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

Alejandro Díaz-Moscoso,[†] Edward Emond,[†] David L. Hughes,[†] Graham J. Tizzard,[‡] Simon J. Coles[‡] and Andrew N. Cammidge[,†]*

[†]School of Chemistry, University of East Anglia, Norwich Research Park, Norwich NR4 7TJ (UK); [‡]UK National Crystallography Service, School of Chemistry, University of Southampton, Southampton SO17 1BJ (UK).

a.cammidge@uea.ac.uk

Abstract

The convenient synthesis of a new class of conjugated aza-BODIPY derivatives is achieved from readily available precursors. 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 application 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] 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 man-made cousins of porphyrins, differing in parent structure through introduction of nitrogen bridges at the *meso*-positions and benzofusion 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 the hybrid porphyrin-phthalocyanine macrocycles[3] (Figure 1) are therefore intriguing structures and here we report the first examples of a new class of aza-benzofused-BODIPY analogues.[4]

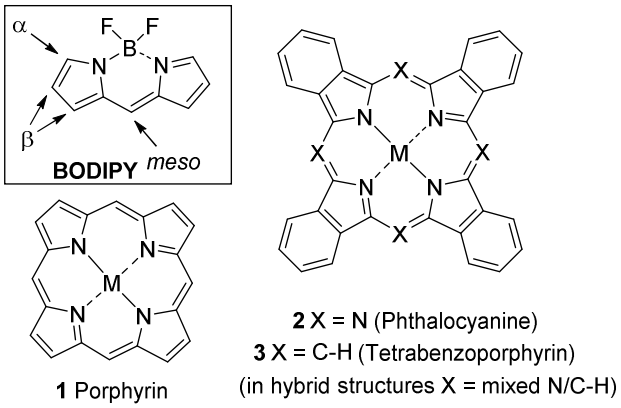
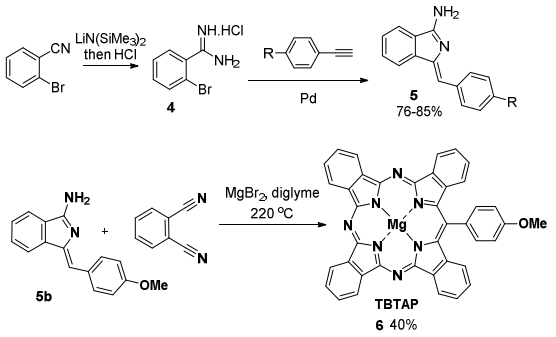


Figure 1. Boron dipyrromethene (BODIPY) parent core indicating positions susceptible for derivatization and the macrocyclic chromophores porphyrin (**1**) and phthalocyanine (**2**).

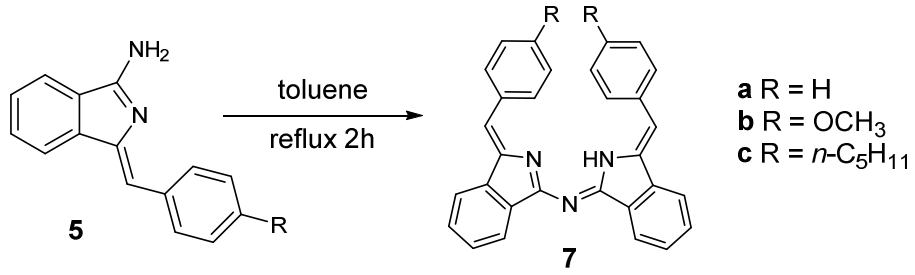
Our entry into this area indeed stemmed from development of a new synthetic protocol for the synthesis of a challenging class of porphyrin-phthalocyanine hybrid macrocycles – tetrabenzotriazaporphyrins (TBTAPs)[3,5] – that can be viewed as phthalocyanine analogues in which a single bridging nitrogen is replaced by carbon. A new synthesis was developed in which macrocyclization of phthalonitrile is initiated by aminoisoindoline **5**, itself smoothly synthesized from bromoamidine **4**.[6] Under the high-temperature reaction conditions, formation of TBTAPs **6** were generally accompanied by self-condensation products but optimization suppressed their formation, leading to the first efficient synthesis of *meso*-aryl TBTAP derivatives (Scheme 1).[5]



Scheme 1. Synthesis of TBTAPs from aminoisoindolines **5**.

