A Platinum Open Access Journal for Organic Chemistry

Paper

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Synthesis of a β-isoindigo-linked 1*H*-3-benzazepine-modified aza-boron dipyrromethene dimer

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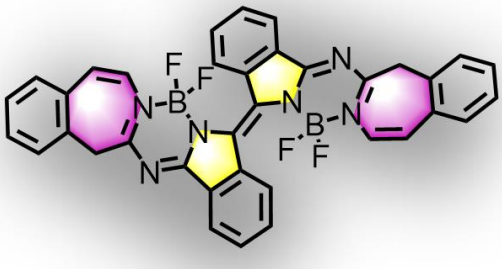
Dedicated to Prof. Tien-Yau Luh on the occasion of his 76th birthday

Received 05-18-2023 **Accepted Manuscript** 08-28-2023 **Published on line** 09-11-2023

Abstract

A 1*H*-3-benzazepine-modified aza-boron dipyrromethene dimer was synthesized by condensation of 2-amino-1*H*-3-benzazepine with a diamino β-isoindigo, followed by complexation with $BF_3{\cdot}OEt_2$. It possesses an axial chirality with a C_i symmetry as shown by heteronuclear NMR spectroscopy. Treatment of this compound with tritylium tetrafluoroborate or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone led to the unexpected mono deborylation instead of yielding the desired fully conjugated benzazepine-modified analogue. Upon mono deborylation, the electronic absorption band at 605 nm became significantly weakened and split, which could be attributed to the lowering of the molecular symmetry.



Keywords: Azepine, axial chirality, boron dipyrromethenes, condensation, β-isoindigo

Introduction

Boron dipyrromethenes (BODIPYs), which comprise two pyrrole units tethered by a methine bridge and a BF_2 group, represent a versatile class of functional dyes.[1] Owing to their strong and tunable electronic absorption and fluorescence emission, high thermal and photo-stability, as well as ease of chemical modification, these compounds have been extensively studied for a wide range of applications. In particular, they can serve as multifunctional theranostic agents for fluorescence bioimaging, photoacoustic imaging, photodynamic therapy, and photothermal therapy.[2] They can also be used as photocatalysts in organic synthesis,[3] building blocks of polymeric materials,[4] photo-active materials for solar cells and photonic devices,[5] and chemosensors for various analytes.[6] With a view to revealing the structure-property relationship and optimizing the properties for various applications, numerous BODIPY derivatives have been designed and synthesized.[7] As an important class of BODIPY derivatives, aza-BODIPYs are of particular interest.[8] By replacing the methine bridge with an aza group at the meso position, the longest-wavelength absorption band of these derivatives is significantly red-shifted (to ca. 650 nm) compared with that of BODIPYs, making them particularly suitable for biomedical applications.[9] Further modification, for example, by introducing fused rings to and restricting the conformation of the aza-BODIPY skeleton could further shift the absorption to the red and significantly alter their photophysical properties.[10]

As another interesting series of BODIPY analogues, one of the pyrrole units has been replaced with a pyridine or quinoline group.[11,12] To maintain a π-conjugated system, these compounds usually contain an exocyclic double bond at the pyrrole ring as shown in Figure 1. With such modification, they exhibit a strong electron-accepting ability with a low LUMO level and can emit strong fluorescence even in the solid state. To expand the π skeleton further, a seven-membered azepine ring can be used to give a fully conjugated system (Figure 1). However, to the best of our knowledge, these analogues have not been reported so far, though BODIPYs fused with a seven-membered ring are known in the literature.[13] We report herein our attempts to prepare these interesting BODIPY derivatives using a β-isoindigo core[14,15] to form a dimeric species. In recent years, different forms of BODIPY dimers have been reported which exhibit superior electronic and optical properties,[16-19] including the intriguing circularly polarized luminescence.[20,21]

