Supporting Information

π-Fused bis-BODIPY as a candidate for NIR dyes

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Experimental Procedure

General: Melting points are uncorrected. Unless otherwise specified, NMR spectra were obtained with a JEOL JNM AL-400 spectrometer at ambient temperature by 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 Voyger DE Pro (Applied Biosystems) in VBL, Ehime University by using sinapinic acid as matrix. IR spectra were measured with a Horiba FT-720 spectrophotometor. UV-vis and fluorescence spectra were measured on JASCO V-570 and HITACHI F-4500, respectively. Absolute quantum yields were measured on a Hamamatsu Photonics C9920-02. TG analysis was done with SII Exstar 600 TG/DTA 6200. Elemental analysis was performed on a Yanaco MT-5 elemental analyzer. X-ray diffraction data were collected by Rigaku Mercury-8 (Mo *Ka* radiation, 3-kW sealed tube), Rigaku VariMax Saturn (Mo *Ka* radiation, 1.2-kW rotating anode), or 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 done by a JAI LC-9801 installed with JAI-1H (Φ20 x 600 mm) and 2H (Φ20 x 600 mm) columns.

Diethyl 3,5-bis(5-ethoxycarbonyl-3,4-diethylpyrrol-2-ylmethyl)-4,8-dihydro-4,8-ethanopyrrolo[3,4-*f*]isoindole-1,7-dicarboxylate (*syn*-**4a**): The reaction of ethyl 5-acetoxylmethyl-3,4-diethylpyrrole-1-carboxylate (**3a**; 0.900 g, 3.37 mmol), and diethyl 4,8-dihydro-4,8-ethanopyrrolo[3,4-*f*]isoindole-1,7-dicarboxylate (*syn*-**2**; 0.500 g, 1.52 mmol) gave 0.615 g (54%) of the title compound as a white powder: mp, 130–132 °C; ^1H NMR δ 8.89 (br s, 2H) , 8.40 (br s, 2H), 5.20 (m, 1H), 4.21–4.33 (m, 8H), 3.85 (m, 4H), 3.66 (m, 1H), 2.72 (m, 4H), 2.39 (m, 4H), 1.72 (m, 2H), 1.59 (m, 2H), 1.37 (t, 6H, *J* = 7.1 Hz), 1.27 (t, 6H, *J* = 7.1 Hz), 1.15 (t, 6H, *J* = 7.6 Hz), 1.06 (t, 6H, *J* = 7.6 Hz); ^{13}C NMR: δ 162.03, 161.46, 136.24, 133.55, 129.20, 128.43, 124.20, 123.27, 116.95, 113.56, 60.02, 59.75, 31.91, 29.04, 28.81, 27.78, 23.06, 18.40, 17.03, 16.31, 15.85, 14.53, 14.37; IR (KBr): ν_{max}, 3316, 1674, 1442, 1257 cm^{-1}; MS (FAB^+): *m/z* 743 (M^++1). Anal. Calcd for $C_{42}H_{54}N_4O_8$: C, 67.90; H, 7.33; N, 7.54. Found: C, 67.67; H, 7.23; N, 7.42.

Diethyl 3,5-bis(3-ethoxycarbonyl-4,7-dihydro-4,7-ethano-2*H*-isoindolylmethyl)-4,8-dihydro-4,8-ethanopyrrolo[3,4-*f*]isoindole-1,7-dicarboxylate (*syn*-**4b**): The reaction of ethyl 3-acetoxylmethyl-4,7-dihydro-4,7-ethano-*2H*-isoindole-1-carboxylate (**3b**; 2.35 g, 8.13 mmol) and *syn*-**2** (1.33 g, 4.05 mmol) gave 1.95 g (61%) of the title compound as a diastereomeric mixture: white powder; mp, 180 – 181 °C (decomp.); ^1H NMR: δ 9.47 (m, 4H), 6.47 (m, 4H), 5.19 (m, 1H), 4.35 (m, 4H), 4.26 (m, 8H), 3.90 (m, 4H), 3.71 (m, 1H), 1.53 (m, 12H), 1.37 (m, 12H); ^{13}C NMR (typical signals): δ 171.41, 162.63, 137.52, 136.45, 136.08, 135.37, 131.66, 128.44, 121.71, 115.16, 113.49, 112.72, 60.07, 56.90, 56.20, 33.94, 32.41, 31.86, 28.97, 27.85, 27.03, 26.28, 23.07, 20.94, 14.51; IR (KBr): ν_{max}, 3309, 2946, 1674 cm^{-1}; MS (FAB): *m/z* 787 (M^++1); HRMS (FAB^+): Calcd for $C_{46}H_{50}N_4O_8$+H^+, 787.3707; Found: 787.3714.

Diethyl 3,7-bis(3-ethoxycarbonyl-4,7-dihydro-4,7-ethano-2*H*-isoindolylmethyl)-4,8-dihydro-4,8-ethanopyrrolo[3,4-*f*]isoindole-1,5-dicarboxylate (*anti*-**4b**): The reaction of **3b** (2.35 g, 8.13 mmol) with *syn*-**2** (1.33 g, 4.05 mmol) afforded 2.13 g (72%) of the title compound as a diastereomeric mixture: white powder; mp, 181–183 °C (decomp.); ^1H NMR (DMSO-d_6): δ 10.69 (m, 4H), 6.36 (m, 2H), 6.24 (m, 2H), 4.78 (m, 2H), 4.60 (m, 2H), 4.28 (m, 2H), 4.18 (m, 8H), 3.60 (m, 4H), 1.47 (m, 8H), 1.35 (m, 12H), 1.12 (m, 4H); ^{13}C NMR (DMSO-d_6; typical signals): δ 216.71, 210.59, 201.60, 161.82, 137.04, 135.55, 128.51, 125.84, 120.36, 119.67, 118.09, 113.64, 65.84, 59.94, 59.73, 34.55, 32.98, 32.27, 31.20, 30.55, 27.45, 26.98, 23.25; IR (KBr): ν_{max}, 3309, 2978, 1666 cm^{-1}; MS (FAB^+): *m/z* 787 (M^++1), 786 (M^+); HRMS (FAB^+): Calcd for $C_{46}H_{50}N_4O_8$+H^+, 787.3707. Found: 787.3695.

1,7-Dimethyl-3,5-bis(3,4-diethyl-5-methylpyrrol-2-ylmethyl)-4,8-dihydro-4,8-ethanopyrrolo[3,4-*f*]isoindole (*syn*-**5a**): Tetra ester *syn*-**4a** (0.615 g, 0.827 mmol) was reduced with $LiAlH_4$ to give 0.406 g (96%) of the title compound as a pale yellow powder: ^1H NMR: δ 7.26 (br s, 2H), 6.85 (br s, 2H), 3.98 (m, 1H), 3.79 (m, 4H), 3.76 (m, 1H), 2.36–2.44 (m, 8H), 2.15 (s, 6H), 2.08 (s, 6H), 1.62–1.70 (m, 4H), 1.11 (t, 6H, *J* = 7.6 Hz), 1.09 (t, 6H, *J* = 7.6 Hz); ^{13}C NMR: δ 126.44, 125.80, 121.97, 120.98, 120.27, 119.85, 116.58,

115.70, 30.23, 30.07, 28.94, 28.77, 22.70, 17.62, 17.55, 16.79, 16.40, 11.19, 11.07; IR (KBr): 3371, 2962, 2931, 2862 cm^{-1}; MS (FAB^+): *m/z* 511 (M^++1), 510 (M^+), 509 (M^+−1); HRMS (FAB^+): $C_{34}H_{46}N_4$+H^+, 511.3801. Found: 511.3777.

1,7-Dimethyl-3,5-bis(3-methyl-4,7-dihydro-4,7-ethano-2*H*-isoindolylmethyl)-4,8-dihydro-4,8-ethanopyrrolo[3,4-*f*]isoindole (*syn*-**5b**): *syn*-Bis-dipyrromethane tetra ester *syn*-**4b** (3.41 g, 4.33 mmol) was reduced to give 1.55 g (65%) of the crude title compound as a mixture of diastereomers: brown powder; ^{1}H NMR: δ 10.69 (m, 4H), 6.36 (m, 2H), 6.24 (m, 2H), 4.78 (m, 1H), 4.60 (m, 1H), 4.28 (m, 2H), 3.75 (m, 4H), 3.60 (m, 2H), 1.47 (m, 8H), 1.35 (m, 6H), 1.27 (m, 6H), 1.12 (m, 4H); MS (FAB^+): *m/z* 555 ($M+1^+$), 554(M^+) ; HRMS (FAB^+): $C_{38}H_{42}N_4$+H^+, 555.3488. Found 555.3493.

1,5-Dimethyl-3,7-bis(3-methyl-4,7-dihydro-4,7-ethano-2*H*-isoindolylmethyl)-4,8-dihydro-4,8-ethanopyrrolo[3,4-*f*]isoindole (*anti*-**5b**): *anti*-Bis-dipyrromethane tetra ester *anti*-**4b** (2.123 g, 2.70 mmol) was converted to give 1.227 g (82%) of the crude title compound as a mixture of diastereomers; brown powder; ^{1}H NMR: δ 6.85 (m, 4H), 6.38 (m, 4H), 3.77 (m, 2H), 3.75 (m, 4H), 3.62 (m, 2H), 3.52 (m, 2H), 2.02 (s, 12H), 1.58 (m, 4H), 1.43 (m, 8H); MS (FAB^+): *m/z* 555 ($M+1^+$), 554(M^+) ; HRMS (FAB^+): $C_{38}H_{42}N_4$+H^+, 555.3488. Found 555.3480.