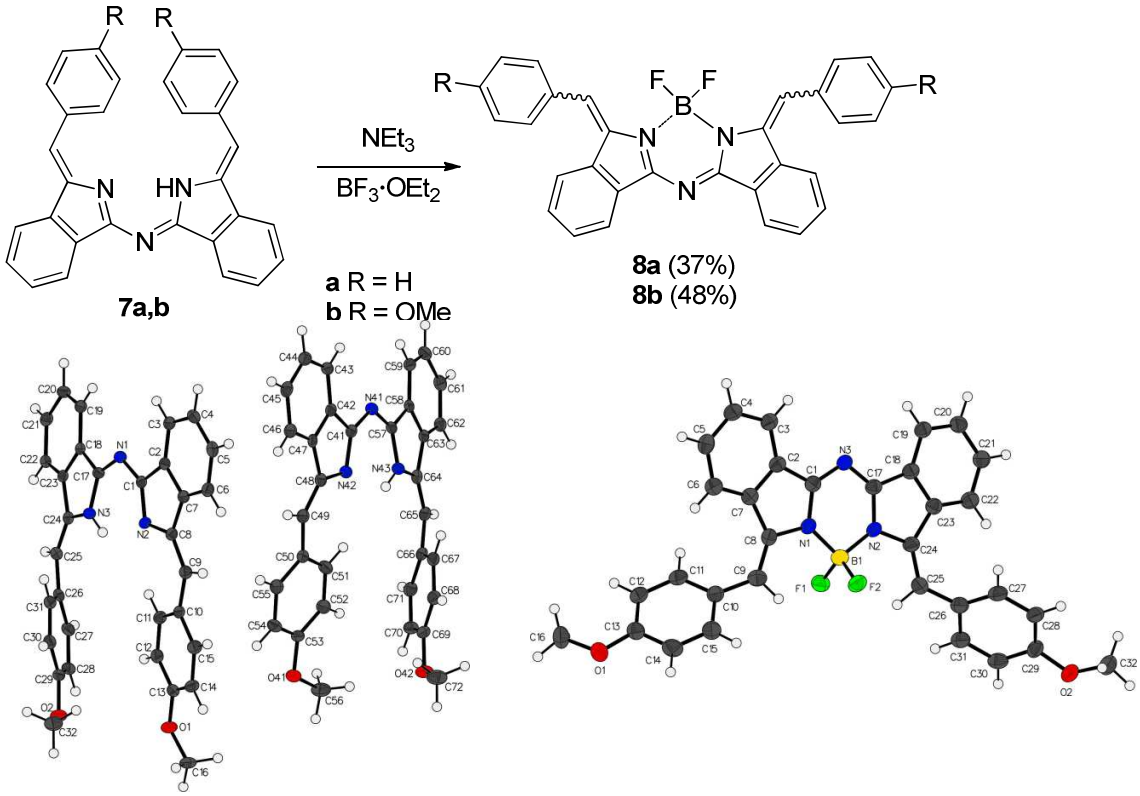
In the present study, alternative reaction conditions were investigated in order to probe further the self-condensation reaction products of aminoisoindolines **5**. Indeed, in the absence of additional co-reactants, aminoisoindolines **5** underwent smooth and efficient self-condensation to form the 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 isolated by crystallization from dichloromethane (Scheme 2). Initial 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-b** and analysis shows that the same *Z, Z* configuration, present in the starting material (see Supporting Information for the X-ray crystal structure of **5b**), is observed in the aza-(dibenzo)dipyrromethene products.[7]



