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### Lattice Expansion of Highly Oriented 2D Phthalocyanine Covalent Organic Framework Films\*\*

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anie\_201107070\_sm\_miscellaneous\_information.pdf

# **Supporting Information**

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A. Materials. All reagents were purchased from commercial sources and used without further purification. Zn octahydroxyphthalocyanine 5,<sup>1</sup> pyrene diboronic acid 1,<sup>2</sup> and diphenylbutadiyne diboronic acid  $2^3$  were prepared via literature procedures. 1,4-Dioxane and propionic acid were purchased from commercial sources and used without further purification. Other solvents were purchased from commercial sources and purified using a custom-built alumina-column based solvent purification system.

#### Instrumentation.

Infrared spectra were recorded on a Thermo Nicolet iS10 with a diamond ATR attachment and are uncorrected.

UV/Vis absorbance spectra were recorded on a Cary 5000 UV-Vis-NIR spectrophotometer with a mercury lamp in either dichloromethane solution or as solids using a praying mantis diffuse reflectance accessory. Emission and excitation spectra were recorded on a Horiba Jobin Yvon Fluorolog-3 fluorescence spectrophotometer equipped with a 450 W Xe lamp, double excitation and double emission monochromators, a digital photon-counting photomultiplier and a secondary InGaAs detector for the NIR range. Correction for variations in lamp intensity over time and wavelength was achieved with a solid-state silicon photodiode as the reference. The spectra were further corrected for variations in photomultiplier response over wavelength and for the path difference between the sample and the reference by multiplication with emission correction curves generated on the instrument. Solid samples were mounted between quartz slides and mounted on a solid sample holder, and emission was observed using a front face detection accessory.

X-ray diffraction patterns were recorded on a Rigaku Smartlab Powder X-Ray Diffractometer in  $2\theta$  medium resolution parallel beam/PSA mode employing CuK $\alpha$  lines focused radiation at 40 kV, 44 mA power and equipped with a Ge crystal detector fitted with a 0.5 mm radiation entrance slit. Samples were mounted on zero background sample holders by dropping powders from a wide-blade spatula and then leveling the sample surface with a glass microscope slide. No sample grinding or sieving was used prior to analysis. Samples were observed using a 0.045°  $2\theta$  step scan from 1.0 – 34° (Omega = 1.0°) with an exposure time of 0.4 s per step. No peaks could be resolved from the baseline for  $2\theta > 34°$  data, which was therefore not considered for further analysis.

Thermogravimetric analysis from 20-600 °C was carried out on a TA Instruments Q500 Thermogravimetric Analyzer in an  $N_2$  atmosphere using a 10 °C/min ramp without equilibration delay.

Scanning electron microscopy (SEM) was performed on a FEI Strata 400 FE-SEM. Materials were deposited onto a sticky carbon surface on a flat aluminum platform sample holder. No metal sputtering of the sample was necessary. Focused ion beam (FIB) patterning and milling was performed using a FEI Strata 400 FIB Ga<sup>+</sup> LIM system. A 1x10  $\mu$ m Pt strip (~1  $\mu$ m thickness) was deposited using the electron gun onto COF films grown on SLG/SiO<sub>2</sub> substrates prior to exposing the sample to the FIB. The sample was then milled with the FIB using a cleaning cross-section. After milling, the samples were imaged at 2 keV using the electron gun. Cross-sectional images were obtained using a stage tilt angle of 52°. Thickness measurements made at this angle were corrected by multiplying by 1.26. SLG/SiO<sub>2</sub> substrates were grounded to the sample holder using sticky carbon prior to imaging to minimize charging.

Mass spectra were obtained on a Waters MALDI micro MX MALDI-TOF mass spectrometer using positive ionization and a reflectron detector. MALDI samples were prepared by wet deposition of a saturated analyte/dithranol matrix solution onto a metallic sample plate and air dried before loading into the instrument.

Surface area measurements were conducted on a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer using ca. 20 mg samples degassed at 180 °C for 12 hours. Nitrogen isotherms were generated by incremental exposure to ultra high purity nitrogen up to ca. 1 atm over 28-hour periods in a liquid nitrogen (77 K) bath, and surface parameters were determined using BET adsorption models included in the instrument software (Micromeritics ASAP 2020 V1.05) using the  $P/P_0$  ranges according to consistency criteria for the BET model in frameworks.<sup>4</sup> Non-local density functional theory (NLDFT) model for N<sub>2</sub> at 77 K and oxide surface with cylindrical pore shape integrated in the Micromeritics data reduction software was used to calculate pore size distribution curves from the adsorption branch of the measures isotherms.

