DOI 10.1007/s10593-020-02847-6
Chemistry of Heterocyclic Compounds **2020**, *56*(12), 1542–1547

Synthesis and photophysical investigation of AIEgen dyes bearing quinoline and BODIPY scaffolds

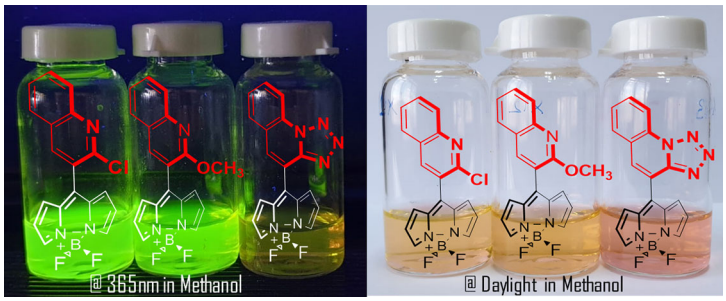
Yavuz Derin[1]*, Barış Seçkin Arslan[1]*, Büşra Albayrak Mısır[1], İlkay Şişman[1,2], Mehmet Nebioğlu[1,2], Ahmet Tutar[1]

[1] *Department of Chemistry, Faculty of Arts and Sciences, Sakarya University, Sakarya 54050, Turkey*

[2] *Biomedical, Magnetic and Semiconductor Materials Research Center (BIMAS-RC), Sakarya University, Sakarya 54050, Turkey; e-mail: yavuzderin@sakarya.edu.tr, barisseckin@gmail.com*

Published in Khimiya Geterotsiklicheskikh Soedinenii, 2020, *56*(12), 1542–1547

Submitted March 22, 2020
Accepted after revision September 30, 2020



Quinoline-based BODIPY AIEgen dyes were synthesized and the structures were elucidated by ^{1}H, ^{13}C, ^{19}F NMR, FT-IR spectroscopy and mass spectrometry methods. Their photophysical properties were investigated. The dyes showed fluorescence quantum yield in the range of 0.16–1.29% in MeOH. It was found that the presence of methoxy group and tetrazole moiety led to blue and red spectral shift, respectively, of the UV absorption maxima of these dyes compared to their chloroquinoline analog. Stokes shifts of the dyes were in the range of 637–955 cm^{-1}. Aggregation-induced emission behavior of the dyes was investigated in EtOH–H_2O mixture so that the dyes exhibited 1.6- to 2.3-fold fluorescence enhancement.

Keywords: BODIPY, quinoline, aggregation-induced emission, fluorescence quantum yield.

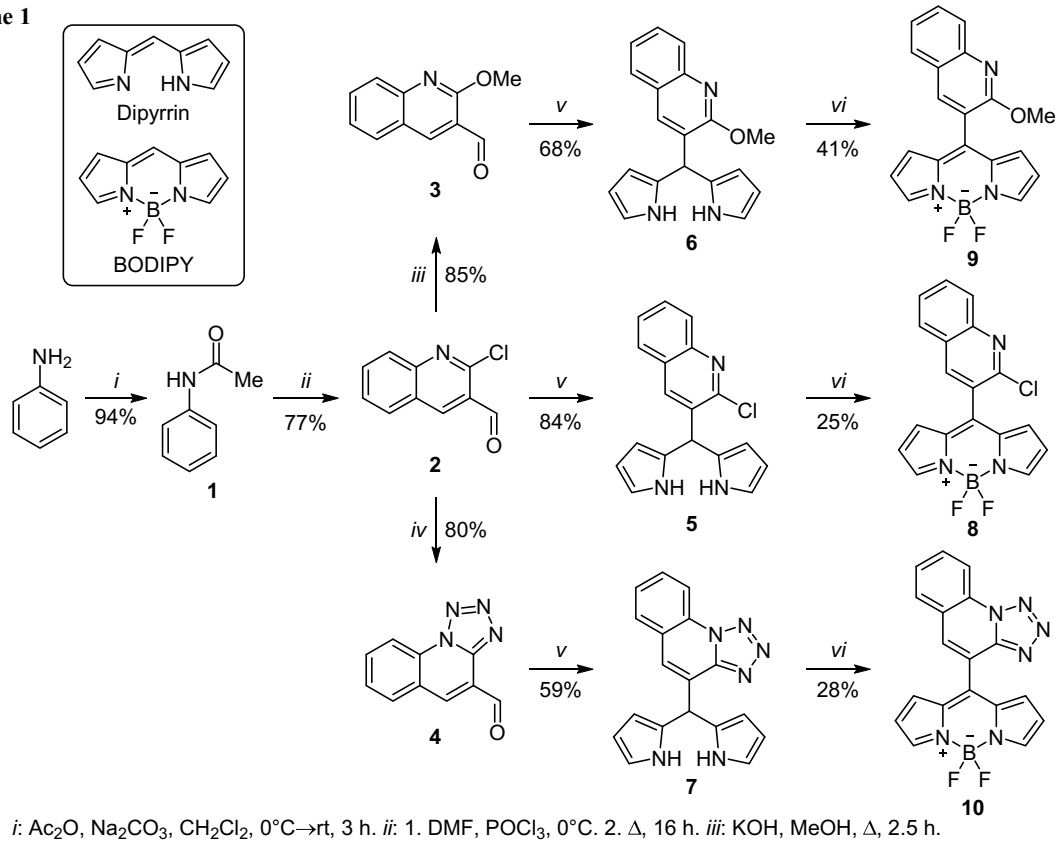
Compounds containing quinoline ring system have been of a particular interest to chemists due to their diverse applications in bioorganic, medicinal, and industrial chemistry, as well as in the field of synthetic organic chemistry.[1,2] Quinolines have been mostly investigated for promising biological activities such as antibacterial, antihypertensive, antimalarial, antitubercular.[3] Due to the extended π-electron system, quinolines also have interesting optical properties and potential to be utilized as optical materials and fluorescent probes.[4–6]

