Electronic Supplementary Information for

TICT fluorescence of *N*-borylated 2,5-diarylpyrroles: A gear like dual motion in the excited state

Takuhiro Taniguchi, Jian Wang, Stephan Irle,* and Shigehiro Yamaguchi*
Department of Chemistry, Graduate School of Science, Nagoya University, and CREST, JST, Furo, Chikusa, Nagoya 464-8602, Japan
yamaguchi@chem.nagoya-u.ac.jp, sirle@chem.nagoya-u.ac.jp

Experimental Section

General. Melting points (mp) were measured on a Stanford Research Systems OptiMelt instrument. ^{1}H, ^{11}B, and ^{13}C NMR spectra were measured with JEOL AL-400 or A-600 spectrometer. UV-vis absorption and fluorescence spectra were recorded at room temperature with a Shimadzu UV-3150 spectrometer and a Hitachi F-4500 spectrometer, respectively, in degassed solvents. Absolute fluorescence quantum yields were determined with a Hamamatsu C9920 calibrated integrating sphere system. Fluorescence lifetimes were measured with a Hamamatsu picosecond fluorescence measurement system C4780 equipped with a N_2 laser (337 nm). Column chromatography was performed using Fuji Silysia silica gel PSQ100B (100 μm). Recycling preparative gel permeation chromatography (GPC) was performed using polystyrene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) with chloroform as an eluent. *N*-(*tert*-butoxycarbonyl)-2,5-dibromopyrrole,[1] bis[2,4,6-tris(trifluoromethyl)-phenyl]fluoroborane,[2] 2,5-di(2-thienyl)pyrrole,[3] 2,5-diphenylpyrrole,[4] and 2,3,4,5-tetraphenyl-pyrrole[5] were prepared according to the methods reported in the literatures. All experiments were carried out under an argon atmosphere.

***N*-(*tert*-Butoxycarbonyl)-2,5-bis(4-dimethylaminophenyl)pyrrole (8)**. To a mixture of *N*-(*tert*-butoxycarbonyl)-2,5-dibromopyrrole (985 mg, 3.0 mmol), 4-(dimethylamino)-phenylboronic acid (1.51 g, 9.2 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (62.5 mg, 0.061 mmol), S-Phos (101 mg, 0.25 mmol), and K_3PO_4 (3.88 g, 18 mmol) was added degassed toluene (15 mL) and H_2O

(6 mL) at room temperature. The reaction mixture was heated at 110 °C and stirred for 20 h. After cooling down to room temperature, water was added and the mixture was extracted with toluene three times. After usual aqueous workup, the mixture was purified by a silica gel column chromatography ($CHCl_3$, $R_f = 0.49$) to give 1.05 g (2.59 mmol) of **8** in 85% yield as pale yellow solids: mp 188–189 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, $J_{HH} = 8.4$ Hz, 4H), 6.75 (d, $J_{HH} = 8.4$ Hz, 4H), 6.14 (s, 2H), 2.98 (s, 12H), 1.23 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.41, 149.70, 136.05, 129.57, 122.62, 111.90, 110.83, 83.23, 40.62, 27.23. Anal. Calcd for $C_{25}H_{31}N_3O_2$: C, 74.04; H, 7.70; N, 10.36. Found: C, 74.20; H, 7.80; N, 10.26.

2,5-Bis[4-(dimethylamino)phenyl]pyrrole (9). A mixture of **8** (1.00 g, 1.81 mmol) and NaOMe (1.95 g, 36.1 mmol) in THF (7.2 mL) and MeOH (7.2 mL) was heated at 80 °C with stirring for 66 h. After cooling down to room temperature, a saturated NH_4Cl aqueous solution was added, and the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was purified by a silica gel column chromatography (CH_2Cl_2, $R_f = 0.39$), followed by recrystallization from CH_2Cl_2 to give 291 mg (0.95 mmol) of **9** in 53% yield as pale yellow solids: mp 206–208 °C (dec); ^1H NMR (400 MHz, THF-d_8) δ 9.92 (s, 1H), 7.43 (d, $J_{HH} = 8.4$ Hz, 4H) 6.70 (d, $J_{HH} = 8.4$ Hz, 4H), 6.24 (quasi d, 2H), 2.91 (s, 12H); ^{13}C NMR (100 MHz, THF-d_8) δ 149.61, 133.63, 125.28, 123.64, 113.29, 105.71, 40.55. Anal. Calcd for $C_{20}H_{23}N_3$: C, 78.65; H, 7.59; N, 13.76. Found: C, 78.45; H, 7.68; N, 13.78.