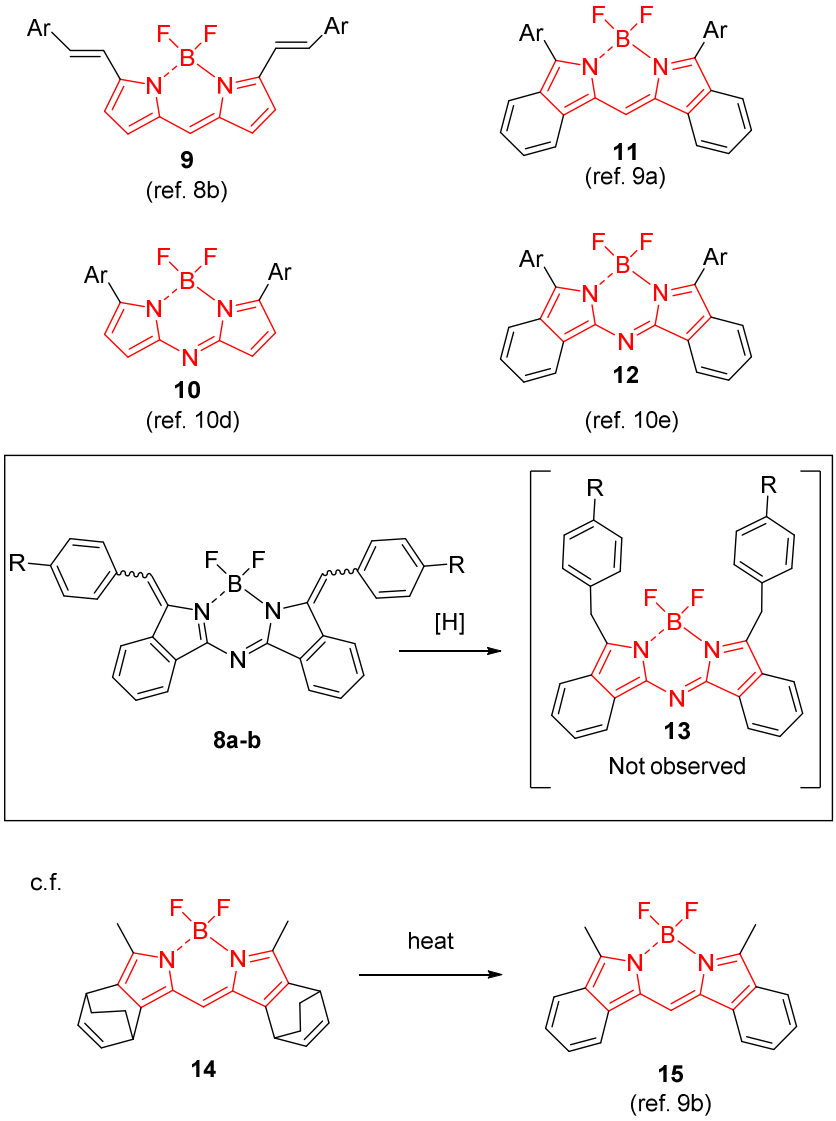
Scheme 2. Self-condensation of aminoisoindolines 5a-c to give aza-(dibenzo)dipyrromethenes **7a-c**.

Aza-(dibenzo)dipyrromethene precursors **7a** and **7b** were converted into the corresponding aza-(dibenzo)BODIPY analogues **8a** and **8b** by straightforward reaction with $BF_3.OEt_2$ (Scheme 3). Isolation and characterization of these adducts proved somewhat more challenging than for their precursors, but crystals were eventually grown from a mixture of dichloromethane:petroleum ether:methanol (1:1:1). The crystal structures for **7b** and **8b** are also shown in Scheme 3 and it is immediately apparent that the BODIPY analogues display the opposite configuration (*E, E*) to those 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 a mixture of *E*/*Z* isomers being observed at equilibrium after several hours.



Scheme 3. Synthesis of aza-(dibenzo)BODIPY derivatives and X-ray crystal structures of **7b** and **8b** (ellipsoids at 50% probability).

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 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 aza-dipyrromethene unit. It appears that maintenance of the formal aromatic system of both fused benzenes drives the overall electronic configuration. Indeed, it can 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**, nitrogen in **13**) and α-substituents (methyl/benzyl).



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 is shown in Figure 2 and displays a relatively broad profile with a visible-region maximum at 465 nm in DCM. Further conjugation through introduction of *para*-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 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 Sup-

porting Information). No appreciable fluorescence is observed in any solvent, presumably due to rapid relaxation (bond rotation) of the molecules in their excited states.

Boron complexes **8a-b** show absorption maxima at 439 and 469 nm respectively, indicating a similar trend of substituent effect. Unlike their precursors however, boron complexes **8a-b** 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 media. As discussed previously, the boron complexes **8a-b** are present as an equilibrating mixture of stereoisomers. The absorption spectra appear similar for each isomer but it is possible that only a single component exhibits the observed fluorescence. The excitation spectrum for **8a** is also shown in figure 2 and it closely resembles the absorption profile suggesting either a similar absorption for each isomer, or that each isomer leads 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.

