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8-AminoBODIPYs: Cyanines or Hemicyanines? The Effect of the Coplanarity of the Amino Group on Their Optical Properties

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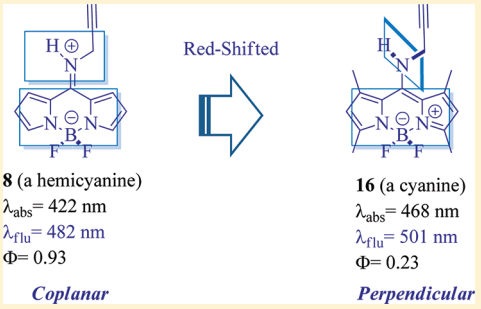
Supporting Information

ABSTRACT: The role of the amino group twisting ability in the BODIPY photophysics for nonsterically hindered and constrained molecular structures was studied. When a coplanar disposition of the amino and the BODIPY core is feasible, a hemicyanine-like delocalized π-system gives rise to novel blue and efficient BODIPY laser dyes. The key role of such rotamer is confirmed by newly synthesized derivatives where the amino and the BODIPY core are electronically decoupled by steric repulsions.



BODIPYs[1] are small compounds that have unique properties: high quantum yields, excellent solubility in organic solvents, high absorption coefficients and stability.[2]

The structure of such compounds is described as the resonance hybrid of canonical forms **1** and **2** (Figure 1).

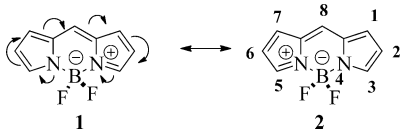
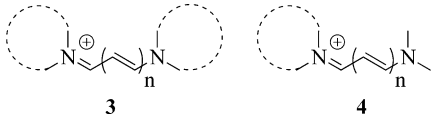


Figure 1. Resonance contributions to the BODIPY structure.

The core BODIPY structure resembles that of a cyanine **3**. Cyanines are conjugated compounds that contain two nitrogen atoms, one of which is positively charged, connected by an odd number of carbon atoms.[3] In the particular case that only one of the N atoms is part of a heterocycle (e.g., **4**), the compound is termed hemicyanine.



Bielmann et al. reported the synthesis of 8-anilinoBODIPY **6** (eq 1). They proposed that **6** (a cyanine-like structure) was best represented by cross-conjugated canonical structure **7** (a hemicyanine-like structure).[4]

We later demonstrated that displacement of thiomethyl group in **5** by nonaromatic amines furnished a family of unprecedented highly fluorescent blue-emitting BODIPY dyes (Figure 2).[5]

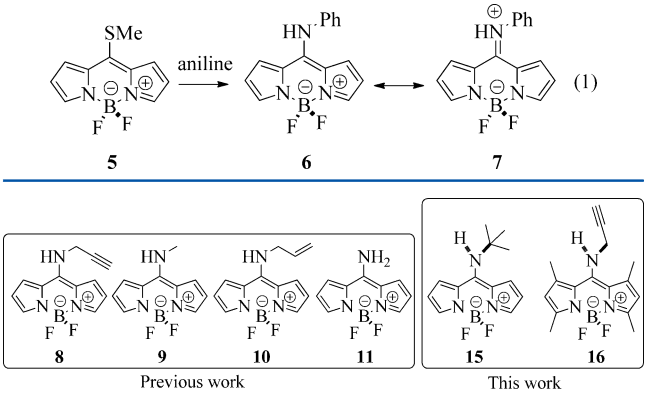


Figure 2. A new family of blue-emitting BODIPY dyes.

One of the questions we tried to answer was why **8**−**11** fluoresce in the blue edge of the visible spectrum. Quantum mechanical calculations indicated that the observed spectral shifts were due to the fact that an amino group at the 8-position generates a net destabilization of the LUMO state while leaving the HOMO unaltered.[5b] This result was in direct contrast with 3-amino-substituted BODIPY derivatives, in which the HOMO−LUMO energy gap remained unchanged by the presence of the amino group in that position.[6] Likewise, it was clear from the X-ray diffraction data of **6**[4] and **8**[5a] that the amino groups adopted a nearly planar geometry. Both ^{1}H and ^{13}C NMR spectra of all of the amino derivatives (except for **11**, vide infra) showed nonequivalent signals of the pyrrolic atoms.

