

Supporting Information for

Dramatic Enhancement of Carrier Mobility via Effective Secondary Structural Arrangement Resulted from the Substituents on Porphyrin Transistor

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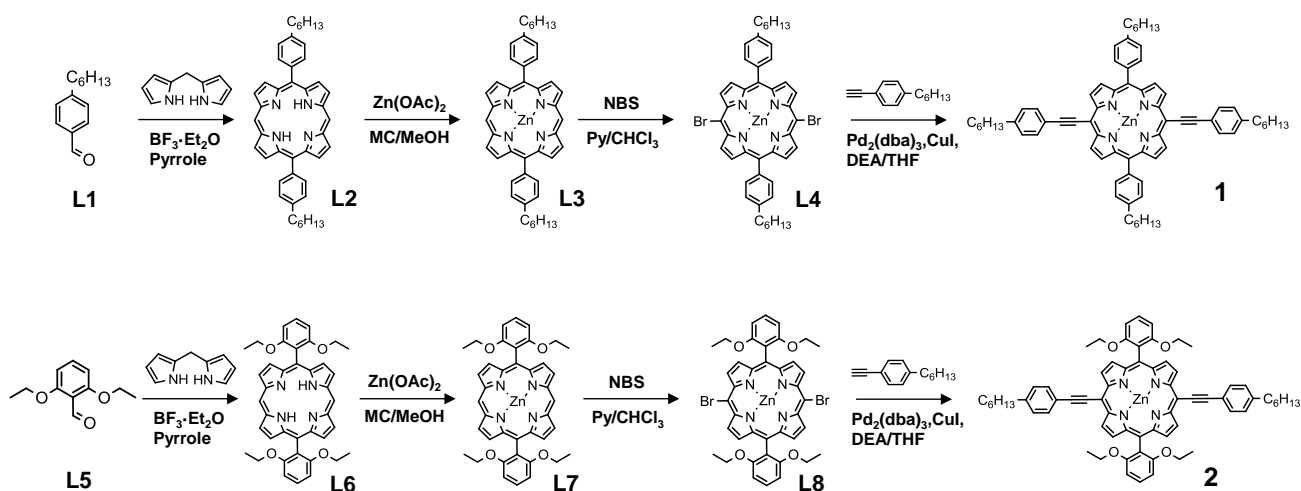
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1. Instrumentations

¹H NMR spectra were recorded on a Varian AS400 (399.937 MHz for ¹H and 100.573 MHz for ¹³C) spectrometer. ¹H chemical shifts are referenced to the proton resonance resulting from protic residue in deuterated solvent and ¹³C chemical shift recorded downfield in ppm relative to the carbon resonance of the deuterated solvents. Absorbance and emission spectra were obtained using an Agilent UV-Vis-NIR spectrophotometer and Hitachi F-7000 fluorescence spectrophotometer. Matrix Assisted Laser Desorption Ionization–Time of Flight (MALDI-TOF) mass spectra were obtained on a Bruker Daltonics LPP20 MALDI TOF Mass Spectrometer Industry-Academic Cooperation Foundation, Yonsei University. The X-ray diffraction experiments were performed using Bruker SMART APEX and Bruker SMART APEX II diffractometers equipped with a monochromator in the Mo K α ($\lambda = 0.71073$ Å) incident beam. The measurements were obtained in a scanning interval of 2θ between 1° and 60° . Powder X-ray diffraction (XRD) measurements were recorded with a Rigaku D/MAX Ultima III using nickel-filtered Cu K α radiation ($\lambda = 1.5418$ Å) over a range of $2^\circ < 2\theta < 40^\circ$ and X'celerator detector operating at 40 kV and 30 mA. The redox properties of the molecules were examined by using cyclic voltammetry (Model: EA161eDAQ). Thin films were prepared on a platinum plate using acetonitrile as a solvent. The employed electrolyte solution was 0.10 M

tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in a freshly dried acetonitrile. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes, respectively. The scan rate was at 50 mV/s. Optical micrographs of crystals was obtained from Metallurgical Microscope (Model: KSM-BA3(T)).



Scheme S1.

2. Synthesis

Materials: All commercially available starting materials and solvents were purchased from Aldrich, TCI, and Acros Co. and used without further purification. All of the reactions and manipulations were carried out under N_2 with standard inert-atmosphere and Schlenk techniques unless otherwise noted. Solvents used in inert-atmosphere reactions were dried using standard procedures. Flash column chromatography was carried out with 230-400 mesh silica-gel from Aldrich using wet-packing method. All deuterated solvents were purchased from Sigma-Aldrich. The porphyrin precursors of 4-hexylbenzaldehyde (L1), 2,2'-dipyrrolemethane, 2,6-diethoxybenzaldehyde (L5), 10,20-bis[2,6-di(ethoxy)phenyl]porphyrin (L6), [10,20-bis[2,6-di(ethoxy)phenyl]porphyrinato] zinc (II) (L7) and [5,15-dibromo-10,20-bis[2,6-di(ethoxy)phenyl]porphyrinato] zinc (II) (L8) were prepared according to the modified literature procedures.^{1,2}

4-Hexylbenzaldehyde (L1). Hexamethylenetetramine (1.65 g, 12 mmol) was added to a solution of hexylbenzene (1.82 g, 11 mmol) in trifluoroacetic acid (TFA, 10 mL) in a 50-mL round-bottom equipped with a magnetic stirbar and the mixture was heated at 80 °C overnight. After cooling to room temperature, the resulting solution was concentrated under reduced pressure, diluted with Et₂O (50 mL), washed with aqueous NaHCO₃ (10 %) and dried over MgSO₄. The resulting residue was purified by silica-gel column chromatography (CH₂Cl₂/hexane, 5:5 v/v) to afford pure **L1** as colorless liquid (1.56 g, 73.2 % yield). ¹H NMR (CDCl₃): δ (ppm) 9.97 (s, 1 H), 7.80 (d, ³J_{H-H} = 8.2 Hz, 2H), 7.34 (d, ³J_{H-H} = 8.2 Hz, 2H), 2.68 (t, ³J_{H-H} = 7.7 Hz, 2H), 1.63–1.58 (m, 2 H), 1.31 (m, 6H), 0.90-0.86 (m, 3H).