NMR spectra were recorded on a Bruker ARX 300 MHz spectrometer using a standard <sup>1</sup>H/X Z-PFG probe at ambient temperature with a 20 Hz sample spin rate.

Grazing incidence X-ray diffraction (GID) was performed at the G2 station at Cornell High Energy Synchrotron Source (CHESS) using a beam energy of  $8.78 \pm 0.01$  keV ( $\lambda = 0.1414$  nm), selected using a Be single-crystal monochromator. Motorized slits were used to define a  $0.2 \times 2$  (V×H) mm<sup>2</sup> beam, with a typical flux of  $2 \times 10^{10}$  photons/s. The data were collected using a 640-element 1D diode-array, of which each element incorporates its own pulse counting electronics capable of count rates of  $\sim 10^5$  photons/s. A set of  $0.1^\circ$ Soller slits were used on the detector arm to define the in-plane resolution. The scattering geometry is described in detail elsewhere.<sup>1</sup> Each data set was collected by scanning the detector with the sample stationary. The incidence angle  $\alpha$  between the beam and sample surface was  $0.175^\circ$ . Axes labels Q<sub>1</sub> and Q<sub>||</sub> are defined using the GISAXS convention Q<sub>1</sub> =  $4\pi/\lambda \sin(\delta/2)$  and Q<sub>||</sub> =  $4\pi/\lambda \sin(\nu/2)$ , where  $\delta$  and  $\nu$  are the vertical and horizontal scattering angles, respectively.<sup>2</sup> At  $\alpha=\delta=0$ , hQ<sub>||</sub> and hQ<sub>1</sub> (where h is Planck's constant) are the components of momentum transfer parallel and perpendicular to the sample surface, respectively.

#### **B.** Synthetic Procedures.

General procedure for COF powder synthesis and ZnPc-Py COF. Pyrene diboronic acid 1 (17 mg, 0.059 mmol) and Zn octahydroxyphthalocyanine 5 (20 mg, 0.028 mmol) were suspended in a mixture of dioxane and MeOH (2:1, 3 mL) and sonicated for 10 min. The dark green suspension was transferred to a 10 mL pre-scored long-necked glass ampoule, flash-frozen in liquid N<sub>2</sub>, and flame-sealed. The ampoule was placed in an oven at 120 °C for 72 h, and the resulting free-flowing dark green powder was collected by filtration on a Hirsch funnel, washed with anhydrous toluene (1 mL), and air-dried. The resulting ZnPc-Py COF powder (10 mg, 52%) was dried under vacuum before characterization by PXRD and IR. ZnPc-Py COF: IR (powder, ATR) 3233, 1607, 1459, 1369, 1337, 1271, 1231, 1106, 1078, 1023, 902, 870, 824, 742, 714 cm<sup>-1</sup>. PXRD [2 $\theta$ (relative intensity)] 3.22 (100), 6.50 (24), 9.92 (5.6), 13.16 (4.3), 26.62 (6.4). UV-Vis (powder, praying mantis DRA) 711, 377 (sh), 336, 284. Anal. Calcd. for (C<sub>64</sub>H<sub>24</sub>B<sub>4</sub>N<sub>8</sub>O<sub>8</sub>Zn)<sub>n</sub>: C, 67.34; H, 2.12; N, 9.82. Found: C, 63.65; H, 2.20; N, 10.34. It has been noted<sup>5,6</sup> that elemental analysis of boronate COFs typically give lowered carbon values from the formation of non-combustible boron carbide byproducts. The presence of boron was confirmed by a characteristic B 1s peak in the XPS with a binding energy of 190.8 eV.

