



Exploring photophysical behavior and fullerene-induced quenching in Difluoroboron Flavanone β -Diketonates for application in organic electronic devices: Experimental and Theoretical Analysis

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ABSTRACT

The photophysical properties of two difluoroboron flavanone β -diketonates (DK1 and DK2) and their interaction with fullerene (C_{60}) in toluene solution and spin-coated films were investigated using time-correlated single-photon counting, absorption spectroscopy, and steady-state fluorescence spectroscopy. In molecular crystal, the complexes exhibited red-shifted absorption and emission relative to their spectra in solution. Additionally, both complexes displayed bi-exponential decay behavior in time-resolved fluorescence measurements, indicating their capability to form both H and J types of aggregates in the solid state. The introduction of C_{60} resulted in significant fluorescence quenching and reduced excited-state lifetimes for both complexes. This quenching, observed in both solution and spin-coated films, was primarily driven by photo-induced electron transfer (PET) processes, underscoring the potential of these complexes as donors in fullerene-based heterojunction organic solar cells. To elucidate the process of aggregate formation and the impacts of different dimerization types within the crystalline structure of the complexes, first-principles calculations using Density Functional Theory (DFT) and time-dependent density functional theory (TD-DFT) were performed. We also employed DFT to explore various DK configurations on the fullerene surface, evaluating intermolecular distances and formation energies. These calculations highlighted the energetically favorable gap between the low-lying LUMO levels of the complexes and C_{60} , confirming their suitability for such applications.

1. Introduction

Organic Electronic (OE) has been the object of intense research in recent decades with promising results in different areas of technological interest such as lighting-emitting devices, photovoltaic cells and transistors. In terms of industrial production, displays and TV screens based on organic light-emitting devices (OLEDs) are already being commercialized [1] whereas organic photovoltaic devices (OPVs) are close to large-scale production mainly due to the significant increase in their efficiency and the possibility of production by printing [2]. However, many challenges still persist, such as the need to increase the efficiencies with a simultaneous reduction in cost production as well as the improvement of the thermal stability leading to a longer lifetime, which is the critical point especially in OPV technology [3,4].

One of the greatest advantages of organic electronics is the possibility of changing and controlling the performance of devices through the synthesis and convenient combination of different materials, that is, the tuning of molecular design [5]. In this context, not only synthesis modification routes were developed, but also new materials were produced, such as organic/inorganic hybrid materials. In the field of the hybrid materials, organoboron materials have stood out with promising results in the field of OPVs due to their high conversion efficiencies which, in turn, are based on the adjustment of their optical and morphological characteristics through synthesis changes of a main group chemistry [6,7]. Among the organoboron materials, difluoroboron β -diketonate (BF2dbm) complexes have emerged as highly promising materials in the field of organic electronic devices and biosensing due to

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their exceptional optical properties and facile synthesis [8–11]. These complexes are derived from the reaction of difluoroboron compounds with β -diketones. They are typically synthesized through a simple and straightforward process wherein a difluoroboron compound, such as boron trifluoride (BF₃), reacts with a β -diketone, such as acetylacetone or dibenzoylmethane. The reaction results in the formation of a stable chelate complex where the BF₂ moiety coordinates to the oxygen atoms of the β -diketone ligand, forming a six-membered ring structure. This coordination imparts unique optical properties to the complex, including high molar extinction coefficient and high quantum fluorescence yields, which make them attractive for various applications in organic electronics such as organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), and organic field-effect transistors (OFETs) [8, 12–14]. Beyond their utility in electronic devices, BF₂dbm complexes have found diverse applications in biosensing, bio-imaging, and self-assembly [12,15–18]. Their strong fluorescence and low cytotoxicity make them ideal candidates for biological applications, where they serve as fluorescent probes for visualizing intricate biological processes at the cellular and molecular levels. However, one of most interesting features of the BF₂dbm complexes is the possibility of tuning their optical and morphological properties through the incorporation of different groups on phenyl rings [19] including the flavonoids, natural substance with enormous potential for use in the pharmaceutical and cosmetics industry [20]. In turn, the morphological changes in the original structure of the BF₂dbm complexes induced by flavonoid groups enables interaction with material with great technological appeal, such as fullerenes.

Moreover, the synergy between flavonoids and fullerene derivatives has garnered significant interest in recent years, particularly in the context of their potential biomedical applications [16]. It has been reinforced in recent research that the implementation of fullerene in the structure of antioxidant substances can considerably expand the range of possibilities for the development of new antioxidants, including DNA antioxidation [21]. This way, fullerene–flavonoid conjugates have emerged as promising candidates for various biomedical applications, including antiviral therapeutics and antioxidant agents [22,23]. Through rational design and computational modeling, novel flavanone derivatives have been synthesized and evaluated as potential inhibitors of the papain-like protease of COVID-19, showcasing the utility of computer-aided design in drug discovery efforts [24]. Additionally, the antioxidant activities of fullerene (C₆₀)-flavonoid conjugates have been extensively investigated, elucidating their dual role as potent chain-breaking antioxidants and radical scavengers [25–27].

On the other hand, fullerenes possess high electron affinity, making them excellent electron acceptors. Their ability to efficiently accept electrons from donor materials is crucial in the operation of Bulk Heterojunction (BHJ) solar cells [28].

In a previous investigation, nine novel difluoroboron flavanone β -diketonates complexes were synthesized by a simple and efficient synthetic route [29] and unequivocally confirmed by single crystal X-ray diffraction. Preliminary findings revealed that the substituent groups and the solvent media significantly affected the electrochemical and photophysical properties of these complexes [29]. In continuation of this study, we report herein, analysis of the photophysical properties of two of difluoroboron flavanone β -diketonate complexes, denoted as DK1 and DK2 (Fig. 1), in both solution and solid phase. In films, both complexes displayed molecular H and J-type aggregates, consistent with the crystalline structure of the molecules in the solid state. First-principles calculations using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) were performed to comprehend the process of aggregate formation within the structure of the complexes. Furthermore, we explore their interaction with fullerene (C₆₀) in order to verify the ability of these complexes to act as electron donors. The investigation was carried out in both toluene solution and spin-coated films. DFT calculations were utilized to describe the molecular interaction mechanisms by analyzing

intermolecular distances and determining formation energies among the molecules. First-principles calculations reveal that the separation distance between the DK molecules and C₆₀ is within the range of 2.1–3.1 Å, with the binding energy associated with the most favorable interaction configuration estimated to be approximately –0.6 eV. Our findings provide valuable insights into the photophysical behavior of difluoroboron flavanone β -diketonates in solid films and their interaction with fullerene, pointing towards their potential application in optoelectronic devices such as organic solar cells.

2. Methods

2.1. Experiments sections

2.1.1. Materials and methods

The structure of the difluoroboron flavanone β -diketonates complexes DK1 and DK2 are shown in Fig. 1. The synthesis and characterization of these complexes has previously been reported by our group [29]. For analysis of the photophysical properties of the complexes, the stock solutions of individual complexes in toluene were diluted to achieve concentrations of 10^{–6} M. The thin films were produced from 10 mg mL^{–1} solutions with 95% toluene and 5% DMF in order to obtain homogeneous films and deposited by spin coating on glass substrates at 3000 rpm for 60 s, followed by heating at 50 °C for 30 min for solvent evaporation.

The buckminsterfullerene or fullerene (C₆₀) (99.5% purity, MW = 720.64 g/mol) was purchased from Luminescence Technology Corp and used without further purification. The chemical structure of buckminsterfullerene (C₆₀) is also shown in Fig. 1. For the fluorescence quenching studies with fullerene in solution, stock solutions of individual complexes were prepared in toluene and the concentrations were kept at 10^{–5} M while the C₆₀ concentration varied from 0 μ M to 450 μ M (from 0 mg/mL to 0.65 mg/mL). For fluorescence quenching studies in solid films, stock solutions of individual complexes were prepared in toluene at 10 mg/mL. The stock solutions of C₆₀ were also prepared in toluene at 2.6 mg/mL for the appropriate solubility of fullerene in toluene [27]. Blended solutions of DK1 (or DK2) with weight ratios of C₆₀ at 3.0, 5.0, 8.0, 10.0 and 13.0 wt% were prepared with a fixed weight of the complexes kept in all samples and spin-coated (3000 rpm, 60 s) onto glass substrates in a glove box and then heated by removing the solvents. All the fluorescence quenching measurements were carried out at room temperature.

2.1.2. Instruments, photophysical and electrochemical measurements

The steady-state UV–Vis absorption and emission spectra in solution and thin film were acquired using a Shimadzu spectrometer (Model UV-1800) and Shimadzu (Model RF-5301PC) fluorescence spectrophotometer, respectively. Singlet excited state photoluminescence decay curves were recorded using the time-correlated single photon counting method of a Fluotime 200 spectrometer (PicoQuant). Excitation was promoted using a 401 nm pulsed diode laser with repetition rates ranging from 5.0 to 20 MHz. Photoluminescence was collected perpendicular to excitation and passed through a polarizer set at magic angle. The detection system consists of a monochromator and a multi-channel base photomultiplier (Hamamatsu R3809U-50). Lifetimes were obtained by fitting a convolution of the instrument response function and a sum of exponentials to the fluorescence data using FluoFit® software. The residual plots and the chi-square (χ^2) were used to accurately determine the quality of the accessories during the analysis procedure. The Cyclic voltammetry (CV) experiments were carried out in an Autolab PGSTAT 128N potentiostat, a sweep rate of 20 mV/s. The tests were performed in 0.1 M acetic acid solution using a platinum wire as counter electrode and saturated calomel electrode (SCE) as reference electrode. The working electrode in a cyclic voltammetry measurement were carried in spin-coated films prepared by dropping the complexes onto ITO glass (resistance of 4–8 Ω /square, Delta technologies Corporation).

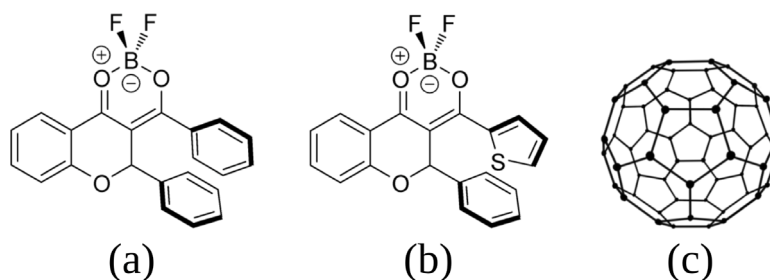


Fig. 1. Structures of the difluoroboron flavanone β -diketonates complexes DK1 (a), DK2 (b) and the buckminsterfullerene C_{60} (c).

2.2. Computational details

Density Functional Theory (DFT) [30,31] and Time-dependent DFT (TD-DFT) [32] calculations were performed with the ORCA 5.0.3 software [33]. A comprehensive benchmark was conducted to ascertain the most suitable exchange–correlation functional for both DFT and TDDFT calculations is presented in the SI. This study assessed several functionals, including the generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE) [34], the hybrid B3LYP [29,35,36], PBE0 [37], and BHLYP [38]; as well as the range-separated hybrid CAM-B3LYP [39], and the hybrid meta-GGA M06-2X [40]. These functionals were utilized in conjunction with the def2-TZVP, applying tight SCF convergence criteria without any imposition of symmetry constraints. To assess the accuracy of the analysis using different basis set, B3LYP functional in combination with def2-TZVP and def2-QZVP was performed. The analysis using different parameters presented similar features as obtained by B3LYP/def2-TZVP, hence, the main discussion will be for this level. UV–Vis spectra were calculated using the Tamm–Dancoff approximation (TDA) [41], and were convoluted with Gaussian functions having a half width at half-maximum (HWHM) of 14 nm. Implicit solvation effects in toluene were considered by employing the conductor-like polarizable continuum model (C-PCM) [42]. Molecular orbitals and TD-DFT difference densities were visualized using VESTA [43]. The band structure calculations for the crystalline system were performed using the GGA-PBE exchange–correlation functional in combination with DZP basis set and D3 dispersion corrections with the SIESTA 5.0.0 software [34,44,45]. The Brillouin zone was sampled with a $3 \times 1 \times 3$ grid.

3. Results and discussion

3.1. Photophysical and electrochemical properties of the difluoroboron flavanone β -diketonates complexes

3.1.1. UV-vis absorption, fluorescence spectra and excited-state lifetime of complexes in toluene solution and spin-coated film

The normalized UV–Vis absorption and emission spectra of DK1 and DK2 complexes in toluene solution and spin-coated films are shown in Fig. 2. The photophysical properties of these complexes, in both solution and spin-coated films, are summarized in Table 1.

The UV–Vis absorption spectrum of the complex DK1 in toluene solution (see Fig. 2a) showed a maximum absorption at 418 nm, with molar absorption coefficient of $0.36 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, and a shoulder at 360 nm (see Table 1). The emission of DK1 in solution (see Fig. 2b) is centered at 478 nm. The spin-coated film of complex DK1 showed both the absorption band and the emission maxima red-shifted compared to solution, with maximum absorption at 430 nm with a shoulder at 367 nm and emission centered at 497 nm. Moreover, the main absorption band of DK1 in film is broader compared to the solution. The absorption spectrum of complex DK2 in solution (Fig. 2b) showed absorption in the region of 430 nm, with a molar absorption coefficient of $0.59 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and a shoulder in 364 nm. The emission of DK1 in solution (Fig. 2c) was centered at 488 nm.

The fluorescence decay curves of the complexes in solution were mono exponentially fitted (see Fig. 2d). The singlet excited-state lifetimes for DK1 and DK2 were found to be 3.59 ns and 4.10 ns, respectively. These lifetimes are typical for monomeric emission of difluoroboron flavanone derivatives, and very similar to those found in chloroform solution [29]. Moreover, the DK1 showed the lowest non-radiative rate constants (k_{nr}) and the highest radiative rate constants (k_r) compared to DK2, which may explain the lower fluorescence quantum yield of DK1 (see Table 1). Thus, the Thienyl group leads to a red-shift of the absorption and fluorescence spectra with an increase in excited states lifetimes and radiative rate constants, consequently decreasing non-radiative rate constants and then improving the fluorescence quantum yield.

Similar trends were observed for the photophysical properties of the difluoroboron flavanone β -diketonates complexes in spin-coated films (see Table 1). The DK1 in film showed main absorption band at 430 nm with a shoulder at 365 nm and emission centered at 497 nm, whilst the film of DK2 showed main absorption band at 445 nm with a shoulder at 370 nm and emission at 517 nm. Moreover, the spin-coated film of complex DK2 showed the highest fluorescence efficiency ($\Phi_F = 0.10$) and consequently the highest radiative rate constants ($k_r = 0.61 \times 10^8 \text{ s}^{-1}$) compared to DK1. The fluorescence quantum yield of complex DK1 in film was found to be 0.04 and its radiative rate constant of $0.34 \times 10^8 \text{ s}^{-1}$. The radiative and non-radiative rate constants of the films were calculated using the respective average lifetimes (τ_{av}). Although radiative and non-radiative rate constant are meaningful for mono-exponential decay (single lifetime), here these constants were evaluated using the average lifetimes in order to provide a qualitative understanding of both radiative and non-radiative processes for the films with multi-exponential decay.

Analogously to the spin-coated film of complex DK1, the film of DK2 showed a broader absorption band, with both absorption and emission spectra red-shifted compared with spectra in solution (see Fig. 2). The red-shift (bathochromic shift) of the main absorption bands of spin-coated films of DK1 and DK2 with respect to the absorption band of the difluoroboron flavanone β -diketonates complexes in toluene solution is typical of formation of aggregates, in particular, the J-type aggregates produced by side-by-side stacking of the complexes. J-type aggregates are very common in non-planar molecules. The head-to-tail dipole interactions in J-aggregates generate energy splitting in excited states, and the lower excited state is optically allowed while the higher one is forbidden, leading to a very moderate red-shift in the absorption spectrum, compared to the region of monomer absorption [48,49]. In addition, the molecular transition dipole moments within the aggregate align due to Coulomb interactions, resulting in a large, collective transition dipole moment. This alignment causes an accelerated radiative decay rate that is proportional to the size of the aggregate. As the number of molecules in the aggregate increases, the fluorescence spectrum becomes more intense. This increase in intensity is also associated with an increase in radiative decay rates and a decrease in the effective fluorescence lifetime [50].

In contrast, H-type aggregates have the cofacial, parallel molecular stacking with molecular transition dipoles oriented side-by-side, in

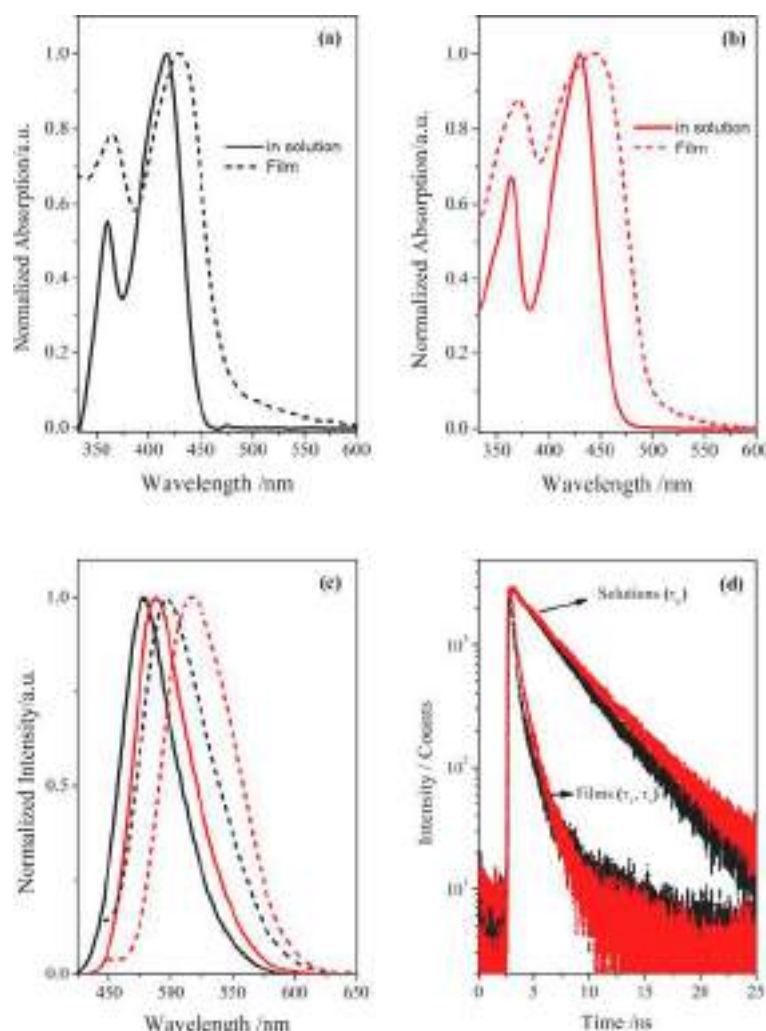


Fig. 2. Normalized absorption (a, b), emission (c) spectra and fluorescence decay curves (d) for complexes DK1 (black) and DK2 (red) in toluene solution at a concentration of 1.80 μM (solid lines) and spin-coated film (dashed lines).

Table 1

The photophysical properties of the complexes DK1 and DK2 in solution and spin-coated films.

Complexes	Absorption λ_{max} (nm)/($\epsilon/10^4$) ^a	Emission (λ_{em})(nm) ^b	Stokes Shift (cm^{-1})	Φ_F^c, Φ_{Ff}^d	τ_0, τ_{av}^e (ns)	$k_r^{f,g}$ ($\times 10^8 \text{ s}^{-1}$)	$k_{nr}^{f,g}$ ($\times 10^8 \text{ s}^{-1}$)
Solutions							
DK1	418, 360sh/(0.36)	478	3003	0.19	3.59	0.53	2.26
DK2	430, 364sh/(0.59)	488	2764	0.31	4.10	0.76	1.68
Solid Films							
DK1	430, 365sh	497	3135	0.04	1.17	0.34	8.21
DK2	445, 370sh	517	3130	0.10	1.63	0.61	5.52

^a Units = $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

^b Excited at maximum absorption band.

^c Fluorescence quantum yields in solution determined with the Anthracene solution as reference ($\Phi_F = 0.27$ in ethanol) [46].

^d Fluorescence quantum yields of the thin films were calculated using $\Phi_{Ff} = \Phi_F \sum \tau_i A_i / \tau_0$, where Φ_F and τ_0 are the fluorescence quantum yield and excited-state lifetimes of complexes in solution, respectively [47].

^e Average lifetimes (τ_{av}) of the complexes in film were calculated using $\tau_{av} = \sum \tau_i^2 A_i / \sum \tau_i A_i$, due to multi-exponential profile, where τ_i and A_i are the excited-state lifetimes and their relative amplitudes, respectively.

^f k_r and k_{nr} are the radiative and non-radiative rate constants calculated using $k_r = \Phi_F / \tau_0$ and $k_{nr} = (1 - \Phi_F) / \tau_0$, respectively.

^g Average lifetimes (τ_{av}) were used to calculate k_r and k_{nr} of the films in order to provide a qualitative understanding of both processes in multi-exponential decay kinetics. sh = Shoulder.

which the lower excited state of the two split energy levels created by dipole interactions is optically forbidden, while the higher one is allowed. Therefore, the main absorption peak is usually blue-shifted (hypsochromic shift) compared to the solution. The H-type aggregates display low radiative decay rate and quenched fluorescence due to the optical forbidden lower excited states, which correspond to the emitting

state. This type of aggregates is very common in planar π -conjugated molecules, where they stack into face-to-face fashion is driven by the strong π - π interactions between adjacent molecules [51].

The fluorescence quantum yields (Φ_F) of the complexes in spin-coated films were lower compared with those found for the complexes in toluene solution, as shown in Table 1. The fluorescence quantum

yields of DK1 and DK2 in spin-coated films were 0.04 and 0.10, respectively. These low yields suggest that H-type aggregates are also present in addition to J-type aggregates in the solid films. In the solid state, molecules typically self-aggregate in various ways due to high molecular packing, which includes the formation of HJ-aggregates [49, 51–61]. This explains the broader absorption band, lower fluorescence quantum yields and the higher non-radiative rate constants displayed for the complexes in spin-coated films compared with those found in toluene solution. The hypothesis that both complexes DK1 and DK2 are capable of forming HJ-aggregates in solid films is supported by time-resolved fluorescence measurements. The fluorescence decay curves at maxima emission of the complexes in spin-coated films (see Fig. 2d) were best fitted with a bi-exponential function, which means that there are at least two emissive species of aggregates. The excited-state lifetimes (τ_i) and their relative amplitudes (A_i) of DK1 and DK2 in spin-coated films, both excited at 401 nm, are listed in Table S1 (see support information). The excited-states lifetimes of complex DK1 in film were found to be 2.22 ns and 0.46 ns. The longest lifetime (2.22 ns) contributed to roughly 12% of the total emission of DK1, while the shortest lifetime (0.46 ns) dominated the emission, contributing to almost 88% of the total emission. The lifetimes of DK2 in film were found to be 2.44 ns and 0.87 ns. Similarly, to DK1 film, the shortest lifetime (0.87 ns) dominated the emission of DK2, contributing to almost 75% of the total emission, while the longest lifetime (2.44 ns) contributed to 25% of the total emission. Assuming that the J-type aggregates are characterized by both the high radiative decay rates and short radiative lifetimes, the short lifetimes (τ_2) of DK1 e DK2 in film are here attributed for the emissions from J-type aggregates, whereas the long lifetimes (τ_1) are attributed for the emissions from H-type aggregates. The average excited-state lifetimes of the films (τ_{av}) are shown in Table 1. The complex DK1 presented average excited-state lifetime slightly shorter compared to average lifetimes of the complex DK2, the average lifetimes were calculated to be 1.17 ns and 1.63 ns, respectively.

The previously reported crystallographic structure of the complex DK2 demonstrated that the molecules exhibit a planar conformation, comprising phenyl, thiophene, and chelate rings, with the phenyl group nearly perpendicular to the molecular plane [29]. Consequently, the molecular conformation of both complexes unequivocally contributes to the formation of J-type aggregates (side by side) of DK1 and DK2.

To elucidate the process of aggregate formation, the impacts of different dimerization types within the crystalline structure of the complexes, and the changes in electronic and optical properties arising from aggregation, we performed first-principles calculations using DFT and TD-DFT formalisms (see Computational Details). Table 2 compares the energies of the frontier orbitals for both molecules DK1 and DK2, [29], in which the former has a p-Tolyl moiety rather than 2-Thienyl; see Fig. 1. Table 2 compares the results obtained with different exchange–correlation functionals, and it is clear that the features do not depend on the level of choice. The HOMO and LUMO electronic density and TD-DFT difference densities are presented in Figure S7 for B3LYP functional. The change of the moiety affects mostly the LUMO, in which the p-Tolyl destabilizes the orbital, shifting the energy in 0.18 eV for B3LYP, 0.22 eV for CAM-B3LYP and 0.14 eV for PBE. HOMO, in contrast, is weakly stabilized by the p-Tolyl moiety, with CAM-B3LYP presenting the largest shift around 0.07 eV. Table 3 shows the experimental energy levels with fairly good agreement with B3LYP results, with an expected overestimation of the DFT HOMO–LUMO gap compared with the measured one, since cyclic voltammetry tends to underestimate this gap, as well systematic variations depending on the different measurements techniques [62–64]. The calculated gap between the low-lying HOMO of DK1 (−6.61 eV) and DK2 (−6.57 eV) with the LUMO of C₆₀ are 3.05 eV and 3.01 eV, respectively.

The change of moiety in the molecule does not remarkably influence the UV–Vis spectral shape, as shown in Figure S9. The reduction

Table 2

Frontier orbital energies and the HOMO–LUMO gap, ΔE (eV), utilizing different exchange–correlation functionals for the molecules DK1 and DK2 in the gas phase, forming dimers, and interacting with C₆₀.

DFT Functional	HOMO	LUMO	ΔE (DFT)
DK1			
B3LYP	−6.61	−2.82	3.79
CAM-B3LYP	−8.11	−1.75	6.36
PBE	−5.88	−3.48	2.40
DK2			
B3LYP	−6.57	−3.00	3.57
CAM-B3LYP	−8.04	−1.97	6.07
PBE	−5.87	−3.62	2.25
C ₆₀			
B3LYP	−6.29	−3.56	2.73
CAM-B3LYP	−7.56	−2.67	4.89
PBE	−5.82	−4.17	1.65
DK1:C ₆₀			
B3LYP/D3BJ	−6.16	−3.45	2.71
DK2:C ₆₀			
B3LYP/D3BJ	−6.16	−3.45	2.71
D _{DK1} ^a /B3LYP	−6.41	−2.90	3.50
D _{DK1} ^b /B3LYP	−6.37	−2.87	3.50
D _{DK2} ^a /B3LYP	−6.42	−2.97	3.45
D _{DK2} ^b /B3LYP	−6.44	−3.00	3.44

^a Most stable dimer.

^b 2nd most stable dimer.

of the HOMO–LUMO gap in molecule DK2 upon the change into 2-Thienyl results in a bathochromic shift of the first excited-state in 0.16 eV, since this state transition contribution is mainly between the frontier orbitals (see Table S8 in Supplementary Information). For both molecules, the first two bands consist of three primary excitations. While the first excitation is responsible for the first band, the second band has contributions from three excitations, in which the second excited state is mostly HOMO-1→LUMO, the third is HOMO-2→LUMO and the fourth is HOMO-3→LUMO. The destabilization of the LUMO induced by p-Tolyl relative to 2-Thienyl results in an overall blue shift in the absorption spectrum of molecule DK1, in alignment with experimental observations, as shown in Figs. 2 and Figure S9. Both molecules presented a solvatochromic effect in toluene, with a redshift of 13 nm for DK1 and 14 nm for DK2 (see Table S12 in Supplementary Information).

To understand the aggregation process within the spin-coated films, especially the spectral variations between these and those observed in a toluene solution, we examined the dimerization process of the DK1 and DK2 molecules. To understand the nature of stacking arrangements and intermolecular interactions among chemical groups that may occur during agglomeration processes, we performed a comprehensive analysis of the crystal structure reported by Ariza et al. [29]. We begin our discussion of dimerization by analyzing the dimers shown in Figs. 3 and S12. We studied two configurations of dimers for each type of molecule, with different types of stacking between them. The dimers labeled D_{DK1}^a and D_{DK2}^a are the most stable for each type of molecule. In an exothermic process, these dimers exhibit π -stacking interactions within the planar segments of the molecules, delineated by formation energies of 18.9 and 22.1 kcal/mol, with interplanar distances of 2.20 Å and 2.31 Å for D_{DK1}^a and D_{DK2}^a, respectively.

Fig. 3(b) and (d) show the UV–Vis spectra of the dimers. To compare with experimental results, we analyze the UV–Vis spectra of the monomer in toluene (see Supplementary Information), alongside the dimer in the gas phase, reflecting solvent-free conditions in spin-coated films. The main absorption peak in the first band for D_{DK2}^a is approximately 398 nm, compared to 404 nm for the monomer in toluene, indicating a subtle blue-shift. The dimer exhibits a solvatochromism in toluene, with a red-shift of 12 nm. Considering the prominence

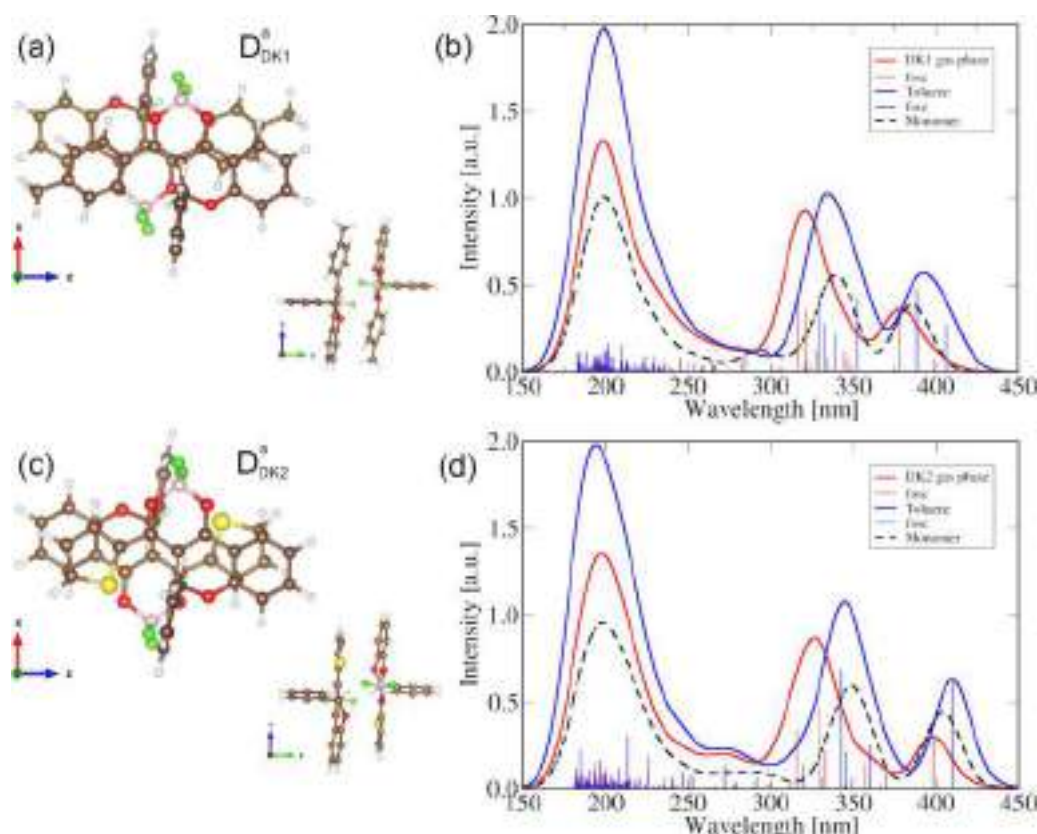


Fig. 3. Geometry configuration of dimer (a) DK1 and (c) DK2. Absorption spectra (b) DK1 and (d) DK2, in gas phase (red), toluene (blue) compared with respective monomers in toluene (dashed-black) Optimized geometric configuration of DK dimers. In the absorption spectrum, the red trace represents the gas-phase conditions, the blue trace denotes the solvent toluene, and the dashed line corresponds to the isolated monomer within the solvent environment.

Table 3
Electrochemical and optical properties of the complexes DK1 and DK2 in solid film.

Complexes	^a λ_{onset} (nm)	^b E_{gap}^{opt} (eV)	^c E_{onset}^{red} (V)	^d E_{onset}^{oxid} (V)	^e HOMO (eV)	^f LUMO (eV)
DK1	430.6	2.88	−0.62	0.83	−5.02	−2.14
DK2	446.0	2.78	−0.63	0.87	−5.03	−2.25
C ₆₀	556.0	2.23	−0.97	1.26	−6.06	−3.83

^a λ_{onset} is the absorption onset wavelength.

^b Optical bandgap calculated on the low energy band edge of the absorption spectrum ($E_{gap}^{opt} = 1240/\lambda_{onset}$) of the films.

^c E_{onset}^{red} is the onset potential of reduction.

^d E_{onset}^{oxid} is the onset potential of oxidation.

^e HOMO = ($E_{onset}^{red} - 4.40$) eV.

^f LUMO = (HOMO + E_{gap}^{opt}) eV. The onset potential of reductions (E_{onset}^{red}), the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of C₆₀ were taken from Ref.[63].

and probable recurrence of this dimer, it is therefore proposed that the observed band broadening can be explained through the hypothesis of a combination of different dimer formations, notably J-type and H-type. We then clarify how this combination of dimers leads to the observed UV–Vis spectra features. Figure S10 and S11 present spectra for various geometries configurations derived from D^a_{DK1} and D^a_{DK2}. We explore alternative stacking in the dimer by rigidly translating the molecules, in steps of 0.77 Å between successive molecular configurations, a procedure analogous to the transition from H-type to J-type dimers. The UV–Vis spectra calculations were performed without geometries relaxation to elucidate the influence of molecular stacking on the absorption characteristics. This is justified as the crystal's packing preserves the different stacking, and relaxing the dimer would alter this characteristic. The results reveal a multifaceted landscape. As illustrated in Figure S11, upon the initial displacement d_1 , an excited state emerges characterized by a red-shift of 25 nm relative to the monomer, resulting in a peak around 429 nm, while another excitation remains

stable around 402 nm. In the subsequent two displacements, d_2 and d_3 , this scenario persists with minor alterations in the positions of these two described peaks. For the final trio of displacements, a systematic reduction in the intermolecular contact surface was initiated, resulting in spectral behaviors that increasingly approximate those observed in the monomer case, retaining a red-shifted spectral profile. A comparable spectral behavior is observed for the DK1 molecule, as can be seen in Figure S9. Upon integration into a spin-coated film, a variety of dimer types may form. Such an ensemble of stacking configurations is likely to broaden the principal absorption band characteristic of DK films.

A model more accurately reflecting the crystal packing observed in DK2 would require a more detailed elucidation of the role of 2-Thienyl, particularly in the context of DK2, in the mechanisms of film formation or crystallization processes. The specific molecular packing configurations for DK2, as detailed by Ariza et al. [29], provide valuable insights into these dynamics. To elucidate this concept, we characterize the

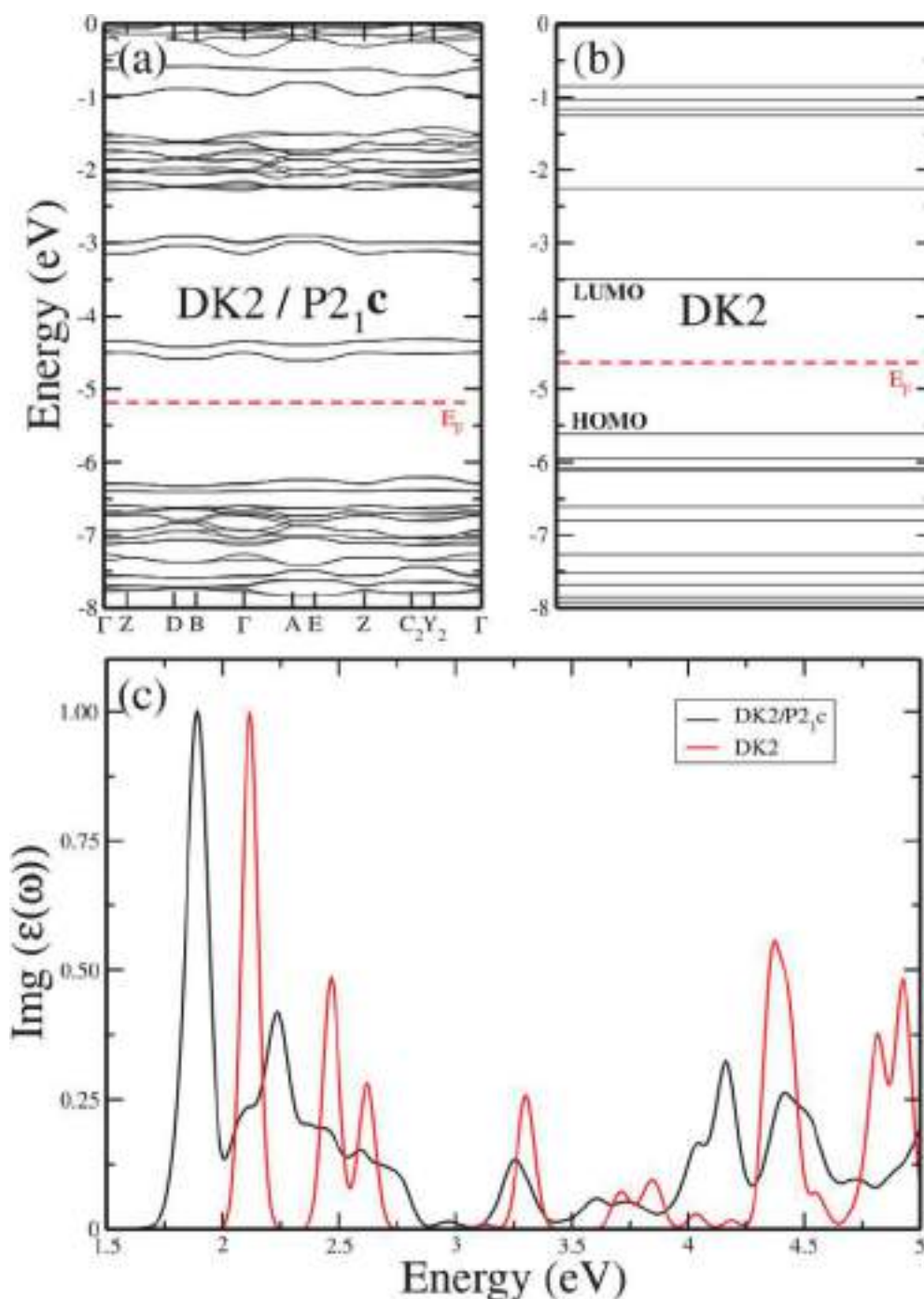


Fig. 4. (a) Electronic band structure of DK2 crystal in the $P2_1/c$ space group [29]. (b) Orbital energies for DK2 molecules with HOMO and LUMO levels indicated. (c) Imaginary part of the dielectric function for DK2/ $P2_1c$ crystal and DK2 molecule with 50 meV optical broadening. The normalization of the spectra was conducted independently. Calculations used SIESTA package version 5.0.0 [44].

optical excitation within this crystal. Furthermore, we conducted a comparative analysis with the isolated molecule employing the same methodology. In these instances, we computed the imaginary part of the dielectric function using dipolar transition matrix elements between the eigenfunctions of the self-consistent Hamiltonian, as shown in Fig. 4.

Fig. 4(a) and (b) illustrate the electronic band structure and orbital energies of the DK2/ $P2_1c$ crystal and the isolated DK2 molecule, respectively. The DK2 crystal exhibits an indirect band gap of 1.58 eV; however, within the C_2 - Y_2 region, it demonstrates a direct band gap of 1.68 eV. Furthermore, an additional band emerges 0.2 eV

above the bottom of the conduction band, with an excitation energy of 1.88 eV. However, the isolated DK2 molecule exhibits a HOMO–LUMO gap of 2.1 eV when investigated using this method. It is crucial to acknowledge the limitations of DFT/PBE in accurately describing energy band gaps, primarily due to issues such as discontinuities [65]. Additionally, the dielectric responses obtained from GGA/PBE are devoid of many-body electron–electron and electron–hole interactions, thereby providing only semi-quantitative approximations for absorption spectra. Hence, a bathochromic shift in the Fig. 4(c) due to the crystallization process. This is a consequence of the reduced energy gap. The initial absorption peak of the crystal is positioned at 1.88

eV, whereas, for the molecule, the first allowed transition corresponds to the HOMO–LUMO transition. Consequently, beyond the spectral broadening attributable to the diversity of dimeric configurations, the crystallization process is posited to contribute to the manifested red shift.

3.1.2. Electrochemical and optical properties of the difluoroboron flavanone β -diketonates in solid films

The electrochemical properties of complexes DK1 and DK2 were investigated by cyclic voltammetry (CV). The data from their electrochemical and optical properties are summarized in Table 3. The potential of oxidation and reduction of the DK1 and DK2 were determined from voltammograms. The cyclic voltammograms of the complexes are provided in the supplementary information (see Fig. S1). The HOMO energy levels were estimated according to their reduction onset (E_{red}^{onset}) potentials from voltammograms where $HOMO = (E_{red}^{onset} - 4.40)eV$. The LUMO energy levels were estimated from optical band gaps (E_{gap}^{opt}) previously determined from the absorption edge of complexes in solid films, according to $LUMO = (HOMO + E_{gap}^{opt})eV$.

As shown in Table 3, the HOMO energy levels of the complexes DK1 and DK2 in solid films were estimated to be -5.02 eV and -5.03 eV, respectively, whereas the LUMO energy levels were found to be -2.14 eV and -2.25 eV, respectively. The optical band gaps of the complexes DK1 and DK2 were found to be 2.88 eV and 2.78 eV, respectively. In fullerene based heterojunction organic solar cells (OSCs), the lowest unoccupied molecular orbital (LUMO) of the donor molecules should be higher than that of molecular orbitals energies of acceptor to energetically favor the intermolecular charge transfer between donors and acceptors [66]. Thus, the optical band gaps energies and the HOMO and LUMO energy levels exhibited for the complexes make them desirable for application as donor in OSCs, since the LUMO and the HOMO of the complexes are higher than that of molecular orbitals energies of fullerene (-3.83 eV and 6.06 eV, respectively), which is energetically favorable to an effective exciton dissociation at the complex and fullerene interface. The interaction of the DK1 and DK2 with fullerene in solution and solid state, also their capability to act as donors, will be discussed further in the following. Additionally, the large gap between the low-lying HOMO level of DK1 (-5.02 eV) and DK2 (-5.03 eV) with LUMO (-3.83 eV) of C_{60} were evaluated to be 1.19 eV and 1.17 eV respectively, which may lead to enhanced organic solar cells (OSCs) with larger open-circuit voltages (Voc) [67].

3.2. Fluorescence quenching of the difluoroboron flavanone β -diketonate complexes by fullerene C_{60} in solution and spin-coated film

While most studies on the interaction between conjugated molecules and C_{60} have focused on the solid state, here the fluorescence quenching of difluoroboron flavanone β -diketonate complexes by fullerene C_{60} was also investigated in solution. The normalized fluorescence of the complexes in toluene solution with variable concentration of fullerene (C_{60}) are shown in Fig. 5. The addition of C_{60} fullerenes to the solutions led to an efficient quenching of the complexes fluorescence. By increasing the C_{60} fullerenes concentration to 450 mM, the DK1 fluorescence intensity was quenched at almost 60% from its initial intensity (without C_{60}), whilst the DK2 fluorescence intensity was reduced to nearly 40%.

Moreover, the excited-state lifetimes of the DK1 and DK2 slightly decrease with increasing fullerenes concentration, suggesting that the decay of the photoexcited complexes in presence of C_{60} occurs via dynamic quenching mechanism [68]. The lifetimes and the fluorescence decay curves as a function of C_{60} concentration can be seen in Table S2 and Figure S2, respectively, in the supplementary information. The Stern–Volmer equation (Eq. (1)) for dynamic (or collisional) quenching process is given by [69]:

$$\frac{\tau_0}{\tau} = \frac{F_0}{F} = 1 + K_{sv}[Q] = 1 + k_q\tau_0[Q] \quad (1)$$

where τ_0 and τ represent the excited-state lifetime in the absence and presence of C_{60} , respectively, F_0 and F are the fluorescence intensity in the absence and presence of C_{60} , respectively, K_{sv} is the Stern–Volmer quenching constant, $[Q]$ is the concentration of C_{60} and k_q is the bimolecular rate constant.

The Stern–Volmer plots for the excited-state lifetimes were linear with good agreement with Eq. (1), as can be seen in Fig. 5c and 5d. The quenching constants K_{sv} and k_q listed in Table 4 were obtained from the fitting of Stern–Volmer plot using Eq. (1). The values of K_{sv} for the DK1 and DK2 were found to be 104.5 M $^{-1}$ and 91.6 M $^{-1}$, respectively. The bimolecular rate constants k_q evaluated for the DK1 and DK2 using Eq. (1) and taking their excited-state lifetimes in absence of C_{60} from Table 1 were found to be 2.93×10^{10} M $^{-1}$ s $^{-1}$ and 2.23×10^{10} M $^{-1}$ s $^{-1}$, respectively. The larger Stern–Volmer quenching constant K_{sv} for DK1: C_{60} system (104.5 M $^{-1}$) compared to DK2: C_{60} system indicates that the fluorescence of DK1 was more efficiently quenched by C_{60} than the fluorescence of DK2 (91.6 M $^{-1}$). Additionally, the magnitude of bimolecular quenching constant k_q (in order of 10^{10} M $^{-1}$ s $^{-1}$) found for the both systems indicates that the bimolecular excited-state process is diffusion-controlled [70].

In the dynamic quenching process, charge transfer may occur when the fullerene collides with the excited complex within an approach close to typical π -stacking distance (~ 3.0 Å). Distances of up to 10 Å are favorable, specially for electron transfer [71,72]. The closest intermolecular distances between fullerene and the complexes were found to be within the range of 2.1 to 3.1 Å. These distances were determined using DFT calculations, and the results will be shown next. Since the interaction between the quencher and the fluorophore affects only the excited state of the fluorophore, no changes in the absorption spectrum are expected. In contrast, the formation of ground-state complexes in static quenching lead to changes on the absorption spectra of the fluorophore [73–76]. The normalized absorption of the complexes in toluene solution with different concentrations of fullerene (C_{60}) are shown in Figure S3, on the supplementary information. The absorption spectra profiles of the complexes remained unchanged upon the addition of fullerene, with no new bands or absorption shoulders observed as a result of ground-state complexation between the complexes and C_{60} . This may be attributed to the spherical shape of fullerene and the twisted structure of the difluoroboron flavanone β -diketonates complexes, which substantially reduces the available surface area for interactions [77]. All the absorption spectra of DK1: C_{60} and DK2: C_{60} systems in solution were recorded against the pristine C_{60} solution as reference. The absorption spectrum of fullerene in toluene is shown in Fig. S4. Fullerene shows its main absorption peak at 335 nm.

The well-known excellent electron-accepting properties of C_{60} , combined with the negligible overlap between its absorption spectrum (300 – 420 nm, see Fig. S4) and the emission spectrum of the complexes (430 – 600 nm, see Fig. 2c), indicate that the fluorescence quenching of the complexes is mainly due to photo-induced electron transfer (PET) from difluoroboron flavanone–diketonate complexes to fullerenes, with no significant energy transfer process involved.

In order to provide further support for the PET mechanism, we estimated the free energy changes (ΔG_0) for electrons transfer reactions in these systems. The ΔG_0 for a PET reaction can be calculated using the Rehm–Weller equation [78]

$$\Delta G_0 = E_{oxid}(D) - E_{red}(A) - E_{0,0}(A) - C \quad (2)$$

where $E_{oxid}(D)$ is the oxidation potential of the donor, $E_{red}(A)$ and $E_{0,0}(A)$ are the reduction potential and the energy of the $S_0 \rightarrow S_1$ transition of the acceptor, and C is the Coulombic term. Since one of the species is neutral and the solvent used is polar in nature, the Coulombic term in the above expression is neglected [79]. Taken the singlet state energy $E_{0,0}(A)$ as the energy of acceptor optical band gap (E_{gap}^{opt}), the oxidation potential of the donor $E_{oxid}(D)$, the reduction potential of the acceptor $E_{red}(A)$ listed in Table 3, the ΔG_0 values for electron transfer for the DK1: C_{60} and DK2: C_{60} systems were negative

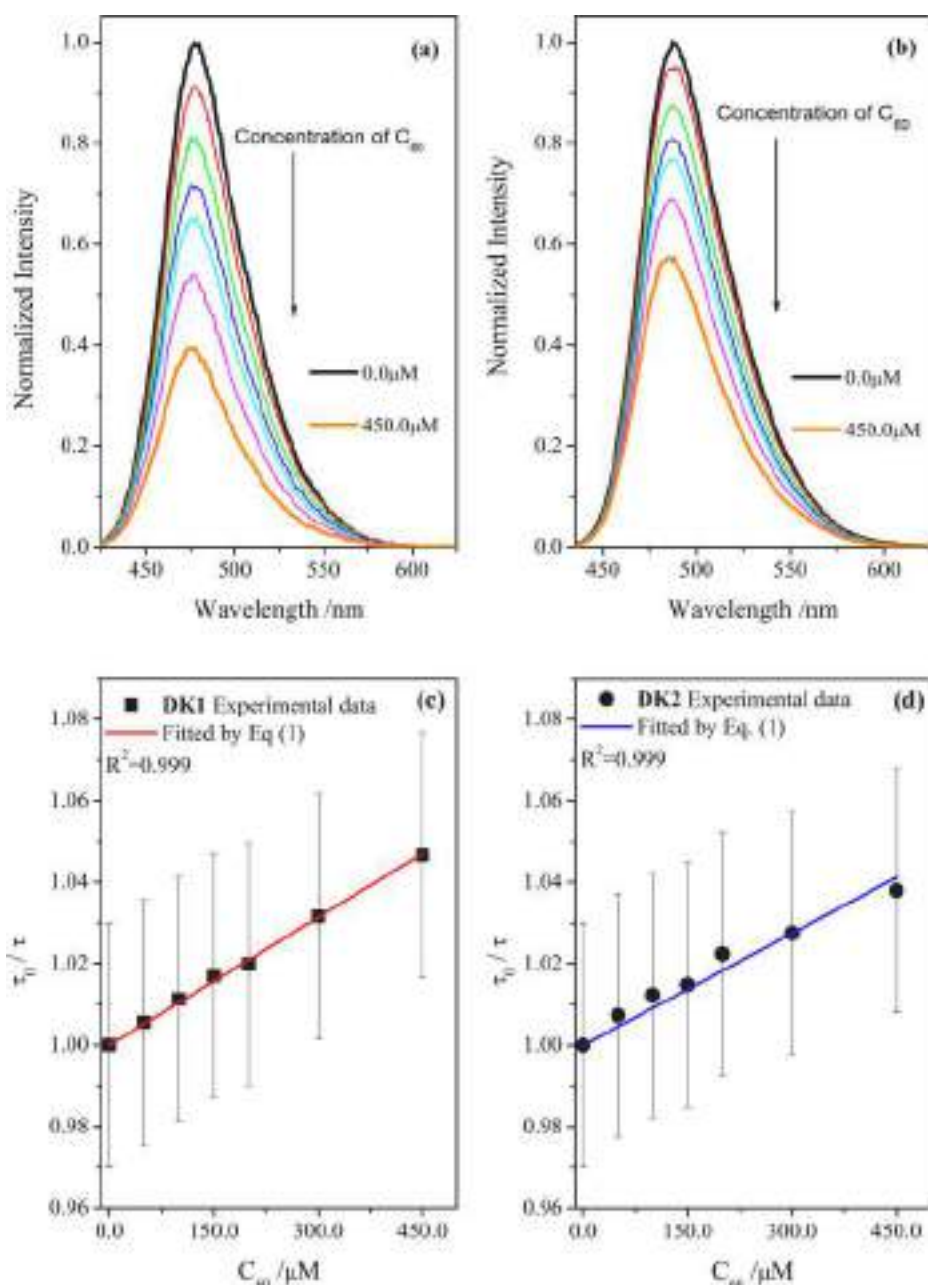


Fig. 5. Fluorescence spectra for complexes DK1 (a) and DK2 (b) in toluene solution with different C_{60} concentration, and Stern-Volmer plots of DK1 (c) and DK2 (d), where τ_0 and τ are the excited-state lifetime in the absence and presence of C_{60} , respectively.

Table 4

Stern-Volmer quenching constant (K_{SV}), bimolecular rate constant (k_q), free energy changes (ΔG_0) for the electron transfer reactions, rate constant of charge separation (k_{CS}) and quantum yield of charge separation (Φ_{CS}) for DK1: C_{60} and DK2: C_{60} systems in toluene solution at room temperature.

Systems	K_{SV} (M^{-1})	k_q ($10^{10} M^{-1} s^{-1}$)	ΔG_0^a (eV)	k_{CS}^b ($10^6 s^{-1}$)	Φ_{CS}
DK1: C_{60}	104.5	2.93	−0.45	13.0	0.05
DK2: C_{60}	91.6	2.23	−0.41	9.3	0.04

^a Calculated by Rhem-Weller equation $\Delta G_0 = E_{oxid}(D) - E_{red}(A) - E_{0,0}(A) - C$.

^b $k_{CS} = \Phi_{CS}/\tau$, where $\Phi_{CS} = 1 - (\tau/\tau_0)$ [70], τ_0 and τ are the lifetime of the excited singlet state of the complexes in absence and presence of C_{60} , respectively.