10,20-Bis(4-hexylphenyl)porphyrin (L2). 4-Hexylbenzaldehyde (596.2 mg, 3.13 mmol) and 2,2'-dipyrrrolemethane (458 mg, 3.13 mmol) were dissolved in dichloromethane (600 mL) in a 1-L Schlenk flask equipped with a magnetic stirbar and degassed with N₂ for 10 min. TFA (130 μL) was added drop-wise with exclusion of light. The resulting mixture was stirred for 3 h at room temperature. After 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.15 g) was added, the solution was stirred for an additional 2 h. TEA (3.25 mL) was then added and the reaction mixture was evaporated to dryness using a rotary evaporator to yield a dark residue, which was purified by silica-gel column chromatography (CH₂Cl₂/hexane, 4:6 v/v) to afford pure **L2** as a purple solid (278 mg, 28.0 % yield). ¹H NMR (CDCl₃): δ 11.91(s, 2H), 10.31 (s, 2H), 9.12 (d, ³J_{H-H} = 4.4 Hz, 4H), 9.39 (d, ³J_{H-H} = 4.4 Hz, 4H), 8.19 (d, ³J_{H-H} = 7.7 Hz, 4H), 7.62 (d, ³J_{H-H} = 7.7 Hz, 4H), 2.99 (t, ³J_{H-H} = 7.7 Hz, 4H), 1.98-1.93 (m, 4H), 1.63-1.52 (m, 12H), 1.04-0.99 (m, 6H). MS (MALDI-TOF): *m/z* = 631.35 for M⁺; Calcd 630.86.

[10,20-Bis(4-hexylphenyl)porphyrinato]zinc(II) (L3). To a solution of **L2** (569 mg, 0.9 mmol) in

dichloromethane (152.5 mL) was added a solution of Zn(OAc)₂ (1.98 g, 9.0 mmol) in methanol (9.7 mL). The reaction mixture was allowed to stir for overnight. After evaporation of solvent, resulting residue was purified by silica-gel column chromatography (CH₂Cl₂/hexane, 5:5 v/v) to afford pure **L3** as a purple solid (560 mg, 89.5 % yield). ¹H NMR (CDCl₃): δ (ppm) 10.30 (s, 2H), 9.42 (d, ³J_{H-H} = 4.9 Hz, 4H), 9.17 (d, ³J_{H-H} = 4.9 Hz, 4H), 8.17 (d, ³J_{H-H} = 7.7 Hz, 4H), 7.61 (d, ³J_{H-H} = 7.7 Hz, 4H), 3.00 (t, ³J_{H-H} = 7.1 Hz, 4H), 1.99-1.94 (m, 4H), 1.68-1.56 (m, 12H), 1.04-1.00 (m, 6H). ¹³C NMR (CDCl₃): δ 150.72, 149.80, 142.72, 140.35, 135.21, 133.07, 132.05, 128.57, 127.27, 120.69, 36.64, 32.53, 32.28, 29.91, 23.38, 14.85. MS (MALDI-TOF): *m/z*= 692.30 for M⁺; Calcd 694.26.

[5,15-Dibromo-10,20-di(4-hexylphenyl)porphyrinato]zinc (II) (L4). **L3** (337 mg, 0.485 mmol) was dissolved in chloroform (511 mL) with pyridine (0.3 mL). The solution mixture was degassed for 10 min and NBS (172.6 mg, 0.97 mmol) was added. The reaction was stirred for 1 h with exclusion of light and then quenched with acetone (1 mL). The solution was concentrated using a rotary evaporator, which was purified by silica-gel column chromatography (CH₂Cl₂/hexane, 6:4 v/v) to afford pure **L4** as a purple solid (350 mg, 84.7 % Yield). ¹H NMR (CDCl₃): δ (ppm) 9.65 (d, ³J_{H-H} = 4.9 Hz, 4H), 8.92 (d, ³J_{H-H} = 4.9 Hz, 4H), 8.02 (d, ³J_{H-H} = 7.1 Hz, 4H), 7.57 (d, ³J_{H-H} = 7.1 Hz, 4H), 2.97 (t, ³J_{H-H} = 7.1 Hz, 4H), 1.97-1.92 (m, 4H), 1.64-1.52 (m, 12H), 1.03-0.99 (m, 6H). ¹³C NMR (CDCl₃): δ 151.55, 150.59, 143.00, 139.99, 135.08, 134.138, 133.53, 128.65, 127.22, 122.91, 36.61, 32.51, 32.27, 29.88, 23.35, 14.82. MS (MALDI-TOF): *m/z*= 852.20 for M⁺; Calcd 852.05.