1,2,10,11-Tetraethyl-4,4,8,8-tetrafluoro-3,5,7,9-tetramethyl-6,13-dihydro-6,13-ethano-4,8-dibora-3a,4a,7a,8a-tetraazabenzo[1,2-*a*:5,4-*a'*]-*s*-indacene (*syn*-**6a**): The title compound was obtained from *syn*-**5a** (28 mg, 0.054 mmol) in 36% yield (12 mg) as pink crystals: mp, 160 °C (decomp.); ^{1}H NMR: δ 7.04 (s, 2H), 4.57 (m, 1H), 4.19 (m, 1H), 2.60 (q, 4H, *J* = 7.6 Hz), 2.54 (s, 6H), 2.51 (s, 6H), 2.39 (q, 4H, *J* = 7.6 Hz), 1.69-1.73 (m, 4H), 1.21 (t, 6H, *J* = 7.6 Hz), 1.09 (t, 6H, *J* = 7.6 Hz); ^{13}C NMR: δ 158.13, 146.31, 145.75, 144.40, 136.79, 132.85, 132.16, 126.36, 119.03, 32.11, 29.85, 29.17, 28.70, 17.93, 17.31, 16.96, 15.02, 12.97, 12.66 IR (KBr): 2966, 2931, 2870, 1603, 1174 cm^{-1}; UV-vis ($CHCl_3$): λ_{max} ($\varepsilon/10^4$ $M^{-1}\cdot cm^{-1}$), 550 (15.1), 503 (7.52), 387 (2.15) nm; MS (FAB^+): *m/z* 603 (M^++1); HRMS (FAB^+): $C_{34}H_{40}B_2F_4N_4$+H^+, 603.3453. Found: 603.3451. Anal. Calcd for $C_{34}H_{40}B_2F_4N_4$+2/3$CHCl_3$: C, 61.03; H, 6.01; N, 8.21. Found: C, 61.08; H, 6.13; N, 7.93.

6,6,10,10-Tetrafluoro-5,7,9,11-tetramethyl-1,4,8,12,15,17-hexahydro-1,4:8,17:12,15-triethano-6,10-dibora-5a,6a,9a,10a-tetraaza-*s*-indaceno[2,3-*b*:6,5-*b'*]difluorene (*syn*-**6b**): Bis-dipyrromethane *syn*-**5b** (862 mg, 1.55 mmol) was reacted to give 698 mg (70%) of the title compound as a mixture of diastereomers: purple powder; mp, 160 °C (decomp.); ^{1}H NMR: δ 7.15 (m, 2H), 6.50 (m, 2H), 6.38 (m, 2H), 4.53 (m, 1H), 4.18 (m 1H), 4.07 (m, 2H), 3.89 (m, 2H), 2.93 (s, 6H), 2.54 (s, 6H), 1.69 (m, 8H), 1.43 (m, 4H); ^{13}C NMR (typical signals): δ 150.95, 150.25, 147.41, 143.24, 136.36, 133.57, 128.15, 127.02, 125.52, 119.76, 118.86, 34.39, 33.12, 29.83, 28.39, 26.42, 26.48, 26.54, 26.61, 12.82, 12.67; IR (KBr): ν_{max} 2866, 1616, 1403, 1176, 1122 cm^{-1} UV-vis ($CHCl_3$): λ_{max} ($\varepsilon/10^4$ $M^{-1}\cdot cm^{-1}$), 553 (10.9), 504 (5.76), 397 (2.15) nm; MS (FAB^+): *m/z* 647 (M^++1); HRMS (FAB^+): $C_{38}H_{36}B_2F_4N_4$+H^+, 647.3140. Found: 647.3165.

6,6,15,15-Tetrafluoro-5,7,14,16-tetramethyl-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 (*anti*-**6b**): *anti*-Bis-dipyrromethane *anti*-**5b** (255 mg, 0.46 mmol) was reacted to give 259 mg (82%) of the title compound as a mixture of diastereomers: purple powder; mp, 160 °C (decomp.); ^{1}H NMR: δ 7.12 (m, 2H), 6.50 (m, 2H), 6.40 (m, 2H), 4.36 (m, 2H), 4.10 (m, 2H), 3.89 (m, 2H), 2.54 (m, 6H), 2.51 (m, 6H), 1.67 (m, 8H), 1.43 (m, 4H); ^{13}C NMR (typical signals): δ 151.18, 150.23, 149.03, 146.95, 138.35, 136.20, 133.61, 128.27, 126.82, 120.05, 118.92, 34.35, 33.12, 31.88, 30.90, 29.57, 28.66, 26.53, 22.64; UV-vis ($CHCl_3$): λ_{max} ($\varepsilon/10^4$ $M^{-1}\cdot cm^{-1}$), 545 (23.4), 509 (6.85), 403 (3.17) nm; MS (FAB^+): *m/z* 647 (M^++1); HRMS (FAB^+): Calcd for $C_{38}H_{36}B_2F_4N_4$ +H^+, 647.3140. Found: 647.3137.

Ethyl 3-(4-*tert*-butylbenzoyl)-4,7-dihydro-4,7-ethano-2*H*-isoindole-1-carboxylate (**11**): 4-*tert*-Butylbenzoic acid (5.36 g, 30.1 mmol) was added to trifluoroacetic anhydride (4.2 ml, 30.0 mmol) at room temperature under an inert atmosphere and the mixture was stirred for 15min. After the vessel was wrapped with an aluminum foil, trifluoroacetic acid (2.7 ml, 35.3 mmol) and ethyl 4,7-dihydro-4,7-ethano-2*H*-isoindole-1-carboxylate (**1**; 2.17 g, 9.99 mmol) were successively added. The mixture was stirred at room temperature for 3 days. The reaction was quenched by the addition of aqueous saturated $NaHCO_3$ and the resulted 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 *in vacuo*. The residue was chromatographed on silica gel (Rf, 0.10; CH_2Cl_2) and alumina (Rf, 0.45; CH_2Cl_2) to give 2.91 g (77%) of the title compound as white solid; mp, 138 °C; ^{1}H NMR: δ 9.20 (br s, 1H), 7.74 (m, 2H), 7.52 (m, 2H), 6.54 (m, 1H), 6.43 (m, 1H), 4.45 (m, 1H), 4.37 (m, 2H), 3.84 (m, 1H), 1.64-1.44 (m, 4H), 1.41 (t, 3H, *J* = 7.1 Hz), 1.39 (s, 9H); ^{13}C NMR: δ 186.01, 161.21, 156.40, 137.54, 137.09, 136.37, 136.09, 135.23, 129.32, 125.57, 125.02, 118.24, 61.07, 35.55, 34.87, 33.93, 31.60, 26.58, 26.55, 14.87; IR (KBr): ν_{max} 3313, 1697, 1628, 1281 cm^{-1}; MS (MALDI-TOF): *m/z* 378 ($M+H^+$), 349 ($M^+-C_2H_4$). Anal. Calcd for $C_{24}H_{27}NO_3$: C, 76.36; H, 7.21; N, 3.71. Found: C, 76.13; H, 7.20; N, 3.76.

Ethyl 3-[(4-*tert*-butylphenyl)hydroxymethyl]-4,7-dihydro-4,7-ethano-2*H*-isoindole-1-carboxylate (**12**): To a stirred solution of ketone **11** (1.12 g, 2.98 mmol) in dry THF (30 ml) and dry MeOH (10 ml) was added $NaBH_4$ (0.375 g, 9.91 mmol) at 0 °C under an inert atmosphere and then the mixture was stirred at room temperature for 2 h. The mixture 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 recrystallized from $CHCl_3$/hexane to give 1.084 g (95%) of the title compound as a mixture of diastereomers: white solid; mp, 170 °C (decomp.); ^{1}H NMR: δ 8.67–8.34 (m, 1H), 7.37 (m, 2H), 7.29 (m, 2H), 6.50–6.33 (m, 2H), 5.88 (m, 1H), 4.32 (m, 1H), 4.27 (m, 2H), 3.54 (m, 1H), 2.49–2.19 (m, 1H), 1.60–1.38 (m, 4H), 1.34 (m, 3H), 1.32 (m, 9H); IR (KBr): ν_{max}, 3360, 3332, 1681, 1639 cm^{-1}; MS (MALDI-TOF): *m/z* 362 (M^++1−H_2O). Anal. Calcd for $C_{24}H_{29}NO_3$+1/6 $CHCl_3$: C, 72.68; H, 7.36; N, 3.51. Found: C, 72.66; H, 7.16; N, 3.60.

Ethyl 3-[acetoxy(4-*tert*-butylphenyl)methyl]-4,7-dihydro-4,7-ethano-2*H*-isoindole-1-carboxylate (**13**): To a stirred solution of alcohol **12** (0.759 g, 2.00 mmol) and 4-(N,N-dimethylamino)pyridine (0.038 g, 0.307 mmol) in dry CH_2Cl_2 (28 ml) was added acetic anhydride (1.9 ml, 20.1 mmol) at room temperature under an inert atmosphere and the mixture was stirred for 30 min. The reaction mixture 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 (Rf, 0.6; 40% EtOAc/hexane) to give 0.840 g (99 %) of the title compound as a mixture of diastereomers: white solid; mp, 170 °C (decomp.); ^{1}H NMR: δ 8.32 (m, 1H), 7.42–7.34 (m, 2H), 7.30–7.24 (m, 2H), 6.93 (m, 1H), 6.46 (m, 1H), 6.39 (m, 1H), 4.35–4.23 (m, 3H), 3.57 (s, 1H), 2.14 (m, 3H), 1.68–1.38 (m, 4H), 1.38–1.33 (m, 3H), 1.32 (s, 9H); IR (KBr): ν_{max}, 3309, 1747, 1660, 1219 cm^{-1}; HRMS (FAB$^+$): Calcd for $C_{26}H_{32}NO_4$+H$^+$, 422.2326. Found: 422.2322. Anal. Calcd for $C_{26}H_{32}NO_4$+1/3H_2O: C, 73.04; H, 7.47; N, 3.28. Found: C, 72.89; H, 7.42; N, 3.32.