(see Table 4), showing that PET is energetically possible. The lower value of $E_{oxid}(D)$ for DK1 led to the largest value of ΔG_0 (−0.45 eV) and the largest amount of PET quenching. The efficiency of charge separation (Φ_{CS}) and rate constant for charge separation (k_{CS}) for

DK1: C_{60} and DK2: C_{60} systems in toluene solution were also determined (see Table 4). The maxima rate constants of charge separation for singlet (k_{CS}) for the DK1: C_{60} and DK2: C_{60} systems in solution were found to be $13.0 \times 10^6 s^{-1}$ and $9.3 \times 10^6 s^{-1}$, respectively, and their

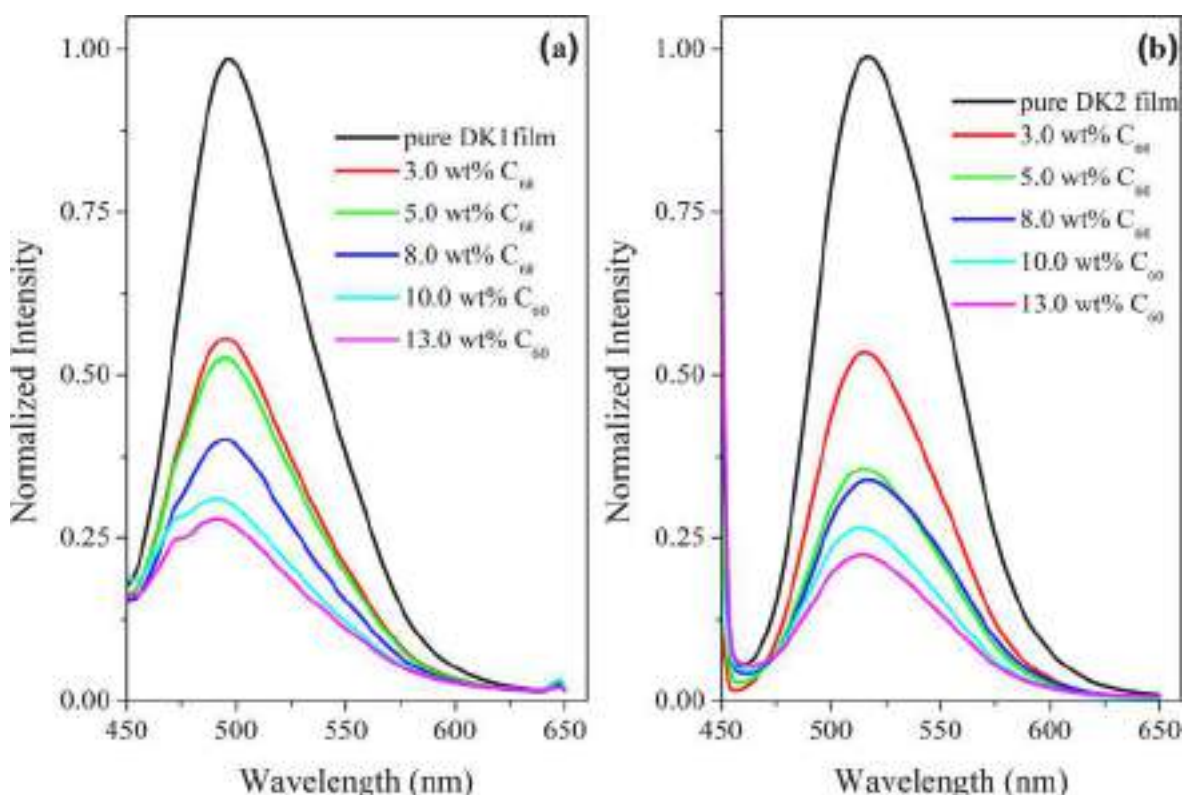


Fig. 6. Normalized emission spectra of the spin-coated films of DK1 (a) and DK2 (b) with different weight ratios of C_{60} .

quantum yields of charge separation for singlet (Φ_{CS}) were found to be 0.05 and 0.04, respectively (taking the τ as 3.43 ns for DK1: C_{60} system and τ as 3.95 ns for DK2: C_{60} system, see Table S2). The DK1: C_{60} system exhibited higher rate constant of charge separation (k_{CS}) and quantum yield of charge separation (Φ_{CS}) compared to the DK2: C_{60} system, suggesting that the DK1: C_{60} system demonstrated a faster rate of charge separation, indicating a more rapid conversion of absorbed light energy into separated charges, while also achieving a greater proportion of photon absorption leading to charge separation.

In spin-coated films, the weight ratios of C_{60} varied from 3.0 wt% to 13.0 wt% and the corresponding normalized fluorescence spectra are shown in Fig. 6. By increasing the weight of C_{60} , the fluorescence intensities of the films notably decreased, while their emission maxima wavelengths kept unchanged. When the weight ratio of C_{60} reached 13.0 wt%, the fluorescence intensities of DK1 and DK2 pure films were quenched by 72% and 78%, respectively and their fluorescence quantum yields (Φ_{FF}) decreased from 0.04 and 0.10 to 0.02 and 0.03, respectively. The fluorescence quantum yields of the films with different weight ratios of C_{60} can be seen in Table S3 and S4, respectively. The fluorescence decay curves for DK1: C_{60} and the DK2: C_{60} spin-coated films (Figure S5) were well-fitted to a bi-exponential decay with a long (τ_1) and a short (τ_2) lifetime. These both lifetimes slightly decreases with increasing the weight of C_{60} as shown in Table S3 and S4 in supplementary information. The excited-states lifetimes of the pure DK1 film were previously found to be 2.22 ns and 0.46 ns, respectively. For the DK1:13.0 wt% film, the longest lifetime decreases to 1.37 ns and the shortest lifetime to 0.25 ns. The average lifetime (τ_{av}) initially of 1.17 ns decreases to 0.63 ns. For the DK2: C_{60} films, their both lifetimes of 2.44 ns and 0.87 ns for pure DK2 film decrease to 1.02 ns and 0.28 ns, respectively, when the weight ratio of C_{60} reached 13.0 wt%, whilst the average lifetime of 1.63 ns decreases to 0.51 ns. The absorption spectra of the complexes spin-coated films with fullerenes were very similar to absorption spectra of the pure complexes films. The normalized absorption spectra of DK1 and DK2 spin-coated films with different weight ratios of C_{60} can be seen in Figure S6 on

the supplementary information. Furthermore, there was any significant overlap between the emission of the complexes in spin-coated films and the absorption spectrum of C_{60} . Therefore, the fluorescence quenching, the decrease in average lifetimes and quantum efficiencies of the films DK1: C_{60} and DK2: C_{60} with no significant energy transfer process were due mainly to photo-induced electron transfer (PET) from the complexes (donors) to C_{60} (acceptor). Thus, the decreases of the lifetimes τ_1 and τ_2 with increasing C_{60} indicate that both existing species of H- and J-aggregates in the films act as electron donors to fullerene. Considering the average lifetimes of the films without (τ_{av}) and with fullerene ($\tau_{av,C60}$) it was possible to obtain the average charge separation rate k_{CS} and quantum yields of charge separation (Φ_{CS}) [61,70]. The average rate constant of charge separation and quantum yield of charge separation for the films are listed in Table S3 and S4. In general, the rate constants of charge separation and quantum yields of charge separation of DK2: C_{60} films were higher compared to the respective films of the DK1: C_{60} system. This suggests that the films of DK2: C_{60} showed a more efficient charge generation process, explaining the more effective quenching of their fluorescence quantum yield (Φ_{FF}) compared to the DK1: C_{60} system. Moreover, the average rate constants of charge separation found for these two difluoroboron flavanone β -diketonates with C_{60} were very similar to those observed by Montoya and Janssen for four thiophene-pyridine-diketopyrrolopyrrole molecules blended with phenyl-C71-butyric acid methyl ester (PC70BM) as cast films for bulk-heterojunction organic solar cells [61]. These findings suggest that the DK: C_{60} systems might also be very suitable for application as active layers in organic solar cells (OSCs).

To understand the C_{60} -DK interaction, DFT calculations were used to explore various DK configurations on the fullerene surface, evaluating intermolecular distances and formation energies (FE) with BSSE corrections. Figures S13 and S14 show the studied geometries, and the results are summarized in Tables S9 and S10. Among the studied configurations, the most stable have really similar formation energies (BEs), with DK2 being slightly more stable than DK1. For both DKs, the interaction with C_{60} leads to a torsional deformation in the planar

region of the molecules, with an adsorption distance of 3.0 Å for DK1 and 2.9 Å for DK2, in which are in agreement with previous studies on flavonoid-carbon interactions [77]. The DK1 and DK2 distances to C₆₀ surface range from 2.07 to 3.12 Å, supporting the quenching hypothesis at distances under 10 Å. In order to further understand the electronic and photophysical properties of the system, Figure S15 shows the absorption spectra for the most energetically favorable configurations of the C₆₀-DK. In the spectra, it is observed that the primary effect of the solvent is a small shift of 10.16 nm and 12.39 nm and an increase in the intensity of f_{osc} for the DK1-C₆₀ and DK2-C₆₀ systems, respectively. In the interacting system for both molecules, the HOMO and LUMO orbitals are localized over C₆₀, with a very weak intensity in the excitation involving these orbitals for wavelengths above 400 nm. With a multiconfigurational character of the transitions, the spectra for DK1-C₆₀ and DK2-C₆₀ systems show a superposition of their monomeric components. While the DK1 monomer has a mostly HOMO-LUMO single excitation in the first band around 373 nm, when interacting with C₆₀ this band becomes a combination of four distinct excitations, with a clear charge transfer character from DK1 to C₆₀. For molecule DK2 a different behavior is observed. With a similar combination of four states on the first band of the absorption spectra, for the system DK2-C₆₀ the most intense excitation is localized within the DK2 molecule. This might be explained by the fact that since 2-Thienyl is an electron-withdrawing group, the excitation has an intramolecular character. However, the other three states in this first band have a similar charge transfer from DK2 to C₆₀. These findings explain the minimal changes observed in the experimental spectra of DK molecules upon interaction with C₆₀ (see Supplementary Figures S15 and S16).

4. Final remarks

In summary, our investigation sheds light on the photophysical properties of two difluoroboron flavanone β -diketonates in spin-coated films and their interaction with fullerene. In solid state, the observed bathochromic shift in absorption spectra, the broader absorption band, lower fluorescence quantum yields exhibited for the complexes in spin-coated films suggested the formation of both H and J-type aggregates. This hypothesis was supported by time-resolved fluorescence measurements and first-principles calculations using density functional theory (DFT) and time-dependent density functional theory (TD-DFT). The addition of C₆₀ resulted in significant fluorescence quenching and a decrease in the excited state lifetimes of the DK1 and DK2 complexes. The fluorescence quenching observed in both solution and spin-coated films was primarily driven by photo-induced electron transfer (PET) processes, where electrons transfer from the complexes (donors) to the fullerene (acceptor) during their collision in solution or at interfaces in the solid film. The intermolecular distance, formation energies and the electronic properties of C₆₀-DK evaluated by DFT and TD-DFT calculations were in agreement with experimental data.

CRediT authorship contribution statement

Sergio Fernando Curcio: Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Data curation. **Gabriel L. Carvalho:** Writing – review & editing, Visualization, Validation, Investigation, Data curation, Formal analysis. **Elida Betania Ariza Paez:** Visualization, Validation, Data curation. **Natália P. Neme:** Writing – review & editing, Visualization, Validation, Investigation, Data curation, Formal analysis. **Rogério Valaski:** Writing – review & editing, Supervision, Methodology, Formal analysis. **Matheus J.S. Matos:** Writing – review & editing, Writing – original draft, Supervision, Visualization, Validation, Investigation, Data curation Funding acquisition, Conceptualization. **Jason Guy Taylor:** Writing – review & editing, Writing – original draft, Supervision, Data curation, Conceptualization. **Thiago Cazati:** Writing – review & editing, Writing – original draft, Supervision, Visualization, Validation, Investigation, Data curation, Conceptualization.

Ethical approval

No studies involving human or animal subjects were conducted in this article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.mtcomm.2024.110878>.

Data availability

Data will be made available on request.

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Charge carrier transport in perylene-based and pyrene-based columnar liquid crystals

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Abstract

Electron and hole transport characteristics were evaluated for perylene-based and pyrene-based compounds using electron-only and hole-only devices. The perylene presented a columnar hexagonal liquid crystal phase at room temperature with strong molecular π -stacking inside the columns. The pyrene crystallizes below 166 °C, preserving the close-packed columnar rectangular structure of the mesophase. Photophysical analysis and numerical calculations assisted the interpretation of positive and negative charge carrier mobilities obtained from fitting the space charge limited regime of current vs voltage curves. The pyrene-based material demonstrated an electron mobility two orders of magnitude higher than the perylene one, indicating the potential of this class of materials as electron transporting layer.

Introduction

Conjugated organic molecules have been widely investigated due to their interesting transport properties and promising applications as active layer in organic photovoltaics (OPVs), organic field effect transistors (OFETs), organic light-emitting diodes

(OLEDs) and sensors [1,2]. Columnar liquid crystals are attractive due to their solution processability and their self-organization in highly anisotropic supramolecular architectures, which favors the mainly one-dimensional migration of charge carriers

with an anisotropy of the charge carrier mobility (parallel vs perpendicular to the columnar axis) of up to ten orders of magnitude [3–7]. In 1994, Adam and collaborators obtained a hole-mobility of up to $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for a triphenylene-based columnar liquid crystal [8], motivating intense research activity to understanding charge transport in columnar mesophases [9–14]. High charge carrier mobilities of $1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for p-type and up to $6.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for n-type liquid-crystalline semiconductors have already been reported [15].

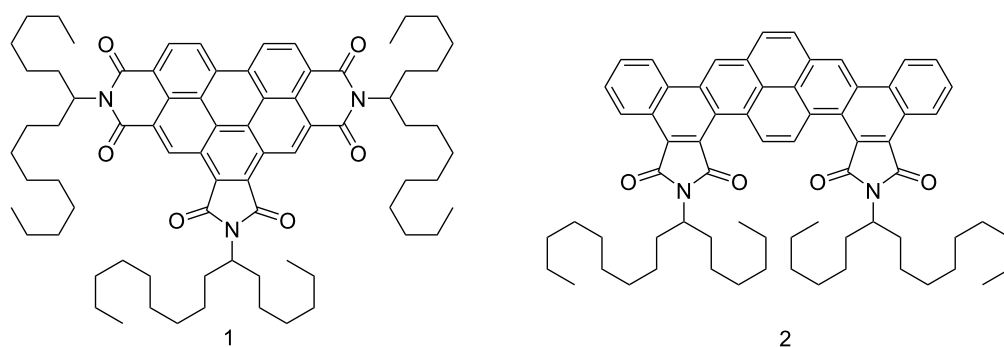
Among the various discotic liquid crystal materials, perylene derivatives are among the most investigated due to their easy functionalization, high chemical and thermal stability, strong photoluminescence, and n-type semiconductor character. They tend to adopt columnar organization due to the strong π – π interaction of the rigid cores, providing a path for the efficient conduction of electrons [16]. Perylene diimide derivatives display good electronic mobilities (10^{-3} to $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and are considered suitable electron acceptors for photovoltaic applications [17–20]. Pyrene derivatives have also been widely investigated in recent decades. They exhibit excellent photoelectric properties such as strong emission, efficient excimer formation, and suitable intermolecular stacking for good charge carrier transport. They have been applied as active layer in OFETs with high ambipolar mobility due to their well-defined monocrystalline microstructures resulting from strong π – π interactions [7,21–24].

In this work, we investigated a perylene and a pyrene-based columnar liquid crystal in hole-only and electron-only devices to compare their charge carrying properties. The molecular organization and photophysical performances are coherent with the charge transport behavior. DFT calculations assisted the interpretation of electron and hole migration mechanism using the frontier orbital energies and the conjugation within the π -system.

Results and Discussion

The syntheses of **1** and **2** were previously published in [25] and [26], respectively. **1** is a benzo[ghi]perylene-hexacarboxylic trialkylimide and **2** a dinaphtho[2,1-*a*;1,2-*i*]pyrene-tetracarboxylic dialkylimide, both with asymmetrically branched alkyl swallow-tails derived from 7-aminoheptadecane (Scheme 1 illustrates their molecular structure). In Table 1, we show the thermal characteristics and observed mesophases. Compound **1** presents a wide range columnar hexagonal phase (Col_{hex}) preserved at room temperature by cooling from the isotropic. Compound **2** shows an additional columnar rectangular phase (Col_{rect}) below the Col_{hex} and crystallizes under 166 °C. The HOMO and LUMO energy levels are also given in Table 1.

Raman spectra of both compounds were acquired off-resonance (Figure 1). Compound **1** presents the main peak at 1609 cm^{-1} assigned to C=C stretching from the chromophore, a peak of



Scheme 1: Molecular structures of compounds **1** and **2**.

Table 1: Characteristics of **1** and **2** extracted from [17] and [18], respectively.

Comp.	Phase sequence (°C) ^a	HOMO (eV)	LUMO (eV)
1	Col _{hex} – 177 – Iso	–6.62	–3.79
2	Cr – 166 – Col _{rect} – 225 – Col _{hex} – 248 – Iso	–5.65	–3.32

^aDetermined by DSC, XRD and POM.

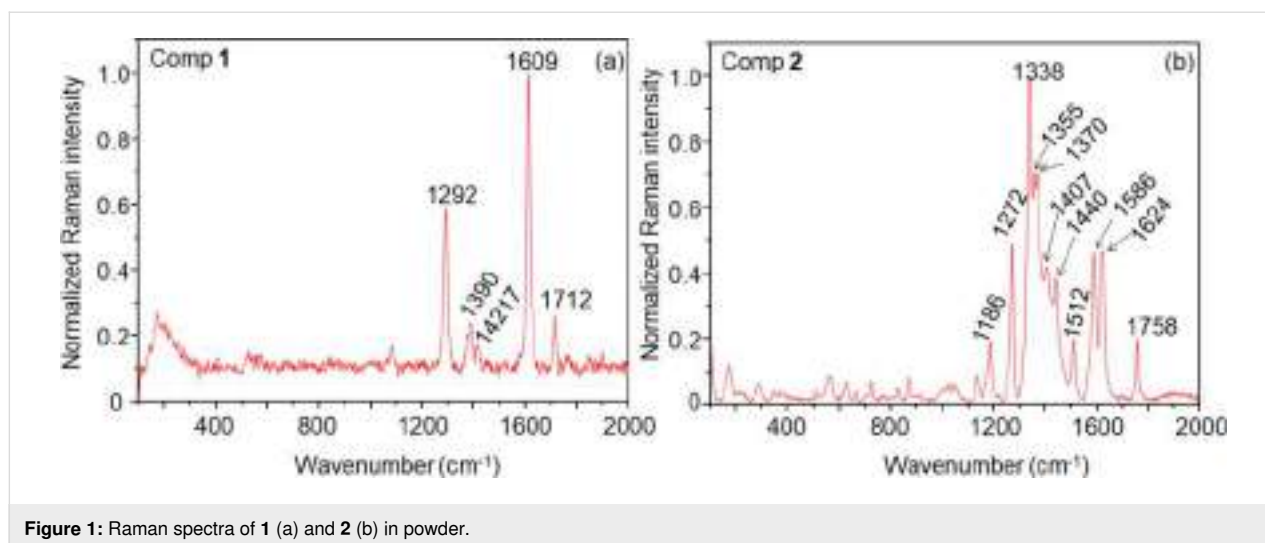


Figure 1: Raman spectra of **1** (a) and **2** (b) in powder.

intermediate intensity at 1292 cm^{-1} assigned to C–H bending and ring stretching, and a less intense peak at 1712 cm^{-1} which corresponds to C=O stretching [27]. The pair at 1390 and 1417 cm^{-1} is attributed to perylene ring stretching [28]. As observed for bis(phenethylimido)perylene (PhPTCD) [29] only a small number of peaks is observed. In contrast, compound **2** presents a larger number of peaks, with the spectrum being dominated by the peak at 1338 cm^{-1} (C–N stretching). The peak at 1272 cm^{-1} (C–H bending and ring stretching), and the pair of peaks at 1586 and 1624 cm^{-1} are assigned to the C=C stretching mode [30]. Less intense peaks can be observed at 1186 cm^{-1} (C–H bending), 1512 cm^{-1} (perylene ring stretching), and 1758 cm^{-1} (C=O).

X-ray diffraction (XRD) measurements of **1** and **2** are shown in Figure 2. The Miller indices indicate the Col_{hex} and Col_{rect}

character of the mesophases [31]. Despite crystallization of **2**, the Col_{rect} order is partially preserved at room temperature. The Col_{hex} lattice parameter (a) obtained is 23.7 Å for **1** and 22.9 Å for **2**. The a/b aspect ratio of the Col_{rect} phase of **2** is equal to 2.08, representing an elongation of around 20% concerning the hexagonal mesophase (where $a/b = 1.73$). The π -stacking distance between neighboring disks inside the columns, indicated by the (001) peak, is $\approx 3.5\text{ Å}$ for all mesophases.

Absorption and photoluminescence (PL) of **1** and **2** are presented in Figure 3 for solution and spin-coated film. Compound **1** shows the three well-defined bands typical of perylene absorption and PL in solution. The absorption becomes broader and the PL deconstructed and red-shifted in the film. These results indicate molecular π -stacking aggregation and excimer formation on the films [2].

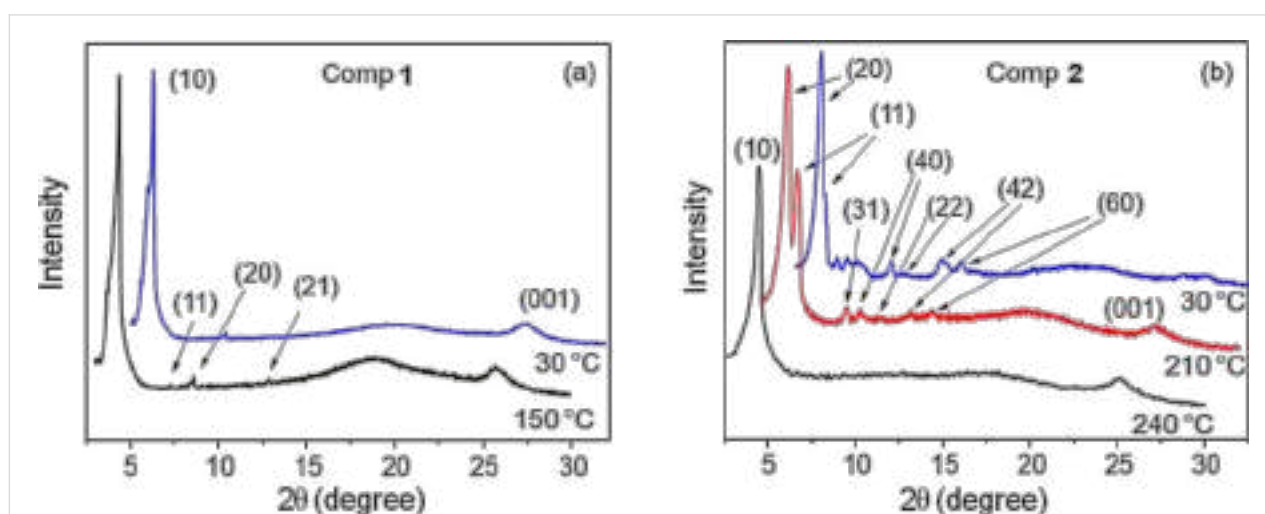
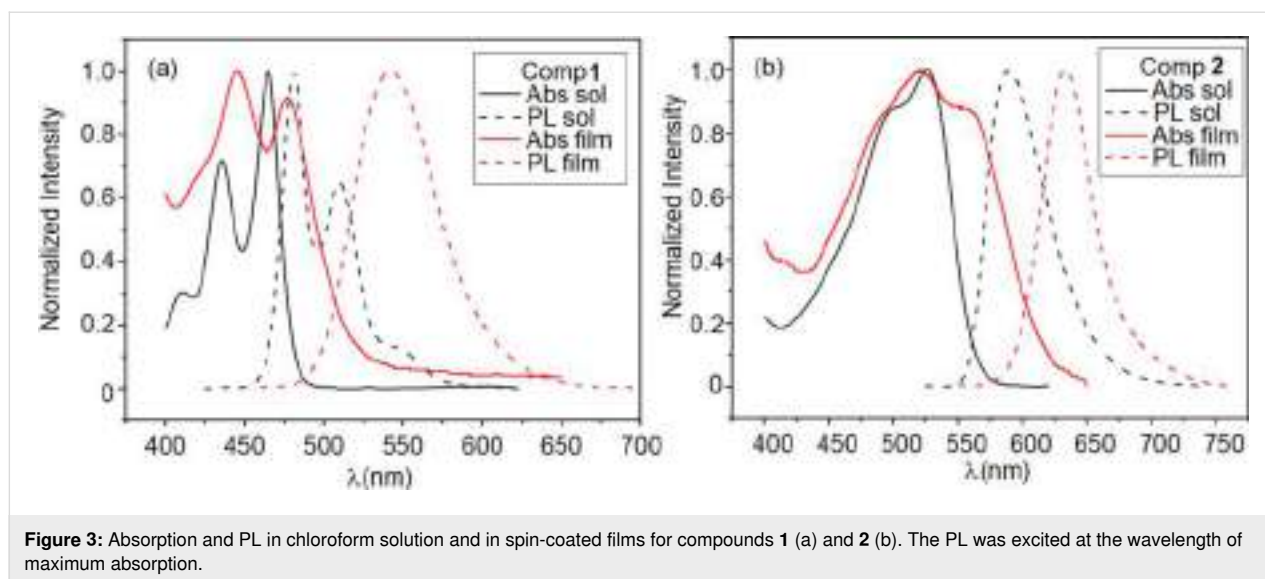


Figure 2: XRD measurements of **1** (a) and **2** (b) captured on cooling from the isotropic phase, indicating the Miller indices.



The PL in film was obtained as a function of temperature (Figure 4). The observed reduction of the PL intensity on heating is expected for organic semiconductors due to self-quenching aggregates and nonradiative decay processes that are thermally activated [32]. However, an increase in the emission intensity can be observed for **1** at the Col_{hex}–Iso transition. The stronger π -stacking aggregates present in the Col_{hex} of **1**, reduce the emission compared to the disordered isotropic phase. The enhanced and blue-shifted emission at the transition to the isotropic phase arise from the excited isolated molecules, where the exciton decays radiatively without diffusion. For the isolated molecules, the more localized π -orbital results in a higher energy emission state. The same effect was previously observed for another perylene-based ColLC compound, indicating the strong molecular interaction between neighboring molecules inside the columnar structure [33]. Due to the high temperature of the Iso phase for **2**, the PL intensity almost vanished. However, a slight increase could also be observed at the Col_{hex}–Iso transition. The reduction of PL at the Cr–Col_{rect} transition also reflects stronger molecular π -stacking of **2** in the Col_{rect} phase compared to the crystalline state.

The excited state lifetimes of **1** and **2** in chloroform solutions and spin-coated films, both excited at 401 nm, are listed in Table 2. The fitted fluorescence decay curves are shown in Supporting Information File 1 (Figure S1). For diluted solutions of **1** and **2**, monoexponential lifetimes in the nanosecond timescale were observed and attributed to emission from monomeric species (6.54 and 4.14 ns, respectively). In the spin-coated films, the best fitting of the decay curves of **1** and **2** indicated three and two lifetimes, respectively. Compound **1** displayed a dominant and longer lifetime compared to solution, 25.9 ns (66.83%), attributed to excimer emission, which usually

presents longer lifetimes compared to the monomeric species [34]. It agrees with the intensity inversion of the vibronic absorption bands and PL redshift in the spin-coated film compared to the solution. The intensity inversion suggests formation of H-aggregates, leading to excimer fluorescence [35]. Due to the similarity to the lifetime in solution, the 6.90 ns lifetime in the film is attributed to monomeric emission. The shortest lifetime of 0.90 ns can be related to the emission of aggregated species driven by π – π interactions [36], contributing to almost 20% of the total emission of **1**. The longer lifetime of **2** in film (3.84 ns) can be attributed to the monomeric emission as it is similar to the value observed in solution, while the shortest lifetime (1.58 ns) of aggregated π – π species dominates with 75.38% of the total emission.

Hole-only (ITO/PEDOT: PSS/**1** or **2**/Au) and electron-only devices (Al/**1** or **2**/Al) were fabricated to evaluate the positive and negative charge carrier transport of **1** and **2**. The active layers of **1** or **2** were spin-coated from chloroform solutions (10 mg/mL). Scheme S1 in Supporting Information File 1 illustrates the device structure with the energy levels of the layers.

Figure 5 shows atomic force microscopy (AFM) images to address the thickness and the morphology of the films of **1** and **2** deposited on the hole-only and electron-only device structures. The thickness of the films in these structures was 40 nm.

The films deposited on PEDOT:PSS for the hole-only devices indicate homogenous properties with low root mean square roughness (R_{rms}) of 1.7 nm and 2.8 nm for **1** (Figure 5a) and **2** (Figure 5b), respectively. The R_{rms} of the films deposited on Al for the electron-only devices are 1.1 nm for **1** (Figure 5c) and

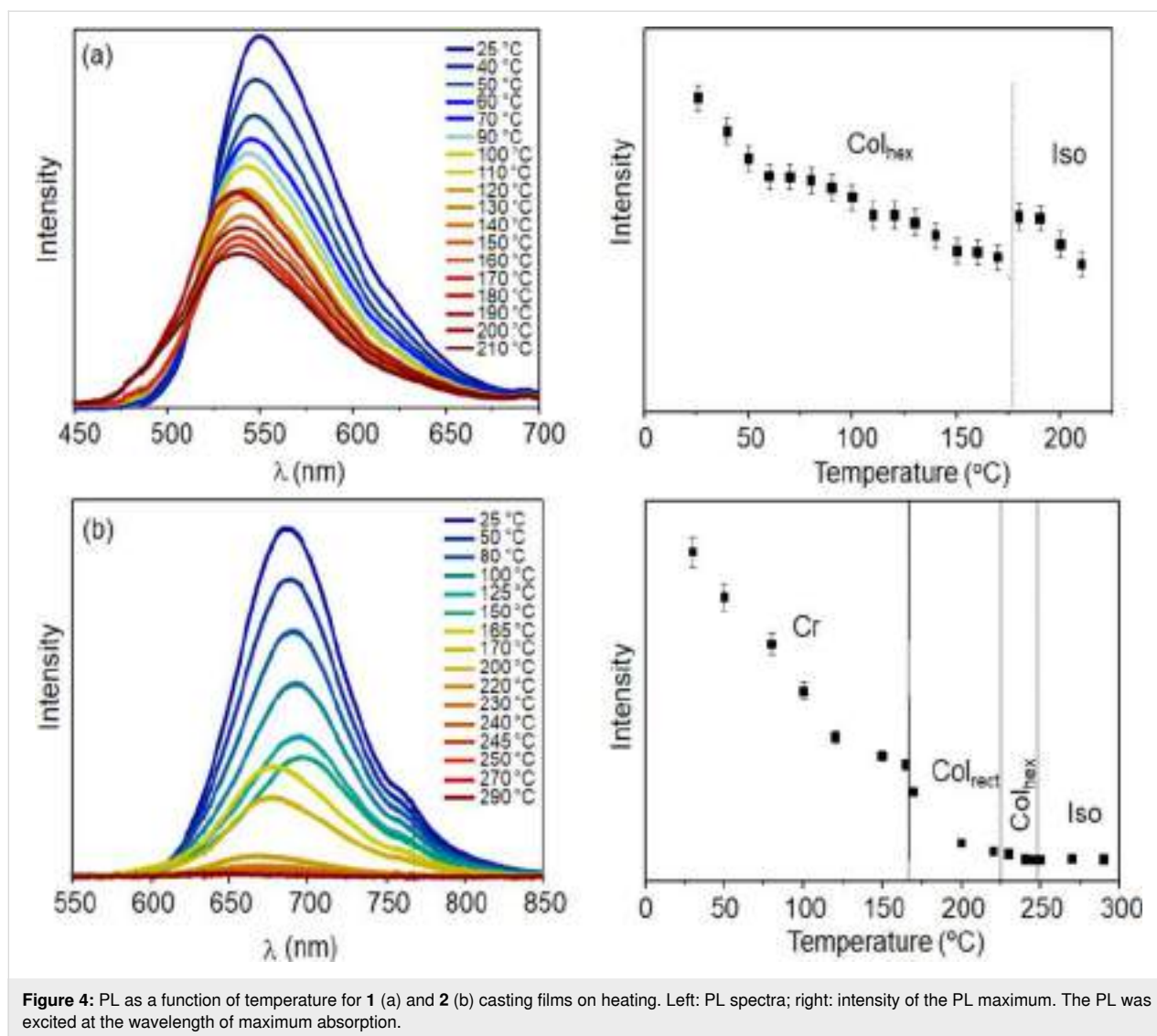


Figure 4: PL as a function of temperature for **1** (a) and **2** (b) casting films on heating. Left: PL spectra; right: intensity of the PL maximum. The PL was excited at the wavelength of maximum absorption.

Table 2: Excited state lifetimes and relative amplitudes of **1** and **2** in chloroform solutions and spin-coated films at room temperature.

Comp.	λ_{max} (nm) ^a	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_3 (ns)	A_3 (%)	χ^2
solution ^b								
1	487	6.54 ± 0.04	100	—	—	—	—	1.063
2	589	4.14 ± 0.03	100	—	—	—	—	1.008
film								
1	542	25.90 ± 0.2	66.83	6.90 ± 0.50	13.18	0.90 ± 0.20	19.99	0.997
2	633	3.84 ± 0.05	24.62	1.58 ± 0.03	75.38	—	—	0.946

^aFluorescence decay collected at maximum emission (λ_{max}), excited at 401 nm. ^bConcentration of 0.17 g L⁻¹.

16.0 nm for **2** (Figure 5d). XRD measurements of as-casted spin-coated films of **1** and **2** confirm their columnar order and polarized optical microscopy show small birefringent domains, indicating locally instead of macroscopic molecular alignment of the films (see Figure S2 in Supporting Information File 1).

Figure 6 shows the log–log plots of the J – V experimental curves for **1** and **2** in both device structures. In all cases, an ohmic regime is observed at low voltages, $J \propto V^n$ with $n \approx 1.0$, followed by a space charge limited current (SCLC) trap-limited regime. To determine the charge carrier mobility, a previously

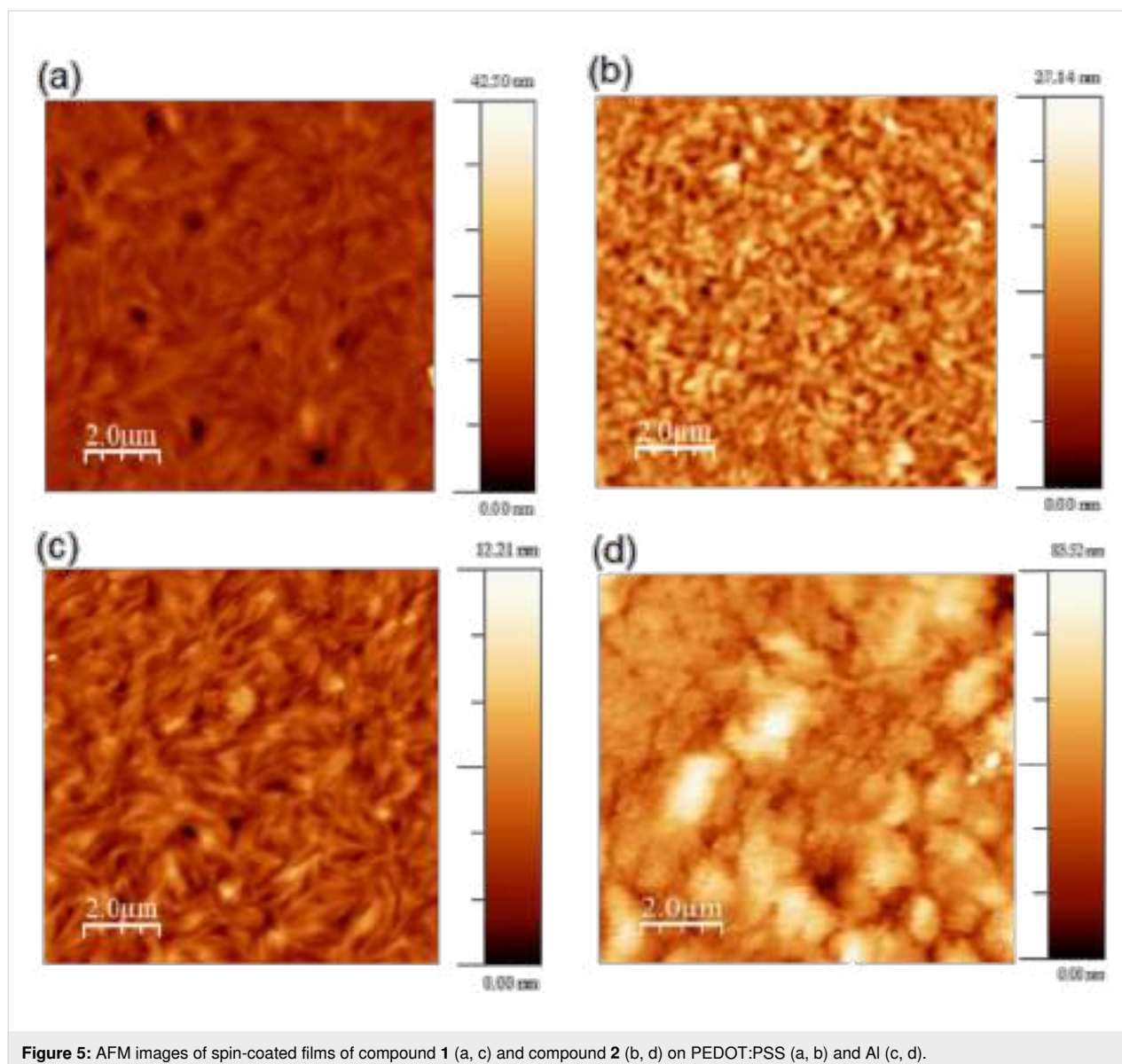


Figure 5: AFM images of spin-coated films of compound **1** (a, c) and compound **2** (b, d) on PEDOT:PSS (a, b) and Al (c, d).

published theoretical model was used [33], where an electric field dependent mobility of the form $\mu(E) = \mu_0 e^{\gamma\sqrt{E}}$ was considered. The parameters μ_0 and γ implicitly include a mono-energetic trap distribution and can be obtained from fitting the SCLC regimes of the experimental J - V curves. The fits for each device are shown as red solid lines in Figure 6, and the values of μ_0 and γ displayed in Table 3 were used to calculate the mobility $\mu(E)$ at an electric field of 6.0×10^5 V/cm.

Figure 7 shows the charge carrier mobility as a function of the applied electric field, calculated from $\mu(E) = \mu_0 e^{\gamma\sqrt{E}}$. The electron mobility of **1** is around one order of magnitude lower than that of holes, depending on the electric field. It suggests that this perylene-based material acts better as a hole-transporting material. The electron mobility of **2** is almost two orders of

magnitude higher than **1**. It may be related to the closer molecular packing of the Col_{rect} phase preserved in the crystal at room temperature, which improves the π -stacking and corroborates with the dominant emission of aggregated π - π species in the film observed in the lifetime measurement. The hole mobility of **2** is similar to **1**, but its electron mobility is slightly higher, indicating that this pyrene-based molecule can act as an ambipolar transporting layer, in agreement with the literature [24]. It is important to emphasize that the charge carrier mobility of columnar liquid crystals can be improved by five orders of magnitude due to molecular alignment of the film in the device structure [33].

Usually, the π -system conjugation and the frontier orbitals energies dominates the charge transport [37,38]. Therefore, to better

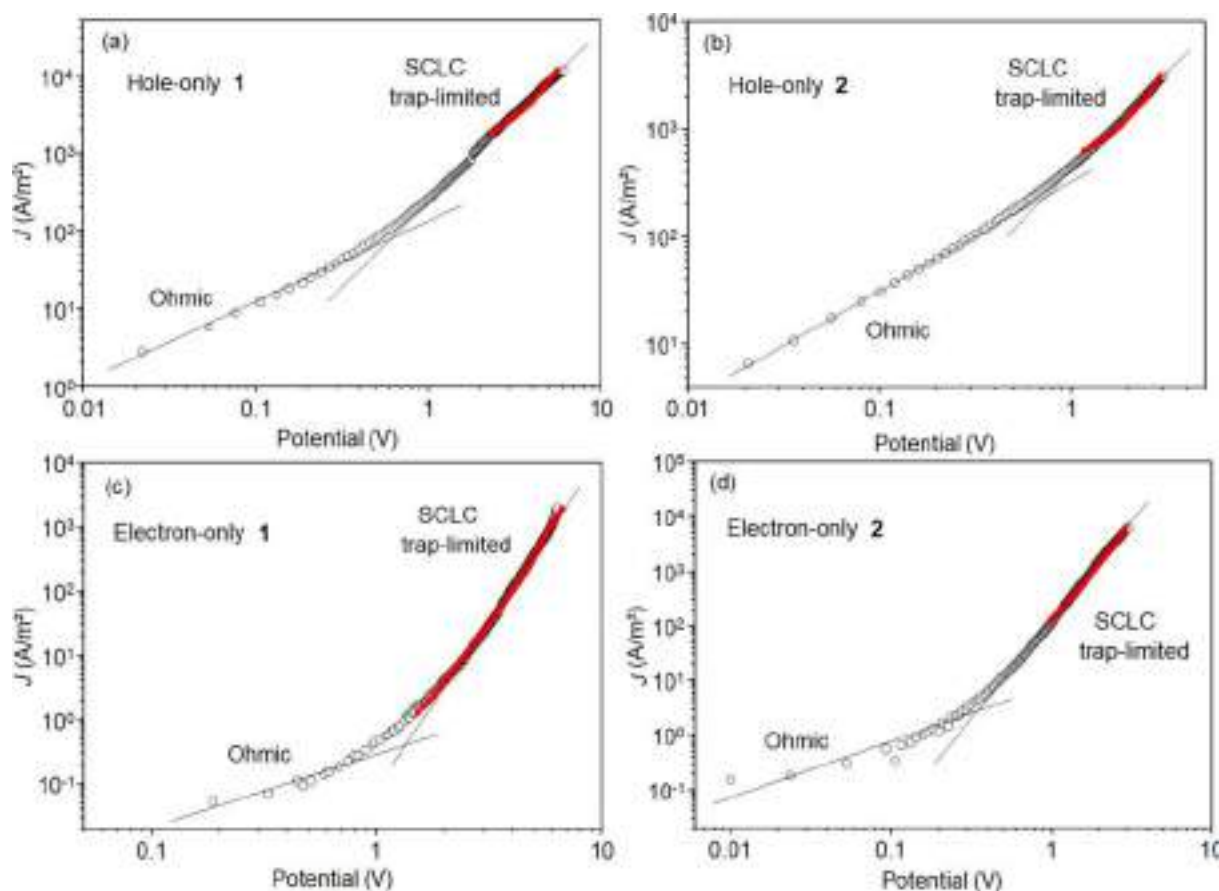


Figure 6: Log–log plot of the J – V curves of the hole-only (a,b) and electron-only (c,d) of **1** (a,c) and **2** (b,d). The open circles are the experimental data, and the red solid lines indicate the theoretical fitting. V_{Ω} is the threshold voltage between the ohmic and SCLC trap-limited regimes.

Table 3: Fitting parameters and charge carrier mobility of hole-only and electron-only devices fabricated with **1** and **2**.

Comp.	γ (cm V ⁻¹) ^{1/2}	μ_0 (cm ² V s ⁻¹)	μ (cm ² V s ⁻¹) ^a	Slope SCLC
hole-only				
1	2.49×10^{-3}	5.82×10^{-7}	1.2×10^{-5}	2.1
2	3.18×10^{-3}	6.62×10^{-7}	2.7×10^{-5}	1.8
electron-only				
1	7.18×10^{-3}	2.54×10^{-10}	6.4×10^{-7}	5.2
2	5.74×10^{-3}	2.24×10^{-7}	1.3×10^{-4}	3.6

^aMobility values for an electric field of 1.0×10^6 V cm⁻¹. Films of **1** and **2** were 40 nm thick.

understand the charge mobility of compounds **1** and **2**, we obtained their ground state geometry using DFT within the B3LYP/def2-TZVP(-f) level of theory (Figure 8a). To reduce computational efforts, isopropyl moieties were used instead of the large aliphatic substituents of molecules **1** and **2**. The π electron systems of both molecules are predominantly planar, with **2-iso** showing a slight deviation from planarity due to the ster-

ical proximity of the dicarboximide oxygens with the adjacent bay hydrogens. The frontier orbitals and their energies are shown in Figure 8b. In **1-iso**, only the two hexagonal imide groups affect the HOMO/LUMO localization, whereas the pentagonal central imide group is little affected. In **2-iso**, both pentagonal are relevant to the HOMO/LUMO localization, whereas the two terminal benzene rings are little affected. The

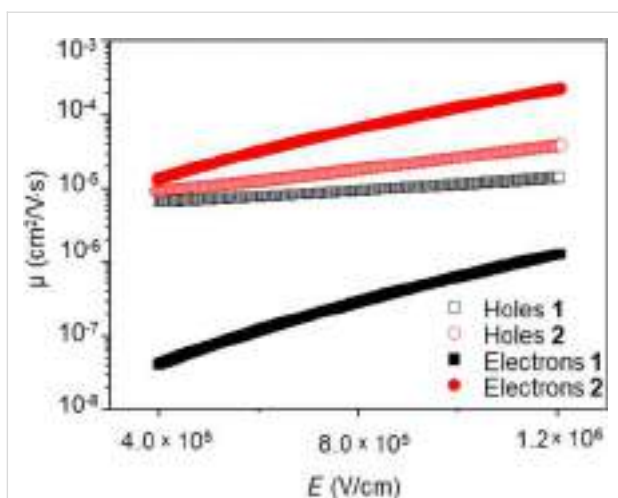


Figure 7: Charge carrier mobility as a function of the applied electric field obtained for the hole-only and electron-only devices of compounds **1** and **2**.

cartesian coordinates of the optimized isopropyl derivatives geometry are presented in Supporting Information File 1.

Conclusion

The electron and hole-transporting characteristics of two columnar liquid crystals were evaluated with electron-only and hole-only devices. Compound **1** is a perylene-based molecule presenting a columnar hexagonal mesophase stable at room temperature, and compound **2** is pyrene-based crystalline with columnar rectangular order preserved at room temperature. Photoluminescence lifetime measurements indicated that molecular aggregation and π -stacking interactions dominate the photophysics of films. While **1** presents majority hole transport, **2** is moderately ambipolar. The electron transport of **2** is around two orders of magnitude higher than **1**, which can be associated to the larger conjugation of **2**. This work highlights the potential of pyrene-based columnar liquid crystals as electron-transporting materials.

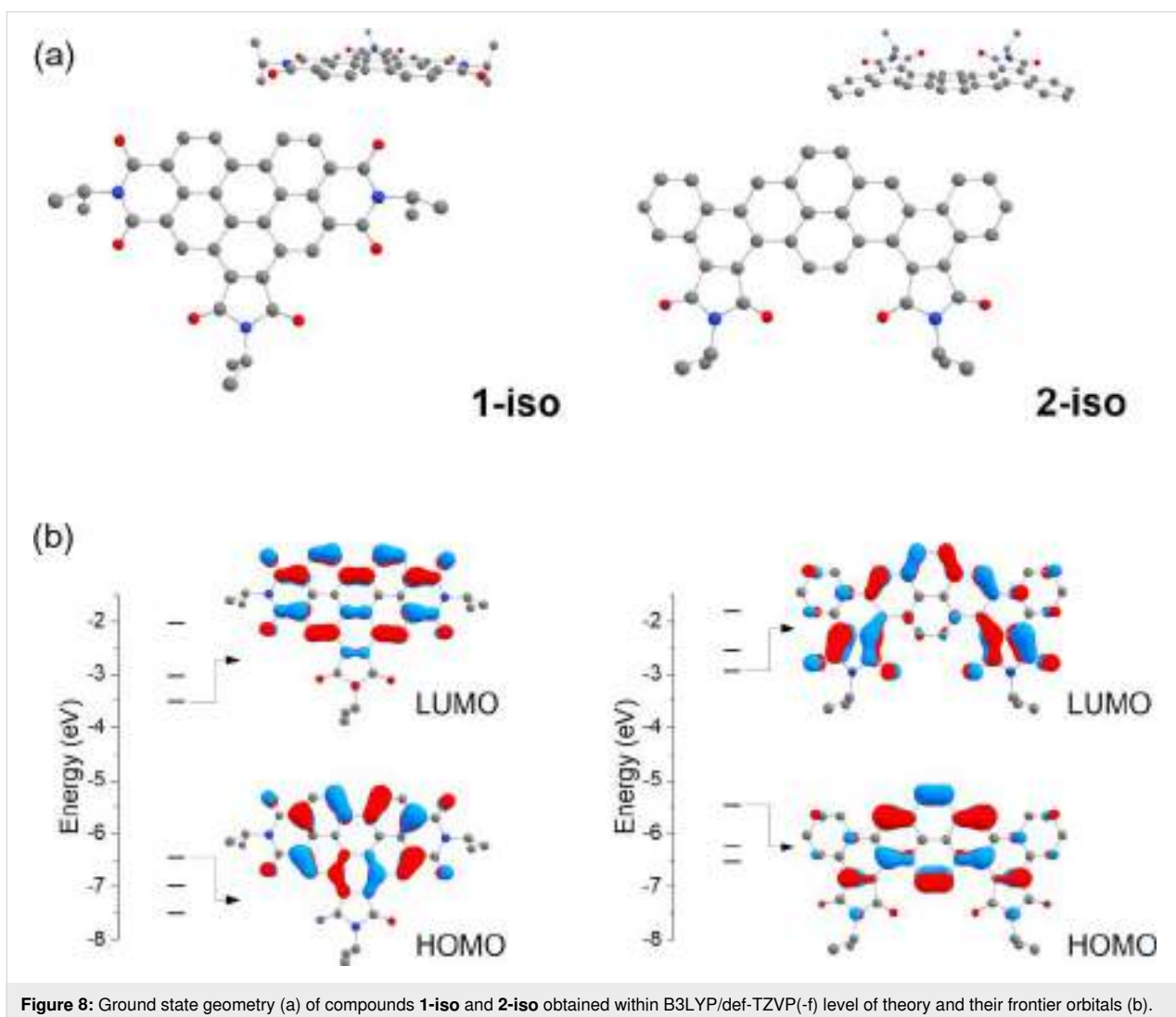


Figure 8: Ground state geometry (a) of compounds **1-iso** and **2-iso** obtained within B3LYP/def-TZVP(-f) level of theory and their frontier orbitals (b).

Experimental

Raman spectra were obtained in an Anton Paar spectrometer, Cora 5001 model, under an excitation laser line at 785 nm and 450 mW power source. The exposure time was around 160 ms and 1 accumulation. The sample powder was placed in a glass slide under the objective lens and performed the autofocus.

XRD measurements were performed with an X'Pert PRO (PANalytical) diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) equipped with an X'Celerator detector. A small amount of **1** or **2** was deposited onto a glass substrate and heated to the isotropic liquid phase. The diffracted radiation was collected in continuous mode from 2° to 30° (2θ angle) at specific temperatures during the cooling down to room temperature. The temperature was controlled with a TCU2000-temperature control unit (Anton Paar).

The absorbance spectra in solution and in spin-coated films were collected with an Ocean Optics USB4000 spectrophotometer. The PL spectra were collected with a Hitachi fluorescence spectrophotometer (Model F-7000) and the samples were excited at the wavelength of maximal absorption. For the PL as a function of the temperature, casting films were placed on a hot stage (Mettler Toledo FP-82) and excited with a UV lamp of 365 nm wavelength. The emission spectra were captured using an optical fiber placed close to the film to guide the light until the Ocean Optics USB4000 spectrophotometer.

Time-resolved fluorescence decay curves were recorded using the technique of time-correlated single photon counting [39] with a FluoTime 200 (PicoQuant). Excitation was provided using a 401 nm pulsed diode laser with repetition rates varying from 5.0 to 20 MHz. Fluorescence was collected perpendicular to excitation and passed through a polarizer set at the magic angle. The detection system consisted of a monochromator and a multichannel bases photomultiplier (Hamamatsu R3809U-50). Lifetimes were obtained by fitting the fluorescence decay curves with exponential functions using FluoFit[®] software and the plots of weighted residuals and reduced chi-square were used to determine the best fits during the analysis procedure.

AFM measurements of the organic films were performed using a Nanosurf EasyScan2 apparatus in tapping mode with a scanning rate of 1.0 Hz covering 512×512 lines.

Hole-only devices were fabricated using indium tin oxide (ITO) coated glass plates (sheet resistance of about $15 \text{ } \Omega/\text{sq}$) with a thin layer of PEDOT:PSS (purchased from Sigma-Aldrich) deposited by spin coating at 3000 rpm during 30 s, followed by annealing at 110°C for 5 min as anodic electrode. For the electron-only devices, the anodic electrode consisted of a 100 nm

thick Al layer vacuum deposited onto a glass substrate, 10^{-7} mbar at a rate of $2 \text{ \AA/s}$. Compounds **1** and **2** were spin-coated from chloroform solutions (10 mg/mL) at 2000 rpm for 30 s, followed by annealing at 40°C for 10 min. The top electrodes were vacuum deposited (10^{-7} mbar at a rate of $2 \text{ \AA/s}$, 100 nm) onto the **1** and **2** layers, Au (for hole-only) and Al (for electron-only). The active area of the devices was 8 mm^2 . The J - V curves were measured at room temperature (25°C) inside a glove box under nitrogen atmosphere using Keithley's Series 2400 Source Measure Unit (SMU) instruments.