**ZnPc-DPB COF.** The above procedure was followed using diphenyl butadiynediboronic acid **2** (17 mg, 0.059 mmol), Zn octahydroxyphthalocyanine **5** (14 mg, 0.020 mmol), and a 3:1 mixture of dioxane and methanol (3:1, 1.3 mL) solvent. 12 mg (53%) of the **ZnPc-DPB COF** were isolated. IR (powder, ATR) 3244, 1607, 1472, 1371, 1338, 1268, 1180, 1081, 1018, 869, 830, 742 cm<sup>-1</sup>. PXRD [ $2\theta$  (relative intensity)] 2.66 (100), 3.74 (4.7), 5.45 (15), 8.29 (5.9), 11.04 (1.9), 13.82 (1.3), 16.48 (0.86), 26.83 (2.2). UV-Vis (powder, praying mantis DRA) 713, 361 (sh), 301, 275 (sh). Anal. Calcd for (C<sub>64</sub>H<sub>24</sub>B<sub>4</sub>N<sub>8</sub>O<sub>8</sub>Zn)<sub>n</sub>: C, 67.34; H, 2.12; N, 9.82. Found: C, 54.15; H, 2.19; N, 9.68. It has been noted<sup>5,6</sup> that elemental analysis of boronate COFs typically give lowered carbon values from the formation of non-combustible boron carbide byproducts. The presence of boron was confirmed by a characteristic B 1s peak in the XPS with a binding energy of 191.7 eV.

**ZnPc-NDI COF.** The above procedure was followed using napthalenediimide diboronic acid **3** (36 mg, 0.071 mmol), Zn octahydroxyphthalocyanine **5** (17 mg, 0.024 mmol), and

a 2:1 mixture of dioxane and MeOH (3 mL) solvent. 23 mg (60%) of the **ZnPc-NDI COF** were isolated. **ZnPc-NDI COF**: IR (powder, ATR) 3338, 1714, 1671, 1613, 1582, 1514, 1479, 1451, 1376, 1342, 1272, 1251, 1200, 1119, 1085, 1022, 984, 870, 835, 768, 742, 719 cm<sup>-1</sup>. PXRD [ $2\theta$  (relative intensity)] 2.44 (100), 5.00 (27), 7.52 (7.0), 12.52 (3.3), 26.92 (2.6). UV-Vis (powder, praying mantis DRA) 693, 333 (sh), 296. Anal. Calcd for ( $C_{84}H_{32}B_4N_{12}O_{16}Zn_{n}$ : C, 64.10; H, 2.05; N, 10.68. Found: C, 55.41; H, 2.56; N, 11.09. It has been noted<sup>5,6</sup> that elemental analysis of boronate COFs typically give lowered carbon values from the formation of non-combustible boron carbide byproducts. The presence of boron was confirmed by a characteristic B 1s peak in the XPS with a binding energy of 191.3 eV.

**ZnPc-PPE COF.** The above procedure was followed using PPE diboronic acid 4 (22 mg, 0.060 mmol), Zn octahydroxyphthalocyanine **5** (15 mg, 0.021 mmol), and a 5:1 mixture of dioxane and MeOH (3 mL) solvent. 20 mg (73%) of the **ZnPc-PPE COF** were isolated. **ZnPc-PPE COF**: IR (powder, ATR) 3060, 2930, 1711, 1605, 1472, 1395, 1351, 1270, 1227, 1187, 1042, 1015, 945, 915, 872, 830, 745, 704 cm<sup>-1</sup>. PXRD [ $2\theta$  (relative intensity)] 2.28 (100), 4.76 (18), 7.20 (6.9), 9.68 (3.4), 12.16 (2.5), 26.52 (2.3). UV-Vis (powder, praying mantis DRA) 693, 331, 308 nm. Anal. Calcd for (C<sub>84</sub>H<sub>32</sub>B<sub>4</sub>N<sub>12</sub>O<sub>16</sub>Zn)<sub>n</sub>: C, 70.56; H, 2.49; N, 8.66. Found: C, 59.20; H, 2.58; N, 8.70. It has been noted<sup>5,6</sup> that elemental analysis of boronate COFs typically give lowered carbon values from the formation of non-combustible boron carbide byproducts. The presence of boron was confirmed by a characteristic B 1s peak in the XPS with a binding energy of 191.3 eV.

Scheme S1. Synthesis of naphthalene diimide diboronic acid 3.