Diethyl 3,7-bis[(3-ethoxycarbonyl-4,7-dihydro-4,7-ethano-2*H*-isoindolyl)(4-*tert*-butylphenyl)methyl]-4,8-dihydro-4,8-ethanopyrrolo[3,4-*f*]isoindole-1,5-dicarboxylate (**14**): To a stirred solution of acetate **13** (0.847 g, 2.01 mmol) and *anti*-dipyrrole *anti*-**2** (0.329 g, 1.00 mmol) in acetic acid (26 ml) was added *p*-toluenesulfonic acid monohydrate (0.10 g, 0.53 mmol) at room temperature in the dark. After being stirred for 3 h, the mixture was quenched by addition of 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 (Rf, 0.5, 40% EtOAc/hexane) to give 1.040 g (99%) of the title compound as a mixture of diastereomers: white powder; mp, 170 °C (decomp.); ^{1}H NMR: δ 8.04 (m, 4H), 7.36–7.27 (m, 4H), 7.15–7.01 (m, 4H), 6.49–5.99 (m, 4H), 5.56–5.16 (m, 2H), 4.45–4.03 (m, 12H), 3.24–2.94 (m, 2H), 1.56–1.34 (m, 8H), 1.34–1.11 (m, 34H); ^{13}C NMR (typical signals): δ 161.75, 150.35, 150.20, 150.10, 137.9−135.1, 129.3−125.5, 113.3−112.5, 59.85, 59.77, 34.47, 33.78, 32.40, 31.33, 30.63, 28.08, 27.97, 26.7−26.1, 14.46; IR (KBr): ν_{max}, 3448, 1697, 1508, 1234 cm^{-1}; MS (MALDI-TOF): *m/z* 1022 [M$^+$+H−(C_2H_4)], 978 [M$^+$+H−(C_2H_4)$_2$]. Anal. Calcd for $C_{66}H_{74}N_4O_8$: C, 75.40; H, 7.09; N, 5.33. Found: C, 75.30; H, 7.09; N, 5.42.

1,5-Dimethyl-3,7-bis[(3-methyl-4,7-dihydro-4,7-ethano-2*H*-isoindolyl)(4-*tert*-butyl-phenyl)methyl]-4,8-dihydro-4,8-ethanopyrrolo[3,4-*f*]isoindole (**15**): Tetra ester **14** (0.526 g, 0.500 mmol) was reduced with $LiAlH_4$ to give 0.351 g (86%) of the title compound as a mixture of diastereomer: orange solid, ^{1}H NMR (CD_2Cl_2): δ 7.7−6.8 (br m, 10H), 6.5−6.2 (br m, 4H), 3.67 (br m, 4H), 3.2−3.0 (br m, 2H), 2.7−2.6 (br m, 2H), 2.10 (m, 12H), 2.0−1.3 (12H), 1.32 (m, 18H); IR (KBr): ν_{max}, 3456, 3417, 2951, 2861 cm^{-1}; MS (FAB$^+$): *m/z* 819 (M$^+$+1), 818 (M$^+$), 817 (M$^+$−1). HRMS (FAB$^+$): Calcd for $C_{58}H_{66}N_4$+H$^+$, 819.5366. Found: 819.5354.

X-ray experiment

Table S1. Crystallographic summary

	syn-**6a**	*anti*-**6a**·PhCl[a]	*syn*-**6b**·$CHCl_3$	*anti*-**6b**·2$CHCl_3$	*syn*-**7**·PhMe
crystal formula	$C_{34}H_{40}B_2F_4N_4$	$C_{40}H_{45}ClB_2F_4N_4$ [$C_{34}H_{40}B_2F_4N_4$]	$C_{39}H_{37}B_2Cl_3F_4N_4$	$C_{40}H_{38}B_2Cl_6F_4N_4$	$C_{39}H_{44}B_2F_4N_4$
space group	*Pbca*	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a[Å]	16.8468(3)	24.4208(4)	16.5658(16)	13.753(3)	11.0884(3)
b[Å]	14.7846(2)	11.8609(2)	15.3933(15)	13.110(3)	23.5088(9)
c[Å]	24.5438(4)	29.0741(5)	14.3780(12)	25.759(5)	13.9282(5)
α[°]	90	90	90	90	90
β[°]	90	118.0000(10)	95.115(4)	119.635(3)	102.6061(14)
γ[°]	90	90	90	90	90
V[Å^3]	6113.20(17)	7435.6(2)	3651.8(6)	4036.9(15)	3543.2(2)
Z	8	8	4	4	4
Radiation	Cu*Kα*	Cu*Kα*	Cu*Kα*	Mo*Kα*	Cu*Kα*
μ[mm^{-1}]	0.766	0.630 [0.629]	2.741	0.480	0.712
unique reflns	5591	13133 [13133]	6636	9252	6472
obsd reflns	4660	10614 [10180]	2317	7147	4116
R_{equiv}	0.0504	0.0469 [0.0471]	0.0901	0.0350	0.0572
Parameters (restrained)	398 (0)	1193 (711) [810 (1)]	512 (388)	584 (0)	613 (527)
R_1 [I > 2σ(I)]	0.0421	0.0438 [0.0455]	0.0975	0.0600	0.0785
wR_2 (All)	0.1109	0.1326 [0.1302]	0.2239	0.1722	0.2203
GOF	1.075	1.177 [1.135]	1.103	1.078	1.059
T[K]	100	100	100	100	100
CCDC No	864644	864645, [865408][a]	864646	864647	864648

[a] The structure of bis-BODIPY *anti*-**6a** ($C_{34}H_{40}B_2F_4N_4$) is also refined without the solvent molecules by Platon Squeeze. The data based on the Squeeze result is shown in brackets.

Table S1 (continued). Crystallographic summary

	anti-**7**·2$C_{10}H_7Cl$[a]	**16**·2$CHCl_3$	**16**·PhCl	**17**·PhCl·1/2i-PA
crystal formula	$C_{52}H_{50}B_2Cl_2F_4N_4$	$C_{60}H_{62}B_2Cl_6F_4N_4$	$C_{64}H_{65}B_2ClF_4N_4$	$C_{123}H_{122}B_4Cl_2F_8N_4O$
space group	*P-1*	$P2_1/c$	$P2_1/c$	*P-1*
a[Å]	7.944(3)	11.3126(2)	11.247(4)	12.9946(3)
b[Å]	10.964(4)	29.2235(6)	27.084(9)	13.0045(3)
c[Å]	13.432(4)	17.1103(3)	17.815(6)	17.9199(4)
α[°]	98.902(13)	90	90	74.7391(8)
β[°]	93.514(13)	92.3136(11)	94.678(6)	88.1657(9)
γ[°]	104.888(14)	90	90	62.0910(10)
V[Å^3]	1110.7(7)	5651.93(18)	5409(3)	2566.87(11)
Z	1	4	4	1
Radiation	Mo*Kα*	Cu*Kα*	Mo*Kα*	Cu*Kα*
μ[mm^{-1}]	0.0530	3.230	0.0439	1.148
unique reflns	5031	10206	12384	9258
obsd reflns	3071	7145	9355	8081
R_{equiv}	0.0530	0.0511	0.0439	0.0474
Parameters (restrained)	293 (0)	870 (867)	733 (243)	739 (269)
R_1 [I > 2σ(I)]	0.1653	0.0667	0.0619	0.0554
wR_2 (All)	0.3974	0.1916	0.1538	0.1572
GOF	1.233	1.064	1.082	1.085
T[K]	100	100	100	100
CCDC No	864649	864650	864651	864652

[a] The crystal is treated as twin.

