

Electronic Supplementary Information (ESI)

Structure-charge transport relationship of 5,15-Dialkylated porphyrins

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Materials Synthesis:

Synthesis of Dipyrromethane Dipyrromethane was produced with slight modification according to the reported literature.¹ Paraformaldehyde (0.9 g, 30 mmol in formaldehyde) was suspended in 20 mL of absolute ethanol and the mixture was refluxed until clear solution appeared. After cooling down, 20-fold of pyrrole (42 mL, 600 mmol) and 1 L of freshly distilled CH₂Cl₂ were added and the mixture was stirred for 5 min to assure that oxygen was removed. Catalyst BF₃·O(Et)₂ (0.5 mL) was then added and stirred at room temperature under N₂ atmosphere in the darkness overnight. After finishing the reaction, removing the solvent under vacuum .excess pyrrole was distilled under reduced pressure. The crude product was purified by silica gel chromatography with an eluent of CH₂Cl₂ /cyclohexane/Et₃N, 100:50:1 and obtained 1.84 g (42%) of the colorless crystalline product.

Synthesis of 5,15-Bis(ethyl) porphyrin (C₂-Por)² Propyl aldehyde (0.58 g, 10.00 mmol) and Dipyrromethane (1.44 g, 10.00 mmol) were added to a dry round-bottomed 2 L flask with 1 L CH₂Cl₂ and degassed with a stream of N₂ for 30 min. BF₃·O(Et)₂ (0.84 mL, 3.3 mmol) was then added, and the solution was stirred under N₂ at room temperature for 1 h and then DDQ (1.72 g, 7.60 mmol) was added. The mixture was stirred at room temperature for an additional 1 hour and then the

solvent was removed. Column chromatography (Silica, CH₂Cl₂:hexane = 1:2, V/V) afforded the porphyrin as the first moving band. Removal of the solvent under vacuum gave product as purple solid. The product was recrystallized with CHCl₂/CH₃OH and obtained the 5,15-Bis(ethyl) porphyrin as light purple crystal. Yield: 0.33 g, 18 %. ¹HNMR (400 MHz, CDCl₃): δ 10.17 (s, 2 H), 9.60 (d, J=4.8 Hz, 4 H), 9.42 (d, J=4.8 Hz, 4 H), 5.08 (m, 4H), 2.19 (t, J=7.6 Hz, 6H), -2.92 (br s, 2 H). ¹³CNMR (400MHz, CDCl₃): d=147.1, 144.2, 132.0, 127.6, 120.1, 104.2, 22.7, 14.2 ppm. MALDI-TOF-MS: m/z=367.2. Elem. Anal. Calcd (%) for C₂₄H₂₂N₄: C, 78.66; H, 6.05; N, 15.29. Found: C, 78.72; H, 6.07; N, 15.79.

Synthesis of 5,15-Bis(n-butyl) porphyrin (C₄-Por) was prepared by a similar procedure as that used for C₂-Por, but with pentanal (0.86 g, 10.00 mmol) and Dipyrromethane (1.44 g, 10.00 mmol) to obtained light purple crystal. Yield: 0.42 g, 20 %. ¹HNMR (400 MHz, CDCl₃): δ 10.18 (s, 2 H), 9.60 (d, J=4.4 Hz, 4 H), 9.42 (d, J=4.4 Hz, 4 H), 5.04 (m, 4H), 2.57 (m, 4H), 1.87 (m, 4H), 1.17 (m, 6H), -2.91 (br s, 2 H). ¹³CNMR (400MHz, CDCl₃): d=147.5, 144.2, 131.9, 127.8, 118.8, 104.3, 40.7, 34.4, 23.7, 14.2 ppm. MALDI-TOF-MS: m/z=423.3. Elem. Anal. Calcd (%) for C₂₈H₃₀N₄: C, 79.59; H, 7.16; N, 13.26 Found: C, 79.62; H, 7.18; N, 13.22.

Synthesis of 5,15-Bis(n-hexyl) porphyrin (C₆-Por) was prepared by a similar procedure as that used for C₂-Por, but with enanthal (1.14 g, 10.00 mmol) and Dipyrromethane (1.44 g, 10.00 mmol) to obtained purple solid. Yield: 0.41 g, 17 %. ¹HNMR (400 MHz, CDCl₃): δ 10.14 (s, 2 H), 9.55 (d, J=4.4 Hz, 4 H), 9.39 (d, J=4.4 Hz, 4 H), 4.98 (m, 4H), 2.57 (m, 4H), 1.85 (m, 4H), 1.56 (m, 4H), 1.45 (m, 4H), 0.99 (m, 6H), -2.97 (br s, 2 H). ¹³CNMR (400MHz, CDCl₃): d=147.4, 144.1, 131.8, 127.7, 118.7, 104.2, 39.7, 34.6, 31.8, 30.3, 22.8, 14.2 ppm. MALDI-TOF-MS: m/z=479.3. Elem. Anal. Calcd (%) for C₃₂H₃₈N₄: C, 80.29; H, 8.00; N, 11.70 Found: C, 80.32; H, 8.03; N, 11.65.