5,15-Bis(4-(hexylbenzene-2-yl)ethynyl)-10,20-di(4-hexylphenyl)porphyrinato]zinc(II) (1). A solution of **L4** (200 mg, 0.235 mmol), 1-ethynyl-4-hexylbenzene (131.2 mg, 0.7 mmol), PPh₃ (30.17 mg) and DEA (14.8 mL) in THF (21.5 ml) was degassed with N₂ for 10 min. Pd₂(DBA)₃ (42 mg) and CuI (10.1 mg) were added in mixture and degassed for 5 min. The reaction mixture was allowed to reflux for 48 h under N₂ atmosphere. The residue was evaporated to dryness in vacuo to afford a

solid product which was purified by silica-gel column chromatography (CH₂Cl₂/hexane, 6:4 v/v) to afford pure **1** as a green solid (188 mg, 73.3 % Yield). ¹H NMR (CDCl₃): δ 9.69 (d, ³J_{H-H} = 4.9 Hz, 4H), 8.92 (d, ³J_{H-H} = 4.9 Hz, 4H), 8.09 (d, ³J_{H-H} = 7.7 Hz, 4H), 7.85 (t, ³J_{H-H} = 7.7 Hz, 4H), 7.59 (d, ³J_{H-H} = 8.2 Hz, 4H), 7.32 (d, ³J_{H-H} = 8.2 Hz, 4H), 2.99 (t, ³J_{H-H} = 7.9 Hz, 4H), 2.70 (t, ³J_{H-H} = 7.7 Hz, 4H), 1.98-1.93 (m, 4H), 1.74-1.68 (m, 4H), 1.51-1.46 (m, 12H), 1.41-1.35 (m, 12H), 1.04-0.99 (m, 6H), 0.95-0.91 (m, 6H). ¹³C NMR (CDCl₃): δ 152.36, 150.63, 144.21, 142.90, 139.94, 134.99, 133.20, 131.94, 131.34, 129.18, 127.29, 123.34, 121.61, 102.36, 97.37, 92.31, 36.64, 36.58, 32.52, 32.35, 32.31, 31.86, 29.91, 29.62, 23.38, 23.25, 14.85, 14.74. MS (MALDI-TOF): *m/z* = 1062.73 for M⁺; Calcd 1062.81.

2,6-Diethoxybenzaldehyde (L5). To a solution TMEDA (7.1 mL, 71.71 mmol), 1,3-diethoxybenzene (10 g, 60.16 mmol) in diethyl ether was added n-BuLi (2.5M in hexane, 26.14 mL, 65.33 mmol) at 0 °C over a 30 min period. The reaction mixture was stirred for 3 h under N₂. After warming up room temperature, DMF (8.88 mL) was added drop wise and the reaction was stirred for an additional 2 h. The mixture was quenched with water and the product was extracted with ethyl acetate 4-times, the solution was evaporated to dryness using a rotary evaporator to yield a yellow residue, which was obtained by recrystallization with hexane to afford **L5** as pure white solid (8.6 g, 73.6 % yield). ¹H NMR (CDCl₃): δ 10.53 (s, 1H), 7.38 (t, ³J_{H-H} = 8.2 Hz, 1H), 6.53(d, ³J_{H-H} = 8.2 Hz, 2H), 4.10 (q, ³J_{H-H} = 7.1 Hz, 4H), 1.45 (t, ³J_{H-H} = 7.1 Hz, 6H).

10,20-Bis[2,6-di(*n*-ethoxy)phenyl]porphyrin (L6). 2,6-Diethoxybenzene (569 mg, 2.93 mmol) and 2,2'-dipyrrrolemethane (428 mg, 2.93 mmol) were dissolved in dichloromethane (516 mL) in a 1-L Schlenk flask equipped with a magnetic stirbar and degassed for 10 min. TFA(142.2 μL) was added drop-wise, the flask was shield from light, and the resulting mixture was stirred for 3 h at room temperature. After DDQ (800 mg) was added, the solution was stirred for an additional 1 h.

TEA (3.04 mL) was then added and the reaction mixture was evaporated to dryness using a rotary evaporator to yield a dark residue, which was purified by silica-gel column chromatography (CH_2Cl_2) to afford pure **L6** as a purple solid (284 mg, 30.35 % yield). ^1H NMR (CDCl_3): δ 11.97 (s, 2H), 10.14 (s, 2H), 9.26 (d, $^3J_{\text{H-H}} = 3.9$ Hz, 4H), 8.96 (d, $^3J_{\text{H-H}} = 3.9$ Hz, 4H), 7.69 (t, $^3J_{\text{H-H}} = 8.6$ Hz, 2H), 7.03 (d, $^3J_{\text{H-H}} = 8.6$ Hz, 4H), 3.87 (q, $^3J_{\text{H-H}} = 7.0$ Hz, 8H), 0.55 (t, $^3J_{\text{H-H}} = 6.9$ Hz, 12H). MS (MALDI-TOF): $m/z = 638.43$ for M^+ ; Calcd 638.75.

[10,20-Bis[2,6-di(*n*-ethoxy)phenyl]porphyrinato] zinc (II) (L7). To a solution of **L6** (282 mg, 0.44 mmol) in dichloromethane (66 mL) was added a solution of $\text{Zn}(\text{OAc})_2$ (965.8 mg, 4.4 mmol) in methanol (4.4 mL) in a 250-mL schlenk flask equipped with a magnetic stirbar. The reaction mixture was allowed to stir for overnight. After evaporation of solvent, resulting residue was purified by column chromatography (CH_2Cl_2 /hexane, 4:6 v/v) to afford pure **L7** as a purple solid (283 mg, 91.6 % yield). ^1H NMR (CDCl_3): δ 10.20 (s, 2H), 9.35 (d, $^3J_{\text{H-H}} = 4.4$ Hz, 4H), 9.06 (d, $^3J_{\text{H-H}} = 4.4$ Hz, 4H), 7.72 (t, $^3J_{\text{H-H}} = 8.2$ Hz, 2H), 7.04 (d, $^3J_{\text{H-H}} = 8.2$ Hz, 4H), 3.89 (q, $^3J_{\text{H-H}} = 7.1$ Hz, 8H), 0.56 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 12H). ^{13}C NMR (CDCl_3): δ 160.47, 151.09, 149.68, 132.25, 131.83, 130.30, 122.15, 112.90, 106.31, 105.53, 64.87, 14.90. MS (MALDI-TOF): $m/z = 702.68$ for M^+ ; Calcd 702.15.