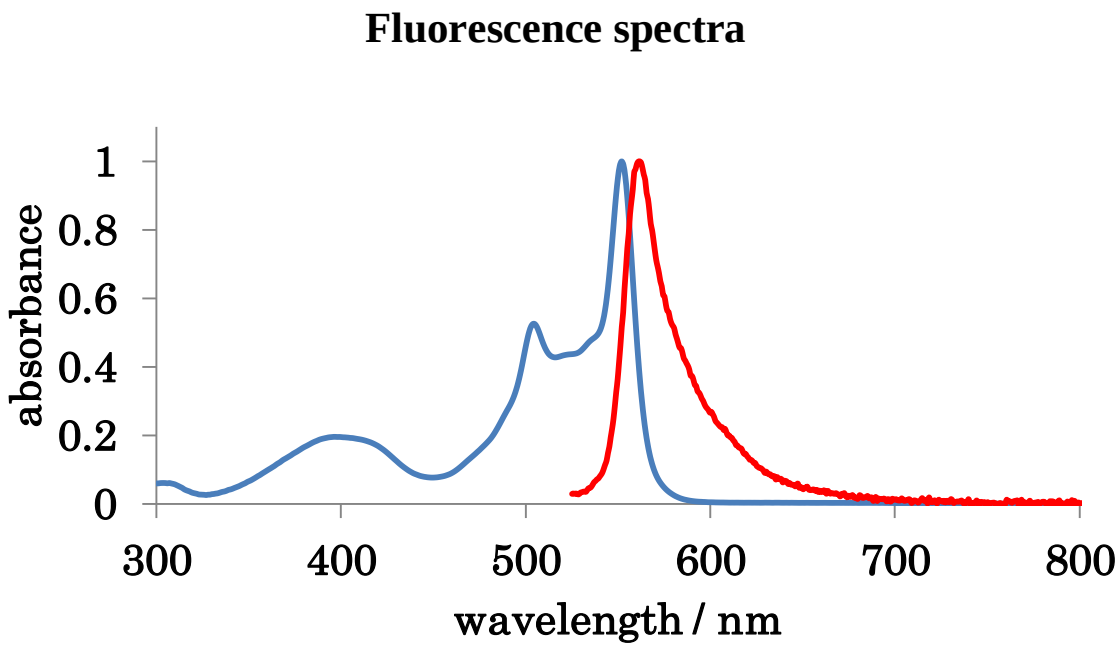


Figure S1. UV (blue) and fluorescence (red) spectra of *syn*-**6b**

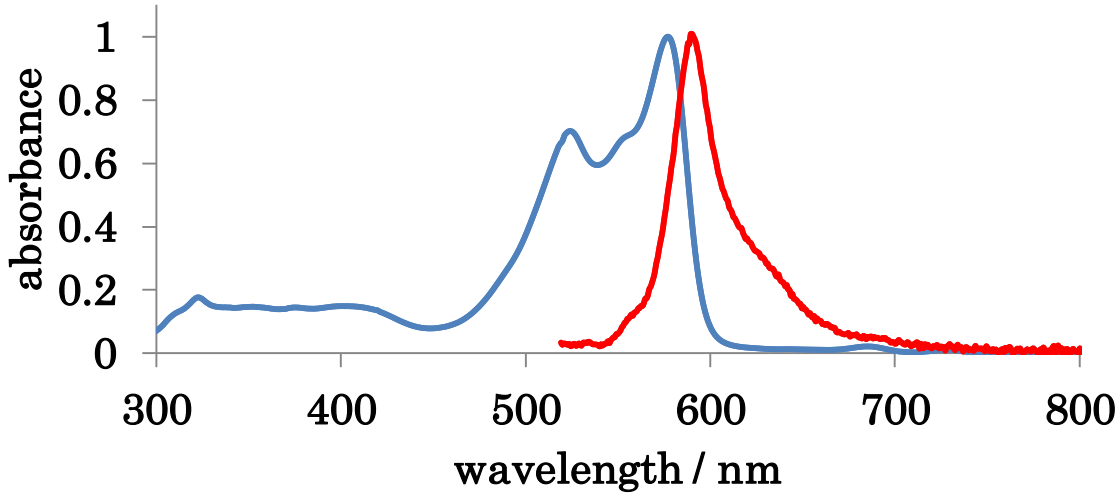


Figure S2. UV (blue) and fluorescence (red) spectra of *syn*-**8**

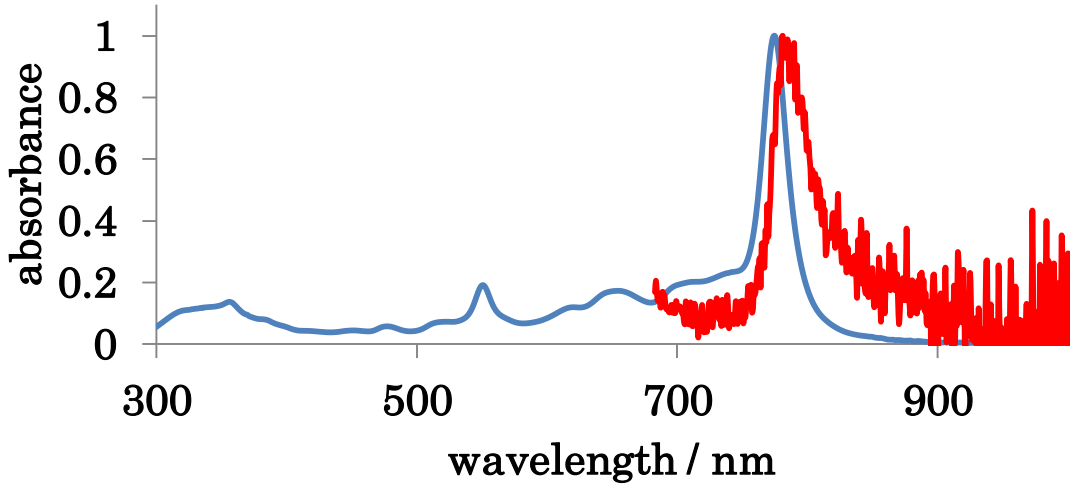


Figure S3. UV (blue) and fluorescence (red) spectra of *syn*-**9**

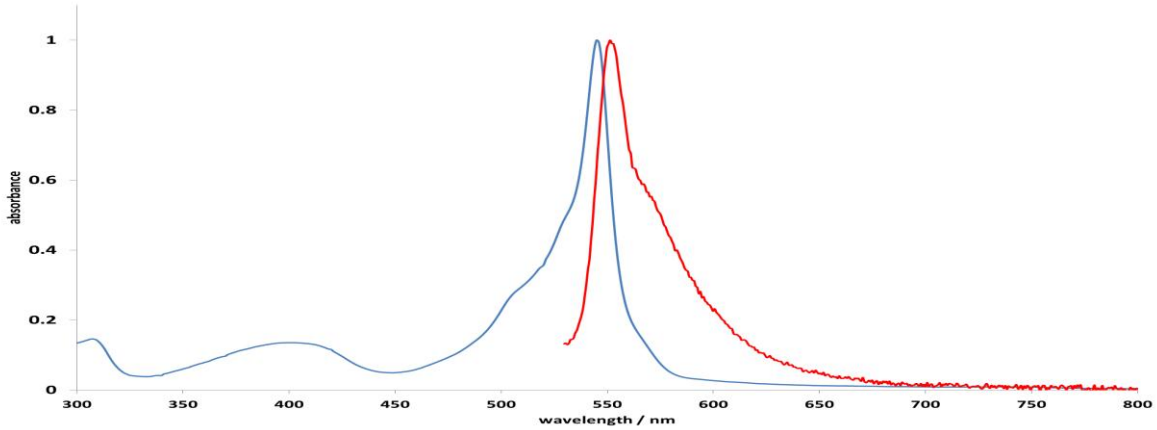


Figure S4. UV (blue) and fluorescence (red) spectra of *anti*-**6b**

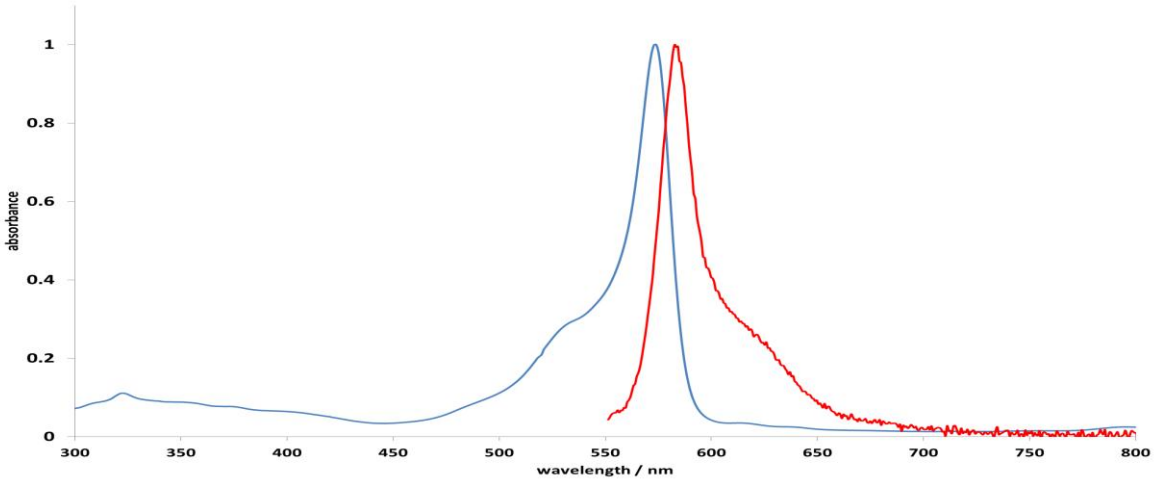


Figure S5. UV (blue) and fluorescence (red) spectra of *anti*-**8**

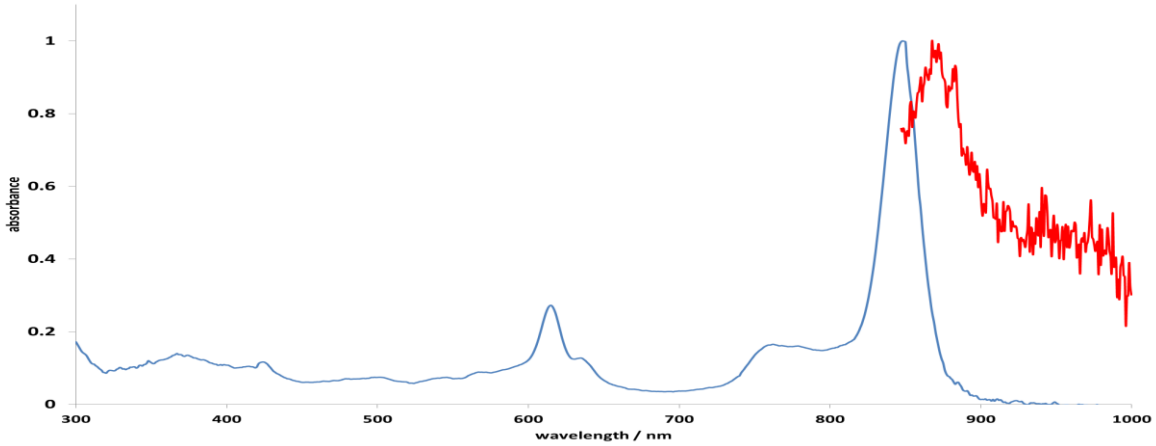


Figure S6. UV (blue) and fluorescence (red) spectra of *anti*-**9**

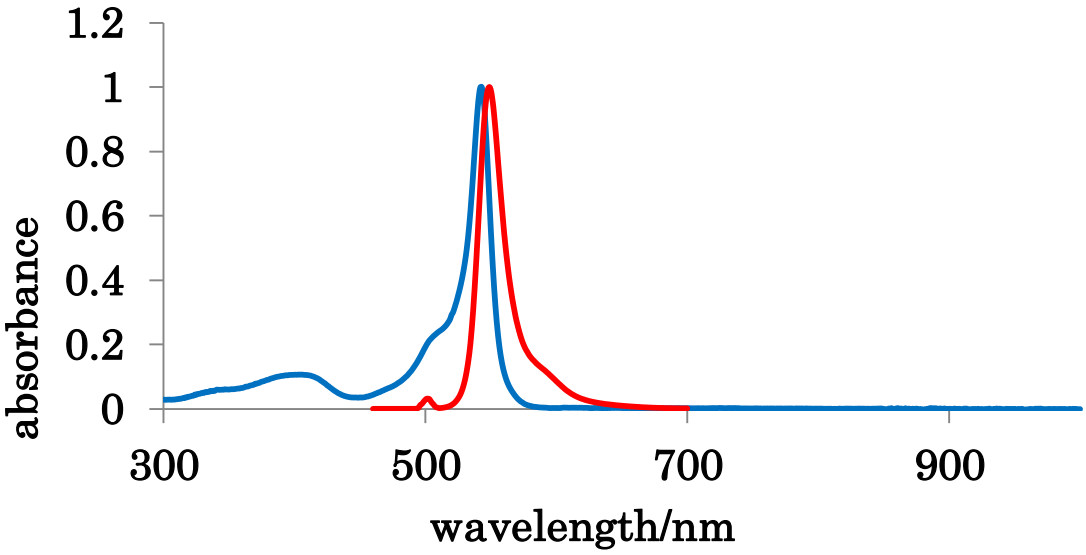


Figure S7. UV (blue) and fluorescence (red) spectra of **16**

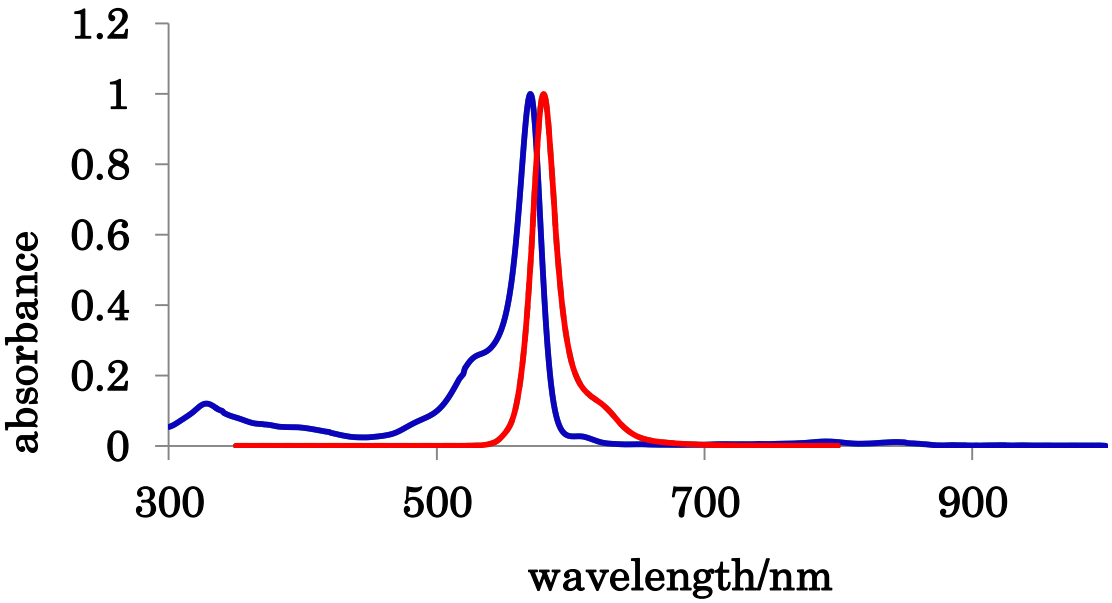


Figure S8. UV (blue) and fluorescence (red) spectra of **17**

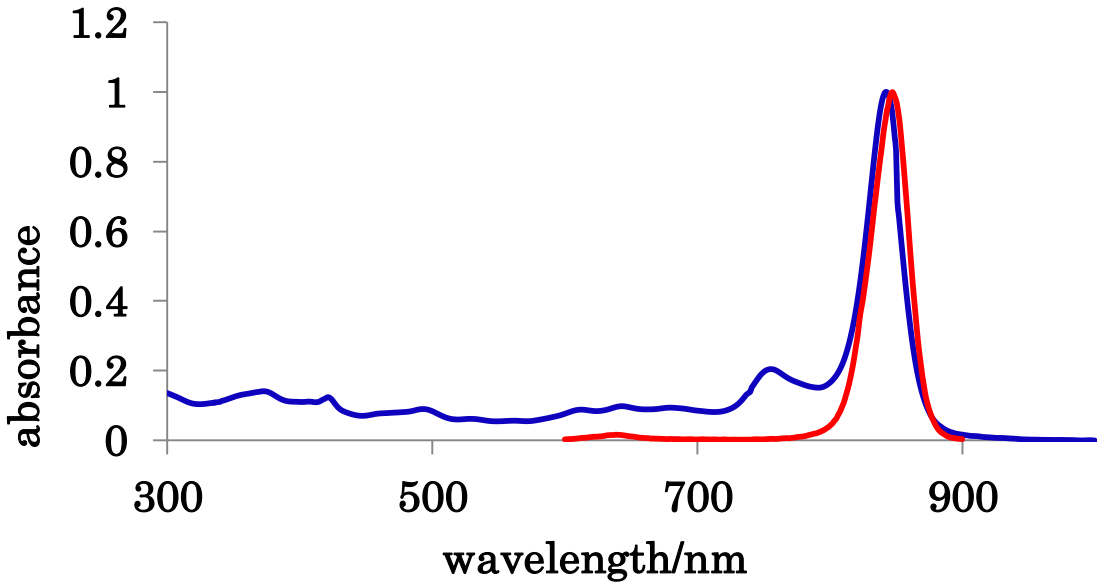


Figure S9. UV (blue) and fluorescence (red) spectra of **10**

TD-DFT calculation

Excitation energies and oscillator strengths

***syn*-6a, HOMO-2: 157; HOMO(s): 158, HOMO(a): 159; LUMO(s): 160, LUMO(a): 161**

Excited State 1: Singlet-A 2.5245 eV 491.12 nm f=0.0602
158 ->161 -0.36991
159 ->160 0.58579
This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.5492 eV 486.37 nm f=0.0035

