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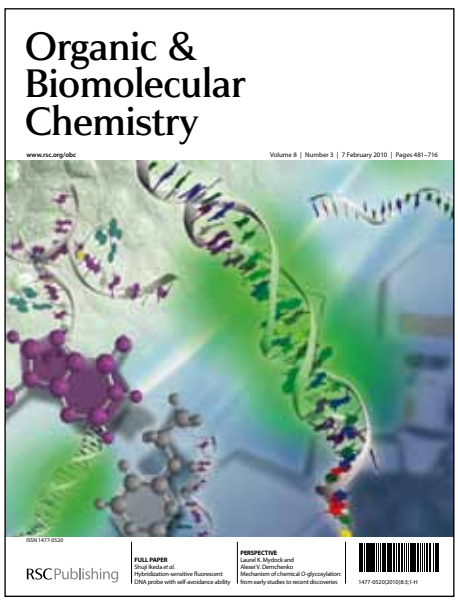

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ARTICLE TYPE

Yellow NIR dye: π-Fused bisbenzoBODIPYs with electron-withdrawing groups

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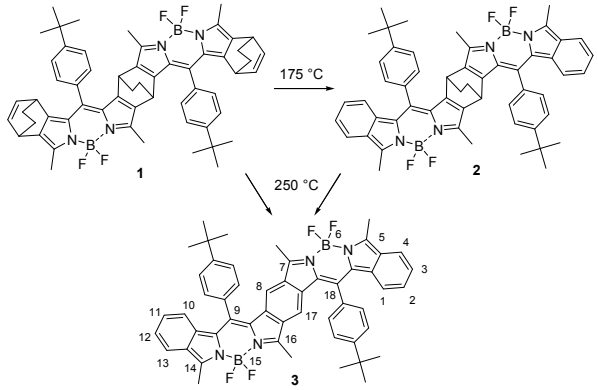
Bicyclo[2.2.2]octadiene-fused (BCOD-fused) bis(benzoborondipyrromethene)s (bisbenzoBODIPYs) bearing electron-withdrawing groups such as fluorine and cyano groups were prepared either by incorporating tetrafluoroisoindole moieties into BODIPY chromophores or by introducing cyano or ethoxycarbonyl groups at the 3,5-positions. The BCOD-fused bisbenzoBODIPYs were quantitatively converted to the corresponding benzene-fused bisbenzoBODIPYs by the retro-Diels-Alder reaction. The π-fused bisbenzoBODIPYs were found to have intensive absorption in the near-infrared region and not to have any strong absorption bands in the visible region. Moreover, the bisbenzoBODIPYs were stable under the atmospheric conditions.

Introduction

Considerable interest is being paid to highly π-conjugated compounds since their electronic properties are applicable to organic semiconducting materials,[1] two-photon microscopic imaging agents,[2] colour-selective cut-filters[3] and other applications.[4] These compounds are rather difficult to synthesize due to their insolubility that arises from the stacking nature of the large, flat chromophores. Many successful preparations of such compounds have been reported, including the introduction of bulky substituents at the peripheral positions of chromophores in order to prevent the stacking. Tetra-tert-butylphthalocyanine is a typical example of the solubilisation of a useful pigment.[5] Moreover, since their HOMO energy levels are high, the chromophores are easily destroyed by oxidation under aerobic conditions. This problem has been solved by the introduction of electro-negative elements into the π-system[6] and/or electron-withdrawing groups such as fluorine and cyano groups.[7] We have explored a synthetic method for the preparation of highly π-conjugated compounds by applying pericyclic cycloreversion of the precursor molecules during the final synthetic steps.[8] The precursor molecules are easily purified because the targeted highly conjugated chromophores are bent and separated by the bulky moieties, which undergo cycloreversion. Thus, the precursors are readily soluble in common solvents and robust under oxidative conditions. This method provides a solution for the preparation of highly conjugated compounds that have been difficult to prepare in a pure form.[9] Recently, π-expanded BODIPYs involving indole and isoindole skeletons have attracted much attention as NIR dyes.[10] We have been interested in preparation of π-expanded BODIPYs based on the precursor method.[11] During the course of our investigation, we have succeeded in the preparation of selective near infrared (NIR) dyes, bisbenzoBODIPY, by the expansion of borondipyrromethene (BODIPY) chromophores followed by fusion of the resulting two boronbenzodipyrro-methene (benzoBODIPY) moieties in the longitudinal direction (Scheme 1).[12] These compounds have large absorption bands (823 nm) in the NIR region and good transparency in the visible region. These compounds are, however, labile under air, although their electronic structures are very attractive. We have planned to prepare stable bisbenzo-BODIPYs by introducing electron-withdrawing groups. In this paper, we discuss the preparation and properties of bisbenzo-BODIPYs bearing fluorine, cyano and ethoxycarbonyl groups.

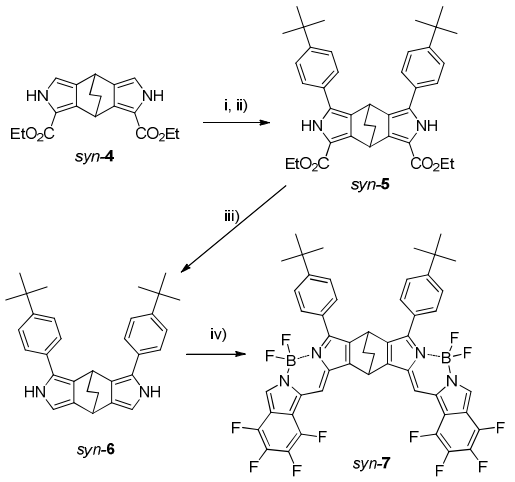


Scheme 1. Pericyclic cycloreversion of BCOD-fused bisBODIPY giving benzene-fused bisbenzoBODIPY

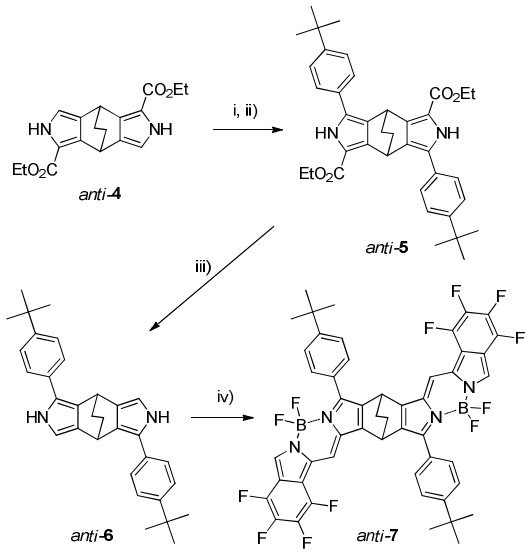
Results and Discussion

First, we chose tetrafluorobenzo as the electron-withdrawing group. As the tetrafluorobenzo group decreased solubility in common solvents,[13] 4-*tert*-butylphenyl group was introduced to the BODIPY dyes. Diiodination of BCOD-fused dipyrrole *syn*-

4[14] was successfully achieved by treatment with benzyltrimethylammonium dichloroiodate (BTMA·ICl_2),[15] which was reported to give chlorinated compounds if the substrates had no NH group.[16] The diiodide was then reacted with 4-*tert*-butylphenyl-boronic acid under Suzuki coupling conditions to give *syn*-**5** in a 27% yield (Scheme 2).[17] The ester groups of *syn*-**5** were removed by heating in an ethylene-glycol solution of KOH to afford *syn*-**6** in a 50% yield.[18] Condensation of *syn*-**6** with 4,5,6,7-tetrafluoro-2*H*-isoindole-1-carbaldehide[19] in the presence of BF_3·OEt_2 followed by treatment with Et_3N[20] gave the targeted BCOD-fused tetrafluorobenzo BODIPY *syn*-**7** in a 19% yield. Similarly, the *anti*-isomer *anti*-**7** was prepared from *anti*-**4**[14] in an overall yield of 8% (Scheme 3).



