Supporting Information

Pyrene-Fused Subphthalocyanine

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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}). Fluorescence spectrum was measured on a Hitachi F-4500 spectrofluorimeter. Fluorescence quantum yield was determined relative to Rhodamine 6G ($\Phi_F = 0.94$, upon excitation at 488 nm).[1] The fluorescence lifetime was measured with a picosecond light pulser (Hamamatsu Photonics C4725; 408 nm; 59 ps FWHM) and a streak-scope (Hamamatsu Photonics, C4334-02). ^{1}H NMR spectrum was recorded on a Bruker AVANCE 400 spectrometer (operating as 400.33 MHz for ^{1}H) using the residual solvent as the internal reference for ^{1}H ($\delta = 7.26$ ppm for $CDCl_3$). High resolution mass spectra were recorded on a Bruker Daltonics Apex-III spectrometer. Preparative separations were performed by silica gel column chromatography (Merck Kieselegel 60H) 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 **4** and cocrystallate (**4-C$_{60}$**) were carried out at –173 °C on a Bruker APEXII CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by a direct method (SHELXS-97 or Sir 2004)[2,3] and refined using a full-matrix least square technique (SHELXL-97).[2] CCDC-780572 and -780573 contain the supplementary crystallographic data for **4** and **4-C$_{60}$**. 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 crystal structure of **4**, two chloroform molecules are positioned in the unit cell with a disordered fashion. Therefore, the chloroform molecules were refined under thermally and positionally restrained conditions, using DFIX, SIMU, ISOR, and DELU commands. The carbon atom of one of the chloroform solvent molecule is disordered at two positions (C51 and C53) with 0.48 and 0.52 occupancies. Although the ADPs of the chloroform molecules are still slightly high, which is listed as C level alerts, this would be acceptable considering that two chloroform molecules lie reasonably in the solvent accessible voids. Some other large electron densities were observed in the unit cell due to another chloroform solvent molecule(s). As we failed to model it properly, the rest molecules were refined without the effect of the unknown solvent molecule(s) by the Platon squeeze technique.[4]

There are 147 restraints in the final refinement, of which 15 for DFIX, 18 for DELU, 60 for SIMU, and 54 for ISOR commands.

In the case of the crystal structure of **4-C$_{60}$**, first, lower symmetry space group, such as triclinic, was utilized for refinement, but the crystal structure was much more properly refined at the current space group (monoclinic, P2/n). The C$_{60}$ resides on a 2-fold axis and the positions of the carbon atoms are severely disordered. Therefore, it was modeled with two C$_{60}$ molecules and the sum of the occupancy of these C$_{60}$ molecules was set to 0.5. Due to the severe disorder of the C$_{60}$ molecules despite the low measurement temperature of –173 °C, they were refined under thermally and positionally restrained conditions, using DFIX, DANG, SIMU, ISOR, and DELU commands.

Some large electron peaks due to a solvent toluene molecule(s) was found in the unit cell. As we failed to model them properly, the rest molecules were refined without the effect of the solvent molecule(s) by the Platon squeeze technique.[4] Despite using Platon squeeze for smoothing the residual electron densities, some peaks having electron densities greater than 1.0 (< 1.28) are still observed at the C$_{60}$ molecule mainly due to its severe disorder.

There are 2877 restraints in the final refinement, of which 178 for DFIX, 358 for DANG, 540 for DELU, 1080 for SIMU, 720 for ISOR, and 1 for SUMP commands.

The Z of 4 in the cif file is correct, but there is a problem in the cif check program that does not estimate Z correctly because the disorder over symmetry element is present in this case.