Dipyrrin or dipyrromethene is a ligand that comprises a methine carbon bridged between two pyrrole rings and forms the complexes with various metals (Scheme 1).[7,8] BODIPY, first reported by Treibs and Kreuzer, is boron difluoride complex of dipyrromethene which is a well-known representative of these complexes.[9] BODIPY has gained the popularity as a functional dye due to high emission and absorption band at visible region, fluorescence quantum yield approaching 100%, being chemically inert toward moisture, solvent, exposure to light, and, most importantly, easily functionalizable to adjust these features.[10–12] Thanks to these properties, BODIPY has many applications such as fluorescence probes,[13,14] biolabeling reagent, laser dyes, photosensitizers for photodynamic therapy,[15] photocatalysts,[16,17] and solar cell components.[18]

In recent years, the dyes that are emissive in the aggregated state have been extensively explored. This class of dyes called AIEgen dyes or AIEgens (aggregation-induced emission luminogens) were discovered in 2001 by Tang et al. and are characterized by increasing emission with the increasing polarity of the medium through aggregate forming as a result of restriction of intramolecular motion.[19] AIEgens have crucial role in biological applications because most conventional dyes are hydrophobic and nonemissive in hydrophilic conditions due to aggregation-caused quenching.[20]

In this study, three quinoline-BODIPY conjugates were designed starting from aniline and pyrrole for the purpose

Scheme 1



i: Ac_2O, Na_2CO_3, CH_2Cl_2, 0°C→rt, 3 h. *ii*: 1. DMF, $POCl_3$, 0°C. 2. Δ, 16 h. *iii*: KOH, MeOH, Δ, 2.5 h.
iv: NaN_3, AcOH, EtOH, Δ, 4 h. *v*: pyrrole, TFA (cat.), rt, 24 h. *vi*: 1. DDQ, CH_2Cl_2, 2 h, rt. 2. Et_3N, 0°C, 15 min. 3. $BF_3{\cdot}Et_2O$, rt.

of investigating their AIEgen-like properties, which could indicate their potential therapeutic effect and ability to serve as fluorescent bioprobes for diagnostics in medicine.

The synthesis of the dyes is shown in Scheme 1. Acetanilide (**1**) formed by acetylation of the aniline was converted to 2-chloroquinoline-3-carbaldehyde (**2**) by the Vilsmeier–Haack reaction.[21,22] Compound **2** reacted with MeOH in strongly basic medium to give 2-methoxyquinoline-3-carbaldehyde (**3**) and in acidic medium with NaN_3 to yield tetrazolo[1,5-*a*]quinoline-4-carbaldehyde (**4**).[23,24] Quinoline derivatives **2**–**4** were condensed with pyrrole in the presence of TFA to give dipyrromethene derivatives **5**–**7**, respectively. Quinoline-BODIPY dyes **8**–**10** were obtained by oxidation of dipyrromethanes with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) followed by complexation with $BF_3{\cdot}Et_2O$.[25] Dyes **8**–**10** were characterized by ^1H, ^{13}C, and ^{19}F NMR and FT-IR spectroscopy and mass spectrometry.

The effect of chloro or methoxy substituents at the quinoline ring or that of fused tetrazole ring on photophysical properties of dyes **8**–**10** was investigated in different solvents by UV/vis and fluorescence spectroscopy. The aggregation-induced luminescence behavior caused by restriction of intramolecular rotations was spectroscopically studied in gradient of EtOH–H_2O mixture.

Absorption and emission spectra of dyes **8**–**10** in MeOH are presented in Figure 1. The absorption and emission spectra in various solvents for each of three compounds **8**–**10** are given in Figure 2 for comparison. Photophysical parameters such as absorption maxima, molar absorption coefficient, emission maxima, fluorescence quantum yield, and Stokes shift (Δυ) are presented in Table 1.