Scheme 2. *Reagents, conditions and yield:* i) BTMA·ICl_2, $CaCO_3$; CH_2Cl_2/MeOH, refl. 4 h; 54%; ii) 4-*tert*-butylphenylboronic acid, $Pd(PPh_3)_4$; toluene, 10% aq-Na_2CO_3, 90 °C, 16 h; 50%; iii) NaOH; ethylene glycol, 160 °C, 2 h; 50%; iv) 4,5,6,7-tetrafluoroisoindole-1-carboxaldehyde; $POCl_3$, CH_2Cl_2, rt, 12 h; diisopropylethylamine, rt, 1 h; BF_3·OEt_2, rt, 5h; 19%.



Scheme 3. *Reagents, conditions and yield*: i) BTMA·ICl_2, $CaCO_3$; CH_2Cl_2/MeOH, refl. 4 h; 91%; ii) 4-*tert*-butylphenylboronic acid, $Pd(PPh_3)_4$; toluene, 10% aq-Na_2CO_3, 90 °C, 16 h; 66%; iii) NaOH; ethylene glycol, 160 °C, 2 h; 74%; iv) 4,5,6,7-tetrafluoro- isoindole-1-carboxaldehyde; $POCl_3$, CH_2Cl_2, rt, 12 h; diisopropylethylamine, rt, 1 h; BF_3·OEt_2, rt, 5h; 18%.

Retro Diels-Alder reaction of *syn*-**7** and *anti*-**7** was conducted at 250 °C to give benzene-fused bisbenzoBODIPYs *syn*-**8** and *anti*-**8** in quantitative yield (Fig 1). The absorption maxima of the longest wavelength in *syn*-**8** and *anti*-**8** were observed at 749 nm and 811 nm, respectively. The *syn* benzene-fused bisbenzo-BODIPY *syn*-**8** was stable under aerobic conditions (see Supporting Information). On the other hand, the *anti* derivative *anti*-**8** was rather labile; the existing absorption bands gradually decreased and a new absorption band gradually appeared around 640 nm. TD-DFT calculation (B3LYP, 6-31G(d))[21] revealed that the HOMO energy levels of *syn*-**8** and *anti*-**8** were −5.11 eV and −5.08 eV, which would be sufficient to lower the HOMO levels. The instability of *syn*-**8** and *anti*-**8** might be due to there being no substituent at the α-positions of the BODIPY chromophore, where the coefficients of HOMOs and LUMOs are large (see Supporting Information).

In order to find candidates for air-stable near-IR dyes, we carried out TD-DFT calculations (B3LYP, 6-31G(d)) of benzene-fused bisbenzoBODIPY with electron-withdrawing groups such as ethoxycarbonyl and cyano groups (Fig 2). The calculated HOMO levels of compounds **9** and **10** were −5.08 eV and −5.66 eV, which were low enough for our purposes.

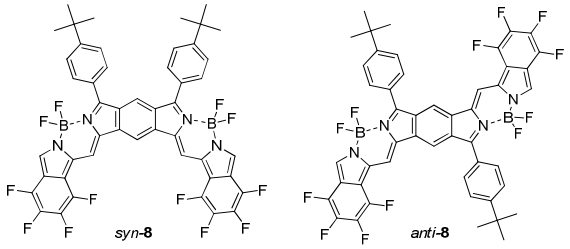


Figure 1. Structures of bis(tetrafluorobenzoBODIPY)s

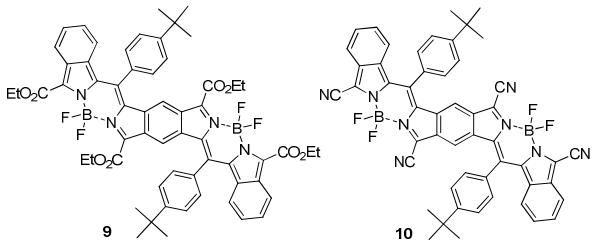
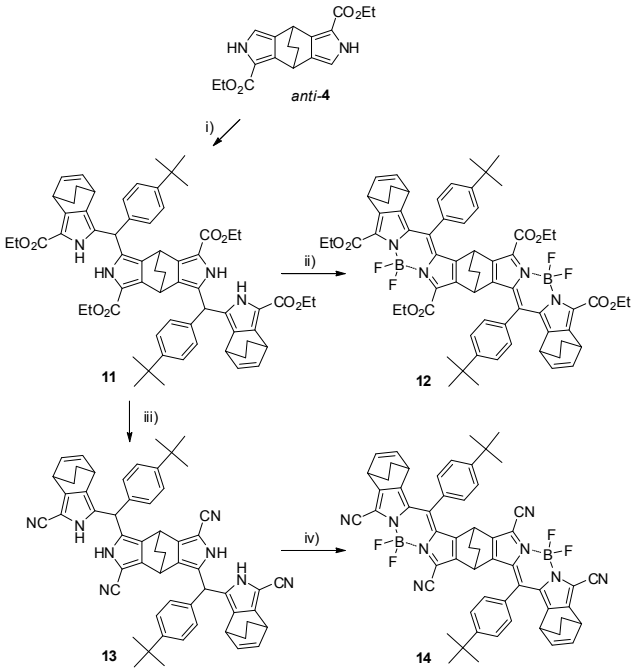


Figure 2. Candidates for air-stable near-IR dyes

The BCOD-fused bisBODIPYs **12** and **14** were prepared from bis(dipyrromethane) **11** reported previously (Scheme 3).[12] Bis(dipyrromethane) **11** oxidized with DDQ in the presence of BF_3·OEt_2 and triethylamine gave BCOD-fused bisBODIPY tetraester **12** in 61% yield. Conversion of ester groups of **12** to cyano groups by the reported method[22] failed. Therefore, the ester groups of **12** were all removed by treatment with KOH in hot ethylene glycol followed by cyanation of the resulting free bis(dipyrromethane) with chlorosulfonyl isocyanate,[23] which gave the desired tetracyano derivative **13** in 88% yield. Oxidation of **13** in the presence of BF_3·OEt_2 and triethylamine afforded BCOD-fused bisBODIPY tetra-nitrile **14** in 28% yield.

Thermal behaviour of the BCOD-fused bisBODIPYs **12** and **14** was examined using thermogravimetric (TG) analysis. The measurements were conducted at a rate of 10 °C/min and the TG curves are shown in Fig 3. In both cases, theoretical amounts of weight due to the extrusion of distal ethylene moieties were lost at 140–200 °C and then the centre ethylene moiety was expelled

at 230–265 °C for the tetra-ester and at 240–275 °C for the tetra-nitrile. There are obvious plateau temperature ranges (205–225 °C for the tetra-ester and 205–235 °C for the tetra-cyanide) between the steep weight-loss ranges of the TG curves. In the case of the tetra-cyano derivative **14**, no obvious weight decrease was observed below 400 °C, while a steep weight loss due to the decomposition of the ester groups in **12** were observed over 300 °C. Bulk thermal treatment of the tetra-cyano derivative **14** at 170 °C for 2 h and at 260 °C for 5 h gave BCOD-fused bisbenzoBODIPY **16** (Fig 4) and benzene-fused bisbenzoBODIPY **10** in almost quantitative yields, respectively. A similar treatment of tetra-ester **12** at 260 °C for 5 h gave benzene-fused bisbenzoBODIPY **9** in a quantitative yield. Contrary to **14**, the thermal treatment of **10** at the first expelling temperature of 175 °C for 1 min gave a mixture of **15** and **9**, probably due to the second extrusion temperature of ethylene being close to the first. Therefore, we abandoned the preparation of pure BCOD-fused bisbenzoBODIPY tetra-ester **15**.