158 ->160 0.52490
159 ->161 -0.47689

Excited State 3: Singlet-A 2.8622 eV 433.17 nm f=0.4961
157 ->160 -0.24261
158 ->161 0.51376
159 ->160 0.24716

Excited State 4: Singlet-A 2.9756 eV 416.67 nm f=0.2811
156 ->160 0.16358
157 ->161 -0.35888
158 ->160 0.31784
159 ->161 0.36885

Excited State 5: Singlet-A 3.1089 eV 398.80 nm f=0.4206
157 ->160 0.63422
158 ->161 0.16025
159 ->160 0.13081

Excited State 6: Singlet-A 3.3502 eV 370.08 nm f=0.1205
155 ->161 0.15030
156 ->160 0.21828
157 ->161 0.56721
158 ->160 0.13904
159 ->161 0.17223

Excited State 7: Singlet-A 3.4806 eV 356.22 nm f=0.0134
155 ->160 0.55006
156 ->161 0.36946

Excited State 8: Singlet-A 3.5032 eV 353.91 nm f=0.3317
155 ->161 0.25535
156 ->160 0.53882
157 ->161 -0.12497
158 ->160 -0.14065
159 ->161 -0.16247

Excited State 9: Singlet-A 3.6999 eV 335.10 nm f=0.0135
154 ->160 0.58307
155 ->161 -0.30611
156 ->160 0.17111

Excited State 10: Singlet-A 3.7073 eV 334.43 nm f=0.0283
154 ->161 0.39649
155 ->160 -0.30831
156 ->161 0.47698

Excited State 11: Singlet-A 3.8143 eV 325.05 nm f=0.0114
154 ->160 0.35486
155 ->161 0.53590
156 ->160 -0.28200

Excited State 12: Singlet-A 3.8503 eV 322.01 nm f=0.0066
154 ->161 0.56565
155 ->160 0.26470
156 ->161 -0.31711