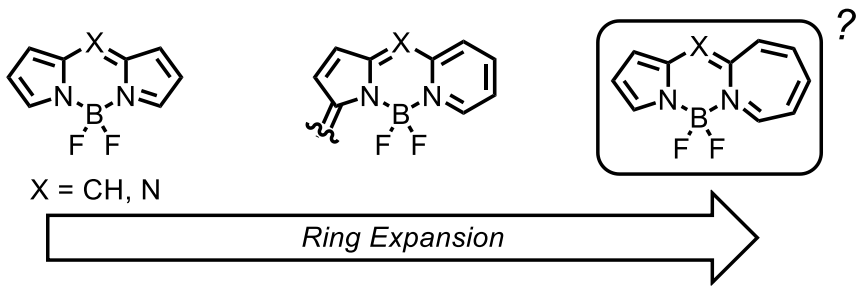


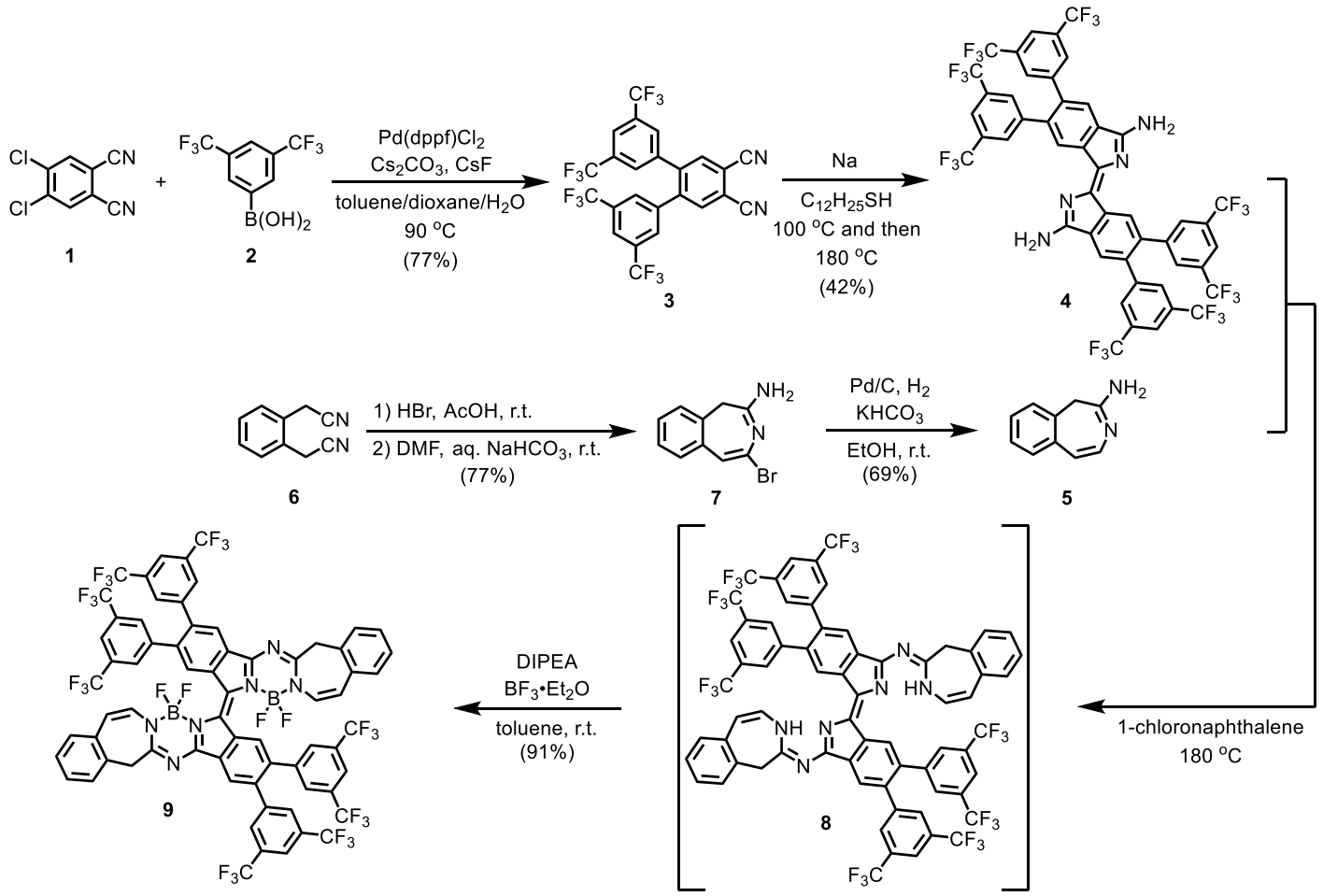
Figure 1. Ring expanded BODIPY analogues.

Results and Discussion

To prepare the β-isoindigo skeleton, 4,5-dichlorophthalonitrile (**1**) underwent Suzuki coupling with 3,5-bis(trifluoromethyl)phenylboronic acid (**2**) in the presence of [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) [$Pd(dppf)Cl_2$], Cs_2CO_3, and CsF in a mixture of toluene,

dioxane, and water to give the disubstituted product **3** in 77% yield (Scheme 1). The two bulky 3,5-bis(trifluoromethyl)phenyl groups were introduced to prevent molecular stacking of the resulting dimer, thereby enhancing its solubility in common organic solvents. With a large hydrophobic core, the dimer was expected to exhibit strong π-π aggregation that would lower its solubility. According to the procedure reported by Kobayashi et al. for the preparation of β-isoindigos,[14] treatment of **3** with Na in 1-dodecanethiol resulted in the formation of unreported β-isoindigo **4**, which was isolated as bright orange microcrystals after purification by silica-gel column chromatography followed by recrystallization from a mixture of tetrahydrofuran (THF) and hexane.