**N,N'-bis(4-iodophenyl)naphthalene-1,4,5,8-tetracarboxylic diimide (7).** Naphthalene-1,4,5,8-tetracarboxylic dianhydride **6** (1.30 g, 4.85 mmol) and 4-iodoaniline (3.20 g, 10.5 mmol) were refluxed in propionic acid (80 mL) for 18 h under N<sub>2</sub>. The brown solution was cooled to rt and the resulting precipitate was collected by filtration and washed with MeOH (4 x 20 mL). The resulting light brown solid **7** (2.40 g, 74%) was used without further purification. Its poor solubility precluded acquisition of a suitable <sup>13</sup>C-NMR spectrum. **7**: <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 300 MHz) δ 8.72 (s, 4H); 7.94 (d, J = 9 Hz, 4H); 7.30 (d, J = 9 Hz, 4H). MALDI-MS m/z (%) 542.9 (44, M<sup>+</sup>-I); 543.9 (52, M<sup>+</sup>+1-I); 669.8 (100, M<sup>+</sup>); 670.8 (53, M<sup>+</sup>+1). IR (powder, ATR) 3100, 3068, 3049, 1711, 1670, 1577, 1484, 1446, 1344, 1248, 1198, 1118, 1006, 980, 884, 850, 827, 766, 741 cm<sup>-1</sup>. UV-Vis [λ /nm (log ε / M<sup>-1</sup> cm<sup>-1</sup>), 6.9 μM in DMF] 380 (4.43), 360 (4.43), 340 (4.34). Anal. Calcd for (C<sub>26</sub>H<sub>12</sub>I<sub>2</sub>N<sub>2</sub>O<sub>4</sub>): C, 46.60; H, 1.80; N, 4.18. Found: C, 47.77; H, 1.84; N, 4.22.

**Naphthalenediimide dipinacolatoboronic ester (8).** Naphthalene diimide diiodide 7 (138 mg, 0.206 mmol) and nickel(II) diphenylphosphinopropane dichloride (9.0 mg, 0.017 mmol) were heated to reflux in toluene (2 mL) and N,N-diisopropylethylamine (1 mL) under N<sub>2</sub>. Pinacol borane (100  $\mu$ L, 0.69 mmol) was added by syringe and the mixture was stirred for 12 h. After cooling to rt, saturated aq. NH<sub>4</sub>Cl (30 mL) was added to the dark brown mixture. The biphasic liquid was diluted with EtOAc (40 mL) and was

washed with H<sub>2</sub>O (3 x 40 mL). The organic layer was evaporated to provide a pale yellow solid, which was suspended in EtOAc (10 mL) and centrifuged for 30 min at 4000 rpm. This suspension/centrifugation procedure was repeated twice. The tan solid **8** (73 mg, 53%) was dried under vacuum and used without further purification. **8**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz) δ 8.84 (s, 4H); 8.04 (d, J = 9 Hz, 4H); 7.36 (d, J = 9 Hz, 4H); 1.38 (s, 24H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 MHz) δ 163, 138, 136, 132, 130, 128, 128, 127, 84, 25. IR (powder, ATR) 3088, 2980, 2940, 1713, 1675, 1607, 1581, 1447, 1399, 1359, 1342, 1321, 1246, 1213, 1198, 1169, 1143, 1120, 1086, 1022, 983, 963, 860, 824, 794, 769, 717 cm<sup>-1</sup>. UV-Vis [λ /nm (log ε / M<sup>-1</sup> cm<sup>-1</sup>), 8.1 μM in DMF] 380 (4.43), 360 (4.42), 343 (4.25). Anal. Calcd for (C<sub>38</sub>H<sub>36</sub>B<sub>2</sub>N<sub>2</sub>O<sub>8</sub>): C, 68.09; H, 5.41; N, 4.18. Found: C, 68.05; H, 5.39; N, 4.28.