Dyes **8**–**10** have a strong absorption peak at the range of 502–515 nm with approximately 50000 (log ε 4.70) molar absorptivity corresponding to S_0–S_1 transition which can also be described as π–π* transition and a shoulder at the higher energy side attributed to 0–1 vibrational transition. Besides, a band appears in the UV region (*ca*. 350 nm) which corresponds to n–π* transition. As for emission spectra, the maximum peak that can be ascribed to emission by the BODIPY unit is located at the range of 522–538 nm when the dyes were excited at 480 nm. These peaks are typical for similarly substituted BODIPY dyes.[25–27]

It was observed that the presence of methoxy group on quinoline ring causes a blue shift of the absorption maximum λ_{abs} in the spectrum of a quinoline-BODIPY dye. On the other hand, a red shift was caused by the presence of tetrazole ring fused quinoline moiety in the dye molecule. It is well known that BODIPY dyes bearing

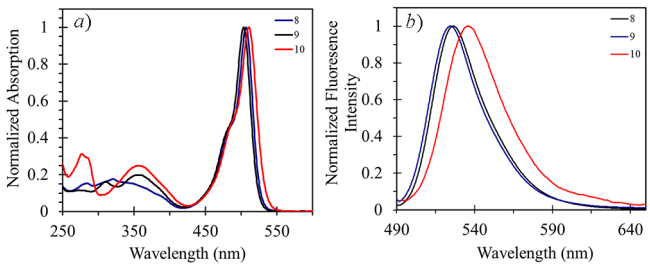


Figure 1. Normalized absorption spectra (*a*) and emission spectra (*b*) of compounds **8**–**10** in MeOH.

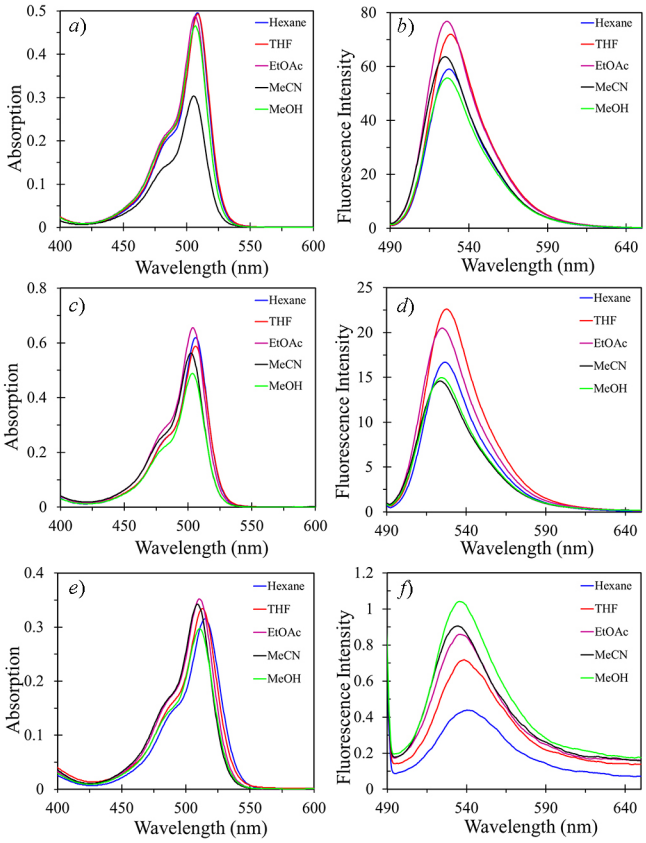


Figure 2. Absorption and emission spectra of compounds **8** (*a*, *b*), **9** (*c*, *d*), and **10** (*e*, *f*) in various solvents, respectively.

electron-donating groups have more blue-shifted spectra than their counterparts with electron-withdrawing groups.[28–30] In the case of dye **10**, tetrazole ring being of a highly electron-withdrawing nature and extending the conjugated π-electron system causes 3 and 7 nm bathochromic shifts of absorption (λ_{abs}) and emission (λ_{em}) maxima, respectively, and the largest Stokes shift (Δυ), whereas the electron-donating methoxy group in the molecule of dye **9** produces opposite shifts of 4 and 2 nm, respectively (Table 1). The reason for which the spectral shift values are quite low is that these groups are not directly attached to BODIPY core. The fluorescence quantum yields φ of the dyes **8**–**10** in MeOH were found to be 5.31, 1.29, and 0.16%, respectively. It is clearly evident that excited state of the BODIPY moiety in dye **10** is quenched by tetrazoloquinoline group which has strong electron-accepting power.[30,31]

When the φ values of dyes **8** and **9** were compared, it was expected that dye **8** would have lower fluorescence quantum yield than dye **9**, as chlorine atom exerts heavy atom effect which is known to diminish the fluorescence quantum yield. However, various articles report that the fluorescence quantum yield of the dyes increases with the introduction of chlorine atom(s)[32,33] and beside that, as an example, chlorinated BODIPY shows higher fluorescence quantum yield than the counterpart with a methoxy group.[34] The increase in fluorescence quantum yield of dye **8** in respect to dye **9** is due to the fact that chlorine atom reduces the nonradiative deactivation process.[32,35] When the photophysical properties of the dyes were evaluated in

Table 1. Photophysical properties of dyes **8**–**10**

Compound	Solvent	λ_{abs}, nm	λ_{em}, nm	Δυ, cm^{-1}	log ε	φ, %
8	Hexane	508	525	637	4.71	6.49
	THF	508	528	746	4.71	7.93
	EtOAc	506	525	715	4.71	7.54
	MeCN	505	523	682	4.50	9.04
	MeOH	507	524	640	4.69	5.31
9	Hexane	506	526	751	4.70	1.40
	THF	506	526	751	4.68	1.98
	EtOAc	504	523	721	4.73	1.45
	MeCN	502	522	763	4.66	1.05
	MeOH	503	522	724	4.60	1.29
10	Hexane	515	538	830	4.60	0.08
	THF	513	534	767	4.62	0.13
	EtOAc	510	536	951	4.64	0.12
	MeCN	509	535	955	4.63	0.11
	MeOH	510	531	775	4.57	0.16

several common organic solvents, it was found that dye **10** displayed higher φ values in polar solvents than in nonpolar solvents (Table 1).