***N*-(Dimesitylboryl)carbazole (3a)**. To a solution of carbazole (1.67 g, 10.0 mmol) in THF (50 mL) was added *n*-BuLi (1.60 M in hexane, 6.56 mL, 10.5 mmol) dropwise at –78 °C. After stirring at the same temperature for 2 h, a THF (20 mL) solution of dimesitylfluoroborane (2.95 g, 11.0 mmol) was added to the mixture at –78 °C. The reaction mixture was gradually warmed to room temperature and a saturated NH_4Cl aqueous solution was added. The organic layer was separated and the aqueous layer was extracted with toluene three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was dissolved into toluene and passed through a silica gel. The mixture was further washed with hexane to give 3.99 g (9.6 mmol) of **3a** in 96%

yield as colorless solids: mp 257–258 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, J_{HH} = 7.6 Hz, 2H), 7.25 (t, J_{HH} = 7.6 Hz, 2H), 7.08 (t, J_{HH} = 7.6 Hz, 2H), 6.93 (d, J_{HH} = 7.6 Hz, 2H), 6.82 (s, 4H), 2.33 (s, 6H), 2.02 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.28, 141.03, 139.17, 138.21 (br), 128.73, 128.09, 126.25, 122.59, 119.44, 115.46, 21.94, 21.31; ^{11}B NMR (128 MHz, CDCl$_3$) δ 52.21. Anal. Calcd for $C_{30}H_{30}BN$: C, 86.75; H, 7.28; N, 3.37. Found: C, 86.63; H, 7.49; N, 3.42.

***N*-{Bis[2,4,6-tris(trifluoromethyl)phenyl]boryl}carbazole (3b)**. To a solution of carbazole (98.9 mg, 0.591 mmol) in Et$_2$O (6 mL) was added *n*-BuLi (1.60 M in hexane, 0.37 mL, 0.59 mmol) dropwise at –78 °C. After stirring for 1 h, a Et$_2$O (2 mL) solution of bis[2,4,6-tris(trifluoromethyl)phenyl]fluoroborane (350 mg, 0.591 mmol) was added to the mixture at –78 °C. The reaction mixture was gradually warmed to room temperature. After the solvent was removed under reduced pressure, CH$_2$Cl$_2$ was added to the resulting mixture and the solution was passed through a celite pad. The mixture was purified by a silica gel column chromatography (1:1 hexane/CH$_2$Cl$_2$, R_f = 0.88) to give 78.1 mg (0.11 mmol) of **3b** in 18% yield as yellow solids: mp 200–201 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.28 (br s, 2H), 8.18 (br s, 2H), 7.96 (d, J_{HH} = 7.6 Hz, 2H), 7.30 (t, J_{HH} = 7.6 Hz, 2H), 7.08 (t, J_{HH} = 7.6 Hz, 2H), 6.36 (d, J_{HH} = 7.6 Hz, 2H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 143.42, 139.94 (br), 138.62 (br q, J_{CF} = 31.0 Hz), 135.79 (br q, J_{CF} = 29.8 Hz), 133.63 (q, J_{CF} = 35.1 Hz), 128.96 (br), 128.69, 126.62 (br, overlapped), 124.20, 122.96 (br q, J_{CF} = 270.4 Hz), 122.41 (q, J_{CF} = 273.3 Hz), 120.29, 115.63 (carbons of trifluoromethyl groups at the 2,6-positions were observed as identical); ^{11}B NMR (128 MHz, CDCl$_3$) δ 44.41; ^{19}F NMR (376 MHz, CDCl$_3$) δ –56.10, –56.77, –63.26. Anal. Calcd for $C_{30}H_{12}BF_{18}N$: C, 48.74; H, 1.64; N, 1.89. Found: C, 48.46; H, 1.61; N, 2.11.