To construct the seven-membered ring, 2-amino-1*H*-3-benzazepine (**5**) was prepared separately through a two-step procedure reported previously.[22] As shown in Scheme 1, treatment of *o*-phenylenediacetonitrile (**6**) with HBr in acetic acid followed by alkaline work up led to the formation of benzazepine **7**, which underwent hydrogenolysis to remove the bromo group to afford **5**. This compound was then condensed with β-isoindigo **4** in 1-chloronaphthalene at 180 °C to give the proposed intermediate **8**. Without purification and characterization, it was then treated in situ with $BF_3{\cdot}Et_2O$ and *N*,*N*-diisopropylethylamine (DIPEA) to give the dimeric product **9** in 91% overall yield. This compound could be isolated readily by column chromatography and was obtained as a dark blue solid.



Scheme 1. Preparation of 1*H*-3-benzazepine-modified dimeric aza-BODIPY analogue **9**.

All the compounds were characterized with various spectroscopic methods (see the spectra given in the Supplementary Material). The dimeric nature of β-isoindigo **4** was confirmed by its ^{1}H, ^{13}C{^{1}H}, and ^{19}F{^{1}H} NMR spectra, which showed that the molecule has a C_2 symmetry and there is free rotation along the aryl–3,5-bis(trifluoromethyl)phenyl bond. For the known 1*H*-3-benzazepines **5** and **7**, their low-field (60 MHz) NMR spectra were reported previously.[22] In this study, their molecular structures were unambiguously confirmed by high-field ^{1}H (400 MHz) and ^{13}C{^{1}H} (100.6 MHz) NMR spectroscopy. For the dimeric aza-BODIPY analogue **9**, its ^{19}F{^{1}H} NMR spectrum showed two singlets at δ -63.17 and -63.22, assignable to the two sets of CF_3 groups, and two broad signals at δ -127.25 and -139.91, assignable to the two fluorine atoms attached to each of the boron centers, for which the coupling due to ^{19}F-^{19}F and ^{19}F-^{11}B could not be resolved (Figure 2a). The ^{11}B{^{1}H} NMR spectrum showed a doublet of doublet for the two equivalent boron centers (Figure 2b). The coupling constants (ca. 24 Hz) were comparable to the values of $^{1}J_{B,F}$ for BODIPYs (28-29 Hz).[23] Its ^{1}H NMR spectrum showed two doublets at δ 3.96 and 3.77 both with a coupling constant of 12.0 Hz for the two geminal methylene protons at the seven-membered ring (Figure 2c). All these spectral data strongly suggested that the molecule is not planar and has an axial chirality with a C_i symmetry probably due to the steric constraint induced by the two BF_2 units.[20] The compound was also characterized with high-resolution electrospray ionization (ESI) mass spectrometry, which showed the molecular ion signal (*m*/*z* = 1486.2432) as the base peak. Its isotopic pattern was also in good agreement with the simulated pattern.

