

Electronic Supplementary Information

Design, synthesis and optical properties of unsymmetrical subphthalocyanine trimer connected by phloroglucinol via axial positions

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Reference [13]

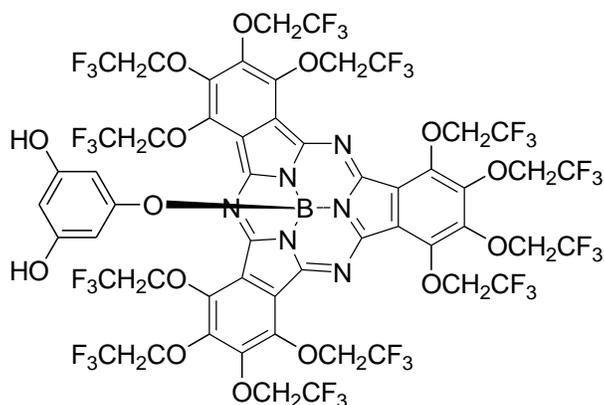
References

Experimental procedure

General information.

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred *via* syringe and were introduced into the reaction vessels through a rubber septum. All solvents were purified by standard method. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or KMnO_4 in water/heat. Column chromatography was carried out on a column packed with silica gel (60N spherical neutral size 63-210 μm). The ^1H NMR (300 MHz) and ^{19}F NMR (282 MHz) (with hexafluorobenzene (δ -162.2 ppm) as an internal standard) spectra for solution in CDCl_3 were recorded on a Varian Mercury 300. Chemical shifts (δ) are expressed in ppm downfield from internal TMS. UV-vis spectra were recorded on a JASCO V-530 spectrometer. IR spectra were recorded on a JASCO FT/IR-200 spectrometer. Fluorescence spectroscopy was recorded on a JASCO FP-6200 Fluorospectrometer. MALDI-TOF mass spectra were taken on a SHIMADZU Axima CFR Plus. Electrochemical experiments were carried out using THF solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) on a HOKUTO DENKO HZ5000 electrochemical measurement system. TBAPF was purchased from TCI and recrystallized from EtOH. The solvent THF (Kanto Chemical Co. Inc., tetrahydrofuran, dehydrated stabilizer free) was passed through Glass Contour Ultimate Solvent System. For CV, 3 mm glassy carbon electrode was used as a working electrode and platinum wire as a counter electrode. Ag/AgNO_3 (0.01 M in MeCN/0.1 M tetrabutylammonium perchlorate) was used as a reference electrode separated by vycor glass. The CV measurements were performed using a concentration of approximately 1.0 mM of the compounds. Ferrocene (Fc) was added as an internal reference and all the potentials were referenced relative to the Fc/Fc^+ couple.

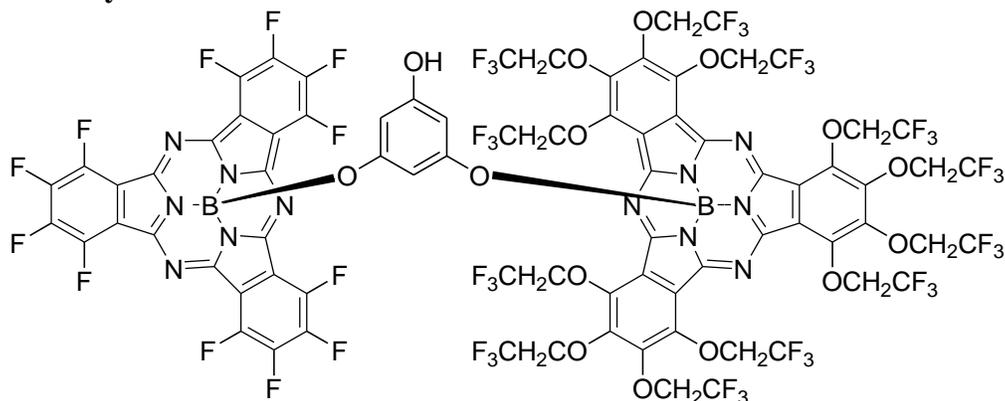
Subphthalocyanine 4



To a solution of phloroglucinol **3** (212.0 mg, 1.68 mmol) and TFE0-SubPc **2a** (539 mg, 0.335 mmol) in toluene (5.0 mL) was added triethylamine (187.3 μL , 1.34 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was heated at 120 $^\circ\text{C}$ and stirred at that temperature for 12 h. After cooling to room temperature, the resulting mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 70/30) to give analog **4** (123 mg,

