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Synthesis, Photophysical and Electrochemical Properties of Novel Online and Highly Fluorescent Difluoroboron Flavanone β-Diketonate Complexes

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Abstract

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 (BF₂dbm) 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 difluouroboron 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, Aricle Online and BF₃. Et₂O 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 excitedstate lifetime in all studied solvent. Computational studies were employed to evaluate ground and excited states 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.

Keywords: Flavanone; Chromanone; Flavonoid; Difluoroboron; Diketonates; UV-VIS, Fluorescence; Luminescence; Quantum Yield; X-ray; Photovoltaic; DFT Studies; Optoelectronic.

Introduction

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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 biological identification applications, detection devices, 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 (BF₂dbm) 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 synthetized by Morgan and Tunstall in 1924 through Claisen condensation reaction using only aromatic carbonyl compounds to obtain fluorescent organoboronic compounds.⁵ The

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difluoroboron β-diketonate complexes are increasingly attracting more att<u>ention wave Article Online</u> 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 BF₂dbm complexes reported showed a strong emission in solution⁶ and further chemical modification at the aromatic 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 synthetized 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

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 synthetized 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 BF_2 dbm 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 synthetized 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 to now, not been reported.

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The flavanone structural motif is an interesting option for complexation with border Article Online diffuoride 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 synthetized 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



Scheme 1. Synthesis of β -diketones.

All the synthetized 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).

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Scheme 2. Synthesis of flavanones 3a-i

The synthetized 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.²⁰

Table 1. Product yield for compounds 3a-1								
Flavanone	R ₁	R ₂	Yield (%)	Melting point (°C)				
3a	Phenyl	Η	59	142-144				
3b	<i>p</i> -anisyl	Н	62	160-162				
3c	<i>p</i> -tolyl	Н	80	167-168				
3d	2-furyl	Н	95	175-176				
3e	2-thienyl	Н	76	118-120				
3f	<i>p</i> -tolyl	2-C1	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				

The difluroboron 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 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**.

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

Compound	R ₁	R ₂	Yield (%)	Melting point (°C)
4a	Phenyl	Н	75	-
4b	<i>p</i> -anisyl	Η	57	-
4c	<i>p</i> -tolyl	Η	61	-
4d	2-furyl	Η	54	-
4e	2-thienyl	Η	87	188-190
4 f	<i>p</i> -tolyl	2-Cl	55	-
4g	2-furyl	4-F	89	165-167
4 h	2-thienyl	4-F	67	172-174
4i	<i>p</i> -anisyl	2-Cl	56	-

Table 2. Product	yield for cor	npounds 4a-i
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The infrared spectrum presented some weak bands between 3100-2900 cm⁻¹ attributed to stretching vibrations of saturated 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

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program with B3LYP functional (see Computational Details) for compound 4a arView Article Online compared them with experimental results. Figure 1S (see supporting information) 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 Figure 1S shows the vibration at 3186 cm⁻¹ (see movies in the SI). 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 simplet 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 nonbinomial 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 Figure 1. The difluoroboron coordination with both oxygens of the 1,3-dicarbonyl moiety was confirmed, forming a six-membered chelate ring. The compound crystalizes 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 Figure 1). Bonding to carbon C14

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exist at the phenyl group that is almost perpendicular (~85°) in comparison with the rever Article Online of molecule and presented a planar conformation formed by the phenyl, thiophene and chelate ring (Figure 1). The principal parameters showing the intermolecular distances and angles are summarized in table 3.



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

_	Tuble 5. Dond distance and angles selecting to molecule R.						
-	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)			

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

C(4)-C(9)	1.317(8)	C(4)-C(9)-O(3)	View Article Online
C(4)-C(5)	1.418(4)	C(4)-C(9)-C(8)	115.4(7)

Analyzing the bond distance of the compound **4e** (Figure 1), some interesting information was obtained involving principally 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 Figure 2, which is akin to some structurally related 3-aroylchromanones that exist exclusively in their keto-enol tautomeric form, stabilized by intramolecular hydrogen bonding.²⁷



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

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 (Figure 3). These interactions form infinite chains along the b axis with the molecules related by the 2₁ screw axis. A

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better packing visualization is shown the Figure 3b where it can be observed that every article Online Dol: 10.1039 DONJ03525D molecule forms a kind of zig zag.