Ground state geometries of the molecules were optimized in a vacuum, using the Orca 5.0.3 [40] software package within B3LYP/Def2-TZVP(-f) level of theory [41-45]. Dispersion effects were included using Grimme's D3 correction with Becke-Johnson (BJ) damping [45,46]. The evaluation of the four-center integrals was accelerated with the RIJCOSX algorithm [47,48]. RIJ requires the specification of an auxiliary basis set for the Coulomb part (Def2/J) and a numerical integration grid for the exchange part (DefGrid-2) [49]. Analytical harmonic vibrational frequency calculations were conducted to verify if the ground state is a minimum on the potential energy surface. Images of the complex geometries were obtained using the Chemcraft program (<http://www.chemcraftprog.com>).

Supporting Information

Supporting Information File 1

Additional data and information.

[<https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-19-128-S1.pdf>]

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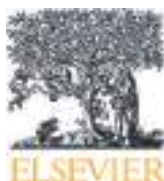
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Strongly luminescent and liquid-crystalline π -conjugated 2-methyl [1,2,3]benzotriazoles with a linear donor-acceptor-donor structure

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ABSTRACT

Symmetrical 2-methyl[1,2,3]benzotriazole (BZT) derivatives with elongated peripheral units connected via acetylenic triple bonds present calamitic thermotropic mesomorphism with nematic and smectic phases. They show intense photoluminescence with near-unity quantum yields in solution. The peripheral groups significantly influence the excited-state lifetime. Fluorescence quenching is observed in the presence of C₆₀, testifying of charge transfer to the fullerene acceptor. The varying sterical demand of the different substituents considerably influences the efficiency of the charge transfer induced fluorescence quenching. HOMO, LUMO and band gap energies ranged from -5.15 to -5.97 eV (ionization potential), -2.47 to -2.96 eV (electron affinity) and 2.68 to 3.08 eV (optical band gap).

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1. Introduction

The electronic properties of linear π -conjugated molecules have acquired a growing importance in various areas of chemistry and condensed matter physics. These molecular materials represent the simplest models of molecular wires and have contributed to the emergence of the concepts of molecular electronics [1,2]. In particular, the π -conjugated compounds based on donor-acceptor (D-A) or donor-acceptor-donor (D-A-D) types are widely investigated as active materials [3], because the band gap and electro-optical properties can be tuned by judicious choice of the fluorophore's donor and acceptor moieties. The fusion of D-A-D units leads to the formation of highly anisotropic and rigid structures which are beneficial to obtain calamitic liquid crystals. Luminescent liquid crystals (LLCs) have gained enormous interest in optoelectronic applications [4–6], as they can self-organize in periodic arrangements leading to good charge transport properties, while retaining fluidity that allows self-healing features and dynamic properties [7–10]. Moreover, LLCs are particularly engaging for applications involving polarized light [11,12].

Fused heterocyclic compounds are valuable scaffolds which play an important role as structural and functional units in LLCs. The benzazoles

such as 2,1,3-benzoxadiazole (BOD), 2,1,3-benzothiadiazole (BTD) and 2,1,3-benzoselenadiazole (BSD) have played an important role as acceptor building blocks in the development of linear π -conjugated materials for applications in organic electronic devices such as organic field effect transistors [13], organic light emitting diodes [14,15] and organic solar cells [16,17]. All these π -conjugated benzazoles have characteristic strong fluorescence properties in both solution and the solid state, large Stokes shifts and good photostabilities [18–20].

A much less explored benzazolic system is 1,2,3-benzotriazole (BTZ). Benzotriazole is a moderate electron acceptor moiety due to its polarizable imine unit [21–25]. Sanchez and Prieto [26,27] synthesized T-shaped structures of 2H-benzo[d][1,2,3]-triazoles and studied their photophysical properties. These BTZ materials exhibited optical waveguiding properties and the possibility of tunable emission and band gap. More recently Zade [28] prepared a series of D-A-D type molecules based on benzazoles modifying the central heteroatom (N, O, S and Se) and observed that the 1,2,3-benzotriazole derivative showed a superior luminescence quantum yield compared to its O, S and Se homologs.

However, there are no reports for linear π -conjugated molecules with LC properties based on 1,2,3-benzotriazoles. In this work, we report the synthesis, characterization and study of thermal properties of symmetrical 2-methyl-1,2,3-benzotriazole derivatives with different peripheral units connected to BTZ core via acetylenic triple bonds. The

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peripheral groups were chosen in order to explore the geometrical limits to mesogenic behavior and to tune the photophysical and electrochemical properties.

2. Results and discussion

2.1. Synthesis

A stepwise synthetic protocol has been followed to develop the final compounds based on 2-methyl[1,2,3]-benzotriazoles. A series of π -conjugated rod-shaped D- π -A- π -D molecules was synthesized with various peripheral units following a Sonogashira cross-coupling protocol as shown in Scheme 1.

4,7-Dibromo-2,1,3-benzothiadiazole **1** was selected as key starting material for a sulfur extrusion reaction using sodium borohydride and catalytic cobalt chloride in a mixture of ethanol/tetrahydrofuran to obtain the diamine **2** in 92% yield. The resulting 3,6-dibromobenzene-1,2-diamine was subjected to reaction with sodium nitrite in acetic acid to afford 4,7-dibromo-1,2,3-benzotriazole **3** in 91% yield. The alkylation of this benzotriazole with iodomethane and potassium carbonate in dimethylformamide gave both 1-methyl-[1,2,3]-benzotriazole and 2-methyl-[1,2,3]-benzotriazole, and the latter building block **4** was easily isolated by column chromatography. In parallel, the aryl acetylenes **5b-g** were prepared from the respective aryl halides via palladium catalyzed cross-coupling using 2-methyl-3-butyn-2-ol, followed by elimination of the protective isopropanol group [29]. The final molecules **6a-g** containing the 2-methyl[1,2,3]benzotriazole core were obtained via the Sonogashira coupling reaction between one equiv. of the 4,7-dibromo-2-methyl[1,2,3]benzotriazole and two equiv. of the corresponding alkyne **5a-g**, using bis(-triphenylphosphine)palladium (II)

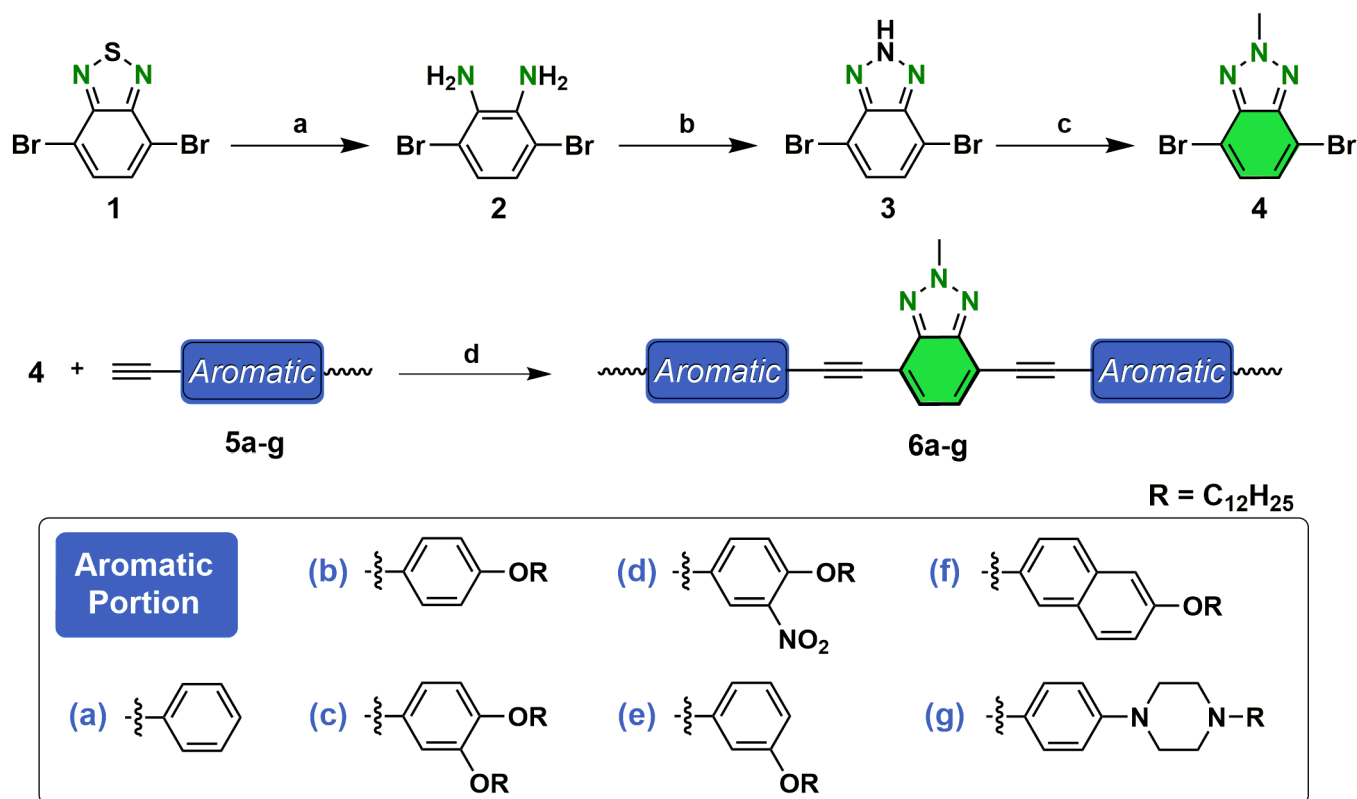
dichloride, triphenylphosphine and copper iodide in triethylamine and tetrahydrofuran. After purification by column chromatography, the desired molecules were obtained in satisfying yields (58–79%).

All of the final compounds synthesized (**6a-g**) were characterized by ^1H and ^{13}C NMR and IR spectroscopy and APPI mass spectrometry.

2.2. Liquid crystalline behavior

The mesomorphic properties of the compounds **6a-g** were investigated by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). The transition temperatures and enthalpy values are given in Table 1.

It is generally observed in liquid crystals that lateral substitution has a greater effect on melting points (i.e. Crystal-to-LC transition temperatures) than terminal substitution [30]. Thus, the 2-methyl-1,2,3-benzotriazole system was designed to produce steric repulsion by the methyl group and hinder close parallel packing, thereby increasing the free volume and lowering the melting point. As lateral alkyl substitution is known to suppress quickly the mesogenic phase range even with moderate alkyl length and number [31], we did not attempt to replace the lateral group by a more voluminous substituent on the nitrogen, but instead aimed at keeping the melting and clearing transitions at moderate temperatures by employing relatively long dodecyl moieties as terminal chains. Further selective lowering of the melting point, to obtain liquid crystalline behavior at or near room temperature, might be predictable by introducing a plurality of terminal chain lengths. The POM analysis allowed to identify that only **6b**, **6f** and **6g** displayed enantiotropic liquid crystalline behavior (Fig. 1) with decreased melting and clearing temperatures compared to similar benzothiadiazoles [32]. The textures observed by POM on cooling **6f** and **6g** from the isotropic phase were



Reagents and Conditions: (a) NaBH_4 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, THF/EtOH; (b) AcOH, NaNO_2 ; (c) CH_3I , K_2CO_3 , butanone; (d) $\text{PdCl}_2(\text{PPh}_3)_2$, CuI, TPP, NEt_3 /THF.

Scheme 1. Synthesis of the rod-shaped benzotriazoles **6a-g**.

Table 1
Phase transition temperatures (°C) and enthalpies (kJ·mol⁻¹) for compounds **6a-g**.

Compound	Transition ^c	T/°C, heating (ΔH /kJ·mol ⁻¹) ^a	T _{dec} /°C ^b
6a	Cr-Iso	153–154	340
6b	Cr-SmC	143 (48.0)	380
	SmC-Iso	146 (broad)	
6c	Cr-Iso	102 (79.4)	391
6d	Cr(I)-Cr(II)	45 (13.5)	336
	Cr(II)-Iso	167 (43.4)	
6e	Cr-Iso	78 (46.2)	384
6f	Cr-SmC	160 (38.9)	386
	SmC-N	203 (5.5)	
	N-Iso	209 (broad)	
6g	Cr-SmC	172 (34.2)	369
	SmC-N	246 (1.8)	
	N-Iso	261 (2.1)	

^a Determined by POM and DSC measurements (10 °C/min) on the second heating cycle.

^b Determined by TGA, onset of decomposition in nitrogen (10 °C/min).

^c Cr = Crystal, N = Nematic, SmC = Smectic C, Iso = Isotropic liquid.

identified as corresponding to nematic (N) and smectic C (SmC) phases [30].

The cooling of these samples from the isotropic phase induced the nucleation of birefringent liquid droplets, which later merge to give the schlieren texture typical of a nematic mesophase. On continuing the cooling of samples, the nematic phase transits slowly to a striated texture like a wave, characterizing a N-SmC transition. Further cooling of these compounds leads to a broken fan-shaped texture of the SmC mesophase.

Fig. 2 shows the thermogram obtained by DSC analysis of second heating and cooling at 10 °C/min and the transitions for sample **6f**. The inserted frame Fig. 2b displays the POM texture of the nucleating nematic phase.

A single mesophase was observed with **6b** by POM. On cooling, this material exhibited a colorful texture from the isotropic that quickly gives way to the crystalline state. During the second heating cycle, the fusion for the mesophase occurred as a fast wave, revealing the same texture. The transition to this mesophase can be observed by differential scanning calorimetry (DSC) during cooling as well as during heating of the material (see ESI). During heating the transition is observed as a shoulder at 146 °C and during cooling a slight separation of the transitions is observed at 138 °C and 134 °C. The energy involved in the process at 138 °C is about 3.4 kJ/mol⁻¹, a typical value for a liquid-to-smectic transition. The XRD study was essential to confirm the mesophase.

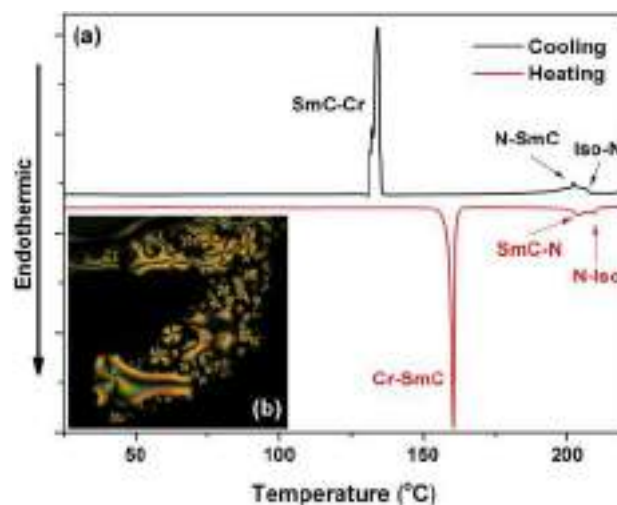


Fig. 2. (a) DSC results for compound **6f** (scan rate 10 °C/min); (b) The inset shows a POM image obtained during the Iso-N transition of **6f** at 202 °C on cooling.

To explore the limits of the mesogenic potential of the diarylethynyl-BTZ structure **6**, we introduced lateral substituents on the terminal aryl units, and found that the introduction of lateral substituents such as nitro (**6d**) or alkoxy (**6c** and **6e**) does efficiently suppress the liquid crystalline behavior.

The thermal stability of the compounds **6a-g** was investigated by thermogravimetric analysis (TGA) under nitrogen atmosphere. The initial thermal decomposition temperatures (T_{dec} , at 5% weight loss) of all the seven compounds were above 330 °C, indicating a good thermal stability in all cases. The nitro derivative **6d** had the lowest decomposition temperature (T_{dec} = 336 °C), compared to the other five (T_{dec} = 369–391 °C).

2.3. X-ray diffraction studies

In order to verify the liquid crystal structure of the BTZ compounds **6b**, **6f** and **6g**, XRD analysis was performed on cooling from the isotropic state at temperatures within the presumed smectic mesophase range. The diffractograms showed in the low angle region two reflection peaks, assigned to the Miller indexes (d_{001}) and (d_{002}), where the ratio of the associated interlayer distance $d_{001}/d_{002} \sim 2$ is in agreement

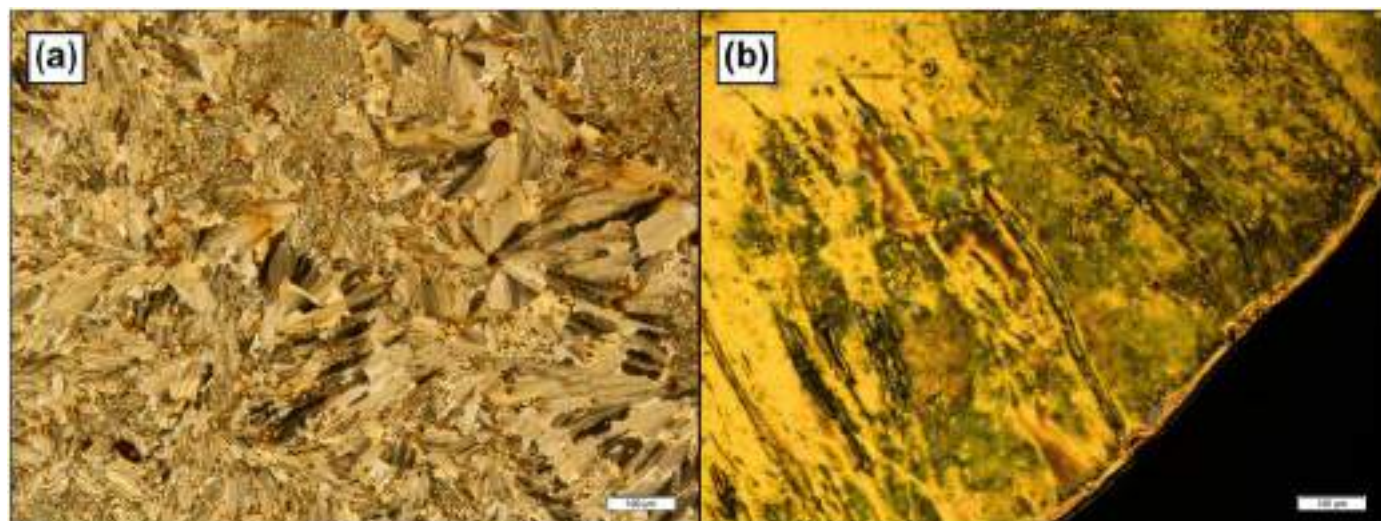


Fig. 1. Polarized optical photomicrographs (100× magnification) of compounds: (a) **6f** at 139 °C and (b) **6g** at 255 °C on cooling.

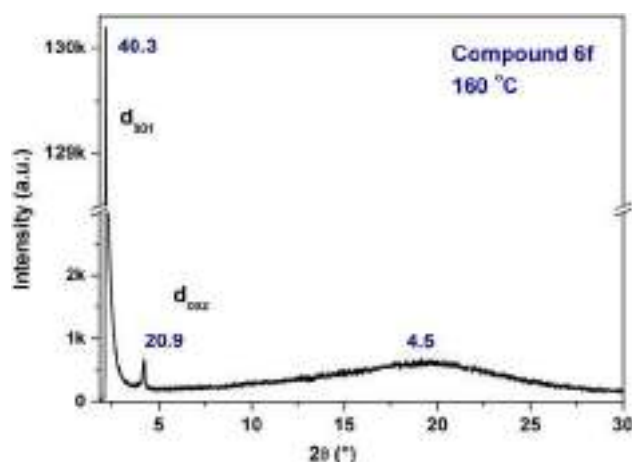


Fig. 3. XRD patterns for **6f** collected at 160 °C in the SmC mesophase.

with a lamellar structure, characteristic of smectic mesophases. Fig. 3 shows a representative diffractogram for **6f**.

The intense peak in the low-angle region (d_{001}), testifies in all three cases of an interlayer spacing that is more than a fifth smaller than the length of the extended molecules, confirming, together with the characteristic POM textures, the transition enthalpies and the absence of diffraction peaks other than d_{001} and d_{002} , the tilted SmC nature of the mesophase (Table 2).

2.4. Photophysical properties

2.4.1. Absorption and fluorescence

The photophysical properties of the 2-methyl[1,2,3]benzotriazoles in solution are depicted in Table 3. Absorption and fluorescence spectra of **6a-g** were taken in diluted solutions of chloroform (10^{-5} M). Representative spectra for the final compounds are given in Fig. 4. All molecules exhibited absorptions of between 325 and 450 nm, with the maxima at around 390 nm. These absorption bands are assigned to $\pi-\pi^*$ transitions due to their high molar absorption coefficients ($\epsilon = 3.5\text{--}4.8 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$).

All of the final benzotriazoles, with the exception of nitro derivative **6d**, exhibited intense fluorescence when excited at the maximum absorption wavelength in solution. The presence of the nitro group completely quenched the fluorescence of molecule **6d** in solution. This behavior points to an efficient intersystem crossing process promoted by the strong electron-withdrawing power of the $-\text{NO}_2$ group [33].

For the other compounds the maximum emission peaks varied between 404 and 472 nm (Fig. 4b).

The homolog **6a** with unsubstituted terminal phenyl groups expectedly showed the shortest-wavelength emission. The presence of electron donor units such as alkoxy (**6b**; **6c**) and piperazine (**6g**) connected to bis(phenylethynyl)BTZ resulted in red shifts of 45, 55 and 65 nm, respectively. Meta-alkoxy substituted **6e** showed a red shift of only 6 nm due to the lesser donor effect of a meta substituent compared to its para analog. The Stokes shifts are in the range of

Table 3
Summary of photophysical properties of **6a-g** in chloroform solution.

Sample	Absorption ^b λ_{max} (nm) ($\epsilon/10^4$) ^a	Emission λ_{max} (nm) ^{b,c}	Stokes shift (cm^{-1})	Φ_{PL}	τ_f/Ns ± 0.01	$K_r/(\text{ns})^{-1}$	$K_{nr}/(\text{ns})^{-1}$
6a	369 (4.1)	404; 424	2348	0.99	1.31	0.76	0.01
6b	383 (4.0)	434; 454	3068	0.99	1.49	0.66	0.01
6c	389 (4.4)	460	3968	0.90	1.59	0.57	0.06
6d	376 (4.8)	–	–	–	–	–	–
6e	373 (4.0)	410; 430	2419	0.96	1.32	0.73	0.03
6f	395 (3.5)	444; 464	2794	0.92	1.16	0.79	0.07
6g	398 (3.9)	472	3939	0.39	1.86	0.21	0.33

K_r and K_{nr} are the radiative and non-radiative rate constant, evaluated by $K_r = \Phi_{\text{PL}}/\tau_f$ and $K_{nr} = (1 - \Phi_{\text{PL}})/\tau_f$, respectively. The excited lifetimes, τ_f , were measured at the maxima of the emission intensity after excitation at 401 nm.

^a Units = $\text{L mol}^{-1} \text{ cm}^{-1}$.

^b Chloroform solution ($1.0 \times 10^{-5} \text{ mol L}^{-1}$).

^c Excited at maximum absorption.

2348–3968 cm^{-1} , with a small overlap region between absorption and emission. The unsubstituted and alkoxy-substituted homologs **6a**, **6b**, **6c**, **6e** as well as the naphthylene homolog **6f** exhibited fluorescence quantum yields (Φ) between 0.90 and 0.99 (see Table 3). Besides the non-fluorescent nitro-derivative **6d**, the only compound that exhibited lower photoluminescence efficiency was **6g** (0.39) with a piperazine donor group. The strongly donating phenylpiperazine portion results in a stronger intramolecular charge transfer (ICT), which induces fluorescence at higher wavelengths, a stronger color dependence on solvent polarity and lower fluorescence quantum yields probably related to the formation of twisted intramolecular charge-transfer (TICT) states. [34]. The excellent quantum yield values for **6a**, **6b**, **6c**, **6e** and **6f** are superior to those of the previously reported 2-benzo[1,2,3]triazoles [26,27]. The high fluorescence quantum yields may result from the nonbonding orbital of the nitrogen atom being perpendicular to the plane of the ring, which allows it to overlap with the π orbitals on the adjacent atoms to enhance the system's conjugation [33].

All homologs except **6d** showed mono-exponential fluorescence decay with lifetimes in the nanosecond timescale (Table 3 and SI), characteristic of monomeric emission. The singlet excited-state lifetimes (τ_f) of compounds **6a-g** were very similar to each other, with a modest increase of lifetime with increasing donor effect in the order **6a** (no alkoxy) – **6e** (meta) – **6b** (para) – **6c** (para + meta) – **6g** (piperazine). **6f**, with its conjugation elongated by the naphthyl group, showed the shortest lifetime. The fluorescence decay curves are shown in the supporting information (see ESI). Moreover, the radiative and non-radiative rate constants of these systems, in chloroform solution, are also affected by the nature of peripheral groups (see Table 2). **6f** with a conjugation elongated by the naphthyl group showed the highest radiative rate constants, while the lowest non-radiative rate constants are exhibited by molecules with peripheral alkoxy donor groups (**6b**, **6c** and **6e**). The piperazine homolog **6g** showed the lowest radiative rate constants and the highest non-radiative rate constants.

The benzotriazoles **6a-g** have also been studied in the form of thin films prepared by spin-coating. In general, the films exhibited hypsochromic shifts between 24 nm and 43 nm for the absorption bands, while the emission showed bathochromic shifts in the range of 6 and 65 nm in relation to the solution. Due to aggregation-induced quenching, the fluorescence quantum yields of the thin films, between 11 and 22%, were much lower than in solution, except for **6b**, which with 43% maintained a rather high quantum yield in the condensed film (see ESI).

2.5. Solvatochromic properties

In order to study the solvatochromic effect, the absorption and fluorescence spectra of **6a-g** were taken in diluted solutions of heptane, toluene, chloroform, tetrahydrofuran, acetone, dimethylformamide and

Table 2
Structural parameters of **6b**, **6f** and **6g**.

Compound	L (Å) ^a	d_{001} SmC (Å) ^b
6b	47.8	37.1
6f	50.6	40.3
6g	51.8	40.2

^a Estimated by ChemBio3D Ultra Software.

^b Experiment taken on cooling from isotropic phase.

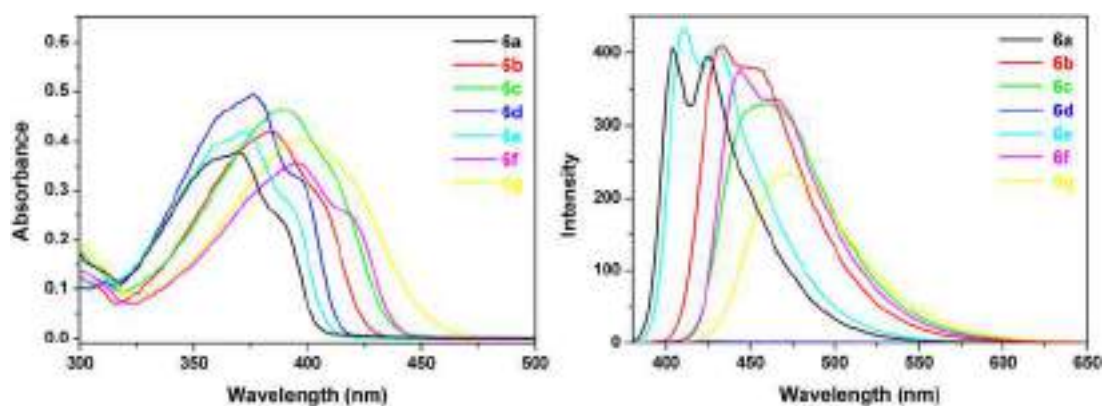


Fig. 4. Absorbance (left) and emission (right) spectra for compounds **6a-g** in chloroform solution (10^{-5} mol L^{-1}).

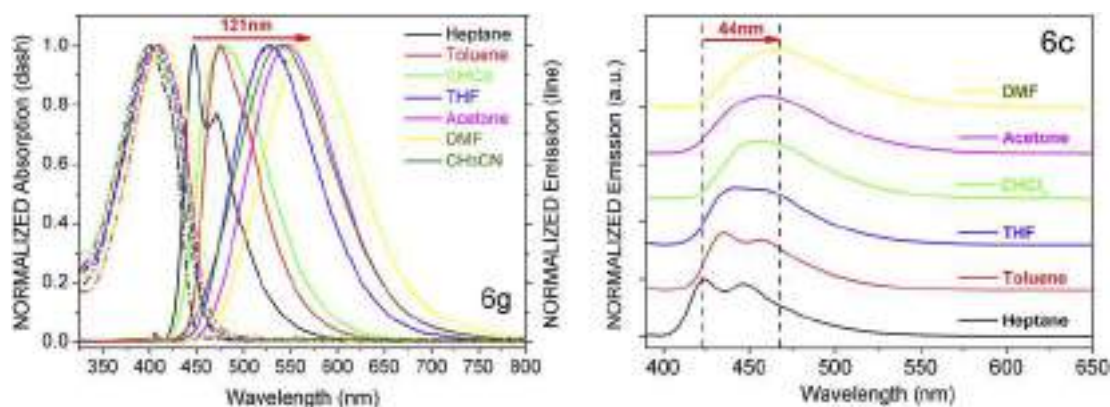


Fig. 5. Normalized absorbance and emission spectra for **6g** in different solvents (left). Normalized emission spectra for **6c** in different solvents (right).

acetonitrile. The absorption and emission spectra of **6g** and **6c** in various solvents are shown in Fig. 5. The photophysical properties of compound **6c** in solution of several solvents are summarized in Table 4. All the samples presented well-resolved absorption and emission bands. Only small spectral variations are observed for the absorption spectra, regardless of the polarity of the solvents. However, there is a prominent red shift in the emission peaks with increasing solvent polarity (see ESI), which is greatest for the homolog **6g** with the strongest donor group.

The maximum emission bands are shifted to longer wavelengths by increasing the solvent polarity, e.g., from 446 nm (hexane) to 567 nm (DMF) in the case of piperazine derivative **6g**. The increase of the Stokes' shift with increase of the dielectric constant of the solvent indicates a stabilization of the excited states by the polar solvents [35]. This behavior implies that the excited state of these compounds is more polar than the ground state.

Table 4
Photophysical properties of compound **6c** in solution of different solvents.

Solvents	$\lambda_{abs}^{a,b}$ (nm)	$\lambda_{em}^{b,c}$ (nm)	Stokes shift (cm^{-1})	τ_1 (ns)
Heptane	386	424	2322	1.12
Toluene	391	435	2587	1.15
$CHCl_3$	389	454	3681	1.59
THF	388	440	3046	1.30
Acetone	385	460	4235	1.63
DMF	389	468	4339	1.75

^a Units = $L \text{ mol}^{-1} \text{ cm}^{-1}$.

^b Chloroform solution (1.0×10^{-5} mol L^{-1}).

^c Excited at maximum absorption.

The excited state lifetimes of **6c** in different solvents are shown in Table 4. The sample exhibited single lifetimes in the nanosecond range in all solvents studied, suggesting that emissions arise only from fluorescent monomers of **6c**. In heptane, toluene and THF solution, the fluorescence decay exhibited a single excited state lifetime of 1.1 to 1.3 ns. For polar solvents (DMF and acetone), **6c** exhibited slightly longer lifetimes in range of 1.6 to 1.8 ns (see ESI for decay curves).

The influence of solvent polarity on the optical properties of a fluorophore can be estimated using the Lippert-Mataga equation [36]. The plot of the Stokes shifts ($\Delta\nu$) as a function of orientation polarizability (Δf) for **6b** is shown in Fig. 6. The increase of $\Delta\nu$ with an increase of

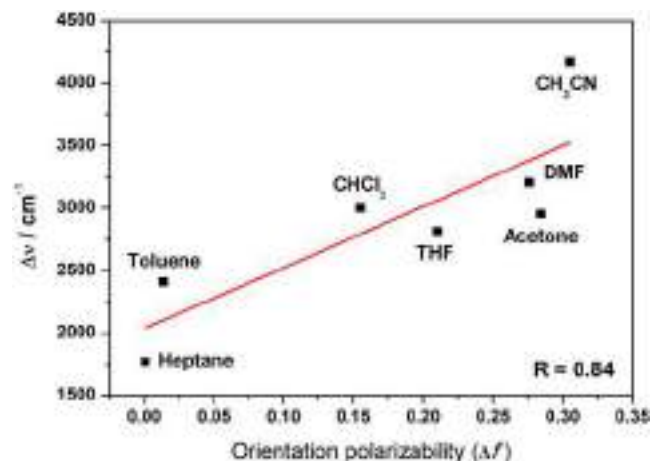


Fig. 6. Changes in the Stokes shifts ($\Delta\nu$) of **6b** versus (Δf) of various solvents.

Table 5
Data obtained by treatment of the Lippert-Mataga correlations.

Compounds	Slope	Linear correlation
6a	771	0.88
6b	4871	0.84
6c	7139	0.91
6d	–	–
6e	1323	0.95
6f	7027	0.79
6g	13,400	0.95

the solvent polarity leads to a linear correlation of 0.84 for this compound. The other derivatives also showed good values of linear correlation (see ESI).

The calculated values for the slope of the linear correlation for all the benzotriazoles are shown in Table 5. A much steeper slope ($13,400 \text{ cm}^{-1}$) was obtained for **6g**, indicating that its dipole moment increase from the ground state to the excited state is more prominent than in to the other compounds.

2.6. Mechanism of photoinduced charge separation

Benzazole-based fluorophores have attracted interest due the potential applications in organic photovoltaic cells [37]. Aware of this phenomenon, the photoinduced charge transfer process was investigated through fluorescence extinction experiments carried out with benzotriazoles in solution. The fluorescence samples in chloroform were gradually quenched by doping with fullerene C_{60} (Fig. 7).

This suggests that electron transfer from photoexcited benzotriazole to fullerene C_{60} occurs in the excited state [38,39]. Moreover, the

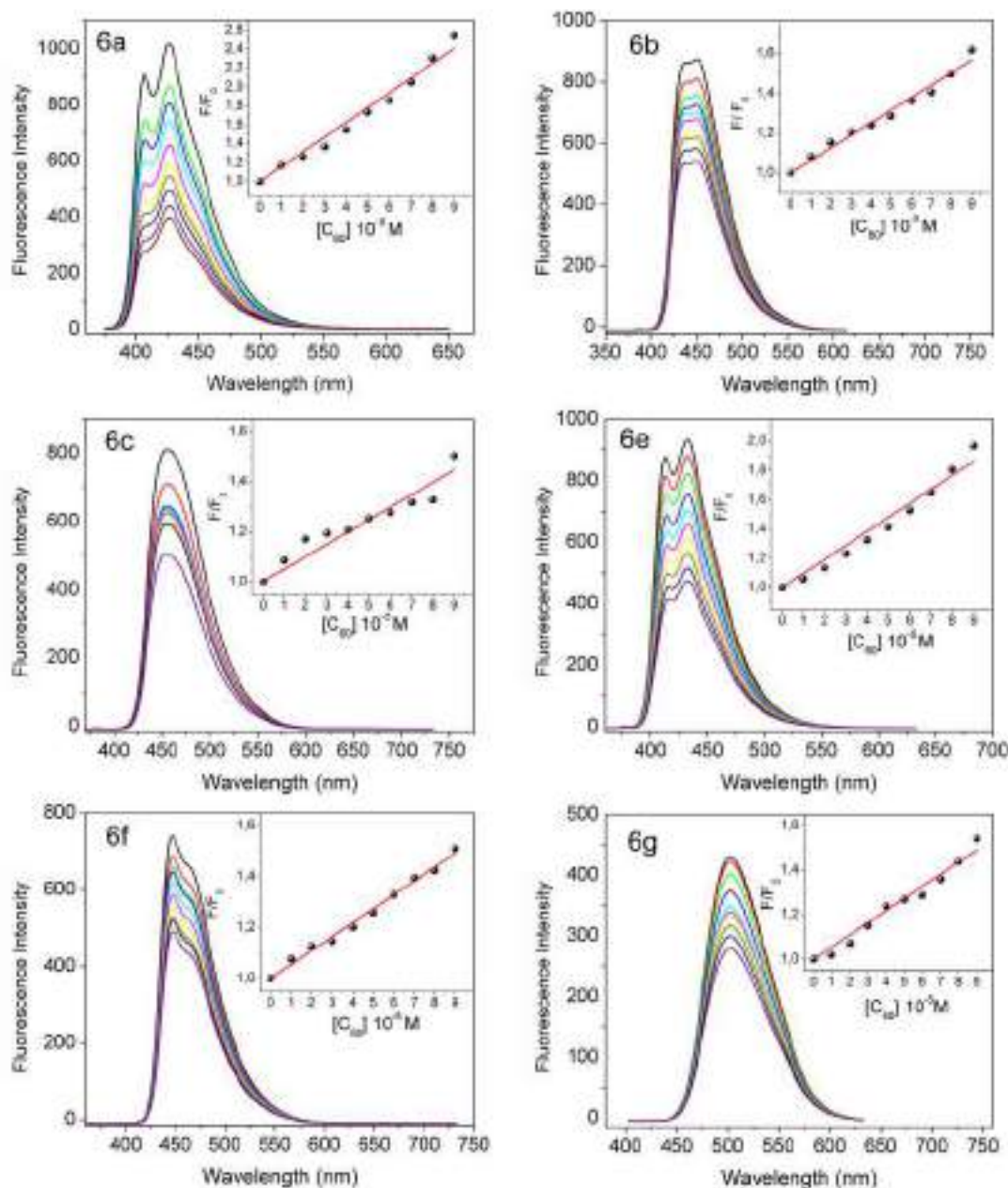


Fig. 7. (a) Emission spectra for **6a-c** and **6e-g** ($1.8 \times 10^{-5} \text{ M}$) in chloroform with concentration of C_{60} : 0.0 (blank), 1.0 equiv. (1), 2.0 equiv. (2), 3.0 equiv. (3), 4.0 equiv. (4), 5.0 equiv. (5), 6.0 equiv. (6), 7.0 equiv. (7), 8.0 equiv. (8), 9.0 equiv. (9). The insets show the Stern-Volmer plots for these samples.

Table 6

Values of Stern-Volmer constant, K_{sv} , and bimolecular rate constant, k_q , obtained from the fitting of Stern-Volmer plot by Eq. (1) for **6a-g** in CHCl_3 with C_{60} .

Compounds	$K_{sv}/10^3 \text{ M}^{-1}$	τ_0/ns	$k_q/10^{11} \text{ M}^{-1} \text{ s}^{-1}$
6a	15.65	1.31 ± 0.01	119.47
6b	6.31	1.49 ± 0.01	42.35
6c	4.96	1.59 ± 0.01	31.19
6d	–	–	–
6e	9.57	1.32 ± 0.01	72.50
6f	5.46	1.16 ± 0.01	47.07
6g	5.45	1.86 ± 0.02	29.30

dependence of the fluorescence intensity on the C_{60} concentration is linear, in accordance with the Stern-Volmer equation:

$$F_0/F = 1 + K_{sv} [C] = 1 + k_q \cdot \tau_0 [C] \quad (1)$$

where F_0 and F represent the fluorescence intensity in the absence and present of C_{60} , respectively, K_{sv} is the Stern-Volmer quenching constant, $[C]$ is the concentration of C_{60} and k_q is the bimolecular rate constant and τ_0 is the lifetime in absence of C_{60} .

Thus, the Stern-Volmer quenching constant K_{sv} and the bimolecular rate constant k_q for the benzotriazoles were obtained from the fitting of Stern-Volmer plot by Eq. (1) (Table 6). The values of K_{sv} range from $15.65 \times 10^3 \text{ M}^{-1}$ to $4.96 \times 10^3 \text{ M}^{-1}$ suggesting that the photoinduced charge separation between the fluorescent compound and C_{60} can be tuned by appropriate peripheral groups [39–41].

Here, the absence of alkoxy chains proved to be beneficial, leading to the highest values of K_{sv} and k_q . Possibly the alkoxy chains affect the approach of BTZ and C_{60} in solution and thus attenuate the quenching processes, since the bimolecular rate constant, k_q , reflects the accessibility of the fluorophore to the quencher. This shielding effect is confirmed when **6c** is compared with **6b**, **6e** or **6f**, as **6c** with four alkoxy chains showed the lowest k_q value of the series. The pattern of alkoxy substitution also influenced the constant, as meta-substituted **6e** had a higher k_q than **6b** substituted in para position.

2.7. Electrochemical behavior

The electrochemical properties of the benzotriazoles derivatives were investigated by cyclic voltammetry (CV) and the data of electrochemical properties of **6a-g** are summarized in Table 7. The cyclic voltammograms reflect the modifications of the donor substitution pattern by changes in the HOMO and LUMO values as well as the width of the

Table 7

Optical and electrochemical properties of compounds **6a-g** where E_{onset}^{ox} is the onset potential of oxidation, E_{onset}^{red} is the onset potential of reduction against NHE, IP (HOMO) is the ionization potential, EA (LUMO) is the electron affinity, is the electrochemical band gap, λ_{onset} is the absorption onset wavelength and E_{gap}^{opt} is the optical band gap.

Parameter	Compounds						
	6a	6b	6c	6d	6e	6f	6g
$E_{onset}^{ox} (\text{V})^a$	1.50	1.26	1.19	1.53	1.44	1.24	0.71
$E_{onset}^{red} (\text{V})^b$	–1.60	–1.66	–1.68	–0.80	–1.62	–1.58	–1.67
IP (HOMO) (eV) ^c	–5.94	–5.70	–5.63	–5.97	–5.88	–5.68	–5.15
EA (LUMO) (eV) ^d	–2.86	–2.77	–2.76	–2.96	–2.83	–2.85	–2.47
$\lambda_{onset} (\text{nm})^e$	402	423	432	411	406	437	463
$E_{gap}^{opt} (\text{eV})^f$	3.08	2.93	2.87	3.01	3.05	2.83	2.68

^a First oxidation process: $E_{onset}^{ox} (\text{vs. NHE}) = E_{onset}^{ox} (\text{vs. Ag/Ag}^+) + 0.25$.

^b First reduction process: $E_{onset}^{red} (\text{vs. NHE}) = E_{onset}^{red} (\text{vs. Ag/Ag}^+) + 0.25$.

^c IP = $-(E_{onset}^{ox} + 4.44) \text{ eV}$.

^d EA = $(E_{onset}^{red} + \text{IP}) \text{ eV}$.

^e λ_{onset} : absorption onsets wavelength.

^f Optical band gap calculated from the low energy edge of the absorption spectrum ($E_{gap}^{opt} = 1240/\lambda_{onset}$).

band gaps, showing that the redox properties are sensitive to the electronic influence of the peripheral groups.

The cyclic voltammograms of **6a-g** (see ESI) exhibit reduction processes in the range of -1.08 V to -1.93 V vs. Ag/Ag^+ (or -0.80 V to -1.68 V vs. NHE). The charge transfer process at negative potentials involves a quasi-reversible reduction of the benzotriazole ring, which is indicated by the fact that the current versus potential curves have the same shape for all compounds. Scanning at positive potential values, the materials showed irreversible oxidation processes, whose potentials were significantly more substituent-dependent than the reduction potentials, leading to a prominent variation of the band gap energies. When an electron-donating alkoxy group is inserted into the 2-methyl-4,7-bis(phenylethynyl)-[1,2,3]benzotriazole core, the oxidation of **6b**, **6c** and **6e** begins at less anodic values, and the reduction process begins at more cathodic values compared to molecule **6a**. A similar effect observed with **6f** due to the elongation of the aromatic portion. The insertion of a nitro group, due to the electron withdrawing effect of the $-\text{NO}_2$ group, caused an increase in the oxidation potential of compound **6d** compared to other molecules that had electron-donating substituents. When a piperazine group is inserted (**6g**), the donating effect is most pronounced, yielding the lowest oxidation potential observed for the entire series.

Comparing the results obtained with benzotriazole-based and similar benzochalcogenodiazole derivatives [19,42,43], the values obtained for the LUMO energies show less negative values for benzotriazoles than for benzoxadiazoles, due to the presence of a less electronegative oxygen atom that reduces the capacity for accepting electrons [28]. The BTZ derivatives also showed slightly lower HOMO energies than the benzoxadiazoles. Compared to derivatives containing sulfur and selenium, higher HOMO energies were observed for the benzotriazoles. The evaluated benzotriazole molecules possess band gaps in the range of 2.68 to 3.08 eV, which are close to the other emitting materials applied in the construction of the light-emitting diode (LED) and organic light-emitting diode (OLED) [44,45]. The HOMO energy levels of our BTZ derivatives are close to the most well-known hole-transporting materials used in the construction of OLED devices. Thus, these compounds may have potential for optoelectronic applications [46].

3. Conclusions

In summary, 2-methyl-BTZ derivatives can present calamitic liquid-crystalline phases as long as the molecule has a high anisometry, with both nematic and smectic C mesophases being observed with two alkoxyarylethynyl or alkylpiperazinylarylethynyl substituents. The decrease on melting and clearing points by lateral substitution occurred in the longest molecules [31]. The presence of lateral group in the shortest aromatic portion did not allow the formation of mesomorphism, probably due to the steric effect and the dependence on length-to-width ratio. An additional decrease of the melting temperatures or suppression of crystallization in ambient conditions is possible by entropy increase through mixing several homologs with different terminal arylene moieties and different alkyl chain lengths. The peripheral groups significantly influence photophysical properties of the benzotriazole derivatives, especially the fluorescence intensity and emission wavelength ($\lambda_{em} = 404\text{--}472 \text{ nm}$). All the final benzotriazoles exhibit intense fluorescence in solution, except for the nitro-derivative. Near-unity quantum yields ($\Phi_{PL} = 0.90\text{--}0.99$) were observed for the homologs with alkoxyarylethynyl peripheral groups. Their excited-state lifetimes of the bis(phenylethynyl)-BTZ homologs, in the nanosecond timescale, increase following the order: unsubstituted (**6a**), meta- (**6e**), para- (**6b**), para- + meta-alkoxy (**6c**), alkylpiperazinyl (**6g**). The emission of the BTZ series is strongly solvatochromic, the most sensitive sample being **6g**. The fluorescence intensity decreases in the presence of C_{60} , indicating photoinduced charge separation, and the steric demand of the peripheral groups affects these charge transfer processes, the highest values of K_{sv} and k_q being observed in the absence

of flexible alkyl tails. The electrochemically determined HOMO and LUMO energy levels revealed moderate band gaps, showing potential for electro-optical applications.

CRediT authorship contribution statement

Elias Regis da Silva: Investigation. **Abad Roger Castillo Hinojosa:** Investigation. **Juliana Eccher:** Data curation, Writing - review & editing. **Michele Duarte Tonet:** Investigation. **Daniela Brondani:** Investigation. **Eduardo Zapp:** Data curation, Writing - review & editing. **Sergio Fernando Curcio:** Investigation. **Bruna Bueno Postacchini:** Data curation. **Thiago Cazati:** Data curation, Writing - review & editing. **André Alexandre Vieira:** Conceptualization, Writing - review & editing, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2020.113616>.

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Reducing lifetime in Cu(I) complexes with thermally activated delayed fluorescence and phosphorescence promoted by chalcogenolate–diimine ligands†

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Luminescent copper(I) complexes have drawn attention due to their promising performance as alternative optoelectronic materials to the well-known heavy transition metal complexes. Herein, we report the synthesis of six luminescent Cu(I) complexes with phosphines and 1,10-phenanthroline-derived ligands with thiadiazole and selenodiazole groups in order to evaluate the effect of the heavy atom on their photophysical properties. Steady-state and time-resolved spectroscopy confirmed delayed fluorescence emission via a thermally activated delayed fluorescence mechanism in all cases. The experimental spectroscopic data were analyzed with detailed quantum-chemical calculations. Interestingly, these complexes did not show the expected “heavy atom effect” that enhances the spin–orbit coupling matrix elements, but nevertheless the addition of the heavier chalcogens contributed to reducing the photoluminescence lifetime to roughly 800 ns, which is the lowest reported so far for such TADF materials.

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Introduction

During the past three decades, many research groups have been studying alternative luminescent materials to replace the most successful, currently employed transition metal complexes, such as those of ruthenium, platinum, osmium, or iridium, in organic light emitting diodes (OLEDs).^{1–4} Cu(I) complexes gained attention due to their promising optoelectronic performance, low cost and high photoluminescence quantum yields (PLQYs), combined with easy color tuning by variation of their ligands.^{5–8} Indeed, copper appears to be particularly interesting due to its spin–orbit coupling (SOC) constant of $\xi_{\text{Cu}} = 851 \text{ cm}^{-1}$, which is known to facilitate ultrafast intersystem crossing (ISC) $S_n \rightarrow T_n$.⁹ Furthermore, mainly due to the pioneering work of

McMillin, it is known that Cu(I) complexes can exhibit thermally activated delayed fluorescence (TADF).^{10–13}

Heteroleptic complexes of the type $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$, where $\text{N}^{\wedge}\text{N}$ and $\text{P}^{\wedge}\text{P}$ indicate chelating diimine and diphosphine ligands, respectively, presented promising photophysical properties, e.g., highly luminescent Cu(I) complexes, with long-lived excited-states. The low-lying metal-to-ligand charge transfer (MLCT) excited state of these copper complexes determines their photophysical properties, and allows emission in the visible region.^{6,14} As the LUMO of these complexes is usually centered on the diimine, the HOMO–LUMO energy gap has been modulated by employing different N-heterocyclics, such as phenanthroline,^{15,16} bipyridyl-, pyrazolyl-,¹⁷ triazolyl-,¹⁸ and tetrazolyl-based ligands.¹⁹ By using these ligands, a variety of emission colors, including blue and green, have already been reported.^{20–24}

In contrast to the heavier metal elements, SOC in copper is much weaker, and the ligands are not generally able to enhance the SOC in these complexes. Consequently, cuprous phosphorescent complexes usually possess long emission lifetimes of up to a hundred microseconds. Unfortunately, the long decay times of triplet states facilitate triplet–triplet annihilation (TTA) and triplet-polaron quenching (TPA) in electroluminescence devices,²⁵ limiting their efficiency. However, this detrimental effect can be avoided by the fact that many emissive cuprous

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complexes can also emit efficiently through a TADF mechanism at room temperature, when there is a small energy gap between singlet (S_1) and triplet (T_1) states.^{26–29} Designing these compounds with short combined TADF and phosphorescence decay times and high PLQYs is still a challenge. For instance, radiative decay times of $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ complexes of less than 2–5 μs have not been reported so far.^{6,28,30}

Recently, we reported two 1,10-phenanthroline-derived ligands with the thiadiazole and selenodiazole groups, where the heavy atom effect was observed in the photophysics of the ligands and ruthenium complexes. The ligand with a selenodiazole group showed an increase of 200 times in the spin–orbit coupling matrix elements and even phosphorescence emission,³¹ and the ruthenium(II) complexes also had their properties altered.³² These results pointed to a promising effect of the heavy atoms in luminescent complexes and a possibility to enhance the SOC in cuprous complexes.

Here, we report the synthesis and characterization of six luminescent Cu(I) complexes with phosphines and 1,10-phenanthroline-derived ligands with thiadiazole and selenodiazole groups, [1,2,5]thiadiazolo[3,4-*f*][1,10]phenanthroline (TDZP) and [1,2,5]selenadiazolo[3,4-*f*][1,10]phenanthroline (PhenSe) (Chart 1). The complexes have been fully characterized using steady-state and time-resolved spectroscopy, and for all of them, crystals have been obtained, allowing a full crystallographic analysis. The experimental spectroscopic data have been further rationalized by means of detailed quantum-chemical calculations.

Results and discussion

Synthesis and characterization

The copper complexes were prepared in excellent yields by a quick reaction of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ with the phosphine and diimine ligands in CH_2Cl_2 . All the final complexes were obtained by crystallization from THF/dichloromethane solutions and used without further purification. A synthetic route for these complexes is shown in Scheme S1 (ESI[†]). The obtained

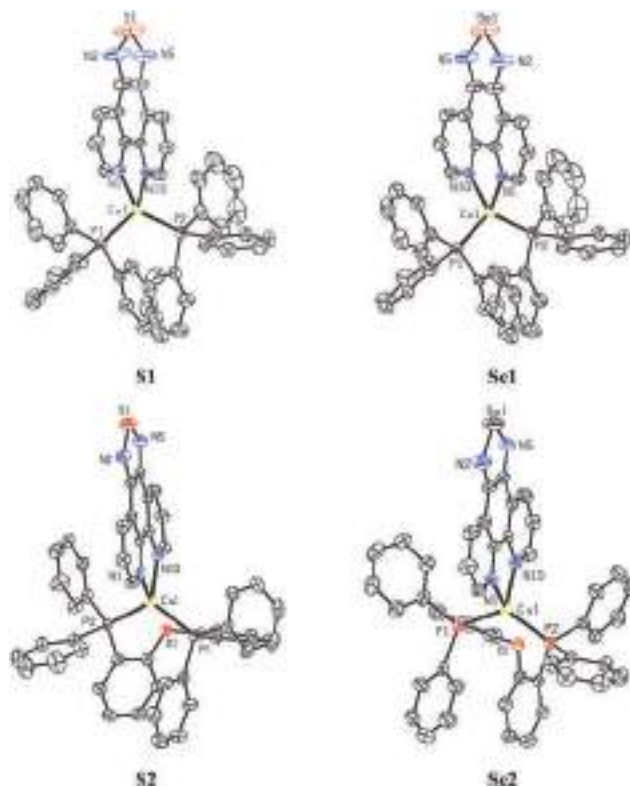


Fig. 1 ORTEP plots (thermal ellipsoids with 50% probability) of the molecular structures of cation complexes **S1**, **Se1**, **S2** and **Se2**. Hydrogen atoms and most atom labels are omitted for clarity.

compounds are stable in air for at least several months without oxidizing (Fig. 1).