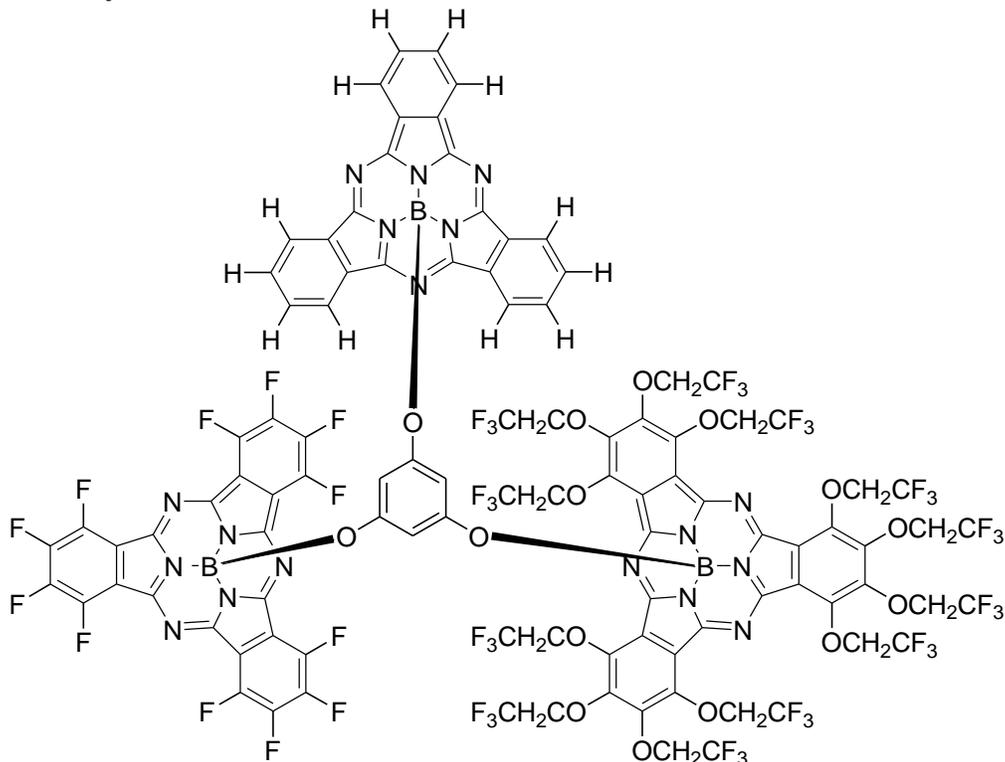
22%) as a purple solid.; ^1H NMR (CDCl_3 , 300 MHz): δ = 4.50 (s, 2H), 4.5 to 4.8 (brm, 12H), 5.1 to 5.4 (brm, 12H), 5.70 (s, 1H); ^{19}F NMR (CDCl_3 , 282 MHz): δ = -75.3 (brs, 18F), -74.7 (brm, 18F); IR (KBr): 3442, 2964, 2919, 2852, 1617, 1507, 1458, 1432, 1281, 1164, 1129, 1067, 970, 833, 670, 548 cm^{-1} ; MALDI-TOF MS (dithranol): 1694.6—1698.8 ($[\text{M}^+]$, isotopic pattern).