Naphthalenediimide diboronic acid (3). Ester 8 (30 mg, 0.045 mmol) and NaIO<sub>4</sub> (20 mg, 0.094 mmol) were suspended in a 4:1 THF:H<sub>2</sub>O solution (0.6 mL). The resulting tan mixture was stirred for 2 h, after which aq. HCl (1M, 1 mL) was added. The pale yellow suspension was stirred for 18 h and diluted with H<sub>2</sub>O (5 mL), filtered, and rinsed with another 5 mL H<sub>2</sub>O. The resulting tan solid was dried under vacuum to provide the diboronic acid **3** (16 mg, 70 %). **3**: <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 300 MHz) δ 8.72 (s, 4H); 8.23 (s, 4H); 7.94 (d, *J* = 6 Hz, 4H); 7.42 (d, *J* = 6 Hz, 4H). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, 300 MHz) δ 164, 138, 135, 131, 130, 129, 128, 127. IR (powder, ATR) 3479, 3378, 1711, 1664, 1606, 1577, 1437, 1416, 1366, 1341, 1275, 1250, 1199, 1151, 1127, 1061, 1028, 1015, 984, 890, 854, 828, 767, 752, 719 cm<sup>-1</sup>. UV-Vis [λ /nm (log ε / M<sup>-1</sup> cm<sup>-1</sup>), 15.0 μM in DMF] 380 (4.40), 360 (4.38), 345(sh) (4.21). Anal. Calcd for (C<sub>26</sub>H<sub>16</sub>B<sub>2</sub>N<sub>2</sub>O<sub>8</sub>): C, 61.71; H, 3.19; N, 5.54.Found: C, 62.31; H, 3.21; N, 5.39.



Scheme S2. Synthesis of phenylbis(phenylethynyl)diboronic acid 4.

Benzene-1,4-bis(phenylethynyl) diboronic acid (4). 4-iodophenylboronic acid (880 mg, 3.55 mmol) and 1,4-diethynylbenzene (205 mg, 1.63 mmol) were dissolved in THF (25 mL) and ethyldiisopropylamine (10 mL) and the solution was sparged with N<sub>2</sub> for 30 min. CuI (63 mg, 0.33 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (43 mg, 0.037 mmol) were added and the solution was sparged with N<sub>2</sub> for another 30 min. The resulting pale yellow mixture was stirred at rt for 12 h, during which a white precipitate formed. The pale yellow solid was recovered by filtration and rinsed with EtOAc (20 mL). The solid was suspended in EtOAc (30 mL), which washed with brine (30 mL) and  $H_2O$  (3 × 30 mL), and the solvent removed to yield 513 mg (86%) of the PPE diboronic acid 4 as a white solid. 4: <sup>1</sup>H-NMR  $(DMSO-d_6, 300 \text{ MHz}) \delta 8.20 \text{ (s, 4H)}; 7.84 \text{ (d, } J = 7.5 \text{ Hz, 4H)}; 7.60 \text{ (d, } J = 3 \text{ Hz, 4H)};$ 7.54 (d, J = 7.5 Hz, 4H). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, 300 MHz)  $\delta$  135, 133, 130, 123, 122, 92,90. MALDI-MS m/z (%) 365.1 (43, M<sup>+</sup>); 366.1 (100, M<sup>+</sup>+1); 367.1 (27, M<sup>+</sup>+2), 368.1 (6, M<sup>+</sup>+3). IR (powder, ATR) 3351, 1701, 1658, 1592, 1576, 1505, 1491, 1434, 1401, 1358, 1256, 1199, 1183, 1143, 1088, 1021, 957, 857, 831, 808, 743, 693 cm<sup>-1</sup>. UV-Vis [λ /nm (log  $\epsilon$  / M<sup>-1</sup> cm<sup>-1</sup>), 9.4  $\mu$ M in DMF] 350 (4.63), 329 (4.83), 321(sh) (4.75). Em ( $\lambda$ /nm in DMF,  $\lambda_{ex} = 350$  nm) 376, 387, 400(sh). Anal. Calcd for (C<sub>22</sub>H<sub>16</sub>B<sub>2</sub>O<sub>4</sub>): C, 72.20; H, 4.41. Found: C, 69.62; H, 4.37.

**Graphene Growth.** Single-layer graphene was grown on 25  $\mu$ m-thick copper foil using previously reported chemical vapor deposition methods.<sup>7</sup> A layer of PMMA (50 nm) was spin-coated on top of the graphene and the copper was etched using aq. FeCl<sub>3</sub>. The graphene was then transferred to fused SiO<sub>2</sub> and the PMMA removed by washing first with chloroform then isopropyl alcohol. The SLG/SiO<sub>2</sub> was finally calcined at 300 °C for 2.5 h.