The molecular structures of the complexes were determined by single crystal X-ray diffraction studies. The Cu(I) center in the four new complexes (**S1**, **Se1**, **S2** and **Se2**) has a distorted tetrahedral geometry, caused by the strong deviation from the tetrahedral angle around the Cu(I) center, where the dihedral angle between N–Cu–N and P–Cu–P planes is measured to be 76.6° for **S1**, 73.0° for **Se1**, 78.3° for **S2** and 70.5° for **Se2**. This situation reflects the specific steric requirements of the ligands,

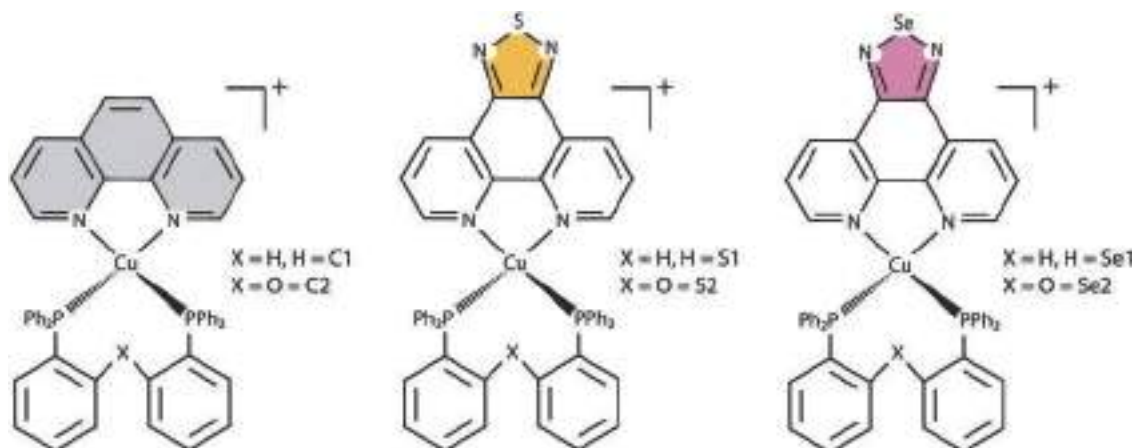


Chart 1 Cu(I) complexes discussed in the introductory part.

Table 1 Selected bond lengths [Å] for **C1–Se2**

	C1^a	S1	Se1	C2^a	S2	Se2
Cu–N1	2.080	2.0877(14)	2.087(2)	2.071	2.0716(13)	2.070(3)
Cu–N10	2.070	2.0827(14)	2.088(2)	2.063	2.0586(12)	2.040(2)
Cu–P1	2.271	2.2588(4)	2.2637(7)	2.261	2.2546(4)	2.2567(8)
Cu–P2	2.245	2.2662(5)	2.2731(8)	2.231	2.2238(4)	2.2197(8)
Cu...O	—	—	—	3.205	3.0391(10)	3.105(2)
N1–Cu–N10	80.90	80.01(5)	79.93(8)	80.83	80.75(5)	81.11(10)
P1–Cu–N1	115.44	117.88(4)	111.09(6)	110.81	105.87(4)	107.31(7)
P2–Cu–P1	118.69	116.151(17)	115.75(3)	108.12	112.573(15)	117.47(3)
N10–Cu–P2	103.60	112.67(4)	113.68(6)	109.08	119.99(4)	110.73(7)

^a 15.

and the stabilization by intramolecular π -stacking interactions, found in many other transition metal complexes with phosphine ligands.¹⁵ Also, for **S2** and **Se2**, most Cu–P and Cu–N distances are closer than those with the PPh₃ ligand. The oxygen atom of the POP ligand in the complexes is at a distance of ≈ 3 Å away from the Cu(I) center, and opposite to the coordinated N atoms, indicating a weak interaction between the oxygen atom and Cu(I) center. This suggests that the POP ligand is in closer proximity to the copper atom due to the ether linkage, which is known to increase the probability of charge transfer from metal to ligand (see below). Bond distances and angles are reported in Table 1 and are similar to those of **C1** and **C2** previously reported.¹⁵

Thermogravimetric analysis (TGA) of **C1–Se2** under a nitrogen atmosphere revealed that the initial decomposition temperatures were close to 130 °C for **C1**, **S1**, **Se1** and **C2** and 350 °C for **S2** and **Se2** (See Fig. S7, ESI†). Such thermal stability indicates that all the complexes can undergo thermal treatments until at least 100 °C in device fabrication.

Cyclic voltammetry in CH₂Cl₂ solution was performed to estimate the HOMO and LUMO levels from the oxidation and reduction potentials, respectively. Fig. 2 shows the cyclic voltammograms and Table 2 summarizes the electrochemical data. All complexes displayed one anodic process, which is attributed to the oxidation of the copper center. This process is usually quite positive and irreversible due to the dissociation of the complex in solution. The phosphine group had a small effect on the oxidation potential, with the complexes bound to triphenylphosphine having a higher potential when compared with the analogues with the POP ligand, in agreement with the obtained Cu–P distances. In addition, a cathodic process was observed for the complexes **S1**, **Se1**, **S2** and **Se2**. The reversible process of reduction was attributed to redox processes of the ligands TDZP and PhenSe, also observed for the free ligands.³¹ The HOMO and LUMO energies obtained from voltammetry agree with the calculated trend from DFT, where the contributions from both the copper atom and the ligands to these frontier orbitals were predicted.

Photophysical properties

The UV-Vis absorption and emission of complexes **C1–Se2** were recorded in CH₂Cl₂ solution (see Fig. 3 and Fig. S9, ESI†), and with the complexes dispersed as 10 wt% in a PMMA matrix

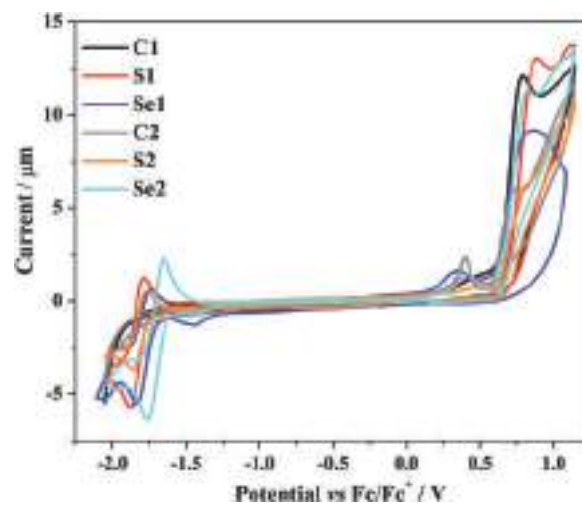


Fig. 2 Cyclic voltammograms of **C1–Se2** in 1×10^{-3} mol L⁻¹ CH₂Cl₂ solutions under a nitrogen atmosphere. The scanning rate is 100 mV s⁻¹. Three electrode electrochemical cell: gold (working), Pt wire (auxiliary), and Ag/Ag⁺ (reference). Supporting electrolyte: 0.1 mol L⁻¹ *n*-Bu₄NBF₄.

Table 2 Electrochemical properties of **C1–Se2**

Complex	$E_{\text{red}}^a/\text{V}$	E_{ox}^a/V	$E_{\text{HOMO}}^b/\text{V}$	$E_{\text{LUMO}}^b/\text{V}$	Electrochemical band gap/eV	Optical band gap ^c /eV
C1	—	0.79	-5.59	-2.66 ^d	—	2.93
S1	-1.83	0.88	-5.68	-2.97	2.71	2.75
Se1	-1.79	0.86	-5.66	-3.01	2.65	2.68
C2	—	0.75	-5.55	-2.81 ^d	—	2.74
S2	-1.81	0.83	-5.63	-2.99	2.64	2.69
Se2	-1.71	0.81	-5.61	-3.09	2.52	2.62

^a Determined from peak potentials. ^b Calculated from $E_{\text{HOMO}} = -(4.8 + E_{\text{ox}})$ and $E_{\text{LUMO}} = -(4.8 - E_{\text{red}})$. ^c Calculated from the onset of the absorption spectra in solution. ^d Obtained from the sum of the LUMO energy and optical band gap.

(Fig. 3 and Fig. S8, ESI†). All photophysical data are summarized in Table 3. The complexes exhibited an intense absorption band around 250 nm, which is attributed to a $\pi \rightarrow \pi^*$ transition of the phosphine ligand. The less intense absorption bands with maxima between 300 and 350 nm are related to the diimine ligand,³¹ and could be mainly attributed to intra-ligand charge transfer transitions. As the lower energy absorption band around 400 nm is not present in the ligands, it is safely assigned

Table 3 Photophysical data for the Cu(I) complexes in CH₂Cl₂ solution and 10 wt% PMMA films

	Solution ^a		PMMA films					
	λ_{abs} (nm)/ ϵ (L mol ⁻¹ cm ⁻¹)	λ_{em} (nm)	λ_{abs} (nm)	λ_{em} (nm)	Φ^b	τ^c (μ s)	k_r^d ($\times 10^5$ s ⁻¹)	k_{nr}^e ($\times 10^5$ s ⁻¹)
C1	352/2772	606	350	550	0.11	2.7	0.41	3.30
S1	370/1808	610	370	577	0.04	1.1	0.36	8.73
Se1	375/3232	615	380	592	0.08	1.1	0.73	8.36
C2	391/2840	628	390	560	0.13	2.1	0.62	4.14
S2	404/3881	624	395	594	0.06	1.2	0.50	7.83
Se2	396/4252	637	400	605	0.08	0.8	1.00	11.50

^a In CH₂Cl₂ at 1.0×10^{-5} mol L⁻¹. ^b The uncertainty in Φ was ± 0.01 . ^c The uncertainty of the lifetime was estimated in ± 0.1 μ s. ^d $k_r = \Phi/\tau$. ^e $k_{\text{nr}} = (1 - \Phi)/\tau$.

to spin allowed MLCT involving 3d orbitals of Cu(I) and π^* orbitals of diimine.^{6,15} Moreover, the molar absorptivity for the MLCT follows the order PhenSe > TDZP > phen (with the exception of **S1**) and POP > PPh₃. However, it is not related to the allowedness of the S₀ → S₁ transition, but to the existence of new MLCT states involving the thiadiazole and selenodiazole moieties with close energy levels, as verified by TD-DFT. The absorption in PMMA was found to be very similar to that in solution.

The emission from a degassed solution under excitation of the MLCT band is in the orange region, with maxima at 606, 610, 615, 628, 624 and 637 nm for **C1–Se2**, respectively. The emission peaks observed using the PMMA matrix were located in the yellow-orange region, with maxima at 550, 577, 592, 560, 594 and 605 nm for **C1–Se2**, respectively. These spectra have broad and unstructured Gaussian line-shapes, which is in accordance with the MLCT nature of the emitting state. Moreover, the luminescence properties strongly depend on the environment. For instance, as depicted in Fig. 3 and Fig. S9 (ESI[†]), **C1** shows emission at $\lambda_{\text{max}} = 604$ nm in solution and $\lambda_{\text{max}} = 550$ nm in PMMA. Similar trends are observed for the other complexes. These observations can be explained considering the changes in the molecular geometry of the Cu(I) compounds, which take place after MLCT excitation. In the electronic ground state (d¹⁰ configuration), the complexes have a pseudo-tetrahedral coordination of the metal ion, whereas in

the MLCT excited state, with a d⁹ configuration of the metal ion, a flattening distortion of the molecular structure occurs.⁷ Therefore, in a rigid matrix, these distortions are less favorable, and a higher energy emission is observed. Furthermore, as the emission results from a CT state, it is also influenced by the polarity of the solvent. Thus, as CH₂Cl₂ has a larger polarity than PMMA, a lower energy emission in CH₂Cl₂ was expected.

The PLQY (Φ) and the excited-state lifetime (τ) values for the complexes embedded in the PMMA matrix are shown in Table 3. Interestingly, the presence of the heavy atom reduced both PLQY values and lifetimes of **S1**, **Se1**, **S2**, and **Se2**, compared to those of their reference compounds **C1** and **C2**. For complexes with TDZP and PhenSe, the lifetimes were measured in the range of 2.7 μ s to 800 ns (Table S3 and Fig. S11, ESI[†]). Based on these results, the radiative and nonradiative constants, k_r and k_{nr} , were calculated (Table 3). The k_r values follow the order **Se1** > **C1** > **S1** and **Se2** > **C2** > **S2**, indicating that the presence of PhenSe with a heavy atom enhances the radiative path, while TDZP does not. On the other hand, for all these new complexes, the nonradiative path is enhanced too. Such an increase of the nonradiative rate is more pronounced in complexes with TDZP and PhenSe, and is attributed to the lower triplet energy (see below) and the intramolecular π -stacking interactions (comparing the dihedral angles). The presence of the thiadiazole and selenodiazole moieties distorts the complexes from their tetrahedral geometry, as mentioned before, increasing the known pseudo-Jahn-Teller effect in the excited state.³³

Time-resolved spectroscopy was used to follow the excited state dynamics of complexes **C1–Se2**. At room temperature, the luminescence is characterized by a fast component followed by a slow bi-exponential decay. The decays obtained as a function of temperature for all complexes exhibit a clear temperature dependence in the delayed fluorescence region (microsecond range), which is characteristic of a TADF mechanism. Fig. 4 shows the emission decays at room temperature (a) and at 80 K (b) for all compounds. In Fig. 4c, a more detailed temperature dependence is shown for compound **C1** from 80 K to 320 K, with a 50 K step. In all compounds, the delayed fluorescence emission (microsecond range) shows higher intensity at higher temperatures, which is a characteristic of the TADF mechanism. On the other hand, the longer-lived emission (millisecond range) shows the opposite behavior, the intensity increases upon cooling down the films, which is also consistent with a

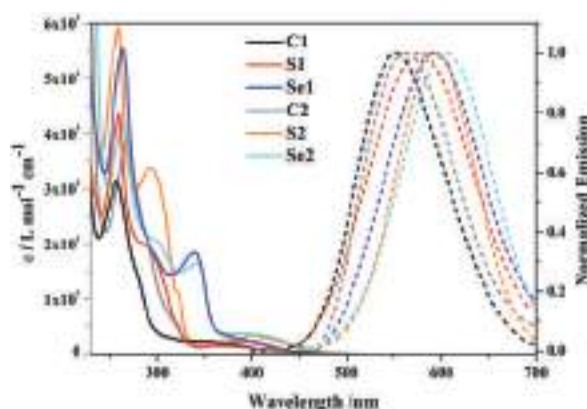


Fig. 3 Optical absorption spectra of the Cu(I) complexes in CH₂Cl₂ solution, at 1.0×10^{-5} mol L⁻¹, and emission spectra of the studied Cu(I) complexes, at 10 wt% in PMMA. Emission spectra were obtained with excitation at the lowest energy band absorption maximum.

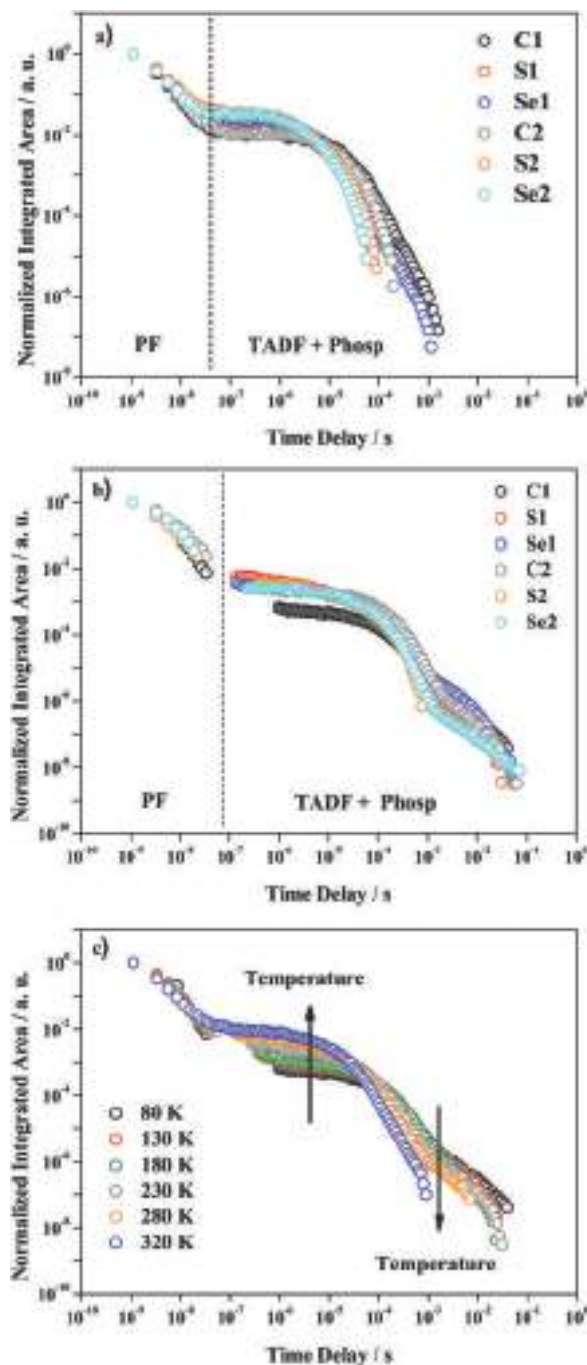


Fig. 4 Time-resolved normalized emission spectra at room temperature for **C1–Se2**, at 10 wt% in PMMA, at 300 K (a) and 80 K (b), and temperature dependence for compound **C1** from 80 K to 320 K, with a 50 K step (c).

slower depopulation of the triplet state *via* RISC, thus increasing the phosphorescence intensity.

The time-resolved emission spectra collected at room temperature and at 80 K are shown in Fig. 5 for **C1** and Fig. S11–S15 in the ESI† for **C2–Se2**. In the early-collected time-resolved emission spectra (1–40 ns), a fast emission at high energy was observed, which is attributed to the prompt fluorescence component, as suggested by Li and co-workers.³⁴ Afterwards, in

the microsecond range, a new emission is observed close to 550 nm, which is attributed to the triplet state of these compounds. Subsequently, a blue shift is observed in the microsecond range due to the thermal repopulation of the singlet state and consequent mixing of emitting species, *i.e.* delayed fluorescence and phosphorescence emission. The time-resolved emission spectra collected at different temperatures show a larger blue-shift at lower temperature. These observations are consistent with the presence of thermalized triplet states at higher temperatures.

The S_1 and T_1 energies (Table 4) were obtained from the onset of the highest and the lowest energy emission from the time-resolved emission spectra at room temperature and 80 K (μ s time frame), respectively. As can be observed, the S_1 energy decreases in the presence of the TDZP and PhenSe ligands and also for the POP complexes, in agreement with the bathochromic shift observed in the absorption spectra and the steady state emission. The T_1 energy follows the same trend, being lower for **S1** and **Se2**. As k_{nr} increases when the energy difference between T_1 and the ground state decreases,³⁵ the higher k_{nr} for complexes with TDZP and PhenSe ligands can be attributed to structural distortions, as mentioned before, and the lower triplet state energy for these complexes. In addition, $\Delta E(S_1 - T_1)$, which is determinant of a faster TADF component in the emission, decreases for complexes with the TDZP and PhenSe and POP ligands. Therefore, the lower lifetime obtained for **Se1** and **Se2** can be partially attributed to the fast reversion from T_1 to S_1 , which corresponds to a faster TADF. However, such a low lifetime for Cu(I) complexes is only possible considering a component of phosphorescence in the emission. Thus, as the phosphorescence decay path depends on both triplet energy and the SOC between the singlet and triplet states, one can expect a lower phosphorescence component for complexes with the TDZP and PhenSe moieties.

Density functional theory/time-dependent DFT approaches and photophysical interpretations

In order to obtain further insights into the nature of the excited states and the emission mechanism, the optimized geometries for the ground state of all complexes were obtained using DFT at the PBE0/def2-TVZP(-f) level. The S_0 geometries are shown in Fig. S16 (ESI†) and the important lengths and angles are listed in Table S4 (ESI†). The vibrational frequencies confirm that the geometries correspond to a minimum of the surface energy potential, since no negative frequencies were found. Moreover, the predicted S_0 geometries for all complexes are in good agreement with the experiment, where the maximum average error found was 2.4% for bond lengths and 6.6% for bond angles, which supports the further use of PBE0 in subsequent investigations.

The first insight into the electronic properties of these complexes can be obtained from the calculated HOMO and LUMO, see Fig. 6. For these complexes, the HOMO (isosurface with transparency) is largely derived from a 3d atomic orbital of the copper(I) center with significant contributions from the coordinating phosphorous atoms, whereas the LUMO is mainly

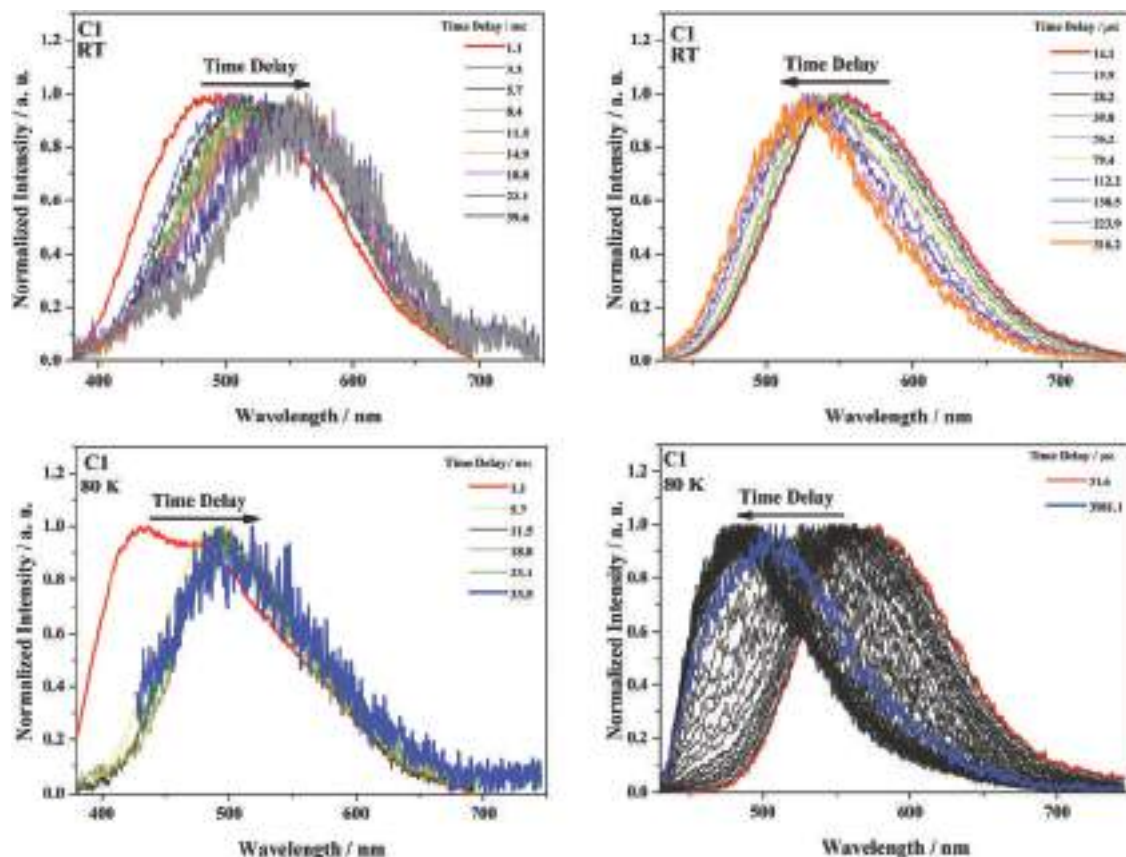


Fig. 5 Time-resolved normalized emission spectra at room temperature (top) and 80 K (bottom) for **C1** at 10 wt% in PMMA. Films were excited at 355 nm.

Table 4 Singlet and triplet energies obtained from time-resolved spectroscopy

	C1	S1	Se1	C2	S2	Se2
S_1/eV	2.77	2.67	2.68	2.73	2.57	2.54
T_1/eV	2.53	2.46	2.51	2.52	2.43	2.42
$\Delta E_{S_1-T_1}/\text{eV}$	0.24	0.21	0.17	0.21	0.14	0.12

distributed over the diimine. However, the LUMO for **C1** and **C2** is mostly distributed over the phenanthroline moiety, while for the complexes with TDZP and PhenSe, the LUMO is centered at the thiazole and selenodiazole, respectively. Thus, the lower energy excited states are expected to be MLCT-like, but involving different π^* orbitals of diimine. Indeed, TD-DFT calculations showed that the low-lying S_1 and T_1 states are more than 88% HOMO $\rightarrow$ LUMO transitions in S_1 and mixed HOMO $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO-1 (both MLCT) for T_1 (Tables S5–S7, ESI[†]), being assigned as $^1\text{MLCT}$ and $^3\text{MLCT}$, respectively.

The LUMO orbital centered at the thiazole and selenodiazole moieties also minimizes the HOMO and LUMO overlap (Fig. S17, ESI[†]) by increasing the spatial separation of these orbitals. That results in a smaller $\Delta E_{S_1-T_1}$, as also obtained from the spectroscopic studies, and agrees well with the calculated $\Delta E_{S_1-T_1}$ using the adiabatic energy for such states (Table 5). This larger spatial

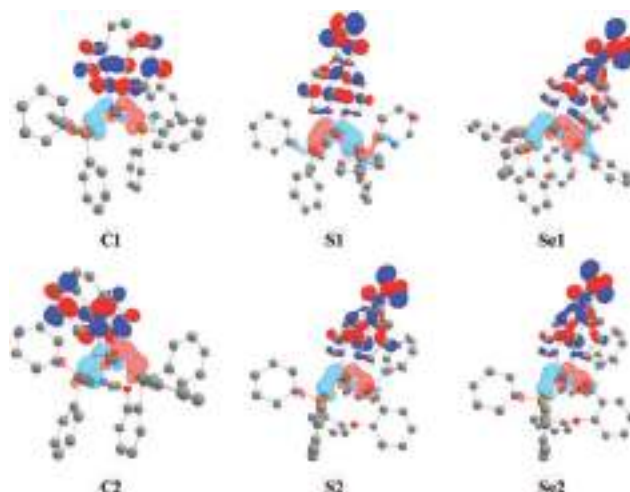


Fig. 6 Frontier molecular orbitals of complexes **C1–Se2** calculated using PBE0/def2-TZVP(-f). The HOMO is shown as the isosurface with transparency.

separation of the HOMO and LUMO also reduces the oscillator strength f of the $S_0 \rightarrow S_1$ transition ($^1\text{MLCT}$) for complexes with the TDZP and PhenSe ligands. Even so, the presence of these ligands resulted in new low energy MLCT states, $d \rightarrow \pi^*$ (thiadiazole or selenodiazole), close to $d \rightarrow \pi^*$ (phen). The net result is a wider and

Table 5 Data of SOC-TD-DFT and adiabatic energy difference for **C1–Se2**

	C1	S1	Se1	C2	S2	Se2
$\langle T_1 \hat{H}_{SO} S_0 \rangle^a$	22.50	24.55	6.09	37.79	26.07	4.44
$\langle T_1 \hat{H}_{SO} S_1 \rangle^a$	17.11	8.12	2.01	27.65	2.76	0.96
$\langle T_1 \hat{H}_{SO} S_2 \rangle^a$	6.37	24.42	9.07	6.32	2.59	9.70
$\langle T_1 \hat{H}_{SO} S_3 \rangle^a$	157.98	156.94	112.72	119.62	152.47	99.99
$\langle T_1 \hat{H}_{SO} S_4 \rangle^a$	166.35	17.36	130.82	128.53	211.05	116.72
$\langle T_1 \hat{H}_{SO} S_5 \rangle^a$	4.70	180.85	66.77	189.82	9.82	99.53
$\langle T_2 \hat{H}_{SO} S_0 \rangle^a$	8.36	5.43	42.32	12.33	26.17	31.84
$\langle T_2 \hat{H}_{SO} S_1 \rangle^a$	15.72	2.46	3.83	21.16	26.17	4.08
$\langle T_2 \hat{H}_{SO} S_2 \rangle^a$	10.24	12.97	18.27	13.55	4.25	12.82
$\langle T_2 \hat{H}_{SO} S_3 \rangle^a$	22.37	2.51	71.51	34.32	14.77	118.22
$\langle T_2 \hat{H}_{SO} S_4 \rangle^a$	34.46	6.79	59.59	87.76	23.44	90.82
$\langle T_2 \hat{H}_{SO} S_5 \rangle^a$	111.44	36.34	88.94	29.88	12.95	123.04
$\Sigma \langle T_i \hat{H}_{SO} S_i \rangle$	577.59	478.73	611.95	707.73	512.50	712.14
S_1^b /eV	2.79	2.35	2.16	2.79	2.46	2.29
T_1^b /eV	2.42	2.09	1.98	2.42	2.32	2.23
$\Delta E_{S_1-T_1}$ Theo/eV	0.37	0.26	0.18	0.37	0.14	0.06
$\Delta E_{S_1-T_1}$ Exp/eV	0.24	0.21	0.17	0.21	0.14	0.12

^a $\sqrt{\Sigma \langle T_i | \hat{H}_{SO} | S_i \rangle^2}$ for the S_0 optimized geometry. ^b Adiabatic energy.

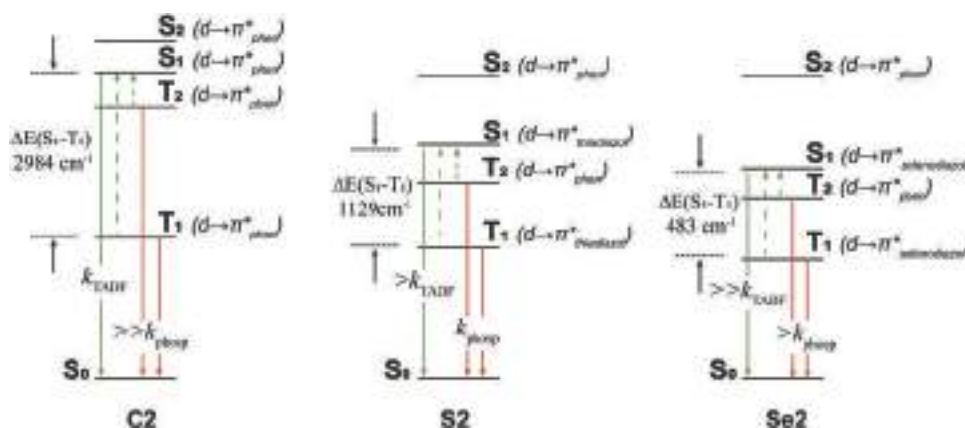
more intense absorption band, as observed in the experimental spectra (compare Tables S5–S7 and Fig. S18, ESI†).

For many Cu(I) complexes, SOC effects provide distinct phosphorescence decay paths in addition to the TADF *via* S_1 . Therefore, to evaluate both the phosphorescence and the TADF decay paths for **C1–Se2** in terms of SOC, we calculated the SOC matrix elements between the first 10 singlet and triplet states,³⁶ on top of the S_0 geometries. The SOC matrix elements, between the first six singlets and the first two triplet states, which should have an appreciable contribution to the phosphorescence and the TADF mechanism in these complexes, are shown in Table 5. As one can see, the SOC between S_1 and T_1 , both mainly involving the MLCT transition with the same d orbital, decreases for complexes with TDZP and PhenSe and shows that the $d \rightarrow \pi^*$ (thiadiazole or selenodiazole) transition does not result in a significant heavy atom effect in the SOC, even for **Se1** and **Se2**, where the selenium atom is present. As the SOC between these states is mostly associated with MLCT transitions,

having components of both the copper and the phenanthroline ligand, the presence of the copper atom ultimately determines the magnitude of the SOC matrix element.³⁷ Also, as the SOC matrix elements have a distance-dependence, it was observed that the ligands with thiadiazole and selenodiazole moieties have a LUMO that is too far from the copper atom, and their contribution to the SOC matrix elements decreases. On the other hand, the SOC between states with the $d \rightarrow \pi^*$ (phen) configuration is close for all complexes and when high energy singlet states, *i.e.* S_3 or S_4 , are involved, as these states result from MLCT transitions involving different d orbitals from that of T_1 or T_2 (see Fig. S19 and Tables S5–S7, ESI†), a high SOC matrix element is observed.

By adding the SOC matrix elements, one can more accurately observe the phosphorescence and TADF decay paths, as both k_{phosp} and k_{TADF} depend on them. In Table 5, the sum of SOC matrix elements of these complexes follows the order **Se1** > **C1** > **S1** and **Se2** > **C2** > **S2**, which is the same order of the radiative constants obtained experimentally. However, k_{phosp} has a dependence on the triplet energy, while k_{TADF} relies on an exponential of $\Delta E(S_1 - T_1)$. Thus, as the triplet energy decreases from **C1** to **Se1** and from **C2** to **Se2**, the phosphorescence rate should be higher for phenanthroline complexes, and the lower contribution of the phosphorescence to the emission should be found for TDZP complexes, due to the combined low triplet energy and SOC matrix elements. On the other hand, for the TADF path, as $\Delta E(S_1 - T_1)$ also decreases from **C1** to **Se1** and from **C2** to **Se2**, this emission component should follow the same order.

We can conclude that, though structurally similar, the presence of TDZP and PhenSe ligands significantly changes the photophysical properties, as shown in Scheme 1 for complexes **C2–Se2**. For these complexes, the introduction of the thiadiazole and selenodiazole moieties resulted in a low-lying ^{1,3}MLCT state involving them. Thus, the lowest $\Delta E_{S_1-T_1}$ values were found for these complexes with chalcogenide atoms, due to the minimization of the HOMO and LUMO overlap through increasing the spatial separation of the HOMO and LUMO, reducing the electron exchange by changing the ligand. Therefore, k_{RISC} ,



Scheme 1 Energy level diagrams for compounds **C2–Se2**. Vertical states and their major configurations obtained using the SOC-TD-DFT approach on top of the S_0 optimized geometry. The calculated $\Delta E_{S_1-T_1}$ is the adiabatic energy difference for these states. The symbols ">" and ">>" compare the contribution of the same constant between the different compounds using **C2** as a reference.

which is determinant of the TADF mechanism and has an exponential dependence on the energy gap between these states, favors the reverse ISC for complexes **Se1** and **Se2**. In addition, the introduction of TDZP and PhenSe provides a slower phosphorescence decay path. Besides, the combined TADF and phosphorescence paths significantly decrease the overall lifetime, which can be explored further in more efficient materials.

Conclusion

The synthesis and characterization of a new series of copper(I) complexes with phenanthroline ligands was presented. The complexes showed thermally activated delayed fluorescence emission determined by steady-state and time-resolved spectroscopy. The experimental spectroscopic data were further rationalized by means of detailed quantum-chemical calculations. The molecules studied here did not show the classical heavy-atom effect in terms of the spin-orbit coupling matrix elements, where a reduction in the $\Delta E_{S_1-T_1}$ energy gap, which is determinant of the TADF mechanism by favoring the reverse ISC, combined with the phosphorescence decay, decreased the lifetime of the complexes. This is achieved through increasing the spatial separation of the HOMO and LUMO. For **Se2**, the lifetime was as low as 800 ns, the lowest reported so far for $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ complexes. These results point to a new way of reducing the lifetime in copper(I) complexes, minimizing the HOMO and LUMO overlap by increasing their spatial distance.

Experimental section

General procedures

All starting materials were purchased from Aldrich, Acros, Merck or Vetec and were used without further purification.

The measurements of carbon, hydrogen and nitrogen percentages of the ligands and the synthesized complexes were performed on a C, H, N – PerkinElmer 2400 elemental analyzer. The spectra in the infrared region were obtained using a PerkinElmer Spectrum 100 spectrophotometer, in the region of 4000 to 450 cm^{-1} . The method of attenuated total reflectance (ATR) was used to analyze all samples.

The X-ray diffraction analysis was performed on a Bruker APEX II DUO diffractometer using radiation generated by a molybdenum tube ($\text{MoK}\alpha\lambda = 0.71073 \text{ \AA}$) and graphite monochromator. During analyses, the samples were maintained at 200 K. The crystal structures were solved by direct methods and refined by the least squares method with a complete matrix, using the Bruker APEX II software package³⁸ and SHELXL-2018, respectively.³⁹ The graphical representations of the molecular structures were generated using the program PLATON.⁴⁰ The squeeze procedure was applied to **S1** and **Se1** complexes using PLATON Crystallographic Tools.⁴⁰ Disordered counterion and solvate were modeled for the **Se2** complex. Full crystallographic tables (including structure factors) for both complexes have been deposited with the Cambridge Crystallographic Data

Centre as supplementary publication numbers CCDC 2006226–2006229.[†] These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk.

Emission decays were obtained using the time-correlated single photon counting technique, using a FluoTime200 (PicoQuant) spectrometer. The excitation was performed by a 401 nm pulsed diode laser with repetition rate ranging from 0.25 to 20.0 MHz. Emission was collected perpendicular to excitation and passed through a polarizer set at the magic angle. The detection system consisted of a monochromator and a microchannel plate photomultiplier (Hamamatsu R3809U-50). Lifetimes were obtained by fitting the emission decays to a convolution of the instrument response function and the sum of exponentials using the FluoFit[®] software. The plots of weighted residuals and reduced chi-squared (χ^2) were used to accurately determine the quality of the fittings during the analysis procedure.

Synthesis and characterization

$[\text{Cu}(\text{Phen})(\text{PPh}_3)_2]\text{BF}_4$ (**C1**). Under argon, PPh_3 (105 mg, 0.4 mmol) was dissolved in dry dichloromethane (20 mL). Tetrakis(acetonitrile)copper(I) tetrafluoroborate (63 mg, 0.2 mmol) was added to this solution, and the reaction mixture was refluxed for 30 min, then Phen (40 mg, 0.2 mmol) was added. The mixture was refluxed for another half hour. The solvent was removed by evaporation. The crude product was further purified by recrystallization from a mixed solvent of tetrahydrofuran/dichloromethane (80:20). Yield: 61%; IR (KBr), in cm^{-1} : $\nu(\text{C-Har})$ 3057–2862, $\nu(\text{C=N-C=C})$ 1670–1432, $\nu(\text{B-F})$ 1055, $\delta(\text{C-Har})$ 843–510; $\text{C}_{48}\text{H}_{38}\text{BCuF}_4\text{N}_2\text{P}_2$ (855.13): calcd C 67.13, H 4.80, N 3.28; found C 67.42, H 4.48, N 3.28.

$[\text{Cu}(\text{TDZP})(\text{PPh}_3)_2]\text{BF}_4$ (**S1**). **S1** was synthesized by the same method as that of **C1**, except that Phen was replaced by TDZP (48 mg, 0.2 mmol). Yield: 90%; IR (KBr), in cm^{-1} : $\nu(\text{C-Har})$ 3057, $\nu(\text{C=N-C=C})$ 1585–1399, $\nu(\text{B-F})$ 1053, $\delta(\text{C-Har})$ 817–515; $\text{C}_{46}\text{H}_{42}\text{BCuF}_4\text{N}_4\text{P}_2\text{S} + 1.5 \text{ THF}$ (1021.35): calcd C 63.35, H 4.51, N 5.12; found C 63.50, H 4.74, N 5.49.

$[\text{Cu}(\text{PhenSe})(\text{PPh}_3)_2]\text{BF}_4$ (**Se1**). **Se1** was synthesized by the same method as that of **C1**, except that Phen was replaced by PhenSe (57 mg, 0.2 mmol). Yield: 87%; IR (KBr), in cm^{-1} : $\nu(\text{C-Har})$ 3050–2849, $\nu(\text{C=N-C=C})$ 1599–1399, $\nu(\text{B-F})$ 1059, $\delta(\text{C-Har})$ 816–512; $\text{C}_{48}\text{H}_{44}\text{BCuF}_4\text{N}_4\text{P}_2\text{Se} + 2 \text{ THF}$: calcd C 60.51, H 4.66, N 4.75; found C 60.91, H 4.75, N 5.07.

$[\text{Cu}(\text{Phen})(\text{POP})]\text{BF}_4$ (**C2**). **C2** was synthesized by the same method as that of **C1**, except that PPh_3 was replaced by POP (107 mg, 0.2 mmol). Yield: 90%; IR (KBr), in cm^{-1} : $\nu(\text{C-Har})$ 3058–2954, $\nu(\text{C=N-C=C})$ 1768–1435, $\nu(\text{C-O})$ 1207, $\nu(\text{B-F})$ 1054, $\delta(\text{C-Har})$ 846–513. $\text{C}_{48}\text{H}_{40}\text{BCuF}_4\text{N}_2\text{OP}_2 + 1 \text{ THF}$: calcd C 64.52, H 4.77, N 2.95; found C 64.76, H 4.64, N 2.89.

$[\text{Cu}(\text{TDZP})(\text{POP})]\text{BF}_4$ (**S2**). **S2** was synthesized by the same method as that of **C2**, except that Phen was replaced by TDZP (48 mg, 0.2 mmol). Yield: 93%; IR (KBr), in cm^{-1} : $\nu(\text{C-Har})$ 3050, $\nu(\text{C=N-C=C})$ 1566–1405; $\nu(\text{C-O})$ 1212; $\nu(\text{B-F})$ 1053; $\delta(\text{C-Har})$ 816–497. $\text{C}_{56}\text{H}_{50}\text{BCuF}_4\text{N}_4\text{O}_3\text{P}_2\text{S}$: calcd C 62.84; H 4.58; N 5.18; found C 62.78; H 4.70; N 5.23.

$[\text{Cu}(\text{PhenSe})(\text{POP})]\text{BF}_4$ (**Se2**). **Se2** was synthesized by the same method as that of **C2**, except that Phen was replaced by

PhenSe (57 mg, 0.2 mmol). Yield: 94%; IR (KBr), in cm^{-1} : $\nu(\text{C-Har})$ 3064–2856, $\nu(\text{C=N-C=C})$ 1566–1434; $\nu(\text{C-O})$ 1212; $\nu(\text{B-F})$ 1059; $\delta(\text{C-Har})$ 872–512. $\text{C}_{56}\text{H}_{50}\text{BCuF}_4\text{N}_4\text{O}_3\text{P}_2\text{Se}$: calcd C 60.34, H 4.23, N 4.87; found: C 60.15, H 4.51, N 5.01.

Thermogravimetric analyses and cyclic voltammetry studies

The thermogravimetric analysis was performed with approximately 2 mg of the sample in a platinum crucible, with a nitrogen flow of 100 mL min^{-1} and a heating ramp of $10^\circ\text{C min}^{-1}$ in a temperature range of 30–900 $^\circ\text{C}$. The equipment used is of the brand Shimadzu, model TGA-50.

The redox behavior of the complexes was investigated by square wave voltammetry in a potentiostat–galvanostat BAS (Bioanalytical Systems, Inc.) model Epsilon. A concentration of $2.5 \times 10^{-4} \text{ mol L}^{-1}$ in CH_2Cl_2 solution was used under a nitrogen atmosphere. Tetrabutylammonium hexafluorophosphate (0.1 mol L^{-1}) was used as a support electrolyte and the electrochemical cell was composed of three electrodes: work – vitreous carbon; auxiliary – platinum wire; reference – Ag/Ag^+ . For correction of the reference electrode, ferrocene ($E_{1/2}$ vs. NHE = 398 mV) was used.

Spectroscopic measurements

The electronic spectra in the ultraviolet, visible and near infrared regions were obtained for all the complexes in the range of 200–800 nm using a PerkinElmer spectrophotometer model Lambda-750. The values of ϵ are given in $\text{L mol}^{-1} \text{ cm}^{-1}$. The emission spectra were obtained on a Varian Cary Eclipse Fluorescence spectrophotometer. The spectroscopy measurements were performed in CH_2Cl_2 solution and in the solid state using a PMMA matrix containing 10 wt% **C1–Se2**. The analyses were performed using spectroscopic grade solvents, substrates and quartz cuvettes with a capacity of 1 mL and 1.00 cm optical path at 25 $^\circ\text{C}$. Absolute quantum yield (Φ) values were obtained using a Hamamatsu Photonics Absolute Quantum Yield Measurement System model c9920-02G, which is based on the integrating sphere method.

Singlet-excited state photoluminescence decay curves were recorded using the time-correlated individual photon counting method on a FluoTime200 (PicoQuant). The excitation was provided using a 401 nm pulsed diode laser with repeating rates ranging from 5.0 to 20 MHz. Photoluminescence was collected perpendicular to the excitation and passed through a polarizer adjusted at the magic angle. The detection system consists of a monochromator and a multichannel base photomultiplier (Hamamatsu R3809U-50). Lifetimes were obtained by fitting the fluorescence for a convolution of the instrument's response function and a sum of exponentials using the FluoFit[®] software. The considered residual plots and the chi-squared (χ^2) were used to accurately determine the quality of the accessories during the analysis procedure.

Time-resolved spectra were obtained by exciting the sample with a Nd:YAG laser (EKSPLA), 10 Hz, 355 nm. Sample emission was directed onto a spectrograph and gated ICCD camera (Stanford Computer Optics). The films were produced by spin coating on quartz substrates.

Theoretical methods

Geometry optimizations of complexes **C1–Se2** were carried out in a vacuum, using the Orca 4.0.1 software package⁴¹ at the DFT level using the PBE0^{42,43} and the basis set Def2-TZVP(-F) for all atoms.^{44–46} The calculations also included Grimme's dispersion correction with damping D3BJ^{47,48} and the RIJCOSX algorithm was employed to accelerate the evaluation of the integrals, using the resolution of identity approximation for the Coulomb part (RIJ), and the chain of spheres approach for the exchange (COSX).^{49,50} RIJCOSX requires the specification of an auxiliary basis set for the Coulomb part and a numerical integration grid for the exchange part, discussed elsewhere. The vibrational frequencies for both complexes showed no imaginary frequencies. Time-dependent density functional theory (TD-DFT) under the Tamn–Dancoff approximation⁵¹ (TDA) was employed to obtain the first 50 singlet excited states, differing only in the basis set chosen: ZORA-Def2-TZVP(-F) for all atoms, including ZORA relativistic corrections.⁵² To include solvent effects in the excited state energies, the conductor-like polarizable continuum model⁵³ (CPCM) was used, using acetonitrile as solvent. TD-DFT/TDA was also employed to optimize the geometry of the first singlet excited state. The first triplet was optimized from the ground state of the UKS calculation. SOC study on top of TD-DFT results was done by using quasi-degenerate perturbation theory.^{36,54} The SOC integrals used here were calculated using a mean-field method named RI-SOMF(1X) and described elsewhere.⁵⁵ The geometric representations of the complexes were obtained using the Chemcraft program.⁵⁶

Conflicts of interest

There are no conflicts to declare.

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Synthesis of 2,1,3-Benzoxadiazole Derivatives as New Fluorophores—Combined Experimental, Optical, Electro, and Theoretical Study

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Herein, we report the synthesis and characterization of fluorophores containing a 2,1,3-benzoxadiazole unit associated with a π -conjugated system (D- π -A- π -D). These new fluorophores in solution exhibited an absorption maximum at around ~ 419 nm (visible region), as expected for electronic transitions of the π - π^* type ($\epsilon \sim 2.7 \times 10^7$ L mol⁻¹ cm⁻¹), and strong solvent-dependent fluorescence emission ($\Phi_{FL} \sim 0.5$) located in the bluish-green region. The Stokes' shift of these compounds is ca. 3,779 cm⁻¹, which was attributed to an intramolecular charge transfer (ICT) state. In CHCl₃ solution, the compounds exhibited longer and shorter lifetimes, which was attributed to the emission of monomeric and aggregated molecules, respectively. Density functional theory was used to model the electronic structure of the compounds **9a–d** in their excited and ground electronic states. The simulated emission spectra are consistent with the experimental results, with different solvents leading to a shift in the emission peak and the attribution of a π - π^* state with the characteristics of a charge transfer excitation. The thermal properties were analyzed by thermogravimetric analysis, and a high maximum degradation rate occurred at around 300°C. Electrochemical studies were also performed in order to determine the band gaps of the molecules. The electrochemical band gaps (2.48–2.70 eV) showed strong correlations with the optical band gaps (2.64–2.67 eV).

Keywords: 2,1,3-benzoxadiazole, heterocycles, luminescence, fluorophore, tetrazole

INTRODUCTION

Conjugated organic compounds, such as benzochalcogenodiazoles, have attracted attention because of their versatility and advantages, including low cost, improved electronic device performance, flexibility, and tuning through structural design (Liu et al., 2015). This class of compounds has been applied in field-effect transistors, sensors, memory devices, and

solar cells (Regis et al., 2018). In general, the incorporation of heterocyclic units with electron-donating groups (donors) and electron-accepting groups (acceptors) in the molecular structure increases the conjugation and alters the performance of organic electronic devices (Niu et al., 2007; Fu et al., 2009; Liu et al., 2015).

The derivatives of the 2,1,3-benzothiadiazole (BTD) heterocycle have been extensively investigated due to their recognized photophysical properties, such as intense fluorescence, large Stokes shift, and high extinction coefficient (Gallardo et al., 2012; Wang et al., 2014; Fang et al., 2017; Aguiar et al., 2018). However, there is very limited literature available on the behavior of molecular materials obtained from the 2,1,3-benzoxadiazole (BOX) heterocycle (Pati, 2016). Interestingly, the 7-nitro-1,2,3-benzoxadiazole is generally used as a fluorophore in the design of many analyte-responsive fluorescent probes (Pati, 2016; Wu et al., 2017).

The BOX heterocycle, also known as benzofuran, has a flat molecular and bicyclic conjugated structure, and its derivative compounds with extended conjugates are extremely fluorescent. Because of the presence of an oxygen atom in the heterocycle, BOX is more electronegative when compared to BTD (Bouffard and Swager, 2008; Lin et al., 2011; Zeng et al., 2012; Göker et al., 2014; Regis et al., 2018), and due to this electronegativity, BOX forms coplanar and quinoid structures, giving better stability to the devices manufactured (Liu et al., 2015).

The main applications of BOX are to obtain fluorescent derivatization reagents and use in the detection of heavy metals (Toyo'oka, 2004; Song et al., 2011; Sumiya et al., 2011), in solar cells, and in liquid crystals (Liu et al., 2015; Regis et al., 2018).

As part of our continued involvement in the chemistry of *N*-heterocycles (Saba et al., 2015, 2016, 2017, 2018, 2020; Rafique et al., 2016, 2018a,b; Silva et al., 2017; Bettanin et al., 2018; Peterle et al., 2018; Rodrigues et al., 2018; Tornquist et al., 2018; Meirinho et al., 2019; Neto et al., 2020; Scheide et al., 2020) and material sciences (Frizon et al., 2014, 2015, 2016, 2018; Bo et al., 2016, 2018; Westrup et al., 2016; Matzkeit et al., 2018; Regis et al., 2018), herein, we report the synthesis and characterization of BOX derivatives containing electron-donor groups (alkylated tetrazole rings) connected to the 2,1,3-BOX group as an electron-acceptor unit. In addition, thermal, electrochemical, and theoretical predictions were made and photophysical analysis was performed to study the stability, likely geometry, and luminescence properties of these compounds in their ground and excited electronic states.

MATERIALS AND METHODS

Materials and Methods

All reagents were used without further purification and were obtained from commercial sources. The solvents acquired were of commercial grade, with the exception of tetrahydrofuran (HPLC grade), and were purified by methods based on the literature (Armarego and Chai, 2003). The compounds were purified by column chromatography (silica gel) and crystallization from analytical-grade solvents. The reactions were monitored by TLC using Silica Gel 60 (Merck Kieselgel 60F254).

Infrared analysis was performed on an Agilent Cary 600 Series Fourier-transform infrared (FTIR) spectrometer in KBr discs or films. The ^1H and ^{13}C NMR spectra were recorded in chloroform-*d* at 400 and 100 MHz, respectively. The chemical shifts are reported in ppm relative to TMS (0.00 ppm), and the coupling constants are reported in Hz. The chromatograms and mass spectra were acquired on a Shimadzu GCMS-QP5050A spectrometer with a DB5-MS [(5%-phenyl)-dimethylpolysiloxane] capillary column (25 m $\times$ 250 μm $\times$ 0.25 μm) using an electron ionization voltage of 70 eV. The oven parameters used in the method were 80°C for 6 min, increasing at 15°C min $^{-1}$ to 280°C and remaining at this temperature for 4 min, giving a run time of 23.33 min with an initial delay of 4 min. The gas flow was He at 0.6 mL min $^{-1}$, with pressure S3 of 2.3301 psi. A Varian Cary 50 UV-Vis spectrophotometer was employed to record the absorption spectra. Fluorescence emission and excitation spectra were acquired on a Shimadzu RF5301pc spectrofluorophotometer. The quantum yield (fluorescent fragment length—FFL) was acquired using the dilute optical method. A solution of H_2SO_4 (0.5 mol L $^{-1}$) and quinine sulfate (QS) ($\Phi_{\text{FL}} = 0.55$) was used as the Φ_{FL} standard (Crosby and Demas, 1971). The uncertainties related to the quantum yield of fluorescence ($\Delta\Phi_{\text{FL}}$) measurements using QS are of the order of 6% (Würth et al., 2011, 2013).

