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Synthesis of a Class of Core-Modified Aza-BODIPY Derivatives

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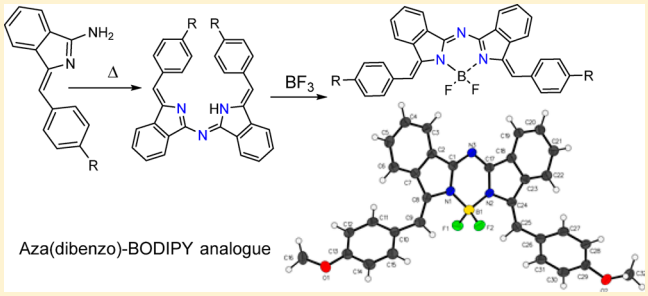
Supporting Information

ABSTRACT: The convenient synthesis of a new class of conjugated aza-BODIPY derivatives from readily available precursors has been achieved. The new materials bear close structural similarity to BODIPYs but differ significantly in electronic configuration from known derivatives, leading to markedly different absorption and emission properties.



Boron dipyrromethenes (BODIPYs) (Figure 1) are developing into an increasingly important class of stable organic dyes. They have proved to be highly fluorescent and sensitive to their environment, leading to potential applications in areas such as sensing and imaging. A rich diversity of chemical tuning has been developed in parallel to physical characterization, and the BODIPY parent structure has been modified through functionalization at the α, β, and *meso* positions, often leading to absorption/fluorescence tuning.[1]

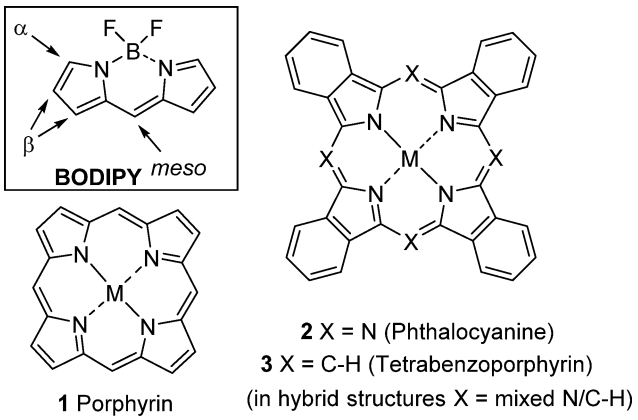
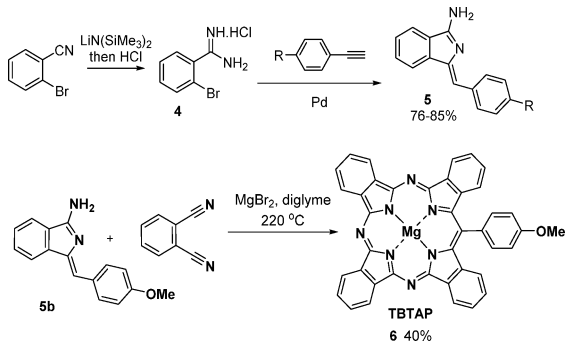


Figure 1. Boron dipyrromethene (BODIPY) parent core, with positions susceptible for derivatization indicated by arrows, and the macrocyclic chromophores porphyrin (**1**) and phthalocyanine (**2**).

Indeed, the dipyrromethene unit can be viewed as a fragment of the ubiquitous porphyrin macrocycle[2] (**1**), where tuning of properties through synthesis has achieved significant advances. Phthalocyanines[2] (**2**) are the synthetic cousins of porphyrins, differing in parent structure through introduction of nitrogen bridges at the *meso* positions and benzo fusion at the pyrrolic β sites. Their longer-wavelength absorption band (close to the near-IR region) and favorable chemical properties have similarly led to intense investigation. BODIPY-like fragments of hybrid porphyrin−phthalocyanine macrocycles[3] (Figure 1) are therefore intriguing structures, and here we report the first examples of a new class of benzo-fused aza-BODIPY analogues.[4]

