Supporting Information

Pyrrolopyrrole aza-BODIPY analogues: a facile synthesis and intense fluorescence

Soji Shimizu,* Taku Iino, Yasuyuki Araki and Nagao Kobayashi*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

Contents:

i. Experimental

General procedure: Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer. Fluorescence spectra and absolute fluorescence quantum yields were measured on a Hamamatsu Photonics C9920-03G calibrated integrating sphere system. The fluorescence lifetimes were measured by a photon counting method with a streak scope (Hamamatsu Photonics, C4334-01) using the second harmonic generation (SHG, 388 nm) of a Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, fwhm 150 fs) as an excitation source. ^{1}H NMR spectra were recorded on a Bruker AVANCE III 500 spectrometer (operating at 500.133 MHz for ^{1}H, 160.462 MHz for ^{11}B, and 470.545 MHz for ^{19}F) using a residual solvent as an internal reference for ^{1}H (δ = 5.32 ppm for CD_2Cl_2) and using $BF_3 \cdot OEt_2$ as external references for ^{11}B (δ = 0 ppm) and ^{19}F (δ = –132 ppm). High resolution mass spectra were recorded on a Bruker Daltonics solariX 9.4T spectrometer. Preparative separations were performed by alumina and silica gel column chromatography (Wako). All reagents and solvents were of commercial reagent grade and were used without further purification except where noted.

Crystallographic data collection and structure refinement: Suitable crystals for X-ray analysis were obtained from slow diffusion of hexane into toluene solutions for **3a** and **3b** and from slow diffusion of methanol into a chloroform solution of **3c**. Data collection for **3a–3c** was carried out at –173(2) ^{o}C on a Bruker APEXII CCD diffractometer with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The structures were solved by a direct method (SHLEXS-97[1] or Sir-97[2]) and refined using a full-matrix least squares technique (SHELXL-97).[1] Yadokari-XG[3] software was used as a GUI for SHELXL-97. CCDC-96328, -96329, -96330 contain the supplementary crystallographic data for **3a**, **3b**, and **3c**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

In the case of **3c**, a chloroform solvent molecule was disordered and refined as two independent molecules with the optimized occupancies of 0.56:0.44 under thermally and positionally restrained conditions, using DFIX, SIMU, ISOR, and DELU commands. There were 108 restraints in the final refinement, of which were 12 for DFIX, 12 for DELU, 36 for SIMU, and 48 for ISOR commands.

Computational methods: Gaussian 09[4] software package was used to carry out DFT and TDDFT calculations using the B3LYP functional with 6-31G(d) basis set. Structural optimization was performed on

model compounds of **3a**, **3b**, and **3c** in which the *p*-octyloxyphenyl substituents at the α-positions were replaced by phenyl groups for simplicity.

General synthetic procedure: 3,6-Bis(4-octyloxyphenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione **1** (100 mg, 0.18 mmol) and 10 equiv of heteroaromatic amine **2** were refluxed in a distilled toluene. To the solution, titanium tetrachloride (0.3 ml, 2.7 mmol) and distilled triethylamine (1.0 ml, 7.2 mmol) were added. After consumption of DPP, borontrifluoride etherate (0.5 ml, 4.1 mmol) was added, and the reaction mixture was refluxed for 4 h. Then the solution was poured into water (300 ml), and the organic phase was extracted with chloroform. The organic layer was dried over sodium sulfate and the solvent was removed. The crude product was purified by alumina and silica gel column chromatography and the pure compound was obtained by recrystallization from chloroform and methanol.

3a: Column chromatography was performed by silica gel column ($CHCl_3$/MeOH = 50:1) and alumina gel column ($CHCl_3$). **3a** was obtained as a blue solid in 21% yield (29.7 mg from 103.1 mg of **1**). HR-MALDI-FT-ICR-MS (*m*/*z*): 792.4112 (calcd for $C_{44}H_{50}B_2F_4N_6O_2$ = 792.4112 [M^+]); ^{1}H NMR (CD_2Cl_2, 500 MHz, 298K): δ = 8.37 (d, *J* = 8.5 Hz, 4H; phenyl), 8.22 (d, *J* = 6.5 Hz, 2H; pyridyl), 7.86 (dd, J_1 = J_2 = 7.5 Hz, 2H; pyridyl), 7.31 (d, *J* = 8.0 Hz, 2H; pyridyl), 7.11 (dd, J_1 = J_2 = 7.0 Hz, 2H; pyridyl), 7.05 (d, *J* = 9.0 Hz, 4H; phenyl), 4.10 (t, *J* = 6.5 Hz, 4H; -OCH_2-), 1.84-0.90 (30H, m, -C_7H_{15}) ppm; ^{11}B NMR ($CDCl_3$, 160 MHz, 298K): δ = 1.2 (t, J_{BF} = 30 Hz) ppm; ^{19}F NMR ($CDCl_3$, 471 MHz, 298K): δ = –110 (q, J_{FB} = 28 Hz) ppm; UV/vis ($CHCl_3$): λ_{max} [nm] (ε) = 316 (23400), 414 (25600), 591 (34100), 638 (78000).