A DropSens BiPotentiostat/Galvanostat (model Stat 400) was used for all electrochemical measurements. The cyclic voltammetry measurements of **9a–d** were obtained in a standard electrochemical cell containing a system of three electrodes: a glassy carbon working electrode, a Pt wire counter electrode, and an Ag/Ag $^+$ (AgNO $_3$ 0.01 mol L $^{-1}$ in acetonitrile) reference electrode. All measurements were performed in an electrolyte solution [0.1 mol L $^{-1}$ tetra-*n*-butyl ammonium hexafluorophosphate (TBAPF $_6$) in CH $_2$ Cl $_2$] purged with purified nitrogen gas. The ferrocene/ferricenium redox pair (Fc/Fc $^+$) was used as an internal reference. The spectra for **9a–d** used to estimate the optical band gaps were obtained on a Shimadzu UV-1800 spectrofluorophotometer. Thermogravimetric analysis (TGA) was carried out using a Shimadzu analyzer with the TGA-50 module. A PerkinElmer 2400 Series II Elemental Analyzer System was used to carry out the elemental analysis of the final compounds. The fluorescence decay was obtained through the time-correlated single-photon counting technique, using a @FluoTime200 (PicoQuant) spectrometer. The excitation was performed by a 401-nm pulsed diode laser, applying a repetition rate of 20 MHz. Fluorescence was collected perpendicular to excitation and passed through a polarizer set at the magic angle. The detection system consisted of a monochromator and a microchannel plate photomultiplier (Hamamatsu R3809U-50). Lifetimes were obtained by fitting the fluorescence decays to a convolution of the instrument response function and the sum of exponentials using FluoFit $^{\text{®}}$ software. The plots of weighted residuals and reduced chi-squared (χ^2) were used to accurately determine the quality of the fittings during the analysis procedure. The geometry optimization of **9** was carried out *in vacuo*, using the Orca 4.1 (Neese, 2012) software package and density functional theory (DFT) with the PBE0 functional

(Perdew et al., 1996, 1997) and the DEF2-TZVP(-F) basis set for all atoms (Schäfer et al., 1992, 1994; Weigend and Ahlrichs, 2005). Grimme D3 correction was used to include dispersion effects with Becke-Johnson (BJ) damping (Becke and Johnson, 2005; Johnson and Becke, 2005, 2006; Grimme et al., 2010, 2011). In order to accelerate the evaluation of the functionals, the RIJCOSX algorithm was employed, using the resolution of identity approximation for the Coulomb part (RIJ) and the chain of spheres approach for the Fock exchange (COSX) (Izsák and Neese, 2011; Izsák et al., 2013). The vibrational frequencies computed on the optimized geometry of **9** included no imaginary frequencies. In order to simulate the absorption spectra, time-dependent density functional theory (TD-DFT) with the Tamn-Dancoff approximation (TDA) (Petrenko et al., 2011) was employed to obtain the first 10 singlet excited states, using the same protocol. To simulate the emission spectra, the path integral approach implemented by our group in the ORCA_ESD module (Souza et al., 2018, 2019) was employed, using PBE0 to obtain the geometries and Hessians for both the ground and excited states. The line width was set to 450 or 500 cm^{-1} , and the default Lorentzian line shape was used to obtain a better fit to the experimental data. The frequencies below 300 cm^{-1} were removed. For the other parameters, the default options were used. Solvent effects were included in the excited-state energies by using the linear response conductor-like polarizable continuum model (LR-CPCM), while the regular CPCM was employed for the ground state (Marenich et al., 2009). Images of the complex geometries were obtained using the Chemcraft program (Chemcraft, 2019).

Synthesis

2,1,3-Benzoxadiazole-1-oxide (6)

A 500-mL flask was used to obtain a mixture of 2-nitroaniline (9.0 g, 6.5 mmol), tetrabutylammonium bromide (0.3 g, 1.1 mmol), diethyl ether (60 mL), and KOH solution (7 mL, 50% wt). To this mixture, a sodium hypochlorite solution (130 mL, activated chlorine > 10%) was added dropwise. After stirring at room temperature for 7 h, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 ($3 \times 1,000$ mL), and the combined organic layers were evaporated under reduced pressure. The yellow solid was obtained without further purification. Yield: 89%. m.p. 68°C . IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3,472, 3,100, 3,080, 2,962, 2,935, 2,875, 1,649, 1,614, 1,584, 1,536, 1,484, 1,440, 1,421, 1,382, 1,351, 1,282, 1,200, 1,145, 1,124, 1,012, 963, 928, 890, 833, 743, 734, 671, 633.

2,1,3-Benzoxadiazole (7)

Compound **6** (1.7 g, 13 mmol), triphenylphosphine (4.0 g, 15 mmol), and toluene (150 mL) were placed in a 250 mL flask. The mix was refluxed for 3 h then cooled and filtered. The solvents were evaporated to afford the crude product. The material was chromatographed on silica gel with CH_2Cl_2 to afford the 2,1,3-benzoxadiazole **7** as a yellow solid. Yield: 80%. m.p. 69°C . IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3,100, 3,080, 3,010, 2,955, 2,924, 2,853, 2,360, 2,332, 1,969, 1,920, 1,721, 1,650, 1,614, 1,583, 1,535, 1,483, 1,440, 1,422, 1,351, 1,282, 1,263, 1,200, 1,146, 1,125, 1,046, 1,012, 973, 961, 891, 834, 742, 732, 671, 633, 617. ^1H NMR (400 MHz,

CDCl_3) δ ppm: 7.85 (dd, 2H, $J = 6.0, 4.0$ Hz), 7.41 (dd, 2H, $J = 6.0, 4.0$ Hz). Anal. Calcd. For $\text{C}_6\text{H}_4\text{N}_2\text{O}$ $[\text{M}]^+$ 120.0 found 120.0.

4,7-Dibromo-2,1,3-benzoxadiazole (8)

Compound **7** (1.23 g, 10 mmol) and Fe powder (0.12 g, 2.0 mmol) were placed in a round-bottom flask and heated to 100°C . Br_2 (1.5 mL, 30 mmol) was added dropwise over 2 h, and then the reaction was refluxed for 3 h. After cooling, the resulting solution was dissolved in CH_2Cl_2 (40 mL) and washed with brine (40 mL). The organic fraction was washed with saturated sodium bicarbonate solution (4×30 mL), brine (4×30 mL), and water (4×30 mL). The organic layer was dried and concentrated under vacuum. The brown crude product was chromatographed on silica gel (hexane/ethyl acetate 98:2) to produce **8** as a cream powder. Yield: 40%. m.p. $98\text{--}100^\circ\text{C}$. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2,923, 2,852, 2,360, 2,342, 1,873, 1,717, 1,695, 1,606, 1,517, 1,493, 1,465, 1,426, 1,378, 1,377, 1,322, 1,300, 1,292, 1,261, 1,204, 1,150, 1,113, 1,085, 107, 1,028, 958, 907, 878, 867, 845, 745, 728, 638, 607. ^1H NMR (400 MHz, CDCl_3) δ ppm: 7.51 (s, 2H). GC-MS: RT: 13.92 min.; Calcd. For $\text{C}_6\text{H}_2\text{Br}_2\text{N}_2\text{O}$ $[\text{M}]^+$ 277.8 found 277.9.

5-(4-Bromophenyl)-2H-tetrazole (2)

First, 4-Bromobenzonitrile (1.0 g, 5.5 mmol), 20 mL of DMF, ammonium chloride (1.8 g, 33.9 mmol) and NaN_3 (2.3 g, 35 mmol) were placed in a 100 mL round-bottom flask. The mixture was refluxed for 24 h. At room temperature, the mixture was poured onto ice-water to obtain a precipitate. Then, the mixture was acidified with HCl solution to pH 1. The yellow precipitate was filtered and recrystallized in water/ethanol (1:1). Yield: 90%. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3,448, 3,090, 3,058, 3,000, 1,905, 1,608. ESI: Anal. Calcd. for $\text{C}_7\text{H}_5\text{BrN}_4$: m/z 226.9; found m/z 246.9 $[\text{M}+\text{Na}]^+$.

General Procedure for the Synthesis of Compounds 3a–d

Tetrazole (**2**) (2 mmol), acetone (60 mL), K_2CO_3 (2.2 mmol), and 2.2 mmol of the respective alkyl bromide (2-ethylhexyl bromide, octyl bromide, or decyl bromide) were placed in a 250 mL two-neck round-bottom flask. After 45 h of refluxing, the mixture was filtered and concentrated under reduced pressure. The white solid was obtained by recrystallization from ethanol.

5-(4-Bromophenyl)-2-(2-ethylhexyl)-2H-tetrazole (3a)

Yield: 72%. ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.04 (d, 2H, $J = 8.8$ Hz), 7.63 (d, 2H, $J = 8.8$ Hz), 4.57 (d, 2H, $J = 6.5$ Hz), 2.10 (m, 2H), 1.33 (m, 9H), 0.95 (t, 3H, $J = 7.04$ Hz), 0.89 (t, 3H, $J = 7.04$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 164.1, 132.1, 128.3, 126.6, 124.5, 56.3, 39.8, 30.4, 28.4, 23.8, 22.8, 14.0, 10.5.

5-(4-Bromophenyl)-2-octyl-2H-tetrazole (3b)

Yield: 76%. ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.04 (d, 2H, $J = 8.31$ Hz), 7.64 (t, 2H, $J = 8.31$ Hz), 4.64 (t, 2H, $J = 7.34$ Hz), 2.06 (m, 2H), 1.37–1.26 (m, 12H), 0.88 (t, 3H, $J = 7.34$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 164.2, 132.1, 128.3, 126.5, 124.6, 53.3, 31.7, 29.4, 28.9, 28.8, 26.4, 22.6, 14.1.

5-(4-Bromophenyl)-2-decyl-2H-tetrazole (3c)

Yield: 88%. ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.03 (d, 2H, $J = 8.80$ Hz), 7.63 (d, 2H, $J = 8.80$ Hz), 4.64 (t, 2H, $J = 7.34$ Hz), 1.26 (m, 16H), 0.87 (t, 3H, $J = 6.85$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 156.9, 124.8, 121.0, 119.2, 117.2, 46.0, 24.6, 22.3, 22.0, 21.6, 19.0, 15.4, 6.8.

5-(4-Bromophenyl)-2-dodecyl-2H-tetrazole (3d)

Yield: 79%. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2,956, 2,920, 2,849, 1,610. ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.03 (d, 2H, $J = 8.80$ Hz), 7.63 (d, 2H, $J = 8.31$ Hz), 4.64 (t, 2H, $J = 6.85$ Hz), 2.06 (m, 2H), 1.37 (m, 2H), 1.26 (m, 16H), 0.89 (t, 3H, $J = 6.85$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 156.8, 124.8, 121.0, 119.2, 117.2, 46.0, 24.6, 22.3, 22.0, 21.6, 19.0, 15.4, 6.8.

General Procedure for the Synthesis of Compounds 4a–d**4-(4-(2-(2-ethylhexyl)-2H-tetrazol-5-yl)phenyl)-2-methylbut-3-yn-2-ol (4a)**

In a 125-mL two-neck round-bottom flask containing a desiccant tube of CaCl_2 , a solution was prepared of tetrazole (3a) (2.000 g, 5.95 mmol), 60 mL of dry $\text{Et}_3\text{N}/\text{THF}$ (1:1), bis(triphenylphosphine)palladium dichloride (0.183 g, 0.26 mmol), and triphenylphosphine (0.069 g, 0.26 mmol). After 48 h of reflux, the mixture was vacuum filtered and a white product was obtained by recrystallization from ethanol. Under argon, the mixture was heated to 55°C ; then, copper iodide (0.025 g; 0.13 mmol) and 2-methyl-3-butyn-2-ol (0.851 g, 10.11 mmol) in 10 mL $\text{Et}_3\text{N}/\text{THF}$ (1:1) were added dropwise over 40 min. After 6 h under reflux, the mixture was filtered at room temperature through Celite® and concentrated under reduced pressure. The resulting product was chromatographed on silica gel. For the preparation of compounds 4b, 4c, and 4d, the same methodology was followed, using 5-(4-bromophenyl)-2-octanotetrazole, 5-(4-bromophenyl)-2-decanotetrazol, and 5-(4-bromophenyl)-2-dodecanotetrazol, respectively.

4-(4-(2-(2-Ethylhexyl)-2H-tetrazol-5-yl)phenyl)-2-methylbut-3-yn-2-ol (4a)

Yield: 71%. ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.1 (d, 2H, $J = 8.31$ Hz), 7.52 (t, 2H, $J = 8.31$ Hz), 4.64 (t, 2H, $J = 6.85$ Hz), 2.51 (s, 1H), 2.11 (m, 1H), 1.65 (s, 6H), 1.33 (m, 8H), 0.95 (t, 3H, $J = 7.34$ Hz), 0.90 (t, 3H, $J = 6.85$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 164.2, 132.1, 128.3, 126.5, 124.6, 53.3, 31.7, 29.4, 28.9, 28.8, 26.4, 22.6, 14.1.

2-Methyl-4-(4-(2-octyl-2H-tetrazol-5-yl)phenyl)but-3-yn-2-ol (4b)

Yield: 77%. ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.1 (d, 2H, $J = 8.80$ Hz), 7.52 (t, 2H, $J = 8.31$ Hz), 4.64 (t, 2H, $J = 7.34$ Hz), 2.47 (s, 1H), 2.05 (m, 2H), 1.64 (s, 6H), 1.27 (m, 10H), 0.87 (t, 3H, $J = 6.85$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 164.4, 132.1, 127.2, 126.6, 124.7, 95.6, 81.7, 65.6, 53.3, 31.7, 31.5, 29.0, 28.8, 26.4, 22.6, 15.1.

4-(4-(2-Decyl-2H-tetrazol-5-yl)phenyl)-2-methylbut-3-yn-2-ol (4c)

Yield: 88%. ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.10 (d, 2H, $J = 8.80$ Hz), 7.53 (d, 2H, $J = 8.80$ Hz), 4.65 (t, 2H, $J = 7.34$ Hz), 2.28 (s, 1H), 2.03 (m, 2H), 1.64 (s, 6H), 1.25 (m, 16H), 0.89 (t, 3H, $J = 6.36$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 164.5, 132.2, 127.2, 126.6, 124.7, 95.5, 81.7, 65.6, 53.3, 31.4, 31.5, 29.4, 28.9, 26.4, 22.7, 14.1.

4-(4-(2-Dodecyl-2H-tetrazol-5-yl)phenyl)-2-methylbut-3-yn-2-ol (4d)

Yield: 96%. m.p.: 65°C . FTIR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3,315, 3,051, 2,956, 2,918, 2,848. ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.04 (d, 2H, $J = 8.80$ Hz), 7.64 (d, 2H, $J = 8.31$ Hz), 4.64 (t, 2H, $J = 6.85$ and 7.34 Hz), 2.06 (m, 2H), 1.26 (m, 16H), 0.89 (t, 3H, $J = 6.85$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 164.2, 132.1, 130.2, 127.2, 126.5, 124.6, 53.3, 29.6, 29.4, 26.4, 22.7, 14.1.

General Procedure for the Synthesis of Compounds 5a–d

Compound (4a) (1.61 g, 4.73 mmol), 50 mL of toluene, and NaOH (0.246 g, 6.15 mmol) were combined in a 100 mL round-bottom flask. The solution was distilled while slowly heating, and a mixture of 8 mL toluene/acetone was also distilled. The reaction was monitored by TLC using hexane/ethyl ether (6:4) as eluent. At room temperature, the solution was filtered through Celite® and vacuum-concentrated. The crude solid was purified by column chromatography elution with a solution of hexane/ethyl acetate (95:5), resulting in the desired product at a yield of 90% [40].

2-(2-Ethylhexyl)-5-(4-ethynylphenyl)-2H-tetrazole (5a)

Yield: 90%. m.p. 67°C . IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3,291, 2,958, 2,920, 2,842. ^1H NMR (CDCl_3 , 400 MHz) δ ppm: 8.10 (d, 2H, $J = 8.31$ Hz), 7.52 (d, 2H, $J = 8.31$ Hz), 4.57 (d, 2H, $J = 6.85$ Hz), 2.10 (m, 1H), 1.39–1.26 (m, 8H), 0.94 (t, 3H, $J = 7.34$ Hz), 0.89 (t, 3H, $J = 6.85$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ ppm: 164.3, 132.1, 127.1, 126.6, 124.6, 95.6, 81.7, 56.2, 39.8, 31.4, 30.3, 28.4, 23.8, 22.8, 13.9, 10.4.

5-(4-Ethynylphenyl)-2-octyl-2H-tetrazole (5b)

Yield: 88%. m.p. 65°C . IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3,286, 2,954, 2,916, 2,846. ^1H NMR (CDCl_3 , 400 MHz) δ ppm: 8.02 (d, 2H, $J = 8$ Hz), 7.62 (d, 2H, $J = 8$ Hz), 4.64 (t, 2H, $J = 8$ Hz), 2.05 (q, 2H, $J = 6.8$ Hz), 1.41–1.32 (m, 2H), 1.32–1.17 (m, 8H), 0.86 (t, 3H, $J = 6.46$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ ppm: 164.0, 131.9, 128.1, 126.4, 124.4, 53.2, 31.5, 29.2, 28.7, 26.2, 22.5, 13.9.

2-Decyl-5-(4-ethynylphenyl)-2H-tetrazole (5c)

Yield: 87%. m.p. 60°C . IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3,286, 2,954, 2,916, 2,846. ^1H NMR (CDCl_3 , 400 MHz) δ ppm: 8.02 (d, 2H, $J = 8$ Hz), 7.62 (d, 2H, $J = 8$ Hz), 4.63 (t, 2H, $J = 6$ Hz), 2.05 (q, 2H, $J = 8$ Hz), 1.4–1.32 (m, 2H), 1.40–1.32 (m, 12H), 0.87 (t, 3H, $J = 6$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ ppm: 164.1, 132.0, 128.2, 125.4, 124.5, 53.2, 31.8, 29.4, 29.2, 28.8, 26.3, 22.6, 14.0. Anal. Calcd. for C, 73.51%; H, 8.44%; N, 18.05% found C, 72.8%; H, 8.56%; N, 18.27%.

2-Dodecyl-5-(4-ethynylphenyl)-2H-tetrazole (5d)

Yield: 88%. m.p. 56°C. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3,290, 2,950, 2,920, 2,844. ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.10 (d, 2H, $J = 8.22$ Hz), 7.53 (d, 2H, $J = 8.22$ Hz), 4.64 (t, 2H, $J = 7.04$ Hz), 2.52 (s, 1H), 2.04 (m, 2H), 1.65 (s, 6H), 1.26 (m, 16H), 0.88 (t, 3H, $J = 6.46$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 164.4, 132.1, 126.6, 124.7, 95.6, 81.7, 65.6, 53.3, 31.9, 31.5, 29.6, 29.3, 29.5, 28.9, 26.3, 22.7, 14.1.

General Procedure for the Synthesis of Compounds 9a–d

In a 100 mL three-neck round-bottom flask, were mixed compound **8** (0.190 g, 0.68 mmol), 45 mL of dry Et_3N , bis(triphenylphosphine)palladium (II) dichloride (0.022 g, 0.03 mmol), and triphenylphosphine (0.080 g, 0.30 mmol). After heating to 55°C, copper iodide (0.030 g, 16 mmol) was added. A 15-mL solution of respective aryl acetylene **5a** (0.50 g, 1.47 mmol) in dry Et_3N was then slowly added dropwise. The reaction remained under reflux for 2 h, being monitored by TLC using a mixture of hexane/ethyl ether (8:2) as the eluent. The mixture was filtered, and the retained solid was dissolved in chloroform and filtered. After concentrating the solvent, a yellow solid was obtained at 71% yield.

4,7-Bis((4-(2-(2-ethylhexyl)-2H-tetrazol-5-yl)phenyl)ethynyl)benzo[c][1,2,5]oxadiazole (9a)

Yield: 71 %. m.p. 175°C. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2,970, 2,951, 2,810, 2,211. ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.20 (dd, 4H, $J = 6.8$ Hz, 2.0 Hz), 7.77 (dd, 4H, $J = 6.8$ Hz, 1.6 Hz), 7.61 (s, 2H), 4.66 (t, 4H, $J = 7.2$ Hz), 2.07 (q, 4H, $J = 7.2$ Hz), 1.42–1.23 (m, 20H), 0.88 (t, 6H, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 164.3, 149.4, 134.4, 132.6, 128.4, 126.9, 123.7, 112.6, 98.8, 85.3, 53.4, 31.7, 29.4, 29.0, 28.9, 26.4, 22.6, 14.1. ESI HRMS: calcd for $[\text{C}_{40}\text{H}_{44}\text{N}_{10}\text{O}+\text{H}]^+$ 681.3772, found 681.3768.

4,7-Bis((4-(2-(2-octyl)-2H-tetrazol-5-yl)phenyl)ethynyl)benzo[c][1,2,5]oxadiazole (9b)

Yield: 77 %. m.p. 206°C. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2955, 2914, 2842, 2207. ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.21 (dd, 4H, $J = 6.8$, 1.6 Hz), 7.77 (dd, 4H, $J = 6.8$ Hz, 1.6 Hz), 7.64 (s, 2H), 4.67 (t, 4H, $J = 7.2$ Hz), 2.07 (q, 4H, $J = 7.2$ Hz), 1.40–1.19 (m, 28H), 0.88 (t, 6H, $J = 6.8$ Hz) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 164.3, 149.4, 134.4, 132.5, 128.4, 126.8, 123.7, 112.6, 98.7, 85.3, 53.4, 31.9, 29.44, 29.38, 29.34, 29.2, 28.9, 26.4, 22.7, 14.1. ESI HRMS: calcd for $[\text{C}_{44}\text{H}_{52}\text{N}_{10}\text{O}+\text{H}]^+$ 737.4398, found 737.4400.

4,7-Bis((4-(2-decyl)-2H-tetrazol-5-yl)phenyl)ethynyl)benzo[c][1,2,5]oxadiazole (9c)

Yield: 82 %. m.p. 202°C. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3,035, 2,968, 2,922, 2,850, 2,202. ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.21 (d, 4H, $J = 8.4$ Hz), 7.78 (d, 4H, $J = 8.4$ Hz), 7.28 (s, 2H), 4.67 (t, 4H, $J = 7.2$ Hz), 2.08 (q, 4H, $J = 7.2$ Hz), 1.41–1.17 (m, 36H), 0.88 (t, 6H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 164.3, 149.4, 134.4, 132.6, 128.4, 126.8, 123.7, 112.6, 98.7, 85.3, 53.4, 31.9, 29.6, 29.5, 29.4, 29.3, 28.9, 26.4, 22.7, 14.1. ESI HRMS: calcd for $[\text{C}_{48}\text{H}_{60}\text{N}_{10}\text{O}+\text{H}]^+$ 793.5024, found 793.5027.

4,7-Bis((4-(2-dodecyl)-2H-tetrazol-5-yl)phenyl)ethynyl)benzo[c][1,2,5]oxadiazole (9d)

Yield: 79 %. m.p. 199°C. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3,031, 2,950, 2,918, 2,850, 2,209. ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.21 (d, 4H, $J = 8.4$ Hz), 7.78 (d, 4H, $J = 8.4$ Hz), 7.64 (s, 2H), 4.59 (d, 4H, $J = 6.8$ Hz), 2.13 (q, 2H, $J = 6.4$ Hz), 1.40–1.27 (m, 16H), 0.97 (t, 6H, $J = 7.2$ Hz), 0.90 (t, 6H, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 164.3, 149.4, 134.4, 132.5, 128.4, 126.8, 123.7, 112.6, 98.7, 85.3, 53.4, 31.9, 29.44, 29.38, 29.34, 29.2, 28.9, 26.4, 22.7, 14.1. ESI HRMS: calcd for $[\text{C}_{40}\text{H}_{44}\text{N}_{10}\text{O}+\text{H}]^+$ 681.3772, found 681.3777.

RESULTS AND DISCUSSION

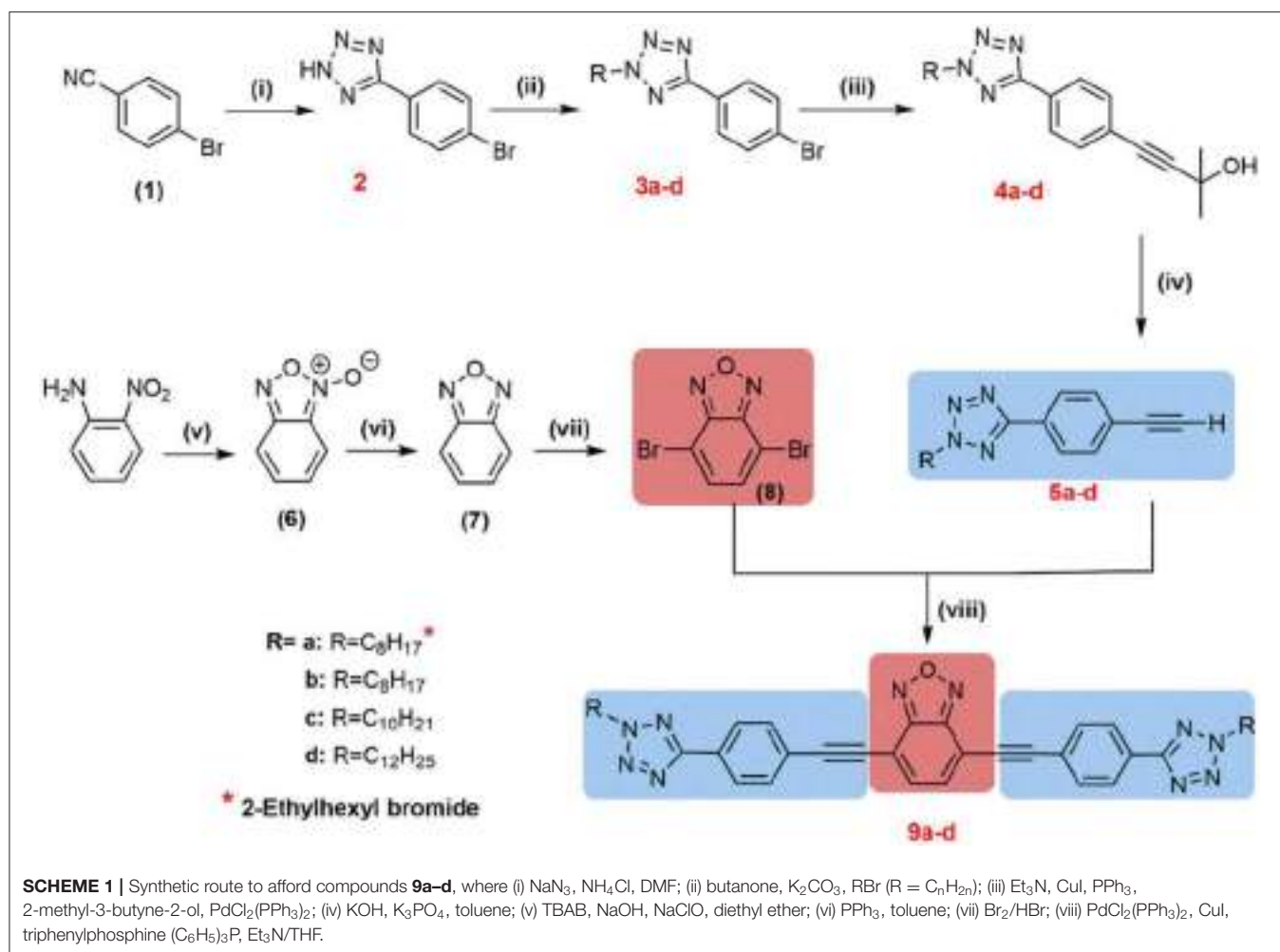
Synthesis and Spectroscopic Characterization

The synthetic route for the preparation of the final desired compounds, based on 1,2,5-benzoxadiazole **9a–d**, is shown in **Scheme 1**. The synthesis procedure adopted has been described in a previous publication (Frizon et al., 2018). The synthesis starts from the cyclization of 2-nitroaniline with sodium hypochlorite with the catalyst TBAB (tetrabutylammonium bromide) in a basic medium to obtain the *N*-oxide **6**. In sequence, the reduction of the *N*-oxide group using PPh_3 in xylene gives the heterocycle 2,1,3-benzoxadiazole **7** at 75% yield. In the next stage, the selective bromination reaction of 2,1,3-benzoxadiazole **7** at positions 4 and 7 was performed to obtain the 4,7-dibromo-2,1,3-benzoxadiazole (**8**). The Sonogashira coupling reaction between the aryl dibromide **8** and two equivalents of terminal aryl acetylenes **5a–d**, synthesized previously, allowed the desired compounds **9a–d** to be obtained. After purification in a chromatographic column, the final desired compounds were obtained at good yields (71–82%). All of the final compounds **9a–d** synthesized were characterized by proton and carbon-13 NMR, IR spectroscopy, and mass spectrometry.

Photophysical Characterization UV-Vis and Fluorescence

The photophysical properties of compounds **9a–d** were determined in chloroform solution at room temperature and are presented in **Table 1**.

The absorption and emission spectra obtained for **9a–d** in chloroform solution are shown in **Figure 1**. All compounds displayed similar absorption spectra with maxima at 419 nm, which are attributed to a π - π^* transition and showed high molar absorption coefficients ($\sim 3.4 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$), which is characteristic of the benzoxadiazole heterocycle. Also, after excitation at the lower energy band, all compounds showed a strong bluish-green fluorescence emission in solution ($\lambda_{\text{FL}} = 450$ – 650 nm), with emission maxima ranging from 494 to 498 nm. The values for the Stokes shifts for compounds **9a–d** are in the range of $3,738$ – $3,786 \text{ cm}^{-1}$, indicating a possible intramolecular charge transfer (ICT) in the excited state (Neto et al., 2007). The fluorescence quantum yields (Φ_{FL}) of **9a–d** were determined in chloroform using quinine sulfate as the standard ($\Phi_r = 0.55$ in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$). The Φ_{FL}



values could be calculated using the equation (Fery-Forgues and Lavabre, 1999): $\Phi_{FL} = \Phi_r (F_s/F_r)(A_r/A_s)(\eta_s/\eta_r)$, where s and r denote the sample and reference, respectively, η is the solvent refractive index, F is the integrated fluorescence intensity, and A is the value of absorbance at the excitation wavelength used to record the fluorescence spectrum. The values obtained are summarized in **Table 1**, where it can be noted that all compounds presented quantum yields (Φ_{FL}) of 0.51 to 0.54. The values obtained for compounds **9a-d** are considerably higher than those reported in our previous articles for compounds containing the heterocycles 2,1,3-benzoselenadiazole (Regis et al., 2018) and 2,1,3-benzotiadiazole (Frizon et al., 2016).

The singlet excited-state lifetimes of compounds **9a-d** in CHCl_3 solvent were investigated by time-resolved fluorescence spectroscopy, using a wavelength of 401 nm for the excitation. Compounds **9a-d** were evaluated in chloroform solution because of the higher affinity of this solvent (due to the alkyl chains) with the aromatic center. The singlet excited-state average lifetimes for compounds **9a-d** are shown in **Table 1**, and their values are similar. All fluorescence decays at emission maxima of compounds **9a-d** (see **Figure S1**) were best fitted by a bi-exponential function. The excited-state lifetimes and

TABLE 1 | Photophysical properties of **9a-d** in CHCl_3 solution.

Compound	$\lambda_{\text{Abs}}^{\text{max}}/\text{nm}^a$ ($\epsilon/10^4 \text{ mol L}^{-1} \text{ cm}^{-1}$) ^b	$\lambda_{\text{FL}}^{\text{max}}/\text{nm}^{a,c}$	Stokes Shift/ cm^{-1a}	Φ_{FL}^d	τ_f^e/ns
9a	417 (3.0)	494	3,738	0.54	2.73
9b	419 (2.7)	498	3,786	0.52	2.68
9c	417 (3.6)	495	3,779	0.52	2.68
9d	419 (4.2)	498	3,786	0.51	2.68

^a $\text{L mol}^{-1} \text{ cm}^{-1}$. ^bIn chloroform solution ($1.0 \times 10^{-5} \text{ mol L}^{-1}$). ^cExcited at absorption maxima. ^dQuantum yields were determined with the quinine sulfate solution as reference ($\Phi_F = 0.55$ in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$). ^eAverage lifetimes were calculated using $\tau_f = \Sigma \tau_i^2 A_i / \Sigma \tau_i A_i$ due to multi-exponential profile. Fluorescence decays were measured at maxima of the emission intensities of the compounds after excitation at 401 nm.

their relative amplitudes for **9a-d** in chloroform solution are shown in **Table S1** (see **ESI**). The longer lifetimes (τ_1) were attributed here to the emission of monomeric **9a-d**, while the shorter lifetimes (τ_2) were attributed to the emission of **9a-d** aggregated in chloroform solution, even at $10^{-5} \text{ mol L}^{-1}$, since the molecular aggregation could reduce the excited-state lifetimes due to the enhanced radiationless path of the

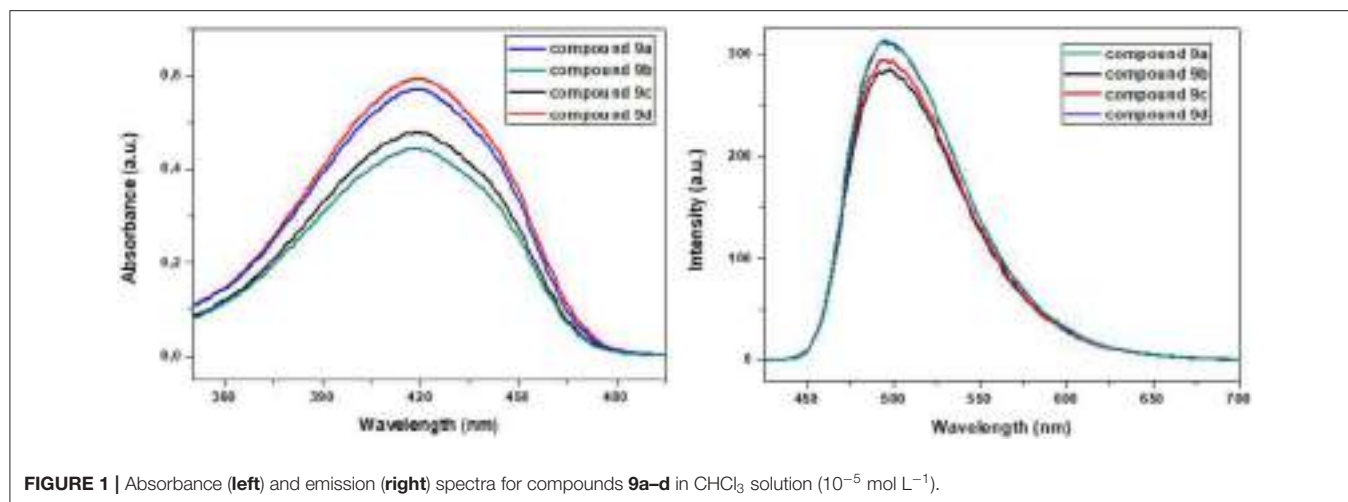


FIGURE 1 | Absorbance (left) and emission (right) spectra for compounds **9a–d** in CHCl_3 solution ($10^{-5} \text{ mol L}^{-1}$).

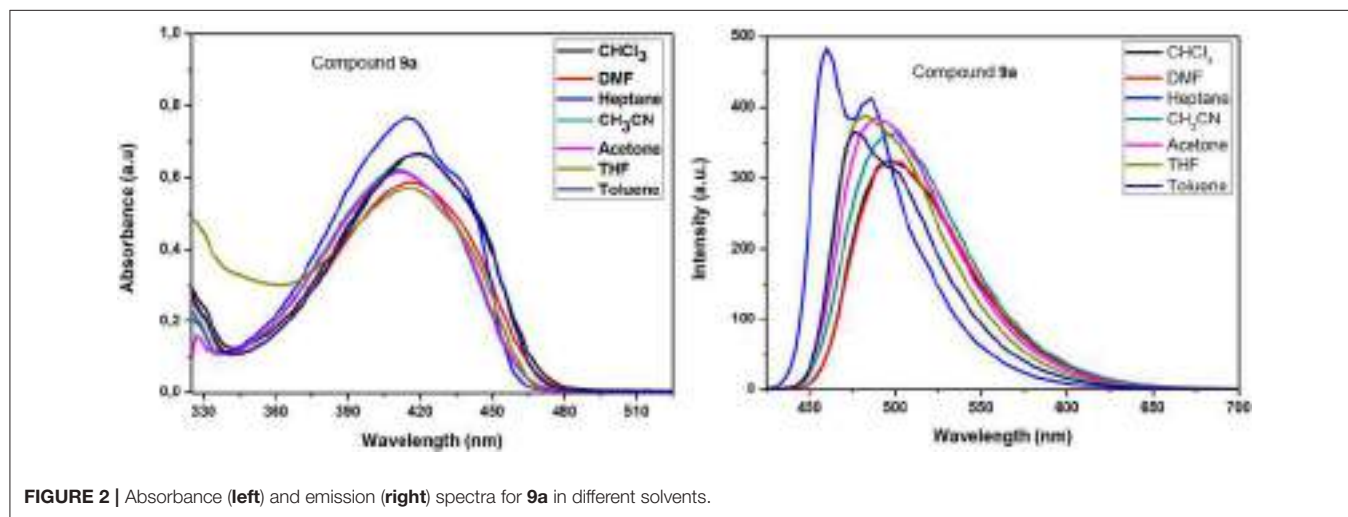


FIGURE 2 | Absorbance (left) and emission (right) spectra for **9a** in different solvents.

excited-state deactivation. With the exception of **9a**, the relative amplitudes of aggregate emissions (A_2) were higher than 70% in dilute chloroform solution (see **Figure S1**). The relative amplitude A_2 of **9a** was close to 50%, showing the possible influence of the branched chain in forming fewer aggregates than the linear chain. A hypothesis of the aggregation of **9a–d** in chloroform solution is proposed based on the fluorescence excitation measurements. The fluorescence excitation spectra for **9a–d** in chloroform solution are shown in **Figure S2** and compared with the absorption spectra. The excitation spectra for the compounds show a different vibrational progression and are red-shifted when compared to the absorption spectra, suggesting aggregation, since the excitation spectrum should be identical in shape to the absorption spectrum, provided that there is a single species in the ground state. In contrast, the excitation and absorption spectra are no longer superimposable when species exist in different forms, such as aggregates, in the ground state (Valeur, 2012). When compared with similar benzothiadiazole derivatives previously reported by our group (Westrup et al., 2016), the benzoxadiazole-based compounds **9a–d** showed a

greater tendency toward aggregate formation. This could be associated with the benzoxadiazole moiety and the higher dipole moment of this heterocycle (Tobiason et al., 1973).

It was observed that the size of the alkyl chain did not significantly influence the deactivation of the excited states, suggesting that only the conjugated aromatic part contributes to the frontier orbitals (HOMO and LUMO), which are responsible for the radiative processes.

Solvatochromism

A solvatochromic study of compounds **9a–d** was performed to ascertain the role of solvent polarity in the absorption and fluorescence emission. The UV-vis absorption and fluorescence emission properties were measured in heptane (Hep), toluene (Tol), chloroform (CHCl_3), tetrahydrofuran (THF), acetone (Acet), *N,N*-dimethylformamide (DMF), and acetonitrile (CH_3CN) solutions. The UV-Vis absorption and emission spectra for **9a** in various solvents are shown in **Figure 2**, and the specifics of the absorption and fluorescence emission of these compounds are listed in **Table 2**.

With increasing solvent polarity, the absorption bands of compound **9a** showed a slight red-shift, indicating a small solvatochromic effect on the ground state. The fluorescence spectra showed a notable hypsochromic shift of the maximum emission in heptane, toluene, and THF (less polar solvents) and higher vibrational resolution when compared to CHCl_3 . The largest hypsochromic shifts were observed for THF and toluene (15 and 22 nm, respectively). This type of optical behavior in apolar organic solvents is similar to that exhibited by benzothiadiazole (Westrup et al., 2016). With the use of a more polar solvent like *N,N*-dimethylformamide or acetonitrile, a small hypsochromic shift in the emission maxima compared to CHCl_3 was also registered. This solvatochromism behavior is observed in molecules exhibiting larger dipole moments and charge transfer characteristics in the excited state, that is, an ICT state (Liang et al., 2015).

The excited-state lifetimes and relative amplitudes of **9a** at $10^{-5} \text{ mol L}^{-1}$ in heptane, toluene, tetrahydrofuran, and acetone are shown in Table S2. In all solvents, **9a** exhibited two excited-state lifetimes. Except in heptane, the longer excited-state lifetimes (τ_1) were over 3 ns and the shorter lifetimes (τ_2) ranged from 2.2 to 1.8 ns. In addition, the shortest lifetime dominates the fluorescence (A_2) of compound **9a**. The longer excited-state lifetimes (τ_1) were attributed here to monomeric emission of **9a**, while the shorter excited-state lifetimes (τ_2) could be associated with the emission provided by aggregates of molecules **9a** in toluene, tetrahydrofuran (THF), and acetone solutions. In heptane solution, the longest lifetime (τ_1) of molecule **9a** was found to be 2.1 ns and the shortest lifetime (τ_2) around 1.4 ns, which could be related to the poor stabilization of the excited state by the non-polar solvent. In addition, the contributions of the longest lifetime (A_1) and the shortest lifetime (A_2) to the emission of **9a** in heptane were similar, suggesting that the emission of **9a** in heptane solution is provided equally by the monomer and the aggregate of **9a**.

The quantum yields of **9a** in different solvents are shown in Table S2. The quantum yields increase with increasing affinity of the solvent for compound **9a**. The quantum yields for **9a** were 0.27 in heptane solution and 0.71 in acetone solution. In toluene, THF, and acetone solutions, the emission lifetime results suggest that the aggregate dominates the emission of compound

9a; however, monomeric emission of **9a** also contributes to the fluorescence, mainly in acetone solution. As the ICT state is known to be able to non-radiatively deactivate excited species, the quantum yield results are in agreement with the proposed molecular aggregation, which suppresses the ICT in the excited state of the monomer and increases the quantum yield in polar solvents (Liang et al., 2015).

Theoretical Modeling of the Electronic Structure and Fluorescence

To gain a better understanding of the absorption and luminescence properties of **9a–d**, we carried out calculations using DFT for a representative molecule without the aliphatic carbon chains (**9**). The calculated frontier orbitals are shown in Figure 3. It can be observed that the HOMO has major contributions from the benzene ring of the benzoxadiazole moiety and from the triple bonds, whereas the LUMO is mostly a π^* orbital delocalized over the benzoxadiazole. The HOMO (−2) and HOMO (−1) are more evenly spread through the molecule, while the LUMO (+1) is more centered in the benzoxadiazole ring and LUMO (+2) in the benzene rings close to the tetrazole.

TD-DFT calculations were performed to acquire information related to the excited states. The absorption spectra were calculated and convoluted with Gaussians, reproducing the experimental spectra, as shown for each molecule in Figure 4. Table 3 shows some of the first two calculated transitions, which were observed in the experimental spectra. To simulate the solvent dependence, the linear response CPCM was used to account for the effect of the solvent on the energy. The two transitions predicted for **9** correspond to those observed in the measured spectra, and, in all solvents, the lowest energy transition originates from a HOMO $\rightarrow$ LUMO (95) excitation. The calculated spectra showed the same solvent-dependence observed in the UV-Vis spectra. With increasing solvent polarity, the first excited state is predicted to be stabilized and the transition matrix element of the dipole moment operator decreases. These results, together with an analysis of the molecular orbitals involved in the first electronic transition, lead to the assignment of a π - π^* transition with the characteristics of a charge transfer excitation, thus explaining the large transition dipole moment and Stokes shift observed.

The fluorescence spectra were also calculated for **9** using the path integral approach developed by our group (Souza et al., 2018, 2019). The PBE0 functional was chosen to obtain the adiabatic electronic energy differences. The emission spectra, shown in Figure 5, are also consistent with the experimental results. The emission peak was shifted for the different solvents; for example, hexane and toluene showed emission at higher energy compared with the other solvents. The main vibrational progression observed in the experimental spectra of non-polar solvents is due to the C=C and C=N stretching modes, with the energy separation of these peaks beginning at around 0.15 eV ($1,200 \text{ cm}^{-1}$).

Thermal Properties

The thermal properties of compounds **9a–d** were obtained by thermogravimetric analysis (TGA) (Figure 6). The DTG

TABLE 2 | The absorption and emission wavelengths, molar absorption coefficient, and Stokes shifts of compound **9a** in various solvents.

Compound	Absorption ^b $\lambda_{\text{max}}(\text{nm}) (\epsilon)^a$	Emission ^c $\lambda_{\text{max}} (\text{nm})$	Stokes shift (cm^{-1})
9a (Hept)	416 (2.7×10^7)	487	3,505
9a (Tol)	420 (2.8×10^7)	477	2,845
9a (CHCl_3)	420 (2.8×10^7)	499	3,769
9a (THF)	416 (2.7×10^7)	484	3,377
9a (Acet)	413 (2.7×10^7)	491	3,846
9a (DMF)	417 (2.8×10^7)	499	3,941
9a (CH_3CN)	413 (2.7×10^7)	499	4,173

^a $\text{L mol}^{-1} \text{ cm}^{-1}$. ^b $[c] = 1.5 \times 10^{-5} \text{ mol L}^{-1}$. ^cExcited at absorption maxima.

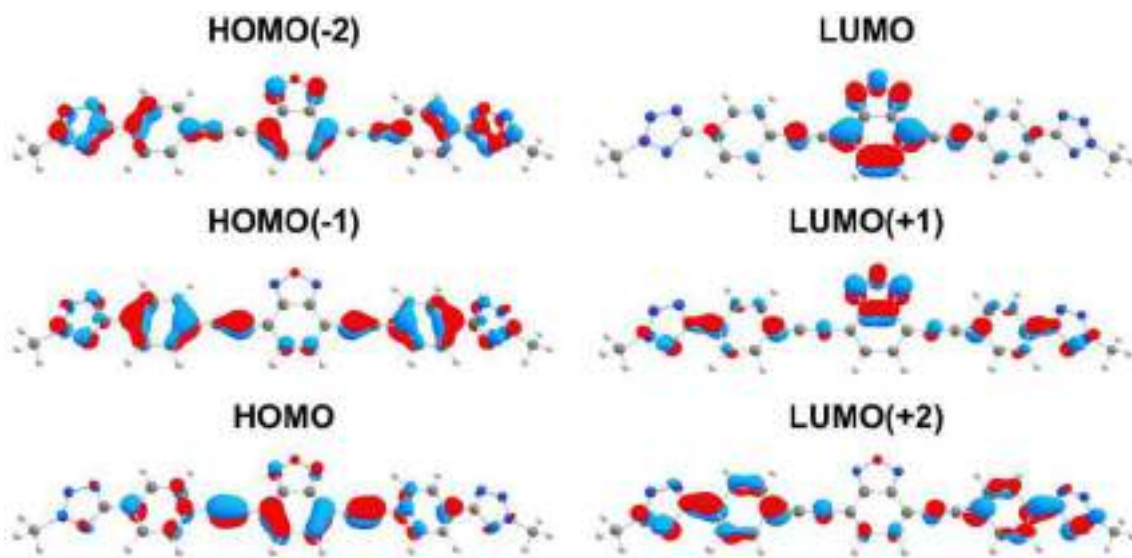


FIGURE 3 | Frontier molecular orbitals of **9** calculated using PBE0/def2-TZVP(-f).

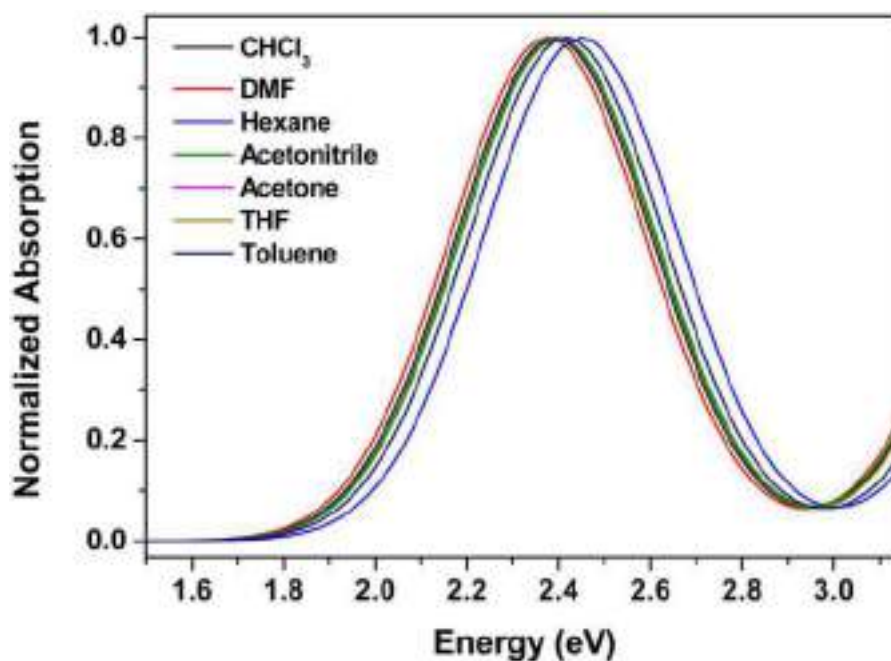


FIGURE 4 | Theoretical absorption spectra calculated in different solvents using PBE0/def2-TZVP(-f) and convoluted with Gaussians of 0.25 eV width.

curves for the final compounds were processed from the TGA curves. The complete degradation process indicates a mass loss of around 100%. Three thermal events were observed for these compounds, corresponding to a mass loss of almost 55% at an initial decomposition temperature of 220°C, with a maximum degradation rate observed at around 300°C. The second thermal event was detected at approximately 305°C, and this event is related to a loss of 51%. A small thermal

event was detected at ~650°C, and this event is related to a loss of 4%.

Electrochemical Characterization

Compounds **9a–d** show very distinct reduction processes in the negative scan (**Figure 7**). The first may be associated with a quasi-reversible reduction of the benzoxadiazole, indicating that the benzochalcogen ring is reduced in preference to the triple

bond. Benzochalcogen is a well-known heteroatomic compound with a high electron-accepting part, because it has two electron-withdrawing imine groups (C=N) (Omer et al., 2009).

TABLE 3 | Data for the TD-DFT excitations using PBE0/def2-TZVP(-f).

State	Energy		<i>f</i>	<I μ F> ²	Attribution ^a
	eV	Solvent shift			
Hexane					
S ₁	2.45	0.14	1.7804	29.67	H → L (95)
S ₂	3.04	0.19	0.0002	0.004	H-1 → L (88)
Toluene					
S ₁	2.42	0.18	1.7323	29.25	H → L (95)
S ₂	3.00	0.23	0.0003	0.004	H-1 → L (88)
CHCl ₃					
S ₁	2.40	0.18	1.6547	28.19	H → L (95)
S ₂	2.98	0.23	0.0003	0.004	H-1 → L (88)
THF					
S ₁	2.40	0.17	1.6347	27.83	H → L (95)
S ₂	2.99	0.22	0.0003	0.004	H-1 → L (88)
Acetone					
S ₁	2.40	0.16	1.6038	27.29	H → L (95)
S ₂	2.99	0.21	0.0003	0.004	H-1 → L (89)
DMF					
S ₁	2.38	0.18	1.5804	27.15	H → L (95)
S ₂	2.95	0.90	0.0037	0.0521	H-3 → L (94)
Acetonitrile					
S ₁	2.40	0.16	1.5962	27.16	H → L (95)
S ₂	3.00	0.21	0.0003	0.004	H-1 → L (89)

^a Transitions with high percentage contributions are shown in parentheses.

Thus, in the case of **9a–d**, this peak can be attributed to the benzoxadiazole group and the reduction peak can probably be assigned to the anion radical species. The second process that occurs at much more cathodic values may be associated with an irreversible electrochemical process with triple bond reduction (Neto et al., 2005, 2013). In the positive scan, various oxidation processes were observed, which probably include oxidation of the tetrazole portion of the molecule, and this process could involve the formation of an intermediate radical cation species.

The energies of HOMO and LUMO boundary orbitals of π -conjugated systems (D- π -A- π -D), such as benzochalcogenic derivatives, can be defined by the electron affinity (EA) and ionization potential (IP). These can be accessed by the evaluation of electron affinity (EA) and the ionization potential (IP), based on the values of reduction and oxidation potentials obtained by electrochemical assays (Neto et al., 2013; Frizon et al., 2014). The EA and IP were determined using the following empirical formula (Neto et al., 2005): $EA = E_{\text{onset}}^{\text{red}} + 4.44 \text{ eV}$ and $IP = E_{\text{onset}}^{\text{oxi}} + 4.44 \text{ eV}$, where $E_{\text{onset}}^{\text{red}}$ and $E_{\text{onset}}^{\text{oxi}}$ are the onset potentials of reduction and oxidation, respectively. These onset potentials were corrected from Ag/Ag⁺ to NHE using the Fc/Fc⁺ pair. Analyses of the HOMO-LUMO energy level calculations of **9a–d** were performed from benzoxadiazole potentials. The band gap values obtained by cyclic voltammetry and UV-vis spectroscopy showed good agreement between the results obtained with the two different techniques. The results of the electrochemical assays conducted with **9a–d** showed that changes in the length of the alkyl group attached to the tetrazole ring did not significantly influence the redox potentials of the molecules. The $E_{\text{gap}}^{\text{ele}}$ values obtained for molecules **9a–d** were higher than those for benzoselenadiazole (Regis et al., 2018).