Scheme 4. *Reagents, conditions and yield*: i) see ref 10; ii) DDQ, CH_2Cl_2, rt, 3 h; diisopropylethylamine, rt, 10 min; $BF_3{\cdot}OEt_2$, rt, 30 min; 61%; iii) NaOH; ethylene glycol, 170 °C, 3 h; 89%; $ClSO_2NCO$; DMF/CH_3CN; −50 °C, 1.5 h then rt overnight; 88%; iv) DDQ, toluene, rt, 1 h; triethylamine, rt, 10 min; $BF_3{\cdot}OEt_2$, 80 °C, overnight; 28%.

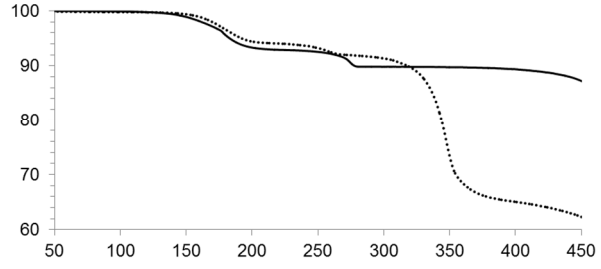


Figure 3. TG experiment of **12** (dotted line) and **14** (solid line) at a rate of 10 °C/min.

Structures of the BCOD- and benzene-fused bisbenzoBODIPYs were determined using X-ray crystallographic analysis. Suitable single crystals of *syn*-**7**, *syn*-**8**, *anti*-**7**·2THF, **14**·$C_2H_4Cl_2$ and **16** were obtained. In all cases, the BODIPY chromophores are almost flat and the mean deviations of twelve BODIPY atoms from their mean planes are less than 0.321(5) Å (the boron atom of *syn*-**7**). The dihedral angles between the mean planes of BCOD-fused BODIPY chromophores vary from 126.21(9)° in *anti*-**7** to 136.75(3)° in **16**. These values are similar to those of BCOD-fused bisporphyrins[22] and bisBODIPYs.[12] In the case of π-fused *syn*-**8**, whole chromophores are almost flat (Fig 5) and a large in-plane distortion is observed in the central benzene ring. Angles of the fused carbons are slightly wider (121.4(3)–122.5(3)°), while those of the unsubstituted carbons are narrower (116.1(3)° and 116.4(3)°). Similar distinctive features have been reported for benzene-fused bisporphyrins[24] and bisBODIPYs.[12]

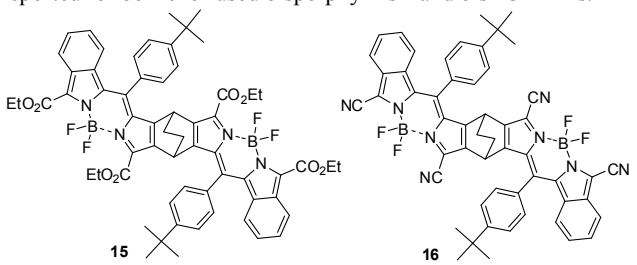


Figure 4. BCOD-fused bisbenzoBODIPY.

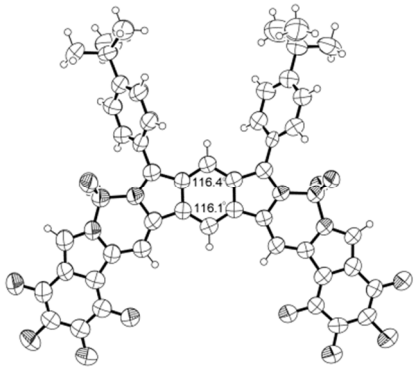


Figure 5. Ortep drawing of *syn*-**8**. Unknown solvent molecules were removed and the BODIPY molecule was refined by the Platon Squeeze technique. Disordered atoms with smaller occupancy are omitted for clarity.

Table 1. UV-vis-NIR and fluorescence spectra of bisBODIPYs in $CHCl_3$

Compound	UV-vis-NIR /nm (ε/10^4 $M^{-1}\cdot cm^{-1}$)				Fluorescence λ_{em} /nm	λ_{ex} /nm	Φ
syn-**7**	420 (1.43)	559	(11.9)	611 (10.5)	624	540	0.41
anti-**7**	384 (1.54)	557[a]	(5.12)	600 (20.8)	609	570	0.28
syn-**8**	562 (5.79)	683	(3.75)	749 (14.3)	755	720	0.16
anti-**8**	599 (1.38)	732	(4.91)	811 (20.6)	819	790	0.13
12	448 (2.57)	520[a]	(5.17)	554 (11.5)	569	500	0.15
15[b]	□	□		585[b]	□[c]	□[c]	□[c]
9	597 (0.91)	796	(3.67)	885 (16.8)	□[d]	□[d]	□[d]
14	462 (3.10)	531[a]	(6.05)	555 (10.3)	571	500	0.01
16	429 (1.62)	557	(5.66)	600 (20.5)	608	540	0.88
10	431 (0.05)[e]	806	(0.15)[e]	903 (1.00)[e]	926[f]	890	0.01

[a] Shoulder peak. [b] This compound was not obtained in a pure form. The UV maximum was measured as a mixture with **9**. [c] Not measured. [d] No fluorescence. [e] Relative intensity. [f] In CH_2Cl_2

Electronic spectra of the bisbenzoBODIPYs were examined. The absorption and fluorescence data are summarized in Table 1 and the spectra of *syn*-**8**, *anti*-**8**, **9** and **10** in CH_2Cl_2 are shown in Fig 6. Only one strong absorption band in the visible-NIR region

was observed for the benzene-fused bisbenzo-BODIPYs (*anti*-**8**, **9** and **10**) with *anti*-geometry. These absorption maxima are in the NIR region (>760 nm); this is particularly evident for **10**, where the absorption tail does not reach the visible region. Contrary to the compounds with *anti*-geometry, *syn*-**8** has another strong band in the visible region at 562 (5.79×10^4 $M^{-1}\cdot cm^{-1}$) nm in addition to the strongest band at 749 (1.43×10^5 $M^{-1}\cdot cm^{-1}$) nm. In the case of the benzene-fused tetra-ester **9**, the molar extinction coefficient of the longest wavelength absorption band (885 nm, 1.68×10^5 $M^{-1}\cdot cm^{-1}$) was smaller than the others ($2.06–2.08 \times 10^5$ $M^{-1}\cdot cm^{-1}$). The full width at half maximum of **9** was 50 nm, while others were far narrower (27 nm for *syn*-**8**, 32 nm for *anti*-**8** and 30 nm for **10**). TD-DFT calculation revealed that the absorptions with the lowest energy consisted of a single HOMO-LUMO transition,[12] and the broadening observed in **9** is ascribed to rotation of the ethyl ester groups.