Figure 3. (a) Representation of the C-H··F intermolecular interactions observed in compound **4e** with one-dimensional chain along the b crystalline axis. (b) View along the c axis of the crystal packing between molecules of **4e**.

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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**.



Scheme 4. Reaction of 4e with methanol.

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 3Hz 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 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 Figure 4.

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Compound	Absorption λ _{max} (nm) / (ε/ 10 ⁴) ^a	Emission λ _{em} (nm)	$\Delta v_{\rm ST}$ (cm ⁻¹)	$\Phi_{\mathtt{PL}}{}^{\mathtt{b}}$	τ _f (ns) ^c	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

 Table 4. Photophysical properties of the compounds 4a-i in chloroform
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^a Units = M^{-1} cm⁻¹, the molar absorption coefficients (ϵ) of the compounds were evaluated from slopes of the curves from inset of Fig. 29S by Beer-Lambert law; ^b Fluorescence quantum yields; ^c Excited-state lifetimes; ^d Radiative rate constant; ^e Non-radiative rate constant.

All compounds exhibited two main absorption bands between 346 nm and 432 nm (Figure 4a-c) whereas molar absorption coefficient of maximum absorption wavelength ranges of 0.2×10^4 M⁻¹cm⁻¹ (for compound 4f) to 1.8×10^4 M⁻¹cm⁻¹ (for compound 4g). The two bands for 4a in CHCl₃ 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 (Δv_{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

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rings can assessed by comparison of **4c** and **4f** with **4a**. In this case, quantum yields weight weight a 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*-hydroxybenzoylmethanate was studied by Fedorenko and co-workers ³⁰ presented a smaller quantum yield (0.26 in CHCl₃) than the analogous cyclic flavanone equivalent **4a** reported here (0.33 in CHCl₃).



Figure 4. Absorption (a-c) and fluorescence (d) spectra for compounds **4a-i** in chloroform solution at a concentration of 10⁻⁴ M

All compounds in chloroform solution at a concentration of 10^{-4} M showed a monoexponential 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 New Journal of Chemistry Accepted Manuscrip

shown in the supporting information (See Figure. 32S). The singlet excited-state lifetime watche online (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 Figure 5.

Compound	Absorption λ _{max} (nm) / (ε/ 10 ⁴) ^a	Emission λ _{em} (nm)	Δυ _{ST} (cm ⁻¹)	$\Phi_{\mathtt{PL}}{}^{\mathtt{b}}$	τ _f (ns) ^c	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
4 c	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
4 h	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

Table 5. Photophysical properties of the compounds 4a-i in acetonitrile

hemistry Accepted Manuscrip ^a Units = M^{-1} cm⁻¹, the molar absorption coefficients (ε) of the compounds were evaluated from slopes of the curves from inset of Fig. 30S 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 (Figure 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 0.2×10^4 M⁻¹cm⁻¹ (for compound 4f) to 1.8×10^4 M⁻¹cm⁻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 (Δv_{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

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acetonitrile solution exhibited fluorescence quantum yields (Φ_{PL}) between 0.19 and 0.4 for which contained 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 R₁ position and 2-Cl at R₂ 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).



Figure 5. Absorption (a-c) and fluorescence (d) spectra for compounds **4a-i** in acetonitrile solution at a concentration of 10⁻⁴ M

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 supporting information (See Figure 33S). The excited-state lifetimes (τ_f) of compounds **4a-i** in acetonitrile were slightly longer compared to lifetimes of the

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compounds in chloroform solution. The lifetimes of the compounds **4a-i** in acetonitrile^W Article Online 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 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. Figure 6 shows the normalized absorption and fluorescence spectra of **4a-i** in THF solution at concentration of 10⁻⁴ M.

Compound	Absorption λ _{max} (nm) / (ε/ 10 ⁴) ^a	Emission λ _{em} (nm)	Δυ _{ST} (cm ⁻¹)	$\Phi_{ extsf{PL}}{}^{ extsf{b}}$	τ _f (ns) ^c	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
4 h	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

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

^a Units = M⁻¹cm⁻¹, the molar absorption coefficients (ε) of the compounds were evaluated from slopes of the curves from inset of Fig. 31S by Beer-Lambert law; ^b Fluorescence quantum yields; ^c Excited-state lifetimes; ^d Radiative rate constant; ^eNon-radiative rate constant.