The absorption and emission spectra were recorded in EtOH–H_2O mixture to study the aggregation-induced emission phenomena in dyes **8**–**10** (Fig. 3). For many BODIPY dyes, aggregation-caused quenching is observed. However, quinoline-BODIPY dyes are known to be AIEgens which fluoresce more intensely with increased

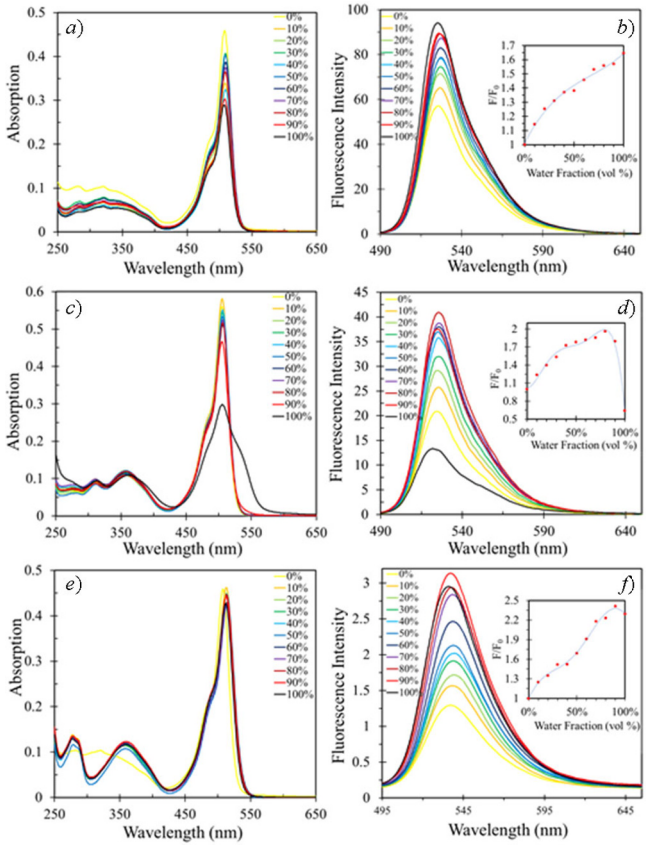


Figure 3. Absorption and emission spectra of compounds **8** (*a*, *b*), **9** (*c*, *d*), and **10** (*e*, *f*) in EtOH–H_2O mixture, respectively. Inset graph: Plot of F/F_0 *versus* water fraction.

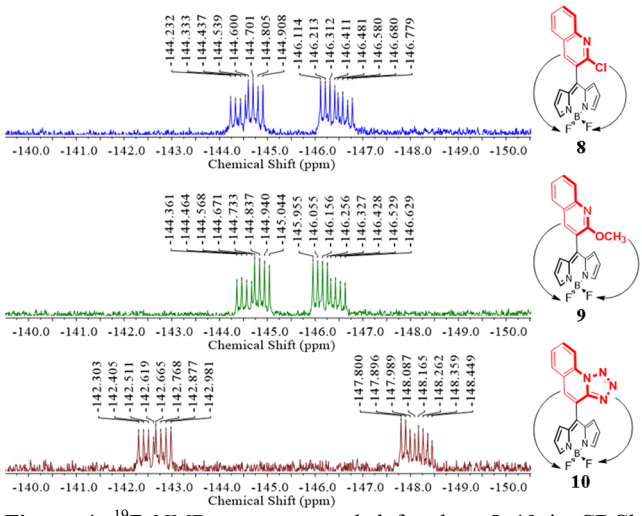


Figure 4. ^{19}F NMR spectra recorded for dyes **8**–**10** in $CDCl_3$ showing the coupling patterns and interaction of fluorine atoms with groups at *meso* position.

water quantity causing the molecules to form aggregates.[36] AIEgens **8**, **9**, and **10** show, in turn, 1.6-, 1.9-, and 2.3-fold fluorescence enhancement F/F_0 at H_2O fraction $f(H_2O)$ 100, 80, and 90%, respectively. Increment of the water content in the dye solutions promotes aggregate formation which results in restriction of intramolecular rotations along with fluorescence intensity.[37]

^{19}F NMR spectra of many BODIPY compounds have typical quartet signals because of coupling to ^{11}B nucleus (I 3/2, $^1J_{BF}$ = 32 Hz).[38,39] However, dyes **8**–**10**, unlike common BODIPY dyes, exhibit doublet of quartets. It indicates that the two fluorine atoms are chemically not equivalent, likely because of the rotation around the C–C bond between BODIPY and quinoline units is slow on NMR time scale. Moreover, in such case, one of the fluorine atoms would be closely interacting with chlorine atom, methoxy group, or fused tetrazole ring (Fig. 4). As a result, the geminal ^{19}F nuclei give rise to a doublet signal. Similar results were reported for BODIPY bearing quinone and thiazolyl groups at *meso* position.[39,40] It is noteworthy that increasing electron-accepting power of the groups on quinoline bring about an increase in the chemical shift difference between both fluorine signals in the order of compounds **9** < **8** < **10**.