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The hypothesis that was proposed suggests that 8-amino-BODIPYs **7**−**11** were best described as coplanar rotamer **13**, in which the lone-pair of the amino group is in the right orientation for efficient overlap with the π-system of the BODIPY core (Figure 3).

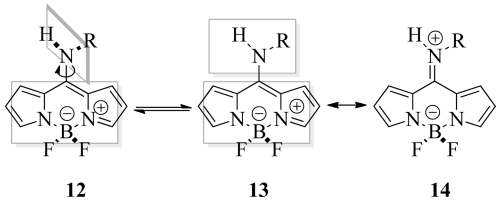


Figure 3. Rotamers of 8-aminoBODIPY dyes.

It follows, therefore, that once the N lone-pair is delocalized over the BODIPY core, *hemicyanine* structure **14** would be the dominant resonance contributor. Structure **14** would be now a cross-conjugated system, where the push−pull interaction of the pyrrole nitrogen atoms would be interrupted. This factor would cause a widening the HOMO−LUMO gap, thereby blue-shifting both the absorption and fluorescence bands. This model would explain the near planarity of the amino group observed on the X-ray diffraction data of **7**−**8**. By the same token, it would explain the NMR spectra of **7**−**10**, for a rigid **14** would render the pyrrole rings nonequivalent. 8-Amino-BODIPY **11** displays equivalent signals for the pyrrole rings in both ^{1}H and ^{13}C NMR spectra since its corresponding hemicyanine structure **14** (R = H) would still be symmetrical.

If our working hypothesis were true, a derivative in which the amino group was to be forced to remain perpendicular to the BODIPY ring (e.g., rotamer **12**) should behave more like a typical cyanine-like BODIPY system, with both absorption and emission bands red-shifted.

Two 8-aminoBODIPY derivatives were designed to support our hypothesis: 8-*tert*-butylaminoBODIPY **15** and 8-propargylamino-1,3,5,7-tetramethylBODIPY **16**.

These systems cannot adopt the coplanar conformation **13** because of steric repulsion of the amino-substituent with the atoms at both the 1- and 7-positions of the BODIPY core (Figure 4).

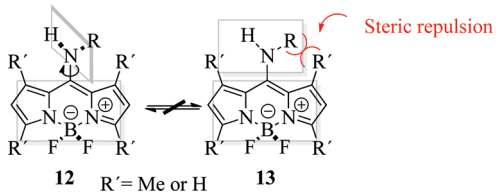
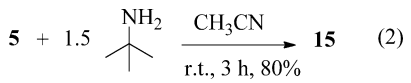


Figure 4. Preferred perpendicular rotamer **12**.

Compound **15** was prepared according to the reported method (eq 2).[4,5a,b]



The synthesis of **16** is illustrated in Scheme 1.

2,4-Dimethylpyrrole was reacted with thiophosgene to give highly colored **17**. Methylation of **17** followed by complexation with BF_3 etherate gave **18**. Finally, **16** was prepared by treating **18** with an excess of propargylamine at rt for 22 h in acetonitrile.

The aromatic section of the ^{1}H NMR spectra of **15** and **16** in CD_3CN is shown in Figure S1, Supporting Information (SI). For purposes of comparison, the spectrum of analogue **8**[5a] is also included.

The coplanar conformation that **8** adopts[5a] renders the six BODIPY protons nonequivalent as can be observed in Figure S1 (SI) (middle). On the other hand, because of the aforementioned sterics arguments, both **15** (Figure S1 (SI), right) and **16** (Figure S1 (SI), left) adopt the perpendicular, plane-symmetric conformation. As a result, the BODIPY protons become magnetically equivalent, displaying only three and one signals, respectively.