[5,15-Dibromo-10,20,-bis[2,6-di(*n*-ethoxy)phenyl]porphyrinato] zinc (II) (L8). **L7** (400 mg, 0.57 mmol) was dissolved in chloroform (600 mL) with pyridine (0.3 mL). The solution mixture was degassed for 10 min and NBS (202.8 mg, 1.14 mmol) was added. The reaction was stirred for 1 h with exclusion of light and then quenched with acetone (1.2 mL). The solution was evaporated using a rotary evaporator, which was purified by silica-gel column chromatography (CHCl_3 /hexane, 4:6 v/v) to afford pure **L8** as a purple solid (470 mg, 95.8 % Yield). ^1H NMR (CDCl_3): δ 9.57 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 4H), 8.83 (d, $^3J_{\text{H-H}} = 4.7$ Hz, 4H), 7.70 (t, $^3J_{\text{H-H}} = 8.6$ Hz, 2H), 7.01 (d, $^3J_{\text{H-H}} = 8.6$ Hz, 4H),

3.91 (q, $^3J_{\text{H-H}} = 7.0$ Hz, 8H), 0.57 (t, $^3J_{\text{H-H}} = 6.7$ Hz, 12H). ^{13}C NMR (CDCl_3): δ 160.44, 151.79, 150.05, 133.01, 132.90, 130.35, 122.55, 115.56, 114.81, 105.94, 64.75, 15.01. MS (MALDI-TOF): $m/z = 858.66$ for M^+ ; Calcd 859.98.

[5,15-Bis(1-ethynyl-4-hexylphenyl)-10,20-bis[2,6-di(n-ethoxy)phenyl]porphyrinato]zinc(II) (2).

A solution of **L8** (200 mg, 0.23 mmol), 1-ethynyl-4-hexylbenzene (127 mg, 0.70 mmol), PPh_3 (29.6 mg) and DEA (14.46 mg) in THF (21 ml) was degassed with N_2 for 10 min. $\text{Pd}_2(\text{dba})_3$ (21 mg) and CuI (9.8 mg) were added in mixture and degassed for 5 min. The reaction mixture was allowed to reflux for 48 h under N_2 atmosphere. The residue was evaporated to dryness in vacuo to afford a solid product which was purified by silica-gel column chromatography (CH_2Cl_2 /hexane, 6.5:3.5 v/v) to afford pure **2** as a green solid (182 mg, 73.9 % Yield). ^1H NMR (CDCl_3): δ 9.61 (d, $^3J_{\text{H-H}} = 4.4$ Hz, 4H), 8.77 (d, $^3J_{\text{H-H}} = 4.4$ Hz, 4H), 7.89 (d, $^3J_{\text{H-H}} = 8.2$ Hz, 4H), 7.66 (t, $^3J_{\text{H-H}} = 8.2$ Hz, 2H), 7.32 (d, $^3J_{\text{H-H}} = 8.2$ Hz, 4H), 6.98 (d, $^3J_{\text{H-H}} = 8.2$ Hz, 4H), 3.89 (q, $^3J_{\text{H-H}} = 8.2$ Hz, 8H), 2.71 (t, $^3J_{\text{H-H}} = 4.4$ Hz, 4H), 1.69-1.66 (m, 4H), 1.35-1.32 (m, 12H), 0.90-0.87 (m, 6H), 0.54 (t, $^3J_{\text{H-H}} = 8.2$ Hz, 12H). ^{13}C NMR (CDCl_3): δ 160.46, 152.00, 150.93, 143.61, 131.95, 130.78, 130.15, 129.26, 123.29, 122.36, 121.97, 115.30, 105.89, 99.67, 95.87, 93.59, 64.72, 36.62, 32.31, 31.94, 29.57, 23.20, 14.95, 14.69. MS (MALDI-TOF): $m/z = 1269.44$ for M^+ ; Calcd 1070.70.

3. Electrochemical Analysis of Porphyrins

Electrochemical characterization of **1** and **2** revealed a reversible oxidation/reduction behavior which is an essential condition for stable semiconducting materials. Cyclic voltammograms (CV) were recorded on a film sample and the potentials were obtained relatively to an internal ferrocene reference (Fc/Fc^+). These CV scans in the range of -2.0 to + 2.0 V (vs Ag/AgCl) show a reversible oxidation behavior. HOMO, LUMO, and bandgap energies of the two porphyrins are shown in Table S1. These values show that two molecules **1** and **2** are suitable semiconducting

materials for OFET fabrication.

Table S1. Optical properties and cyclic voltammetry analysis of **1** and **2**.

