Supporting Information

Synthesis and properties of β,β-sp^3-hybridized subphthalocyanine analogues

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Contents:

i. Experimental

General procedure: Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer. Magnetic circular dichroism (MCD) spectra were recorded on a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet, which produces magnetic fields of up to 1.09 T (1 T = 1 tesla) with both parallel and antiparallel fields. The magnitudes were expressed in terms of molar ellipticity per tesla ($[\theta]_M$ / deg dm^3 mol^{-1} cm^{-1} T^{-1}). ^{1}H NMR spectra were recorded on a JEOL Alfa-500 spectrometer (operating at 500.00 MHz) and a Bruker AVANCE 400 spectrometer (operating at 400.33 MHz) using a residual solvent as an internal reference for ^{1}H (δ = 7.26 ppm for $CDCl_3$). High resolution mass spectra were recorded on a Bruker Daltonics Apex-III spectrometer or on an AB SCIEX 4800 *Plus* MALDI TOF/TOF Analyzer. CV measurements were recorded with a Hokuto Denko HZ5000 potentiostat under nitrogen atmosphere in distilled *o*-dichlorobenzene (*o*-DCB) solutions with 0.1 M of tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. Measurements were made with a glassy carbon electrode (area = 0.07 cm^2), an Ag/AgCl reference electrode, and a Pt wire counter electrode. The concentration of the solution was fixed at 0.5 mM and the sweep rates were set to 100 mV/s and 50 mV/s for CV measurements. The ferrocenium/ferrocene (Fc^+/Fc) couple was used as an internal standard. Preparative separations were performed by silica gel column chromatography (Silica gel 60, Merck) and recycling preparative GPC-HPLC (JAI LC-9201 with preparative JAIGEL-2H, 2.5H, and 3H columns). All reagents and solvents were of commercial reagent grade and were used without further purification except where noted.

Crystallographic data collection and structure refinement: Data collection for **1** was carried out at –173 °C on a Bruker APEXII CCD diffractometer with MoKα radiation (λ = 0.71073 Å). The structures were solved by a direct method (SHELXS-97)[1] and refined using a full-matrix least square technique (SHELXL-97).[1] Yadokari-XG 2009 software was used as a GUI for SHELXL-97.[2] CCDC-861339 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational methods: The Gaussian 09 software package[3] was used to carry out DFT and TDDFT calculations at the B3LYP/6-31G(d) level. Structural optimization was performed on model compounds of **1**-**4**.

General synthetic procedures:

Dibenzotriazasubchlorin 1: To a 1,2,4-trichlorobenzene solution (1.0 ml) of tetrafluorophthalonitrile (200 mg, 1.0 mmol) and tetramethylsuccinonitrile (299 mg, 2.2 mmol) was added a 1.0 M *p*-xylene solution of boron trichloride (1.0 ml), and the resultant mixture was heated at 200 °C for 30 min. After removing the solvent, the residue was purified on silica gel column using chloroform as an eluent. **1** was further purified by recycling GPC HPLC and finally recrystallized from chloroform and hexane to provide pure **1** in 1.2% yield (3.5 mg).

HR-ESI-FT-ICR-MS (m/z): 605.0668 (calcd for $C_{24}H_{12}N_6F_8BClNa$ = 605.0669 $[M+Na]^+$); ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 2.03 (s, 6H; β-methyl), 1.16 ppm (s, 6H; β-methyl); UV/vis ($CHCl_3$): λ_{max} [nm] (ε) = 269 (23300), 454 (10900), 632 (42900).

Triazasubchlorin 3: To a 1,2,4-trichlorobenzene solution (1.0 ml) of fumaronitrile (78 mg, 1.0 mmol) and tetramethylsuccinonitrile (136 mg, 1.0 mmol) was added a 1.0 M *p*-xylene solution of boron trichloride (1.0 ml), and the resultant mixture was heated at 200 °C for 30 min. The same reaction was performed several times and the combined reaction mixture was purified by silica gel chromatography and GPC HPLC to provide **3** as a pure form in less than 0.1% yield.

HR-MALDI-TOF-MS (m/z): 338.1228 (calcd for $C_{16}H_{16}N_6BCl$ = 338.1218 $[M]^+$); ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.92 (d, 2H, J = 4.8 Hz; β-CH), 7.38 (d, 2H, J = 4.8 Hz; β-CH), 1.13 (s, 6H; β-methyl), 1.09 ppm (s, 6H; β-methyl); UV/vis ($CHCl_3$): λ_{max} [nm] (ε) = 300 (41300), 383 (9450), 561 (52200).

ii. Packing diagram of the crystal structure of 1

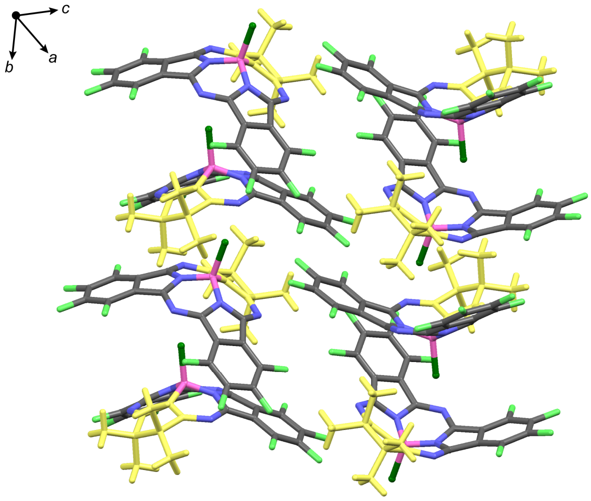

Figure S2. Packing diagram of the crystal structure of **1**. The pyrroline units are highlighted as a yellow color.