Our entry into this area indeed stemmed from the development of a new synthetic protocol for the synthesis of a challenging class of porphyrin−phthalocyanine hybrid macrocycles, tetrabenzotriazaporphyrins (TBTAPs),[3,5] which can be viewed as phthalocyanine analogues in which a single bridging nitrogen is replaced by carbon. A new synthesis was developed in which macrocyclization of phthalonitrile is initiated by aminoisoindoline **5**, which itself can be smoothly synthesized from bromoamidine **4** (Scheme 1).[6] Under the high-temperature reaction conditions, formation of TBTAPs **6**

Scheme 1. Synthesis of TBTAPs from Aminoisoindolines 5



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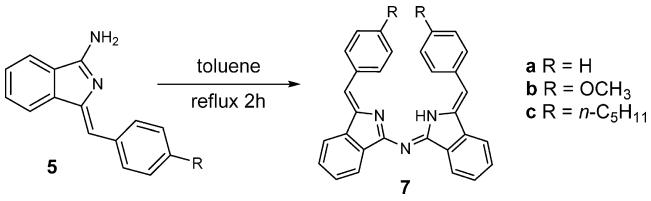
were generally accompanied by self-condensation products, but optimization suppressed their formation, leading to the first efficient synthesis of *meso*-aryl TBTAP derivatives.[5]

In the present study, alternative reaction conditions were investigated in order to probe further the self-condensation reaction products of aminoisoindolines **5**. Indeed, in the absence of additional coreactants, aminoisoindolines **5** underwent smooth and efficient self-condensation to form the π-extended aza-(dibenzo)dipyrromethene derivatives **7**. In a typical reaction, aminoisoindolines **5a–c** were heated under reflux in toluene for 2 h, and the products were isolated by crystallization from dichloromethane (Scheme 2). Initial

Scheme 2. Self-Condensation of Aminoisoindolines 5a–c To Give Aza-(dibenzo)dipyrromethenes 7a–c

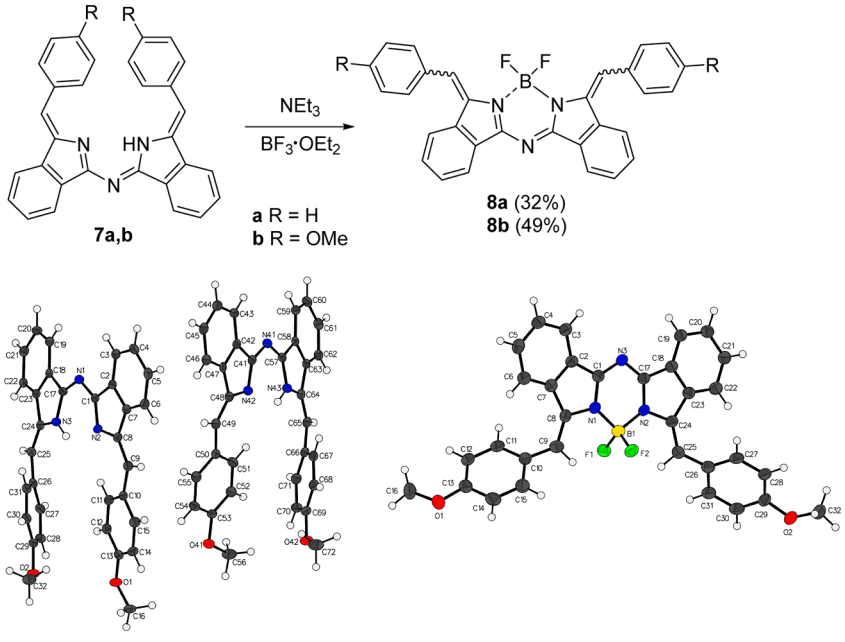


characterization of the deep-red crystals by NMR spectroscopy indicated that a single dipyrromethene species was present in each case. Crystals suitable for X-ray crystallography were obtained for **7a** and **7b**, and analysis showed that the same *Z*,*Z* configuration present in the starting material (see the Supporting Information for the X-ray crystal structure of **5b**) was observed in the aza-(dibenzo)dipyrromethene products.[7]