3b: Column chromatography was performed by silica gel column ($CHCl_3$). **3b** was obtained as a green solid in 20% yield (35.0 mg from 97.1 mg of **1**). HR-MALDI- FT-ICR-MS (*m*/*z*): 904.3551 (calcd for $C_{48}H_{50}B_2F_4N_6O_2S_2$ = 904.3554 [M^+]); ^{1}H NMR (CD_2Cl_2, 500 MHz, 298K): δ = 8.41 (d, *J* = 6.8 Hz, 4H; phenyl), 7.94 (d, *J* = 8.0 Hz, 2H; benzothiazolyl), 7.74 (d, *J* = 8.0 Hz, 2H; benzothiazolyl), 7.52 (dd, J_1 = J_2 = 8.0 Hz, 2H; benzothiazolyl), 7.41 (dd, J_1 = J_2 = 8.0 Hz, 2H; benzothiazolyl), 7.11 (d, *J* = 7.0 Hz, 4H; phenyl), 4.15 (t, *J* = 6.5 Hz, 4H; -OCH_2-), 1.88-0.92 (30H, m, -C_7H_{15}) ppm; ^{11}B NMR ($CDCl_3$, 160 MHz, 298K): δ = 1.2 (t, J_{BF} = 30 Hz) ppm; ^{19}F NMR ($CDCl_3$, 471 MHz, 298K): δ = –111 (q, J_{FB} = 30 Hz) ppm; UV/vis ($CHCl_3$): λ_{max} [nm] (ε) = 327 (35400), 444 (33200), 603 (39900), 655 (110000).

3c: Column chromatography was performed by silica gel column ($CHCl_3$/MeOH 50:1). **3c** was obtained as a green solid in 18% yield (29.0 mg from 97.3 mg of **1**). HR-MALDI- FT-ICR-MS (*m*/*z*): 892.4424 (calcd for $C_{52}H_{54}B_2F_4N_6O_2$ = 892.4425 [M^+]); ^{1}H NMR (CD_2Cl_2, 500 MHz, 298K): δ = 8.56-8.53 (m, 6H; phenyl and quinolyl), 8.12 (d, *J* = 9.0 Hz, 2H; quinolyl), 7.76 (d, *J* = 7.8 Hz, 2H; quinolyl), 7.71 (dd, J_1 = J_2 = 8.0 Hz, 2H; quinolyl), 7.49 (dd, J_1 = J_2 = 7.5 Hz, 2H; quinolyl), 7.26 (d, *J* = 9.0 Hz, 2H; quinolyl), 7.10 (d, *J* = 9.0 Hz, 4H; phenyl), 4.14 (t, *J* = 6.5 Hz, 4H; -OCH_2-), 2.25-0.91 (30H, m, -C_7H_{15}) ppm; ^{11}B NMR ($CDCl_3$, 160 MHz, 298K): δ = 2.2 (t, J_{BF} = 33 Hz) ppm; ^{19}F NMR ($CDCl_3$, 471 MHz, 298K): δ = –104 (q, J_{FB} = 32 Hz) ppm; UV/vis ($CHCl_3$): λ_{max} [nm] (ε) = 435 (22000), 619 (36300), 671 (100000).