In this study, BODIPY dyes substituted by quinoline moiety at *meso* position were synthesized and characterized by ^{1}H, ^{13}C, and ^{19}F NMR, FT-IR spectroscopy and mass spectrometry methods. Doublet of quartet splitting patterns were observed in ^{19}F NMR spectra of the synthesized compounds, which is not common for BODIPY dyes. Photophysical parameters, such as fluorescence quantum yield, molar absorption coefficient, Stokes shifts, and absorption/emission peak maxima were evaluated in several common organic solvents. Dye containing tetrazolo-[1,5-*a*]quinoline moiety exhibited very low fluorescence quantum yield due to highly electron-withdrawing nature of the tetrazole group. Nevertheless, this dye showed higher aggregation-induced fluorescence enhancement than dyes containing methoxy- or chloroquinoline unit. It can be concluded that tetrazoloquinoline-BODIPY system is a versatile AIEgen scaffold. Through synthetic modification of quinoline or BODIPY moiety, more functional dyes will be produced and explored in due course.

Experimental

FT-IR (ATR) spectra were recorded on a PerkinElmer Spectrum Two instrument. The absorption and emission spectra of the dyes were measured in quartz cuvette with 1 cm optical path using a Shimadzu UV 2600 spectrophotometer and a Hitachi F7000 spectrofluorometer. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian Infinity Plus spectrometer (300, 75, and 282 MHz, respectively) with TMS as reference. High-resolution ESI mass spectra were recorded on a Waters SYNAPT MS series system. The melting points were determined using a Schorpp MPM-H1 apparatus.

All reagents and solvents used in reactions were of reagent grade quality and were procured from commercial suppliers. Solvents used in column chromatography were obtained as technical grade and purified by standard methods before use.[41] Synthesis of compounds **1**–**4** according to the literature-described method[23,24] is reported in the Supplementary information file.

2-Chloro-3-[di(1*H*-pyrrol-2-yl)methyl]quinoline (5).[25] In a flask, pyrrole (10.0 ml, 144.1 mmol) and 3 drops of TFA were added to 2-chloroquinoline-3-carbaldehyde (**2**) (1.42 g, 7.4 mmol). The mixture was stirred at room temperature for 24 h. After the reaction was complete, the excess pyrrole was removed under reduced pressure. The crude product was purified by column chromatography on silica gel, eluent hexane–EtOAc, 10:1. Yield 1.92 g (84%), white-off solid. IR spectrum, ν, cm^{-1}: 3379 (N–H), 3104 (C–H Ar), 2985 (C–H aliphatic), 1615 (C=N), 1568 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.13 (2H, br. s, NH); 8.00 (1H, d, *J* = 8.8, H Ar); 7.79 (1H, s, H Ar); 7.74–7.64 (2H, m, H Ar); 7.55–7.47 (1H, m, H Ar); 6.77 (2H, td, *J* = 2.7, *J* = 1.6, H pyrrole); 6.19 (2H, dd, *J* = 6.0, *J* = 2.7, H pyrrole); 5.97 (1H, s, CH); 5.90–5.84 (2H, m, H pyrrole). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 151.0; 146.7; 138.1; 135.0; 130.7; 130.5; 128.0; 127.8; 127.5; 127.3; 118.1; 108.9; 108.1; 41.2.

3-[Di(1*H*-pyrrol-2-yl)methyl]-2-methoxyquinoline (6) was synthesized analogously starting from 2-methoxyquinoline-3-carbaldehyde (**3**) (1.39 g, 7.4 mmol). Yield 1.52 g (68%), white-off solid. IR spectrum, ν, cm^{-1}: 3454 (N–H), 3100 (C–H Ar), 2998 (C–H aliphatic), 1618 (C=N), 1571 (C=C), 1096 (C–O).^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.13 (2H, br. s, 2NH); 7.85 (1H, d, *J* = 8.3, H Ar); 7.70 (1H, s, H Ar); 7.66–7.53 (2H, m, H Ar); 7.40–7.28 (1H, m, H Ar); 6.72 (2H, td, *J* = 2.7, *J* = 1.6, H pyrrole); 6.17 (2H, dt, *J* = 5.5, *J* = 2.7, H pyrrole); 5.93–5.89 (2H, m, H pyrrole); 5.82 (1H, s, CH); 4.05 (3H, s, OCH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 160.3; 145.8; 137.2; 131.6; 129.4; 127.6; 127.2; 127.0; 125.6; 124.3; 117.5; 108.7; 107.3; 54.1; 37.0.