Aza-(dibenzo)dipyrromethene precursors **7a** and **7b** were converted into the corresponding aza-(dibenzo)BODIPY analogues **8a** and **8b** by straightforward reaction with $BF_3{\cdot}OEt_2$ (Scheme 3). Isolation and characterization of these adducts proved somewhat more challenging than for their precursors, but crystals were eventually grown from a 1:1:1 dichloromethane/petroleum ether/methanol mixture. The crystal structures of **7b** and **8b** are also shown in Scheme 3, and it is immediately apparent that the BODIPY analogues display the *E*,*E* configuration, which is the opposite of the configuration of their precursors. However, it appears that in this case the *E*,*E* configuration is favored solely by the crystal packing and solid-state interactions. The ^{1}H NMR spectrum of a freshly dissolved sample of the crystals shows essentially one molecular species corresponding to the *E*,*E* configuration, but isomerization then takes place slowly at room temperature, resulting in the observation of a mixture of *E* and *Z* isomers at equilibrium after several hours.

As mentioned previously, the parent BODIPY molecule has been significantly modified to achieve chemical tuning. Separately, BODIPY has been modified through conjugation at the α positions[8] (e.g., **9–12**), benzo fusion at the β sites[9] (e.g., **11**, **12**), and replacement of the *meso*-carbon with a nitrogen bridge[10] (e.g., **10**, **12**). The new structures **8** incorporate all of these modifications simultaneously, and it is noteworthy that the synthetic pathway is significantly more straightforward than routes previously described for related compounds (especially for the aza-BODIPY derivatives).[10a,b] However, the resulting stable materials are significantly different from previous analogues. In the new framework, the rigid π system extends beyond the azadipyrromethene unit. It appears that maintenance of the formal aromatic system of both fused benzenes drives the overall electronic configuration. Indeed, it could be envisaged that reduction of the new derivatives **8** would yield the aza-(dibenzo)BODIPY chromophores **13** with the classic BODIPY π system (Scheme 4, shown in red), but both boron complexes **8** and their precursors **7** proved resistant to chemical reduction using reagents such as hydrazine or sodium borohydride. This observation is in direct contrast to the observations of Ono and co-workers, who reported the synthesis of dimethyl analogues **15**.[9b] Compounds **13** and **15** differ only in the bridging atom (carbon in **15** vs nitrogen in **13**) and α substituents (methyl vs benzyl).

Scheme 3. Synthesis of Aza-(dibenzo)BODIPY Derivatives and X-ray Crystal Structures of 7b and 8b (Ellipsoids at 50% Probability)



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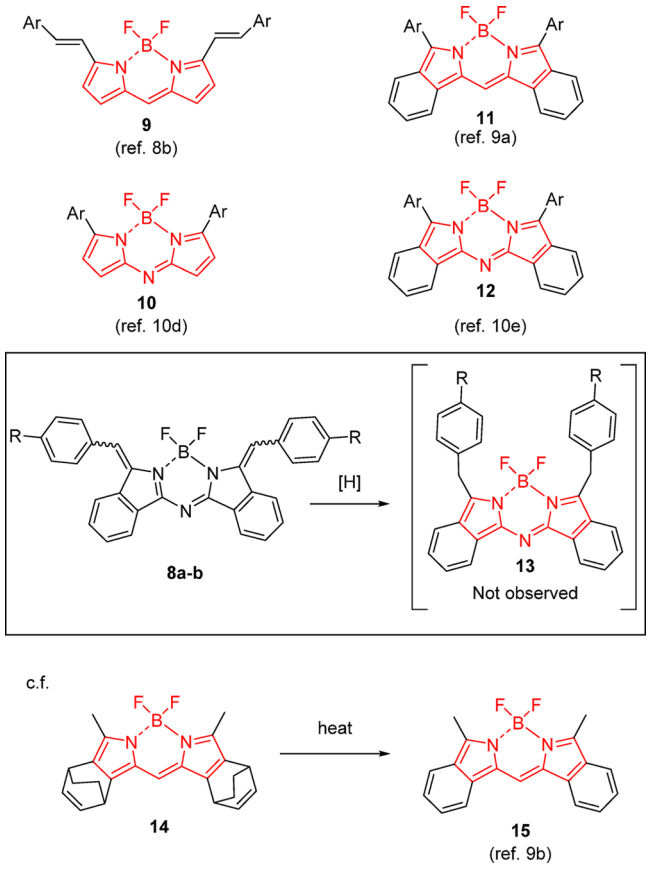
Scheme 4. Attempted Reduction of Complexes 8 To Give the Common Aza-(dibenzo)BODIPY Substructure (red) Present in All Known Analogues and Examples of Conjugated Derivatives