In THF, the absorption spectra of the compounds **4a-i** exhibited peaks and shoulders ranging of 323 nm to 415 nm (Figure 6a-c). The main absorption bands of the compounds are given in Table 6. THF bears a sp³ 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 $_{DO}$ solve M_{DO} wavelength are molecule itself.²¹ The molar absorption coefficients of main absorption wavelength are between 0.1×10^4 M⁻¹cm⁻¹ (for compound 4d and 4f) to 1.1×10^4 M⁻¹cm⁻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 (Δv_{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).



Figure 6. Absorption (a-c) and fluorescence (d) spectra for compounds **4a-i** in tetrahydrofuran solution at a concentration of 10⁻⁴ M

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

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timescale (see Table 5). The fluorescence decay curves of the compounds in $_{DOF, 1010397DONJ03525D}^{THE, 04897}$ Article Online shown in the supporting information (See Figure 34S). The excited-state lifetimes (τ_f) of the compounds **4a-i** in THF were similar to 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 Figure 7. The photophysical properties of compound **4a** in solution of several solvents at 10⁻⁴ M are summarized in Table 7.



Figure 7. Normalized absorption (a) and fluorescence (b) spectra of compound 4a in CHCl₃, CH₃CN and THF

Concerning the polarities of each solvent, CHCl₃ and THF both have similar polarity whereas CH₃CN is a more polar solvent. The absorption spectra of compound **4a** in CHCl₃ and CH₃CN 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 CH₃CN is shifted to longer wavelengths from 488-489 nm (THF and CHCl₃) to 502 nm (CH₃CN). This implies 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 $\mu^{CS} = 7.28$ D to $\mu^{ES} = 10.60$ D for the first excited state. The fluorescence quantum yields of **4a** in CHCl₃ was slightly higher.

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

Solvent	Absorption λ_{max} (nm) / (ϵ / 10 ⁴) ^a	Emission λ _{em} (nm)	Δυ _{ST} (cm ⁻¹)	$\Phi_{\mathtt{PL}}{}^{\mathtt{b}}$	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⁻¹cm⁻¹; ^b Fluorescence quantum yields; ^c Excited-state lifetimes; ^d Radiative rate constant; ^e Non-radiative rate constant.

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 Figure 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.

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

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 **4ai** are summarized in Table 8. The HOMO was estimated according to the reduction onset (E_{onset}^{red}) potentials from voltammograms using the following equation: HOMO= $-(E_{onset}^{red} + 4.44)$ eV. The LUMO was estimated from optical band gaps (E_{gap}^{opt}) previously determined from the absorption edge of compounds in solution, according to equation: LUMO = $(HOMO - E_{gap}^{opt})$ eV. The cyclic voltammograms of the compounds are provided in the supporting information (See Figures 35S – 43S).

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

Compounds	E ^{onset} (V) ^a	HOMO (eV) ^b	LUMO (eV) ^c	E ^{opt} gap (eV) d	λ _{onset} (nm) ^e
4a	-1.09	5.53	2.67	3.07	404

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4b	-1.10	5.54	2.72	2.97	417
4 c	-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_{red}^{onset} is the onset potential of reduction, ^b HOMO = $-(E_{red}^{onset} - 4.44)$ eV; ^c LUMO = $(HOMO - E_{gap}^{opt})$ eV; ^d E_{gap}^{opt} is optical band gap calculated from the low energy edge of the absorption spectrum (E_{gap}^{opt} = 1240 / λ_{onset}); ^e λ_{onset} is the absorption onsets wavelength.

The cyclic voltammograms of the compounds (see ESI) exhibit reduction processes with E_{red}^{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 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

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experimental results, we studied different properties with six different functional we Article Online B3LYP, PBE0, CAM-B3LYP, BHLYP, 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 Figures 9 and 10 and 41S.



Figure 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.



Figure 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.

Tables 3S and 4S show the optimized parameters for bonds and angles between the atoms in the gas phase for molecules **4a** and **4e**. The labeling scheme is presented in Figure 41S for molecule **4e**. Comparing these results with those obtained by X-ray crystallography for compound **4e** (see Figure 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,

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respectively. The angles obtained with the DFT calculations do not show deviations watches and a show deviation and a show deviating a show deviating a show

In order to understand the experimental absorption spectra, the four lowest excited states responsible for the main absorption bands observed were investigated. Figures 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 5S and 6S 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, Figures 9 and 10 show difference densities only for excited state 1 for both molecules. The excited state 3 has an excitation energy of 3.900eV (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 5S and 6S.