4-[Di(1*H*-pyrrol-2-yl)methyl]tetrazolo[1,5-*a*]quinoline (7) was synthesized analogously starting from tetrazolo[1,5-*a*]-quinoline-4-carbaldehyde (**4**) (1.47 g, 7.4 mmol). Yield

1.37 g (59%), off-white solid. IR spectrum, ν, cm^{-1}: 3326 (N–H), 3091 (C–H Ar), 2988 (C–H aliphatic), 1608 (C=N), 1567 (C=C).^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.15 (2H, br. s, 2NH); 8.64 (1H, d, *J* = 8.2, H Ar); 7.91 (1H, d, *J* = 8.0, H Ar); 7.87–7.79 (2H, m, H Ar); 7.69 (1H, t, *J* = 7.6, H Ar); 6.76 (2H, d, *J* = 1.5, H pyrrole); 6.13 (2H, dd, *J* = 5.7, *J* = 2.9, H pyrrole); 6.03 (2H, s, H pyrrole); 5.99 (1H, s, CH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 147.9; 131.2; 131.1; 130.2; 129.6; 129.0; 128.4; 127.8; 124.4; 118.4; 116.9; 108.7; 107.7; 42.3.

10-(2-Chloroquinolin-3-yl)-5,5-difluoro-4λ^5-5*H*-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-4-ylium-5-uide (8). A solution of DDQ (0.812 g, 3.58 mmol) in THF (15 ml) was added dropwise to a solution of 2-chloro-3-[di(1*H*-pyrrol-2-yl)methyl]quinoline (**5**) (1.0 g, 3.25 mmol) in CH_2Cl_2 (25 ml). After stirring the reaction mixture for 2 h, the mixture was cooled in ice bath, and Et_3N (0.75 ml) was added cooling the flask in the ice bath. The reaction mixture was then stirred for 15 min. Afterward, $BF_3 \cdot Et_2O$ (3 ml, 24.3 mmol) was added and the reaction mixture was brought to room temperature and stirred overnight. After the reaction was complete, the solvent was removed. The crude product was purified by column chromatography on silica gel; eluent hexane–CH_2Cl_2, 3:1. Yield 0.287 g (25%), red-green solid, mp 185–186°C. IR spectrum, ν, cm^{-1}: 3091 (C–H Ar), 1620 (C=N), 1558 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.25 (1H, s, H Ar); 8.15 (1H, d, *J* = 8.4, H Ar); 7.99 (2H, s, H pyrrole); 7.89 (2H, t, *J* = 8.1, H Ar); 7.69 (1H, t, *J* = 7.6, H Ar); 6.75 (2H, d, *J* = 4.2, H pyrrole); 6.54 (2H, d, *J* = 4.1, H pyrrole). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 148.3; 145.9; 141.0; 140.3; 135.7; 132.3; 131.1 (2 signals); 128.9; 128.4; 128.1; 126.6; 126.0; 119.6. ^{19}F NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): –144.58 (dq, J_{FF} = 104.2, J_{BF} = 28.8); –146.46 (dq, J_{FF} = 103.8, J_{BF} = 27.9). Found, *m*/*z*: 354.0806 $[M+H]^+$. $C_{18}H_{12}BClF_2N_3$. Calculated, *m*/*z*: 354.0775.

5,5-Difluoro-10-(2-methoxyquinolin-3-yl)-4λ^5-5*H*-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-4-ylium-5-uide (9) was synthesized analogously starting from 3-[di(1*H*-pyrrol-2-yl)methyl]-2-methoxyquinoline (**6**) (0.986 g, 3.25 mmol). Yield 0.465 g (41%), red-green solid, mp 174–175°C. IR spectrum, ν, cm^{-1}: 3110 (C–H Ar), 2954 (C–H aliphatic), 1624 (C=N), 1549 (C=C), 1108 (C–O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.02 (1H, s, H Ar); 8.00–7.88 (3H, m, H Ar, H pyrrole); 7.79–7.69 (2H, m, H Ar); 7.53–7.40 (1H, m, H Ar); 6.80 (2H, d, *J* = 4.1, H pyrrole); 6.49 (2H, d, *J* = 4.0, H pyrrole); 4.02 (3H, s, OCH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 159.3; 147.4; 144.8; 142.2; 140.8; 135.8; 131.4; 131.0; 128.2; 127.5; 125.3; 124.1; 118.9; 118.5; 54.2. ^{19}F NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): –144.71 (dq, J_{FF} = 105.1, J_{BF} = 29.1); –146.31 (dq, J_{FF} = 105.4, J_{BF} = 28.3). Found, *m*/*z*: 350.1264 $[M+H]^+$. $C_{19}H_{15}BF_2N_3O$. Calculated, *m*/*z*: 350.1271.