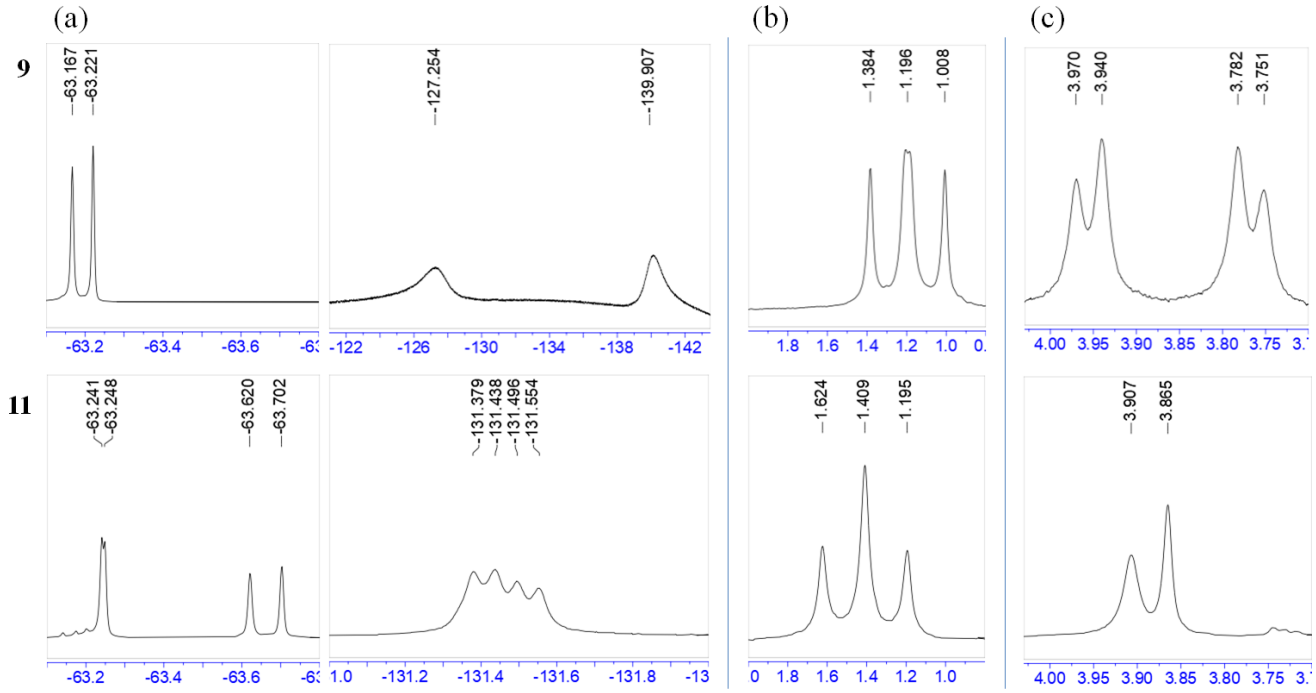
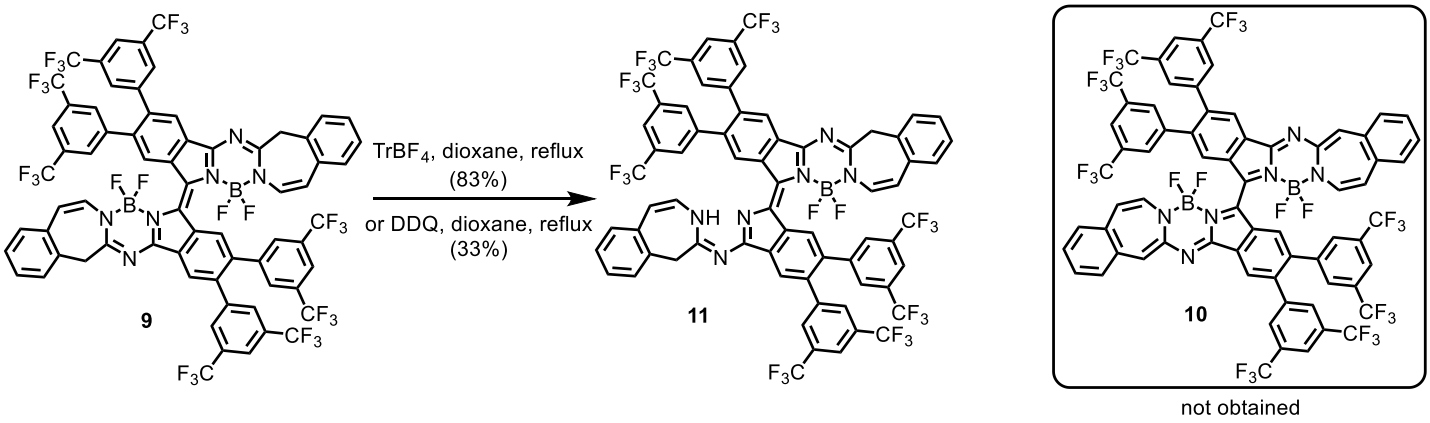


Figure 2. Partial (a) ^{19}F{^{1}H}, (b) ^{11}B{^{1}H}, and (c) ^{1}H NMR spectra of **9** and **11** in $CDCl_3$.