Subphthalocyanine **5**



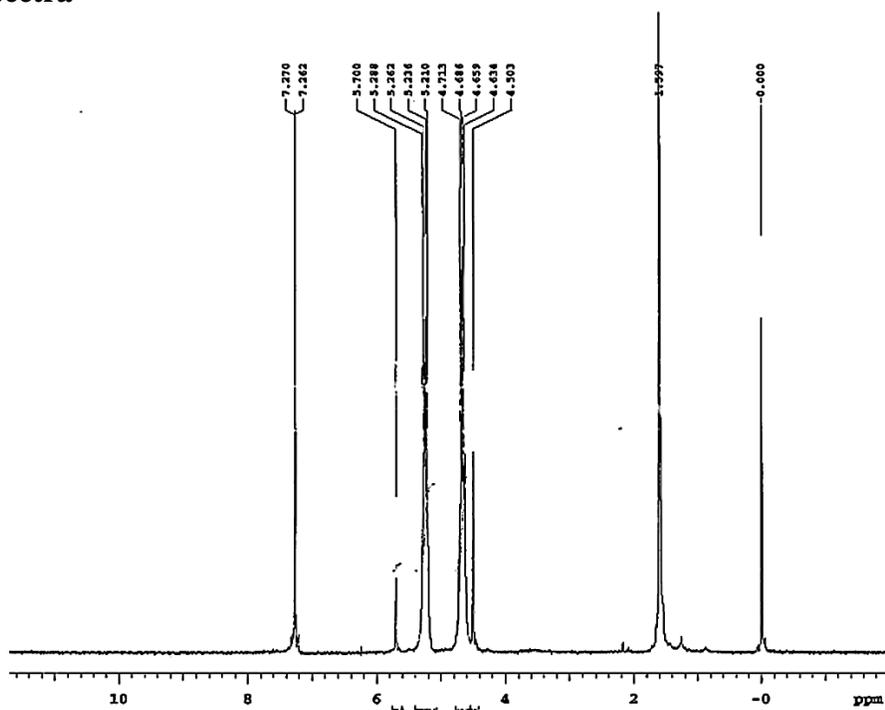
A mixture of F-SubPc **2b** (50.3 mg, 0.0779 mmol) and silver trifluoromethanesulfonate (25.0 mg, 0.0973 mmol) in toluene (5.0 mL) was stirred at room temperature under nitrogen atmosphere for 2 h. After generating trifluoromethanesulfonated F-SubPc, **4** (110 mg, 0.0649 mmol) and *N,N*-diisopropylethylamine (16.9 μL , 0.0973 mmol) were added. The reaction mixture was heated at 70 $^\circ\text{C}$ and stirred at that temperature for 12 h. After cooling to room temperature, the resulting mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 70/30) to give analog **5** (35.7 mg, 24%) as a purple solid.; ^1H NMR (CDCl_3 , 300 MHz): δ = 2.98 (s, 1H), 3.59 (s, 1H), 4.45 (s, 1H), 4.5 to 4.8 (brm, 12H), 5.1 to 5.3 (brm, 12H); ^{19}F NMR (CDCl_3 , 282 MHz): δ = -147.67 (d, J = 13.0 Hz, 6F), -137.34 (d, J = 14.1 Hz, 6F), -75.4 (brm, 18F), -74.7 (brm, 18F); IR (KBr): 3420, 2957, 2850, 1652, 1488, 1435, 1281, 1164, 1110, 1068, 967 cm^{-1} ; MALDI-TOF MS (dithranol): 2304.6—2309.5 ($[\text{M}^+]$, isotopic pattern).