5,5-Difluoro-10-(tetrazolo[1,5-*a*]quinolin-4-yl)-4λ^5-5*H*-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-4-ylium-5-uide (10) was synthesized analogously starting from 4-[di(1*H*-pyrrol-2-yl)methyl]tetrazolo[1,5-*a*]quinoline (**7**) (1.022 g, 3.25 mmol). Yield 0.327 g (28%), red-green solid, mp 247–248°C. IR spectrum, ν, cm^{-1}: 3116 (C–H Ar), 1605 (C=N), 1558 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.82 (1H, d, *J* = 8.2, H Ar); 8.18 (1H, s, H Ar); 8.12–8.05 (2H, m, H Ar); 8.02 (2H, s, H pyrrole); 7.84 (1H, t, *J* = 7.1, H Ar); 6.88 (2H, d, *J* = 4.2, H pyrrole); 6.55 (2H, d, *J* = 3.7, H pyrrole). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 148.3; 147.0; 139.1; 136.9; 135.4; 133.3; 133.1; 131.5; 131.1; 129.1; 124.4; 120.1; 118.5; 117.0. ^{19}F NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): –142.65 (dq, J_{FF} = 88.8, J_{BF} = 28.9); –148.14 (dq, J_{FF} = 81.0, J_{BF} = 26.7). Found, *m*/*z*: 361.1207 $[M+H]^+$. $C_{18}H_{12}BF_2N_6$. Calculated, *m*/*z*: 361.1179.

Photophysical studies. All absorption and emission spectra were acquired for 10 μM dye solutions in common organic solvents. The dyes were excited with 480 nm wavelength to record emission spectra. Molar absorption coefficients were calculated from Lambert–Beer equation.[42] Relative fluorescence quantum yields were calculated using a solution of rhodamine B in EtOH (φ_{ref} 0.49)[43] as reference dye *via* the following equation.

$$\varphi_{smp} = \varphi_{ref} \times \left(\frac{I_{smp}}{I_{ref}}\right) \times \left(\frac{A_{ref}}{A_{smp}}\right) \times \left(\frac{\mu_{smp}{}^2}{\mu_{ref}{}^2}\right)$$

Subscripts smp and ref stand for sample and reference, respectively. Variables φ, *I*, *A*, and μ stand for fluorescence quantum yield, area under the maximum emission peak, absorbance at the excitation wavelength (480 nm), and refractive index of solvent, respectively. Stokes shifts were estimated from the difference between maximum emission and absorption wavenumber.[44,45] The dye solutions in 10 μM concentration were prepared in EtOH–H_2O gradient (from 0 to 100%) to investigate aggregation-induced emission behavior of the dyes *via* fluorescence and UV/vis spectroscopic methods.

Supplementary information file containing ^{1}H, ^{13}C, ^{19}F NMR and mass spectra as well as synthetic methods for all compounds is available at the journal website at http://link.springer.com/journal/10593.

References

1. Arslan, B. S.; Güzel, E.; Kaya, T.; Durmaz, V.; Keskin, M.; Avcı, D.; Nebioğlu, M.; Şişman, İ. *Dyes Pigm.* **2019**, *164*, 188.
2. Gupta, S. S.; Kumari, S.; Kumar, I.; Sharma, U. *Chem. Heterocycl. Compd.* **2020**, *56*, 433. [*Khim. Geterotsikl. Soedin.* **2020**, *56*, 433.]
3. Prajapati, S. M.; Patel, K. D.; Vekariya, R. H.; Panchal, S. N.; Patel, H. D. *RSC Adv.* **2014**, *4*, 24463.
4. Liu, Y.; Yang, L.; Ma, C.; Tang, A. *Dyes Pigm.* **2020**, *173*, 107981.
5. Wang, L.; Qian, Y. A. *J. Photochem. Photobiol., A* **2019**, *372*, 122.
6. Benelhadj, K.; Retailleau, P.; Massue, J.; Ulrich, G. *Tetrahedron Lett.* **2016**, *57*, 1976.
7. Matsuoka, R.; Nabeshima, T. *Front. Chem.* **2018**, *6*, 349.
8. Dudina, N. A.; Nikonova, A. Y.; Antina, Y. V.; Berezin, M. B.; Vyugin, A. I. *Chem. Heterocycl. Compd.* **2014**, *49*, 1740. [*Khim. Geterotsikl. Soedin.* **2013**, 1878.]
9. Treibs, A.; Kreuzer, F. H. *Justus Liebigs Ann. Chem.* **1968**, *718*, 208.
10. Boens, N.; Leen, V.; Dehaen, W. *Chem. Soc. Rev.* **2012**, *41*, 1130.
11. Boens, N.; Verbelen, B.; Ortiz, M. J.; Jiao, L.; Dehaen, W. *Coord. Chem. Rev.* **2019**, *399*, 213024.

12. Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891.
13. Gao, J.; Tao, Y.; Wang, N.; He, J.; Zhang, J.; Zhao, W. *Spectrochim. Acta*, *Part A* **2018**, *203*, 77.
14. Qin, W.; Dou, W.; Leen, V.; Dehaen, W.; Van der Auweraer, M.; Boens, N. A. *RSC Adv.* **2016**, *6*, 7806.
15. Kamkaew, A.; Lim, S. H.; Lee, H. B.; Kiew, L. V.; Chung, L. Y.; Burgess, K. *Chem. Soc. Rev.* **2013**, *42*, 77.
16. Yadav, R. K.; Baeg, J. O.; Kumar, A.; Kong, K. J.; Oh, G. H.; Park, N. J. *J. Mater. Chem. A* **2014**, *2*, 5068.
17. Yang, H.; Zhao, M.; Zhang, J.; Ma, J.; Wu, P.; Liu, W.; Wen, L. *J. Mater. Chem. A* **2019**, *7*, 20742.
18. Thumuganti, G.; Gupta, V.; Singh, S. P. *New J. Chem.* **2019**, *43*, 8735.
19. Luo, J.; Xie, Z.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. *Chem. Commun.* **2001**, 1740.
20. Yamaguchi, M.; Ito, S.; Hirose, A.; Tanaka, K.; Chujo, Y. *Mater. Chem. Front.* **2017**, *1*, 1573.
21. Cheng, B.; Xu, J. *Phosphorus*, *Sulfur Silicon Relat. Elem.* **2017**, *192*, 518.
22. Meth-Cohn, O.; Narine, B.; Tarnowski, B.; Hayes, R.; Keyzad, A.; Rhouati, S.; Robinson, A. A. *J. Chem. Soc*., *Perkin Trans. 1* **1981**, 2509.
23. Chandraprakash, K.; Ramesh, P.; Ravichandran, K.; Mohan, P. S.; Ponnuswamy, M. N. *Acta Crystallogr*., *Sect. E*: *Struct. Rep. Online* **2010**, *66*, o2510.
24. Ladani, N. K.; Patel, M. P.; Patel, R. G. *ARKIVOC* **2009**, (vii), 292.
25. Singh, R. S.; Gupta, R. K.; Paitandi, R. P.; Dubey, M.; Sharma, G.; Koch, B.; Pandey, D. S. *Chem. Commun.* **2015**, 9125.
26. Choi, S.; Bouffard, J.; Kim, Y. *Chem. Sci.* **2014**, *5*, 751.
27. Prasannan, D.; Raghav, D.; Sujatha, S.; Hareendrakrishna Kumar, H.; Rathinasamy, K.; Arunkumar, C. *RSC Adv.* **2016**, *6*, 80808.
28. Sørensen, M. L. H.; Vosch, T.; Laursen, B. W.; Hansen, T. *Photochem. Photobiol. Sci.* **2019**, *18*, 1315.
29. Patalag, L. J.; Jones, P. G.; Werz, D. B. *Chem.–Eur. J.* **2017**, *23*, 15903.
30. Patalag, L. J.; Loch, M.; Jones, P. G.; Werz, D. B. *J. Org. Chem.* **2019**, *84*, 7804.
31. Dumas-Verdes, C.; Miomandre, F.; Lépicier, E.; Galangau, O.; Vu, T. T.; Clavier, G.; Méallet-Renault, R.; Audebert, P. *Eur. J. Org. Chem.* **2010**, 2525.
32. Duran-Sampedro, G.; Agarrabeitia, A. R.; Garcia-Moreno, I.; Costela, A.; Bañuelos, J.; Arbeloa, T.; López Arbeloa, I.; Chiara, J. L.; Ortiz, M. J. *Eur. J. Org. Chem.* **2012**, 6335.
33. Zhang, X. F.; Zhang, I.; Liu, L. *Photochem. Photobiol.* **2010**, *86*, 492.
34. Rohand, T.; Baruah, M.; Qin, W.; Boens, N.; Dehaen, W. *Chem. Commun.* **2006**, 266.
35. Qin, W.; Rohand, T.; Baruah, M.; Stefan, A.; Van der Auweraer, M.; Dehaen, W.; Boens, N. *Chem. Phys. Lett.* **2006**, *420*, 562.
36. Singh, R. S.; Kumar, A.; Mukhopadhyay, S.; Sharma, G.; Koch, B.; Pandey, D. S. *J. Phys. Chem. C* **2016**, *120*, 22605.
37. Qian, J.; Tang, B. Z. *Chem* **2017**, *3*, 56.
38. Goud, T. V.; Tutar, A.; Biellmann, J. F. *Tetrahedron* **2006**, *62*, 5084.
39. Neena, K. K.; Thilagar, P. *ChemPlusChem* **2016**, *81*, 955.
40. Benniston, A. C.; Copley, G.; Elliott, K. J.; Harrington, R. W.; Clegg, W. *Eur. J. Org. Chem.* **2008**, 2705.
41. Armarego, W. L. F. *Purification of Laboratory Chemicals*; Elsevier: Amsterdam, 2008, 8th ed.
42. Swinehart, F. *J. Chem. Educ.* **1962**, *39*, 333.
43. Casey, K. G.; Quitevis, E. L. *J. Phys. Chem.* **1988**, *92*, 6590.
44. Rurack, K.; Spieles, M. *Anal. Chem.* **2011**, *83*, 1232.
45. Derin, Y.; Yılmaz, R. F.; Baydilek, İ. H.; Atalay, V. E.; Özdemir, A.; Tutar, A. *Inorg. Chim. Acta* **2018**, *482*, 130.