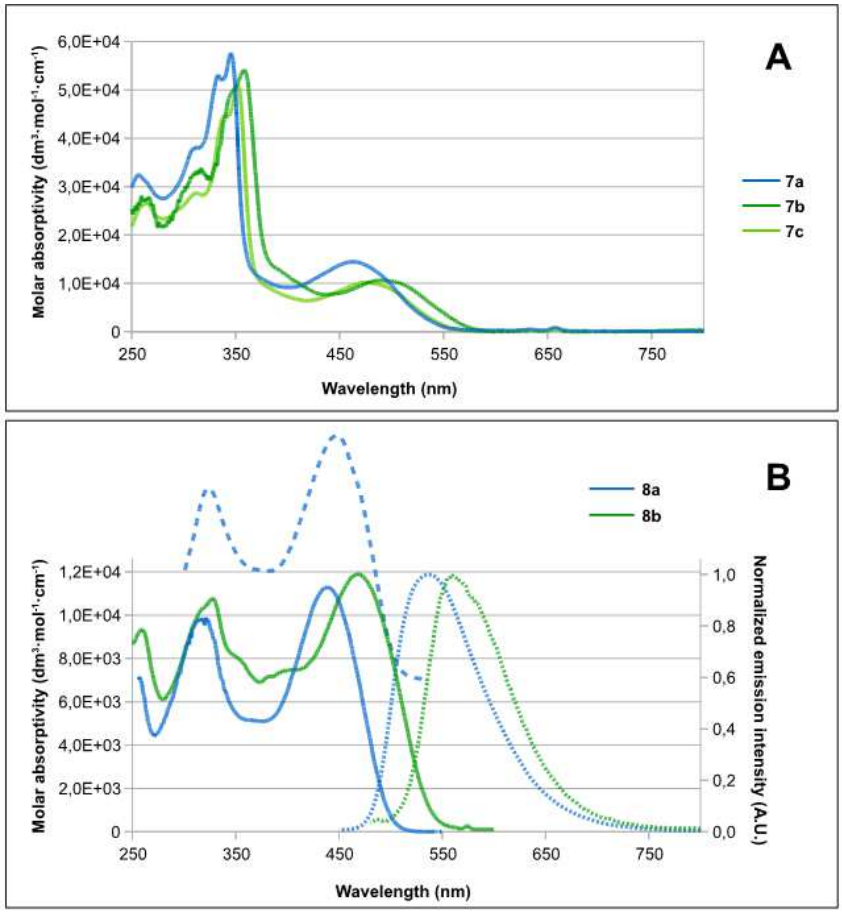


Figure 2. (A) UV-Vis absorption spectra of **7a-c** in DCM. (B) Normalized UV-Vis absorption (solid line) and fluorescence emission (dotted line) spectra of **8a** and **8b** in DCM; excitation spectrum for **8a** (dashed line, Em = 537 nm).

In summary, we report here a new type of boron aza-(dibenzo)dipyrromethene derivatives and their precursor dipyrromethene analogues. The new structures are relatively straightforward to prepare and incorporate, simultaneously on the parent BODIPY core, conjugation at the α-positions, benzofusion 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 traditional BODIPY chromophores and is presumably driven by preservation of local aromaticity of the benzene rings (Figure 3). 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, present as an equilibrating mixture of stereoisomers, show weak fluorescence with Stokes shifts of over 90 nm.

Experimental Section

(Z)-1(4-Pentylphenylmethylene)-1H-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 eq) and $PdCl_2$(MeCN) (39 mg, 0.05 eq) was sealed in a microwave vessel with a magnetic bar and then purged and refilled with N_2 three times. Then, a solution of 4-pentylphenylacetylene (0.7 ml, 1.2 eq) and DBU (1.12 ml, 2.5 eq) 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 ^oC for 1 h. After cooling, 50 ml of AcOEt were added and the mixture 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 eluent to afford a yellow compound that was recrystallized from a DCM:Petroleum ether (1:1) mixture to yield yellow needles (660 mg, 76%).

Mp 94-95 ^oC; 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); 7.78 (br d, 1H, *J* = 7.5); 7.46 (br td, 1H, *J* = 7.5, 1.1); 7.43 (br d, 1H, *J* = 7.5); 7.34 (td, 1H, , *J* = 7.5, 1.0); 7.22 (br d, 2H, *J* = 8.1); 6.76 (s, 1H); 6.2 – 5.2 (br s, 2H, NH_2); 2.63 (t, 2H, *J* = 7.7); 1.60-1.70 (m, 2H); 1.27-1.45 (m, 4H); 0.91 (t, 3H, *J* = 6.8); ^{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 (MADLI-TOF) *m/z* = 290.1 $[M]^+$ (100%); HR-MS (ESI) ($C_{20}H_{23}N_2$) $[M+H]^+$: Calc.: 291.1856; Found: 291.1857; UV-vis (MeOH): λ max (nm) (ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)) = 366 ($9.34 \cdot 10^3$); 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 ºC for 2 h under N_2 atmosphere, allowing the solvent to slowly evaporate during the process. After cooling, the residue was purified by column chromatography using DCM as solvent to afford a red compound that was recrystallized from a DCM to yield red needles. The needles were washed twice with MeOH. (Yield 82.1 mg, 82%).