Subphthalocyanine trimer 1

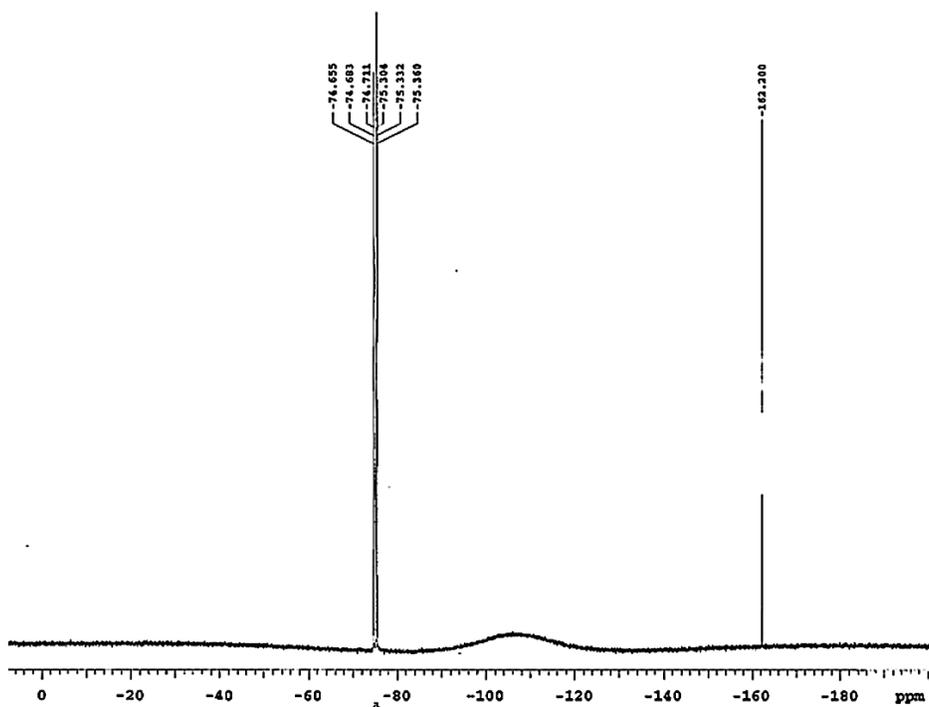


A mixture of H-SubPc **2c** (13.4 mg, 0.0311 mmol) and silver trifluoromethanesulfonate (11.9 mg, 0.0463 mmol) in toluene (5.0 mL) was stirred at room temperature under nitrogen atmosphere for 2 h. After generating trifluoromethanesulfonated H-SubPc, **5** (35.7 mg, 0.0155 mmol) and *N,N*-diisopropylethylamine (8.1 μ L, 0.0465 mmol) were added. The reaction mixture was heated at 70 $^{\circ}$ C and stirred at that temperature for 12 h. After cooling to room temperature, the resulting mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 80/20) to give SubPc trimer **1** (19.3 mg, 46%) as a purple solid.; ^1H NMR (CDCl_3 , 300 MHz): δ = 2.59 (s, 1H), 2.83 (s, 1H), 2.94 (s, 1H), 4.5 to 4.8 (brm, 12H), 4.9 to 5.2 (brm, 12H), 7.92 (brm, 6H), 8.73 (brm, 6H); ^{19}F NMR (CDCl_3 , 282 MHz): δ = -147.9 (brm, 6F), -137.2 (brm, 6F), -75.3 (brm, 18F), -74.8 (brm, 18F); IR (KBr): 2959, 2918, 2850, 1487, 1458, 1437, 1283, 1166, 1128, 1066, 967, 805, 744, 595 cm^{-1} ; MALDI-TOF MS (dithranol): 2698.6—2703.7 ($[\text{M}^+]$, isotopic pattern).