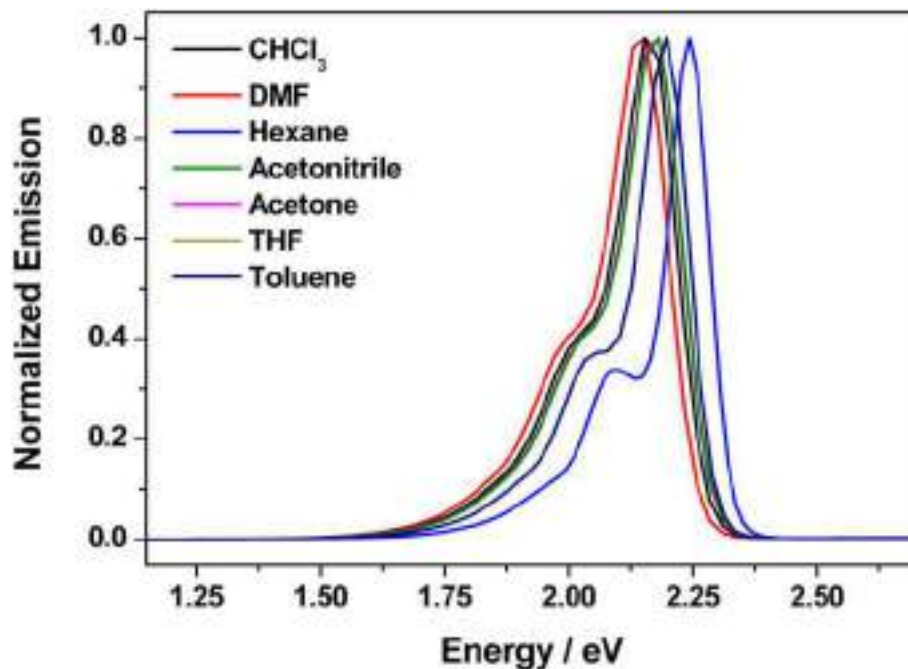


FIGURE 5 | Predicted emission spectra calculated in different solvents using PBE0/def2-TZVP(-f).

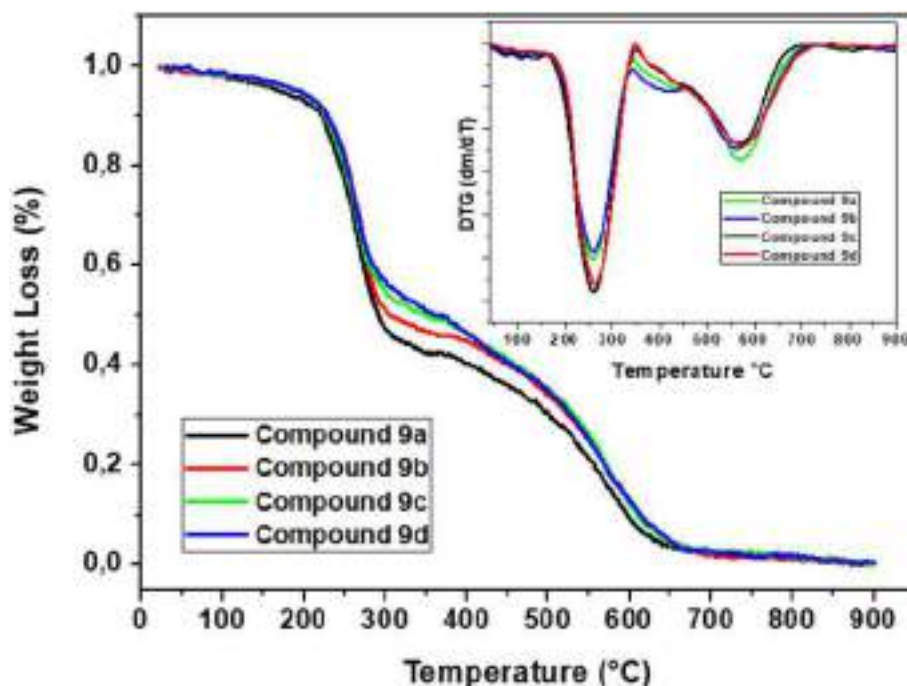


FIGURE 6 | Thermograms (TGA) and DTG curves of compounds **9a–d**.

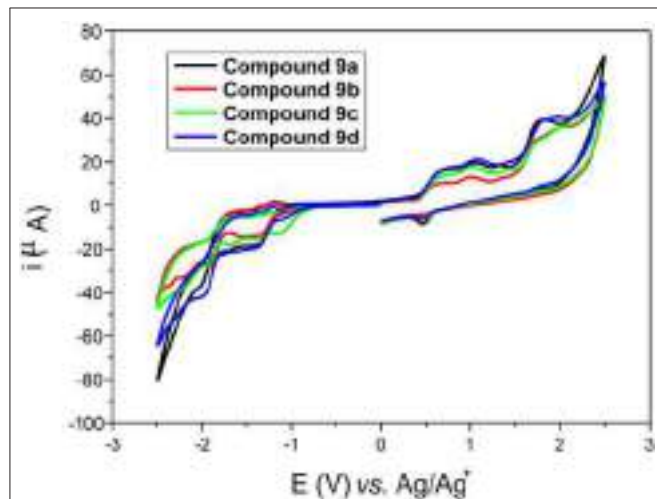


FIGURE 7 | Cyclic voltammogram of compounds **9a–d** on a glassy carbon electrode in 0.1 TBAPF₆/CH₂Cl₂ at 100 mV s⁻¹.

TABLE 4 | Optical and electrochemical properties of compounds **9a–d**, where E_{oxi}^{onset} is the onset potential of oxidation, E_{red}^{onset} is the onset potential of reduction, I_p (HOMO) is the ionization potential, E_a (LUMO) is the electron affinity, E_g is the band gap, and λ_{onset} is the absorption onset wavelength.

Parameter	Compound			
	9a	9b	9c	9d
E_{oxi}^{onset} (V) ^a	1.964	1.934	2.001	1.953
E_{red}^{onset} (V) ^a	-0.726	-0.756	-0.476	-0.746
IP (HOMO) (eV) ^b	-6.404	-6.374	-6.441	-6.393
EA (LUMO) (eV) ^c	-3.714	-3.684	-3.994	-3.964
E_{ele}^{gap} (eV)	2.69	2.69	2.48	2.70
λ_{onset} (nm)	467.1	468.9	468.8	468.1
E_{gap}^{opt} (eV) ^d	2.65	2.64	2.64	2.65

^a vs. NHE; ^b $IP = -(E_{ox} + 4.44)$ eV; ^c $EA = -(E_{red} + 4.44)$ eV; ^d Optical bandgap calculated on the low energy band edge of the absorption spectrum ($E_{gap}^{opt} = 1240/\lambda_{onset}$).

CONCLUSIONS

In this study, a new series of fluorophores, with D- π -A- π -D molecular architectures, based on 2,1,3-benzoxadiazole derivatives, was synthesized and characterized. The photophysical behavior of the compounds was evaluated by combining the following spectroscopic techniques: UV-vis absorption spectroscopy, stationary fluorescence spectroscopy, and time-resolved spectroscopy. The series of molecules in solution exhibited, in the visible region, a maximum absorption (~ 419 nm) that can be attributed to electronic transitions of the

type π - π^* ($\epsilon \sim 3.4 \times 10^{-4} \text{ L mol}^{-1}\text{cm}^{-1}$). Compounds **9a–d** exhibited intense fluorescence ($\Phi_{\text{FL}} \sim 0.5$) located in the bluish-green region (494–498 nm) with a solvent polarity dependence resulting in a large Stokes shift (ca. $3,779 \text{ cm}^{-1}$), which was associated with an ICT in the excited state. The data obtained from DFT and TD-DFT indicate that the ground and first excited states are a π -type orbital. Therefore, a π - π^* transition with the characteristics of a charge transfer excitation can be assumed, confirming the ICT state. Compounds **9a–d** showed a strong tendency to form aggregates even in dilute solution, exhibiting in CHCl_3 solution longer and shorter lifetimes, on the nanosecond timescale, which were here attributed to the emission of monomeric and aggregated molecules, respectively. The thermal characterization allowed the thermal stability of compounds **9a–d** to be evaluated, and a high maximum degradation rate was observed at around 300°C . Small electrochemical band gap (2.48 to 2.70 eV) and optical band gap (2.64 to 2.67 eV) values were obtained for compounds **9a–d**, these being in agreement with results for similar compounds previously reported in the literature. The redox potentials of **9a–d** did not change significantly with variations in the length of the alkyl group attached to the tetrazole ring. The recognition of the structure–property relationship of benzoxadiazole could guide further studies in the search for luminescent materials with better performance than benzothiadiazole.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/**Supplementary Material**.

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AUTHOR CONTRIBUTIONS

TF, AV, and JR conceived the project and wrote the manuscript. TF, JR, AV, SS, and ML performed the synthesis and characterization. AV, FS, TF, and TC studied the photophysical properties (absorption and fluorescence spectra). HB, FG, and TF studied the thermal properties. EZ performed the electrochemical studies. GF and BS made the theoretical predictions. SC and TC studied the singlet excited-state lifetimes. All authors discussed the results and commented on the manuscript.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fchem.2020.00360/full#supplementary-material>

For compounds **9a–d**, the absorption (Abs) and fluorescence excitation (Ex) spectra, NMR spectra, FTIR spectra, and HRMS are available in **Figures S3–S23**.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Synthesis, photophysical and electrochemical properties of novel and highly fluorescent difluoroboron flavanone β -diketonate complexes†

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Difluoroboron β -diketonates complexes are highly luminescent with extensive properties such as their fluorescence both in solution and in solid state and their high molar extinction coefficients. Due to their rich optical properties, these compounds have been studied for their applications in organic electronics such as in self-assembly and applications in biosensors, bio-imaging and optoelectronic devices. The easy and fast synthesis of difluoroboron β -diketonate (BF_2dbm) complexes makes their applications even more attractive. Although many different types of difluoroboron β -diketonates complexes have been studied, the cyclic flavanone analogues of these compounds have never been reported in the literature. Therefore, the present work aims to synthesize difluoroboron flavanone β -diketonate complexes, study their photophysical and electrochemical properties and assess their suitability for applications in optoelectronic devices. The synthesis was based on a Baker–Venkataraman reaction which initially provided substituted diketones, which were subsequently reacted with aldehydes to afford the proposed flavanones. The complexation was achieved by reacting flavanones and $\text{BF}_3\cdot\text{Et}_2\text{O}$ and in total 9 novel compounds were obtained. A representative difluoroboron flavanone complex was subjected to single crystal X-ray diffraction to unequivocally confirm the chemical structure. A stability study indicated only partial degradation of these compounds over a few days in a protic solvent at elevated temperatures. Photophysical studies revealed that the substituent groups and the solvent media significantly influence the electrochemical and photophysical properties of the final compounds, especially the molar absorption coefficient, fluorescence quantum yields, and the band gap. Moreover, the compounds exhibited a single excited-state lifetime in all studied solvents. Computational studies were employed to evaluate ground and excited state properties and carry out DFT and TDDFT level analysis. These studies clarify the role of each state in the experimental absorption spectra as well as the effect of the solvent.

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1 Introduction

Organic luminophores stand out as important compounds within a diverse set of different areas of science because of their applications in technology as part of chemical detection devices, biological identification applications, bio-imaging and

photoelectronic devices.^{1,2} The last decade has seen continued efforts to develop a new class of compounds known as organoboronic complexes.^{3,4} The difluoroboron β -diketonates (BF_2dbm) belonging to the tetracoordinate organoboron complexes are highly fluorescent and can present very useful photophysical properties,^{1–6} with potential technological applications. The first compound of this type was synthesized by Morgan and Tunstall in 1924 through Claisen condensation reaction using only aromatic carbonyl compounds to obtain fluorescent organoboronic compounds.⁵ The difluoroboron β -diketonate complexes are increasingly attracting more attention as fluorescent organic materials because they have so many advantages including easy preparation, high molar extinction coefficient, high quantum fluorescence yields and important photo physical properties.⁴ Most of BF_2dbm complexes reported showed a strong emission in solution⁶ and further chemical modification at the aromatic

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ring substituents of the molecule and conjugation expansion allows for adjustments in emission color throughout the visible region up until NIR region.⁷

Although the synthesis and photophysical characterization of many BF₂dbm complexes has been described in the literature,^{3,8–13} only a few notable examples demonstrating their potential applications have been reported. For example, the BF₂dbm-PLA polymer synthesized by Zhang and collaborators was found in the solid state to display unique optical properties and good stability of nanoparticles in aqueous suspension and thus making them suitable for biological imaging, biological detection and photodynamic therapies.¹⁴ The NIR emission characteristic of the curcuminoid based BF₂dbm complexes made them suitable candidates for NIR imaging. Their capacity to penetrate deeply into the tissues, low auto-fluorescence background and low toxicity to biological samples allowed Ran and collaborators to use the curcuminoid complexes as NIR imaging probe for detecting insoluble aggregates of β -amyloid *in vitro*, an pathological marker of Alzheimer disease and differentiate *in vivo* mice and 19 month old transgenic mice.¹⁵ Mo and collaborator reported the use of a BF₂dbm complexes as an organic light-emitting diode emission material as part of a device capable of exhibiting high quantum yields of 12.8%.¹⁶ A BF₂dbm derivative containing a triphenylamine moiety was synthesized as a new type of π electron donor–acceptor system. The compound showed long wavelength absorption in the UV/visible spectra and redox properties ideal for applications in sensitized solar cells. The fabricated device showed solar-to-electric power conversion efficiencies of 2.7–4.4% under 1.5 AM solar light.¹⁷

Almost all BF₂dbm complexes described in the literature have the same basic structural scaffold with substituents mainly being introduced on the benzenoid rings. Structural modifications of BF₂dbm complexes at the α -carbon of the dicarbonyl moiety or variants of the 1,3-diketone as cyclic ketone, have up until now, not been reported. The flavanone structural motif is an interesting option for complexation with boron difluoride given that the extra aromatic ring at the C2

position of the dihydropyrone could contribute to the absorption and fluorescent properties. Therefore, in order to discern how the aforementioned structural modifications affect the photophysical and electrochemical properties of BF₂dbm complexes, we describe the synthesis and evaluate the photophysical properties of novel difluoroboron flavanone β -diketonates complexes in different media.

2 Results and discussion

2.1 Synthesis of difluoroboron flavanone β -diketonates complexes

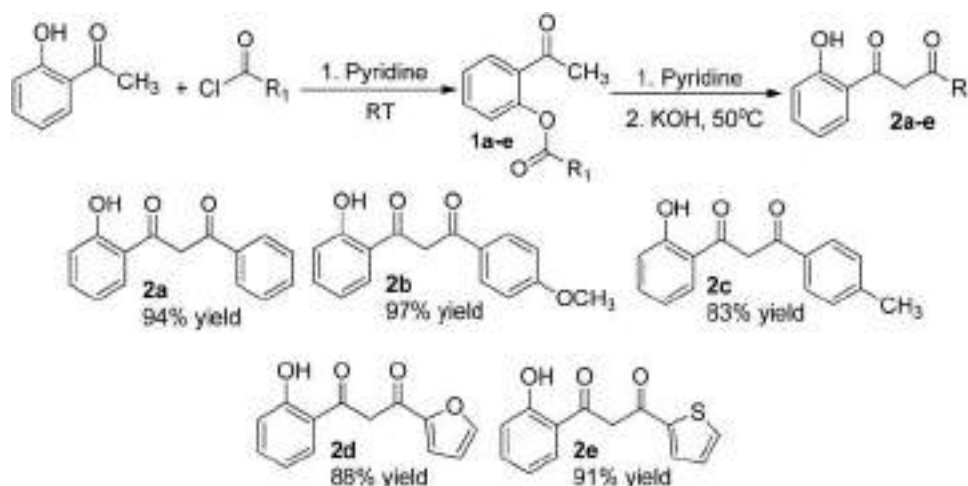
The synthesized β -diketones were obtained by esterification of 2-hydroxyacetophenones with substituted benzoyl chlorides in the first step. Esters **1a–e** were subjected to a Baker–Venkataraman rearrangement in the second step to afford diketones **2a–e** in excellent yields (Scheme 1).^{18,19}

All the synthesized β -diketones are known compounds in the literature and therefore were confirmed by comparison of their physical and spectroscopy data with the reported data in the literature (see Experimental section).

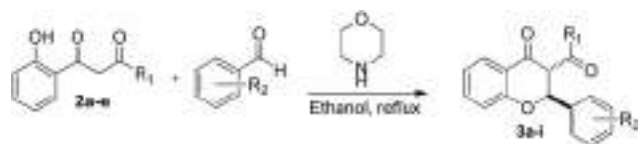
Next, with diketones **2a–e** in hands, flavanones **3a–i** were synthesized *via* an Aldol–Oxi domino reaction between β -diketones **2a–e** and substituted benzaldehydes (Scheme 2) according to the procedure describe in the literature.²⁰

The synthesized flavanones were purified by recrystallization to provide crystalline compounds in good yield (46–95%). Flavanones **3a–i** are all known compounds and therefore confirmed by comparison of their melting points and spectroscopic data with those reported in the literature (Table 1).²⁰

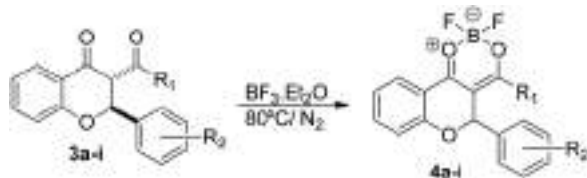
The difluoroboron flavanone β -diketonate complexes **4a–i** were obtained by reacting flavanones **3a–i** with BF₃·Et₂O in an inert atmosphere of nitrogen (Scheme 3). The methodology was optimized to obtain the best possible yields. Carrying the reaction out initially in dichloromethane (DCM) as solvent and at room temperature for two hours provided a final product



Scheme 1 Synthesis of β -diketones.

Scheme 2 Synthesis of flavanones **3a-i**.Table 1 Product yield for compounds **3a-i**

Flavanone	R ₁	R ₂	Yield (%)	Melting point (°C)
3a	Phenyl	H	59	142–144
3b	<i>p</i> -Anisyl	H	62	160–162
3c	<i>p</i> -Tolyl	H	80	167–168
3d	2-Furyl	H	95	175–176
3e	2-Thienyl	H	76	118–120
3f	<i>p</i> -Tolyl	2-Cl	97	175–176
3g	2-Furyl	4-F	68	171–172
3h	2-Thienyl	4-F	46	144–146
3i	<i>p</i> -Anisyl	2-Cl	79	173–175

Scheme 3 Synthesis of difluoroboron flavanones complexes **4a-i**.

yield of only 27% after purification. Increasing the temperature to 80 °C and increasing the stoichiometric excess of BF₃·Et₂O to 8 equivalents not only permitted to elimination of DCM as solvent but also improved the reaction yield to 78%. The optimized reaction conditions established for the synthesis of **4a** were applied to the synthesis of compounds **4b-i**.

In total, 9 novel compounds were prepared in good yield (Table 2). Amongst the flavanone compounds prepared, only one flavanone containing a 2-pyridyl group at R₂ position (structure not shown) failed to react with BF₃·Et₂O and form the corresponding difluoroboron flavanone β-diketonate complex. This may possibly be due to a competitive complexation between the pyridine nitrogen and boron trifluoride. Only compounds **4e**, **4g** and **4h** bearing a 2-furyl or 2-thienyl at R₁ were obtained as solids whereas in comparison the other compounds formed yellow-greenish oils.

The infrared spectrum presented some weak bands between 3100–2900 cm^{−1} attributed to stretching vibrations of saturated

Table 2 Product yield for compounds **4a-i**

Compound	R ₁	R ₂	Yield (%)	Melting point (°C)
4a	Phenyl	H	75	—
4b	<i>p</i> -Anisyl	H	57	—
4c	<i>p</i> -Tolyl	H	61	—
4d	2-Furyl	H	54	—
4e	2-Thienyl	H	87	188–190
4f	<i>p</i> -Tolyl	2-Cl	55	—
4g	2-Furyl	4-F	89	165–167
4h	2-Thienyl	4-F	67	172–174
4i	<i>p</i> -Anisyl	2-Cl	56	—

and unsaturated C–H bonds. More intense absorptions bands were observed between 1600–1540 and 1500–1400 cm^{−1} corresponding to C=O and C=C (enolic tautomerism) stretching vibrations. The bands observed in the region of 1180–1170 cm^{−1} were attributed to the B–O stretching vibration and the bands at 1030–1050 cm^{−1} were attributed to the B–F stretching vibrations.^{21,22}

In order to describe vibrational modes that are infrared active we performed calculations using the ORCA program with B3LYP functional (see Computational details) for compound **4a** and compared them with experimental results. Fig. S1 (see ESI†) shows the infrared spectrum of compound **4a** theoretically calculated including the main vibrational normal modes. Weak bands between 3207–3094 cm^{−1} are formed by fifteen infrared active modes where fourteen are due to stretching of C–H bonds of the benzenoid rings. The inset in Fig. S1 (ESI†) shows the vibration at 3186 cm^{−1} (see movies in the ESI†). There is a vibration at 3094 cm^{−1} that is due to C–H stretching from the γ-dihydropyrone ring. The next main band with a maximum at 1632 cm^{−1} is formed by six vibrations, where the first two are due to C–C bond stretching within the benzenoid rings and rocking of their H atoms. The last two have, in addition, a weak contribution from C–O stretching. The third band at 1580 cm^{−1} is attributed to a single vibration from C–O stretching of the dicarbonyl fragment. The most intense band of the spectrum at 1520 cm^{−1} is a result of seven vibrations. These modes correspond to C–C bond stretching of the benzenoid rings and from rocking of H atoms. The most intense peak at 1519 cm^{−1} also has some weak contributions from C–O bond stretching of dihydropyrone moiety. The stretching of the B–F bonds occur at 1076 and 1070 cm^{−1}. The proton NMR displayed a characteristic singlet resonance at approximately 6.60 ppm which corresponded to the methine hydrogen on the γ-dihydropyrone ring and thus strongly suggesting the formation of a difluoroboron β-diketonate complex. Likewise, the ¹³C NMR showed only one ketone signal at approximately 181 ppm which further supports this conclusion. Furthermore, a ¹⁹F NMR analysis was carried out and the spectrum revealed non-binomial quartets in the range of −141.4 and −143.6 ppm which is an agreement with similar BF₂dbm complexes reported in the literature.^{23–26}

2.2 Single crystal X-ray diffraction

The crystal structure of compound **4e** is represented in Fig. 1. The difluoroboron coordination with both oxygens of the 1,3-dicarbonyl moiety was confirmed, forming a six-membered chelate ring. The compound crystallizes in a centrosymmetric *P2₁/c* space group, existing an inverted center inside a unitary cell with an equal 50:50 ratio of the *S* and *R* isomer. (Only the *S* isomer was presented in Fig. 1). Bonding to carbon C14 exist at the phenyl group that is almost perpendicular (~85°) in comparison with the rest of molecule and presented a planar conformation formed by the phenyl, thiophene and chelate ring (Fig. 1). The principal parameters showing the intermolecular distances and angles are summarized in Table 3.

Analyzing the bond distance of the compound **4e** (Fig. 1), some interesting information was obtained involving principally

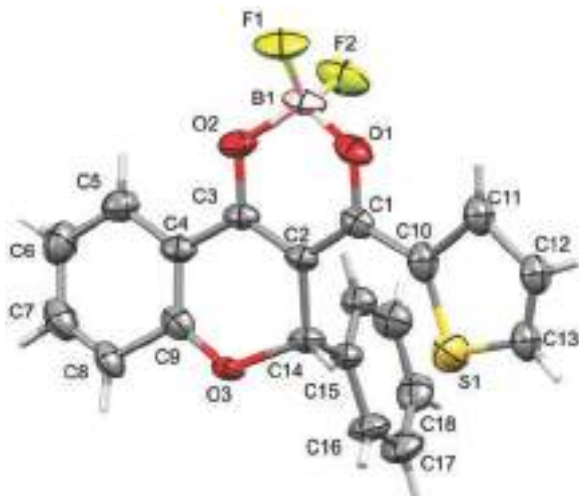


Fig. 1 Crystallographic structure of compound **4e** with no-hydrogen atoms labeled. Ellipsoids are represented at 30% probability.

Table 3 Bond distance and angles selecting to molecule **4e**

Bond	Distance (Å)	Bond	Angle (°)
O(2)–C(3)	1.307(3)	C(3)–O(2)–B(1)	120.6(3)
O(1)–C(1)	1.316(3)	C(1)–O(1)–B(1)	122.2(2)
O(2)–B(1)	1.476(5)	F(1)–B(1)–F(2)	112.1(3)
O(1)–B(1)	1.458(5)	F(1)–B(1)–O(1)	109.0(3)
F(2)–B(1)	1.371(5)	F(2)–B(1)–O(1)	108.3(4)
F(1)–B(1)	1.361(4)	F(1)–B(1)–O(2)	108.4(4)
C(3)–C(2)	1.380(4)	F(2)–B(1)–O(2)	109.4(3)
C(3)–C(4)	1.439(4)	O(1)–B(1)–O(2)	109.7(2)
C(2)–C(1)	1.402(4)	O(2)–C(3)–C(2)	122.1(3)
C(2)–C(14)	1.513(3)	O(2)–C(3)–C(4)	115.3(3)
C(14)–C(15)	1.518(3)	C(2)–C(3)–C(4)	122.6(2)
C(10)–S(1)	1.598(10)	C(3)–C(2)–C(1)	118.4(2)
C(10)–C(11)	1.635(12)	C(3)–C(2)–C(14)	119.4(2)
C(12)–C(11)	1.572(16)	C(10)–S(1)–C(13)	95.5(8)
C(4)–C(9)	1.317(8)	C(4)–C(9)–O(3)	129.0(6)
C(4)–C(5)	1.418(4)	C(4)–C(9)–C(8)	115.4(7)

the 6 member planar ring formed by B1–O1–C1–C2–C3–O2 atoms. The bond distance of C1–O1 and C3–O2 are 1.316(3) and 1.307(3) Å, respectively, which is remarkable given that bond lengths for C–O and C=O bonds according to Mogul analysis 1.41(3) and 1.22(2) Å, respectively were expected. Moreover, the bond length of C1–C2 was 1.402(4) Å and C2–C3 was 1.380(4) Å, where typically C=C bonds lengths are 1.33(3) Å. These aspects suggest electronic delocalization density along the molecular fragment O1–C1–C2–C3–O2 (resonance hybrid). Therefore, it is suggested that one way to represent the chelate ring is represented in the Fig. 2, which is akin to some structurally related 3-arylchromanones that exist exclusively in their keto-enol tautomeric form, stabilized by intramolecular hydrogen bonding.²⁷

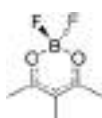


Fig. 2 Representation of resonate chelate ring formed in the actual structure.

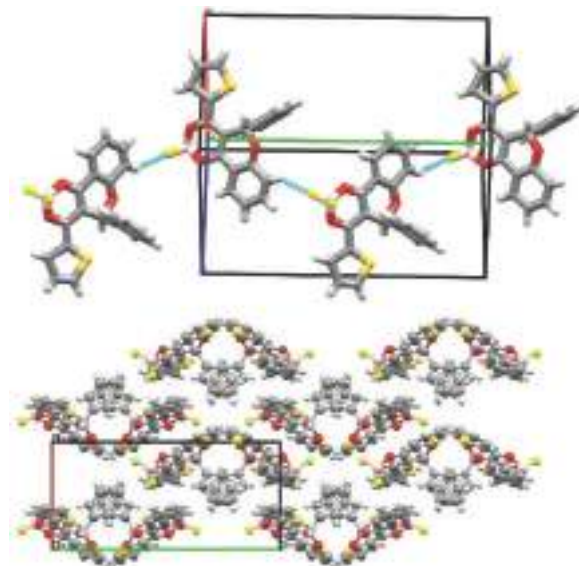


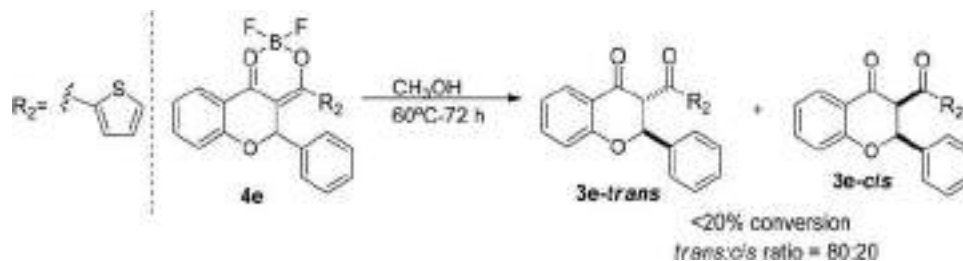
Fig. 3 Top image shows representation of the C–H...F intermolecular interactions observed in compound **4e** with one-dimensional chain along the *b* crystalline axis. Bottom image shows the view along the *c* axis of the crystal packing between molecules of **4e**.

The B–O distance bond was 1.476(5) and 1.458(5) for B1–O2 and B1–O1, respectively, which are similar with reported values recently reported in the literature.²⁶ The B1–F1 distance bond [1.361(4)] and B1–F2 [1.371(5)] agree with B–F bond lengths (1.36–1.37) reported for structures containing the BF₂ fragment coordinated to acetyl-ketones as O–O donors. The boron atom with sp³ hybridization orbitals presented a tetrahedral geometry distorted with O–B–O and O–B–F angles very close of 109.5° and the F1–B1–F2 angle (121.3(3)°) is a little bigger because repulsion between electron clouds of fluorine atoms (F...F). The crystalline structure is stabilized by weak intermolecular interactions, such as the C–H...F contacts with atoms distance of 2.402 Å (Fig. 3). These interactions form infinite chains along the *b* axis with the molecules related by the 2₁ screw axis. A better packing visualization is shown the Fig. 3b where it can be observed that every molecule forms a kind of zig zag.

2.3 Stability of difluoroboron flavanone β-diketonate complexes

The β-diketonate complex **4e** was reacted with methanol at 60 °C for 3 days under refluxing conditions (Scheme 4). The mixture of products was characterized by proton NMR which confirmed the partial conversion of **4e** to the flavanone starting material **3e**.

The proton NMR revealed that **4e** mostly remained unreacted but 20% of the mixture as determined from the NMR peak integrals was comprised of flavanones **3e-trans** and **3e-cis** indicated by the presence of 4 sets of doublets. Two smaller doublets corresponded to *cis* isomer at 4.61 and 5.82 ppm with a coupling constant of 3 Hz and the other two doublets at 4.94 and 5.99 ppm with a coupling constant of 12 Hz corresponded to the *trans* isomer were observed. The ratio between the diastereoisomers (80:20) was calculated by integration of the signal of both isomers. Thus, based on this result, the complexes would

Scheme 4 Reaction of **4e** with methanol.

be expected to slowly lose their fluorescent properties in protic solvents or in the presence of nucleophilic species.

2.4 Photophysical properties

The photophysical properties of the final compounds, **4a–i** are summarized in Table 4 and normalized absorption and fluorescence spectra of **4a–i** in chloroform as solvent at a concentration of 10^{-4} M are also shown in Fig. 4.

All compounds exhibited two main absorption bands between 346 nm and 432 nm (Fig. 4a–c) whereas molar absorption coefficient of maximum absorption wavelength ranges of $0.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (for compound **4f**) to $1.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (for compound **4g**). The two bands for **4a** in CHCl_3 correspond to π – π^* transitions of the conjugated systems that involve the aromatic rings.^{28,29} The maxima emission wavelength of most compounds in chloroform roughly take place at 486 nm, except for compounds **4d**, **4e**, **4g** and **4h** where their maxima emission wavelength occur around 495 nm (see Table 4). The Stokes shifts ($\Delta\nu_{\text{ST}}$) of the compounds in chloroform are in the range of 2946 to 4303 cm^{-1} , respectively, for **4g** and **4a**. The compounds in chloroform solution exhibited fluorescence quantum yields (Φ_{PL}) between 0.28 and 0.75 (see Table 4). Although no clear correlations between the electronic properties of the different substituents present in compounds **4a–i** with the quantum yields could be established, a few standout compounds with promising photophysical properties were identified. Specifically, compound **4d** bearing a 2-furyl moiety achieved up to 0.75 in chloroform as solvent making it a lead compound for further studies in the solid state and potential applications in optoelectronic devices. Furthermore, compound **4b** bearing a *p*-anisyl moiety displayed a significant quantum yield of 0.51 and thus

indicates that the introduction of a methoxy group improved this property of the difluoroboron β -diketonate complexes. The influence of methyl groups and halogens on the benzenoid rings can be assessed by comparison of **4c** and **4f** with **4a**. In this case, quantum yields were very similar which suggests that these functional groups do not increase quantum yields of the difluoroboron β -diketonate complexes. Comparison of compounds **4g–i** with their non halogen bearing counterparts **4d** and **4e** suggests that the introduction of halogens does not favor larger quantum yields. All difluoroboron flavanone complexes emitted in the green region. The fluorescent boron-difluoride *o*-hydroxybenzoyl methanate was studied by Fedorenko and co-workers³⁰ presented a smaller quantum yield (0.26 in CHCl_3) than the analogous cyclic flavanone equivalent **4a** reported here (0.33 in CHCl_3).

All compounds in chloroform solution at a concentration of 10^{-4} M showed a mono-exponential fluorescence decays with lifetimes in the nanosecond timescale (see Table 4), which is a feature of monomeric emission from difluoroboron β -diketonate dyes in diluted solutions.³ The fluorescence decay curves of the compounds in chloroform are shown in the ESI† (see Fig. S32). The singlet excited-state lifetimes (τ_{f}) of compounds **4a–i** varied from 4.88 ns (**4g**) to 3.56 ns (**4b**) in chloroform. Moreover, compound **4d** showed the highest radiative rate constants and the lowest non-radiative rate constants, which explains the higher fluorescence efficiency observed for **4d** (0.75) in chloroform. Compounds **4g** and **4h** containing 4-F group at R2 position displayed the lowest radiative rate constants, whilst compound **4i** exhibited the highest non-radiative rate constants. The photophysical properties of the final compounds, **4a–i**, in acetonitrile solution are summarized in Table 5. Normalized absorption and fluorescence spectra of **4a–i** in acetonitrile solution at concentration of 10^{-4} M are showed in Fig. 5.

Table 4 Photophysical properties of the compounds **4a–i** in chloroform

Compound	Absorption λ_{max} (nm)/($\epsilon/10^4$) ^a	Emission λ_{em} (nm)	$\Delta\nu_{\text{ST}}$ (cm^{-1})	Φ_{PL} ^b	τ_{f} ^c (ns)	k_{r} ^d (ns^{-1})	k_{nr} ^e (ns^{-1})
4a	346; 404/(0.5)	489	4303	0.33	4.20	0.079	0.160
4b	360; 417/(0.3)	484	3262	0.51	3.56	0.143	0.138
4c	359; 418/(0.8)	485	3191	0.32	3.69	0.087	0.184
4d	364; 430/(0.4)	494	3013	0.75	4.78	0.157	0.052
4e	364; 430/(0.7)	495	3054	0.48	4.16	0.115	0.125
4f	351; 410/(0.2)	489	3940	0.36	3.91	0.092	0.164
4g	364; 432/(1.8)	495	2946	0.35	4.88	0.072	0.133
4h	364; 429/(0.8)	496	3149	0.30	4.15	0.072	0.169
4i	362; 421/(0.3)	487	3163	0.28	3.69	0.076	0.195

^a Units = $\text{M}^{-1} \text{ cm}^{-1}$, the molar absorption coefficients (ϵ) of the compounds were evaluated from slopes of the curves from inset of Fig. S29 (ESI) by Beer–Lambert law. ^b Fluorescence quantum yields. ^c Excited-state lifetimes. ^d Radiative rate constant. ^e Non-radiative rate constant.

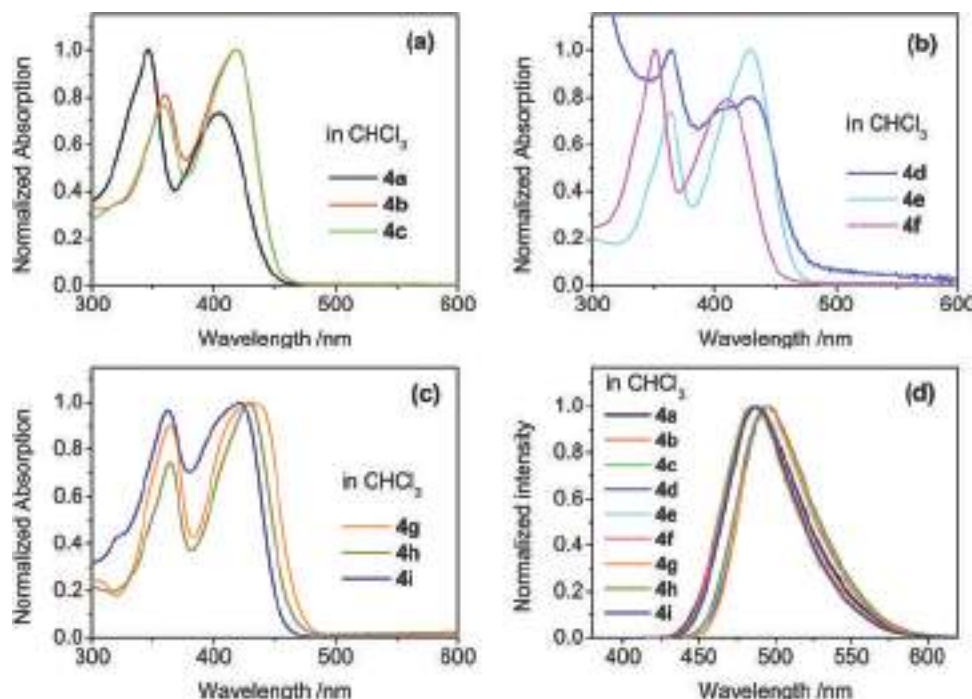


Fig. 4 Absorption (a–c) and fluorescence (d) spectra for compounds **4a–i** in chloroform solution at a concentration of 10^{-4} M.

Table 5 Photophysical properties of the compounds **4a–i** in acetonitrile

Compound	Absorption λ_{max} (nm)/($\epsilon/10^4$) ^a	Emission λ_{em} (nm)	$\Delta\nu_{\text{ST}}$ (cm ⁻¹)	Φ_{PL} ^b	τ_{f} ^c (ns)	k_{r} ^d (ns) ⁻¹	k_{nr} ^e (ns) ⁻¹
4a	344; 404/(0.4)	502	4832	0.20	6.56	0.030	0.122
4b	360; 417/(0.3)	496	3820	0.46	4.47	0.103	0.121
4c	358; 413/(0.3)	497	3689	0.22	4.54	0.048	0.172
4d	362; 433/(0.3)	507	3371	0.34	5.78	0.059	0.114
4e	362; 430/(0.8)	513	3763	0.36	5.35	0.067	0.120
4f	352; 410/(0.2)	499	4350	0.19	6.26	0.030	0.129
4g	361; 432/(1.8)	495	2946	0.35	4.88	0.072	0.133
4h	362; 428/(0.6)	512	3833	0.32	5.32	0.060	0.128
4i	359; 418/(0.4)	496	3762	0.48	4.44	0.108	0.117

^a Units = $\text{M}^{-1} \text{cm}^{-1}$, the molar absorption coefficients (ϵ) of the compounds were evaluated from slopes of the curves from inset of Fig. S30 (ESI) by Beer–Lambert law. ^b Fluorescence quantum yields. ^c Excited-state lifetimes. ^d Radiative rate constant. ^e Non-radiative rate constant.

Compounds **4a–i** also exhibited two main absorption bands between 344 nm and 433 nm in acetonitrile solution (Fig. 4a–c) corresponding to π – π^* transitions of the conjugated systems that involve the aromatic rings²⁹ whereas molar absorption coefficient of maximum absorption wavelength ranges were $0.2 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$ (for compound **4f**) to $1.8 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$ (for compound **4g**). The maxima emission wavelength in acetonitrile occurs between 495 nm (for the compounds **4b**) and 513 nm (compound **4e**) as showed in Table 5. The Stokes shifts ($\Delta\nu_{\text{ST}}$) of the compounds in acetonitrile are in the range of 2946 to 4832 cm^{-1} , respectively, for **4g** and **4a**. The fluorescence quantum yields (Φ_{PL}) of compounds **4a–i** in acetonitrile are shown in Table 5. The compounds in acetonitrile solution exhibited fluorescence quantum yields (Φ_{PL}) between 0.19 and 0.48. The fluorescence quantum yields of compounds **4a–i** in acetonitrile were smaller compared to quantum yields of the compounds in chloroform solution. Compound **4i** containing *p*-anisyl group at R_1 position and 2-Cl at R_2 position exhibited the

highest fluorescence efficiency (0.48). It is worth noting that the fluorescence efficiency of compound **4d** in acetonitrile solution (0.34) was significantly lower than in chloroform (0.75).

The fluorescence decays of all compounds in acetonitrile solution at concentration of 10^{-4} M were also best fitted using a mono-exponential with lifetimes in the nanosecond timescale (see Table 5). The fluorescence decay curves of the compounds in acetonitrile are shown in the ESI† (see Fig. S33). The excited-state lifetimes (τ_{f}) of compounds **4a–i** in acetonitrile were slightly longer compared to lifetimes of the compounds in chloroform solution. The lifetimes of the compounds **4a–i** in acetonitrile range from 6.56 ns (**4a**) to 4.44 ns (**4i**), as shown in Table 5. The highest radiative rate constant was exhibited by compound **4i**, which also showed the higher fluorescence efficiency (0.48) in acetonitrile. In addition, the non-radiative rate constant of the compound **4d** in acetonitrile solution was higher than the radiative rate constant, which explains the decreased of fluorescence efficiency of the compound **4d** in

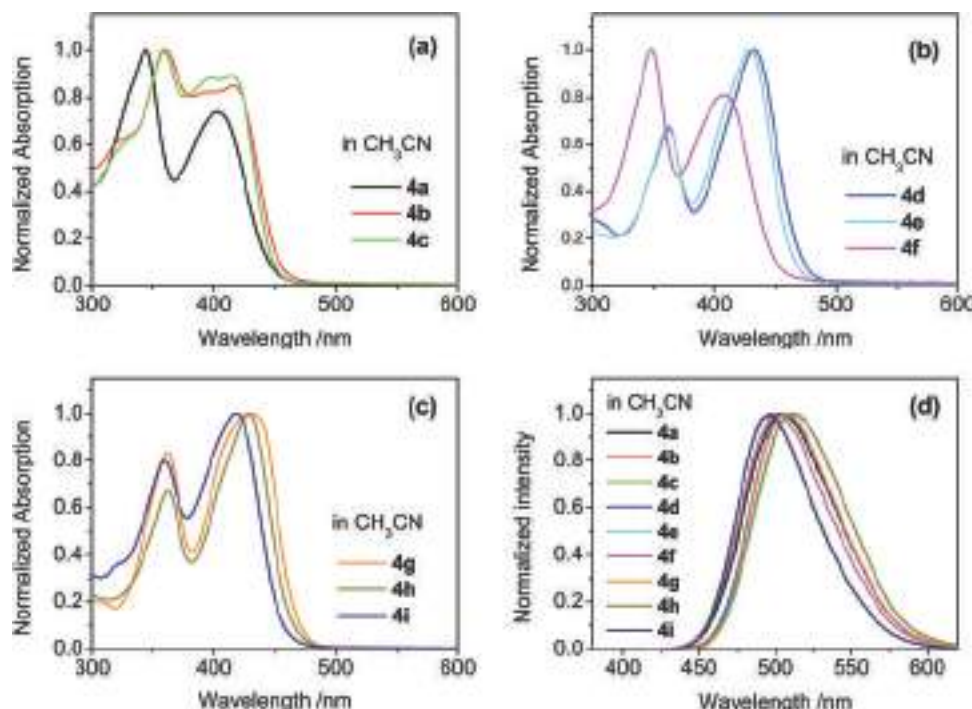


Fig. 5 Absorption (a–c) and fluorescence (d) spectra for compounds **4a–i** in acetonitrile solution at a concentration of 10^{-4} M.

Table 6 Photophysical properties of the compounds **4a–i** in tetrahydrofuran

Compound	Absorption λ_{max} (nm)/($\epsilon/10^4$) ^a	Emission λ_{em} (nm)	$\Delta\nu_{\text{ST}}$ (cm^{-1})	Φ_{PL} ^b	τ_{r} ^c (ns)	k_{r} ^d (ns^{-1})	k_{nr} ^e (ns^{-1})
4a	323; 348/(0.3)	488	6608	0.21	4.58	0.046	0.172
4b	358; 415/(0.3)	482	3408	0.56	3.91	0.143	0.113
4c	358; 414/(0.8)	483	3335	0.36	3.96	0.091	0.162
4d	362/(0.1)	490	2740	0.40	5.25	0.076	0.114
4e	366; 387/(0.5)	495	2786	0.08	4.27	0.019	0.215
4f	328; 352/(0.1)	487	6204	0.27	4.46	0.061	0.141
4g	366; 398/(1.1)	491	2835	0.10	4.88	0.020	0.184
4h	364; 402/(0.5)	496	3149	0.11	4.28	0.026	0.208
4i	361; 414/(0.2)	483	3106	0.25	3.98	0.063	0.188

^a Units = $\text{M}^{-1} \text{cm}^{-1}$, the molar absorption coefficients (ϵ) of the compounds were evaluated from slopes of the curves from inset of Fig. S31 (ESI) by Beer–Lambert law. ^b Fluorescence quantum yields. ^c Excited-state lifetimes. ^d Radiative rate constant. ^e Non-radiative rate constant.

acetonitrile compared to its efficiency in chloroform. Compounds **4a** and **4f** showed the lowest radiative rate constants, whilst compound **4c** exhibited the highest non-radiative rate constant. The photophysical properties of compounds, **4a–i**, in tetrahydrofuran (THF) solution are summarized in Table 6. Fig. 6 shows the normalized absorption and fluorescence spectra of **4a–i** in THF solution at concentration of 10^{-4} M.

In THF, the absorption spectra of the compounds **4a–i** exhibited peaks and shoulders ranging of 323 nm to 415 nm (Fig. 6a–c). The main absorption bands of the compounds are given in Table 6. THF bears a sp^3 hybridized oxygen atom with lone pairs of electrons and as a result is capable of different interactions with compounds **4a–i** that cause the observed changes in the spectra. Based on theoretical and experimental demonstrations, Gelfand *et al.* suggested that the deformation of the spectral shape observed in THF is due to numerous vibrations outside the plane and explicit solvation which results in several low-frequency intermolecular vibrations and vibrations

from the solvent molecule itself.²¹ The molar absorption coefficients of main absorption wavelength are between $0.1 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$ (for compound **4d** and **4f**) to $1.1 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$ (for compound **4g**). The maxima emission wavelength in THF occurs between 482 nm and 496 nm (compound **4h**) as shown in Table 5. The Stokes shifts ($\Delta\nu_{\text{ST}}$) of the compounds are in the range of 2740 to 6608 cm^{-1} , respectively, for **4d** and **4a**. The fluorescence quantum yields (Φ_{PL}) of compounds **4a–i** in THF were between 0.08 and 0.56 (Table 6) and compound **4b** exhibited the highest fluorescence efficiency (0.56) in THF. Compound **4d** in THF exhibited fluorescence efficiency (0.40) that was close to its efficiency recorded in acetonitrile (0.34).

The fluorescence decays of all compounds in THF solution at concentration of 10^{-4} M were also best fitted using a mono-exponential with lifetimes in the nanosecond timescale (see Table 5). The fluorescence decay curves of the compounds in THF are shown in the ESI† (see Fig. S34). The excited-state lifetimes (τ_{r}) of the compounds **4a–i** in THF were similar to

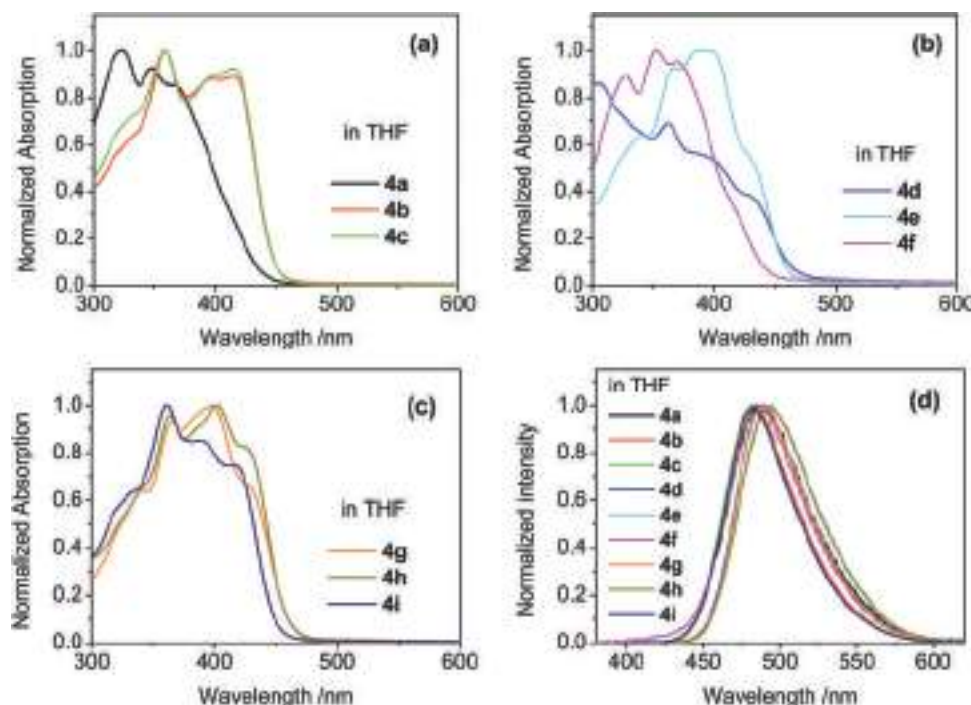


Fig. 6 Absorption (a–c) and fluorescence (d) spectra for compounds **4a–i** in tetrahydrofuran solution at a concentration of 10^{-4} M.

those of the compounds in chloroform solution. The lifetimes of the compounds **4a–i**, showed in Table 6, are between 5.25 ns (**4d**) and 3.91 ns (**4b**). Compound **4b** showed the highest radiative rate constants and the lowest non-radiative rate constants, explaining the higher fluorescence efficiency observed for **4b** (0.56) in THF. In contrast, compound **4e** exhibited the lowest radiative rate constant and the highest non-radiative rate constant. This explains the low fluorescence quantum yields of compound **4e** (0.08) in THF. Similarly as observed in acetonitrile, compound **4d** in THF exhibited a non-radiative rate constant higher than the radiative rate constant leading to a decrease in fluorescence efficiency of compound **4d** when compared to its efficiency in chloroform.

2.5 Solvatochromic properties

In order to study in detail the solvatochromic effect, the absorption and fluorescence spectra of **4a** were taken in solutions of

chloroform, acetonitrile and tetrahydrofuran. The compounds were found to be insoluble in nonpolar solvents such as hexane, cyclohexane and heptane. In addition, alcohols such as methanol or ethanol caused an immediate loss in the fluorescent properties of compounds **4a–i**. The absorption and emission spectra of **4a** in those solvents are shown in Fig. 7. The photophysical properties of compound **4a** in solution of several solvents at 10^{-4} M are summarized in Table 7.

Concerning the polarities of each solvent, CHCl_3 and THF both have similar polarity whereas CH_3CN is a more polar solvent. The absorption spectra of compound **4a** in CHCl_3 and CH_3CN were very similar. However, the shape of absorption spectrum of **4a** in THF was totally modified with a remarkable hypsochromic shift. Moreover, the maximum emission wavelength of **4a** in CH_3CN is shifted to longer wavelengths from 488–489 nm (THF and CHCl_3) to 502 nm (CH_3CN). This implies

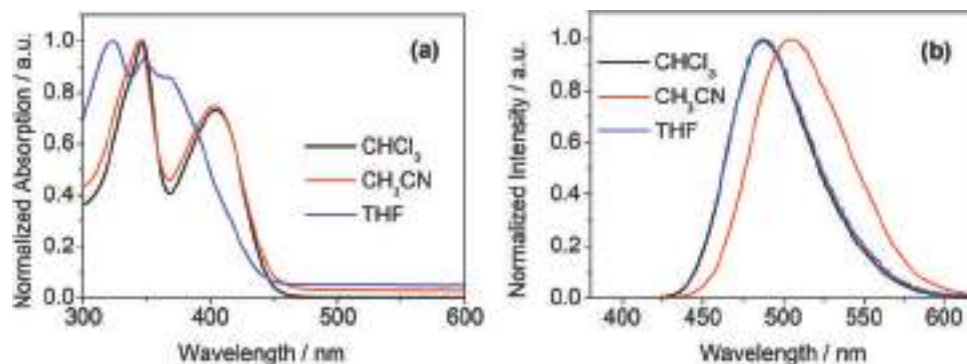
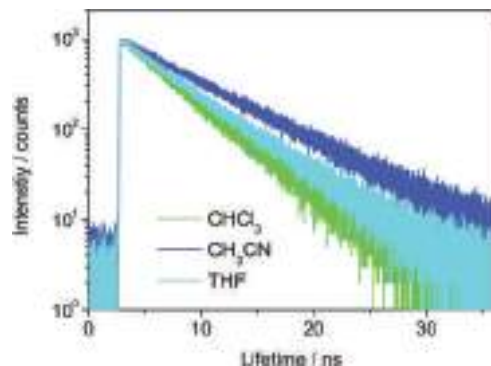


Fig. 7 Normalized absorption (a) and fluorescence (b) spectra of compound **4a** in CHCl_3 , CH_3CN and THF.