Aza-(dibenzo)dipyrromethene **7a** is orange in color. Its absorption spectrum, shown in Figure 2, displays a relatively broad profile with a visible-region maximum at 465 nm in DCM. Further conjugation through the introduction of *p*-methoxy substituents in **7b** red-shifts the absorption by around 25 nm, comparable to related examples in classical BODIPYs.[10e] The compounds show moderate solvatochromism, shifting a further 20−40 nm when the solvent is changed from DCM to DMSO/water (see the Supporting Information). The spectra remain essentially unchanged in base and weak acid media, but a distinct and reversible color change from orange to deep red is observed in strong acid media (see the Supporting Information). No appreciable fluorescence is observed in any solvent, presumably because of rapid relaxation (bond rotation) of the molecules in their excited states.

Boron complexes **8a** and **8b** show absorption maxima at 439 and 469 nm, respectively, indicating a similar trend of the substituent effect. Unlike their precursors, however, boron complexes **8a** and **8b** show fluorescence with significant Stokes shifts of around 90 nm (Figure 2), albeit with low quantum yields (**8a** ∼5%, **8b** ∼0.5%). This fluorescence behavior is not affected by the presence of oxygen in the medium. As discussed previously, the boron complexes **8a** and **8b** are present as an equilibrating mixture of stereoisomers. The absorption spectra of the two isomers appear to be similar, but it is possible that only a single component exhibits the observed fluorescence. The excitation spectrum of **8a** is also shown in Figure 2, and it closely resembles the absorption profile, suggesting either similar absorption for the two isomers or that both isomers lead to a common emission profile. Furthermore, we know that *E*/*Z* isomerism occurs thermally, and it is therefore reasonable to assume that a major deactivation mechanism for the excited state involves classic photoisomerization of all isomers.

In summary, we have reported here a new type of boron aza-(dibenzo)dipyrromethene derivatives and their precursor dipyrromethene analogues. The new structures are relatively straightforward to prepare, and they simultaneously incorporate on the parent BODIPY core conjugation at the α positions, benzo fusion at the β sites, and replacement of the *meso* carbon with a nitrogen bridge. The combination leads to stabilization of an electronic configuration that is subtly different from that of traditional BODIPY chromophores and is presumably driven by preservation of local aromaticity of the benzene rings. The electronic structure also leads to contrasting spectroscopic behavior, with the new derivatives displaying their main visible-region absorption around 460 nm. The boron complexes, which are present as an equilibrating mixture of stereoisomers, show weak fluorescence with Stokes shifts of over 90 nm.

EXPERIMENTAL SECTION

(*Z*)-1-(4-Pentylphenylmethylene)-1*H*-isoindol-3-amine (5c). A previously reported strategy was used.[5,6] A mixture of amidine **4**[11] (706.5 mg), BINAP (102 mg, 0.055 equiv), and $PdCl_2(MeCN)$ (39 mg, 0.05 equiv) was sealed in a microwave vessel with a magnetic stir bar, and the vessel was purged and refilled with N_2 three times. Then a solution of 4-pentylphenylacetylene (0.7 mL, 1.2 equiv) and DBU (1.12 mL, 2.5 equiv) in dry DMF (12 mL) was added. The mixture was stirred under N_2 for 5 min to give a clear yellow solution with a white solid. Finally, the mixture was irradiated in a microwave reactor at 120 °C for 1 h. After the mixture was cooled, 50 mL of AcOEt was added, and the mixture was washed with a saturated solution of $NaHCO_3$ (75 mL) three times. The organic layer was dried ($MgSO_4$), filtered, and concentrated. The residue was finally purified by column chromatography using AcOEt followed by AcOEt/EtOH/H_2O (90:5:3) as the eluent to afford a yellow compound that was recrystallized from DCM/petroleum ether (1:1) to yield yellow needles (660 mg, 76%).