iii. Cyclic voltammogram of 1

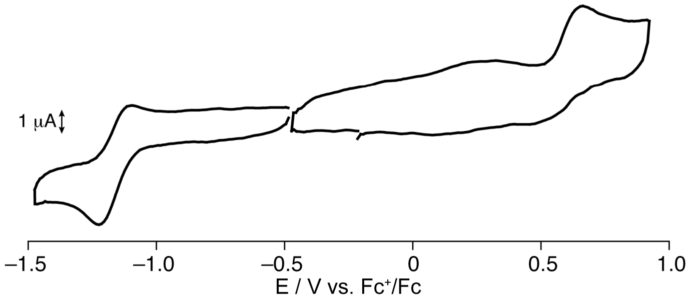

Figure S2. Cyclic voltammogram of **1** in *o*-DCB containing 0.1 M TBAP (Sample concentration = 0.5 mM).

Table S1. Redox potentials of **1** and **2** (V vs. Fc⁺/Fc). ΔE is the difference between the first oxidation and reduction potentials.

compound	Ox.	Red.	ΔE
1	0.67	–1.15	1.82
2	1.14	–0.97	2.11

iv. Molecular orbital diagram of 3 and 4

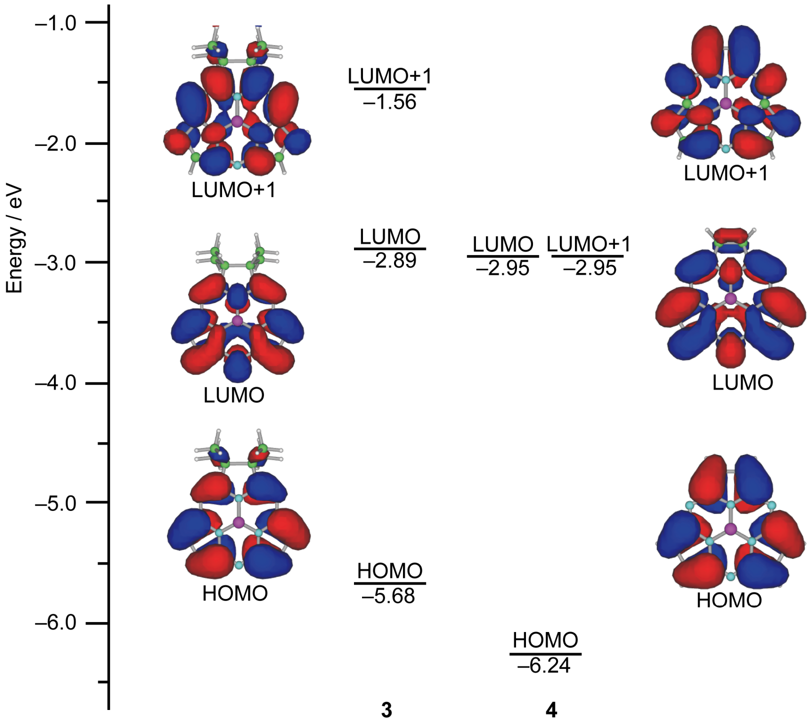

Figure S3. Partial frontier molecular orbital diagram of **3** (left) and **4** (right).

v. TDDFT calculations

Table S2. Selected transition energies and wave functions calculated by the TDDFT (B3LYP/6-31G(d)) method.

compd	energy [nm]	*f*[a]	wave function[b]
1	545	0.40	+ 0.704 |147 ← 146> + …
	430	0.12	+ 0.677 |148 ← 146> – 0.133 |147 ← 141> + 0.150 |147 ← 143> + …
2	515	0.32	+ 0.692 |160 ← 158> + 0.118 |159 ← 153> + …
	515	0.32	+ 0.692 |159 ← 158> – 0.118 |160 ← 153> + …
3	460	0.19	+ 0.694 |89 ← 88> + 0.133 |90 ← 86> + …
	352	0.021	+ 0.564 |90 ← 88> – 0.203 |89 ← 85> – 0.362 |89 ← 86> + …
4	412	0.114	+ 0.653 |73 ← 71> + 0.261 |72 ← 68> + …
	412	0.114	+ 0.653 |72 ← 71> – 0.261 |73 ← 68> + …

[a] Oscillator strength. [b] Wave functions based on the eigenvectors predicted by TDDFT. The |146>, |158>, |88>, and |71> represent the HOMO of **1**, **2**, **3**, and **4**, respectively.

vi. References

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2. Yadokari-XG, Software for Crystal Structure Analyses, K. Wakita, (2001); Release of Software (Yadokari-XG 2009) for Crystal Structure Analyses, C. Kabuto, S. Akine, T. Nemoto, and E. Kwon, *J. Cryst. Soc. Jpn.*, 2009, **51**, 218.

3. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.