Growth Single Crystal of C₂-Por: Methanol was carefully layered onto the dichloromethane solution of C₂-Por. Slow diffusion over two weeks yielded light purple crystals.

Growth Single Crystal of C₄-Por: Methanol was carefully layered onto the dichloromethane solution of C₄-Por. Slow diffusion over two weeks yielded light purple crystals.

Single Crystal X-ray Diffraction: Small needle-shaped crystal (maximum dimensions <20 μm) of C₂-Por, and C₄-Por were mounted on glass fiber. All measurements were made on a X8 PROTEUM system with a MICROSTAR micro-focus copper rotation anode x-ray generator and a PLATINUM135 CCD detector at 100 K.

Thermo Gravimetric Analysis (TGA): A few milligrams of as synthesized porphyrins materials were loaded on an aluminum/platinum crucible. Weight loss of sample was recorded using a Perkin-Elmer TGA-7 analyzer in the temperature range

50-800 °C under a flowing N₂ stream.

Atomic Force Microscopy (AFM): Images of film surface morphology of as deposited films (50 nm) formed on SiO₂/Si substrate made from porphyrin complexes were recorded using atomic force microscope (AFM, VEECO Multimode V) operating in the tapping mode.

Grazing Incidence X-ray Diffraction (GIXRD): Grazing incidence X-ray diffraction patterns of as-deposited films formed on SiO₂/Si substrate were recorded using a Bruker D8 Advance (θ/θ) diffractometer with a Göbel mirror attachment. Irradiation of the parallel CuK _{α 1,2} X-ray beam was fixed at a grazing incident angle of 1.000° (θ) and the detector was independently moved to collect the diffraction data in 2θ range of 3-30° with a step-size of 0.02° (2θ) at a fixed speed of *ca* 5 second/step.

Fabrication of Field-Effect Transistors and Charge Mobility Measurements: A heavily doped silicon substrate was used as the gate electrode. A silicon dioxide dielectric layer (100 nm) was thermally grown on the silicon substrate. Image reversal photolithography followed by standard lift-off process was used to form the Ti/Au source/drain contact patterns. The fabricated field-effect transistors had a channel width W around 1000 μm and a channel length L of 100 μm . The bottom-contact field-effect transistors based on thin film samples (50 nm) of porphyrins were fabricated on the patterned SiO₂/Si substrate by vacuum-deposition and measured according to standard method.³

Table S1. Crystal data for X-ray structures of C₂-Por and C₄-Por

Compound name	C ₂ -Por	C ₄ -Por
Crystal system /Space group	Monoclinic <i>P21/c</i>	Monoclinic <i>P21/c</i>
Lattice Parameters	<i>a</i> = 13.1977 (4) Å <i>b</i> = 12.7229 (4) Å <i>c</i> = 11.5658 (4) Å β = 103.008 (2)° <i>V</i> = 1892.21 (11) Å ³	<i>a</i> = 9.8980 (6) Å <i>b</i> = 9.3449 (6) Å <i>c</i> = 12.9197 (8) Å β = 107.261 (4)° <i>V</i> = 1141.20 (12) Å ³
Molecular Formular	C ₂₄ H ₂₂ N ₄	C ₂₈ H ₃₀ N ₄
Molecular Weight	366.46	422.56
Z	4	2
D_c(gcm⁻³)	1.286	1.230
μ, mm⁻¹ (CuKα)	0.08	0.07
F(000)	776	452
Max 2θ, °	55°	52.8°
Unique data	4303	2312
Observed data [I > 2σ(I)]	3043	1284
Parameters/restraints	312/0	188/0
R₁/wR₂^[a]	0.064, 0.212	0.074/0.283
Goodness of fit S	1.00	1.00
Residual peak /hole, eÅ⁻³	0.27 e Å ⁻³ -0.27 e Å ⁻³	0.29 e Å ⁻³ -0.23 e Å ⁻³

[a] $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ and $R_w = \frac{[\sum w(|F_o| - |F_c|)^2]^{1/2}}{\sum w|F_o|^2}^{1/2}$ based on the number of observed data $I > 2\sigma(I)$.

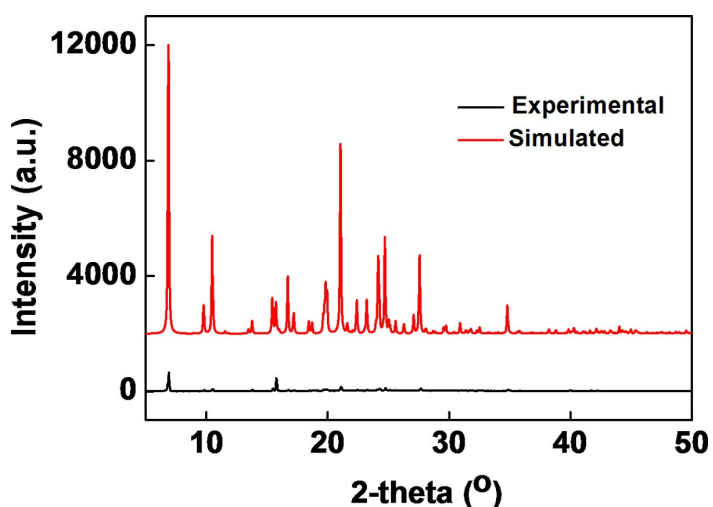


Fig. S1 Experimental PXRD patterns of solid samples of C₂-Por and simulated PXRD patterns calculated from the single crystal X-ray structures.