***N*-(Dimesitylboryl)-2,5-di(2-thienyl)pyrrole (4)**. To a solution of 2,5-di(2-thienyl)pyrrole (371 mg, 1.6 mmol) in toluene (10 mL) was added *n*-BuLi (1.60 M in hexane, 1.0 mL, 1.6 mmol) dropwise at room temperature. After stirring for 2 h, a solution of dimesitylfluoroborane (473 mg, 1.76 mmol) in toluene (5 mL) was added. The reaction mixture was refluxed for 50 h. After addition of water, the organic layer was separated, and the aqueous layer was extracted with toluene three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was dissolved in toluene and passed through a silica gel column. Further purification by recycling GPC followed by recrystallization with hot toluene gave 448 mg (0.93 mmol) of **4** in 58% yield as pale yellow solids: mp 167–168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (dd, $J_{HH} = 5.1$, 1.2 Hz, 2H), 6.60 (dd, $J_{HH} = 3.6$, 1.2 Hz, 2H), 6.59 (br s, 2H), 6.57 (dd, $J_{HH} = 5.1$, 3.6 Hz, 2H), 6.46 (s, 2H), 6.36 (br s, 2H), 2.18 (s, 6H), 2.12 (s, 6H), 1.69 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.90, 141.00, 139.13, 139.03 (br), 135.87, 131.64, 128.06, 127.99, 127.34, 125.80, 125.10, 117.48, 22.61, 22.06, 21.09; ^{11}B NMR (128 MHz, $CDCl_3$) δ 56.34. Anal. Calcd for $C_{30}H_{30}BNS_2$: C, 75.14; H, 6.31; N, 2.92. Found: C, 75.48; H, 6.45; N, 2.61.

***N*-(Dimesitylboryl)-2,5-diphenylpyrrole (5)**. To a solution of 2,5-diphenylpyrrole (266 mg, 1.21 mmol) in toluene (4.8 mL) was added *n*-BuLi (1.60 M in hexane, 0.83 mL, 1.32 mmol) dropwise at room temperature. After stirring for 1 h, a toluene (1.5 mL) solution of dimesitylfluoroborane (360 mg, 1.32 mmol) was added to the mixture at room temperature. The reaction mixture was refluxed for 46 h. After addition of water, the organic layer was separated, and the aqueous layer was extracted with toluene three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was dissolved in a 1:1 hexane/toluene mixed solvent and passed through a silica gel column. Purification by a recycling GPC followed by recrystallization from hot hexane gave 228 mg (0.49 mmol) of **5** in 41% yield as pale yellow solids: mp 158–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14–7.12 (m, 4H), 6.97–6.94 (m, 6H), 6.48 (br s, 2H), 6.36 (s, 2H), 6.26 (br s, 2H), 2.21 (s, 6H), 2.05 (s, 6H), 1.73 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.64, 140.54, 140.16, 139.49 (br), 138.81, 135.76, 129.23, 127.95, 126.53, 126.08, 115.39, 22.55, 22.16, 20.93 (carbons at the meta-positions of the mesityl group were observed as identical.); ^{11}B NMR (128 MHz, $CDCl_3$) δ 55.75. Anal. Calcd for $C_{34}H_{34}BN$: C, 87.36; H, 7.33; N, 3.00. Found: C, 87.49; H, 7.38; N, 2.64.

***N*-(Dimesitylboryl)-2,5-bis(4-dimethylaminophenyl)pyrrole (6)**. To a solution of **9** (203 mg, 0.664 mmol) in toluene (13 mL) was added *n*-BuLi (1.30 M in hexane, 0.56 mL, 0.73

mmol) dropwise at room temperature. After stirring at 80 °C for 2 h, a solution of dimesitylfluoroborane (199 mg, 0.743 mmol) in toluene (1.5 mL) was added. The reaction mixture was refluxed for 46 h. After addition of water, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (1:1 toluene/CH_2Cl_2, R_f = 0.34) followed by recrystallization from hot hexane gave 75.3 mg (0.14 mmol) of **6** in 21% yield as yellow solids: mp 164–165 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.96 (d, J_{HH} = 8.8 Hz, 4H), 6.48 (s, 2H), 6.33 (d, J_{HH} = 8.8 Hz, 4H), 6.27 (s, 2H), 6.24 (s, 2H), 2.79 (s, 12H), 2.19 (s, 6H), 2.05 (s, 6H), 1.72 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.42, 141.38, 140.46, 139.99 (br), 139.93, 137.90, 130.03, 127.97, 127.69, 124.92, 114.15, 111.63, 40.96, 22.57, 22.16, 20.91; ^{11}B NMR (192 MHz, $CDCl_3$) δ 56.29. Anal. Calcd for $C_{38}H_{44}BN_3$: C, 82.45; H, 8.01; N, 7.59. Found: C, 82.53; H, 8.06; N, 7.42.