The free twist of the amine group can be hindered by either adding bulky substituents (**15**) or by replacing the hydrogens of adjacent positions 1 and 7 of the BODIPY by methyl groups (**16**) (Figure 4). With regard to their counterparts, without such steric hindrance (**9** and **8**, respectively), quantum mechanical calculations (structural data for **8**, **9**, **15**, and **16** amino derivatives are collected in Tables S2 and S3 (SI)) confirm the blockade of the amine in a twisted disposition (mainly in the excited state) with regard to the chromophoric plane, preventing a coplanar arrangement between the amine and the indacene chromophore (Figure 5). For instance, the calculated dihedral angle for the twist of the amine was ∼3° for dye **8**, according to a coplanar disposition (rotamer **13** in Figure 3); consequently, the amine electronic coupling with the chromophore is allowed, giving rise to a hemicyanine-like resonance structure where the amine is characterized by a sp^2 hybridization (rotamer **14** in Figure 3). The presence of such entity in related *meso* substituted BODIPYs has been previously reported.[5,7] The twist angle for the sterically hindered derivative **16** increases up to ∼50° (Table S2 (SI)) upon the methylation of the adjacent positions, which corresponds to a nonplanar sp^3 hybridization and a cyanine-like delocalized π-system (rotamer **12** in Figure 3). Similar results were obtained for pairs **9** and **15**, where the amine was fixed in a perpendicular disposition in the excited state (∼ 90°, Table S3 (SI)) by the presence of a bulky *tert*-butyl moiety in the amino group. Indeed, the theoretical simulation suggests that whereas in compound **9** an electronic coupling between the indacene core and the amino is allowed, in the sterically hindered derivative **15**, such delocalization is interrupted (Figure 5). Thus, these sets of derivatives are adequate to evaluate the effect of coplanarity of the amino group on the photophysical properties of the BODIPY.

Previous results of related 8-amino derivatives showed also wide spectral bands placed at the blue region of the visible. This occurs because of the electron releasing effect of the amine group leading to an energy rise of the LUMO.[5] Such blue-shift is not so pronounced for derivatives **15** and **16** in comparison with reference dyes **8** and **9** (Figure 6). In these last derivatives, the contribution of a rotamer characterized by a hemicyanine-like delocalized π-system is responsible for the large spectral shift to higher energies. Nonetheless, the constrained structure of **15** and **16**, induced by the steric repulsion of their substitution pattern (Figure 4), hampers the required coplanar disposition of the amine and the BODIPY, consequently decreasing the formation probability of such hemicyanine and rendering a less pronounced blue-shift of the spectral bands (Figure 6). Furthermore, for nonconstrained amino substituted BODIPYs, a direct relationship between the electron donor

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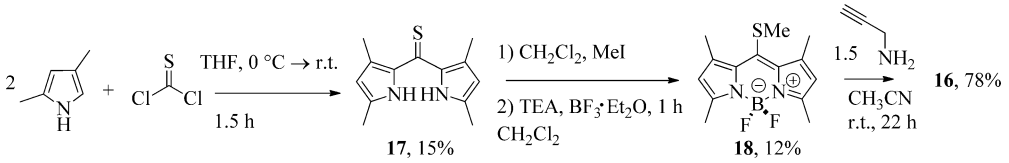
Scheme 1. Synthesis of 16



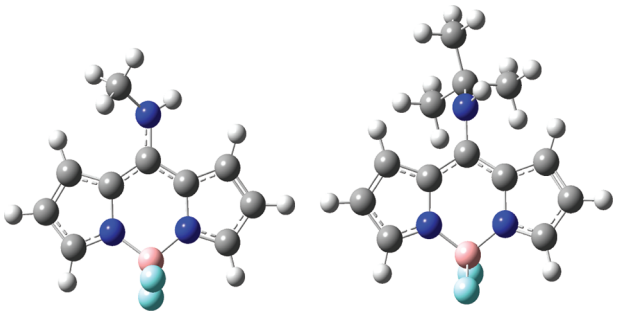


Figure 5. Optimized first excited state geometry for the fluorophores **9** and **15**.

character of the amine and the extent of the spectral blue-shift has been established.[5b] Accordingly, a larger spectral shift should be expected for derivative **15** (*N*-*tert*-butyl) than for dye **9** (*N*-methyl) because the *tert*-butyl substituent (Hammet parameter $\sigma_p^+ = -0.275$) has a higher donor capacity than the methyl ($\sigma_p^+ = -0.256$). This is not the case here, which indicates the influence of the formation of the hemicyanine in the spectral shift.