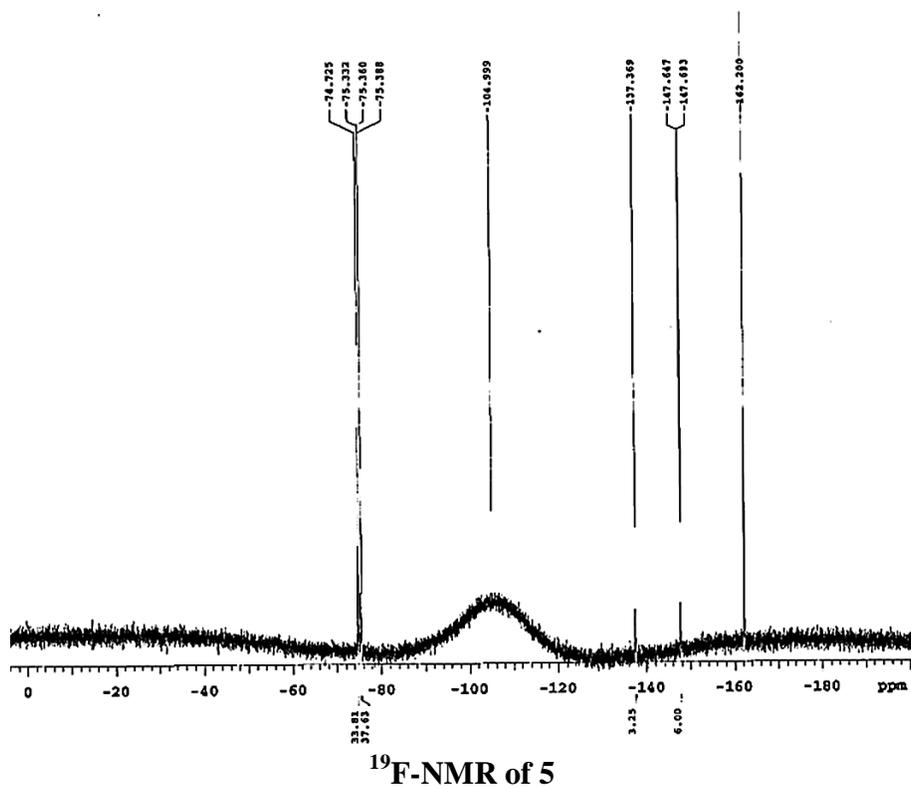
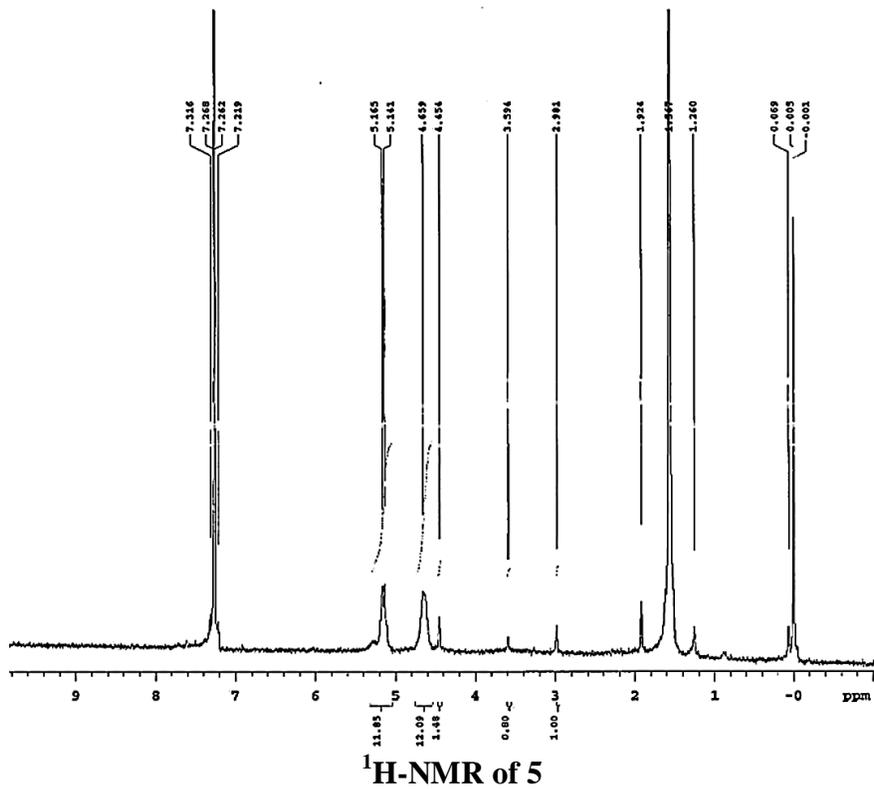
NMR spectra