Excited State 13: Singlet-A 4.8175 eV 257.36 nm f=0.0078
152 ->160 0.61241
153 ->161 -0.33044

Excited State 14: Singlet-A 4.8185 eV 257.31 nm f=0.0029
152 ->161 -0.34117
153 ->160 0.60836

Excited State 15: Singlet-A 5.0245 eV 246.76 nm f=0.0401
152 ->160 0.25352

153 ->161 0.57197
158 ->163 0.14033
159 ->162 -0.18540

Excited State 16: Singlet-A 5.0515 eV 245.44 nm f=0.0491
152 ->161 0.56237
153 ->160 0.25871
158 ->162 -0.18756
159 ->163 0.15737

Excited State 17: Singlet-A 5.1916 eV 238.82 nm f=0.0000
150 ->161 -0.40720
151 ->160 0.56622

Excited State 18: Singlet-A 5.1976 eV 238.54 nm f=0.0000
149 ->161 0.10169
150 ->160 0.54810
151 ->161 -0.42402

Excited State 19: Singlet-A 5.4937 eV 225.68 nm f=0.0003
149 ->160 0.56757
150 ->161 0.30227
151 ->160 0.27731

Excited State 20: Singlet-A 5.5850 eV 222.00 nm f=0.0002
149 ->161 0.42160
150 ->160 0.29248
151 ->161 0.46958

***anti*-6a, HOMO-2: 157; HOMO(s): 158, HOMO(a): 159; LUMO(s): 160, LUMO(a): 161**
Excited State 1: Singlet-A 2.5669 eV 483.01 nm f=0.0015
158 ->160 0.53303
159 ->161 0.46278
This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.5695 eV 482.52 nm f=0.0564
158 ->161 0.44247
159 ->160 0.54265

Excited State 3: Singlet-A 2.8830 eV 430.06 nm f=0.9828
156 ->160 0.11280
157 ->161 0.17858
158 ->161 0.46238
159 ->160 -0.34316

Excited State 4: Singlet-A 2.9326 eV 422.77 nm f=0.0611
156 ->161 0.13060
157 ->160 0.43283
158 ->160 0.26125
159 ->161 -0.37493

Excited State 5: Singlet-A 3.2248 eV 384.47 nm f=0.4103
157 ->161 0.65471
158 ->161 -0.12155

Excited State 6: Singlet-A 3.2841 eV 377.53 nm f=0.1067
155 ->160 0.15621
156 ->161 -0.14230
157 ->160 0.51926
158 ->160 -0.23397
159 ->161 0.21287

Excited State 7: Singlet-A 3.4855 eV 355.72 nm f=0.1851
155 ->161 -0.36692
156 ->160 0.54770

Excited State 8:	Singlet-A	3.5105 eV	353.18 nm	f=0.0151
155 ->160	0.47505			
156 ->161	-0.40630			
158 ->160	0.11147			
159 ->161	-0.12519			
Excited State 9:	Singlet-A	3.7112 eV	334.08 nm	f=0.0231
154 ->160	0.53264			
155 ->161	0.35774			
156 ->160	0.24203			
Excited State 10:	Singlet-A	3.7179 eV	333.48 nm	f=0.0175
154 ->161	0.44675			
155 ->160	0.32671			
156 ->161	0.40630			
Excited State 11:	Singlet-A	3.8315 eV	323.59 nm	f=0.0054
154 ->160	-0.43636			
155 ->161	0.45211			
156 ->160	0.31710			
Excited State 12:	Singlet-A	3.8462 eV	322.36 nm	f=0.0031
154 ->161	0.52089			
155 ->160	-0.33840			
156 ->161	-0.32663			
Excited State 13:	Singlet-A	4.8534 eV	255.46 nm	f=0.0005
152 ->161	-0.36605			
153 ->160	0.59607			
Excited State 14:	Singlet-A	4.8623 eV	254.99 nm	f=0.0006
152 ->160	0.52739			
153 ->161	-0.46783			
Excited State 15:	Singlet-A	5.0277 eV	246.60 nm	f=0.0128
152 ->161	0.54880			
153 ->160	0.29144			
158 ->163	0.14216			
159 ->162	-0.18658			
Excited State 16:	Singlet-A	5.0358 eV	246.21 nm	f=0.0824
152 ->160	0.39658			
153 ->161	0.46587			
158 ->162	0.18477			
159 ->163	-0.16201			
Excited State 17:	Singlet-A	5.2155 eV	237.72 nm	f=0.0006
150 ->161	-0.45647			
151 ->160	0.52461			
Excited State 18:	Singlet-A	5.2181 eV	237.60 nm	f=0.0000
150 ->160	0.51150			
151 ->161	-0.46828			
Excited State 19:	Singlet-A	5.5320 eV	224.12 nm	f=0.0001
149 ->160	0.53299			
150 ->161	-0.30291			
151 ->160	-0.33375			
Excited State 20:	Singlet-A	5.5783 eV	222.26 nm	f=0.0004
149 ->161	0.47217			
150 ->160	-0.29995			
151 ->161	-0.41657			

***syn*-7, HOMO: 151; LUMO: 152**

Excited State 1:	Singlet-A	2.1893 eV	566.32 nm	f=1.2907
151 ->152	0.59919			

This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State	2:	Singlet-A	2.2406 eV	553.36 nm	f=0.0451
150 ->152		0.25165			
151 ->153		0.63318			
Excited State	3:	Singlet-A	2.8397 eV	436.61 nm	f=0.1228
148 ->152		0.12145			
150 ->152		0.56141			
151 ->153		-0.12525			
151 ->154		-0.27611			
Excited State	4:	Singlet-A	3.0189 eV	410.69 nm	f=0.0137
149 ->152		0.11031			
150 ->153		0.65055			
Excited State	5:	Singlet-A	3.2134 eV	385.84 nm	f=0.0088
148 ->152		0.55714			
149 ->153		0.15576			
151 ->154		0.35244			
Excited State	6:	Singlet-A	3.2539 eV	381.03 nm	f=0.0162
148 ->153		0.17221			
149 ->152		0.64587			
150 ->153		-0.10882			
Excited State	7:	Singlet-A	3.4693 eV	357.38 nm	f=0.2317
147 ->152		0.21319			
148 ->152		-0.34347			
150 ->152		0.17309			
151 ->154		0.45466			
Excited State	8:	Singlet-A	3.7069 eV	334.47 nm	f=0.0444
148 ->153		0.66088			
149 ->152		-0.19927			
150 ->154		-0.10164			
Excited State	9:	Singlet-A	3.7266 eV	332.70 nm	f=0.0469
147 ->152		-0.12204			
148 ->152		-0.15817			
149 ->153		0.66583			
Excited State	10:	Singlet-A	3.8645 eV	320.83 nm	f=0.2249
146 ->152		0.14823			
148 ->153		0.10196			
150 ->154		0.66228			
Excited State	11:	Singlet-A	3.9003 eV	317.88 nm	f=0.0215
147 ->152		0.62902			
149 ->153		0.10179			
151 ->154		-0.16412			
Excited State	12:	Singlet-A	4.0944 eV	302.81 nm	f=0.3227
146 ->152		-0.30084			
147 ->153		0.60242			
Excited State	13:	Singlet-A	4.2558 eV	291.33 nm	f=0.0029
146 ->152		0.55765			
147 ->153		0.25538			
147 ->154		-0.22130			
150 ->154		-0.11633			
Excited State	14:	Singlet-A	4.5342 eV	273.44 nm	f=0.0088
145 ->152		-0.17860			
146 ->153		0.65987			

Excited State 15: Singlet-A 4.7282 eV 262.22 nm f=0.0095
149 ->154 0.69497

Excited State 16: Singlet-A 4.7359 eV 261.80 nm f=0.0120
148 ->154 0.68897

Excited State 17: Singlet-A 4.9549 eV 250.23 nm f=0.0522
145 ->152 0.63076
146 ->153 0.12131
150 ->155 -0.10789
151 ->157 -0.16353

Excited State 18: Singlet-A 5.1060 eV 242.82 nm f=0.0896
144 ->152 0.16520
145 ->153 0.45646
147 ->154 0.31956
151 ->155 0.36269

Excited State 19: Singlet-A 5.1607 eV 240.25 nm f=0.0634
144 ->152 -0.30575
145 ->153 0.42059
146 ->152 -0.10043
147 ->154 -0.37981
151 ->156 -0.22363

Excited State 20: Singlet-A 5.2992 eV 233.97 nm f=0.0002
142 ->153 -0.25498
143 ->152 0.63111

***anti*-7, HOMO: 151; LUMO: 152**

Excited State 1: Singlet-A 1.9399 eV 639.13 nm f=1.0350
151 ->152 0.59308
This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.3966 eV 517.33 nm f=0.0000
150 ->152 0.52544
151 ->153 -0.47088

Excited State 3: Singlet-A 2.8726 eV 431.61 nm f=0.0005
148 ->152 0.28791
149 ->152 0.13041
150 ->152 0.33593
150 ->154 -0.10501
151 ->153 0.39159

Excited State 4: Singlet-A 3.0350 eV 408.52 nm f=0.0806
148 ->152 -0.16277
149 ->152 0.49336
151 ->154 0.42139

Excited State 5: Singlet-A 3.1097 eV 398.71 nm f=0.3511
147 ->152 0.12265
149 ->152 -0.41424
151 ->154 0.49724

Excited State 6: Singlet-A 3.1557 eV 392.89 nm f=0.0024
148 ->152 0.58365
149 ->152 0.14541
150 ->152 -0.14669
150 ->154 0.11288
151 ->153 -0.19172