Table S1 (SI) summarizes the photophysical properties of **15** and **16**. A comparison is made with their structural analogues **9** and **8** respectively, as well as with the parent BODIPY chromophore **1**. In all amine derivatives, the blue-shift in absorption is much more evident than in fluorescence, leading to a clear enhancement in the Stokes shift. This is an important feature because BODIPYs are usually characterized by a close absorption and emission region, thus, the negative influence of reabsorption/reemission phenomena are of great relevance.[2] Most of the 8-amine derivatives (including **8** and **9**) overcome such limitations while maintaining a high fluorescence efficiency.[5b] Furthermore, although the absorption intensity (ε_{max}) decreases by the presence of the amine, the overall absorption probability (described by the oscillator strength) remains similar to their reference BDP chromophore, because of their wider spectra.

As seen in Table S1 (SI), the derivatives with no sterically hindered amines (**8** and **9**) are characterized by bright blue emission with a fluorescence efficiency that is close to that of the BDP (at around 0.90). This can be explained in terms of the formation probability of the hemicyanine π-system (rotamer **14** in Figure 3). However, for a more electron donor amine (**9**), the fluorescence quantum yield and lifetime decreased in polar media because of the activation of an intramolecular charge transfer (ICT).[5b]

On the other hand, restricting the movement of the amines (**15** and **16**) implies a larger absorption coefficient in comparison with their respective counterparts free from steric repulsions (**9** and **8**). These trends, and the registered spectral band blue-shift, were theoretically corroborated by quantum mechanics simulation of the absorption transition. The perpendicular conformation of the amine preventing its electronic coupling with the chromophore explains why the photophysics of derivatives **15** and **16** tends to that of the BODIPY **1**. Nonetheless, this conformation of the 8-amine implies a drastic reduction in the fluorescence ability (Table S1 (SI)). Furthermore, in polar media such decrease is more evident, the fluorescence quantum yield tends to zero (<0.1), and the lifetimes become very short (lower than 1 ns, see Table S1 (SI)). In general, a more constrained geometry, that is, hindering the mobility of the functional groups attached to the chromophore, benefits fluorescence ability because it reduces the internal conversion processes, typically related with rigidity/flexibility of the fluorophore.[8] However, in this study, entirely opposite features are achieved. Steric hindrance prevents a coplanar disposition of the amine and the BODIPY and consequently the formation of the hemicyanine, avoiding the high efficient blue emission signal observed in dyes **8** and **9**. Alternatively, such twisted disposition seems to activate a new nonradiative pathway, responsible for the quenching of the fluorescence emission in the LE state.

Considering the electron donor character of the amine and the sensibility of the fluorescence quantum yield and lifetime with the solvent nature, such extra quenching process, mainly

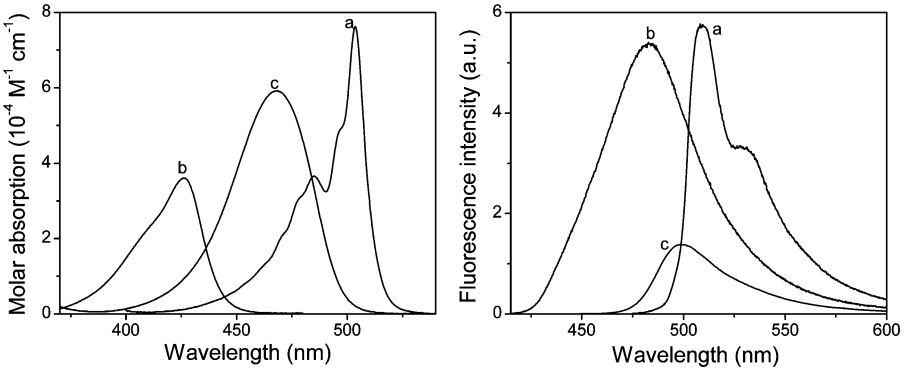


Figure 6. Absorption (left) and fluorescence (right) spectra of diluted solutions of reference compound **1** (a) and its 8-amino derivatives **8** (b) and **16** (c) in c-hexane.