ii. MO diagrams of PPABs

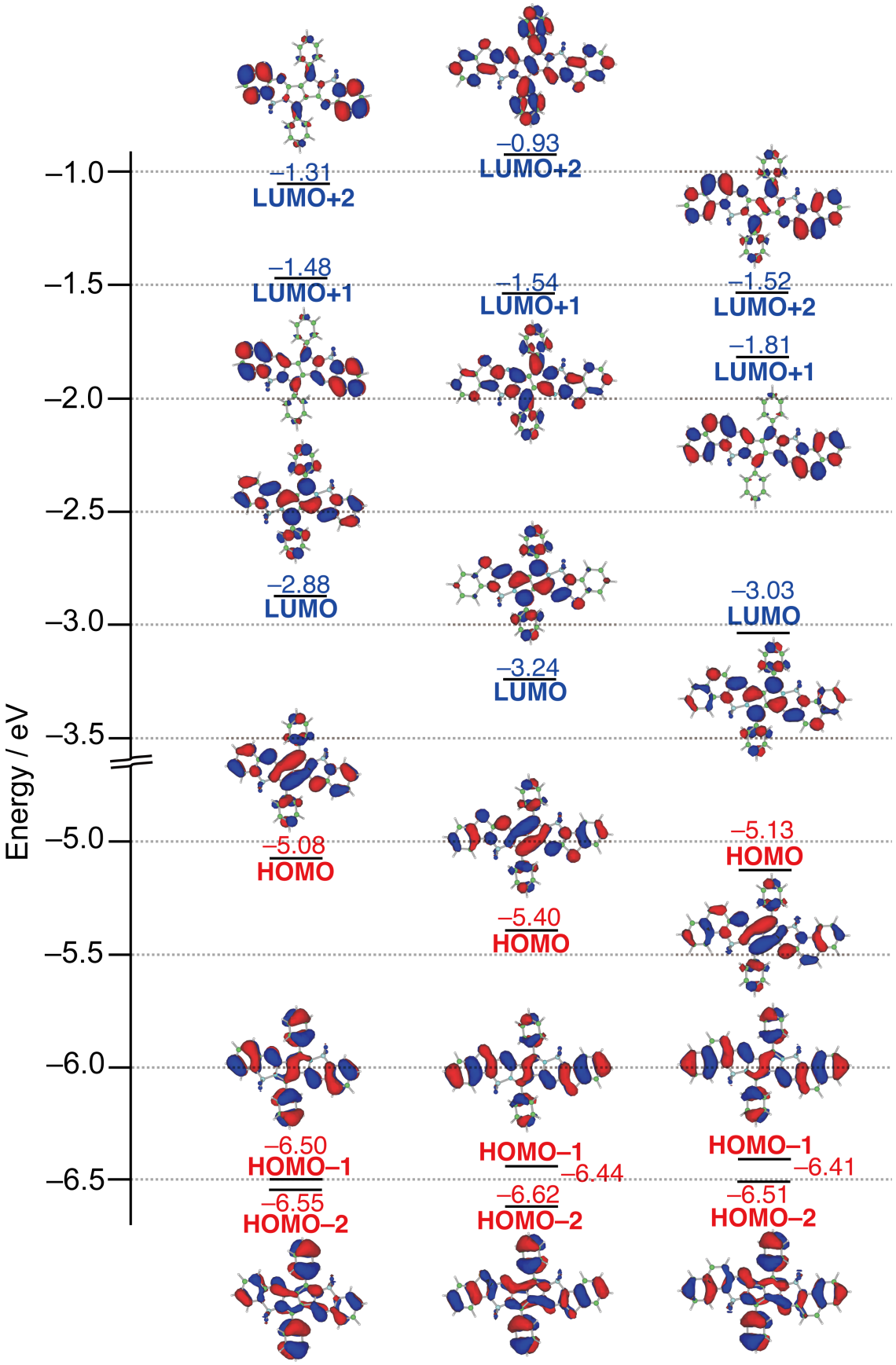

Fig. S4. Partial molecular orbitals of **3a** (left), **3b** (middle), and **3c** (right) based on B3LYP/6-31G(d). *p*-Octyloxyphenyl substituents were replaced by phenyl substituents for simplicity.

iii. TD DFT calculations of PPABs

Table S1. Selected transition energies and wave functions of **3a**, **3b**, and **3c** calculated by the TDDFT method (B3LYP/6-31G(d)).

compd	energy [nm]	f [a]	wave function[b]
3a	580	0.65	+ 0.713 | L ← H> +…
	391	0.22	+ 0.647 | L ← H–2> – 0.228 | L+2 ← H> + 0.117 | L ← H–4> +…
	375	0.14	+ 0.565 | L+2 ← H> + 0.250 | L ← H–2> – 0.331 | L ← H–4> +…
	305	0.58	+ 0.682 | L+4 ← H> – 0.102 | L ← H–2> +…
	273	0.19	+ 0.675 | L+1 ← H–1> +…
3b	600	0.81	+ 0.711 | L ← H> +…
	420	0.33	+ 0.694 | L ← H–2> +…
	310	0.58	+ 0.596 | L+2 ← H> – 0.351 | L ← H–10> +…
	280	0.36	+ 0.689 | L+1 ← H–1> +…
3c	613	0.91	+ 0.712 | L ← H> +…
	413	0.16	+ 0.650 | L ← H–2> – 0.252 | L+2 ← H> +…
	386	0.24	+ 0.545 | L+2 ← H> + 0.318 | L ← H–6> – 0.194 | L ← H–3> + 0.230 | L ← H–2> + …
	306	0.35	+ 0.641 | L+4 ← H> – 0.258 | L+1 ← H–1> +…
	297	0.22	+ 0.627 | L+1 ← H–1> + 0.265 | L+4 ← H> +…
	277	0.22	+ 0.533 | L+1 ← H–4> – 0.319 | L+1 ← H–5> + 0.115 | L+1 ← H–7> – 0.173 | L+2 ← H–3> – 0.196 | L+6 ← H> +…
	273	0.13	+ 0.585 | L+2 ← H–2> – 0.292 | L+1 ← H–7> +…
	269	0.12	+ 0.598 | L+1 ← H–7> + 0.298 | L+2 ← H–2> +…

[a] Oscillator strength. [b] Wave functions based on the eigenvectors predicted by TD DFT. H and L represent HOMO and LUMO, respectively.

iv. References

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