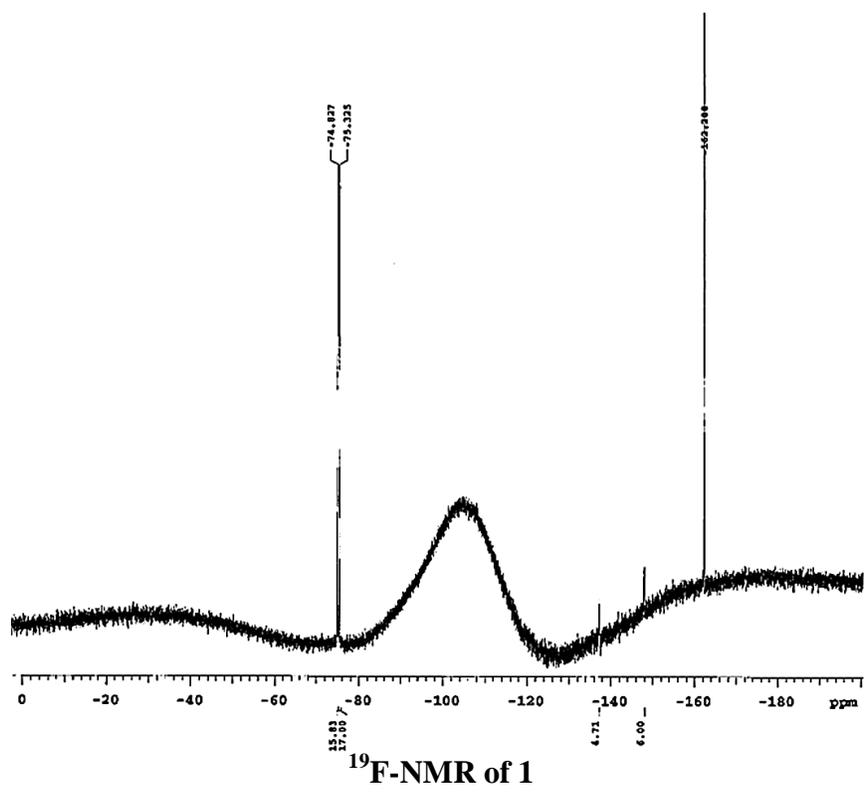
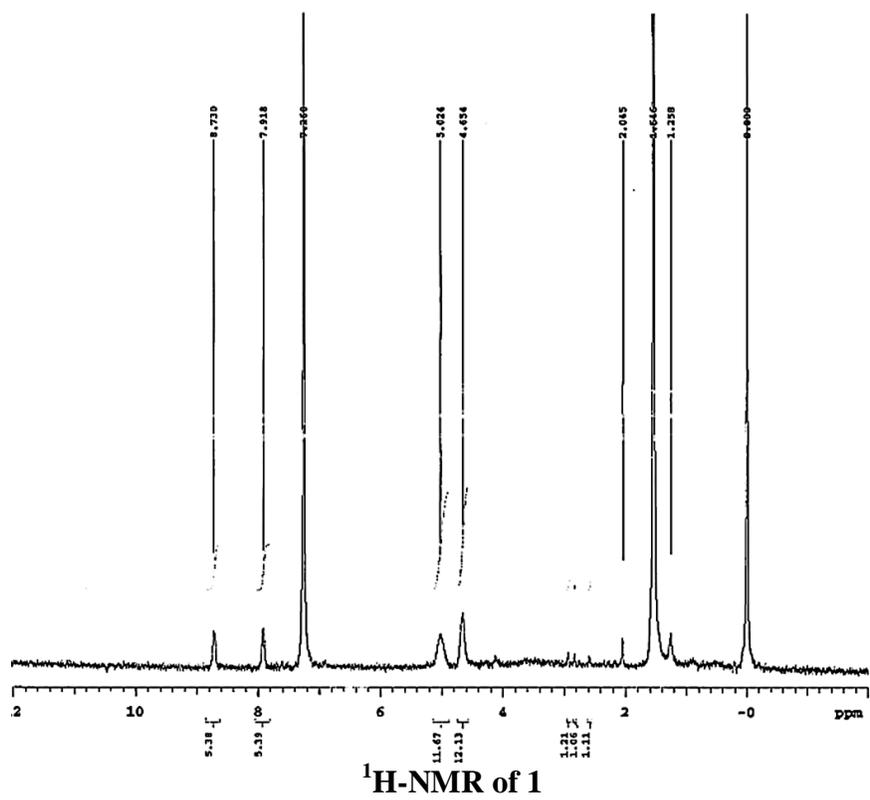