General procedure for ZnPc COF film growth on SLG. The appropriate diboronic acid (0.109 mmol) and zinc octahydroxyphthalocyanine (0.035 g, 0.050 mmol) were added to a 15 mL cylindrical pressure vessel and suspended in a mixture of 1,4-dioxane, methanol, N,N-dimethylacetamide, and 1,2-dichlorobenzene (v/v 3:1:2:1; 3.0 mL). After capping, the mixture was sonicated for 30 minutes and a graphene-containing substrate was added. The sealed vessel was heated in a 120 °C oven for 24 h. The vessel was cooled to room temperature and the resulting green powder was recovered by filtration and dried under vacuum. The graphene-containing substrate was submerged in anhydrous toluene and sonicated for 5 seconds, and finally dried under vacuum.

### C. NMR Spectra.





Figure S2. <sup>1</sup>H-NMR spectrum of NDI ester 8 in CDCl<sub>3</sub>.



Figure S3. <sup>13</sup>C-NMR spectrum of NDI ester 8 in CDCl<sub>3</sub>.







Figure S5. <sup>13</sup>C-NMR spectrum of NDI diboronic acid **3** in DMSO-*d*<sub>6</sub>.





Figure S7. <sup>13</sup>C-NMR spectrum of PPE diboronic acid 4 in DMSO- $d_6$ .



**Figure S6.** <sup>1</sup>H-NMR spectrum of PPE diboronic acid **4** in DMSO-*d*<sub>6</sub>.

**D. FT-IR Spectra.** 

Figure S8. FT-IR of pyrene diboronic acid 1 (blue) and ZnPc-Py COF (red).



**Figure S9.** Expansion of 700-1800 cm<sup>-1</sup> region of the above spectrum.





Figure S10. FT-IR of DPB acid 2 (blue) and ZnPc-DPB COF (red).







Figure S12. FT-IR of NDI diiodide 7 (blue) and pinacolboronate ester 8 (red).

**Figure S13.** Expansion of 700-1800 cm<sup>-1</sup> region of the above spectrum.





Figure S14. FT-IR of NDI acid 3 (blue) and ZnPc-NDI COF (red).

**Figure S15.** Expansion of 700-1800 cm<sup>-1</sup> region of the above spectrum.





Figure S16. FT-IR of diboronic acid 4 (blue) and ZnPc-PPE COF (red).

**Figure S17.** Expansion of 700-1800 cm<sup>-1</sup> region of the above spectrum.



### **E. UV-Vis-NIR Characterization**

Figure S18. Diffuse reflectance absorption spectra of ZnPc-Py COF (gold), ZnPc-DPB COF (blue), ZnPc-NDI COF (red) and ZnPc-PPE COF (purple) powders.



**F. Simulation & Refinement of the COF Structures.** Crystal modeling of the COFs was carried out using the Materials Studio (ver.5.0) suite of programs by Accelrys.<sup>8</sup> The initial structures were constructed piecewise starting with a primitive tetragonal unit cell with space group *P4/mmm*. The *a* cell parameter was estimated according to the distance between the center of the vertices for each COF as shown in Figure S19, and *c* parameter was arbitrarily chosen as 3.35 Å. The structures were optimized using the Geometry Optimization routine including energy minimization with cell parameters optimization, using the parameters from the Universal Force Field. Modeling of the staggered structures was performed in a similar manner but starting with the space group *I4/mmm*, and *c* = 6.70 Å. Calculation of the simulated powder diffraction patterns and Pawley refinements were performed the Materials Studio Reflex Plus Module. The observed diffraction patterns were subjected to Pawley refinement wherein peak profile were refined using the Pseudo-Voigt peak shape function and asymmetry was corrected using the Berar-Baldinozzi function.<sup>5</sup>



Figure S19. Precursor structures used for initial modeling of the COF structures.





ZnPc-DPB COF

ZnPc-PPE COF

**Figure S21**. Observed (blue) versus Pawley-refined (red) PXRD pattern profiles for **ZnPc-Py COF**. Residuals are indicated.



**Figure S22**. Observed (blue) versus Pawley-refined (red) PXRD pattern profiles for **ZnPc-DPB COF**. Residuals are indicated.



**Figure S23**. Observed (blue) versus Pawley-refined (red) PXRD pattern profiles for **ZnPc-NDI COF**. Residuals are indicated.



**Figure S24**. Observed (blue) versus Pawley-refined (red) PXRD pattern profiles for **ZnPc-PPE COF**. Residuals are indicated.