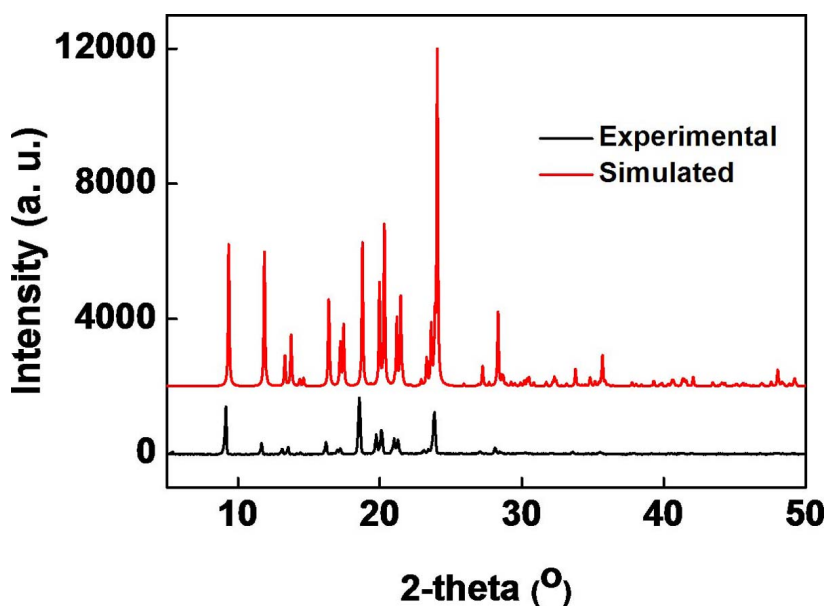


Fig. S2 Experimental PXRD patterns of solid samples of C₄-Por and simulated PXRD patterns calculated from the single crystal X-ray structures.

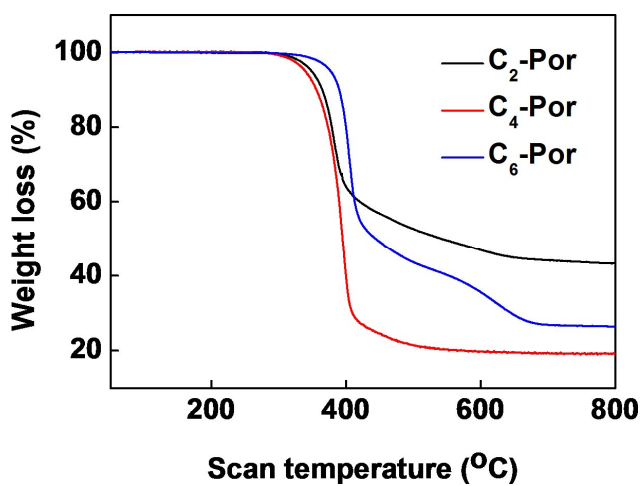


Fig. S3 TGA curve of C_n-Por (n=2, 4, and 6).

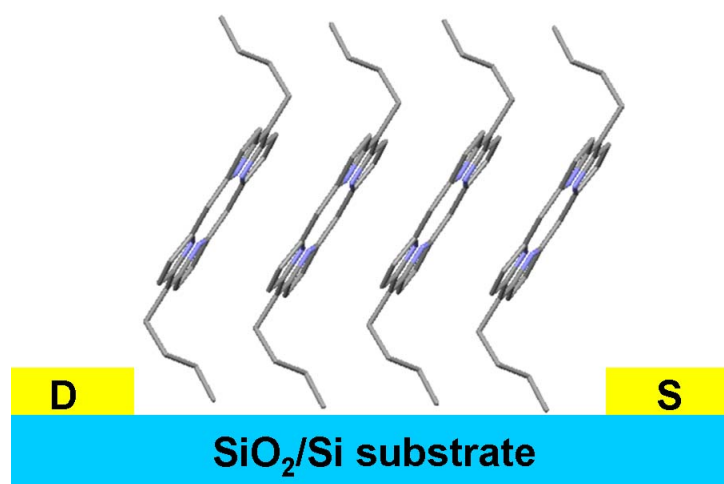


Fig. S4 A schematic drawing of probable molecular alignment of Cn-Por compounds molecules in the films (C₄-Por as example).

Reference

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