Computational methods: The Gaussian 03 software package[5] was used to carry out DFT and TDDFT calculations using the B3LYP functional with 6-31G(d) basis sets. Structural optimization was performed on model compounds of **2** and **4** based on the crystal structure in which the *tert*-butyl substituents and axial phenoxy ligand were replaced with hydrogen atoms and hydroxy group for simplicity.

ii. Synthesis

Synthesis of 2,7-di-*tert*-butyl-4,5,9,10-tetracyanopyrene (1): A mixture of 2,7-di-*tert*-butyl-4,5,9,10-tetrabromopyrene (1.1 g, 1.7 mmol) and CuCN (1.5 g, 17 mmol) in DMI (1,3-dimethyl-2-imidazolidinone, 50 ml) was stirred at 220 °C for 2 hours. The resultant mixture was poured into aqueous ammonia and O_2 was bubbled into the solution overnight. The suspension was then filtered and the filtrate was collected. The filtrate was purified by silica gel column using $CHCl_3$ as an eluent and the product was recrystallized from hexane/toluene to give yellow powder (0.19 g, 29%). EI-MS (*m*/*z*): 414.1842 ($C_{28}H_{22}N_4$ = 414.1844 [M^+]); ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.93 (s, 4H; pyrene), 1.66 ppm (s, 18H; *tert*-butyl).

Synthesis of pyrene-fused subphthalocyanine (4): A mixture of 2,7-di-*tert*-butyl-4,5,9,10-tetracyanopyrene **1** (41 mg, 0.1 mmol) and tetrafluorophthalonitrile (400 mg, 2.0 mmol) in 1-chloronaphthalene (1.0 ml) was stirred at 230 °C for 5 seconds. Then 1.0 M *p*-xylene solution of BCl_3 (0.8 ~ 1.0 ml) was added, and the resultant mixture was stirred for 1 hour. After the solvent was removed, excess amount of phenol (985 mg, 10.5 mmol) was added, and the mixture was heated at 120 °C for 5 hours. Phenol was removed by careful washing of the mixture with aqueous NaOH solution. The residue was purified by silica gel column and subsequently by GPC-HPLC to give axially phenoxy substituted PySubPc **4** in 0.9% (0.8 mg) yield. ESI-FT-ICR-MS (*m*/*z*): 941.2160 ($C_{50}H_{27}BN_8F_8O_1Na$ = 941.2165 [M^++Na]); ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 10.71 (s, 2H; pyrene), 8.85 (s, 2H, pyrene), 6.85 (dd, 2H, J_1 = 8.01 Hz, J_2 = 8.01 Hz; *meta*-phenyl), 6.72 (t, 1H, J = 8.01 Hz; *para*-phenyl), 5.50 (d, 2H, J = 8.01 Hz; *ortho*-phenyl), 1.85 ppm (s, 18H; *tert*-butyl); UV/vis ($CHCl_3$): λ_{max} [nm] (ε) = 305 (69400), 565 (50200), 593 (89200).

iii. ^{1}H NMR spectrum

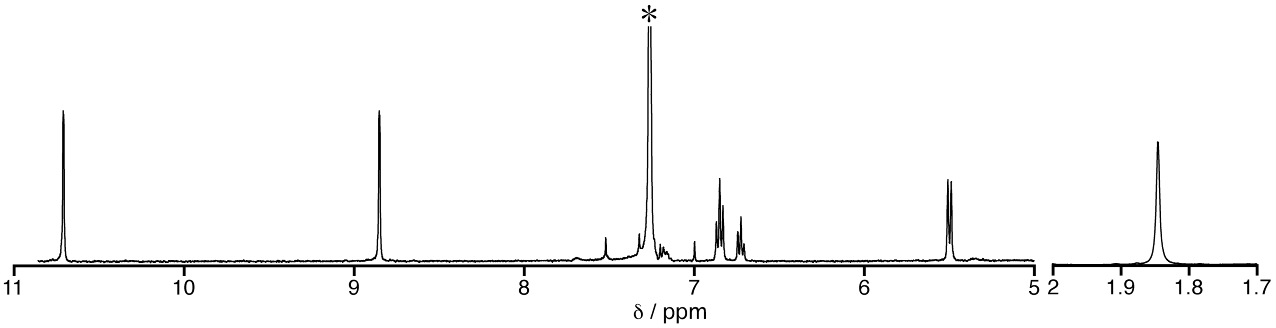

Figure S1. ^{1}H NMR spectrum of **4** in $CDCl_3$. Asterisk indicates the solvent residual peak.