Molecules	Absorption (nm)		Emission (nm)		Energy levels (eV) ^a		
	Solution	Film	Solution	Film	HOMO	LUMO	E _g
	λ_{max}	λ_{max}	λ_{max}	λ_{max}			
1	448	478	649	723	-5.34	-3.37	1.96
2	450	472	647	712	-5.37	-3.58	1.81

^a Sample: film on Pt electrode

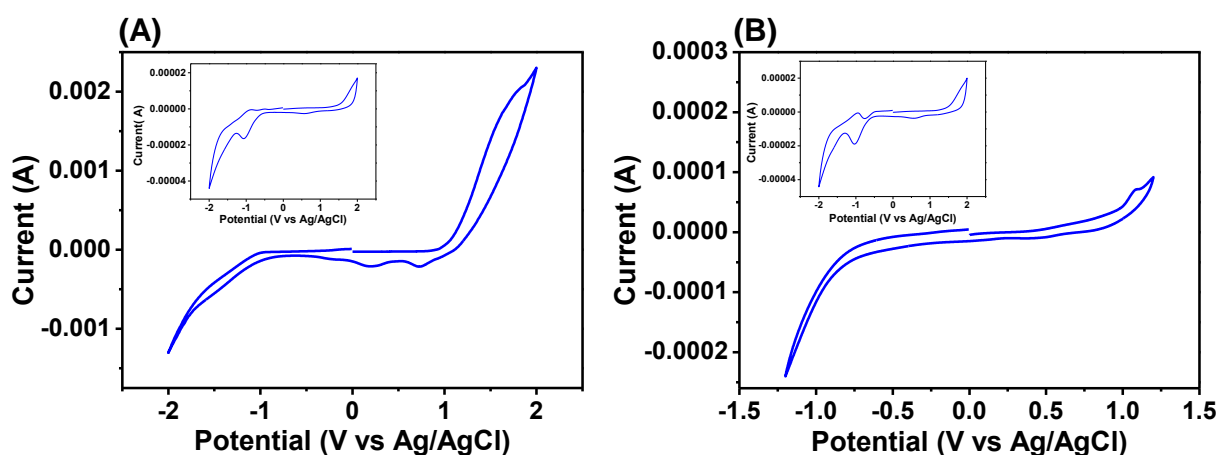


Figure S1. CV voltammograms of **1** (A) and **2** (B) in solution phases (insets) and film states.

4. Single-crystal X-ray Crystallography

Single crystals of **1** and **2** were grown in air by careful layering a 1-mM chloroform and toluene solution of the respective compounds over hexanes inside a glass tube (5-8 mm in diameter). The tubes were then capped and allowed to reach equilibrium under darkness. Single crystals appear at the interface of the two solvents over a period of ~10 days. The X-ray diffraction data were collected on a Bruker SMART APEX diffractometer for **1** and Bruker SMART APEX II diffractometer for **2** equipped with a monochromator in the Mo K α ($k = 0.71073 \text{ \AA}$) incident beam. Each crystal was mounted on a glass fiber. The CCD data were integrated and scaled using the

Bruker-S SAINT software package, and the structure was solved and refined using SHELXTL V6.12.

All hydrogen atoms were placed in the calculated positions.

Crystal data for 1: $C_{72}H_{76}N_4Zn$, MW = 1062.74, Monoclinic ($P2_1/n$), $a = 10.725(2)$ Å, $b = 15.113(3)$ Å, $c = 35.434(7)$ Å, $\beta = 91.85(3)^\circ$, $V = 5740(2)$ Å³, $Z = 4$, (Mo-K α) = 0.475 mm⁻¹, 30656 reflections measured, 11180 unique ($R_{int} = 0.2769$) which were used in all calculations, final $R = 0.0871$ ($R_w = 0.1779$) with reflections having intensities greater than 2σ , GOF (F^2) = 0.740. CCDC reference number 915238.

Crystal data for 2: $C_{68}H_{68}N_4O_4Zn$, MW = 1070.63, Monoclinic ($P2_1/c$), $a = 10.2621(11)$ Å, $b = 23.923(3)$ Å, $c = 11.1250(12)$ Å, $\beta = 90.800(10)^\circ$, $V = 2730.9(5)$ Å³, $Z = 2$, (Mo-K α) = 0.505 mm⁻¹, 37502 reflections measured, 6268 unique ($R_{int} = 0.1124$) which were used in all calculations, final $R = 0.0522$ ($R_w = 0.1075$) with reflections having intensities greater than 2σ , GOF (F^2) = 0.837. CCDC reference number 915239.

Table S2. Crystal data and structure refinement for **1** and **2**.

	1	2
Empirical formula	$C_{72}H_{76}N_4Zn$	$C_{68}H_{68}N_4O_4Zn$
Formula weight	1062.74	1070.63
Temperature (K)	170(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Space group	$P2_1/n$	$P2_1/c$
a (Å)	10.725(2)	10.2621(11)
b (Å)	15.113(3)	23.923(3)
c (Å)	35.434(7)	11.1250(12)
α (°)	90.00	90.00
β (°)	91.85(3)	90.800(10)
γ (°)	90.00	90.00
Volume(Å ³)	5740(2)	2730.9(5)

Z	4	2
Density (calc.) (Mg/m ³)	1.230	1.302
Absorption coeff. (mm ⁻¹)	0.475	0.505
Crystal size (mm ³)	0.30 x 0.25 x 0.15	0.10 x 0.05 x 0.02
Reflections collected	30656	37502
Independent reflections	11180 [R(int) = 0.2769]	6268 [R(int) = 0.1124]
Data/restraints/parameters	11180 / 24 / 651	6268 / 0 / 353
Goodness-of-fit on F ²	0.740	0.837
Final R indices [I > 2σ(I)]	R ₁ = 0.0871, wR ₂ = 0.1779	R ₁ = 0.0522, wR ₂ = 0.1075
R indices (all data)	R ₁ = 0.3002, wR ₂ = 0.2344	R ₁ = 0.1119, wR ₂ = 0.1201
Extinction coefficient	0.0333(15)	0.0016(4)
Largest diff. peak and hole (e.Å ⁻³)	0.601 and -1.060	0.416 and -0.569