Attempts were made to convert **9** into the fully conjugated benzazepine-modified analogue, which contains two benzazepine-modified aza-BODIPY units (compound **10**, Scheme 2). We first treated **9** with an excess amount of tritylium tetrafluoroborate ($TrBF_4$) in refluxing dioxane in order to remove a hydride from the seven-membered ring. Surprisingly, mono deborylation occurred to afford **11** as a red-purple solid in 83% yield (Scheme 2). Oxidation of **9** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) also gave **11** (in 33% yield), but the desired product **10** could not be obtained. It is worth mentioning that treatment of the

intermediate **8** generated in situ with a less amount of $BF_3{\cdot}Et_2O$ (1.5 equiv. with respect to **4**) could not give **11**, but a significant amount of **8** was recovered. The unsymmetrical structure of this compound was inferred from its $^{19}F\{^1H\}$ NMR spectrum, which exhibited four instead of two singlets (at δ -63.24, -63.25, -63.62, and -63.70) for the CF_3 groups (Figure 2a). In addition, a distorted quartet at δ -131.47 was also observed for the two equivalent fluorine atoms, which were coupled with the boron center with a $^1J_{F,B}$ of 27.6 Hz.[23] The presence of only one BF_2 group was also supported by the triplet at δ 1.41 ($^1J_{B,F}$ = 27.6 Hz) in the $^{11}B\{^1H\}$ NMR spectrum (Figure 2b). Furthermore, the four methylene protons now resonated as two singlets at δ 3.91 and 3.87 in the ^1H NMR spectrum (Figure 2c), showing that the axial chirality was lost in this compound. A very downfield signal at δ 13.68 was also observed, which could be assigned to the NH proton at the seven-membered ring. Compound **11** was further characterized by high-resolution ESI mass spectrometry. Both the accurate mass and the isotopic pattern of the molecular ion signal were in good agreement with the theoretical values, providing strong evidence to support the identity of this compound.



Scheme 2. Attempted synthesis of the fully conjugated benzazepine-modified aza-BODIPY dimer **10**.

The electronic absorption spectra of compounds **9** and **11** were recorded in $CHCl_3$ (Figure 3). It can be seen that while the dimeric aza-BODIPY analogue **9** exhibited a broad band at 605 nm, the mono-deborylated analogue **11** displayed a much weaker and split signal at around 570 nm, which might be due to the loss of symmetry caused by the removal of one of the BF_2 units. Upon excitation at the respective λ_{max}, both compounds showed negligible fluorescence. It is worth noting that while the absorption of **9** was slightly red shifted compared with that of general BODIPYs due to the extended conjugation, the non-fluorescent property of **9** was in contrast with the highly emissive nature of BODIPYs.[1]

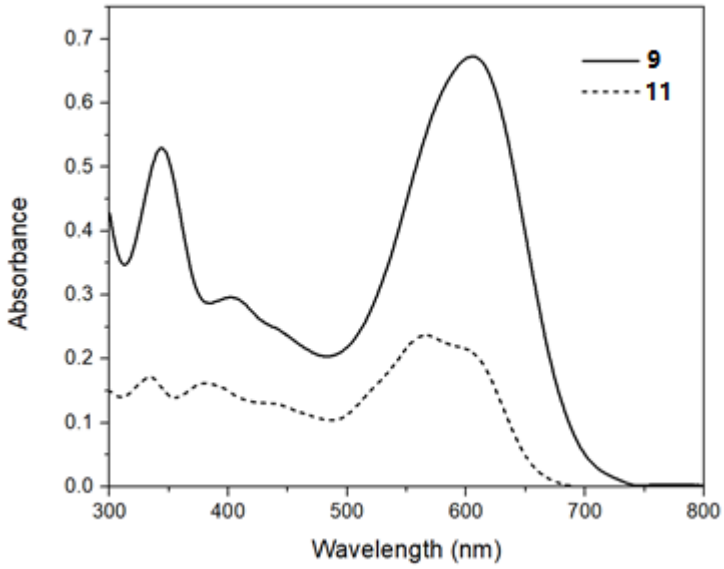


Figure 3. Electronic absorption spectra of **9** and **11** in $CHCl_3$ (18 μM).

Conclusions

In summary, we have successfully synthesized a novel β-isoindigo-linked 1*H*-3-benzazepine-modified aza-BODIPY dimer (compound **9**) in 91% yield through a one-pot condensation of β-isoindigo **4** with 2-amino-1*H*-3-benzazepine (**5**) followed by borylation with $BF_3{\cdot}OEt_2$. To the best of our knowledge, it is the first example of BODIPY analogue in which one of the five-membered pyrrole rings is replaced with a seven-membered azepine ring. Unfortunately, attempts to convert this compound to the fully conjugated benzazepine-modified aza-BODIPY dimer were unsuccessful. As shown by heteronuclear NMR spectroscopy, the axial chirality of **9** was lost upon mono deborylation, which also resulted in weakening and splitting of the electronic absorption band at 605 nm.