Table 7 Photophysical properties of the compounds **4a** in different solvents

Solvent	Absorption λ_{max} (nm)/($\epsilon/10^4$) ^a	Emission λ_{em} (nm)	$\Delta\nu_{\text{ST}}$ (cm ⁻¹)	Φ_{PL} ^b	τ_{f} (ns) ^c	k_{r} ^d (ns) ⁻¹	k_{nr} ^e (ns) ⁻¹
CHCl ₃	346; 404/(0.5)	489	4303	0.33	4.20	0.079	0.160
CH ₃ CN	344; 404/(0.4)	502	4832	0.20	6.56	0.030	0.122
THF	323; 348/(0.3)	488	6608	0.21	4.58	0.046	0.172

^a Units = M⁻¹ cm⁻¹. ^b Fluorescence quantum yields. ^c Excited-state lifetimes. ^d Radiative rate constant. ^e Non-radiative rate constant.

**Fig. 8** The fluorescence decay curves of the compound **4a** in acetonitrile, chloroform and tetrahydrofuran solution.

that the excited state of **4a** is more polar than the ground state. Our TD-DFT/B3LYP calculations (see Computational details) show a change in the dipole moment of the ground state from $\mu^{\text{GS}} = 7.28$ D to $\mu^{\text{ES}} = 10.60$ D for the first excited state. The fluorescence quantum yields of **4a** in CH₃CN and THF (Table 7) were very similar whereas the quantum yield of **4a** in CHCl₃ was slightly higher.

The excited state lifetimes of **4a** in different solvents are shown in Table 7. In polar solvent such as CH₃CN compound **4a** showed a longer excited state lifetime compared to it excited state lifetimes in CHCl₃ and THF. The fluorescence decay curves of the compound **4a** in acetonitrile and tetrahydrofuran solution is shown in Fig. 8. Compound **4a** exhibited the highest radiative rate constants in CHCl₃ and the lowest radiative rate constants in CH₃CN (Table 7). The highest non-radiative rate constant of **4a** was observed in THF as solvent.

2.6 Electrochemical characterization

The electrochemical properties of the final compounds were investigated by cyclic voltammetry (CV). The data from the electrochemical study and optical properties of **4a-i** are summarized in Table 8. The HOMO was estimated according to the reduction onset ($E_{\text{red}}^{\text{onset}}$) potentials from voltammograms using the following equation: $\text{HOMO} = -(E_{\text{red}}^{\text{onset}} + 4.44)$ eV. The LUMO was estimated from optical band gaps ($E_{\text{gap}}^{\text{opt}}$) previously determined from the absorption edge of compounds in solution, according to equation: $\text{LUMO} = (\text{HOMO} - E_{\text{gap}}^{\text{opt}})$ eV. The cyclic voltammograms of the compounds are provided in the ESI† (see Fig. S35–S43).

The cyclic voltammograms of the compounds (see ESI†) exhibit reduction processes with $E_{\text{red}}^{\text{onset}}$ varying from -0.9 to -1.3 V vs. SCE (see Table 8). Moreover, the substituent group changes the HOMO and LUMO values as well as the width of

Table 8 Electrochemical and optical properties of compounds **4a-i**

Compounds	$E_{\text{red}}^{\text{onset}}$ ^a (V)	HOMO ^b (eV)	LUMO ^c (eV)	$E_{\text{gap}}^{\text{opt}}$ ^d (eV)	λ_{onset} ^e (nm)
4a	−1.09	5.53	2.67	3.07	404
4b	−1.10	5.54	2.72	2.97	417
4c	−0.95	5.39	2.58	2.97	418
4d	−1.23	5.67	2.97	2.88	430
4e	−1.26	5.70	2.96	2.88	430
4f	−0.89	5.33	2.50	3.02	410
4g	−1.28	5.72	3.02	2.87	432
4h	−1.19	5.63	2.88	2.89	429
4i	−0.89	5.33	2.58	2.95	421

^a $E_{\text{red}}^{\text{onset}}$ is the onset potential of reduction. ^b $\text{HOMO} = -(E_{\text{red}}^{\text{onset}} - 4.44)$ eV. ^c $\text{LUMO} = (\text{HOMO} - E_{\text{gap}}^{\text{opt}})$ eV. ^d $E_{\text{gap}}^{\text{opt}}$ is optical band gap calculated from the low energy edge of the absorption spectrum ($E_{\text{gap}}^{\text{opt}} = 1240/\lambda_{\text{onset}}$). ^e λ_{onset} is the absorption onsets wavelength.

the optical band gaps. As shown in Table 8, HOMO of the compounds **4a-i** was estimated to be between 5.33 eV and 5.72 eV whereas the LUMO varied from 2.50 eV to 3.02 eV. The HOMO and LUMO energy levels of the present compounds are comparable to other boron difluoride derivatives applied as dye sensitizers material in dye-sensitized solar (DSC's).¹⁷ Comparing these results obtained with (dibenzoylmethanato) boron difluoride derivatives containing triphenylamine moieties, the values obtained for the LUMO and HOMO energy levels energies were similar to values found for compounds **4a-i**.¹⁷ Moreover, the optical band gaps of the compounds **4a-i** are between 2.70 and 2.86 eV, which are close to the other emitting materials applied in the construction of the organic light-emitting diode (OLED).¹⁶ Thus, these new compounds have potential for applications in optoelectronic devices.

2.7 Theoretical studies

In order to explore the theoretical photophysical properties, compounds **4a** and **4e** were chosen as representative examples. We performed first-principle calculations based on DFT and TDDFT formalisms (see Computational details) to determine UV-VIS spectra, TD-DFT difference densities and ground state properties. In order to find out which approximation to the exchange–correlation functional best describes the experimental results, we studied different properties with six different functionals: B3LYP, PBE0, CAM-B3LYP, B3LYP, M06-2X, and PBE. The first set of results were analyzed in detail for the B3LYP functional. The ground state geometry optimization of molecules **4a** and **4e** determined by DFT/B3LYP can be seen in Fig. 9, 10 and Fig. S41 (ESI†).

Tables S3 and S4 (ESI†) show the optimized parameters for bonds and angles between the atoms in the gas phase for

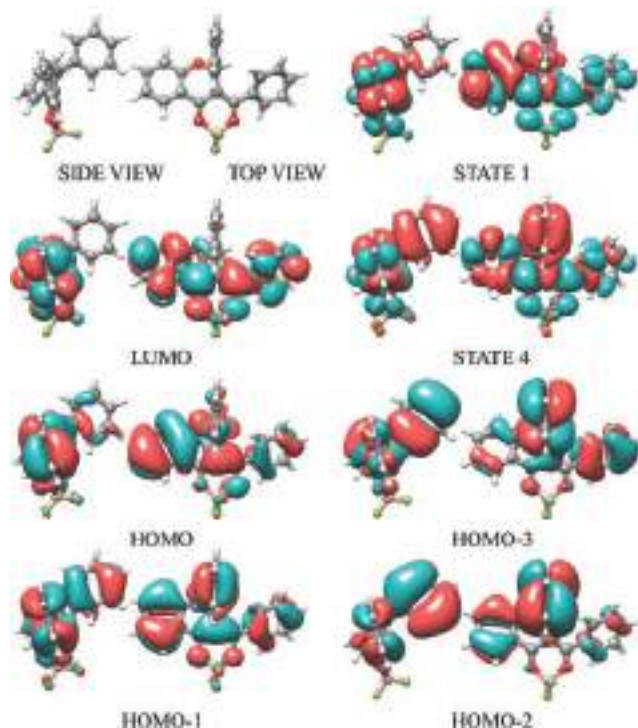


Fig. 9 Molecular Orbital plots and TDDFT difference densities and main excitation states for full TDDFT calculations for molecule **4a**. In the TDDFT difference densities, red indicates a loss of electron upon excitation and blue indicates a gain of electron density. The colour difference in MO of the isosurfaces indicates a difference in sign.

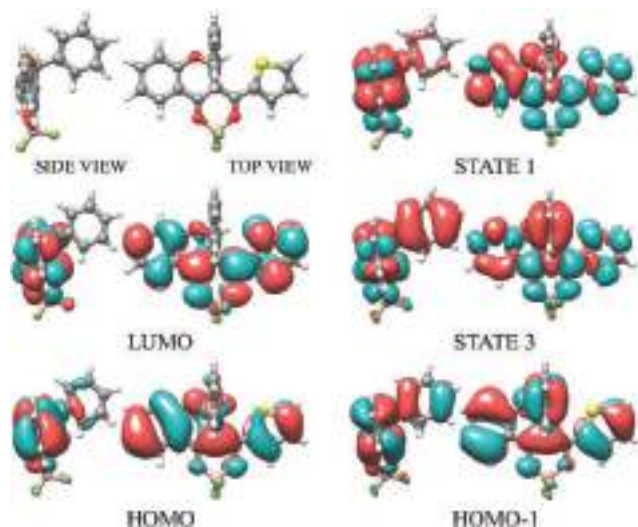


Fig. 10 Molecular orbital plots and TDDFT difference densities and main excited states for full TDDFT calculations for molecule **4e**. In the TDDFT difference densities, red indicates a loss of electron upon excitation and blue indicates a gain of electron density. The colour difference in MO of the isosurfaces indicates a difference in sign.

molecules **4a** and **4e**. The labeling scheme is presented in Fig. S41 (ESI[†]) for molecule **4e**. Comparing these results with those obtained by X-ray crystallography for compound **4e** (see Fig. 1 and Table 3) it is possible to see small differences for

some bonds and angles. For C1–O1 and C3–O2 the calculations show bond distances only 1.3% and 1.2% shorter than the experimental values. For C1–C2 bond the differences only appear in the third decimal place and we have a C2–C3 distance 2% longer than experimental results. B–O distance bond were 2.2% and 3.1% longer for B1–O2 and B1–O1, respectively. The B–F bond distances do not show any significant differences. The largest deviations appear for atoms in the 2-thienyl group. While C10–S1 bond is almost 9% longer, C10–C11 and C12–C11 are 15.4 and 10.5% shorter, respectively. The angles obtained with the DFT calculations do not show deviations greater than 6%. In general, geometry optimization with solvation effects can slightly change the bonding distances of some groups in the molecule. F–B (O–B) distance bonds can be shorter or longer by up to 1.7% in relation to the gas phase using C-PCM model with chloroform, THF and acetonitrile. This same effect occurs for molecule **4a** with differences of 1.6% being observed.

In order to understand the experimental absorption spectra, the four lowest excited states responsible for the main absorption bands observed were investigated. Fig. 9 and 10 present the main molecular orbitals (MO) and the TDDFT difference densities of many excited states with the highest oscillator strength (f_{osc}) for a full TDDFT/B3LYP calculation. Side and top view are shown in the figures. HOMO and LUMO plots are mainly localized at the flavanone framework and benzoyl (**4a**) or 2-thienyl (**4e**) moieties.

Tables S5 and S6 (ESI[†]) provide the main transitions for each excited state and the degree of each individual MO contribution. Excited state 1 represents 95% of the HOMO/LUMO transition for **4a** and 93% for **4e**. An excitation energy of 3.210 eV for molecule **4a** and 3.066 eV for compound **4e** was also calculated, and a small contribution from the HOMO–1/LUMO transition was noted. This transition is mostly responsible for the excited state 2 in both molecules contributing 94% for molecule **4a** and 87% for **4e**. Excitation occurs for energies at 3.693 eV and 3.524 eV for molecules **4a** and **4e**, respectively. These two states have the same main set of excitations with different contributions and similar TDDFT difference densities. Therefore, Fig. 9 and 10 show difference densities only for excited state 1 for both molecules. The excited state 3 has an excitation energy of 3.900 eV (3.671 eV) contributing 98% (87%) for HOMO–2/LUMO transition for molecule **4a** (**4e**) and a small HOMO–3/LUMO transition contribution. By contrast, state 4 has a greater contribution from HOMO–3/LUMO with 96% for both molecules and small contribution in the HOMO–2/LUMO excitation, with energy of 3.914 and 3.714 eV for molecules **4a** and **4e**, respectively. For states 5 and 6, the transitions follow the same logic as shown in Tables S5 and S6 (ESI[†]).

The absorption spectra for molecules **4a** and **4e** in gas phase are presented in Fig. 11(a) and (b), respectively.

The 30 excited states obtained from a full TDDFT/B3LYP/def2-TZVP are shown and the resulting spectra display four peaks, where the first two are formed by the first four excited states. These excited states might be responsible for the experimental absorption bands between 346 nm and 432 nm for the

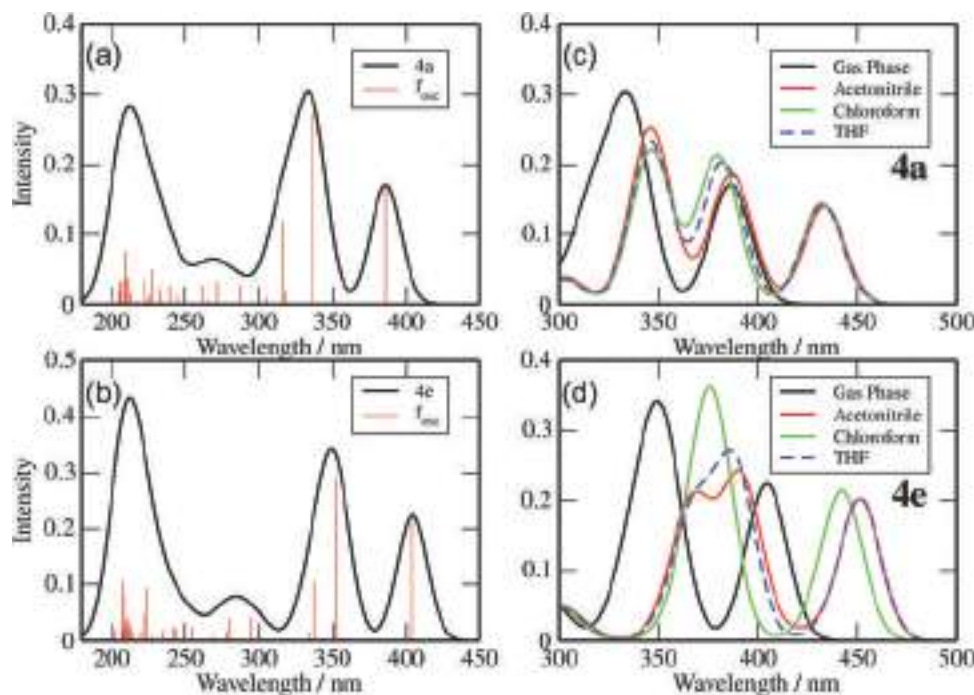


Fig. 11 Theoretical absorption spectra for molecules **4a** and **4e**. (a) and (b) show the spectra for gas phase for 30 excited states. Red stick shows the value of oscillator strength (f_{osc}). On the right (c) and (d) the spectra for different types of solvents was presented.

compounds **4a** and **4e**. The first peak consists of only the state 1, while the second consists of states 2 to 4. It is important to note that, for the first two peaks, only 3 states have relevant values for the oscillator strength. Results in gas phase and with inclusion of solvent effects for the main excited states are summarized in Table S7 (ESI[†]). For molecule **4a**, state 1 has a $f_{osc} = 0.17$ with λ_{max} in 386 nm (see Fig. S11 and ESI[†]) which results in an intense peak. Using C-PCM model to consider the solvent effects a bathochromic shift of 46 nm for all solvents used was observed: acetonitrile, chloroform and THF. The peak shifts to $\lambda_{max} = 433$ nm and the oscillator strength decreases to approximately 0.14 (see Fig. 11c). A similar effect is observed for the molecule **4e** with a bathochromic shift of approximately 47 nm for acetonitrile and THF and 38 nm for chloroform (see Fig. 11d). Solvents hardly changed the oscillator strength in this case. If we directly compare the experimental and theoretical spectra, it is possible to see differences between λ_{max} values. The deviations come from the well-known shift between vertical excitations and band maximum and for the non-description of vibrational effects.^{31–34} The difference in electron densities for the two molecules for state 1 are similar (Fig. 10 and 11) showing that the electron density decreases in part of the dihydropyrone moiety and benzenoid rings while it increases in the R_1 group and the dicarbonyl fragment (see Fig. 1).

In gas phase the second peak is formed mainly by states 2 ($f_{osc} = 0.27$) and 4 ($f_{osc} = 0.12$) for molecule **4a** and by states 2 ($f_{osc} = 0.29$) and 3 ($f_{osc} = 0.11$) for molecule **4e**. State 2 has the highest oscillator strength of the spectra with wavelength of 336 and 352 nm for molecules **4a** and **4e**, respectively. The inclusion of solvents results in a bathochromic shift between 44–52 nm for **4a** and 27–40 nm for **4e** (see Table S7, ESI[†]) with a

oscillator strength decrease of 36% for molecule **4a** and 20% for **4e**. States 3 and 4 for molecules **4a** and **4e**, respectively, have the largest shift, but a small value of oscillator strength. State 4 of **4a** presents a excitation in wavelength of 316.8 nm. All solvents used presented, approximately, a 30 nm bathochromic shift and the oscillator strength increases between 90 and 115%. Because of the bathochromic shifts together with the decrease and increase of f_{osc} for states 2 and 4, respectively, the spectra shows a third peak around 346 nm. For molecule **4e** the oscillator strength of state 3 increased between 90 and 98% with also a shift around 30 nm with solvation effects. In this case, the solvation effects only changes the shape of the spectra for THF and acetonitrile with the appearance of a small shoulder around 388 nm.

Fig. S44 and S45 (ESI[†]) compare the absorption spectra calculated for different functionals for compounds **4a** and **4e** in the gas phase or in acetonitrile. We used 10 excited states in these cases. Unlike B3LYP, the other hybrid functionals presented one well-defined excited states for each of the first two bands (states 1 and 2) for gas phase calculations. Furthermore, except for the B3LYP, all hybrid functionals showed an increase in intensity for the first peak in the calculations performed with the C-PCM model. The bathochromic shift is observed for all functionals. It is important to note that each excited state has a different shift. For the other hybrid functionals we observed a bigger shift for excited states 2 and a smaller shift for excited state 1. Consequently, the first two excited states stay together, increasing the intensity of the band. For these cases, no significant differences in the spectra were observed for the three solvents used. The smallest deviation for λ_{max} is obtained for PBE0 and B3LYP functionals for both molecules. Using the C-PCM model

Table 9 Orbital energies and energy gap (in eV) using different methodologies for molecules **4a** and **4e**. ΔE^{gap} (TDDFT) was estimated using the lowest excitation energy from the TDDFT calculations. For ΔE^{gap} (DFT) we use the difference between HOMO and LUMO energies from DFT calculations

Functional	HOMO	LUMO	ΔE^{gap} (DFT)	ΔE^{gap} (TDDFT)			
				Gas phase	CH ₃ CN	CHCl ₃	THF
Compound 4a							
B3LYP	−6.65	−2.89	3.77	3.21	2.86	2.87	2.87
PBE0	−6.96	−2.81	4.15	3.35	3.09	3.10	3.10
CAM- B3LYP	−8.16	−1.82	6.34	3.69	3.53	3.55	3.54
BHLYP	−7.82	−1.85	5.97	3.85	3.70	3.71	3.71
M06-2X	−8.13	−2.25	5.88	3.62	3.44	3.44	3.44
PBE	−5.94	−3.56	2.38				
Compound 4e							
B3LYP	−6.57	−3.00	3.57	3.07	2.75	2.80	2.75
PBE0	−6.86	−2.93	3.94	3.21	3.01	3.00	3.01
CAM- B3LYP	−8.05	−1.97	6.08	3.54	3.42	3.43	3.42
BHLYP	−7.70	−2.01	5.69	3.67	3.50	3.50	3.50
M06-2X	−8.07	−2.22	5.85	3.56	3.39	3.40	3.40
PBE	−5.86	−3.63	2.24				

with acetonitrile, the absolute deviation using PBE0 for compound **4a** is only 3 nm for the two absorption bands, whilst B3LYP presents a deviation of 30 and 41 nm for the first and second bands, respectively. For compound **4e**, PBE0 (B3LYP) underestimates (overestimates) the first band λ_{max} by approximately 22 nm.

The HOMO and LUMO energies as well as the molecular energy gap were also calculated. We estimated the energy gap using the excitation energy of the first singlet excited state calculated by TDDFT^{33–35} and the difference between HOMO and LUMO energies were calculated by DFT. These results are presented in Table 9. First, the HOMO energies, obtained from B3LYP/DFT calculation, showed an absolute deviation of 1.13 eV compared to the experimental results which is consistent with other reports for the exchange–correlation functional used.^{32–35} For CAM-B3LYP a maximal absolute deviation of 2.63 eV was observed. For HOMO energies, the best agreement with experimental data was obtained using the PBE functional. The differences are close to 7% for molecule **4a** and less than 3% for the molecule **4e**. It is noteworthy that there is a greater difficulty in theoretically describing virtual orbitals with DFT as pointed out in other reports.^{34–36} B3LYP functional LUMO energies show differences of 7% in relation to the experimental data for **4e**. In the case of **4a**, B3LYP overestimates the LUMO by almost 18%. PBE functional overestimates the LUMO energies with maximal absolute deviation of 1.10 eV. The best estimate for LUMO energy for compound **4a** was obtained with M06-2X functional, with maximal absolute deviation of 0.21 eV. On the other hand, for compound **4e**, PBE0 shows the best estimate for LUMO energy with a maximal absolute deviation of 0.10 eV.

The calculated energy gap using PBE/DFT shows an underestimation of about 0.7 eV for the both **4a** and **4e**. DFT with hybrid functionals overestimates the energy gap. B3LYP/DFT

overestimates the gap by approximately 0.70 eV and the maximal deviation reaches 3.27 eV using CAM-B3LYP. Among the hybrid functionals, B3LYP has the smallest deviation. In addition to the intrinsic problems of DFT calculations for gap energy,^{32–35} the lack of solvent model in this calculation brings an additional difference between theoretical and experimental values. We reduced this difference using TD-DFT calculations with the C-PCM model. The lowest excitation energy is a good estimation to the HOMO–LUMO gap as can be seen in Table 9. The gas phase calculation shows differences of less than 7% in relation to the experimental data. An overestimation of 0.14 and 0.19 eV for molecules **4a** and **4e**, respectively was observed. The inclusion of solvent effects decreases the excitation energy between 0.27 and 0.35 eV due to the bathochromic shift. These results underestimate the energy gap between 3 and 7% in relation to the experimental data. The use of C-PCM model gives good agreement between the experimental and theoretical energy gap. TD-DFT with PBE0 shows better estimation for energy gap for compound **4a** when calculated with the C-PCM model. In contrast, for compound **4e**, B3LYP and PBE0 show similar performance when compared with experimental results. With solvent effects B3LYP always underestimates the energies' gap with maximal deviation of 0.21 eV and 0.08 eV for compound **4a** and **4e**, respectively. PBE0, on the other hand, overestimates with maximal deviation of 0.03 eV and 0.13 eV for compound **4a** and **4e**, respectively. Hybrid functionals containing more exact exchange (BHLYP and M06-2X) and the range-separated hybrid CAM-B3LYP always overestimate the energies' gap. Calculations with C-PCM model, for the three solvents used, show similar deviation. For example, M06-2X shows deviations of 0.37 eV and 0.51 eV for compound **4a** and **4e**, respectively. This analyzes for hybrid functionals are in agreement with previous work on singlet-excited states of organic molecules.³³ Our calculations show that most accurate estimates are obtained for hybrid functionals with less exact exchange like PBE0 and B3LYP.

3 Conclusion

In conclusion, we describe the synthesis of nine novel difluoroboro flavanone complexes by a simple and efficient synthetic route that allows for easy structural variation and inclusion of electron donating and withdrawing groups. The obtained compounds were confirmed and characterized by infrared spectroscopic, ¹H, ¹⁹F and ¹³C NMR spectroscopy and X-ray diffraction. The photophysical properties of the final compounds were studied in different solvents. The substituents groups and the solvent media significantly influenced the electrochemical and photophysical properties of the final compounds and lead to molar absorption coefficient ranges from 10⁴ to 10⁵ M^{−1} cm^{−1} and the fluorescence quantum yield to vary of 0.08 to 0.75. Compound **4d** bearing a 2-furyl moiety presented the highest quantum yield value of 0.75 in CHCl₃ and an excited-state lifetime 4.78 ± 0.03 nanoseconds. All compounds showed single exponential decays in all studied solvent suggesting that the emission originated from monomeric species of the

compounds. These complexes exhibited optical properties and band gaps suitable for applications in organic optoelectronic devices, in particular as active layer of organic light emitting diodes (OLEDs) and organic solar cells (OSCs). The computational study was used to describe ground and excited states properties of representative compounds using DFT and TDDFT calculations. We presented HOMO and LUMO energies and energies gap calculated with two exchange–correlation functionals. It was possible to compare the energies with the results obtained experimentally and a good agreement for HOMO energy using PBE/DFT and for the energy gap calculated with B3LYP/TDDFT method were obtained. Furthermore, full TDDFT calculations show that the two bands of the experimental spectra are formed by the four lowest excited states. The first band is formed only by state 1 with an almost pure HOMO/LUMO transition and with a large oscillator strength. In addition, there is a reasonable bathochromic shift caused by solvation effects.

4 Experimental section

All commercial reagents were used as received. Anhydrous solvents were purchased from Sigma Aldrich. Flash column chromatography was performed using silica gel 200–400 Mesh. TLC analyses were performed using silica gel plates, using ultraviolet light (254 nm and 365 nm), for visualization. Melting points are uncorrected and were recorded on a Buchi B-540 apparatus. The ^1H and ^{13}C Nuclear Magnetic Resonance spectra were recorded on a Bruker Avance 400 MHz spectrometer. The chemical displacement values (δ) are presented in ppm relative to the internal standard tetramethylsilane (TMS) and the coupling values (J) are expressed in Hz. The multiplicities are abbreviated as follows: singlet (s), doublet (d), doublet doublet (dd), triplet (t), and multiplet (m). Electronic absorption spectra, UV and visible, were carried out in non-degasified solvents using a Thermo-Scientific Genesys 10s UV-vis Spectrophotometer. The absorption spectra in the infrared region (FTIR) were recorded in an ABB Bomem MB 3000 (FTIR) device, a high frequency region (4000 to 400 cm^{-1}), with a resolution of 4 cm^{-1} and 32 scans per sample. The liquid samples were analysed by Total Attenuated Reflectance (ATR), in ZnSe crystal. The solid samples were analysed in the form of a KBr tablet in the proportion 100:2 KBr/sample (Department of Chemistry, UFOP). High Resolution Mass Spectra were obtained on a Shimadzu HPLC-ESI-IT-TOF. The synthesis of esters, diketones and flavanones and their characterization data have previously been reported in the literature.^{18,19,37–42}

4.1 Typical procedure for synthesis of difluoroboron flavanone diketone complexes

In a Schlenk tube equipped with a magnetic bar, the synthesized flavanone (**3a–i**) (1 equivalent) was added and the air atmosphere was exchanged for an inert N_2 atmosphere. Then, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (8 equivalents) was added using a syringe and the reaction was left under constant stirring for 24 h at 80 $^\circ\text{C}$. After the reaction time, the obtained mixture was cooled to room

temperature and transferred to a column containing silica gel for purification by column chromatography using the appropriate solvent mixtures.

2,2-Difluoro-4,5-diphenyl-2,5-dihydro-[1,3,2]dioxaborinino[5,4-c]chromen-1-ium-2-uide (4a). Flavanone **3a** (0.91 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (7.31 mmol) provided compound **4a** as a yellow oil in 76% yield; R_f : 0.60 (30% ethyl acetate/hexane, UV Lamp 365 nm); IR (cm^{-1}): 3026, 1615, 1593, 1564, 1490, 1476, 1350, 1215, 1182, 1150, 1037, 750; ^1H -NMR (400 MHz, CDCl_3): δ 6.58 (s, 1H), 6.98 (d, 1H, J 12.0), 7.08–7.12 (m, 1H), 7.28–7.65 (m, 11 H), 8.05 (dd, 1H, J 8.0 and 1.6); ^{13}C -NMR (100 MHz, CDCl_3): δ 75.2, 104.4, 117.3, 118.4, 122.6, 127.5, 127.7, 127.8, 128.1, 128.5, 128.9, 129.2, 132.2, 133.3, 138.3, 139.1, 159.3, 177.4, 181.9; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{16}\text{O}_3 \cdot \text{BF}_2$: 377.1155; found: 377.1161; CHCl_3 $\lambda_{\text{abs}} = 404$ nm, $\epsilon = 0.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 489$ nm, Φ : 0.33721, $t = 4.20 \pm 0.03$ ns, $k_r = 0.08 \text{ ns}^{-1}$, $k_{nr} = 0.16 \text{ ns}^{-1}$; CH_3CN $\lambda_{\text{abs}} = 404$ nm, $\epsilon = 0.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 502$ nm, $\Phi = 0.20452$, $t = 6.56 \pm 0.04$ ns; THF: $\lambda_{\text{abs}} = 369$ nm, $\epsilon = 0.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 488$ nm, $\Phi = 0.21117$, $t = 4.58 \pm 0.03$ ns, $k_r = 0.046 \text{ ns}^{-1}$, $k_{nr} = 0.172 \text{ ns}^{-1}$.

2,2-Difluoro-4-(4-metoxiphenyl)-5-phenyl-2,5-dihydro-[1,3,2]dioxaborinino[5,4-c]chromen-1-ium-2-uide (4b). Flavanone **3b** (0.67 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (5.36 mmol) provided compound **4b** as a green oil in 61% yield; R_f : 0.60 (50% CH_2Cl_2 /hexane, UV Lamp 365 nm); IR (cm^{-1}): 3022, 2958, 1614, 1588, 1491, 1478, 1453, 1444, 1263, 1214, 1172, 1149, 1037, 751; ^1H -NMR (400 MHz, CDCl_3): δ 3.88 (s, 3H), 6.62 (s, 1H), 6.94–6.97 (m, 3H), 7.04–7.08 (m, 1H), 7.32–7.54 (m, 6H), 7.66–7.68 (m, 2H), 8.03 (dd, 1H, J 8.0 and 1.6); ^{13}C -NMR (100 MHz, CDCl_3): δ 55.6, 75.3, 103.6, 114.4, 117.6, 118.4, 122.5, 124.5, 127.7, 127.8, 128.9, 129.2, 131.8, 138.3, 138.4, 158.7, 164.0, 176.2, 181.0; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{18}\text{O}_4 \cdot \text{BF}_2$: 407.1261; found: 407.1256; CHCl_3 $\lambda_{\text{abs}} = 418$ nm, $\epsilon = 0.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 484$ nm, Φ : 0.50929, $t = 3.56 \pm 0.001$ ns, $k_r = 0.142 \text{ ns}^{-1}$, $k_{nr} = 0.137 \text{ ns}^{-1}$; CH_3CN $\lambda_{\text{abs}} = 417$ nm, $\epsilon = 0.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 496$ nm, $\Phi = 0.46429$, $t = 4.47 \pm 0.002$ ns, $k_r = 0.103 \text{ ns}^{-1}$, $k_{nr} = 0.119 \text{ ns}^{-1}$; THF: $\lambda_{\text{abs}} = 414$ nm, $\epsilon = 0.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 482$ nm, $\Phi = 0.55691$, $t = 3.91 \pm 0.001$ ns, $k_r = 0.142 \text{ ns}^{-1}$, $k_{nr} = 0.113 \text{ ns}^{-1}$.

2,2-Difluoro-5-phenyl-4-(p-tolyl)-2,5-dihydro-[1,3,2]dioxaborinino[5,4-c]chromen-1-ium-2-uide (4c). Flavanone **3c** (0.73 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (5.76 mmol) provided compound **4c** as a green oil in 57% yield; R_f : 0.60 (30% CHCl_3 /hexane, UV Lamp 365 nm); IR (cm^{-1}): 3077, 2932, 1608, 1586, 1516, 1477, 1477, 1350, 1272, 1219, 1182, 1149, 1035, 1033, 758; ^1H -NMR (400 MHz, CDCl_3): δ 2.44 (s, 3H) 6.60 (s, 1H), 6.97 (d, 1H, J 8.0), 7.07 (t, 1H, J 8.0), 7.28–7.57 (m, 9H), 8.04 (d, 1H, J 8.0); ^{13}C -NMR (100 MHz, CDCl_3): δ 21.9, 75.2, 104.1, 117.4, 118.4, 122.6, 127.6, 128, 128.9, 129.1, 129.2, 129.7, 138.3, 138.9, 144.7, 159.1, 176.8, 181.6; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{18}\text{O}_3 \cdot \text{BF}_2$: 391.1312; found: 391.1319; CHCl_3 $\lambda_{\text{abs}} = 420$ nm, $\epsilon = 0.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 485$ nm, Φ : 0.31762, $t = 3.69 \pm 0.03$ ns, $k_r = 0.085 \text{ ns}^{-1}$, $k_{nr} = 0.184 \text{ ns}^{-1}$; CH_3CN $\lambda_{\text{abs}} = 420$ nm, $\epsilon = 0.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 497$ nm, $\Phi = 0.21586$, $t = 4.54 \pm 0.03$ ns, $k_r = 0.047 \text{ ns}^{-1}$, $k_{nr} = 0.172 \text{ ns}^{-1}$; THF: $\lambda_{\text{abs}} = 416$ nm, $\epsilon = 0.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 483$ nm, $\Phi = 0.36177$, $t = 3.96 \pm 0.03$ ns, $k_r = 0.091 \text{ ns}^{-1}$, $k_{nr} = 0.161 \text{ ns}^{-1}$.

2,2-Difluoro-4-(furan-2-yl)-5-phenyl-2,5-dihydro-[1,3,2]dioxaborinino[5,4-c]chromen-1-ium-2-uide (4d). Flavanone **3d** (0.91 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (7.29 mmol) provided compound **4d** as a green oil in 54% yield; R_f : 0.60 (30% $\text{CHCl}_3/\text{hexane}$, UV Lamp 365 nm); IR (cm^{-1}): 3014, 1613, 1578, 1529, 1493, 1453, 1352, 1211, 1148, 1036, 747; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 6.71 (dd, 1H, J 3.6 and 1.6), 6.98 (d, 1H, J 8.0), 7.04 (t, 1H, J 8.0), 7.29–7.33 (m, 4H), 7.41–7.43 (m, 2H), 7.51–7.56 (m, 1H), 7.69–7.72 (m, 2H), 8.01 (dd, 1H, J 8.0 and 1.6); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 74.1, 102.4, 113.9, 117.4, 118.3, 122.5, 124.3, 127.2, 127.6, 128.7, 128.9, 138.6, 138.7, 148.8, 149.8, 159.4, 165.8, 176.6; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{14}\text{O}_4\text{BF}_2$: 367.0948; found: 367.0953; CHCl_3 $\lambda_{\text{abs}} = 430$ nm, $\epsilon = 0.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 494$ nm, $\Phi = 0.75012$, $t = 4.78 \pm 0.03$ ns, $k_r = 0.156 \text{ ns}^{-1}$, $k_{nr} = 0.052 \text{ ns}^{-1}$; CH_3CN $\lambda_{\text{abs}} = 433$ nm, $\epsilon = 0.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 507$ nm, $\Phi = 0.33749$, $t = 5.78 \pm 0.04$ ns, $k_r = 0.058 \text{ ns}^{-1}$, $k_{nr} = 0.114 \text{ ns}^{-1}$; THF: $\lambda_{\text{abs}} = 432$ nm, $\epsilon = 0.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 490$ nm, $\Phi = 0.40149$, $t = 5.25 \pm 0.03$ ns, $k_r = 0.076 \text{ ns}^{-1}$, $k_{nr} = 0.114 \text{ ns}^{-1}$.

2,2-Difluoro-5-phenyl-4-(thiophen-2-yl)-2,5-dihydro-[1,3,2]dioxaborinino[5,4-c]chromen-1-ium-2-uide (4e). Flavanone **3e** (1.02 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (8.20 mmol) provided compound **4e** as an orange solid in 69% yield; melting point: 188–190 °C; R_f : 0.60 (30% $\text{CHCl}_3/\text{hexane}$, UV Lamp 365 nm); IR (cm^{-1}): 2921, 1608, 1587, 1488, 1475, 1450, 1354, 1217, 1184, 1149, 1030, 756; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 6.85 (s, 1H), 6.95 (d, 1H, J 8.4), 7.06 (t, 1H, J 8.0), 7.16 (t, 1H, J 4.0), 7.34–7.54 (m, 6H), 7.60 (d, 1H, J 4.0), 7.86 (d, 1H, J 4.0), 8.02 (dd, J 8.0 and 1.6); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 75.3, 102.5, 117.6, 118.3, 122.6, 127.7, 127.7, 129.1, 129.2, 129.5, 135.9, 136.2, 137.0, 137.0, 138.5, 158.6, 172.3, 176.2; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{14}\text{O}_3\text{SBF}_2$: 383.0719; found: 383.0708; CHCl_3 $\lambda_{\text{abs}} = 430$ nm, $\epsilon = 0.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 495$ nm, $\Phi = 0.47797$, $t = 4.16 \pm 0.03$ ns, $k_r = 0.114 \text{ ns}^{-1}$, $k_{nr} = 0.125 \text{ ns}^{-1}$; CH_3CN $\lambda_{\text{abs}} = 430$ nm, $\epsilon = 0.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 513$ nm, $\Phi = 0.36432$, $t = 5.35 \pm 0.03$ ns, $k_r = 0.068 \text{ ns}^{-1}$, $k_{nr} = 0.119 \text{ ns}^{-1}$; THF: $\lambda_{\text{abs}} = 435$ nm, $\epsilon = 0.5104 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 495$ nm, $\Phi = 0.07757$, $t = 4.27 \pm 0.03$ ns, $k_r = 0.018 \text{ ns}^{-1}$, $k_{nr} = 0.216 \text{ ns}^{-1}$.

5-(2-Chlorophenyl)-2,2-difluoro-4-(p-tolyl)-2,5-dihydro-[1,3,2]dioxaborinino[5,4-c]chromen-1-ium-2-uide (4f). Flavanone **3f** (0.82 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (6.58 mmol) provided compound **4f** as a green oil in 69% yield; R_f : 0.60 (50% $\text{CH}_2\text{Cl}_2/\text{hexane}$, UV Lamp 365 nm); IR (cm^{-1}): 3191, 2929, 1608, 1587, 1489, 1476, 1451, 1440, 1353, 1319, 1218, 1110, 1184, 1149, 1034, 756; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 2.44 (s, 3H), 6.86 (d, 1H, J 8.4), 6.93 (s, 1H), 7.10 (t, 1H, J 8.20), 7.18–7.41 (m, 7H), 7.49–7.53 (m, 2H), 8.09 (d, 1H, J 8.0); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 21.8, 72.9, 102.9, 117.1, 118.3, 122.6, 127.3, 127.7, 129, 129.7, 129.9, 130.7, 131, 134.2, 135.2, 138.9, 144.9, 158.5, 176.7, 182.2; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{17}\text{O}_3\text{ClBF}_2$: 425.0922; found: 425.0919; CHCl_3 : $\lambda_{\text{abs}} = 410$ nm, $\epsilon = 0.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 489$ nm, $\Phi = 0.35751$, $t = 3.91 \pm 0.002$ ns, $k_r = 0.091 \text{ ns}^{-1}$, $k_{nr} = 0.164 \text{ ns}^{-1}$; CH_3CN : $\lambda_{\text{abs}} = 410$ nm, $\epsilon = 0.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 499$ nm, $\Phi = 0.18627$, $t = 6.26 \pm 0.03$ ns, $k_r = 0.029 \text{ ns}^{-1}$, $k_{nr} = 0.129 \text{ ns}^{-1}$; THF: $\lambda_{\text{abs}} = 374$ nm, $\epsilon = 0.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 487$ nm, $\Phi = 0.27184$, $t = 4.46 \pm 0.03$ ns, $k_r = 0.060 \text{ ns}^{-1}$, $k_{nr} = 0.163 \text{ ns}^{-1}$.

2,2-Difluoro-5-(4-fluorophenyl)-4-(furan-2-yl)-2,5-dihydro-[1,3,2]dioxaborinino[5,4-c]chromen-1-ium-2-uide (4g). Flavanone **3g** (0.89 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (7.20 mmol) provided compound **4g** as a yellow solid in 85% yield; melting point: 165–167 °C; R_f : 0.60 (30% $\text{CHCl}_3/\text{hexane}$, UV Lamp 365 nm); IR (cm^{-1}): 2920, 1607, 1588, 1487, 1475, 1435, 1354, 1217, 1184, 1150, 1030, 756; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 6.72–6.73 (m, 1H), 6.95–7.02 (m, 3H), 7.06–7.10 (m, 1H), 7.26 (s, 1H), 7.39–7.42 (m, 2H), 7.53–7.57 (m, 1H), 7.72–7.73 (m, 2H), 8.03 (dd, J 8.0 and J 1.6); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 73.5, 102.2, 114, 115.8 and 115.6 (J 8.0), 117.5, 118.3, 122.6, 124.4, 127.7, 129.1 ($J_{\text{C-F}}$ 22.0), 134.5 ($J_{\text{C-F}}$ 3.0), 138.7, 149.8, 159.1, 161.6, 164.1 ($J_{\text{C-F}}$ 181.0), 176.6; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{13}\text{O}_4\text{BF}_3$: 385.0854; found: 385.0862. CHCl_3 $\lambda_{\text{abs}} = 432$ nm, $\epsilon = 1.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 495$ nm, $\Phi = 0.3492$, $t = 4.88 \pm 0.04$ ns, $k_r = 0.071 \text{ ns}^{-1}$, $k_{nr} = 0.133 \text{ ns}^{-1}$; CH_3CN $\lambda_{\text{abs}} = 430$ nm, $\epsilon = 1.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 507$ nm, $\Phi = 0.34243$, $t = 5.89 \pm 0.04$ ns, $k_r = 0.058 \text{ ns}^{-1}$, $k_{nr} = 0.111 \text{ ns}^{-1}$; THF: $\lambda_{\text{abs}} = 431$ nm, $\epsilon = 1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 491$ nm, $\Phi = 0.09793$, $t = 4.88 \pm 0.03$ ns, $k_r = 0.020 \text{ ns}^{-1}$, $k_{nr} = 0.184 \text{ ns}^{-1}$.

2,2-Difluoro-5-(4-fluorophenyl)-4-(thiophen-2-yl)-2,5-dihydro-[1,3,2]dioxaborinino [5,4-c]chromen-1-ium-2-uide (4h). Flavanone **3h** (0.95 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (7.61 mmol) provided compound **4h** as a yellow solid in 67% yield; melting point: 172–174 °C; R_f : 0.60 (30% $\text{CHCl}_3/\text{hexane}$, UV Lamp 365 nm); IR (cm^{-1}): 2920, 1608, 1587, 1487, 1476, 1450, 1354, 1218, 1184, 1147, 1030, 756; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 6.83 (s, 1H), 6.94 (d, 1H, J 8), 7.04–7.11 (m, 3H), 7.18–7.20 (m, 1H), 7.47–7.61 (m, 4H), 7.88 (dd, 1H, J 4.8 and 1.2), 8.03 (dd, 1H, J 8.00 and J 1.6); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 74.7, 102.4, 115.6, 116.0 ($J_{\text{C-F}}$ 8.0), 117.5, 118.2, 122.8, 127.7, 129.2, 129.6, 129.7 ($J_{\text{C-F}}$ 21.8), 132.9 ($J_{\text{C-F}}$ 3.2), 136.2, 137.2, 138.6, 158.4, 161.9 ($J_{\text{C-F}}$ 248); 172.4, 176.1; ^{19}F NMR (376.5 MHz, CDCl_3): δ -112.51 (C-F), -141.39 (B-F), -143.66 (B-F); HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{13}\text{O}_3\text{SBF}_3$: 401.0625; found: 401.0630; CHCl_3 $\lambda_{\text{abs}} = 429$ nm, $\epsilon = 0.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 496$ nm, $\Phi = 0.30428$, $t = 4.15 \pm 0.03$ ns, $k_r = 0.073 \text{ ns}^{-1}$, $k_{nr} = 0.167 \text{ ns}^{-1}$; CH_3CN $\lambda_{\text{abs}} = 428$ nm, $\epsilon = 0.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 512$ nm, $\Phi = 0.32155$, $t = 5.32 \pm 0.03$ ns, $k_r = 0.060 \text{ ns}^{-1}$, $k_{nr} = 0.127 \text{ ns}^{-1}$; THF: $\lambda_{\text{abs}} = 429$ nm, $\epsilon = 0.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 496$ nm, $\Phi = 0.10864$, $t = 4.28 \pm 0.03$ ns, $k_r = 0.025 \text{ ns}^{-1}$, $k_{nr} = 0.208 \text{ ns}^{-1}$.

5-(2-Chlorophenyl)-2,2-difluoro-4-(4-methoxyphenyl)-2,5-dihydro-[1,3,2] dioxaborinino[5,4-c]chromen-1-ium-2-uide (4i). Flavanone **3i** (0.46 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (3.62 mmol) provided compound **4i** as a green oil in 56% yield; R_f : 0.60 (30% $\text{CHCl}_3/\text{hexane}$, UV Lamp 365 nm); IR (cm^{-1}): 3010, 2960, 1603, 1588, 1488, 1477, 1450, 1358, 1308, 1263, 1218, 1170, 1149, 1026, 836, 754; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 3.87 (s, 3H), 6.85 (d, 1H, J 12.0), 6.91–6.96 (m, 3H), 7.05–7.09 (m, 1H), 7.19–7.22 (m, 1H), 7.30–7.37 (m, 2H), 7.46–7.55 (m, 4H), 8.07 (dd, 1H, J 8.0 and J 1.6); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 55.7, 73.1, 102.5, 114.5, 117.3, 118.2, 122.6, 127.3, 127.5, 128.9, 130.8, 131.1, 131.8, 134.3, 135.0, 138.6, 158.2, 164.3, 176.0, 181.2; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{17}\text{O}_4\text{ClBF}_2$: 441.0871; found: 441.0869; CHCl_3 $\lambda_{\text{abs}} = 422$ nm, $\epsilon = 0.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 487$ nm, $\Phi = 0.27644$, $t = 3.69 \pm 0.03$ ns,

$k_r = 0.074 \text{ ns}^{-1}$, $k_{nr} = 0.196 \text{ ns}^{-1}$, CH_3CN $\lambda_{\text{abs}} = 418 \text{ nm}$, $\varepsilon = 0.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 496 \text{ nm}$, $\Phi = 0.47881$, $t = 4.44 \pm 0.03 \text{ ns}$, $k_r = 0.107 \text{ ns}^{-1}$, $k_{nr} = 0.117 \text{ ns}^{-1}$, THF: $\lambda_{\text{abs}} = 429 \text{ nm}$, $\varepsilon = 0.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{em}} = 483 \text{ nm}$, $\Phi = 0.24643$, $t = 3.98 \pm 0.03 \text{ ns}$, $k_r = 0.061 \text{ ns}^{-1}$, $k_{nr} = 0.189 \text{ ns}^{-1}$.

4.2 Photophysical properties

For the study of the photophysical properties, a stock solution was prepared in CHCl_3 , CH_3CN and THF and then diluted to the desired concentrations. After preparation, the solutions were homogenized in an ultrasonic bath for 5 min and then subjected to UV-vis absorption, steady state and time resolved fluorescence measurements. All measurements were carried out at room temperature in 10 mm quartz cuvettes. All commercial reagents were purchased from Synth and used as received. The electronic absorptions in solution were investigated using UV-vis absorption measurements carried out with a U-2001 UV-vis (Hitachi) spectrometer. The molar absorption coefficients (ε) were evaluated from slopes of the linear relationship between the absorbance at a wavelength (λ) and the concentration of the compounds using the Beer–Lambert law, whereas the absorbance (Abs) is proportional to the molar concentration (c), light path length (l), and molar extinction coefficient (ε) expressed by the following equation:

$$\text{Abs}(\lambda) = \varepsilon(\lambda) \cdot l \cdot c \quad (1)$$

The fluorescence spectra were monitored using a RF-5301PC (Shimadzu) spectrofluorophotometer with the excitation wavelength corresponding to the respective maximum of the absorption band. The relative fluorescence quantum yields (Φ_{PL}) of the compounds were calculated with the following equation:

$$\Phi_{\text{PL}} = \left(\frac{A_S F n^2}{A_{\text{FS}} n_0^2} \right) \Phi_S \quad (2)$$

where the subscript S refers to the standard solution (reference). Φ_S is the quantum yields of standard, A is absorbance at the excitation wavelength, F the integrated emission area across the fluorescence spectra and the n are respectively index of refraction of the solvent containing the unknown (n) and the standard (n_0). Optical densities were set lower than 0.1 at the respective maximum of absorption, and corrected fluorescence emission spectra were recorded following the technique described by Eaton.⁴³ The fluorescence quantum yields (Φ_{PL}) of the compounds were determined using rhodamine-B in methanol diluted solution as standard solution ($\Phi_S = 0.8$).⁴⁴ The fluorescence spectra of dilute solutions of the compounds and the standard were recorded under exactly the same experimental conditions and temperature. Singlet-excited state photoluminescence decay curves were recorded using the time-correlated single photon counting method of a FluoTime 200 (PicoQuant) spectrometer. The excitation was promoted using a 401 nm diode laser pulsing at 20 MHz. Photoluminescence was collected perpendicular to the excitation and passed through a polarizer adjusted at the magic angle. The detection system consists of a monochromator and a multi-channel base

photomultiplier (Hamamatsu R3809U-50). Excited-state lifetimes were obtained by fitting a convolution of the instrument's response function and a sum of exponentials to the fluorescence data using the FluoFit[®] software. The residual plots and the chi-square (χ^2) were used to accurately determine the quality of the accessories during the analysis procedure. The radiative and non-radiative rate constant were evaluated by $k_r = \Phi_{\text{PL}}/\tau_f$ and $k_{nr} = (1 - \Phi_{\text{PL}})/\tau_f$.

4.3 Electrochemical measurements

The electrochemical properties of the compounds were investigated by cyclic voltammetry (CV) using *Microquímica* potentiostat/galvanostat (model MQPG-01) coupled to a personal computer with *Microquímica software*. Platinum wire and ITO on glass were used as counter and working electrodes, respectively. An acetic acid solution (0.1 M) was used as a supporting electrolyte, the values were obtained at a scan speed of 200 ms^{-1} with a saturated calomel electrode (SCE) as standard. Through the fabrication of a film using the spin-coating technique as a working electrode in a cyclic voltammetry measurement assembly, it was possible to estimate the HOMO energy level of compounds.

4.4 X-ray diffraction measurement

Compound **4e** was crystalized by the solvent evaporation method. The solid was dissolved in the minim quantity of CHCl_3 and was covered with aluminum foil and left in a dark place without external perturbations. The crystal form finally appeared after 6 days. The data collection was performed on an Agilent SuperNova diffractometer, equipped with a dual source of radiation (Cu and Mo) and an Atlas S2 CCD detector at room temperature (293 K). The data collection routine, unit cell determination and intensity data integration were carried out with the CrysAlisPro software, using $\text{CuK}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). The structure of **4e** was solved by direct methods (SHELXS) and refined by full-matrix least-squares against F^2 (SHELXL).⁴⁵ Anisotropic displacement parameters were introduced for all non-hydrogen atoms. Hydrogen atoms were observed by Fourier Maps and constrained at geometrically calculated positions and refined with the appropriate riding model considering $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Also, the thiophene disordered over two positions with site-occupation factors of 0.60 and 0.40. The intramolecular parameters were analyzed using MOGUL⁴⁶ and the molecular geometry derived from the CSD (Cambridge Structural Database),⁴⁷ which gives a rapid access to information on the preferred values of bond lengths, valence angles, and acyclic torsion angles. Structure data files for **4e** are deposited at Cambridge Crystallographic Data Centre (CCDC 1996094[†]). Summary of crystal, data collection procedures, structure determination methods and refinement results are summarized in Table S1 (ESI[†]). Representation of the structure was drawn with the Mercury 4.3.1 program.⁴⁸

4.5 Computational details

First-principle calculations based on density functional theory (DFT) and time-dependent density functional theory (TDDFT) formalisms^{49–51} were performed on ORCA version 4.2.0 program package.^{52,53} DFT and TD-DFT methods were used with the

generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE),⁵⁴ the hybrid B3LYP,^{55–57} PBE0,⁵⁸ M06-2X⁵⁹ and B3LYP⁶⁰ and range-separated hybrid CAM-B3LYP⁶¹ for exchange and correlation functionals. Full TD-DFT were performed to explore the electronic levels involved in the excitations and to calculate the UV/Vis spectra. The def2-TZVP basis set with tight SCF convergence criteria were employed.^{62,63} The first 30 and 10 singlet excited states were calculated for B3LYP and for the other functionals, respectively. The UV-Vis spectra were convoluted with Gaussian functions having 12 nm of half width at half-maximum (HWHM). Solvation effects in chloroform, THF and acetonitrile were considered by adopting the conductor-like polarizable continuum model (C-PCM).⁶⁴ An excited state gradient calculation was performed to obtain the dipole moment of the excited state. All graphics of molecular orbitals and TD-DFT difference densities were performed with UCSF Chimera.⁶⁵ Infrared active vibrations were visualized with Jmol.⁶⁶

Conflicts of interest

There are no conflicts of interest to declare.