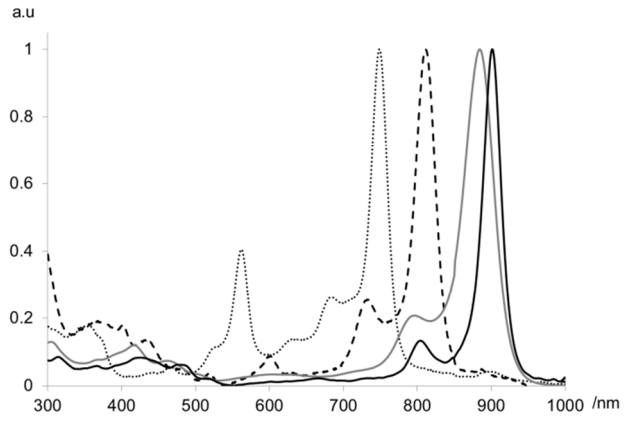


Figure 6. UV-vis-NIR spectra of *syn*-**8** (dotted line), *anti*-**8** (broken line), **9** (grey solid line) and **10** (black solid line)

Benzene-fused derivatives *syn*-**8**, *anti*-**8** and **10** showed obvious fluorescence at 755, 819 and 926 nm with quantum yields of Φ = 0.16, 0.13 and 0.01, respectively, while no fluorescence was observed in **9**. A high quantum yield (Φ = 0.88) was observed in BCOD-fused bisbenzoBODIPY tetra-ester **16**, although the reason for this is unclear. The UV-vis-NIR spectra of **9** and **10** did not change even after irradiation with room lights under aerobic conditions. The stability was also confirmed by cyclic voltammetry (CV). Unfortunately, CV of syn-8, anti-8 and **10** could not be measured due to their poor solubility. The CV of **9** revealed the stability of the benzene-fused bisbenzoBODIPYs. The first half-wave oxidation potential of **9** was 0.44 V (Pt electrodes, *vs* Fc/Fc^+, CH_2Cl_2, tetrabutylammonium hexafluorophosphate; 0.78 V *vs* SCE). The value was a little lower than those of alkyl-substituted BODIPYs (0.95–1.12 V *vs* SCE),[25] comparable to those of sulphur-substituted BODIPYs (0.48–0.68 V *vs* Fc/Fc^+)[26] and higher than that of distyryl-substituted BODIPY (0.50 V *vs* SCE).[27]

Conclusion

We succeeded in the preparation of benzene-fused benzoBODIPY dimers bearing strong absorption and fluorescence in NIR region. These dyes are stable in the presence of oxygen and irradiation with room lights. As the benzene-fused bisbenzoBODIPY with four cyano groups retains good transparency in the visible region, these dyes are thought to be promising selective NIR dye candidates.

Experimental Section

General

Melting points are uncorrected. Unless otherwise specified, NMR spectra were obtained with a JEOL JNM AL-400 spectrometer at ambient temperature using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard for ^1H and ^{13}C. Mass spectra (EI and FAB) were measured with an MStation spectrometer (JEOL MS-700). MALDI-TOF mass spectra were measured on Voyager DE Pro (Applied Biosystems) in VBL, Ehime University by using sinapinic acid as matrix. IR spectra were obtained using a Thermo Scientific Nicolet iS5 FT-IR spectrometer with an iD5 ATR diamond plate. UV-vis and fluorescence spectra were measured using a JASCO V-570 and HITACHI F-4500, respectively. Absolute quantum yields were measured on a Hamamatsu Photonics C9920-02. TG analysis was performed with a SII Exstar 600 TG/DTA 6200. Elemental analysis was performed on a Yanaco MT-5 elemental analyser. X-ray diffraction data was collected using a Rigaku VariMax RAPID (Cu *Ka* radiation, 1.2-kW rotating anode). The X-ray diffraction, NMR, IR, TG and EA measurements were performed in INCS, Ehime University. Preparative GPC was performed using a JAI LC-9801 installed with JAI-1H (Φ 20 × 600 mm) and 2H (Φ 20 × 600 mm) columns. DMF was distilled under reduced pressure and then stored over MS 4Å. Pyridine and DMSO were distilled from CaH_2 and stored over MS 4Å. Other dry solvents were purchased from Kanto Chemical Co. Ethyl isocyanoacetate was kindly provided by The Nippon Synthetic Chemical Industry Co. Ltd.

X-ray crystal structure analysis

Single crystals were prepared by vapour diffusion of isopropanol into a solution of bisBODIPYs in THF, $C_2H_4Cl_2$ or chlorobenzene. The crystals were taken with a Cryoloop and mounted. Determination of cell parameters and collection of reflection intensities were performed using RAPID AUTO software.[28] The data was corrected for Lorentz, polarization and absorption effects. The structures were solved using SIR2004[29] and expanded using the Fourier technique.[30] Hydrogen atoms were placed in calculated positions and refined by using riding models. All calculations were performed using the Crystal-Structure crystallographic software package.[31] Shelxl64[32] was used for structure refinement. The data was validated by the Platon program.[33] Crystallographic data and the Platon validation results are shown in the Supporting Information.

Materials

Diethyl 3,5-di(4-*tert*-butylphenyl)-4,8-dihydro-4,8-ethanopyrrol[3,4-*f*]isoindole-1,7-dicarboxylate (*syn*-5): Benzyltrimethylammonium dichloroiodate (BTMA·ICl_2, 1.20 g, 3.45 mmol) was added to a stirred suspension of *syn*-dipyrrole *syn*-**4** (520 mg, 1.59 mmol) and $CaCO_3$ (500 mg, 5 mmol) in a mixture of CH_2Cl_2 (33 mL) and MeOH (13 mL) at rt. The mixture was refluxed for 4 h. After being cooled to rt, the reaction was quenched by the addition of a saturated Na_2SO_3 solution. The organic layer was separated and the aqueous layer

was extracted with $CHCl_3$. The combined organic extract was washed with water and brine, dried over $NaSO_4$ and concentrated *in vacuo*. The residual syrup was triturated with hexane/methanol (9:1) to give 500 mg (54%) of diethyl 3,5-diiodo-4,8-dihydro-4,8-ethanopyrrol[3,4-*f*]isoindole-1,7-dicarboxylate as a white powder: mp 271 °C (decomp.); ^{1}H NMR δ 1.42 (t, 6H), 1.71 (m, 4H), 3.82 (m, 1H), 4.34 (q, 4H), 5.23 (m, 1H), 8.50 (br, 1H);^{13}C NMR δ 14.8, 27.8, 28.8, 32.5, 60.6, 62.9, 120.2, 136.2, 137.6, 160.8; IR ν_{max} (KBr) 3201, 1658, 1415, 1331, 1230, 1146 cm^{-1}; MS (FAB$^+$) *m/z* 581 (M$^+$+1); HRMS calcd. for $C_{18}H_{18}I_2N_2O_4$+H$^+$: 580.9434, found: 580.9432.

Syn diiodo dipyrrole (100 mg, 0.172 mmol), 4-*tert*-butylphenylboronic acid (62 mg, 0.38 mmol) and $Pd(PPh_3)_4$ (10 mg, 0.009 mmol) were placed in a flask, which was then flashed with argon. Dry toluene (5 mL) was added and the mixture was degassed by Freeze-Pump-Thaw (FPT) cycling. After the addition of degassed 10w% aqueous Na_2CO_3 solution (56 mg, 0.56 mL), the mixture was stirred at 90 °C for 16 h. After being cooled, the mixture was filtered through a Celite pad. The organic layer was separated, washed with water and brine, dried over $NaSO_4$ and concentrated. The residue was chromatographed on silica gel ($CHCl_3$) to give 53 mg (50%) of the title compound as a white powder: mp 280 °C (decomp.); ^{1}H NMR δ 1.36 (s, 18H), 1.44 (t, 6H, J = 7 Hz), 1.76–1.85 (m, 4H), 4.37 (q, 4H, J = 7.0 Hz), 4.86 (m, 1H), 5.35 (m, 1H), 7.45 (m, 8H), 8.44 (br, 2H); ^{13}C NMR δ 14.1, 14.7, 22.6, 27.8, 28.6, 30.8, 34.6, 60.0, 77.1, 114.5, 125.8, 127.6, 128.2, 129.2, 136.6, 150.3, 161.7; IR ν_{max} (KBr) 3287, 2953, 1666, 1265, 1140, 1051 cm^{-1}; MS (FAB$^+$) *m/z* 593(M$^+$+1); HRMS calcd. for $C_{38}H_{44}N_2O_4$+H$^+$: 593.3379, found 593.3345. Anal. Calcd. for $C_{38}H_{44}N_2O_4$ +1/3$CHCl_3$, C, 72.79; H, 7.06; N, 4.43. Found: C, 72.59; H, 6.89; N, 4.25%.