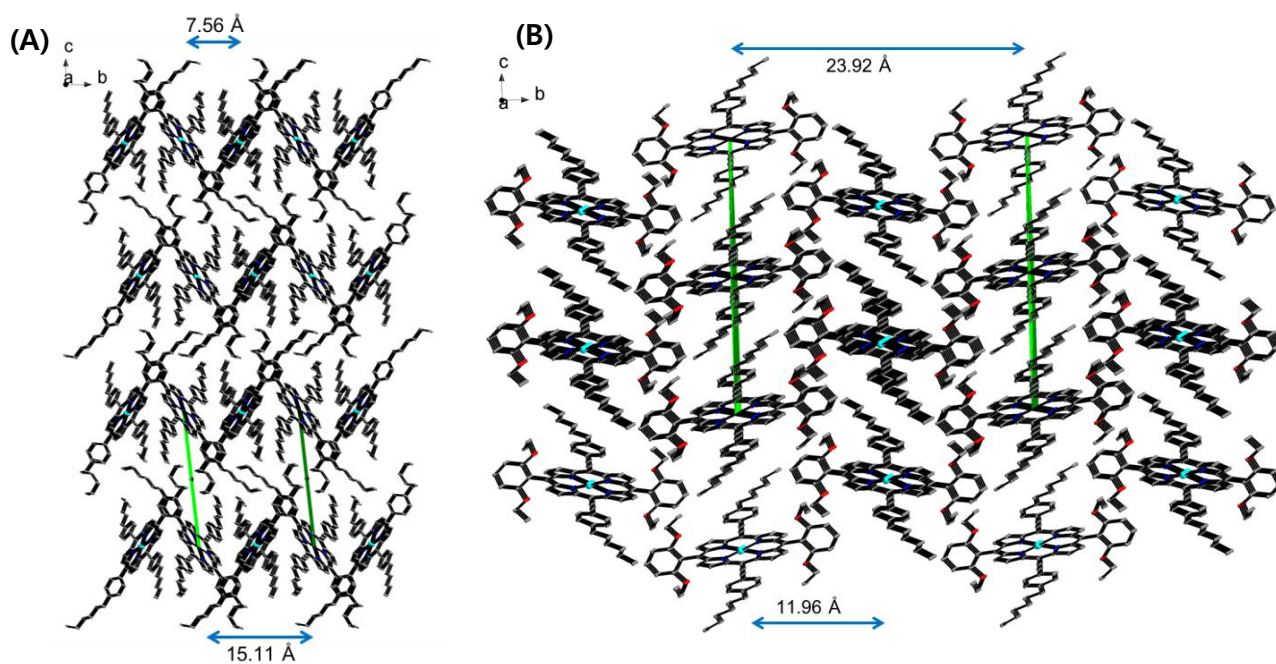


Figure S2. Crystal packing diagram representations looking down through 'a' axis of **1** (A) and **2** (B) showing clear J-aggregated arrays (Zn = sky blue, and O = red). These J-aggregated arrays of both **1** and **2** are stacked in the zigzag fashion with distances between arrays of 7.56 Å for **1** and 11.96 Å for **2**.

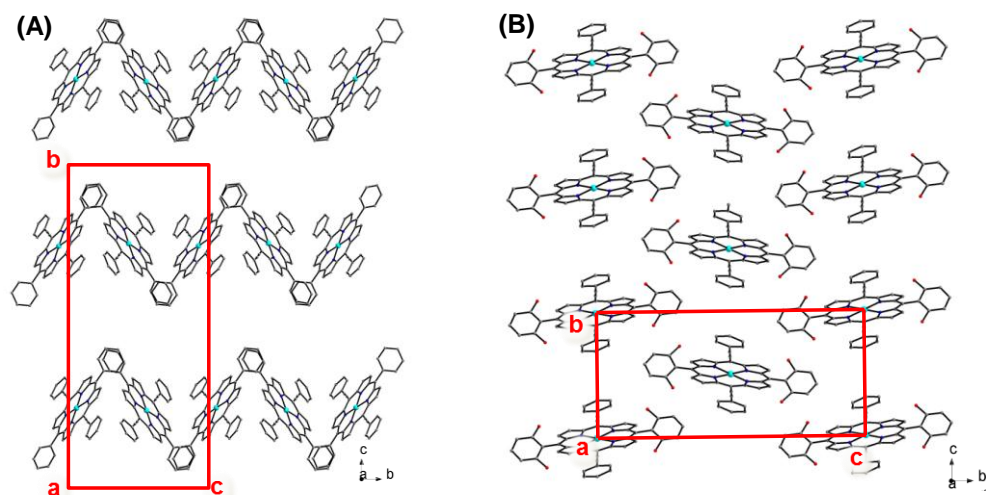


Figure S3. Crystal packing diagram looking down through 'a' axis of **1** (A) and **2** (B) with omitting hexyl groups and hydrogen atoms for clarity showing higher stacking density of arrays for **1** confirmed by their total numbers of lattice points in the unit cells ($Z = 4$ for **1** and $Z = 2$ for **2**).

5. OFET Fabrication

Bottom-gate top contact OFET devices were consisted of heavily n-type doped <100> silica as a gate electrode and 300 nm thick thermally grown SiO₂ as a gate insulator. The source and drain electrodes (120 nm Au) were deposited by thermal evaporation through a shadow mask. The resulting wafers were washed with acetone, isopropanol, followed by ultraviolet-ozone exposure for further cleaning. The silicon oxide layer was treated with *n*-octyltrichlorosilane (OTS) by immersing freshly cleaned wafers in a 100 mmol/L solution of OTS in anhydrous toluene for 30 min, followed by sonication in toluene and isopropanol, consecutively. The TFTs were fabricated by directly spin-coating a 1 wt% solution of porphyrins onto the dielectric substrate (OTS-SiO₂/Si) at 2000 rpm. The single-crystal FET devices were fabricated by growing porphyrin crystals directly on the top of OTS-treated wafers before depositing the source and drain electrodes. All field effect mobilities were extracted in the saturation regime using the relationship $\mu_{sat} = (2I_{DS}L)/(WC(V_G - V_{th})^2)$, where I_{DS} means saturation drain current, C is the capacitance of SiO₂ dielectric, V_G is the gate bias, and V_{th} is the

threshold voltage. The device performance was evaluated in air using Keithley 4200-SCS semiconductor characterization system under ambient conditions. (Note, due to some uncertainty in contact area of crystals on the gate insulator, small deviation in the mobility measurement may be anticipated.)