***N*-(Dimesitylboryl)-2,3,4,5-tetraphenylpyrrole (7)**. To a solution of 2,3,4,5-tetraphenylpyrrole (387 mg, 1.04 mmol) in xylene (10 mL) was added *n*-BuLi (1.60 M in hexane, 0.68 mL, 1.09 mmol) dropwise at room temperature. After stirring for 1.5 h, dimesitylfluoroborane (307 mg, 1.15 mmol) was added to the mixture. The reaction mixture was refluxed for 12 h. After addition of water, the organic layer was separated, and the aqueous layer was extracted with toluene three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography followed by recrystallization from toluene/hexane gave 263 mg (0.42 mmol) of **7** in 41% yield as colorless solids: mp 234–235 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04–7.01 (quasi d, 5H), 7.00–6.98 (quasi t, 5H), 6.90–6.80 (m, 10H), 6.51 (s, 2H), 6.21 (s, 2H), 2.38 (s, 6H), 2.06 (s, 6H), 1.64 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.41, 140.33, 139.89 (br), 138.64, 135.53, 135.13, 134.47, 130.94, 130.74, 128.38, 128.00, 127.75, 127.16, 126.43, 126.23, 125.38, 22.44, 22.39, 20.92; ^{11}B NMR (192 MHz, $CDCl_3$) δ 56.08. Anal. Calcd for $C_{46}H_{42}BN$: C, 89.16; H, 6.83; N, 2.26. Found: C, 89.44; H, 6.87; N, 2.17.

X-Ray Crystallographic Analysis of 3a. Single crystals of **3a** suitable for X-ray crystallographic analysis were obtained by recrystallization from a hot toluene solution. Intensity data were collected at 123 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo Kα radiation (λ = 0.71070 Å). A total of 7634 reflections were measured with the maximum 2θ angle of 50.0°, of which 2069 were independent reflections (R_{int} = 0.0310). The structure was solved by direct methods (SHELXS-97)[6] and refined by the full-matrix least-squares on F^2 (SHELXL-97).[6] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{30}H_{30}BN$; FW = 415.36, crystal size 0.20 × 0.15 × 0.15 mm^3, Monoclinic, $C_{2/c}$, a = 12.716(3) Å, b = 10.577(2) Å, c = 17.530(4) Å, β = 90.626(3)°, V = 2357.7(9) Å^3, Z = 4, D_c = 1.170 g cm^{-3}. The refinement converged to R_1 = 0.0417, wR_2 = 0.1115 ($I > 2\sigma(I)$), GOF = 1.093.

X-Ray Crystallographic Analysis of 4. Single crystals of **4** suitable for X-ray crystallographic analysis were obtained by recrystallization from a hot toluene solution. Intensity data were collected at 173 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo Kα radiation (λ = 0.71070 Å). A total of 8656 reflections were measured with the maximum 2θ angle of 50.0°, of which 4408 were independent reflections (R_{int} = 0.0402). The structure was solved by direct methods (SHELXS-97)[6] and refined by the full-matrix least-squares on F^2 (SHELXL-97).[6] The thiophene ring consisting of (S2, C9-C12) was disordered and was solved using appropriate models. Thus, two sets of thiophene ring, *i.e.*, (S2A, C9, C10A, C11A, C12A) and (S2B, C9, C10B, C11B, C12B), were placed and their occupancies were refined to be 0.85 and 0.15. These disordered thiophene rings were restrained by SADI and SIMU instruction during refinement. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{30}H_{30}BNS_2$; FW = 479.48, crystal size 0.20 × 0.10 × 0.10 mm^3, Triclinic, P_{-1}, a = 8.49(3) Å, b = 12.61(4) Å, c = 12.72(6) Å, α = 105.34(9)°, β = 91.55(8)°, γ = 102.24(8)°, V = 1278(9) Å^3, Z = 2, D_c = 1.246 g cm^{-3}. The refinement converged to R_1 = 0.0639, wR_2 = 0.1834 ($I > 2\sigma(I)$), GOF = 1.074.