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Highly luminescent liquid crystals by connecting 1,3,4-oxadiazole with thiazolo[5,4-d]thiazole units

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ABSTRACT

The direct bonding between a thiazolo[5,4-d]thiazole and two 1,3,4-oxadiazole units allowed us to create a new and versatile rigid core for luminescent liquid crystal, which showed interesting and variable mesomorphic and photophysical properties. From the 5-bis(5-phenyl-1,3,4-oxadiazol-2-yl)thiazolo[5,4-d]thiazole new core, three molecules with different number of alkoxy chains were synthesized and had their properties correlated with the molecular structure. The molecule with two chains showed a smectic C mesophase, while the mesogens with four and six chains presented hexagonal columnar mesomorphism, which was confirmed by POM and XRD measurements. In addition, the molecule with six chains presented liquid crystalline behavior close to room temperature. In solution, the molecules presented strong photoluminescence ranging from blue to yellow, with quantum yields higher than 0.6. Excited state lifetimes allowed to correlate the fluorescence component associated to the different emitting species to the molecular organization in spin coated films. The molecular energy levels, together with thermal stability and possible charge carrier transport due to molecular packing, suggest that these molecules are promising for optoelectronic applications. Overall, this work contributes to the development of the use of thiazolo[5,4-d]thiazole in liquid crystals, demonstrating its great efficiency and versatility.

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1. Introduction

Liquid crystals (LCs) have unique properties and features [1–3] that lead to many applications as organic semiconductors, especially in the manufacture of efficient, ultra-light, low power consuming, low cost and flexible components for electrical devices [4–8]. Therefore, the interesse in synthesis of new liquid crystal molecules have increase, and it is of paramount importance an adequate molecular planning in order to propose a structure that is synthetically viable and that contains the desired properties [9–11].

Thus, in the search for new and more robust materials, heterocycles have played an important role, providing rigid cores with different polarities and geometries, and allowing the tailoring of physical and chemical properties, such as stability, mesomorphic behavior and luminescence [11–13]. One of the most commonly employed heterocycles in the synthesis of LCs is the five-membered 1,3,4-oxadiazole ring

(OXA), which can be found in different mesogenic cores, such as calamitic, bent-cores, polycatenar and discotics [14–17]. The reason for such wide use is related to their easy and synthesis versatility, high thermal and chemical stability and usually high luminescence quantum yield [18].

Another important class of heterocycles is the thiazolo[5,4-d]thiazole (**Thz**), which is composed of two fused five-membered thiazole rings containing sulfur and nitrogen. It shows a rigid planar structure, an electron deficient characteristic, luminescence, high oxidative stability and may form π -stacking interaction, which is essential for good charge transfer in optoelectronic devices [19]. Due to these characteristics, it has been explored for several electro-optical applications, including as electron acceptor in Organic Solar Cells [20–23]. However, despite its potential, the **Thz** heterocycle is still underexplored in the synthesis of liquid crystalline materials, both polymeric [24,25] and low molecular mass mesogens [26,27].

Therefore, our group has recently reported the first discotic liquid crystals based on the **Thz** heterocycle connected to four OXA units via two benzene rings, converting the linear **Thz** structure into discotic core [28]. It was observed that the combination of both heterocycles generated

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products with great thermal stability, significant mesomorphism range, good molecular packing and high quantum yield.

In this work, we investigated the direct covalent bonding between **Thz** and **OXA** heterocycles, leading to a better conjugation among them. The synthesis of three new compounds containing different numbers of long alkoxy chains ($C_{12}H_{25}O-$) was successfully performed and showed that the better conjugation promoted a strong bathochromic shift of the emission band. Furthermore, the number of alkoxy chains had strong influence over the photophysical and mesomorphic arrangement, as both smectic and columnar mesophases could be obtained. Overall, this work contributes to the development of the use of heterocycles in the search for better materials for different applications, in addition to demonstrating the great efficiency and versatility of thiazolo [5,4-*d*]thiazole in liquid crystals.

2. Experimental

Reagents and solvents were acquired in analytical grade from Merck and Aldrich and used without further purification unless noted here. Anhydrous pyridine was obtained by distillation over KOH, stored in molecular sieves (4 Å), and used when described. Reactions were monitored by Thin Layer Chromatography (TLC) on aluminum plates coated with a thin layer of silica gel 60, with the indicator UV₂₅₄ – Marcherey – Nagel. The synthesized compounds were isolated by chromatography in a silica-gel 60 column (Aldrich, 70–230 mesh). NMR spectra were obtained in VARIAN Unity Plus spectrometers, in $CDCl_3$ or $CDCl_3/CF_3COOD$ solution with TMS as an internal standard, and the chemical shifts were expressed in δ (ppm) unit. For high-resolution mass spectrometry analysis (HRMS), the MicroTOFII Bruker was used with an APPI ionization source, and the samples were injected with a syringe Hamilton 500 μ L model 1750 RN SYR. Thermal properties such as melting point, phase transitions, and mesomorphic textures were initially investigated using a polarized optical microscope, Olympus BX50 coupled to a Mettler Toledo FP-82 hot stage and an Olympus DP73 digital camera. Thermal transitions and enthalpies were determined by DSC measurements, carried out using a DSC Q2000 calorimeter (TA Instruments) equipped with a RCS90 cooling system. During measurements, a heating/cooling rate of $10^\circ C\ min^{-1}$ and a nitrogen flow of $50\ mL\ min^{-1}$ were employed. Thermal stability was investigated by TGA using a Shimadzu equipment with a TGA-50 module and a heating rate of $10^\circ C\ min^{-1}$ and a nitrogen flow of $20\ mL\ min^{-1}$. The absorption and photoluminescence spectra in solution and thin film were recorded in the UV–Vis region by using the spectrophotometer SpectroVision UV–Vis model DB-1880S and Hitachi-F-4500, respectively. The X-ray diffraction (XRD) analysis was performed with a X'PERTPRO (PANalytical) diffractometer with Cu K α radiation ($\lambda = 1.5418\ \text{\AA}$) and applied power of 1.2 kVA. The scan was carried out in continuous mode from 2° to 30° (2θ) angle) with the sample in the mesophase, obtained by cooling from the isotropic state. Synthesis and analytical data of molecules synthesized in this work are found in the supporting information. Cyclic voltammograms (CV) were recorded using an AUTOLAB Potentiostat/Galvanostat PGSTA30 system from solutions of approximately $10^{-3}\ mol\ L^{-1}$ of the analyte in dried dichloromethane containing $0.1\ mol\ L^{-1}$ tetrabutylammonium hexafluorophosphate (TBAPF₆) under argon atmosphere, using a gas-tight single-compartment three-electrode cell equipped with glass carbon working, platinum wire auxiliary and Ag/AgCl *pseudo*-reference electrodes. The thickness and morphological aspects of thin films deposited by spin coating from 10 mg/mL in chloroform solution (2000 rpm during 60 s) were determined with a Nanosurf Flex AFM, operating in tapping mode with a scanning rate of 1.0 Hz and 512 pixels $\times$ 512 pixels. Fluorescence decay were obtained through the time-correlated single photon counting technique, using aFluoTime200 (PicoQuant) spectrometer. The excitation was performed by a 401 nm pulsed diode laser with repetition rate ranging from 0.25 to 20.0 MHz. Fluorescence was collected perpendicular to excitation and passed through a polarizer set at the

magic angle. The detection system consisted of a monochromator and a microchannel plate photomultiplier (Hamamatsu R3809U-50). Lifetimes were obtained by fitting the fluorescence decays to a convolution of the instrument response function and the sum of exponentials using the FluoFit® software. The plots of weighted residuals and reduced chi-squared (χ^2) were used to accurately determine the quality of the fittings during the analysis procedure.

3. Results and discussions

3.1. Synthesis

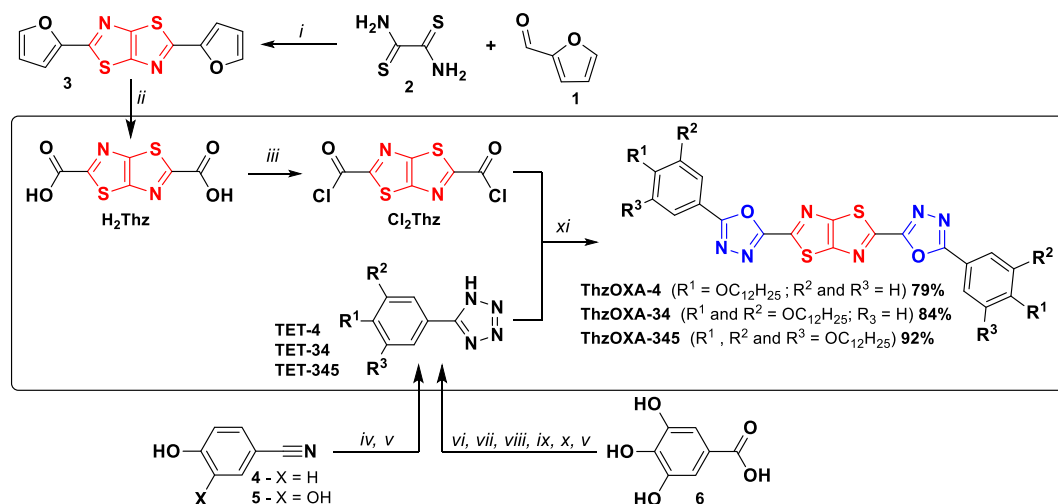
All planned compounds were prepared by a partial convergent route as described in Scheme 1. Initially, all tetrazoles (**TET**) and the thiazolo [5,4-*d*]thiazole-2,5-dicarboxylic acid (**H₂Thz**) were prepared in parallel. The **H₂Thz** synthesis started by an oxidative condensation between dithioxamide (**2**) and furfuraldehyde (**1**), resulting in the intermediate **3**, which was then oxidized with $KMnO_4$ [29,30]. For the tetrazoles, two different routes were necessary. For **TET-4** and **TET-34**, initially the respective commercial 4-hydroxybenzonitrile (**4**) and 3,4-dihydroxybenzonitrile (**5**) had their phenolic groups alkylated with $C_{12}H_{25}Br$ in the presence of K_2CO_3 as base. Later, the nitrile group was converted into the respective tetrazole heterocycle by a Huisgen 1,3-dipolar cycloaddition reaction using NaN_3 and NH_4Cl in DMF [31]. For the **TET-345** tetrazole, a longer synthetic route was necessary, starting with the esterification of the gallic acid (**6**) followed by alkylation with 1-dodecylbromide, reduction of the ester unit with $LiAlH_4$ and subsequent partial oxidation with PCC, resulting in the 3,4,5-tris (dodecyloxy)benzaldehyde. In a later step, the aldehyde was treated with a solution of I_2 and NH_4OH (*in situ* formation of nitrogen triiodide) that promoted the oxidation of nitrogen intermediates, thus obtaining the corresponding nitriles [32]. At the end, the Huisgen 1,3-dipolar cycloaddition between the nitrile, NaN_3 and NH_4Cl in DMF resulted in the desired **TET-345** tetrazole with excellent yields. To obtain the desired target compounds the thiazolo[5,4-*d*]thiazole-2,5-dicarboxylic acid (**H₂Thz**) was initially converted in the respective acid chloride (**Cl₂Thz**) by the reaction with thionyl chloride in the presence of catalytic amount of DMF. The freshly prepared **Cl₂Thz** was subsequently reacted with the corresponding tetrazoles derivatives in anhydrous pyridine solution, resulting in the target 1,3,4-oxadiazole compounds (**ThzOXA-n**) in good yields after purification (79–92%). The structure and purity of the target compounds was determined by spectroscopic measurements such as ^1H and ^{13}C NMR and HRMS. In addition, the sharp and reproducible thermal transitions observed by POM and DSC, along with the large texture domains, are additional indications of purity. Detailed synthetic routes, experimental procedures and analytical data can be found in the Supporting Information.

3.2. Mesomorphic behavior

The thermal and mesomorphic behavior of all target compounds were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC), while their thermal stability was measured by thermogravimetric analysis (TGA). These results are summarized in Table 1 (The transitions on cooling were omitted, but can be found on Table S1). All mesophases were also characterized by X-ray diffraction measurements (XRD), the results being presented and discussed later in the work.

The thermogravimetric data presented in Table 1 show that all final compounds are highly thermal stable, with decomposition temperatures (T_{dec}) above $320^\circ C$. This indicates that the rigid core 2,5-bis(5-phenyl-1,3,4-oxadiazol-2-yl)thiazolo[5,4-*d*]thiazole (**Thz-OXA**) explored herein is suitable for applications that require a high thermal stability. The mass loss profile for all compounds can be found on Fig. S7.

As summarized on Table 1, all target molecules presented liquid crystalline behavior, demonstrating the efficacy of the **ThzOXA** core.



Scheme 1. Synthetic route to obtain the target molecules. *Reagents and conditions:* i) DMF, reflux; ii) KMnO_4 , Py, H_2O , 40°C ; iii) SOCl_2 , toluene, DMF_{cat} , reflux; iv) $\text{C}_{12}\text{H}_{25}\text{Br}$, butanone, K_2CO_3 , TBAB, reflux; v) NaN_3 , NH_4Cl , DMF; vi) MeOH , H_2SO_4 , reflux; vii) $\text{C}_{12}\text{H}_{25}\text{Br}$, CH_3CN , K_2CO_3 , KI, reflux; viii) LiAlH_4 , THF, reflux; ix) PCC , CH_2Cl_2 , *r.t.*; x) I_2 , NH_3 , H_2O , THF, *r.t.*; xi) anhydrous Py, reflux.

Table 1

Transition temperatures, associated enthalpy values and decomposition temperatures for the final compounds.

Compound	Temperature/ $^\circ\text{C}$ [$\Delta\text{H}/\text{kJ}\cdot\text{mol}^{-1}$] ^a	$T_{\text{dec}}/^\circ\text{C}$ ^b
ThzOXA-4	Cr 193 [4.9] Cr₁ 203 [38.8] (SmC 193 [11.0]) ^c Iso	326
ThzOXA-34	Cr 149 [24.8] Col_h 152 [15.6] Iso	350
ThzOXA-345	Cr 84 [22.1] Col_h 94 [2.8] Iso	342

Abbreviations: Cr and Cr₁ = crystalline state, Iso = isotropic liquid; SmC = smectic C mesophase; Col_h = hexagonal columnar mesophase.

^a Determined by DSC (peak temperatures) during the second heating/cooling cycle using a rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

^b T_{dec} measured by TGA under nitrogen atmosphere with a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. The values refer to the temperature in which 1% of mass was lost by the material.

^c Transition within parentheses indicates a monotropic mesophase. A complete version of the table can be found on the SI (Table S1).

Additionally, the mesophase type and transition temperatures are strongly dependent on the number of alkoxy chains (Scheme 1). Compound **ThzOXA-4**, which contains only two long alkoxy chains and a more linear structure, did not exhibit any liquid crystalline behavior by POM on heating, melting directly to the isotropic liquid at 203°C . On cooling, formation of *batonnets* at 193°C followed by their coalescence resulting in a *broken fan-shaped* texture (inset of Fig. 1a) indicates the transition to a monotropic SmC liquid crystalline phase. Upon further cooling, the sample crystallizes at 183°C . The monotropic behavior was ratified by DSC measurements (Fig. 1a) where a high enthalpy endothermic peak was observed on heating (203°C) and two exothermic peaks were present on cooling (193 and 183°C). The small transition observed on heating, before the melting, was attributed to a Cr—Cr₁ transition since no fluidity nor texture change was observed by POM.

Compound **ThzOXA-34**, with two additional alkoxy chains, presented an enantiotropic mesomorphism, which was confirmed both by POM and DSC (Fig. 1b). Two transitions were observed on heating (149 and 152°C) and two on cooling (151 and 137°C). The additional chains promoted a large decrease in the melting point (about 50°C). On cooling from the isotropic liquid, the formation of a pseudo-focal conic texture with rectilinear defects and large homeotropic domains was observed (inset of Fig. 1b), indicating a columnar mesophase. This observed behavior is consistent with the increase in the number of alkoxy chains that leads to a polycatenar mesogen, in this case tetracatenar, rather than the calamitic character presented by **ThzOXA-4**.

The last compound of the series, the hexacatenar **ThzOXA-345** also shows an enantiotropic columnar phase, as indicated by the texture observed on cooling from the isotropic liquid, with rectilinear defects and the presence of homeotropic regions (inset of Fig. 1c). DSC measurements ratified the enantiotropic mesomorphism and demonstrated that the increase in the alkoxy chain number promoted a significant decrease of the transition temperatures (both melting and clearing) and an increase of the mesomorphism range from $\Delta T = 13^\circ\text{C}$ for **ThzOXA-34**, to 36°C for **ThzOXA-345** (Table 1). The thermogram (Fig. 1c) suggests that on the second heating, an initial melting is observed at 67°C , immediately followed by a crystallization at 76°C and a new melting at 84°C . In addition, it can be observed that the crystallization enthalpy on cooling ($4.7\text{ kJ}\cdot\text{mol}^{-1}$) is significantly lower than the melting on heating at 84°C ($22\text{ kJ}\cdot\text{mol}^{-1}$). This enthalpy discrepancy, allied to the complex transition behavior, suggest that the compound does not completely crystallizes on cooling, or that the crystallization does not lead to the most thermodynamically stable solid. Therefore, on heating the sample again, when the molecules gain some structural mobility (first melting), they have enough energy and mobility to reorganize and be able to crystallize in a better structure, as suggested by the crystallization at 76°C . Furthermore, the similar enthalpies involved in the crystallization at 76°C ($23\text{ kJ}\cdot\text{mol}^{-1}$) and the melting at 84°C ($22\text{ kJ}\cdot\text{mol}^{-1}$), corroborate this explanation.

X-ray diffraction measurements were performed to confirm the mesophases proposed by POM and to gain information about the molecular organization in the mesophase. All diffractograms are presented in Fig. 2, and the data are summarized in Table 2.

For the molecule **ThzOXA-4**, three diffraction peaks were observed in the low-angle region (Fig. 2a), in addition to a broad and diffuse peak around $4.4\text{ \AA}$, which indicates the liquid like character of the phase [33,34]. The peaks were indexed to the Miller indices (001), (002) and (003) due the ratio $\approx 1:2:3$ in relation to the first peak (d_{001}). This confirms the lamellar character of the molecular structure, as expected for smectic mesophases. The first and most intense diffraction peak ($d_{001} = 30.0\text{ \AA}$) is associated to the distance between adjacent layers, i.e., the layer size. To understand how the molecules are accommodated in this lamellar mesophase, the molecular length (L) was estimated [35] assuming a transoid conformation, in which the molecule is completely stretched and allows for better lateral packing, as shown in Fig. 3a. Comparing the layer size with the molecular length results in a ratio d_{001}/L value of 0.62. This ratio is significantly smaller than what is expected for a Sm_A phase, when only interdigitation and chain folding

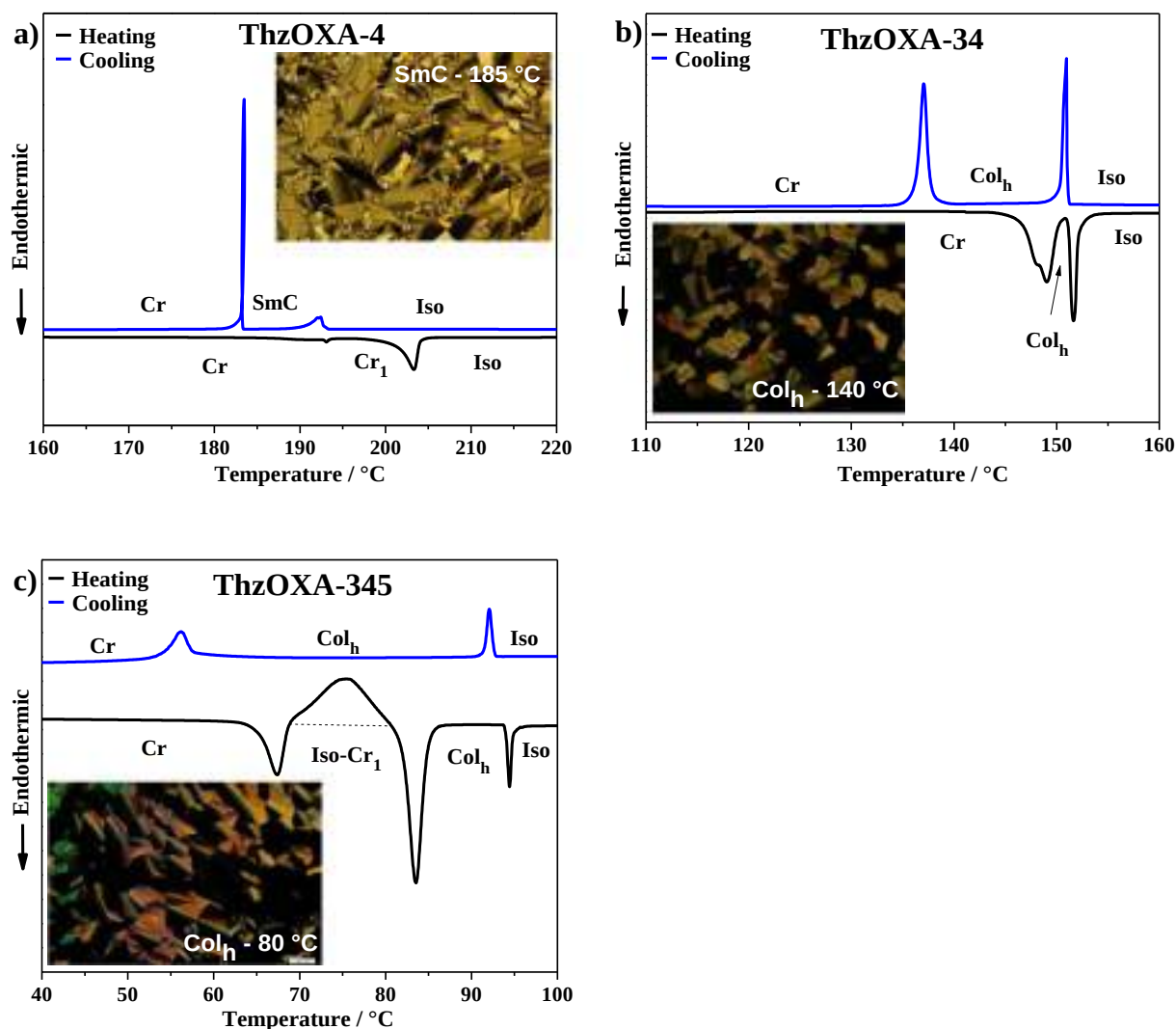


Fig. 1. DSC traces obtained for all target compounds during the second heating (black) and cooling (blue) cycles using a rate of 10 °C min⁻¹: a) THZOXA-4; b) THZOXA-34 c) THZOXA-345. Inset shows the optical texture observed for the respective mesophases (polarizers are crossed and aligned with the figure borders).

are occurring (0.9–0.8) [36,37]. Therefore, this indicates that the molecules are tilted in relation to the layer as represented in Fig. 3a, resulting in an even lower d_{001}/L and corroborating the SmC textures observed by POM [38]. From the data presented and based on the relation $\cos$

$\theta = d_{001}/L$, a tilt angle of $\theta \approx 51^\circ$ could be estimated, which indicates a highly tilted smectic phase. However, it is important to note that this calculation is an estimative that does not take into account interdigitation and/or chain folding. Even though a proper texture was not

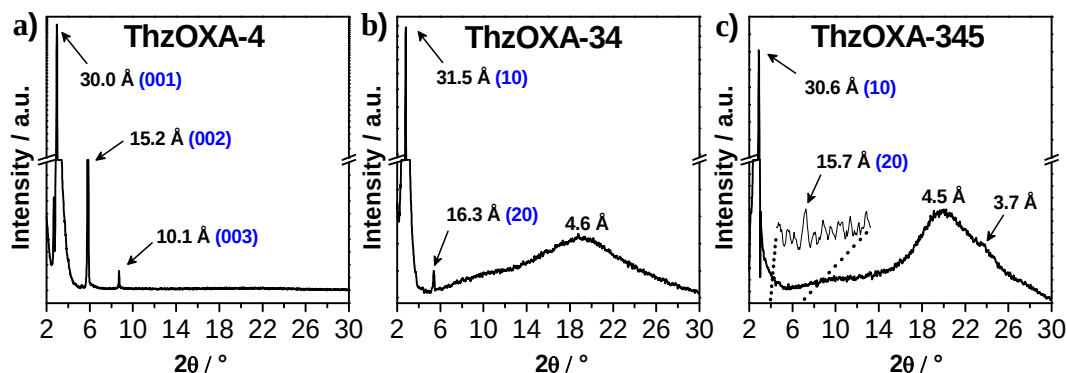


Fig. 2. XRD pattern for the target compounds at their respective mesophases: a) SmC phase for THZOXA-4 at 185 °C; b) Col_h phase for THZOXA-34 at 140 °C; c) Col_h phase for THZOXA-345 at 80 °C.

Table 2
XRD data and lattice parameters for all target compounds.

Compound	Mesophase (T/°C)	$d_{\text{obs}}/\text{\AA}$	hkl^a	$\alpha/\text{\AA}^b$	Z^c
ThzOXA-4	SmC (185)	30.0	001	37.0	2.8
		15.2	002		
		10.1	003		
		4.4	diff		
ThzOXA-34	Col _h (140)	31.5	10	35.8	1.6
		16.3	20		
		4.6	diff		
		30.6	10		
ThzOXA-345	Col _h (80)	31.5	10	35.8	1.6
		16.3	20		
		4.5	diff		
		3.7	π -stacking		

^a Miller Indices.

^b Columnar hexagonal lattice parameter determined by the following equation:

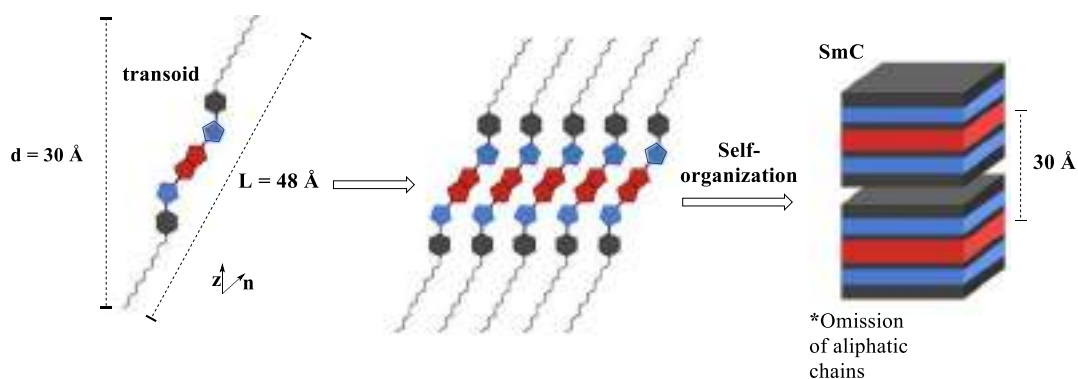
$$\alpha = (d_{10} + 2d_{20})/\sqrt{3}.$$

^c Number of molecules in the cross section of a column in the Col_h phase, assuming that the height of the disk (h) corresponds to the maximum of the diffuse (*diff*) peak or the π -stacking when present.

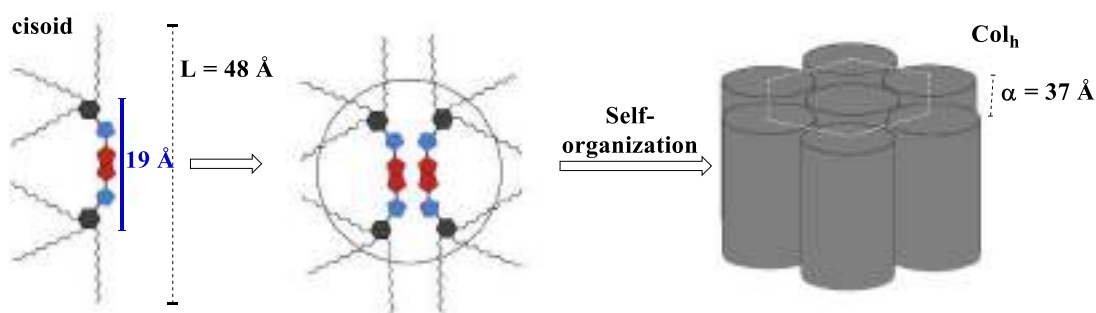
achieved, comparison of the estimated tilt (θ) with optical tilt (mainly the tilt of the π -conjugated system) was performed with the few fractions of circular domains found in the SmC texture. The result indicates an optical tilt of about 40°, which is lower than the tilt estimated by XRD measurements. Since the tilt of the aromatic cores is usually higher than the tilt of the chains [39], it is proposed that some interdigitation and/or chain folding are contributing to the layer shrinkage.

The diffractograms of **ThzOXA-34** and **ThzOXA-345** (Fig. 2b, c and Table 2) exhibited two low-angle diffraction peaks whose ratio is approximately 2. Although this pattern could indicate a lamellar mesophase, the textures are typical of columnar phases (inset of Fig. 1), thus discarding the smectic mesomorphism. In addition, the absence of other intense peak close to the first, most intense one, also allows the exclusion of rectangular and oblique patterns. Thus, as already suggested by the textures, the mesophases were assigned as Col_h, with the peaks indexed as d_{10} and d_{20} . The absence of the d_{11} peak, which is characteristic of the Col_h mesophase, is common and often reported in the literature and indicates a lower degree of order

a) ThzOXA-4



b) ThzOXA-34



c) ThzOXA-345

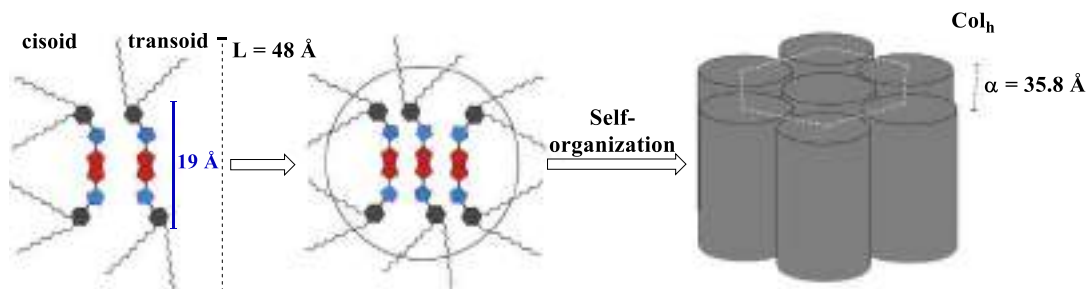


Fig. 3. Schematic representation suggesting a molecular arrangement for mesophases formation: a) SmC of **ThzOXA-4**; b) Col_h of **ThzOXA-34**; c) Col_h of **ThzOXA-345**.

[40–43]. The diffuse halo around 4.6 Å for **ThzOXA-34** and 4.5 Å for **ThzOXA-345** is related to the liquid-like order, as already discussed for **ThzOXA-4**. A small shoulder around 3.7 Å is additionally observed for **ThzOXA-345** indicating a certain periodicity in the packing of disks within a column.

Crystallization of the compounds was also investigated through XRD measurements at 30 °C (Fig. S8). The presence of additional small peaks at lower angles for compounds **ThzOXA-4** and **ThzOXA-34** indicates some crystallization of the material, even though no defined peaks could be observed at higher angles. On the other hand, the diffractogram for **ThzOXA-345** remains nearly identical to the one observed for the mesophase, indicating the same the molecular organization of the Col_h phase. This could be a consequence of the small crystallization enthalpy on cooling (Fig. 1c) and to the fact that the most energetic crystallization was observed on the subsequent heating process.

From the data presented in Table 2 the lattice parameter (α), which is equivalent to the diameter of each disk in a Col_h phase, could be calculated resulting in 37.0 Å for compound **ThzOXA-34** and 35.8 Å for **ThzOXA-345**. Since both compounds are classified as polycatenar mesogens, *i.e.*, they have a linear elongated core and contain multiple terminal long alkoxy chains, they do not show a proper discotic anisotropy. Thus, it would be expected that they alone do not fill the requisites for a proper Col_h molecular packing.

The mesophase formation can be explained by a molecular arrangement model where the mesogenic core of the polycatenar molecules self-assemble side-by-side resulting in dynamic disks (or ellipses), whose orientation is approximately perpendicular to the long axis of the resulting column [44–46]. To better understand this, the number of molecules (Z) present in one fictitious slice of the column, *i.e.*, a disk of height h , was estimated using eq. $Z = \sqrt{3}/2(\alpha^2 h \rho N_A)/M$, in which α corresponds to the lattice parameter, ρ is the material density (assumed to be 1.0 g cm⁻³), N_A the Avogadro's number and M the molar mass [43,47,48]. For compound **ThzOXA-345**, the disk height (h) is 3.7 Å, which is related to the periodical packing of disks. However, for **ThzOXA-34**, the stacking diffraction peak is not observed. In this case, h was assumed to be the diffuse peak (4.6 Å) which refers to the lateral mean distance of the aliphatic chains and mesogens. With this information, it was determined that each disk of the Col_h phase of compound **ThzOXA-34** is composed by approximately three molecules ($Z = 2.8$), while approximately two molecules ($Z = 1.6$) constitute the disks of **ThzOXA-345**. This apparent contradiction, since the size of the disks are slightly similar (lattice parameter), can be explained by the total number of alkoxy chains. For compound **ThzOXA-345**, when two molecules pack to form the aggregate, they possibly prefer to assume a cisoid conformation, which is shaped like a half-disk, as schematically illustrated in Fig. 3c. Two mesogens together then form a complete disk containing 12 long peripheral chains, which completely fill the surrounding space, thus reducing the free volumes. These disks, due to their specific anisotropy and through π - π stacking interaction, pack in columns, which in turn are distributed in a 2-dimensional hexagonal pattern, resulting in a Col_h mesophase (Fig. 3c). Similar behavior was already reported in the literature for hexacatenar mesogens of similar size [43,49–51]. The difference between the molecular length ($L = 48$ Å) and the disk size ($\alpha = 37$ Å) can be due to a large chain folding and/or considerable interdigitation of the chains between neighboring disks, or better fill some empty spaces. Another possible explanation is that the molecular arrangement results in an approximately elliptical structure, which is tilted at a certain angle in the column, generating a circular projection that allows the formation of the symmetrical Col_h mesophase [41,52]. Such an inclination would satisfactorily explain the difference between L and α , in the same way as described for the SmC mesophase of **ThzOXA-4**. It is likely that both processes are working together to form the Col_h mesophase. It is also worth mentioning that for sake of symmetry conditions, there cannot exist a correlation of tilt between neighboring columns.

The tetracatenar molecule **ThzOXA-34** has a similar lattice parameter, despite of this molecule having two fewer alkoxy chains. Therefore, if two molecules assumed a cisoid conformation and constituted a disk like in the case of **ThzOXA-345**, it would have only eight peripheral chains, creating free volumes and destabilizing the molecular organization. In this case, as calculated before, a third molecule is present, resulting in a disk with three mesogens and totaling 12 alkoxy chains, which seems to be the ideal number in this case. The representation of the new structure is illustrated in Fig. 3b, in which 2 molecules are represented in the cisoid conformation and one in the transoid conformation, filling the space more efficiently. It is important to note that liquid crystals are a dynamic and fluid system, where the mesogens adopt different conformations and even diffuse between adjacent disks, so that this representation is not permanent and valid for all disks, just a possible average representation [53]. It is also worth mentioning that some tilt of the mesogens (uniform or randomized) inside the column, resulting in a more circular projection of the disks, is possible, as already discussed for **ThzOXA-345** to explain the difference between the molecular length and cell parameter [41,52]. The higher Z value for **ThzOXA-34** may help to explain why it has a slightly larger disk size (see α in Table 2) than **ThzOXA-345**, even though the later compound is bigger due to the presence of additional alkoxy chains.

3.3. Spectroscopy, theoretical predictions and electrochemistry

The UV–Vis absorption and emission spectra of the **ThzOXA-4**, **ThzOXA-34**, and **ThzOXA-345** in chloroform solution and spin-coated film before and after annealing are presented in Fig. 4, with the photophysical data summarized in Table 3. In solution, all the compounds display two intense absorption bands between 280 nm and 400 nm, with molar absorption coefficients around 21,000 and 37,000 M⁻¹ cm⁻¹, which can be assigned to π - π^* transitions. The steady-state emission of the compounds exhibit maximum emission wavelengths at 464, 499 and 545 nm after excitation at their maximum absorption wavelength, with a quantum yield (Φ) of 0.61, 0.71, and 0.72, respectively. By increasing the number of the side chains, the emission spectra are progressively red-shifted and the quantum yield increases. Therefore, it is possible to tune the emission wavelength of these compounds by varying the number and position of the side chains. The photophysical data presented here also demonstrates the advantages of direct bonding between the thiazolo[5,4-*d*]thiazole and the 1,3,4-oxadiazole units. This promoted a significant bathochromic shift of the absorption and emission bands and an increase of the quantum yield, when compared to compounds whose heterocycles are separated by a phenylene ring and not directly conjugated due the *meta* position ($\Phi = 25$ and 47) [28].

The theoretical modeling of the **ThzOXA-4**, **ThzOXA-34**, and **ThzOXA-345** showed the same trends of the measured photophysical properties. First, we have optimized the conformer for each compound considering the rotation through the bond that connects the oxadiazole and thiazole moieties and for **ThzOXA-34** the relative methoxy positions, leading to the lowest conformer energy, presented in Figs. S9–S11. It is important to note that a methyl group was used instead of the long aliphatic carbon chains, since this reduced computational effort. For the lowest energy conformer of each compound, the electronic excitations were modeled by time-dependent density functional theory (TD-DFT), using linear response of the conductor-like polarizable continuum model (CPCM) to account for the solvent effect on the energy. For these molecules, the HOMO is a π orbital spread throughout the aromatic rings, while the LUMO is a π^* orbital centered on the oxadiazole and thiazole moieties (see Fig. S12). In addition, the HOMO increases in energy from **ThzOXA-4** to **ThzOXA-34** as the number of donating substituents increases, due to the major contributions from the benzene moiety for this orbital, thus decreasing the energy of this transition in agreement with the observed red-shift in the absorption and emission spectra. On other hand, for **ThzOXA-345**, the HOMO energy is slightly

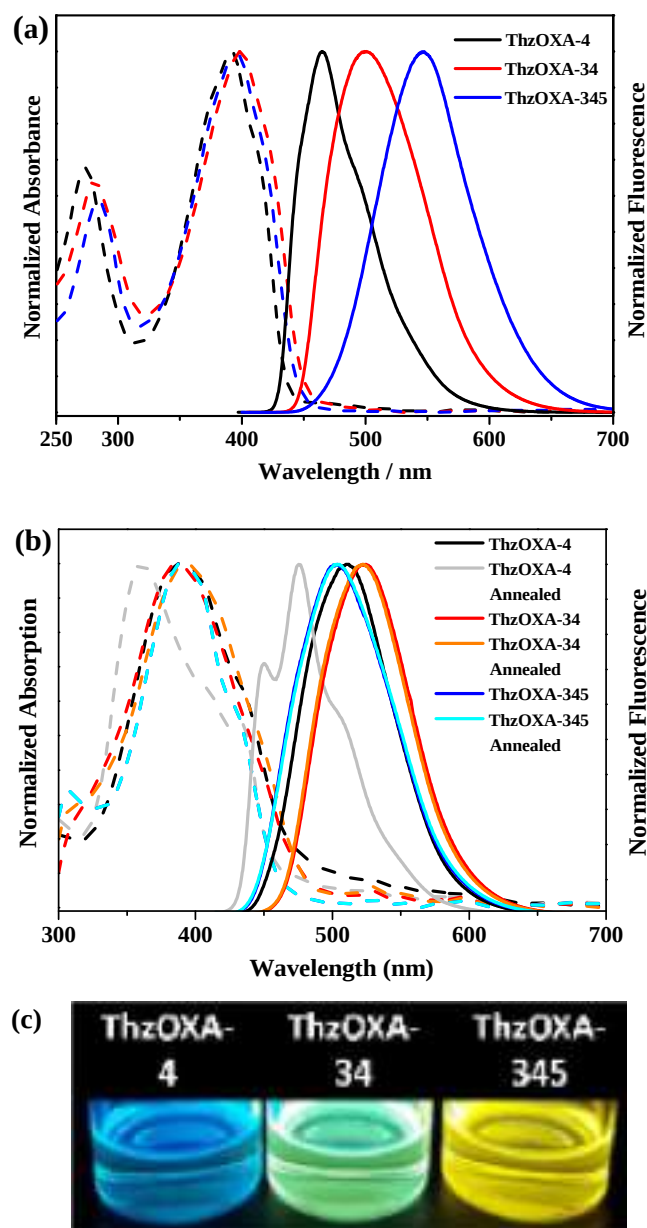


Fig. 4. a) Normalized UV-vis absorption and emission spectra of the **ThzOXA-4**, **ThzOXA-34**, and **ThzOXA-345** in chloroform solution of 10^{-5} mol L $^{-1}$; b) Spin-coated films before and after annealing; c) differences emission colors for the target compounds in chloroform solution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

lower than **ThzOXA-4**. This is due to the loss of planarity, which decreases the extension of the π electron system. The calculated absorption spectra of the molecules are shown in Fig. S13, which agree very well with the experimental data also shown.

The analysis of the TD-DFT results suggest that the lowest energy absorption band (around 400 nm at the experimental spectra) for **ThzOXA-4** and **ThzOXA-34** results from a HOMO $\rightarrow$ LUMO transition (S_1), with a contribution higher than 96% (Table S2). Thus, for **ThzOXA-4** and **ThzOXA-34**, the lowest energy band and the low-lying emission state can be assigned to a π - π^* -like transition. For the compound **ThzOXA-345**, the most intense transition is also a HOMO $\rightarrow$ LUMO transition (S_4). However, the low-lying state for **ThzOXA-345** results from a HOMO-2 $\rightarrow$ LUMO transition (S_1). This is ascribed to a π - π^* -like transition with charge transfer characteristics and with lower energy compared to the S_1 state of **ThzOXA-4** and **ThzOXA-34**, in accordance

with the larger shift of the emission band for that compound. The high energy band observed in the experimental spectra close to 280 nm for these compounds is also assigned to π - π^* -like transitions, involving mixed transitions for the most intense calculated transitions, with the corresponding largest excitation amplitudes.

The main absorption bands of the spin-coated films before and after annealing are around 390 nm, similarly to the main absorption bands of the compounds **ThzOXA-34** **ThzOXA-345** and in solution. The exception was the annealed spin-coated films of **ThzOXA-4** that presented a main absorption band centered at 360 nm with a shoulder close to 410 nm. The emission spectra of the films are red-shifted with respect to the emission spectra in solution, with the exception of **ThzOXA-345**, which showed a blue-shift of 45 nm. In solid film (as coated) the molecular torsional motion is spatially limited by the molecular stacking, thus reducing the conformational changes during excited-state. This increases the energy of the excite-state when compared to relaxed states in solution, leading to a shift of the emission to shorter wavelengths. This effect is more prominent for **ThzOXA-345**, which features six lateral chains.

The blue-shifted main absorption band of the annealed spin-coated films of **ThzOXA-4** with respect to absorption band of non-annealed film suggests formation of *H*-type aggregates (face to face or sandwich), mostly driven by the π - π stacking between the molecules [54]. The smectic mesophase (SmC) structure observed for this compound represents the ideal configuration for the formation of *H*-type aggregates [55], which is enhanced by the annealing process. AFM images of **ThzOXA-4** clearly show formation of large microscale domains after annealing (see first column of Fig. 5). In addition, *H*-type aggregates mostly lead to enhancement of the non-radiative pathways of de-excitation, which explains the decreasing fluorescence quantum yields. Moreover, the emission spectrum of the annealed spin-coated film of **ThzOXA-4** is also blue-shifted, with additional vibrational resolution, compared to the non-annealed film. The emission spectra and quantum yields of the annealed spin-coated films of **ThzOXA-34** and **TzhOXA-345** were both very similar to those of the non-annealed films.

Fig. 5 shows the morphology of the spin-coated films of **ThzOXA-4**, **ThzOXA-34** and **ThzOXA-345**, determined with AFM. The thickness of all films is around 80 nm. The root mean square roughness (R_{RMS}) of the films as casted are 3.7, 2.7 and 3.6 nm, respectively. The morphology and consequently the molecular organization clearly change after thermal annealing. This is particularly evident for **ThzOXA-4** ($R_{\text{RMS}} = 3.7$ nm) and **ThzOXA-34** ($R_{\text{RMS}} = 7.0$ nm), which may indicate different molecular organizations. The morphology of compound **ThzOXA-345** ($R_{\text{RMS}} = 5.5$ nm) is not significantly affected by thermal annealing, which can be due to the larger number of chains.

The excited-state lifetime data of compounds **ThzOXA-4**, **ThzOXA-34**, and **ThzOXA-345** in chloroform solution and spin-coated films before and after thermal annealing when excited at 401 nm are shown in Table 3. The fluorescence decay curves are demonstrated in Fig. S14. In solution, all compounds exhibit single lifetimes in the nanosecond range, which are s to the monomeric fluorescent emission. Moreover, the lifetimes increase (0.90–3.09 ns) with increasing the number of the side chains of the compounds, which is agreement with the red-shift observed in the absorption and emission spectra. The lifetime curves of the films before and after annealing were best fitted using multi-exponential decays (see Fig. S14 and Table S3).

For **ThzOXA-4** before annealing, a bi-exponential decay was used, resulting in two lifetimes, one longer ($\tau_1 = 1.52$ ns) and the other shorter ($\tau_2 = 0.66$ ns) than the emission in solution. τ_1 is attributed to molecular interactions driven by the non-covalent interaction between excited π - π stacked molecules, in which emission lifetimes are usually longer than those of monomeric states [56]. τ_2 is slightly shorter than the monomeric emission in solution. Considering the reduction of the fluorescence quantum yields in the film and the enhancement of non-radioactive pathways, which results in lifetime reduction, it is suggested that τ_2 represents the monomeric emission in film. For the

Table 3Photophysical data for compounds **ThzOXA-4**, **ThzOXA-34**, and **ThzOXA-345** in chloroform solution and spin-coated films (before and after annealing).

Compound	Solution ^a				Film		
	$\lambda_{\text{abs}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	$\lambda_{\text{em}}/\text{nm}$	τ_s^b/ns	Φ^c	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	Φ^c
ThzOxa-4	391 (3.7) 274 (2.5)	465	0.90	0.61	391	512	0.39
ThzOxa-34	400 (3.3) 283 (2.1)	500	2.20	0.71	388	522	0.40
ThzOxa-345	393 (3.7) 281 (2.2)	547	3.09	0.72	389	502	0.19
ThzOxa-4 Annealed^d					360	476	0.28
ThzOxa-34 Annealed^d					393	522	0.45
ThzOxa-345 Annealed^d					389	502	0.15

^a In CHCl_3 at $10^{-5} \text{ mol L}^{-1}$.^b Excited-state lifetimes were measured at maxima of the emission spectra after excitation at 401 nm, the uncertainty is $\pm 0.01 \text{ ns}$.^c The uncertainty is ± 0.01 .^d Thermal annealing until isotropic phase.

annealed **ThzOXA-4** film, three exponentials were necessary to best fit the decay, where the longer lifetime ($\tau_1 = 2.52 \text{ ns}$) was longer than the one before annealing. The SmC structure of the annealed film of **ThzOXA-4**, reduces the molecular free volume and slightly increases molecular interactions, being responsible for this increase. The intermediated lifetime $\tau_2 = 0.86 \text{ ns}$ is attributed to monomeric emission due to similarity with the lifetime in solution, while the much shorter lifetime $\tau_3 = 0.23 \text{ ns}$ is attributed to the emission of the *H*-type aggregates formed after thermal annealing. This is in agreement with the evidence from the absorption measurements, in which a blue-shift of the main absorption band was observed for the annealed films.

The fluorescence decays of **ThzOXA-34** and **ThzOXA-345** were best fitted with three-exponentials before and after annealing, exhibiting three distinct excited-state lifetimes. The longer lifetimes (τ_1) arise from molecular interactions, as observed for **ThzOXA-4**. After the thermal annealing of **ThzOXA-34** and **ThzOXA-345**, the intermediate lifetimes also associated with the monomeric emission remain practically

unchanged, suggesting that the shortest lifetime might be due to emission of aggregated species formed by π -stacking of the packing disks [57]. Cyclic voltammograms of the compounds were collected at scan rates 100 mV s^{-1} and are shown in Fig. S15. The HOMO, LUMO and optical band gap (E_g) are shown in Table 4. The compounds showed only oxidation processes, from which the $E_{1/2}$ could be calculated as -1.35 V for **ThzOXA-4**, and -1.37 V for **ThzOXA-34** and **ThzOXA-345** versus Fc/Fc^{+1} . The $E_{1/2}$ potential was used to estimate the LUMO energy levels. The optical band gap values calculated from the onset of the absorption spectra were used to estimate the HOMO.

The results demonstrate that the thiazolo[5,4-*d*]thiazole and the 1,3,4-oxadiazole units directly connected are promising for electronic device application. The liquid crystalline behavior within accessible temperatures and over a wide temperature range ($\Delta T = 40^\circ \text{C}$), the photophysical properties, particularly the high quantum yields and molar absorptivity coefficients, the possibility of modulating the frontier orbitals by varying the number and position of side chains, and the redox-active states capable of first electron reduction at low potentials

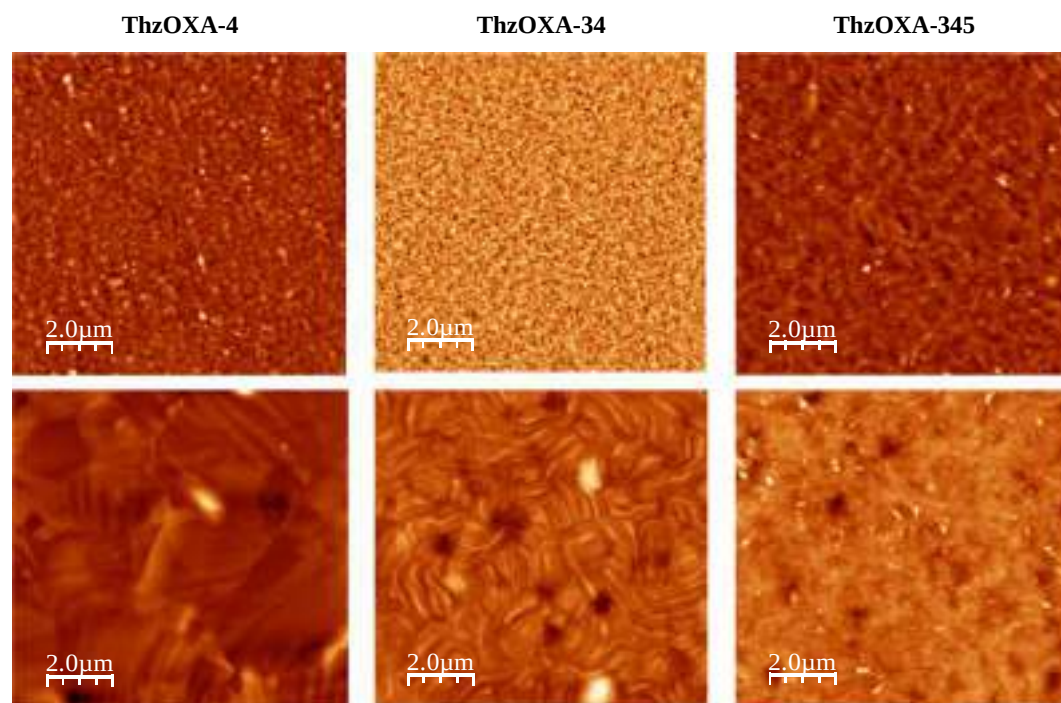
**Fig. 5.** AFM images of thin films. As casted on top and after annealing on bottom. First column **ThzOXA-4**, second column **ThzOXA-34** and third column **ThzOXA-345**.

Table 4

Electrochemical data and optical band gap.

Compound	LUMO (eV) ^a	HOMO (eV) ^b	E _g ^c (eV)
ThzOXA-4	−3.4	−6.2	2.8
ThzOXA-34	−3.5	−6.2	2.7
ThzOXA-345	−3.4	−6.2	2.8

^a Determined from peak potentials.^b Calculated from E_g = −(HOMO–LUMO).^c Calculated from the onset of the absorption spectra in solution.

make these soft materials good candidates for organic photovoltaics (OPV), organic LEDs and field-effect transistors (OFETs), and other devices.

4. Conclusions

The synthesis of new liquid crystalline molecules in which the thiazolo[5,4-*d*]thiazole and 1,3,4-oxadiazole heterocycles are directly connected was successfully accomplished, with high yields. In addition to a high thermal stability, it was demonstrated that this new rigid core shows great versatility, as the mesomorphic organization can be changed from a smectic (SmC) to a columnar (Col_h) phase by varying the number of terminal chains, as confirmed by POM and XRD measurements. XRD investigations also demonstrated that, for this core to be able to form a Col_h phase, 2 **ThzOXA-345** molecules must pack together to form a disk, while for **ThzOXA-34**, 3 molecules are required to do so, always resulting in 12 peripheral long alkoxy chains.

The direct conjugation between thiazolo[5,4-*d*]thiazole and 1,3,4-oxadiazole heterocycles also improved the photophysical behavior, in comparison to molecules in which they are separated by a phenylene ring. In addition, we demonstrated a significant change of photophysical properties with the number of chains, with a higher emission and a bathochromic shift for compounds with increased number of alkoxy chains (emission ranging from 465 to 547 nm). Fluorescence quantum yields higher than 0.60 were obtained in solution, but quenching due to molecular aggregation reduced these values for spin-coated films. Moreover, excited state lifetime studies highlighted the fluorescence components of these compounds, and the dependence with their distinct molecular organization in solid films, especially after thermal annealing. Their thermal stability, and the self-organizing molecular packing induced by annealing may contribute for optimized charge carrier transport. Finally, this work demonstrated how the combination of both heterocycles bring about promising properties for electronic device applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2020.114887>.

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