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active in polar media, should be an intramolecular charge transfer (ICT) state, which should be nonfluorescent (no new emission bands were detected). Furthermore, considering the steric hindrance, which forces the amine into a more perpendicular disposition, it could be a twisted ICT state (TICT), where the donor and acceptor are electronically decoupled.[9] The stabilization of this ICT state leads to the appearance of a fast component in the fluorescence decay curves (Table S1 (SI)). Such state has also been proposed for aniline substituted BODIPY derivatives.[10] The fluorescence quenching effect of the ICT state is more obvious in derivative **15** than in **16**. In polar media, the former derivative is almost nonfluorescent, and the decay curves are better suited as a biexponential fit with fast lifetime (<0.1 ns).

The *tert*-butyl group electron releasing effect is higher than that of the propargyl; hence, the formation of the ICT state is further favored in derivative **15** in comparison with derivative **16**. In fact, the higher electron donor nature of the amine in the former entity is reflected in the shift of the spectral bands, which are placed deeper into the blue upon *tert*-butyl substitution in the amine.

In summary, two new rigid 8-aminoBODIPY dyes **15** and **16** were prepared. The disposition of the amino group at the *meso* position plays a key role on the photophysical properties of the BODIPYs. If the amine substituents are small enough or the chromophoric adjacent positions to the *meso* are not substituted, the amine can adopt a coplanar disposition and give rise to a hemicyanine-like delocalized π-system. Such entity is responsible for the spectral blue shift and is characterized by very high fluorescence efficiency, mainly in apolar media, allowing their use in tunable dye lasers. Nonetheless, if the amine motion is blocked, the coplanar rotamer cannot be achieved, and hence the hemicyanine formation is forbidden. Consequently, the blue shift is lower and an ICT state is activated because of the electron releasing ability and twisted disposition of the amine group. Such new state efficiently quenches the fluorescence emission of the BODIPY even in apolar environments.

EXPERIMENTAL SECTION

General Procedures. All reactions were performed under a dry N_2 atmosphere in oven- and/or flame-dried glassware unless otherwise noted. Analytical thin-layer chromatography was performed on Merck silica gel plates with F-254 indicator. THF was dried over activated 4 Å molecular sieves. Column chromatography was performed on 100−200 mesh silica gel.

Starting Materials. 8-ThiomethylBODIPY, thiophosgene, 2,4-dimethylpyrrole, methyl iodide, triethylamine, propargylamine, *tert*-butylamine, and BF_3−OEt_2 are commercially available and were used as received. ***Caution!*** *Handling thiophosgene requires a fume hood and the container has to be kept tightly closed for storage.* ***Thiophosgene is highly toxic.***

Synthesis of Bis(3,5-dimethyl-1*H*-pyrrol-2-yl)methanethione 17. A solution of 2,4-dimethylpyrrole (2.0 g, 21.0 mmol, 2.1 equiv) in dry tetrahydrofuran (20 mL) was added dropwise thiophosgene (1.15 g, 10.0 mmol, 1 equiv) at 0 °C. After TLC showed that the reaction went to completion (1.5 h), the reaction mixture was allowed to reach rt and was adsorbed on SiO_2-gel. After flash-chromatography (SiO_2-gel, EtOAc/hexanes gradient). The pure compound fraction was collected, which after removal of the solvents under reduced pressure yielded **17** (348.0 mg, 15%) as a crystalline orange red solid: TLC (30% EtOAc/hexanes, R_f = 0.5); mp 185−186 °C; IR (KBr, cm^{-1}) 3271 (s), 2916 (m), 1558 (s), 1531 (s), 1487 (s), 1439 (s), 1329 (m), 1259 (s), 1221 (s), 1138 (s); ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.0 (1H, br s), 5.90 (d, J = 2.2 Hz, 2H), 2.24 (s, 6H), 2.05 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$), δ 191.8, 137.5, 137.2, 127.8, 114.1, 13.6, 13.2. Anal. Calcd for $C_{13}H_{16}N_2S$: C, 67.20; H, 6.94; N, 12.06. Found: C, 67.16; H, 6.89; N, 12.10.