Mp = 94−95 °C. R_f = 0.57 (AcOEt/EtOH/H_2O 90:5:3). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 8.01 (br d, 2H, J = 8.1 Hz); 7.78 (br d, 1H, J = 7.5 Hz); 7.46 (br td, 1H, J = 7.5, 1.1 Hz); 7.43 (br d, 1H, J = 7.5 Hz); 7.34 (td, 1H, J = 7.5, 1.0 Hz); 7.22 (br d, 2H, J = 8.1 Hz); 6.76 (s, 1H); 6.2−5.2 (br s, 2H, NH_2); 2.63 (t, 2H, J = 7.7 Hz); 1.60−1.70 (m, 2H); 1.27−1.45 (m, 4H); 0.91 (t, 3H, J = 6.8 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K): δ (ppm) = 164.8; 146.5; 143.1; 142.6; 134.1; 130.9; 130.5; 129.2; 128.8; 127.1; 119.8; 119.0; 115.7; 36.0; 31.6; 31.2; 22.7; 14.2. MS (MALDI-TOF): m/z = 290.1 $[M]^+$ (100%). HR-MS (ESI) ($C_{20}H_{23}N_2$) $[M + H]^+$: calcd 291.1856, found 291.1857. UV−vis (MeOH) λ_{max}/nm (ε/dm^3·mol^{-1}·cm^{-1}): 366 (9.34 × 10^3). FT-IR (NaCl) ν (cm^{-1}): 3329, 3143, 2955, 2928, 2855, 1652, 1622, 1606, 1532, 1466, 1422, 1377, 1179, 1113, 1046, 864, 759, 689, 537.

Azadipyrromethene 7a. A solution of **5a**[6] (104 mg) in toluene (2 mL) was heated at 120 °C for 2 h under a N_2 atmosphere, and the solvent was allowed to slowly evaporate during the process. After cooling, the residue was purified by column chromatography using DCM as the solvent to afford a red compound that was recrystallized from DCM to yield red needles. The needles were washed twice with MeOH (82.1 mg, 82%).

Mp = 238−239 °C. R_f = 0.63 (DCM). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 12.80 (br s, 1H, NH); 8.09 (br dt, 2H, J = 7.4, 1.2 Hz); 7.91−7.88 (m, 4H); 7.82 (br dt, 2H, J = 7.4, 1.0 Hz); 7.55 (td, 2H, J = 7.4, 1.2 Hz); 7.50 (td, 2H, J = 7.4, 1.0 Hz); 7.08−7.11 (m, 6H); 6.81 (s, 2H). ^{13}C NMR (125.7 MHz, $CDCl_3$, 298 K): δ (ppm) = 166.3; 141.9; 139.8; 135.7; 134.9; 130.3; 129.7; 129.3; 128.4; 128.3; 122.5; 119.5; 114.4. MS (MALDI-TOF): m/z = 423.2 $[M]^+$ (100%).