Mp 238-239 ºC; 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); 7.91-7.88 (m, 4H); 7.82 (br dt, 2H, *J* = 7.4, 1.0); 7.55 (td, 2H, *J* = 7.4, 1.2); 7.50 (td, 2H, *J* = 7.4, 1.0); 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 (MADLI-TOF) *m/z* = 423.2 $[M]^+$ (100%); HR-MS (ESI) ($C_{30}H_{22}N_3$) $[M+H]^+$: Calc.: 424.1808; Found: 424.1807 $[M+H]^+$; UV-vis (CH_2Cl_2): λ max (nm) (ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)) = 465 ($1.99 \cdot 10^4$), 343 ($5.75 \cdot 10^4$); 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 ºC for 2 h under N_2 atmosphere, letting the solvent to slowly evaporate during the process. After cooling, the residue was purified by column chromatography using DCM then DCM:MeOH (50:1) as eluent to afford a red compound that was recrystallized from a DCM and washed twice with MeOH to yield red (84 mg, 87%).

Mp 203-204 ºC; 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); 7.85 (br d, 4H, *J* = 8.7); 7.79 (br dt, 2H, *J* = 7.4, 0.9); 7.53 (td, 2H, *J* = 7.4, 1.0); 7.48 (td, 2H, *J* = 7.4, 0.9); 6.77 (s, 2H); 6.62 (br d, 4H, *J* = 8.7); 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 (MADLI-TOF) *m/z* = 483.7 $[M]^+$ (100%); HR-MS (ESI) ($C_{32}H_{26}O_2N_3$) $[M+H]^+$: Calc.: 484.2020; Found: 484.2012 $[M+H]^+$; UV-vis (CH_2Cl_2): λ max (nm) (ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)) = 491 ($1.07 \cdot 10^4$), 358 ($5.41 \cdot 10^4$); 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 ºC for 30 min under N_2 atmosphere. After cooling, water (50 ml) was added and the mixture stirred for 15 min. The solid was filtered off and dissolved in DCM, dried ($MgSO_4$), filtered and concentrated. The residue was purified by column chromatography using petroleum ether:DCM (1:1), (1:2) then neat DCM as 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 ºC; R_f 0.56 (Pet. 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); 7.83 (br d, 2H); 7.81 (br d, 4H, *J* = 8.1); 7.54 (td, 2H, *J* = 7.3, 1.3); 7.49 (td, 2H, *J* = 7.3, 1.1); 6.93 (br d, 4H, *J* = 8.1); 6.84 (s, 2H); 2.50 (t, 4H, *J* = 7.9); 1.50-1.55 (m, 4H); 1.26-1.40 (m, 8H); 0.89 (t, 6H, *J* = 6.9); ^{13}C-NMR (105.6 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 (MADLI-TOF) *m/z* = 564.4 $[M]^+$ (100%); HR-MS (ESI) ($C_{40}H_{42}N_3$) $[M+H]^+$: Calc.: 564.3373; Found: 564.3364 $[M+H]^+$; UV-vis (CH_2Cl_2): λ max (nm) (ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)) = 475 ($1.02 \cdot 10^4$), 352 ($5.10 \cdot 10^4$); FT-IR (NaCl), ν($cm^{-1}$): 2953, 2925, 2847, 1601, 1587, 1467, 1415, 1372, 1180, 1148, 1121, 859, 816, 757, 706, 550, 527.

AzaBODIPY (8a). A solution of **7a** (138 mg) and Et_3N (0.455 ml, 10 eq) in CH_2Cl_2 (12 ml) was stirred for 15 min at rt under N_2 atmosphere before adding $BF_3 \cdot Et_2O$ (2.2 ml, 25 eq) 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 (1M) (50 ml) twice. The residue was dried ($MgSO_4$), filtered and concentrated. Finally, the residue was purified by column chromatography using DCM as eluent to afford a bright yellow compound that was recrystallized from a DCM:Pet.Ether:MeOH (1:1:1) to yield orange-yellow needles (49 mg, 32%).