$^1\text{H-NMR}$ of 4



$^{19}\text{F-NMR}$ of 4





Computational method

The geometries of **1** and **2a-c** were first optimized by AM1 method using SPARTAN program (Ref. S1). The optimized geometries were further optimized at the B97D/6-31G* level. The HOMO and LUMO energy levels of **1** and **2a-c** were calculated using the optimized geometries. The HOMO and LUMO energy levels calculated for **1** and **2a-c** at the B97D/6-31G* and B3LYP/6-31G* levels are summarized in Table S1. The trend of HOMO and LUMO energy levels for the **2a-c** obtained by the B97D/6-31G* level calculations is the same as that obtained by the B3LYP/6-31G* level calculations. The molecular orbital energy levels calculated for **1** (trimer) are summarized in Table S2. The distributions of the eight molecular orbitals (from HOMO-3 to LUMO+3) obtained by the B3LYP/6-31G* level calculations (Fig. 6) are nearly identical to those obtained by the B97D/6-31G* and B3LYP/6-311G** level calculations.

Supplemental table

Table S1. Calculated HOMO and LUMO energy levels for 1 (trimer) and 2a-c (TFEO-subPc, F-subPc and H-subPc) in eV.

	B97D/6-31G*		B3LYP/6-31G*	
	HOMO	LUMO	HOMO	HOMO
TFEO-subPc 2a	-4.85	-3.23	-5.48	-5.48
F-subPc 2b	-5.39	-3.74	-6.03	-6.03
H-subPc 2c	-4.81	-3.02	-5.30	-5.30
trimer 1	-4.93	-3.58	-5.46	-5.46

Table S2. Calculated energy levels of molecular orbitals for 1 (trimer) in eV.

	B97D/6-31G*	B3LYP/6-31G*	B3LYP/6-311G**
LUMO+3	-3.40	-3.14	-3.46
LUMO+2	-3.44	-3.19	-3.51
LUMO+1	-3.55	-3.29	-3.63
LUMO	-3.58	-3.33	-3.67
HOMO	-4.93	-5.46	-5.74
HOMO-1	-5.01	-5.65	-5.96
HOMO-2	-5.20	-5.86	-6.20
HOMO-3	-5.33	-6.27	-6.62

Reference [13]

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S1 SPARTAN 14, Wavefunction Inc., Irvine, CA, 2014.

Except for molecular mechanics and semi-empirical models, the calculation methods used in *Spartan* have been documented in: Y. Shao, L. F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. T. Brown, A. T. B. Gilbert, L. V. Slipchenko, S. V. Levchenko, D. P. O'Neill, R. A. DiStasio Jr., R. C. Lochan, T. Wang, G. J. O. Beran, N. A. Besley, J. M. Herbert, C. Y. Lin, T. Van Voorhis, S. H. Chien, A. Sodt, R. P. Steele, V. A. Rassolov, P. E. Maslen, P. P. Korambath, R. D. Adamson, B. Austin, J. Baker, E. F. C. Byrd, H. Dachsel, R. J. Doerksen, A. Dreuw, B. D. Dunietz, A. D. Dutoi, T. R. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C-P. Hsu, G. Kedziora, R. Z. Khalliulin, P. Klunzinger, A. M. Lee, M. S. Lee, W. Z. Liang, I. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. M. Rhee, J. Ritchie, E. Rosta, C. D. Sherrill, A. C. Simmonett, J. E. Subotnik, H. L. Woodcock III, W. Zhang, A. T. Bell, A. K. Chakraborty, D. M. Chipman, F. J. Keil, A. Warshel, W. J. Hehre, H. F. Schaefer, J. Kong, A. I. Krylov, P. M. W. Gill and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3172.

A discussion and assessment of commonly-used calculation methods is found in: W. J. Hehre, *A Guide to Molecular Mechanics and Quantum Chemical Calculations*, Wavefunction, Inc., Irvine, CA, 2003. This is available as a PDF under the Help menu.