Diethyl 3,7-di(4-*tert*-butylphenyl)-4,8-dihydro-4,8-ethanopyrrol[3,4-*f*]isoindole-1,5-dicarboxylate (*anti*-5): Benzyltrimethylammonium dichloroiodate (BTMA·ICl_2, 1.053 g, 3.03 mmol) was added to a stirred suspension of *anti*-dipyrrole *anti*-**4** (456 mg, 1.39 mmol) and $CaCO_3$ (439 mg, 4.39 mmol) in a mixture of CH_2Cl_2 (29 mL) and MeOH (11 mL) at rt. The mixture was refluxed for 4 h. After being cooled to rt, the reaction was quenched by the addition of a saturated Na_2SO_3 solution. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The combined organic extract was washed with water and brine, dried over $NaSO_4$ and concentrated *in vacuo*. The residue was triturated with hexane/methanol (9:1) to give 500 mg (54%) of diethyl 3,7-diiodo-4,8-dihydro-4,8-ethanopyrrol[3,4-*f*]isoindole-1,5-dicarboxylate as a white powder: mp, 227 °C (decomp.); ^{1}H NMR δ 1.42 (t, 6H, J = 7.0 Hz), 1.70–1.73 (m, 4H), 4.34 (q, 4H, J = 7.0 Hz), 4.54 (m, 2H), 8.35 (br, 2H); ^{13}C NMR δ 14.6, 27.9, 32.2, 60.3, 63.0, 119.5, 136.5, 136.6, 160.3; IR ν_{max} (KBr) 3275, 1674, 1412, 1323, 1207, 1142 cm^{-1}; MS (FAB$^+$) *m/z* 580(M$^+$+1); HRMS (FAB$^+$) calcd. for $C_{18}H_{18}I_2N_2O_4$ +H$^+$: 580.9434, found: 580.9438. Anal. Calcd. for $C_{18}H_{18}I_2N_2O_4$+2/3H_2O +1/6C_6H_{14}: C, 37.26; H, 3.13; N, 4.83. Found: C, 37.78; H, 3.94; N, 4.80%.

Anti diiodo dipyrrole (764 mg, 1.32 mmol), 4-*tert*-butylphenylboronic acid (474 mg, 2.65 mmol) and $Pd(PPh_3)_4$ (76.4 mg, 0.066 mmol) were placed in a flask, which was then flashed with argon. Dry toluene (21 mL) was added and the mixture was degassed by FPT cycling. After the addition of degassed 10w% aqueous Na_2CO_3 solution (430 mg, 4.3 mL), the mixture was stirred at 90 °C for 16 h. After being cooled, the mixture was filtered through a Celite pad. The organic layer was separated, washed with water and brine, dried over $NaSO_4$, and concentrated. The residue was chromatographed on silica gel ($CHCl_3$) to give 513 mg (66%) of the title compound as a white powder: mp >300 °C (decomp.); ^{1}H NMR δ 1.36 (s, 18H), 1.44 (t, 6H, J = 7 Hz), 1.76–1.79 (m, 4H), 4.43–4.45 (m, 4H), 5.15 (m, 2H), 7.45–7.55 (m, 8H), 8.42 (br, 2H); ^{13}C NMR δ 14.3,31.0, 31.1, 31.3, 34.5, 59.9, 114.0, 125.8, 127.7, 128.1, 129.0, 137.8, 150.4, 161.6; IR ν_{max} (KBr) 3305, 2958, 1673, 1288, 1257 cm^{-1}; MS (FAB$^+$) *m/z* 593 (M$^+$ +1); HRMS calcd. for $C_{38}H_{44}N_2O_4$ +H$^+$: 593.3379, found: 593.3372. Anal. Calcd. for $C_{38}H_{44}N_2O_4$ +1/3$CHCl_3$: C, 72.79; H, 7.06; N, 4.43. Found: C, 72.61; H, 6.79; N, 4.12%.

1,7-Di(4-*tert*-butylphenyl)-4,8-dihydro-4,8-ethanopyrrol[3,4-*f*]isoindole (*syn*-6): A mixture of *syn*-**5** (50 mg, 0.084 mmol) and NaOH (90 mg, 2.25 mmol) in ethylene glycol (4 mL) was stirred and heated at 160 °C for 2 h under nitrogen. After being cooled to rt, the mixture was diluted with water and extracted with ethyl acetate. The organic extract was washed with water and brine, dried over Na_2SO_4 and concentrated. The residue was washed with hexane to give 53 mg (50%) of the title compound, which was used without further purification: ^{1}H NMR δ 1.36 (s, 18H), 1.80 (m, 4H), 4.26 (m, 1H), 4.88 (m, 1H), 6.56 (m, 2H), 7.38–7.47 (m, 8H), 7.57 (br, 2H); ^{13}C NMR δ 30.0, 31.0, 30.9, 31.3, 34.4, 52.4, 108.4, 123.2, 125.0, 125.6, 126.4, 130.9, 131.2, 148.3; IR ν_{max} (KBr) 3395, 2955, 1435, 1160, 1074, 830 cm^{-1}; MS (FAB$^+$) *m/z* 449 (M$^+$ +1), 448 (M$^+$), 420 (M$^+$ −C_2H_4); HRMS calcd. for $C_{38}H_{44}N_2O_4$ +H$^+$: 449.2957, found: 449.2962.

1,5-Di(4-*tert*-butylphenyl)-4,8-dihydro-4,8-ethanopyrrol[3,4-*f*]isoindole (*anti*-6): A mixture of anti-**5** (140 mg, 0.24 mmol) and NaOH (250 mg, 6.25 mmol) in ethylene glycol (11 mL) was stirred and heated at 160 °C for 2 h under nitrogen. After being cooled to rt, the mixture was diluted with water. The mixture was extracted with ethyl acetate. The organic extract was washed with water and brine, dried over Na_2SO_4 and concentrated. The residue was washed with hexane to give 80 mg (74%) of the title compound, which was used without further purification: white solid; ^{1}H NMR δ 1.35(s, 18H), 1.82 (m, 4H), 4.56 (m, 2H), 6.55 (m, 2H), 7.41 (m, 8H), 7.59 (br, 2H); ^{13}C NMR δ 29.8, 31.0, 31.4, 34.5, 108.6, 123.1, 125.2, 125.6, 126.7, 131.0, 131.2, 148.5; IR ν_{max} (KBr) 3432, 2952, 1527, 1163, 833, 752 cm^{-1}; MS (FAB$^+$) *m/z* 449 (M$^+$+1), 448 (M$^+$), 420 (M$^+$−C_2H_4); HRMS calcd. for $C_{38}H_{44}N_2O_4$ +H$^+$: 449.2957, found 449.2941. Anal. Calcd. for $C_{32}H_{36}N_2$ +H_2O: C, 82.36; H, 8.21; N, 6.00. Found: C, 82.50; H, 7.90; N, 6.08%.