ZnPc-Py COF	a (Å)	<i>c</i> (Å)
MS modeling	27.185	3.535
$d_{100}$	27.056	
Pawley refinement	26.980	3.338
ZnPc-DPB COF	<i>a</i> (Å)	<i>c</i> (Å)
MS modeling	32.469	3.556
$d_{100}$	33.060	
Pawley refinement	32.183	3.356
ZnPc-NDI COF	<i>a</i> (Å)	<i>c</i> (Å)
MS modeling	36.064	3.542
$d_{100}$	36.176	
Pawley refinement	35.701	3.361
ZnPc-PPE COF	<i>a</i> (Å)	<i>c</i> (Å)
MS modeling	36.718	3.552
$d_{100}$	37.403	
Pawley refinement	38.533	3.367

**Table S1.** Comparison of unit cell parameters of the simulated crystals, the *d*-spacing of the 100 diffraction peaks and the refined patterns for each prepared COF.

Tetrago (P4/mn	onal, nm)	2 2 2 Q Å	
a = 0 =	20.900  A, C = 3	5.330 A	7
<u>C1</u>	0.027462	<u>y</u> 0.500000	0.50000
C2	0.027462	0.300000	0.50000
C2	0.027402	0.455430	0.50000
C3	0.053700	0.455450	0.50000
04	0.105074	0.455450	0.50000
65	0.131288	0.500000	0.50000
C6	0.265000	0.475000	0.50000
C7	0.309000	0.450000	0.50000
C8	0.355000	0.475000	0.50000
C9	0.401000	0.462000	0.50000
01	0.212025	0.546591	0.50000
B1	0.182823	0.500000	0.50000
N1	0.430000	0.500000	0.50000
N2	0.416000	0.584000	0.50000
Zn1	0.500000	0.500000	0.50000

Table S2. Fractional atomic coordinates for refined unit cell of ZnPc-Py COF.

Table S3. Fractional atomic coordinates for refined unit cell of ZnPc-DPB COF.

Tetrago	Tetragonal			
(P4/mn	(P4/mmm)			
a = b =	a = b = 32.183 Å, c = 3.356 Å			
atom	X	Ζ		
C1	0.020491	0.500000	0.50000	
C2	0.057698	0.500000	0.50000	
C3	0.102075	0.500000	0.50000	
C4	0.123748	0.464739	0.50000	
C5	0.166807	0.464739	0.50000	
C6	0.188528	0.500000	0.50000	
C7	0.300642	0.480551	0.50000	
C8	0.337406	0.457860	0.50000	
C9	0.373823	0.480551	0.50000	
C10	0.414478	0.469042	0.50000	
01	0.261315	0.464137	0.50000	
B1	0.236652	0.500000	0.50000	
N1	0.440321	0.500000	0.50000	
N2	0.428054	0.428054	0.50000	
Zn1	0.500000	0.500000	0.50000	

**Table S4.** Fractional atomic coordinates for unit cell of **ZnPc-NDI COF** calculated using the Materials Studio ver.5.0 modeling program.

Tetragonal	
(PA/mmm)	

(F4/1111	(F4///////)			
a = b =	= 35.701 Å, <i>c</i> = 3.361 Å			
atom	x	У	Ζ	
C1	0.019879	0.500000	0.50000	
C2	0.019879	0.433099	0.50000	
C3	0.039699	0.466552	0.50000	
C4	0.079187	0.466552	0.50000	
C5	0.140886	0.500000	0.50000	
C6	0.162059	0.466552	0.50000	
C7	0.201335	0.466552	0.50000	
C8	0.221662	0.500000	0.50000	
C9	0.319419	0.480860	0.50000	
C10	0.352942	0.460236	0.50000	
C11	0.386323	0.480974	0.50000	
C12	0.423494	0.470264	0.50000	
01	0.095827	0.435714	0.50000	
02	0.285292	0.467504	0.50000	
B1	0.263921	0.500000	0.50000	
N1	0.099281	0.500000	0.50000	
N2	0.447162	0.500000	0.50000	
N3	0.434520	0.434520	0.50000	
Zn1	0.500000	0.500000	0.50000	