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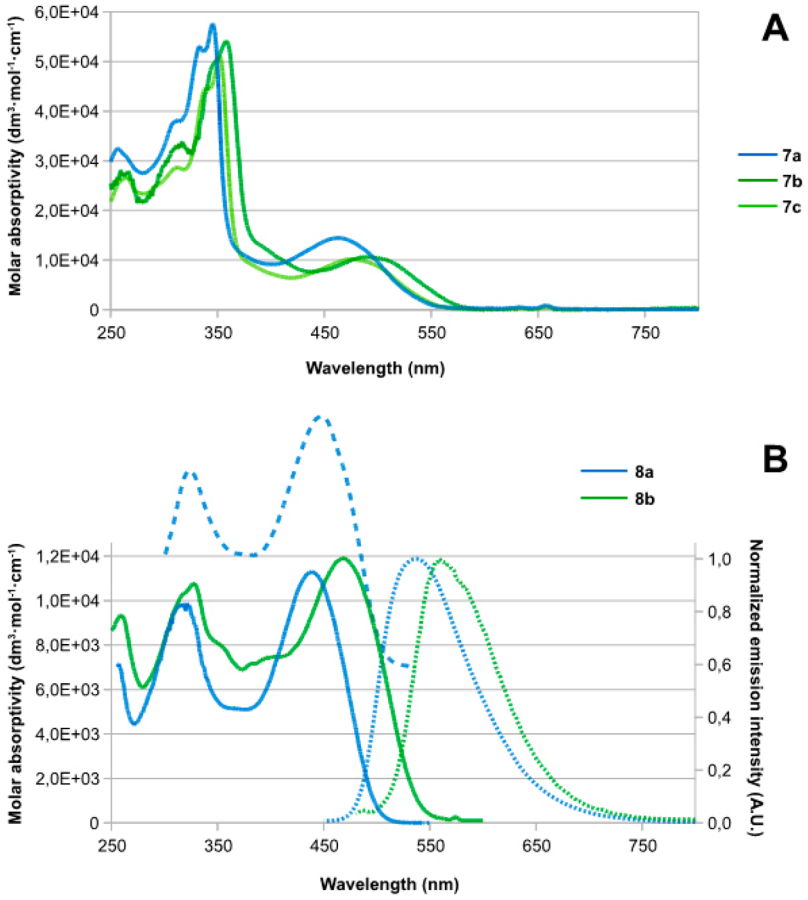

Figure 2. (A) UV−vis absorption spectra of **7a**−**c** in DCM. (B) UV−vis absorption (solid line) and normalized fluorescence emission (dotted line) spectra of **8a** and **8b** in DCM and the excitation spectrum of **8a** (dashed line, λ_{em} = 537 nm).

HR-MS (ESI) ($C_{30}H_{22}N_3$) $[M + H]^+$: calcd 424.1808, found 424.1807 $[M + H]^+$. UV−vis (CH_2Cl_2) λ_{max}/nm (ε/dm^3·mol^{-1}·cm $^{-1}$): 465 (1.44×10^4), 343 (5.75×10^4). FT-IR (NaCl) ν (cm^{-1}): 3002, 2835, 1599, 1585, 1470, 1421, 1372, 1188, 1122, 1047, 1029, 780, 743, 725.

Azadipyrromethene 7b. A solution of **5b**[5] (100 mg) in toluene (2 mL) was heated at 120 °C for 2 h under a N_2 atmosphere, and the solvent was allowed to slowly evaporate during the process. After cooling, the residue was purified by column chromatography using DCM and then DCM/MeOH (50:1) as the eluent to afford a red compound that was recrystallized from DCM and washed twice with MeOH to yield red crystals (84 mg, 87%).

Mp = 203−204 °C. R_f = 0.62 (DCM/MeOH 50:1). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 13.07 (br s, 1H, NH); 8.09 (br dt, 2H, J = 7.4, 1.0 Hz); 7.85 (br d, 4H, J = 8.7 Hz); 7.79 (br dt, 2H, J = 7.4, 0.9 Hz); 7.53 (td, 2H, J = 7.4, 1.0 Hz); 7.48 (td, 2H, J = 7.4, 0.9 Hz); 6.77 (s, 2H); 6.62 (br d, 4H, J = 8.7 Hz); 3.69 (s, 6H). ^{13}C NMR (125.7 MHz, $CDCl_3$, 298 K): δ (ppm) = 165.8; 159.2; 140.3; 139.8; 134.7; 131.3; 130.0; 128.6; 128.0; 122.4; 119.3; 114.8; 114.1; 55.1. MS (MALDI-TOF): m/z = 483.7 $[M]^+$ (100%). HR-MS (ESI) ($C_{32}H_{26}O_2N_3$) $[M + H]^+$: calcd 484.2020, found 484.2012 $[M + H]^+$. UV−vis (CH_2Cl_2) λ_{max}/nm (ε/dm^3·mol^{-1}·cm^{-1}): 491 (1.07×10^4), 358 (5.41×10^4). FT-IR (NaCl) ν (cm^{-1}): 3000, 2833, 1598, 1585, 1510, 1473, 1370, 1252, 1175, 1122, 1031, 855, 822, 708, 578, 532.