Excited State 7: Singlet-A 3.3388 eV 371.34 nm f=0.4700
147 ->152 -0.18176
150 ->153 0.63741

Excited State 8:	Singlet-A	3.7526 eV	330.40 nm	f=0.2497
147 ->152	0.62297			
150 ->153	0.15239			
151 ->154	-0.11338			
Excited State 9:	Singlet-A	3.7965 eV	326.58 nm	f=0.0001
149 ->153	0.12964			
150 ->154	0.65393			
Excited State 10:	Singlet-A	3.9882 eV	310.87 nm	f=0.0048
149 ->153	0.65923			
150 ->154	-0.12875			
Excited State 11:	Singlet-A	4.0253 eV	308.01 nm	f=0.0821
146 ->152	-0.16279			
148 ->153	0.64665			
Excited State 12:	Singlet-A	4.0367 eV	307.14 nm	f=0.1203
146 ->152	0.62238			
147 ->154	0.14685			
148 ->153	0.18889			
Excited State 13:	Singlet-A	4.3072 eV	287.85 nm	f=0.0000
147 ->153	0.68326			
Excited State 14:	Singlet-A	4.6195 eV	268.39 nm	f=0.0056
145 ->152	0.46608			
146 ->153	-0.21310			
148 ->154	0.16672			
149 ->154	0.43116			
Excited State 15:	Singlet-A	4.6252 eV	268.06 nm	f=0.0135
145 ->152	-0.38797			
146 ->153	0.18586			
149 ->154	0.53998			
Excited State 16:	Singlet-A	4.6486 eV	266.71 nm	f=0.0051
145 ->152	-0.12606			
148 ->154	0.67715			
Excited State 17:	Singlet-A	4.8519 eV	255.54 nm	f=0.0001
145 ->152	0.21854			
146 ->153	0.59885			
151 ->155	0.20536			
Excited State 18:	Singlet-A	5.0200 eV	246.98 nm	f=0.1081
144 ->152	0.46936			
146 ->152	-0.10250			
147 ->154	0.43312			
151 ->156	0.21670			
Excited State 19:	Singlet-A	5.1434 eV	241.05 nm	f=0.0003
142 ->153	-0.16010			
143 ->152	0.67056			
Excited State 20:	Singlet-A	5.2157 eV	237.71 nm	f=0.0216
142 ->152	0.58895			
143 ->153	-0.17237			
144 ->152	0.20535			
147 ->154	-0.16884			
151 ->157	0.10092			

***syn*-9, HOMO: 145; LUMO: 146**

Excited State 1:	Singlet-A	1.9858 eV	624.34 nm	f=1.3464
145 ->146	0.59412			

This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State	2:	Singlet-A	2.0183 eV	614.31 nm	f=0.0512
144 ->146		-0.25822			
145 ->147		0.62565			
Excited State	3:	Singlet-A	2.6576 eV	466.53 nm	f=0.1837
144 ->146		0.54990			
145 ->147		0.11435			
145 ->148		-0.33052			
Excited State	4:	Singlet-A	2.7923 eV	444.03 nm	f=0.0442
144 ->147		0.65821			
Excited State	5:	Singlet-A	3.0683 eV	404.09 nm	f=0.0989
140 ->146		0.11187			
144 ->146		0.21126			
145 ->148		0.56584			
Excited State	6:	Singlet-A	3.4639 eV	357.93 nm	f=0.0077
141 ->146		0.10123			
142 ->146		0.20375			
145 ->149		0.64276			
Excited State	7:	Singlet-A	3.5747 eV	346.84 nm	f=0.0019
141 ->147		-0.10937			
142 ->147		-0.10951			
143 ->146		0.47371			
145 ->150		0.47173			
Excited State	8:	Singlet-A	3.5810 eV	346.22 nm	f=0.0881
142 ->146		0.19164			
144 ->148		0.65902			
Excited State	9:	Singlet-A	3.7125 eV	333.97 nm	f=0.0375
141 ->146		0.56231			
142 ->146		0.24539			
143 ->147		-0.22020			
145 ->149		-0.19271			
Excited State	10:	Singlet-A	3.7747 eV	328.46 nm	f=0.1813
143 ->146		-0.45958			
145 ->150		0.46889			
Excited State	11:	Singlet-A	3.8278 eV	323.90 nm	f=0.0872
140 ->147		0.19866			
141 ->146		-0.23507			
142 ->146		0.54437			
143 ->147		0.13638			
144 ->148		-0.15281			
145 ->149		-0.10362			
Excited State	12:	Singlet-A	3.8457 eV	322.40 nm	f=0.0100
140 ->146		0.65911			
141 ->147		0.15730			
Excited State	13:	Singlet-A	3.9883 eV	310.87 nm	f=0.2307
140 ->147		0.34924			
141 ->146		0.25237			
143 ->147		0.49233			
Excited State	14:	Singlet-A	4.1094 eV	301.71 nm	f=0.0237
141 ->147		-0.22120			
142 ->147		0.62560			
144 ->149		0.12417			
Excited State	15:	Singlet-A	4.1415 eV	299.37 nm	f=0.0204
140 ->146		-0.14699			

141 ->147 0.62421
142 ->147 0.21841
143 ->146 0.16184

Excited State 16: Singlet-A 4.1724 eV 297.15 nm f=0.0169
140 ->147 0.52701
141 ->146 -0.12359
142 ->146 -0.12329
143 ->147 -0.40291

Excited State 17: Singlet-A 4.2216 eV 293.69 nm f=0.0103
139 ->146 0.65598
144 ->149 0.13643

Excited State 18: Singlet-A 4.3776 eV 283.22 nm f=0.1548
139 ->146 -0.12164
142 ->147 -0.11461
144 ->149 0.65198

Excited State 19: Singlet-A 4.4667 eV 277.58 nm f=0.0003
138 ->146 0.13746
139 ->147 -0.37137
144 ->150 0.55492

Excited State 20: Singlet-A 4.5217 eV 274.20 nm f=0.0803
138 ->146 -0.22764
139 ->147 0.48441
140 ->147 0.10345
140 ->148 0.14332
144 ->150 0.37307

***anti*-9, HOMO: 145; LUMO: 146**

Excited State 1: Singlet-A 1.7631 eV 703.21 nm f=1.1956
145 ->146 0.58401
This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.1593 eV 574.19 nm f=0.0000
144 ->146 0.49465
145 ->147 0.50546

Excited State 3: Singlet-A 2.6958 eV 459.91 nm f=0.0000
144 ->146 0.40898
145 ->147 -0.39048

Excited State 4: Singlet-A 2.8615 eV 433.28 nm f=0.3398
142 ->146 0.10754
145 ->148 0.65843

Excited State 5: Singlet-A 3.0604 eV 405.12 nm f=0.3121
140 ->146 -0.11168
144 ->147 0.65698

Excited State 6: Singlet-A 3.4314 eV 361.32 nm f=0.0083
141 ->147 -0.10110
143 ->146 0.52895
145 ->149 0.42704

Excited State 7: Singlet-A 3.4726 eV 357.04 nm f=0.0000
141 ->146 0.49046
143 ->147 -0.11286
145 ->150 -0.46486

Excited State 8: Singlet-A 3.5601 eV 348.26 nm f=0.0000
144 ->148 0.65090
145 ->150 0.16561

Excited State 9:	Singlet-A	3.5740 eV	346.91 nm	f=0.3632
142 ->146	-0.34168			
143 ->146	-0.33690			
145 ->149	0.47610			
Excited State 10:	Singlet-A	3.6175 eV	342.74 nm	f=0.0000
141 ->146	0.46306			
144 ->148	-0.17789			
145 ->150	0.45604			
Excited State 11:	Singlet-A	3.6494 eV	339.74 nm	f=0.0495
140 ->146	-0.21163			
142 ->146	0.54112			
143 ->146	-0.23488			
145 ->149	0.21740			
Excited State 12:	Singlet-A	3.7254 eV	332.81 nm	f=0.1394
140 ->146	0.62154			
142 ->146	0.16231			
Excited State 13:	Singlet-A	4.0355 eV	307.24 nm	f=0.0000
139 ->146	0.66370			
140 ->147	-0.10353			
Excited State 14:	Singlet-A	4.1352 eV	299.82 nm	f=0.0000
140 ->147	-0.45254			
142 ->147	0.16864			
143 ->147	0.47000			
144 ->149	-0.10508			
Excited State 15:	Singlet-A	4.3192 eV	287.06 nm	f=0.0000
137 ->146	-0.11116			
140 ->147	-0.11699			
142 ->147	0.55384			
143 ->147	-0.24790			
144 ->149	0.27122			
Excited State 16:	Singlet-A	4.3528 eV	284.84 nm	f=0.0213
141 ->147	0.59326			
143 ->146	0.11076			
144 ->150	0.32215			
Excited State 17:	Singlet-A	4.3929 eV	282.23 nm	f=0.0000
140 ->147	0.46646			
141 ->146	0.11087			
142 ->147	0.32827			
143 ->147	0.27332			
144 ->149	-0.23793			
Excited State 18:	Singlet-A	4.4337 eV	279.64 nm	f=0.1897
141 ->147	-0.30440			
144 ->150	0.59128			
Excited State 19:	Singlet-A	4.4407 eV	279.20 nm	f=0.0000
140 ->147	0.17082			
143 ->147	0.30555			
144 ->149	0.56591			
Excited State 20:	Singlet-A	4.4871 eV	276.31 nm	f=0.1255
138 ->146	0.61206			
139 ->147	0.19318			
140 ->148	-0.15254			
141 ->147	-0.10919			