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





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.

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 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 7S. For molecule **4a**, state 1 has a f_{osc} = 0.17 with λ_{max} in 386 nm (see Figure 11 and Supporting Information) 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 λ_{max} = 433 nm and the oscillator strength decreases to approximately 0.14 (see Figure 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 Figure 11d). Solvents

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hardly changed the oscillator strength in this case. If we directly compare the Article Online 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 (Figure 10 and 11) showing that the electron density decreases in part of the dihydropyrone moiety and benzenoid rings while it increases in the R₁ group and the dicarbonyl fragment (see Figure 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 75) 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 stogether 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.

Figures 44S and 45S 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

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first two excited states stay together, increasing the intensity of the band. For these case we watcher online on 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 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

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smallest deviation. In addition to the intrinsic problems of DFT calculations for gap on the intrinsic problems of DFT calculations for gap on the intrinsic problems of DFT calculations for gap on the intrinsic problems of DFT calculations for gap on the intrinsic problems of DFT calculations for gap on the intrinsic problems of DFT calculations for gap of the intrinsic 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.

 Table 9. Orbital Energies and energy gap (in eV) using different methodologies from 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	номо	LUMO	ΔE ^{gap} (DFT)	ΔE^{gap} (TDDFT)			
				Gas Phase	CH₃C N	CHCl 3	THF
Compound 4a							
B 3LYP	-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				

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 Article Online final compounds and lead to molar absorption coefficient ranges from 10⁴ to 10⁵ M⁻¹cm⁻¹ and the fluorescence quantum yield to vary of 0.08 to 0.75. Compound 4d bearing a 2furyl moiety presented the highest quantum yield value of 0.75 in CHCl₃ and an excitedstate 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

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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 ¹³C 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: simplet (s), doublet (d) , doublet doublet (dd),

triplet (t), and multiplet (m). Electronic absorption spectra, UV and visible, were carried warde online 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 Bomen 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 Diketonate 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, BF₃.Et₂O (8 equivalents) was added using a syringe and the reaction was left under constant stirring for 24 h at 80 °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.

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2,2-difluoro-4,5-diphenyl-2,5-dihydro-[1,3,2]dioxaborinino[5,4-c]chromen-1-ium-2, View Article Online

uide (4a): flavanone **3a** (0.91 mmol) and BF₃.Et₂O (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, CDCl₃): 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); ¹³C-NMR (100 MHz, CDCl₃): 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* [M + H]⁺ Calcd for C₂₂H₁₆O₃.BF₂: 377.1155; Found: 377.1161; **CHCl**₃ λ_{abs} = 404 nm, ε = 0.5.10⁴ M⁻¹.cm⁻¹, λ_{em} =489 nm, Φ: 0.33721. *t*= 4.20±0.03 ns, k_r= 0.08 ns⁻¹, k_{nr}= 0.16. ns⁻¹; **CH₃CN** λ_{abs} = 404 nm, ε = 0.4.10⁴ M⁻¹.cm⁻¹. λ_{em} = 488 nm, Φ= 0.21117 *t*= 4.58±0,03 ns, k_r= 0.046 ns⁻¹. k_{nr}= 0.172 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 BF₃.Et₂O (5.36 mmol) provided compound **4b** as a green oil in 61% yield; R_f: 0.60 (50% CH₂Cl₂/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, CDCl₃): 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); ¹³C-NMR (100 MHz, CDCl₃): 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* [M + H] ⁺ Calcd for C₂₃H₁₈O₄.BF₂: 407.1261; Found: 407.1256; **CHCl**₃ λ_{abs}= 418 nm, ε = 0.3.10⁴ M-1.cm⁻¹, λ_{em}= 496 nm, Φ= 0.46429, *t*= 4.47±0.002 ns, k_r= 0.103 ns⁴, k_{nr}= 0.119. ns⁴; **THF**: λ_{abs}= 414 nm, ε = 0.3.10⁴ M⁻¹.cm⁻¹, λ_{em}= 482 nm, Φ= 0.55691, *t*= 3.91±0.001 ns, k_r= 0,142 ns⁴, k_{nr}= 0.113 ns⁴.