Experimental Section

General. Toluene was dried using an INERT solvent drying system prior to use. All other solvents and reagents were of reagent grade and used without further purification. All the reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC; Merck pre-coated silica gel 60F254 plates). For reactions that required heating, oil bath was used as the heating source. Chromatographic purification was performed on silica gel (Macherey-Nagel, 230–400 mesh) column with the indicated eluent.

^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$, and $^{11}B\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance III 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100.6 MHz; ^{11}B, 128.4 MHz) or a Bruker Avance III 500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125.8 MHz; ^{19}F, 470.4 MHz) in a deuterated solvent. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced internally using the residual solvent [^{1}H: δ = 7.26 (for $CDCl_3$), δ = 2.5 (for DMSO-d_6)] or solvent [^{13}C: δ = 77.2 (for $CDCl_3$), δ = 39.7 (for DMSO-d_6)] resonance relative to tetramethylsilane. For $^{19}F\{^{1}H\}$ and $^{11}B\{^{1}H\}$ NMR spectra, trifluoromethylbenzene (δ = -64 ppm) and $BF_3{\cdot}OEt_2$ (δ = 0 ppm) were used as the external reference,

respectively. High-resolution ESI mass spectra were recorded on a Q Exactive Focus Orbitrap mass spectrometer. UV-Vis spectra were taken on a Cary 5G UV-Vis-NIR spectrophotometer. Melting points were measured on a Büchi melting point apparatus (model B-545).

4,5-Bis[3',5'-bis(trifluoromethyl)phenyl]phthalonitrile (3). A mixture of 4,5-dichlorophthalonitrile (**1**) (1.03 g, 5.2 mmol), 3,5-bis(trifluoromethyl)phenylboronic acid (**2**) (2.80 g, 10.9 mmol), Pd(dppf)Cl_2 (430 mg, 10 mol%), Cs_2CO_3 (2.56 g, 7.8 mmol), and CsF (1.18 g, 7.8 mmol) in toluene (30 mL), dioxane (30 mL), and water (20 mL) was stirred at 90 ℃ until compound **1** was fully consumed as indicated by TLC. After cooling to room temperature, the mixture was mixed with ethyl acetate (100 mL) and water (100 mL). The organic phase was washed with water and brine sequentially, and then it was dried over anhydrous Na_2SO_4. The solvent was then evaporated under vacuum, and the crude product was purified by silica-gel column chromatography using *n*-hexane/EtOAc (19:1 v/v) as the eluent to give the product as a white solid (2.23 g, 77%). mp 168-169 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01 (s, 2 H, Ar*H*), 7.89 (s, 2 H, Ar*H*), 7.51 (s, 4 H, Ar*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 142.8, 138.2, 135.1, 132.8 (quartet, $^2J_{C,F}$ = 34.1 Hz, *C*CF_3), 129.5, 122.9, 122.4 (quartet, $^1J_{C,F}$ = 273.0 Hz, *C*F_3), 116.8, 114.2. ^{19}F{^{1}H} NMR ($CDCl_3$, 470.4 MHz): δ -63.36 (s, C*F*$_3$). HRMS (ESI): *m*/*z* calcd for $C_{24}H_8F_{12}N_2$ $[M]^-$ 552.0501, found 552.0504.

Diamino β-isoindigo 4. Sodium metal (32 mg, 1.4 mmol) was dissolved in dodecanethiol (2.5 mL) at 100 °C. After the sodium was completely dissolved, phthalonitrile **3** (770 mg, 1.4 mmol) was added, and the mixture was stirred at this temperature for 1 h. The reaction temperature was then elevated to 180 °C, and the mixture was kept stirring for 1 h. The reaction was then quenched with an excess of *n*-hexane. The precipitate that was collected by filtration was purified by silica-gel column chromatography using $CHCl_3$ as eluent, followed by recrystallization from THF/hexane to give the product as bright yellow microcrystals (324 mg, 42%). mp >310 ºC. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.85 (s, 2 H, Ar*H*), 8.18 (s, 2 H, Ar*H*), 8.06 (s, 2 H, Ar*H*), 8.00 (s, 2 H, Ar*H*), 7.93 (s, 4 H, Ar*H*), 7.85 (s, 4 H, Ar*H*), 7.67 (s, 2 H, NH_2). ^{13}C{^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 163.3, 143.6, 143.0, 141.5, 141.1, 138.2, 136.4, 133.3, 131.1, 130.4 (quartet, $^2J_{C,F}$ = 33.2 Hz, *C*CF_3), 130.2 (quartet, $^2J_{C,F}$ = 32.7 Hz, *C*CF_3), 126.7, 126.6, 124.4, 122.2, 120.9, 120.7, 120.1 (the two *C*F_3 quartets could not be identified). ^{19}F{^{1}H} NMR (DMSO-d_6, 470.4 MHz): δ -61.55 (s, C*F*$_3$), -61.67 (s, C*F*$_3$). HRMS (ESI): *m*/*z* calcd for $C_{48}H_{20}F_{24}N_4$ $[M+H]^+$ 1109.1378, found 1109.1377.