7,9-Di(4-*tert*-butylphenyl)-1,2,3,4,12,13,14,15-octafluoro-8,17-dihydro-8,17-ethano-6,10-dibora-5a,6a,9a,10a-tetraaza-*s*-indaceno[2,3-*b*:6,5-*b′*]difluorene (*syn*-7): $POCl_3$ (0.1 mL, 1 mmol) was added to a stirred solution of *syn*-**6** (90 mg, 0.20 mmol) and 4,5,6,7-tetrafluoroisoindole-1-carbaldehyde (70 mg, 0.32 mmol) in dry CH_2Cl_2 (20 ml) at rt and in the dark. After the mixture was stirred at rt for 12 h, diisopropylethylamine (0.2 mL, 1.1 mmol) was added and stirred at rt for 1 h. Then BF_3·OEt_2 (0.14 mL, 1.1 mmol) was added and the mixture was further stirred at rt for 5 h. The reaction was quenched with water and the mixture was filtered through a Celite pad, which was washed with ethyl acetate. The organic phase was separated and the

aqueous phase was extracted with ethyl acetate. The organic extract was washed with aqueous saturated $NaHCO_3$, water and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was chromatographed on silica gel (CH_2Cl_2/ hexane) to give 29 mg (19%) of the title compound as a purple solid: mp 250 °C (decomp.); ^{1}H NMR δ 1.38 (s, 18H), 1.84 (m, 2H), 2.01 (m, 2H), 4.48 (m, 1H), 4.94 (m, 1H), 7.45 (m, 4H), 7.58 (m, 4H), 7.80 (s 2H), 8.32 (s 2H); ^{13}C NMR (typical signals) δ 28.4, 29.7, 31.3, 31.8, 35.0, 53.4, 125.3, 127.6, 129.2, 135.3, 139.4, 151.7, 153.1, 155.2, 159.3, 174.0, 181.2, 182.3, 186.6; ^{19}F NMR δ −136.1 (m, 2F), −138.4 (m, 2F), −141.9 (m, 2F), −146.4 (m, 2F), −151.1 (m, 2F), −158.7 (m, 2F); IR ν_{max} (KBr) 2959, 1485, 1233, 1194, 1116, 1027 cm^{-1}; UV-vis-NIR ($CHCl_3$) λ_{max} (ε/10^4 M^{-1}·cm^{-1}) 420 (1.43), 559 (11.9), 611 (10.5) nm; Fluorescence ($CHCl_3$) λ_{em} 624 nm (λ_{ex} 540 nm, Φ = 0.41); MS (FAB$^+$) *m/z* 915 (M$^+$ −C_2H_4 + 1), 914 (M$^+$ −C_2H_4); HRMS (FAB$^+$) calcd. for $C_{50}H_{36}B_2F_{12}N_4$ −C_2H_4 +H$^+$: 915.2700, found 915.2689. Anal. Calcd. for $C_{50}H_{36}B_2F_{12}N_4$ +C_6H_{14}: C, 65.39; H, 4.90; N, 5.45. Found: C, 65.76; H, 4.55; N, 5.09%.

7,16-Di(4-*tert*-butylphenyl)-1,2,3,4,10,11,12,13-octafluoro-8,17-dihydro-8,17-ethano-6,15-dibora-5a,6a,14a,15a-tetraaza-*s*-indaceno[2,3-*b*:6,7-*b′*]difluorene (*anti*-7): $POCl_3$ (0.3 mL, 3 mmol) was added to a stirred solution of *anti*-**6** (200 mg, 0.45 mmol) and 4,5,6,7-tetrafluoroisoindole-1-carbaldehyde (200 mg, 0.92 mmol) in dry toluene (40 ml) at rt in the dark. After the mixture was stirred at rt for 12 h, diisopropylethylamine (0.6 mL, 3.3 mmol) was added and stirred at rt for 1 h. Then BF_3·OEt_2 (0.42 mL, 3.3 mmol) was added and the mixture was further stirred at rt for 5 h. The reaction was quenched with water and the mixture was filtered through a Celite pad, which was washed with ethyl acetate. The organic phase was separated and the aqueous phase was extracted with ethyl acetate. The organic extract was washed with aqueous saturated $NaHCO_3$, water and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was chromatographed on silica gel (CH_2Cl_2/ hexane) to give 75 mg (18%) of the title compound as a purple solid: mp 250 °C (decomp.); ^{1}H NMR δ 1.43 (s, 18H), 1.88 (m, 2H), 1.99 (m, 2H) 4,72 (m, 2H), 7.62 (m 4H), 7.68 (m, 2H), 7.74 (m, 4H), 8,31 (m, 2H); ^{13}C NMR (typical signals) δ 28.6, 31.3, 32.2, 35.1, 123.1, 125.5, 127.8, 129.1, 129.2, 135.3, 136.9, 151.6, 152.0, 153.2, 164.7, 164.9, 182.7; ^{19}F NMR δ −136.1 (m, 2F), −138.2 (m, 2F), −142.2 (m, 2F), −146.4 (m, 2F), −151.4 (m, 2F), −159.0 (m, 2F); IR ν_{max} (KBr) 2961, 1462, 1232, 1109, 1025, 1008 cm^{-1}; UV-vis-NIR ($CHCl_3$) λ_{max} (ε/10^4 M^{-1}·cm^{-1}) 384 (1.54), 557 (5.12), 600 (20.8) nm; Fluorescence ($CHCl_3$) λ_{em} 609 nm (λ_{ex} 570 nm, Φ = 0.28); MS (FAB$^+$) *m/z* 915 (M$^+$ −C_2H_4 +1), 914 (M$^+$ −C_2H_4); HRMS (FAB$^+$) calcd. for $C_{50}H_{36}B_2F_{12}N_4$ −C_2H_4 +H$^+$: 915.2700, found: 915.2719. Anal. Calcd. for $C_{50}H_{36}B_2F_{12}N_4$ +1/4C_6H_{14} +1/2H_2O: C, 63.57; H, 4.20; N, 5.76. Found: C, 63.49; H, 4.57; N, 5.39%.

7,9-Di(4-*tert*-butylphenyl)-1,2,3,4,12,13,14,15-octafluoro-6,10-dibora-5a,6a,9a,10a-tetraaza-*s*-indaceno[2,3-*b*:6,5-*b′*]difluorene (*syn*-8): *Syn*-**7** (8.1 mg, 8.6 µmol) was weighed in a micro-tube, which was placed in a 30-mL round-bottomed flask. The flask was evacuated using a rotary oil pump and placed in a pre-heated (250 °C) glass-tube oven for 2 h. After being cooled, the micro-tube was taken out and weighed (7.9 mg, quantitative). The black solid was taken up by hexane and dried *in vacuo*: ^{1}H NMR δ 1.34 (s, 18H), 7.56 (m, 4H), 7.76 (m, 4H), 7.91 (m, 2H), 8.02 (m, 2H), 8.39 (m, 2H); ^{19}F NMR δ −134.7 (m, 4F), −144.1 (m, 2F), −148.3 (m, 2F), −154.5 (m, 2F), −161.0 (m, 2F); IR ν_{max} (KBr) 2963, 1481, 1244, 1191, 983 cm^{-1}; UV-vis-NIR ($CHCl_3$) λ_{max} (ε/10^4 M^{-1}·cm^{-1}) 562 (5.79), 683 (3.75), 749 (14.3) nm; Fluorescence ($CHCl_3$) λ_{em} 755 nm (λ_{ex} 720 nm, Φ = 0.16); MS (FAB$^+$) *m/z* 915 (M$^+$+1); HRMS calcd. for $C_{48}H_{32}B_2F_{12}N_4$: 915.2700, found: 915.2710. Anal. Calcd. for $C_{48}H_{32}B_2F_{12}N_4$ +2/3C_6H_{14}: C, 64.26; H, 4.29; N, 5.76. Found: C, 64.43; H, 4.20; N, 6.01%.