Computational Details. The electronic structure calculations were carried out using the TURBOMOLE 5.10 program.[7] The B3LYP method was employed in combination with Ahlrich's def2-SV(P) basis set.[8] For excited singlet states, we employed time-dependent density functional theory (TD-DFT) using the B3LYP functional and the def2-SV(P) basis set to predict absorption and emission frequencies in the gas-phase. The minimum energy geometries were obtained by geometry optimizations on the potential energy surfaces of ground and low-lying excited singlet states. Harmonic vibrational frequencies were computed for ground state geometries to ensure that the optimized structures are indeed minima. The SCF convergence threshold was 10^{-6} hartree for ground state calculations, and an additional density convergence threshold of 10^{-7} was applied to compute ground state Kohn Sham orbitals for subsequent excited state energy and gradient calculations. Geometry convergence for optimization of minimum energy molecular structures in ground and excited states was requested by applying 10^{-6} hartree and 10^{-3} a.u. threshold values for subsequent energies and the maximum nuclear gradient, respectively.

Table S1 Fluorescence lifetimes and excited state dynamics for compounds **4–7**

Compd.	τ_s/ns[a]	$k_r/10^{-6}$ s^{-1} [b]	$k_{nr}/10^{-6}$ s^{-1} [b]
4	8.7	8.1	107.0
5	64.0	9.2	6.4
6	8.2	7.3	115.0
7	35.0	12.9	15.7

[a] Fluorescence lifetimes measured in cyclohexane. [b] The radiative rate constant (k_r) and nonradiative rate constant (k_{nr}) are calculated by the following equations: $k_r = \Phi_F/\tau_s$, $k_{nr} = (1-\Phi_F)/\tau_s$.

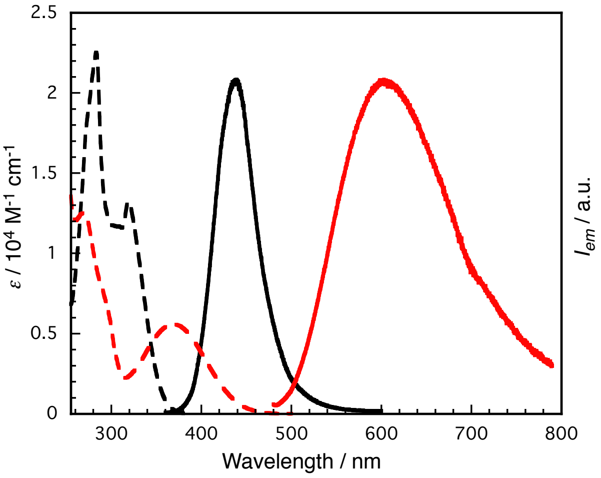

Fig. S1. UV-vis absorption (dashed lines) and fluorescence spectra (solid lines) of **3a** (black) and **3b** (red) in cyclohexane.

Table S2 Cartesian coordinates (Å) for optimized geometry of **3a** in the S_0 state