Azadipyrromethene 7c. A solution of **5c** (200 mg) in dry diglyme (5 mL) was heated at 220 °C for 30 min under a N_2 atmosphere. After the solution was cooled, water (50 mL) was added, and the mixture was stirred for 15 min. The solid was filtered off, dissolved in DCM, dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography using petroleum ether/DCM (1:1, 1:2) and then neat DCM as the eluent to afford a red compound that was recrystallized from DCM and washed twice with MeOH to yield red needles (67 mg, 34%).

Mp = 171−172 °C. R_f = 0.56 (petroleum ether/DCM 1:1). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 12.98 (br s, 1H, NH); 8.11 (br d, 2H, J = 7.3 Hz); 7.83 (br d, 2H); 7.81 (br d, 4H, J = 8.1 Hz); 7.54 (td, 2H, J = 7.3, 1.3 Hz); 7.49 (td, 2H, J = 7.3, 1.1 Hz); 6.93 (br d, 4H, J = 8.1 Hz); 6.84 (s, 2H); 2.50 (t, 4H, J = 7.9 Hz); 1.50−1.55 (m, 4H); 1.26−1.40 (m, 8H); 0.89 (t, 6H, J = 6.9 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K): δ (ppm) = 165.9; 143.1; 141.2; 140.0; 134.7; 133.3; 130.2; 129.8; 129.3; 128.2; 122.5; 119.5; 114.5; 36.0; 31.8; 30.9; 22.7; 14.2. MS (MALDI-TOF): m/z = 564.4 $[M+H]^+$ (100%). HR-MS (ESI) ($C_{40}H_{42}N_3$) $[M + H]^+$: calcd 564.3373, found 564.3364 $[M + H]^+$. UV−vis (CH_2Cl_2) λ_{max}/nm (ε/dm^3·mol^{-1}·cm^{-1}): 475 (1.02×10^4), 352 (5.10×10^4). FT-IR (NaCl) ν (cm^{-1}): 2953, 2925, 2847, 1601, 1587, 1467, 1415, 1372, 1180, 1148, 1121, 859, 816, 757, 706, 550, 527.

Aza-BODIPY 8a. A solution of **7a** (138 mg) and Et_3N (0.455 mL, 10 equiv) in CH_2Cl_2 (12 mL) was stirred for 15 min at rt under a N_2 atmosphere before BF_3·Et_2O (2.2 mL, 25 equiv) was added dropwise. The mixture was further stirred for 24 h. Then more CH_2Cl_2 (15 mL) was added, and the mixture was washed with dilute hydrochloric acid (1 M, 50 mL) twice. The residue was dried ($MgSO_4$), filtered, and concentrated. Finally, the residue was purified by column chromatography using DCM as the eluent to afford a bright-yellow compound that was recrystallized from DCM/petroleum ether/MeOH (1:1:1) to yield orange-yellow needles (49 mg, 32%).