2-Amino-4-bromo-1*H*-3-benzazepine (7). According to the reported procedure,[22] a 30% solution of HBr in acetic acid (11 mL) was added dropwise into a solution of *o*-phenylenediacetonitrile (**6**) (3.61 g, 23 mmol) in acetic acid (6 mL) with stirring. After 2 h, the precipitate formed was collected by filtration and washed with acetic acid and diethyl ether. The solid was then redissolved in *N*,*N*-dimethylformamide (DMF) (20 mL), and the solution was added dropwise into a saturated $NaHCO_3$ solution (100 mL). After vigorous stirring for 30 min, the precipitate was collected by filtration, washed thoroughly with water, and dried. The crude product was purified by recrystallization from acetone as colorless crystals (4.23 g, 77%). mp 195 ºC (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.23-7.35 (m, 3 H, Ar*H*), 7.13 (d, *J* = 7.2 Hz, 1 H, Ar*H*), 6.78 (s, 1 H, C=C*H*), 3.30 (s, 2 H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 153.6, 135.3, 131.5, 129.1, 128.2, 127.7, 127.1, 117.0, 40.0. HRMS (ESI): *m*/*z* calcd for $C_{10}H_9BrN_2$ $[M+H]^+$ 237.0022, found 237.0023.

2-Amino-1*H*-3-benzazepine (5). According to the reported procedure,[22] a mixture of **7** (1.20 g, 5.1 mmol), $KHCO_3$ (1.02 g, 10.2 mmol), and 10% Pd/C (150 mg) in ethanol (150 mL) was stirred under an atmosphere of hydrogen at normal pressure. After 2 h, the mixture was filtered through Celite and the filtrate was evaporated in vacuo with temperature lower than 40 ℃. The crude product was purified by recrystallization from CH_2Cl_2 to afford colorless crystals (0.55 g, 69%). mp 154 ºC (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28-7.34 (m, 3 H, Ar*H*), 7.15 (d, *J* = 7.6 Hz, 1 H, Ar*H*), 6.90 (d, *J* = 8.8 Hz, 1 H, C=C*H*), 6.37 (d, *J* = 8.8 Hz, 1 H, C=C*H*),

3.23 (s, 2 H, C*H*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 152.7, 137.9, 135.6, 130.6, 127.7, 127.5, 127.3, 126.7, 115.3, 40.0. HRMS (ESI): *m*/*z* calcd for $C_{10}H_{10}N_2$ $[M+H]^+$ 159.0917, found 159.0917.

1*H*-3-Benzazepine-modified aza-BODIPY dimer 9. A mixture of β-isoindigo **4** (57 mg, 0.05 mmol) and 2-amino-1*H*-3-benzazepine (**5**) (40 mg, 0.25 mmol) in 1-chloronaphthalene (2.5 mL) was stirred at 180 ℃ for 1 h. The mixture turned to deep red purple gradually. It was expected that the intermediate **8** was formed, which was not purified and characterized. After cooling to room temperature, DIPEA (55 μL) and toluene (10 mL) were added, followed by the dropwise addition of $BF_3{\cdot}Et_2O$ (80 μL, 0.65 mmol). The mixture was stirred at room temperature for 30 min. It was then evaporated in vacuo, and the residue was loaded onto a silica-gel column and eluted with hexane/CH_2Cl_2 (1:3 v/v) to give the product as a dark blue solid (70 mg, 91%). mp >310 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.54 (s, 2 H, Ar*H*), 8.18 (s, 2 H, Ar*H*), 7.81 (s, 2 H, Ar*H*), 7.78 (s, 2 H, Ar*H*), 7.58 (s, 4 H, Ar*H*), 7.56 (s, 4 H, Ar*H*), 7.43-7.49 (m, 4 H, Ar*H*), 7.34-7.39 (m, 4 H, Ar*H*), 7.05 (d, *J* = 9.6 Hz, 2 H, C=C*H*), 6.97 (d, *J* = 9.6 Hz, 2 H, C=C*H*), 3.96 (d, *J* = 12.0 Hz, 2 H, C*H*), 3.77 (d, *J* = 12.0 Hz, 2 H, C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 165.6, 161.9, 141.4, 141.3, 141.1, 139.0, 137.4, 134.3, 133.7, 132.5, 132.2, 132.0 (quartet, $^2J_{C,F}$ = 33.7 Hz, *C*CF_3), 131.9 (quartet, $^2J_{C,F}$ = 33.7 Hz, *C*CF_3), 130.5, 130.2, 129.9, 129.6, 129.5, 128.5, 127.9, 127.7, 126.9, 126.7, 125.0, 124.6, 124.2, 121.5, 118.8, 42.6 (the two *C*F_3 quartets could not be identified). ^{19}F{^{1}H} NMR ($CDCl_3$, 470.4 MHz): δ -63.17 (s, C*F*$_3$), -63.22 (s, C*F*$_3$), -127.25 (br s, B*F*), -139.91 (br s, B*F*). ^{11}B{^{1}H} NMR ($CDCl_3$, 128.4 MHz): δ 1.20 (virtual t, $^1J_{B,F}$ = 24.1 Hz). HRMS (ESI): *m*/*z* calcd for $C_{68}H_{32}B_2F_{28}N_6$ $[M]^-$ 1486.2453, found 1486.2432. UV-Vis ($CDCl_3$) λ_{max}/nm (log ε): 344 (4.47), 605 (4.56).