atom	*x*	*y*	*z*
H	0.5781431	1.2142879	-5.3534996
C	0.7053639	1.5139553	-4.3085276
C	1.0593798	2.266798	-1.5959829
C	0.2964068	0.6617389	-3.2731762
C	1.2819156	2.7419483	-3.9862022
C	1.4590756	3.1060926	-2.63971
C	0.457307	1.0420378	-1.9176389
H	1.6068369	3.4207306	-4.7809427
H	1.9239241	4.0670353	-2.3965487
H	1.2170281	2.5693864	-0.5617323
N	0	0	-1.0639716
B	0	0	0.3903458
C	-0.1186116	1.3751789	1.1762482
C	-0.4553968	3.7898263	2.6698012
C	0.8283164	1.7624708	2.1638067
C	-1.2412928	2.2221931	0.9541935
C	-1.3929861	3.3945977	1.7085383
C	0.6506016	2.9564137	2.8770996
H	-2.2748027	4.0224876	1.5366243
H	1.3989843	3.2406294	3.6255973
C	2.0597803	0.9317214	2.4653516
H	2.7146611	1.4468253	3.188889
H	2.6611991	0.7398837	1.5582341
H	1.7971178	-0.053328	2.8888223
C	-2.3036716	1.9147321	-0.0845374
H	-1.956056	2.1723971	-1.1017655
H	-3.2183616	2.5013928	0.1077175
H	-2.5910874	0.849986	-0.1062335
C	-0.6177558	5.0811772	3.4370269
H	-0.1522057	5.9285869	2.8960657
H	-0.1377389	5.0263708	4.4297572
H	-1.6824782	5.3354549	3.5829968
H	-0.5781431	-1.2142879	-5.3534996
C	-0.7053639	-1.5139553	-4.3085276
C	-1.0593798	-2.266798	-1.5959829
C	-0.2964068	-0.6617389	-3.2731762
C	-1.2819156	-2.7419483	-3.9862022
C	-1.4590756	-3.1060926	-2.63971
C	-0.457307	-1.0420378	-1.9176389
H	-1.6068369	-3.4207306	-4.7809427
H	-1.9239241	-4.0670353	-2.3965487
H	-1.2170281	-2.5693864	-0.5617323
C	0.1186116	-1.3751789	1.1762482
C	0.4553968	-3.7898263	2.6698012
C	-0.8283164	-1.7624708	2.1638067
C	1.2412928	-2.2221931	0.9541935
C	1.3929861	-3.3945977	1.7085383
C	-0.6506016	-2.9564137	2.8770996
H	2.2748027	-4.0224876	1.5366243
H	-1.3989843	-3.2406294	3.6255973
C	-2.0597803	-0.9317214	2.4653516
H	-2.7146611	-1.4468253	3.188889
H	-2.6611991	-0.7398837	1.5582341
H	-1.7971178	0.053328	2.8888223
C	2.3036716	-1.9147321	-0.0845374
H	1.956056	-2.1723971	-1.1017655
H	3.2183616	-2.5013928	0.1077175
H	2.5910874	-0.849986	-0.1062335
C	0.6177558	-5.0811772	3.4370269
H	0.1522057	-5.9285869	2.8960657
H	0.1377389	-5.0263708	4.4297572
H	1.6824782	-5.3354549	3.5829968

Table S3 Cartesian coordinates (Å) for optimized geometry of **3a** at S_1' in the S_1 state

atom	*x*	*y*	*z*
H	1.1203328	0.9005406	-5.2851357
C	1.3352179	1.0594485	-4.2242112
C	1.920833	1.5474277	-1.4721823
C	0.5746227	0.4494907	-3.2378054
C	2.4002853	1.9038818	-3.836303
C	2.6831562	2.1413477	-2.4827617
C	0.8752411	0.6848534	-1.8579847
H	3.0051375	2.3897902	-4.6075082
H	3.5033837	2.8123998	-2.2128531
H	2.1074183	1.7525708	-0.4178604
N	0	0	-1.0495474
B	0	0	0.5481811
C	-0.2546897	1.3825064	1.2122453
C	-0.5668629	3.9720027	2.4677455
C	0.5237613	1.7698734	2.3628832
C	-1.1964706	2.3575655	0.72853
C	-1.3326063	3.5999479	1.3534851
C	0.3509303	3.0298508	2.9490167
H	-2.0817106	4.3035917	0.9692014
H	0.971834	3.2929374	3.8141207
C	1.5983108	0.8792368	2.9518319
H	2.2083417	1.4376491	3.6832077
H	2.2723085	0.4822745	2.1699266
H	1.1880622	-0.0076493	3.467132
C	-2.1363071	2.0576916	-0.4201195
H	-1.6248333	2.0439489	-1.4001656
H	-2.931786	2.8197556	-0.4866746
H	-2.6267451	1.0733765	-0.2996522
C	-0.706873	5.3364247	3.0993989
H	-0.0634762	6.0887336	2.5990923
H	-0.4176053	5.322414	4.1655218
H	-1.7453347	5.7099014	3.034836
H	-1.1203328	-0.9005406	-5.2851357
C	-1.3352179	-1.0594485	-4.2242112
C	-1.920833	-1.5474277	-1.4721823
C	-0.5746227	-0.4494907	-3.2378054
C	-2.4002853	-1.9038818	-3.836303
C	-2.6831562	-2.1413477	-2.4827617
C	-0.8752411	-0.6848534	-1.8579847
H	-3.0051375	-2.3897902	-4.6075082
H	-3.5033837	-2.8123998	-2.2128531
H	-2.1074183	-1.7525708	-0.4178604
C	0.2546897	-1.3825064	1.2122453
C	0.5668629	-3.9720027	2.4677455
C	-0.5237613	-1.7698734	2.3628832
C	1.1964706	-2.3575655	0.72853
C	1.3326063	-3.5999479	1.3534851
C	-0.3509303	-3.0298508	2.9490167
H	2.0817106	-4.3035917	0.9692014
H	-0.971834	-3.2929374	3.8141207
C	-1.5983108	-0.8792368	2.9518319
H	-2.2083417	-1.4376491	3.6832077
H	-2.2723085	-0.4822745	2.1699266
H	-1.1880622	0.0076493	3.467132
C	2.1363071	-2.0576916	-0.4201195
H	1.6248333	-2.0439489	-1.4001656
H	2.931786	-2.8197556	-0.4866746
H	2.6267451	-1.0733765	-0.2996522
C	0.706873	-5.3364247	3.0993989
H	0.0634762	-6.0887336	2.5990923
H	0.4176053	-5.322414	4.1655218
H	1.7453347	-5.7099014	3.034836