7,16-Di(4-*tert*-butylphenyl)-1,2,3,4,10,11,12,13-octafluoro-6,15-dibora-5a,6a,14a,15a-tetraaza-*s*-indaceno[2,3-*b*:6,7-*b′*]difluorene (*anti*-8): *Anti*-**7** (5.4 mg, 5.7 µmol) was weighed in a micro-tube, which was placed in a 30-mL round-bottomed flask. The flask was evacuated using a rotary oil pump and placed in a pre-heated (250 °C) glass-tube oven for 2 h. After being cooled, the micro-tube was taken out and weighed (5.2 mg, quantitative) yielding a black solid, mp >350 °C; ^{1}H NMR δ 1.42 (s, 18H), 7.68 (m, 4H), 7.78 (m, 2H), 7.87 (m, 4H), 8.03 (m, 2H), 8.23 (m, 2H); ^{19}F NMR δ −135.1 (m, 4F), −144.1 (m, 2F), −148.3 (m, 2F), −154.7 (m, 2F), −161.1 (m, 2F); IR ν_{max} (KBr) 2963, 1480, 1182, 1150, 1082, 984 cm^{-1}; UV-vis-NIR ($CHCl_3$) λ_{max} (ε/10^4 M^{-1}·cm^{-1}) 599 (1.38), 732 (4.91), 811 (20.6) nm; Fluorescence ($CHCl_3$) λ_{em} 819 nm (λ_{ex} 790 nm, Φ = 0.13); MS (FAB$^+$) *m/z* 915 (M$^+$ +1); HRMS (FAB$^+$) calcd. for $C_{48}H_{32}B_2F_{12}N_4$: 915.2700, found: 915.2711. Anal. Calcd. for $C_{48}H_{32}B_2F_{12}N_4$: C, 63.05; H, 3.53; N, 6.13. Found: C, 62.83; H, 3.77; N, 6.14%.

Tetraethyl 9,18-di(4-*tert*-butylphenyl)-1,4,8,10,13,17-hexahydro-1,4:8,17:10,13-triethano-6,15-dibora-5a,6a,14a,15a-tetraaza-*s*-indaceno[2,3-*b*:6,7-*b′*]difluorene-5,7,14,16-tetracarboxylate (12): DDQ (0.176 g, 0.775 mmol) was added to a stirred solution of BCOD-fused dipyrromethane **11** (0.402 g, 0.382 mmol) in dry CH_2Cl_2 (4 mL) at rt in the dark and the mixture was stirred for 3 h. Diisopropylethylamine (0.95 mL, 5.59 mmol) was added and the mixture was stirred at rt for 10 min. BF_3·OEt_2 (0.7 mL, 5.67 mmol) was then added. After the mixture was stirred at rt for 30 min, water was added. The mixture was extracted with $CHCl_3$. The organic extract was washed with aqueous saturated $NaHCO_3$, water and brine, dried over Na_2SO_4 and concentrated. The residue was chromatographed on silica gel (40% EtOAc/hexane,). The eluate (Rf = 0.47) was concentrated and the resulting solid was recrystallized from $CHCl_3$/hexane to give 0.267 g (61%) of the title compound as an orange powdery solid: ^{1}H NMR δ 7.61 (m, 4H), 7,29 (m, 4H), 6.39 (m, 2H), 6.05 (m, 2H), 4.49–4.32 (m, 8H), 4.30 (m, 2H), 3.51 (s, 2H), 2.51 (s, 2H), 1.48 (s, 18H), 1.45–1.40 (m, 12H), 1.40–1.05 (m, 12H); ^{13}C NMR δ 160.93, 160.91, 160.76, 160.72, 154.05, 153.81, 151.49, 149.21, 142.57, 139.89, 138.68, 138.48, 135.88, 135.81, 133.65, 130.83, 130.43, 129.76, 128.47, 128.08, 127.64, 126.05, 125.89, 125.21, 61.56, 61.50, 35.46, 35.06, 34.08, 34.03, 32.76, 31.33, 27.05, 25.79, 25.74, 25.65, 25.57, 14.11, 14.06; IR (KBr) ν_{max} 2962, 1701, 1558, 1111 cm^{-1}; UV-vis-NIR ($CHCl_3$) λ_{max} (ε/10^4 M^{-1}·cm^{-1}) 448 (2.69), 520 (5.17 sh), 553 (11.5) nm; Fluorescence ($CHCl_3$) λ_{em} 569 nm (λ_{ex} 540 nm, Φ = 0.15); HRMS (FAB$^+$) calcd. for $C_{66}H_{68}B_2F_4N_4O_8$ +H$^+$, 1143.5238. Found: 1143.5247. Anal. Calcd. for $C_{66}H_{68}B_2F_4N_4O_8$ +1/2$CHCl_3$: C, 66.42; H, 5.74; N, 4.66. Found: C, 66.25; H, 5.68; N, 4.54%.

1,5-Dicyano-3,7-bis[(3-cyano-4,7-dihydro-4,7-ethano-2*H*-

isoindolyl)(4-*tert*-butylphenyl)methyl]-4,8-dihydro-4,8-ethanopyrrol[3,4-*f*]isoindole (13): A mixture of bisdipyrromethane tera-ester **11** (0.526 g, 0.500 mmol) and NaOH (0.32 g 8.00 mmol) in ethylene glycol (10 mL) was heated at 170 °C for 3 h under argon in the dark. After being cooled to rt, the mixture was diluted with water and extracted with ethyl acetate. The organic extract was washed with water and brine, dried over Na_2SO_4 and concentrated. The residue was chromatographed on silica gel (40% EtOAc/hexane). The eluate (Rf = 0.74) was collected to give 0.341 g (89%) of 13,7-bis[(4,7-dihydro-4,7-ethano-2*H*-isoindolyl)(4-*tert*-butyl-phenyl)methyl]-4,8-dihydro-4,8-ethanopyrrol[3,4-*f*]isoindole as a black powdery solid, which was used in the next step without further purification: ^{1}H NMR (CD_2Cl_2) δ 7.33–6.89 (m, 12H), 6.38–6.06 (m, 8H), 5.34 (m, 2H), 3.65 (s, 2H), 3.27 (m, 2H), 2.99 (s, 2H), 1.50–1.34 (m, 12H), 1.23 (m, 18H); IR (KBr) ν_{max} 3394, 2951, 2862, 1508 cm^{-1}; HRMS (FAB$^+$) calcd. for $C_{54}H_{58}N_4$ +H$^+$, 763.4740. Found: 763.4740.

A solution of chlorosulfonyl isocyanate in CH_3CN (1.97 mmol in 2 mL) was added to a stirred solution of the above bisdipyrromethane (0.341 g, 0.447 mmol) in dry DMF (11 mL) and dry CH_3CN (4.5 mL) at −50 °C under argon. After being stirred for 1.5, the mixture was warmed to rt and then further stirred overnight. The reaction was quenched with water and the mixture was extracted with EtOAc. The organic extract was washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (40% EtOAc/hexane). The eluate (Rf = 0.46) was collected to give 0.342 g (88%) of the title compound as a brown solid, which was used in the next step without further purification: ^{1}H NMR δ 8.16–7.77 (m, 4H), 7.41 (m, 4H), 7.05 (m, 4H), 6.53–6.20 (m, 4H), 5.51 (m, 2H), 4.01 (s, 2H), 3.86–3.70 (m, 2H), 3.34–2.93 (m, 2H), 1.64–1.41 (m, 12H), 1.34 (m, 18H); IR (KBr) ν_{max} 3275, 2958, 2866, 2210, 1508 cm^{-1}; HRMS (FAB$^+$) calcd. for $C_{58}H_{54}N_8$ +H$^+$, 863.4550. Found: 863.4547.