Synthesis of 5,5-Difluoro-1,3,7,9-tetramethyl-10-(methylthio)-5*H*-dipyrrolo[1,2-c:2′,1′-f][1,3,2]diazaborinin-4-ium-5-uide 18. To a solution of compound **17** (0.34 g, 1.46 mmol, 1 equiv) in anhydrous dichloromethane (1.5 mL) was added methyl iodide (0.46 mL, 7.4 mmol, 5 equiv) at rt. The reaction mixture was stirred for 24 h until completion (TLC monitoring). The solvent was removed under reduced pressure, and to the residue, dissolved in anhydrous dichloromethane (1.5 mL) under N_2 atmosphere at rt was added triethylamine (0.49 mL, 3.50 mmol, 2.4 equiv). After stirring for 30 min, BF_3·OEt_2 (0.47 mL, 4.9 mmol, 3.3 equiv) was added. The mixture was stirred for 30 min at rt. After the evaporation of solvents under reduced pressure, the crude product was adsorbed on SiO_2-gel. After flash-chromatography (SiO_2-gel, EtOAc/hexanes gradient), **18** (51.5 mg, 12%) was isolated as a dark red solid: TLC (30% EtOAc/hexanes, R_f = 0.8); mp 150−151 °C; IR (KBr, cm^{-1}) 3436 (m), 1535 (s), 1505 (s), 1471 (w), 1369 (w), 1299 (s), 1196 (s), 1221 (s); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.08 (s, 2H), 2.61 (s, 6H), 2.52 (s, 6H), 2.45 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$), δ 155.7, 143.8, 141.3, 122.5, 22.5, 17.2, 15.0, 14.4. Anal. Calcd for $C_{14}H_{17}BF_2N_2S$: C, 57.16; H, 5.82; N, 9.52. Found: C, 57.12; H, 5.89; N, 9.49.

Typical Procedure (TP) for the Addition of Amines to ThiomethylBODIPY Dyes. To a CH_3CN (2 mL) solution of the corresponding thiomethylBODIPY (either **5** or **18**, typically 20 mg) was added the corresponding amine (1.5 equiv) in a 20 mL scintillation vial under air. The vial was capped, and the mixture was stirred at rt until completion (TLC). Flash chromatography (SiO_2-gel, EtOAc/hexanes gradient) purification yielded the pure compounds.

5,5-Difluoro-1,3,7,9-tetramethyl-10-(prop-2-yn-1-ylamino)-5*H*-dipyrrolo[1,2-c:2′,1′-f][1,3,2]diazaborinin-4-ium-5-uide 16. According to TP: TLC (30% EtOAc/hexanes, R_f = 0.5); yellow crystals; mp 161−163 °C; yield 78% (16 mg); IR (KBr, cm^{-1}) 3423 (m), 3283 (m), 1571 (s), 1531 (s), 1508 (m), 1462 (w), 1392 (m), 1283 (w), 1221 (s); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 (s, 2H), 5.25 (br signal, 2H), 4.18 (dd, J_1 = 3.6 Hz, J_2= 8.7 Hz, 2H), 2.51 (s, 6H), 2.42 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$), δ 150.7, 150.1, 134.3, 124.4, 119.4, 79.5, 75.16, 41.8, 15.4, 14.4. Anal. Calcd for $C_{16}H_{18}BF_2N_3$: C, 63.81; H, 6.02; N, 13.95. Found: C, 63.83; H, 6.09; N, 13.90.

10-(*tert*-Butylamino)-5,5-difluoro-5*H*-dipyrrolo[1,2-c:2′,1′-f]-[1,3,2]diazaborinin-4-ium-5-uide 15. According to TP: TLC (30% EtOAc/hexanes, R_f = 0.4); yellow crystals; mp 130−131 °C; yield 80% (17.6 mg); IR (KBr, cm^{-1}) 3369 (s), 2981 (w), 1582 (s), 1554 (s), 1457 (m), 1404 (m), 1381 (s), 1278 (m), 1225 (m); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.60 (s, 2H,), 7.09 (s, 2H), 6.69 (br s, 1H), 6.47 (s, 2H), 1.70 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$), δ 148.0, 134.5, 124.0, 120.9, 114.4, 55.6, 29.2. Anal. Calcd for $C_{13}H_{16}BF_2N_3$: C, 59.35; H, 6.13; N, 15.97. Found: C, 59.41; H, 6.19; N, 15.91.

ASSOCIATED CONTENT

Supporting Information

Tables S1−S3 and Figure S1. Full photophysical data of the BDP chromophore and its 8-amino derivatives **8**, **9**, **15**, and **16** in different solvents ranging from apolar to polar/protic media. Theoretically calculated structural data of these amino derivatives, NMR spectra of the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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