Mp = 215−216 °C. R_f = 0.77 (DCM). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, data for the main isomer (*E*,*E*)): δ (ppm) = 8.18 (br dt, 2H, J = 7.6, 1.0 Hz); 7.88 (s, 2H); 7.66−7.60 (m, 6H, H-7); 7.53 (td, 2H, J = 7.6, 0.8 Hz); 7.49 (t, 4H, J = 7.3 Hz); 7.46−7.41 (m, 4H). ^{13}C NMR (125.7 MHz, $CDCl_3$, 298 K, data for the main isomer (*E*, *E*)): δ (ppm) = 163.9; 138.7; 136.2; 135.2; 132.4, 129.8; 129.4; 128.8; 128.7;

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127.8; 125.7; 123.8; 123.6. MS (MALDI-TOF): m/z = 471.2 $[M + H]^+$ (100%). HR-MS (MALDI) ($C_{30}H_{21}N_3{}^{10}BF_2$) $[M + H]^+$: calcd 471.1827, found 471.1824 $[M + H]^+$. UV−vis (CH_2Cl_2) λ_{max}/nm (ε/$dm^3{\cdot}mol^{-1}{\cdot}cm^{-1}$): 439 ($1.13 \times 10^4$), 317 ($9.87 \times 10^3$). Fluorescence ($CH_2Cl_2$) λ^{em}_{max}/nm (λ_{ex} = 440 nm): 537. FT-IR (NaCl) ν (cm^{-1}): 3052, 3024, 2954, 2926, 2853, 1735, 1630, 1567, 1536, 1502, 1453, 1336, 1232, 1181, 1158, 1074, 1031, 938, 848, 765, 724, 696.

Aza-BODIPY 8b. A solution of **7b** (47 mg) and Et_3N (0.13 mL, 10 equiv) in CH_2Cl_2 (10 mL) was stirred for 15 min at rt under a N_2 atmosphere before $BF_3{\cdot}Et_2O$ (0.64 mL, 25 equiv) was added dropwise. The mixture was further stirred for 24 h. Then more CH_2Cl_2 (15 mL) was added, and the mixture was washed with dilute hydrochloric acid (1 M, 50 mL) twice. The residue was dried ($MgSO_4$), filtered, and concentrated. Finally, the residue was purified by column chromatography using DCM as the solvent to afford a bright-yellow compound that was recrystallized from from DCM/petroleum ether/MeOH (1:1:1) to yield orange-yellow needles (25.3 mg, 49%).

Mp = 229−230 °C. R_f = 0.58 (DCM). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, data for the main isomer (*E,E*)): δ (ppm) = 8.18 (br d, 2H, J = 7.4 Hz); 7.82 (s, 2H); 7.80 (br d, 2H, J = 7.7 Hz); 7.58 (br d, 4H, J = 8.5 Hz); 7.53 (td, 2H, J = 7.4, 0.9 Hz); 7.46 (td, 2H, J = 7.7, 1.2 Hz); 7.00 (br d, 4H, J = 8.5 Hz); 3.91 (s, 6H). ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K, data for the main isomer (*E, E*)): δ (ppm) = 163.3; 160.2; 142.6; 137.9; 136.4; 132.2; 131.5; 129.2; 127.5; 125.8; 123.7; 123.4; 114.2; 55.5. MS (MALDI-TOF): m/z = 531.08 $[M + H]^+$ (100%). HR-MS (MALDI) ($C_{32}H_{24}O_2N_3{}^{10}BF_2$) $[M]^+$: calcd 530.1960, found 530.1964 $[M]^+$. UV−vis (CH_2Cl_2) λ_{max}/nm (ε/$dm^3{\cdot}mol^{-1}{\cdot}cm^{-1}$): 469 ($1.19 \times 10^4$), 328 ($1.08 \times 10^4$); Fluorescence ($CH_2Cl_2$): λ^{em}_{max}/nm (λ_{ex} = 440 nm): 560. FT-IR (NaCl) ν (cm^{-1}): 3052, 2954, 2836, 1728, 1599, 1567, 1554, 1503, 1258, 1172, 1089, 1024, 860, 798, 726.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization spectra for new compounds and X-ray crystal structures of **5b** and **7a**. 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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(4) Such structures can also be termed azadiisoindolomethenes, but throughout this paper we retain the nomenclature based around the parent dipyrromethene and BODIPY cores.

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