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 BF₃.Et₂O (5.76 mmol) provided compound **4c** as a green oil in 57% yield; R_f: 0.60 (30% CHCl₃/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, CDCl₃): 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); ¹³C-NMR (100 MHz, CDCl₃): δ 21.9, 75.2,

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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 View Article Online 176.8, 181.6; HRMS (ESI-TOF) m/z [M + H] ⁺ Calcd for C₂₃H₁₈O₃.BF₂: 391.1312; Found: 391.1319; CHCl₃ λ_{abs} = 420 nm, ε = 0.8.10⁴ M⁻¹.cm⁻¹, λ_{em} =485 nm, Φ : 0.31762, t= 3.69±0,03 ns, kr= 0.085, ns⁻¹, knr= 0.184 ns⁻¹; CH₃CN λ_{abs} = 420 nm, ε = 0.3.10⁴ M⁻¹.cm⁻¹, λ_{em} = 497 nm, Φ = 0.21586, t= 4.54±0.03 ns, kr= 0.047ns⁻¹, knr= 0.172, ns⁻¹; THF: λ_{abs} = 416 nm, ε = 0.8.10⁴ M⁻¹.cm⁻¹. λ_{em} = 483 nm, Φ = 0.36177, t= 3.96±0.03 ns, kr= 0.091 ns⁻¹, knr= 0.161 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 BF₃.Et₂O (7.29 mmol) provided compound **4d** as a green oil in 54% yield; R_f: 0.60 (30% CHCl₃/hexane, UV Lamp 365 nm); IR (cm⁻¹): 3014, 1613, 1578, 1529, 1493, 1453, 1352, 1211, 1148, 1036, 747; ¹H-NMR (400 MHz, CDCl₃): 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); ¹³C-NMR (100 MHz, CDCl₃): 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* [M + H] ⁺ Calcd for C₂₀H₁₄O₄.BF₂: 367.0948; Found: 367.0953; CHCl₃ λ_{abs}= 430 nm, ε = 0.4.10⁴ M⁻¹.cm⁻¹, λ_{em}= 494 nm, Φ= 0.75012, *t* = 4.78±0.03 ns, k_r= 0.156 ns⁻¹, k_{nr}= 0.052. ns⁻¹; CH₃CN λ_{abs}= 433 nm. ε = 0.3.10⁴ M⁻¹.cm⁻¹, λ_{em}= 507 nm, Φ= 0.33749, *t*= 5.78±0.04 ns, k_r= 0.058 ns⁻¹, k_{nr}= 0.114 ns⁻¹; THF: λ_{abs}= 432 nm, ε = 0.1.10⁴ M⁻¹.cm⁻¹. λ_{em}= 490 nm, Φ= 0.40149, *t*= 5.25±0.03 ns, k_r= 0.076 ns⁻¹, k_{nr}= 0.114 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 BF₃.Et₂O (8.20 mmol) provided compound 4e as an orange solid in 69% yield; Melting point: 188-190 °C; R_f: 0.60 (30% CHCl₃/hexane, UV Lamp 365 nm); IR (cm⁻¹): 2921, 1608, 1587, 1488,1475, 1450, 1354, 1217, 1184, 1149, 1030, 756; ¹H-NMR (400 MHz, CDCl₃): 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); ¹³C-NMR (100 MHz, CDCl₃): 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* [M + H] + Calcd for C₂₀H₁₄O₃S.BF₂: 383.0719; Found: 383.0708; CHCl₃ λ_{abs} = 430 nm, ε = 0.7.10⁴ M⁻¹.cm⁻¹, λ_{em} = 495 nm, Φ = 0.47797, *t*= 4.16±0.03 ns, kr= 0.114 ns⁻¹, knr= 0.125, ns⁻¹; CH₃CN λ_{abs} = 430 nm, ε = 0.8.10⁴ M⁻¹.cm⁻¹. λ_{em} = 513 nm, Φ = 0.36432, *t*= 5.35±0.03