Mono deborylated aza-BODIPY dimer 11. A mixture of **9** (15 mg, 0.01 mmol) and $TrBF_4$ (3.4 mg, 0.01 mmol) in dioxane (1 mL) was stirred under reflex for 1 h. The solvent was removed in vacuo and the residue was subject to column chromatography using hexane/CH_2Cl_2 (1:4 v/v) as eluent to give the product as a red-purple solid (12 mg, 83%). mp >310 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.68 (s, 1 H, N*H*), 8.53 (s, 1 H, Ar*H*), 8.37 (s, 1 H, Ar*H*), 8.33 (s, 1 H, Ar*H*), 8.12 (s, 1 H, Ar*H*), 7.79 (s, 1 H, Ar*H*), 7.78 (s, 1 H, Ar*H*), 7.73 (s, 1 H, Ar*H*), 7.70 (s, 1 H, Ar*H*), 7.53 (s, 2 H, Ar*H*), 7.51 (s, 2 H, Ar*H*), 7.37-7.49 (m, 8 H, Ar*H*), 7.35 (s, 2 H, Ar*H*), 7.32 (s, 2 H, Ar*H*), 7.19 (d, *J* = 7.6 Hz, 1 H, C=C*H*), 7.03 (d, *J* = 8.4 Hz, 1 H, C=C*H*), 6.89 (dd, *J* = 3.2, 7.6 Hz, 1 H, C=C*H*), 6.73 (d, *J* = 7.6 Hz, 1 H, C=C*H*), 3.91 (s, 2 H, C*H*$_2$), 3.87 (s, 2 H, C*H*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 169.8, 162.2, 162.1, 161.2, 144.5, 141.7, 141.64, 141.60, 141.3, 141.2, 141.1, 139.3, 138.8, 138.7, 138.4, 136.2, 134.6, 133.9, 133.5, 132.8, 132.7, 132.5, 132.4, 132.3, 132.2, 132.1, 131.9, 131.8, 131.7, 131.5, 130.1, 129.9, 129.5, 129.1, 128.7, 127.8, 127.7, 127.6, 127.4, 126.0, 125.5, 125.3, 125.2, 124.6, 124.5, 124.2, 124.1, 124.0, 123.8, 121.6, 121.4, 121.1, 120.6, 43.2, 29.7 (the *C*F_3 and *C*CF_3 quartets could not be identified). ^{19}F{^{1}H} NMR ($CDCl_3$, 470.4 MHz): δ -63.24 (s, C*F*$_3$), -63.25 (s, C*F*$_3$), -63.62 (s, C*F*$_3$), -63.70 (s, C*F*$_3$), -131.47 (quartet, $^1J_{F,B}$ = 27.6 Hz, B*F*$_2$). ^{11}B{^{1}H} NMR ($CDCl_3$, 128.4 MHz): δ 1.41 (t, $^1J_{B,F}$ = 27.6 Hz, *B*F_2). HRMS (ESI): *m*/*z* calcd for $C_{68}H_{33}BF_{26}N_6$ $[M-H]^-$ 1437.2384, found 1437.2371. UV-Vis ($CDCl_3$) λ_{max}/nm (log ε): 567 (4.07).

Acknowledgements

L.Z. thanks The Chinese University of Hong Kong for the award of CUHK Vice-Chancellor's PhD Scholarship.

Supplementary Material

NMR and ESI mass spectra of all the compounds are available on the supplementary material file associated with this paper.

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