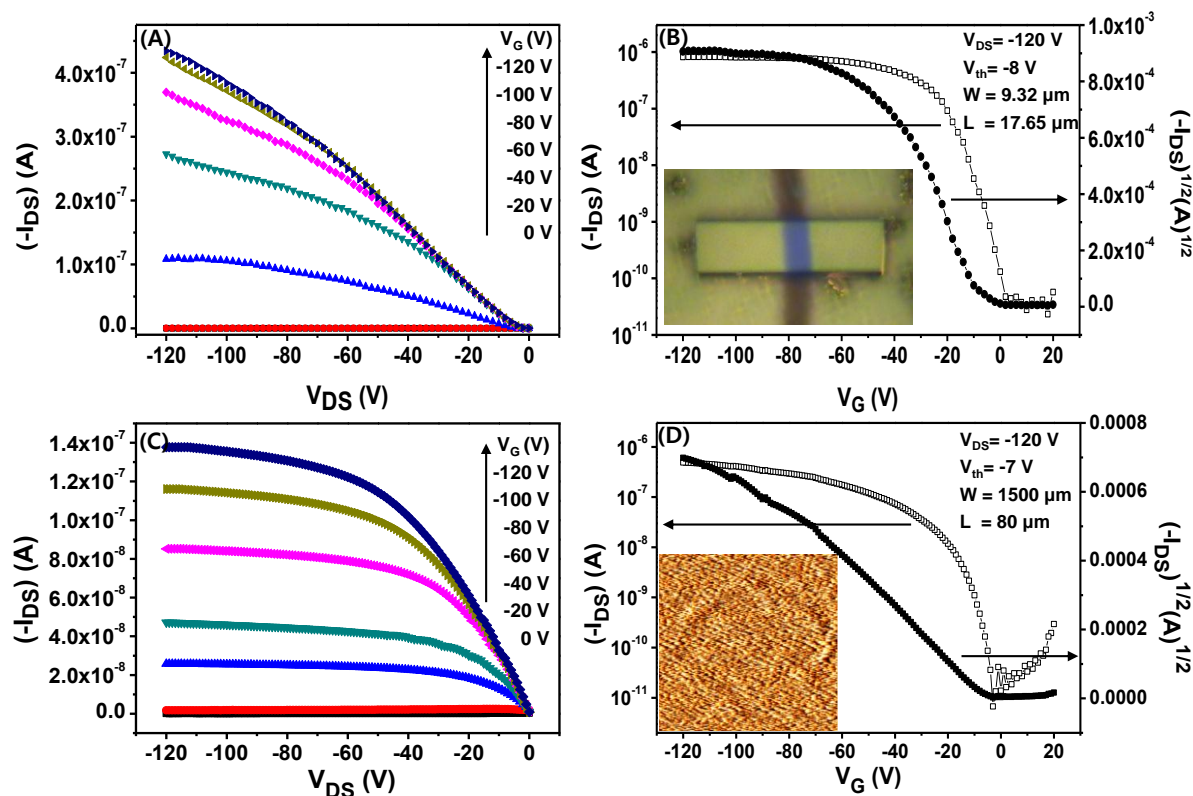


Figure S4. Electrical characterization of single-crystal and thin-film OFET of **2**. Output (A) and transfer (B) curves of OFET device made of single-crystal, and output (C) and transfer (D) curves of OFET device made of thin-film (Insets: Optical microscopic images of single-crystal device and AFM image of film, $V_{DS} = -120$ V).

Table S3. OFET device performance of **1** and **2**.

Sample	μ_{max}		$I_{\text{on/off}}$	
	Film ($\times 10^{-2}$)	Crystal	Film	Crystal
1	1.63	2.57	6.0×10^5	2.0×10^5
2	0.06	0.48	7.2×10^5	3.0×10^3

6. Additional Data

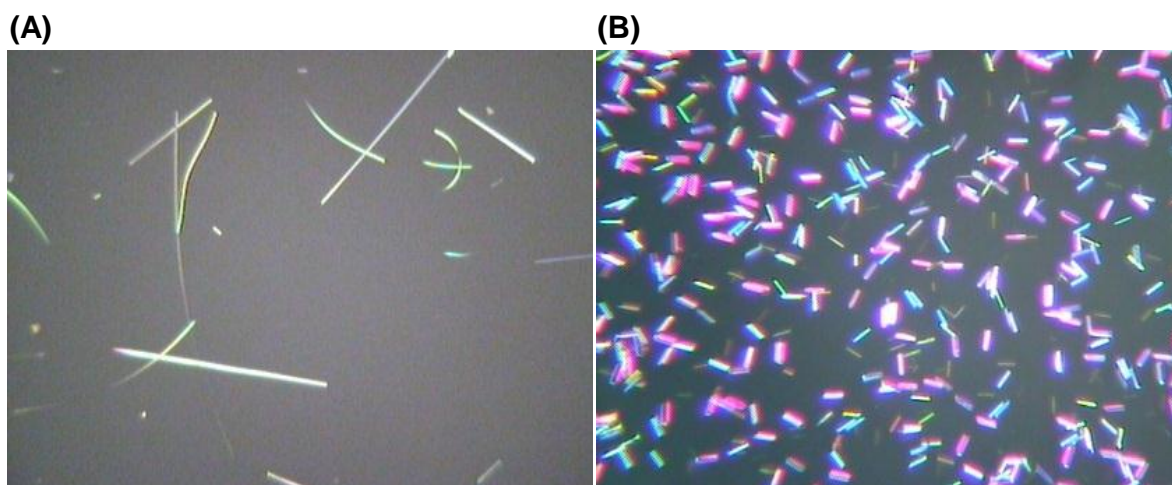


Figure S5. Optical microscopy images of single crystals of **1** (A) and **2** (B) under a cross-polarizers.