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ns, kr= 0.068 ns⁻¹, knr= 0.119 ns⁻¹; **THF:** λ_{abs} = 435 nm, ε = 0.5.10⁴ M⁻¹.cm⁻¹, λ_{em} = 495 nm, $\Phi_{DOI: 10.1039/DONJ03525D}^{tem}$ 0.07757, t= 4.27±0.03 ns, kr= 0.018 ns⁻¹, knr= 0.216 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 BF₃.Et₂O (6.58 mmol) provided compound 4f as an green oil in 69% yield; R_f: 0.60 (50% CH₂Cl₂/hexane, UV Lamp 365 nm); IR (cm⁻¹): 3191, 2929, 1608, 1587, 1489, 1476, 1451, 1440, 1353, 1319, 1218, 1110, 1184, 1149, 1034, 756; ¹H-NMR (400 MHz, CDCl₃): 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); ¹³C-NMR (100 MHz, CDCl₃): 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* [M + H] ⁺ Calcd for C₂₃H₁₇O₃Cl.BF₂: 425.0922; Found: 425.0919; CHCl₃: λ_{abs} = 410 nm, ε = 0.2.10⁴ M⁻¹.cm⁻¹, λ_{em} = 489 nm, Φ = 0.35751, *t*= 3.91±0.002 ns, k_r= 0.091 ns⁻¹, k_{nr}= 0.164 ns⁻¹, CH⁻¹Cm⁻¹, λ_{em} = 499 nm, Φ = 0.18627, *t*= 6.26±0.03 ns, k_r= 0.029 ns⁻¹, k_{nr}= 0.129 ns⁻¹, THF: λ_{abs} = 374 nm, ε = 0.1.10⁴ M⁻¹.cm⁻¹, λ_{em} = 487 nm Φ = 0.27184, *t*= 4.46±0.03 ns, k_r= 0.060 ns⁻¹, k_{nr}= 0.163 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 BF₃.Et₂O (7.20 mmol) provided compound **4g** as an yellow solid in 85% yield; Melting point: 165-167 °C; R_f: 0.60 (30% CHCl₃/hexane, UV Lamp 365 nm); IR (cm⁻¹): 2920, 1607, 1588, 1487, 1475, 1435, 1354, 1217, 1184, 1150, 1030, 756; ¹H-NMR (400 MHz, CDCl₃): 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); ¹³C-NMR (100 MHz, CDCl₃): 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*_{C-F} 22.0), 134.5 (*J*_{C-F} 3.0), 138.7, 149.8, 159.1, 161.6, 164.1 (*J*_{C-F} 181.0), 176.6; HRMS (ESI-TOF) *m*/*z* [M + H] ⁺ Calcd for C₂₀H₁₃O₄BF₃: 385.0854; Found: 385.0862. CHCl₃ λ_{abs}= 432 nm, ε = 1.8.10⁴ M⁻¹.cm⁻¹, λ_{em}= 495 nm, Φ= 0.3492, *t*= 4.88±0.04 ns, k_r= 0.071 ns³, k_{nr}= 0.133 ns⁻¹, CH₃CN λ_{abs}= 430 nm, ε = 1.8.10⁴ M⁻¹.cm⁻¹, λ_{em}= 495 nm, ε = 1.1.10⁴ M⁻¹.cm⁻¹, λ_{em}= 491 nm, Φ= 0.09793, *t*= 4.88±0.03ns, k_r= 0.020 ns⁻¹, k_{nr}=.0.184 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 BF₃.Et₂O (7.61 mmol) provided compound **4h** as an yellow solid in 67% yield; Melting point: 172-174 °C; R_f:

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0.60 (30% CHCl₃/hexane, UV Lamp 365 nm); IR (cm⁻¹): 2920, 1608, 1587, 1487, 1476 1456 per Article Online 397DONJ03525D 1354, 1218, 1184, 1147, 1030, 756; ¹H-NMR (400 MHz, CDCl₃): 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); ¹³C-NMR (100 MHz, CDCl₃): δ 74.7, 102.4, 115.6, 116.0 (*J_{CF}* 8.0), 117.5, 118.2, 122.8, 127.7, 129.2, 129.6, 129.7 (*J_{CF}* 21.8), 132.9 (*J_{CF}* 3.2), 136.2, 137.2, 138.6, 158.4, 161.9 (*J_{CF}* 248); 172.4, 176.1; ¹⁹F NMR (376.5 MHz, CDCl₃): δ -112.51 (C-F), -141.39 (B-F), -143.66 (B-F); HRMS (ESI-TOF) *m*/*z* [M + H] ⁺ Calcd for C₂₀H₁₃O₃SBF₃: 401.0625; Found: 401.0630; CHCl₃ λ_{abs} = 429 nm, ε = 0.8.10⁴ M⁻¹.cm⁻¹, λ_{em} = 496 nm, Φ = 0.30428, *t*= 4.15±0.03 ns, kr= 0.073 ns⁴, knr= 0.167 ns⁴, CH₃CN λ_{abs} = 428 nm, ε = 0.6.10⁴ M⁻¹.cm⁻¹, λ_{em} = 496 nm, Φ = 0.10864, *t*= 4.28±0.03 ns, kr= 0.025 ns⁴, knr= 0.208 ns⁴.