Table S4 Cartesian coordinates (Å) for optimized geometry of **4** in the S_0 state

atom	*x*	*y*	*z*
C	4.3678399	-1.0482501	-2.1489005
H	5.0035832	-0.6152393	-2.9227039
C	4.7456544	-1.6224513	-0.9610767
H	5.7869508	-1.7202072	-0.6432999
C	3.6314325	-2.0626857	-0.1843292
H	3.7196116	-2.5408296	0.7940846
C	2.4108758	-1.810793	-0.7738989
C	1.0884943	-2.2470993	-0.3074951
C	0.6790583	-3.5629771	-0.2034723
H	1.3044494	-4.426934	-0.4270821
C	-0.6845141	-3.5619762	0.1932705
H	-1.3121241	-4.4251729	0.4136685
C	-1.0902336	-2.2454253	0.3029653
C	-2.4094791	-1.8065547	0.7763401
C	-3.6336201	-2.0449059	0.1886669
H	-3.7282979	-2.5118476	-0.7945573
C	-4.7423818	-1.6065284	0.9742511
H	-5.7853966	-1.6950847	0.659474
C	-4.3569336	-1.0471101	2.1666364
H	-4.9873294	-0.6189423	2.9474414
S	2.6503031	-1.0572681	-2.3397283
S	-2.638845	-1.0679385	2.3509786
N	0.0001557	-1.4083825	-0.0010701
B	0.0003764	0.0735965	-0.0009417
C	-1.276011	0.8367874	-0.5343092
C	-3.4872321	2.3099195	-1.5948867
C	-1.8444918	1.9279008	0.1846517
C	-1.8375389	0.5073904	-1.8021802
C	-2.9133786	1.2510651	-2.3064698
C	-2.9396793	2.6224745	-0.3452775
H	-3.3198082	0.9894832	-3.2902617
H	-3.3780402	3.4411623	0.2369856
C	1.2757588	0.8385561	0.531925
C	3.48574	2.314878	1.5909503
C	1.8403685	0.5084908	1.7983044
C	1.8400339	1.9327557	-0.1858556
C	2.9345813	2.6289007	0.3433077
C	2.9159809	1.2531859	2.3015107
H	3.3693928	3.4502768	-0.2378668
H	3.3253972	0.9902398	3.2836818
C	1.3111285	-0.6154992	2.6699892
H	1.549571	-1.6106242	2.2544723
H	0.2151247	-0.5767189	2.7937461
H	1.7548733	-0.5634539	3.6787167
C	1.3071446	2.3918978	-1.5294049
H	2.0254802	3.072732	-2.0180402
H	0.3507905	2.9345943	-1.4236133
H	1.1248216	1.5524486	-2.2202191
C	-1.3144642	2.3856933	1.5297445
H	-0.3590893	2.9305294	1.4261901
H	-1.1314608	1.5452099	2.2191069
H	-2.0348286	3.0641077	2.0187525
C	-4.6345152	3.1087082	-2.1664144
H	-4.2679208	4.0078613	-2.6998336
H	-5.31928	3.4589315	-1.3736846
H	-5.2210031	2.5162718	-2.890256
C	4.6324593	3.1151121	2.1615394
H	5.3142084	3.4692351	1.3679316
H	5.2223811	2.5222731	2.8822516
H	4.264936	4.0118993	2.6982944
C	-1.3047016	-0.6146568	-2.6742715
H	-1.7460797	-0.5616934	-3.6840005
H	-1.5430383	-1.6106526	-2.2606635
H	-0.2084231	-0.5746835	-2.7953989