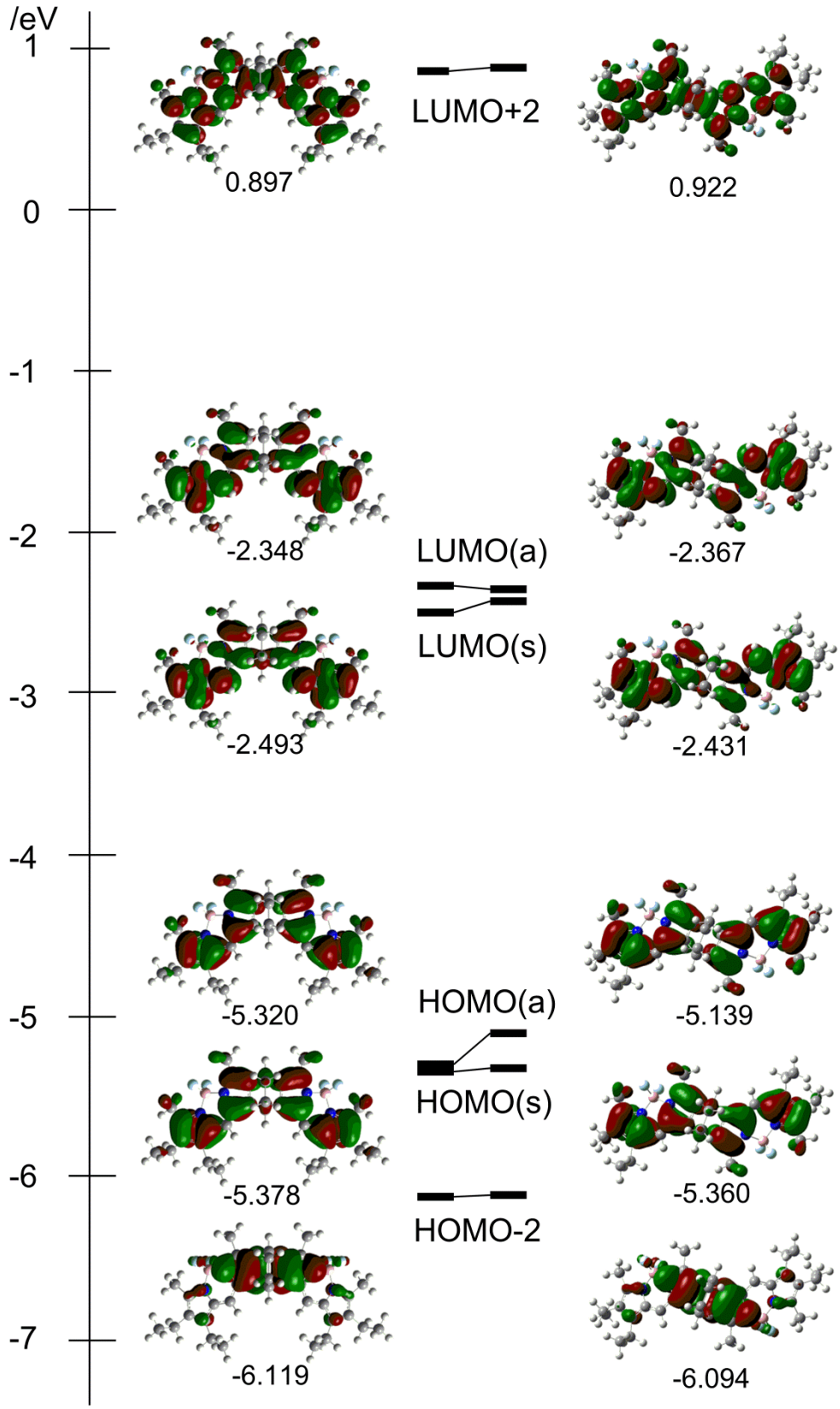


Figure S1. The calculated frontier orbitals of *syn*-**6a** (left) and *anti*-**6a** (right)

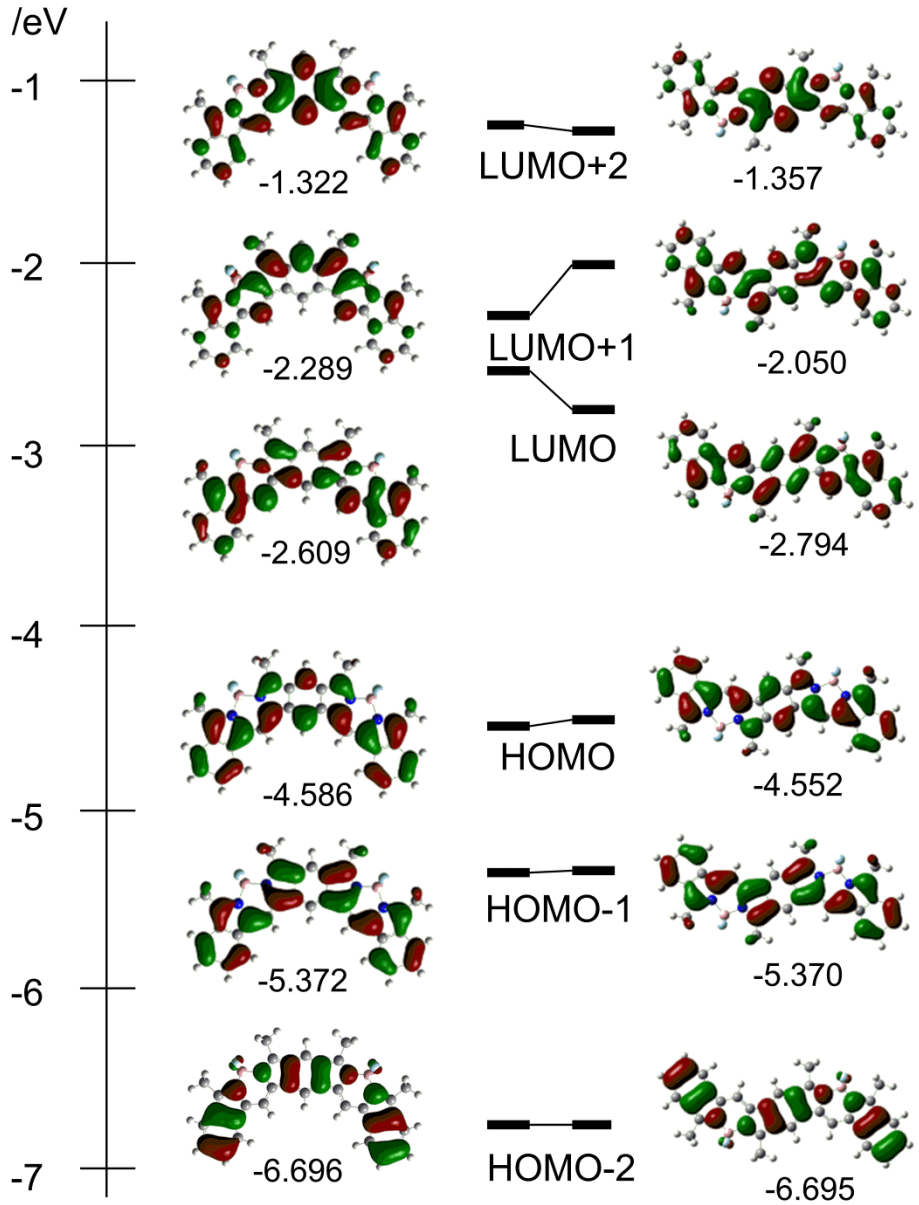
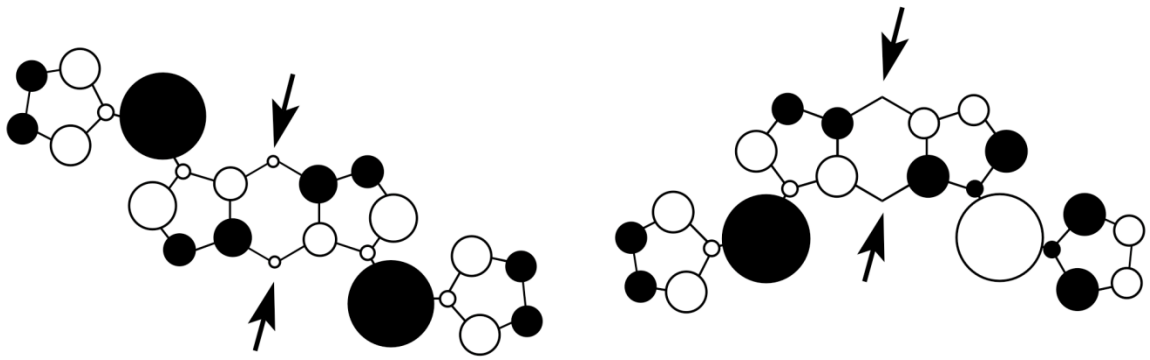


Figure S2. The calculated frontier orbitals of *syn*-**9** (left) and *anti*-**9** (right)

Hückel-type calculation



α + 0.3501 |β| α + 0.3565 |β|

Figure S3. The Hückel LUMOs of the *syn/anti* isomers of **7**. Only the atoms contained in the π-electron system are considered, and the nitrogen atoms are replaced by sp^2 carbon atoms to emphasize the effect of topology. The presence and absence of the interaction between the LUMOs of the two BODIPY moieties are indicated by the AO coefficients of fused benzo atoms (marked with arrows). The orbital energy of the *anti* isomer is slightly lower than that of the *syn* isomer.