iv. UV/vis absorption spectra in various solvents

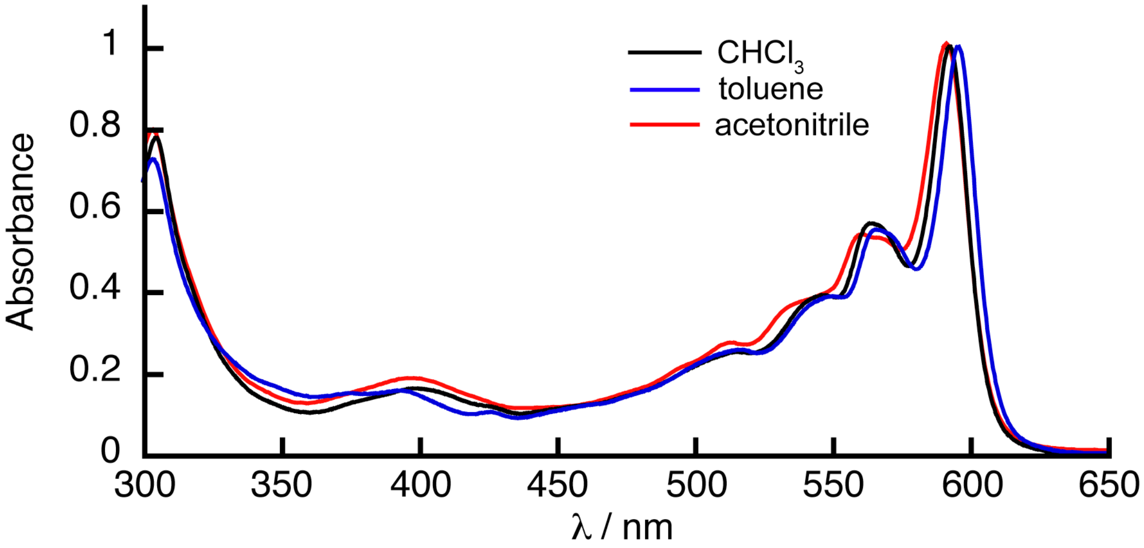

Figure S2. UV/vis absorption spectra of **4** in various solvents.

v. TDDFT calculation of 4

Table S1. Selected transition energies and wave functions calculated by the TDDFT (B3LYP/6-31G(d)) method.

<table>
<tr><th>compd</th><th>energy [nm]</th><th><i>f</i> [a]</th><th>wave function[b]</th></tr>
<tr><td>4</td><td>535</td><td>0.39</td><td>+ 0.619|183 ← 182> + 0.103|184 ← 174>
– 0.110|184 ← 176> – 0.160|184 ← 181> + …</td></tr>
<tr><td></td><td>485</td><td>0.31</td><td>+ 0.561|184 ← 182> – 0.125|183 ← 174>
+ 0.141|183 ← 176> – 0.256|183 ← 181> + …</td></tr>
<tr><td></td><td>469</td><td>0.13</td><td>+ 0.679|184 ← 181> + 0.119|183 ← 182> + …</td></tr>
<tr><td></td><td>393</td><td>0.11</td><td>+ 0.619|185 ← 181> – 0.129|186 ← 180>
– 0.139|183 ← 181> + …</td></tr>
<tr><td></td><td>320</td><td>0.15</td><td>+ 0.537|183 ← 176> + 0.121|183 ← 174>
– 0.132|183 ← 177> – 0.209|184 ← 178>
– 0.315|186 ← 182> + …</td></tr>
<tr><td></td><td>306</td><td>0.15</td><td>0.585|184 ← 176> – 0.148|183 ← 173>
+ 0.164|184 ← 174> – 0.113|183 ← 175>
+ 0.167|184 ← 177> – 0.164|187 ← 182> + …</td></tr>
<tr><td></td><td>296</td><td>0.32</td><td>+ 0.500|186 ← 181> + 0.135|183 ← 171>
+ 0.106|185 ← 175> – 0.311|185 ← 180>
+ 0.138|190 ← 182> + …</td></tr>
</table>

[a] Oscillator strength. [b] The wave functions based on the eigenvectors predicted by TDDFT. Eigenvectors greater than 0.10 are included. The |182> represents the HOMO of **4**.

vi. References

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