9,18-Di(4-*tert*-butylphenyl)-5,7,14,16-tetracyano-1,4,8,10,13,17-hexahydro-1,4:8,17:10,13-triethano-6,15-dibora-5a,6a,14a,15a-tetraaza-s-indaceno[2,3-*b*:6,7-*b′*]difluorene (14): A mixture of **13** (0.342 g, 0.396 mmol) and DDQ (0.181 g, 0.797 mmol) in dry toluene (15 mL) was stirred at rt for 1 h in the dark and then dry Et_3N (2.0 mL, 14.3 mmol) was added with stirring. After 10 min, $BF_3{\cdot}OEt_2$ (0.7 mL, 5.67 mmol) was added and the mixture was heated at 80 °C overnight. After being cooled to rt, the mixture was quenched with water. The mixture was extracted with EtOAc. The organic extract was washed with water and brine, dried over Na_2SO_4 and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2) and the eluate (Rf = 0.33) was collected and concentrated. The residual solid was recrystallized from $CHCl_3$/hexane to give 0.267 g (61%) of the title compound as orange crystals: mp 165 °C (decomp.); ^{1}H NMR δ 7.90 (br-s, 2H), 7.68 (br-s, 2H), 7.36 (m, 4H), 6.45 (m, 2H), 6.16 (m, 2H), 4.14 (m, 2H), 3.17 (m, 2H), 2.98 (m, 2H), 1.48 (s,18H), 1.47–1.15 (m, 12H); ^{13}C NMR δ 156.72, 156.56, 156.22, 156.21, 156.17, 150.46, 150.32, 150.29, 146.25, 146.05, 142.22, 142.15, 135.25, 134.98, 133.72, 133.37, 131.90, 131.84, 130.84, 128.52, 128.48, 128.27, 127.99, 127.69, 127.38, 125.77, 120.51, 120.45, 116.60, 116.55, 111.09, 110.77, 110.70, 36.13, 36.03, 35.43, 35.42, 33.36, 33.31, 32.53, 32.45 31.24, 26.92, 26.87, 26.81, 25.69, 25.57; IR (KBr) ν_{max} 2962, 2225, 1543, 1176 cm^{-1}; UV-vis-NIR ($CHCl_3$) λ_{max} (ε/10^4 M$^{-1}{\cdot}$cm^{-1}) 462 (3.10), 531 (6.05, sh), 555 (10.2) nm; Fluorescence ($CHCl_3$) λ_{max} 571 nm (Φ = 0.014); HRMS (FAB$^+$) Calcd. for $C_{58}H_{48}B_2F_4N_8$ +H$^+$, 955.4197. Found: 955.4201. Anal. Calcd. for $C_{58}H_{48}B_2F_4N_8$ +1/5hexane: C, 73.16; H, 5.27; N, 11.53. Found: C, 73.15; H, 5.26; N, 11.48%.

Tetraethyl 9,18-di(4-*tert*-butylphenyl)-6,15-dibora-5a,6a,14a,15a-tetraaza-*s*-indaceno[2,3-*b*:6,7-*b′*]difluorene-5,7,14,16-tetracarboxylate (9): BCOD-fused bisBODIPY **12** (22.9 mg, 20.0 μmol) was weighed in a micro-tube, which was placed in a 30-mL round-bottomed flask. The flask was evacuated using a rotary oil pump and placed in a glass-tube oven. The oven was heated at 175 °C for 1 h and then cooled to rt. A small amount of the sample was taken and monitored in the UV-vis-NIR regions. As the absorption due to fully conjugated bisbenzoBODIPY **9** in addition to **15** appeared, the sample was further heated at 250 °C for 1 h. After being cooled, the micro-tube was taken out and weighed (21.0 mg, 99%): a black solid, mp 333 °C (decomp.); ^{1}H NMR δ 8.13 (m, 2H), 7.76 (m, 4H), 7.44 (m, 4H), 7.20 (s, 2H), 7.04 (m, 2H), 6.13 (m, 2H), 4.57 (q, J = 6.8 Hz, 4H), 4.47 (q, J = 6.8 Hz, 4H), 1.57 (s, 18H), 1.54 (m, 12H); IR (KBr) ν_{max} 2961, 1712, 1307, 1166, 1129, 1082 cm^{-1}; UV-vis-NIR ($CHCl_3$) λ_{max} (ε/10^4 M$^{-1}{\cdot}$cm^{-1}) 597 (0.91), 796 (3.67), 885 (16.8) nm; HRMS (FAB$^+$) calcd. for $C_{60}H_{56}B_2F_4N_4O_8$ +H$^+$: 1059.4299. Found: 1059.4301. Anal. Calcd. for $C_{60}H_{56}B_2F_4N_4O_8$ +1/2H_2O: C, 67.49; H, 5.38; N, 5.25. Found: C, 67.41; H, 5.35; N, 5.27%.

9,18-Di(4-*tert*-butylphenyl)-5,7,14,16-tetracyano-8,17-dihydro-8,17-ethano-6,15-dibora-5a,6a,14a,15a-tetraaza-*s*-indaceno[2,3-*b*:6,7-*b′*]difluorene (16): BCOD-fused tetracyano bisBODIPY **14** (4.8 mg, 5.0 μmol) was weighed in a micro-tube, which was placed in a 30-mL round-bottomed flask. The flask was evacuated using a rotary oil pump and placed in a glass-tube oven. The oven was heated at 170 °C for 2 h and then cooled to rt. After being cooled, the micro-tube was taken out and weighed (3.8 mg, 84%) yielding a dark gold solid: mp 268 °C (decomp.); ^{1}H NMR (CD_2Cl_2) δ 7.87 (m, 4H), 7.67 (m, 2H), 7.45 (m, 2H), 7.40–7.31 (m, 6H), 6.60 (m, 2H), 2.93 (s, 2H), 1.44 (s,18H), 1.36 (br-s, 4H); ^{13}C NMR (CD_2Cl_2) δ 155.6, 147.5, 145.4, 142.4, 135.9, 133.7, 132.9, 130.6, 129.4, 129.1, 128.2, 127.9, 127.7, 126.8, 123.6, 123.2, 112.4, 111.7, 110.7, 35.6, 32.4, 31.5, 27.2; IR (KBr) ν_{max} 2958, 2222, 1558, 1311 cm^{-1}; UV-vis-NIR ($CHCl_3$) λ_{max} (ε/10^4 M$^{-1}{\cdot}$cm^{-1}) 429 (1.62), 557 (5.66), 600 (20.5) nm; Fluorescence (CH_2Cl_2) λ_{max} 608 nm (Φ = 0.88); HRMS (FAB$^+$) calcd. for $C_{54}H_{40}B_2F_4N_8$ +H$^+$: 899.3571. Found: 899.3571.

9,18-Di(4-*tert*-butylphenyl)-5,7,14,16-tetracyano-6,15-dibora-5a,6a,14a,15a-tetraaza-*s*-indaceno[2,3-*b*:6,7-*b′*]difluorene (10): BCOD-fused tetracyano bisBODIPY **14** (4.9 mg, 5.1 μmol) was weighed in a micro-tube, which was placed in a 30-mL round-bottomed flask. The flask was evacuated using a rotary oil pump and placed in a glass-tube oven. The oven was heated at 260 °C for 5 h and then cooled to rt. After being cooled, the micro-tube was taken out. The dark black powder was weighed (4.4 mg, 100%). When the powder was dissolved in $CHCl_3$, the solution was yellow: UV-vis-NIR ($CHCl_3$) λ_{max} (rel. intensity) 431 (0.05), 806 (0.33), 903 (1.00) nm; Fluorescence (CH_2Cl_2) λ_{max} 926 nm (Φ = 0.01); HRMS (FAB$^+$) calcd. for $C_{52}H_{36}B_2F_4N_8$

$+H^+$: 871.3258. Found: 871.3273.

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ARTICLE TYPE

Graphical abstract

Stable benzene-fused bisbenzoBODIPY with four cyano groups is ideal for a NIR-selective dye, which shows strong absorption in NIR region and good transparency in the visible region.