Mp 215-216 ºC; R_f 0.77 (DCM); ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K, *Data for main isomer (E,E)*): δ (ppm) = 8.18 (br dt, 2H, *J* = 7.6, 1.0); 7.88 (s, 2H); 7.66 – 7.60 (m, 6H, H-7); 7.53 (td, 2H, *J* = 7.6, 0.8); 7.49 (t, 4H, *J* = 7.3); 7.46 – 7.41 (m, 4H); ^{13}C-NMR (125.7 MHz, $CDCl_3$, 298 K, *Data for main isomer (E,E)*): δ (ppm) = 163.9; 138.7; 136.2; 135.2; 132.4, 129.8; 129.4; 128.8; 128.7; 127.8; 125.7; 123.8; 123.6; MS (MADLI-TOF) *m/z* = 471.2 $[M+H]^+$ (100%); HR-MS (MALDI) ($C_{30}H_{21}N_3{}^{10}BF_2$) $[M+H]^+$: Calc.: 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 ($1.13 \cdot 10^4$), 317 ($9.87 \cdot 10^3$); Fluorescence ($CH_2Cl_2$): λ max em (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.

AzaBODIPY (8b). A solution of **7b** (47 mg) and Et_3N (0.13 ml, 10 eq) in CH_2Cl_2 (10 ml) was stirred for 15 min at rt under N_2 atmosphere before adding $BF_3 \cdot Et_2O$ (0.64 ml, 25 eq) 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 (1M) (50 ml) twice. The residue was dried ($MgSO_4$), filtered and concentrated. Finally, the residue was purified by column chromatography using DCM as solvent to afford a bright yellow compound that was recrystallized from a DCM:Pet.Ether:MeOH (1:1:1) to yield orange-yellow needles (25.3 mg, 49%).

Mp 229-230 ^{o}C; R_f 0.58 (DCM); ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K, *Data for main isomer (E,E)*): δ (ppm) = 8.18 (br d, 2H, *J* = 7.4); 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); 7.46 (td, 2H, *J* = 7.7, 1.2); 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 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 (MADLI-TOF) *m/z* = 531.08 $[M+H]^+$ (100%); HR-MS (MALDI) ($C_{32}H_{24}O_2N_3{}^{10}BF_2$) $[M]^+$: Calc.: 530.1960; Found: 530.1964 $[M]^+$; UV-vis (CH_2Cl_2): λ max (nm) (ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)) = 469 ($1.19 \cdot 10^4$), 328 ($1.08 \cdot 10^4$); Fluorescence ($CH_2Cl_2$): λ max em (nm) (λ ex 470 nm) = 560; FT-IR (NaCl), ν(cm^{-1}): 3052, 2954, 2836, 1728, 1599, 1567, 1554, 1503, 1258, 1172, 1089, 1024, 860, 798, 726.

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Supporting Information: Characterization spectra for new compounds; X-ray crystal structures of **5b** and **7a**. This information is available free of charge via the internet at http://pubs.acs.org/.

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(7) The crystal structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre with the following reference numbers; **5b** 992705, **7a** 992691, **7b** 992706, and **8b** 992707.

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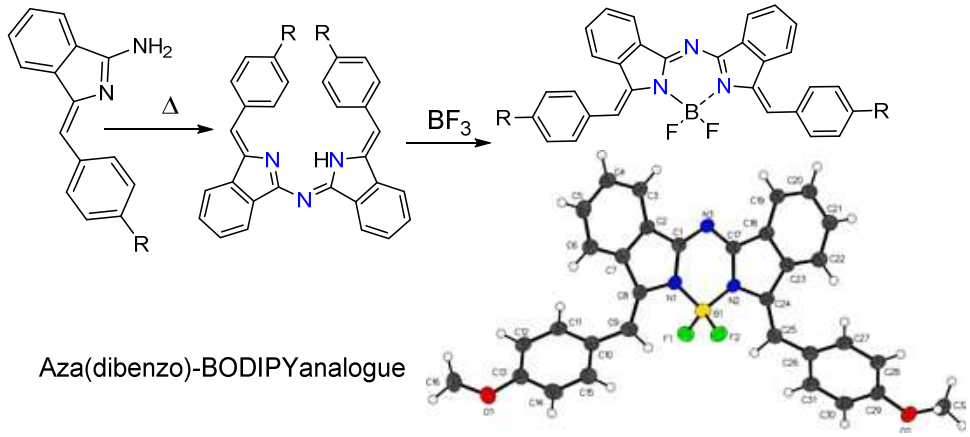
SYNOPSIS TOC



Aza(dibenzo)-BODIPYanalogue