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 BF₃.Et₂O (3.62 mmol) provided compound 4i as an green oil in 56% yield; R_f: 0.60 (30% CHCl₃/hexane, UV Lamp 365 nm); IR (cm⁻¹): 3010, 2960, 1603, 1588, 1488, 1477, 1450, 1358, 1308, 1263, 1218, 1170, 1149, 1026, 836, 754; ¹H-NMR (400 MHz, CDCl₃): 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); ¹³C-NMR (100 MHz, CDCl₃): 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* [M + H] + Calcd for C₂₃H₁₇O₄ClBF₂: 441.0871; Found: 441.0869; CHCl₃ λ_{abs} = 422 nm, ε = 0.3.10⁴ M⁻¹.cm⁻¹, λ_{em} = 487 nm, Φ = 0.27644, *t*= 3.69±0.03 ns, kr= 0.074 ns⁴, knr= 0.196 ns⁴, CH₃CN λ_{abs} = 418 nm, ε = 0.4.10⁴ M⁻¹.cm⁻¹, λ_{em} = 496 nm, Φ = 0.47881, *t*= 4.44±0.03 ns, kr= 0.107 ns⁴, knr= 0.117 ns⁴, THF: λ_{abs} = 429 nm, ε = 0.2.10⁴ M⁻¹.cm⁻¹, λ_{em} = 483 nm, Φ = 0.24643 *t*= 3.98±0.03 ns, kr= 0.061 ns⁴, knr= 0.189 ns⁴.

4.2 Photophysical properties

For the study of the photophysical properties, a stock solution was prepared in CHCl₃, CH₃CN 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 wArticle Online 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:

Abs
$$(\lambda) = \varepsilon(\lambda).l.c$$
 Eq. (1)

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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:

where the subscript *S* refers to the standard solution (reference). $\Phi_{\rm S}$ 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 (n₀). 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 ($\Phi_{\rm PL}$) of the compounds were determined using rhodamine-B in methanol diluted solution as standard solution ($\Phi_{\rm S} = 0.8$).⁴⁴ The fluorescence spectra of dilute solutions of the compounds and the standard were recorded under exactly the same experimental conditions and temperature. Singletexcited 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 Article Online 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 $k_r = \Phi_{PL}/\tau_f$ and $k_{nr} = (1-\Phi_{PL})/\tau_f$.

4.3 Electrochemical measurements

The electrochemical properties of the compounds were investigated by cyclic voltammetry (CV) using *Microquimica* potentiostat /galvanostat (model MQPG-01) coupled to a personal computer with *Microquimica 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 CHCl₃ 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 CuK α radiation ($\lambda = 1.54184$ Å). The structure of **4e** was solved by direct methods (SHELXS) and refined by full-matrix least-squares against F² (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 with the appropriate riding model considering $U_{iso}(H) = 1.2U_{eq}(C)$. 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). Copies of the data can be obtained, free of charge, via <u>www.ccdc.cam.ac.uk</u>. Summary of crystal, data collection procedures, structure determination methods and refinement results are summarized in Table 1S. Representation of the structure was drawn with the Mercury 4.3.1 program.⁴⁸

4.5 Computational details

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First-principle calculations based on density functional theory (DFT) and timedependent density functional theory (TDDFT) formalisms⁴⁹⁻⁵¹ 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 M06-2X 59 and BHLYP 60 and range-separated hybrid CAM-B3LYP ⁶¹ 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

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Conflicts of interest: There are no conflicts of interest to declare.

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A convenient method for the synthesis of flavanone difluoroboron complexes with strong absorption and fluorescence properties is described.