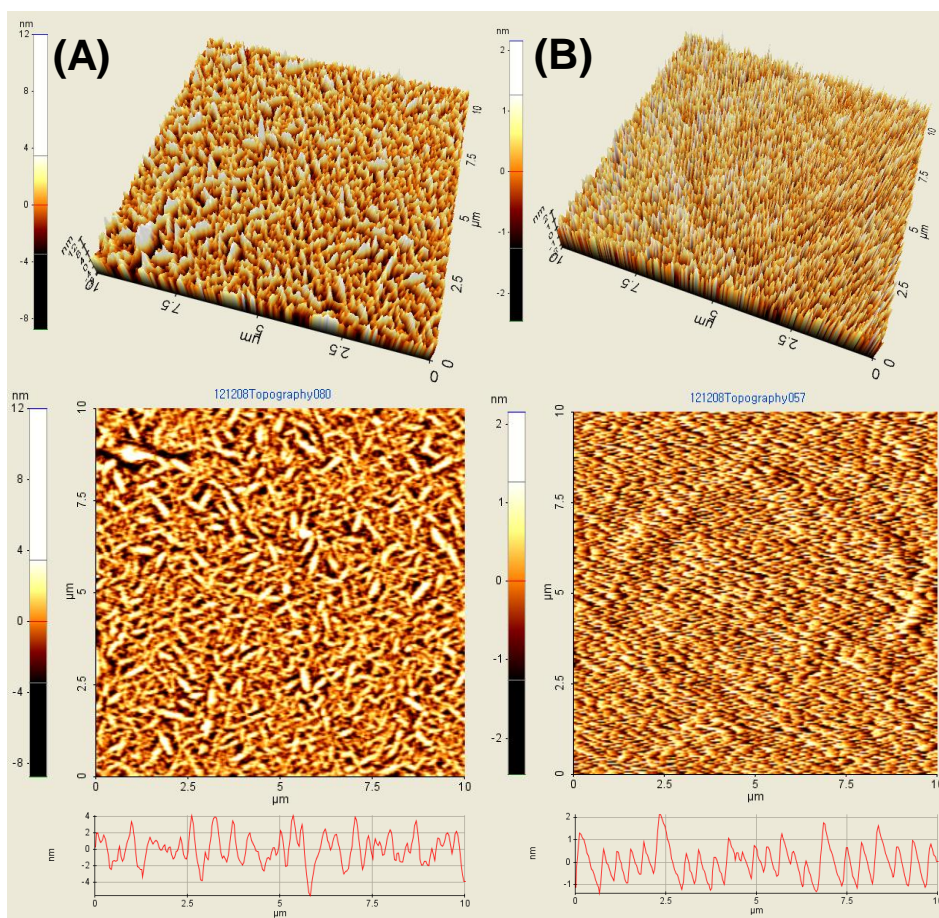


Figure S6. AFM images of thin-films of **1** (A) and **2** (B).

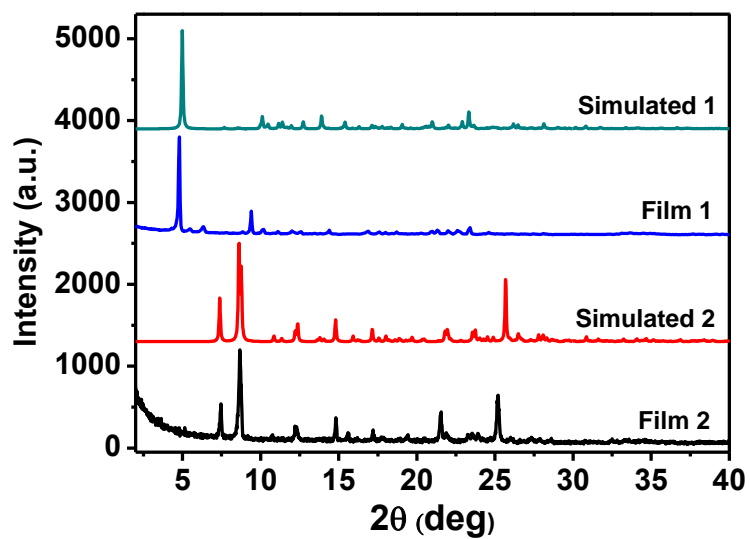


Figure S7. Powder X-ray diffraction (PXRD) patterns of thin-films and simulated patterns obtained from the X-ray crystal structures of **1** and **2**.

7. References

1. M. A. Peshkova, N. V. Timofeeva, A. L. Grekovich, S. M. Korneev and K. N. Mikhelson, *Electroanalysis*, 2010, **19**, 2147
2. S. Choi, S. H. Chae, M. H. Hoang, K. H. Kim, J. A. Hur, Y. Kim, S.-J. Kim, D. H. Choi and S. J. Lee, *Chem. Eur. J.*, 2012, DOI: 10.1002/chem.201202894.