Table S5. Cartesian coordinates (Å) for optimized geometry of **4** at S_1' in the S_1 state

atom	*x*	*y*	*z*
C	4.1377515	-0.8441387	-2.4179732
H	4.8079506	-0.177318	-2.9634939
C	4.3296311	-2.1838616	-2.1286864
H	5.2147408	-2.7507957	-2.4255955
C	3.2526293	-2.7227863	-1.4017366
H	3.2181169	-3.7604377	-1.0682846
C	2.2351674	-1.7915201	-1.1220061
C	1.0037291	-2.130749	-0.4724866
C	0.6240464	-3.503355	-0.2789991
H	1.2147409	-4.37063	-0.5636891
C	-0.6208844	-3.5045069	0.2826158
H	-1.2097229	-4.37307	0.5671269
C	-1.0041112	-2.1325694	0.4741684
C	-2.2357294	-1.7954126	1.1241256
C	-3.2459042	-2.731079	1.4163418
H	-3.2043508	-3.7722708	1.0950739
C	-4.3253389	-2.1922147	2.1394464
H	-5.2054169	-2.7625	2.4447677
C	-4.1429932	-0.8478262	2.4131018
H	-4.8172141	-0.1799158	2.9523076
S	2.668641	-0.2288411	-1.7799174
S	-2.6796585	-0.2286996	1.7655659
N	-0.0011784	-1.3088883	-0.0001107
B	-0.0017534	0.2817489	-0.0002559
C	-1.17505	0.9862569	-0.7571869
C	-3.3544572	2.3413465	-2.106905
C	-1.7677883	2.1932104	-0.2325108
C	-1.7411883	0.4928493	-1.9864403
C	-2.7915675	1.1635967	-2.6192286
C	-2.8199195	2.8256893	-0.9081877
H	-3.1779073	0.7618933	-3.5637514
H	-3.2526827	3.7323638	-0.4680851
C	1.1725564	0.9860663	0.7557632
C	3.3566151	2.3368688	2.1021773
C	1.7383102	0.4926523	1.9851171
C	1.7669505	2.1916393	0.2300026
C	2.8216416	2.8218465	0.9039506
C	2.7910479	1.1612344	2.6163156
H	3.2558463	3.7273668	0.4629147
H	3.177141	0.7594956	3.5609251
C	1.1919945	-0.7297124	2.6973889
H	1.4586372	-1.6778143	2.1949655
H	0.0905688	-0.7010042	2.7734061
H	1.5903527	-0.7910035	3.7250285
C	1.3450663	2.8228414	-1.0839629
H	2.1517862	3.4676743	-1.4768192
H	0.4438814	3.4541741	-0.9848428
H	1.0942347	2.0734686	-1.8508007
C	-1.3473037	2.8225948	1.082766
H	-0.4458068	3.4538503	0.9858049
H	-1.0977211	2.0718964	1.8487637
H	-2.1543715	3.467031	1.475584
C	-4.4622654	3.0668074	-2.8331274
H	-4.06298	3.7486345	-3.6114006
H	-5.0645345	3.6841855	-2.1424852
H	-5.1453286	2.3635261	-3.3439513
C	4.4674161	3.0598521	2.8263247
H	5.0700861	3.6754524	2.1344507
H	5.1495629	2.355045	3.3362745
H	4.0711112	3.7429521	3.6049913
C	-1.1979763	-0.7320792	-2.6966641
H	-1.5969925	-0.7944277	-3.7239845
H	-1.4665018	-1.6785708	-2.1922302
H	-0.0965351	-0.7061296	-2.7733908