Table S5. Fractional atomic coordinates for unit cell of ZnPc-PPE COF calculated using
the Materials Studio ver.5.0 modeling program.
Tetragonal

retrage	onai		
(P4/mn	nm)		
a = b =	38.533 Å, <i>c</i> = 3.367 Å		
atom	x	У	Ζ
C1	0.018677	0.468853	0.50000
C2	0.038444	0.500000	0.50000
C3	0.078109	0.500000	0.50000
C4	0.110866	0.500000	0.50000
C5	0.150530	0.500000	0.50000
C6	0.170299	0.468853	0.50000
C7	0.207616	0.468853	0.50000
C8	0.227438	0.500000	0.50000
C9	0.327400	0.481973	0.50000
C10	0.359425	0.462877	0.50000
C11	0.391299	0.482008	0.50000
C12	0.426676	0.471666	0.50000
01	0.293260	0.468194	0.50000
B1	0.270958	0.500000	0.50000
N1	0.437864	0.437864	0.50000
N2	0.448380	0.500000	0.50000
Zn1	0.500000	0.500000	0.50000

Figure S25. Crystal models of ZnPc-Py COF (top left), ZnPc-DPB COF (top right), ZnPc-NDI COF (bottom left) and ZnPc-PPE COF (bottom right) in a staggered conformation and corresponding simulated PXRD patterns. Similarly colored sheets are in alternating unit cells. Note the lack of match to observed PXRD patterns (*vide supra*).



**G. Thermogravimetric Analysis.** TGA traces of the COFs were obtained up to 600  $^{\circ}$ C using a linear 10  $^{\circ}$ C/min ramp method.





#### H. Surface Area Determinations.



Figure S27. BET plot for ZnPc-DPB COF calculated from isotherm data.

Figure S28. BET plot for ZnPc-Py COF calculated from isotherm data.





Figure S29. BET plot for ZnPc-NDI COF calculated from isotherm data.

Figure S30. BET plot for ZnPc-PPE COF calculated from isotherm data.





**Figure S31.** Differential (top) and cumulative (bottom) pore size distribution plot of ZnPc-Py COF from the application of the NLDFT model to the N<sub>2</sub> isotherm.



**Figure S32.** Differential (top) and cumulative (bottom) pore size distribution plot of ZnPc-DPB COF from the application of the NLDFT model to the N<sub>2</sub> isotherm.

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**Figure S33.** Differential (top) and cumulative (bottom) pore size distribution plot of ZnPc-NDI COF from the application of the NLDFT model to the  $N_2$  isotherm.



**Figure S34.** Differential (top) and cumulative (bottom) pore size distribution plot of ZnPc-PPE COF from the application of the NLDFT model to the  $N_2$  isotherm.

### I. Scanning Electron Microscopy

Figure S35. Scanning electron micrographs of powder samples of (a) ZnPc-Py COF, (b) ZnPc-DPB COF, (c) ZnPc-NDI COF and (d) ZnPc-PPE COF.



**Figure S36.** Top down SEM of (a) **ZnPc-Py COF** thin film, (b) **ZnPc-DPB COF** thin film, (c) **ZnPc-NDI COF** thin film, and (d) **ZnPc-PPE COF** thin film



### J. Higher Resolution X-ray Reflectivity of ZnPc-DPB COF Film

**Figure S7.** Background subtracted off-specular X-ray reflectivity of **ZnPc-DPB COF** thin film showing improved resolution compared to Fig. 5c.



**Figure S38.** 2D projection of the intensity along  $Q_1$  at Chi = 4.5 degrees. The FWHM of this peak gives the average domain size along the *c*-axis. For this sample, the FWHM is 0.02 Å<sup>-1</sup> corresponding to a 31 nm (94 layers) correlation length.



### K. References.

- 1. Youssef, T. E. Efficient green procedures for the preparation of novel tetraalkynyl-substituted phthalocyanines. *Polyhedron* **29**, 1776-1783.
- 2. Tzschucke, C. C., Murphy, J. M. & Hartwig, J. F. Arenes to anilines and aryl ethers by sequential iridium-catalyzed borylation and copper-catalyzed coupling. *Org. Lett.* **9**, 761-764 (2007).
- 3. Spitler, E. L., Koo, B. T., Colson, J. W., Gutierrez, G. D., Clancy, P. & Dichtel, W. R. Oriented covalent organic framework films with 4.7 nm pores. Submitted.
- 4. Walton, K. S. & Snurr, R. Q. Applicability of the BET method for determining surface areas of microporous Metal-Organic Frameworks *J. Am. Chem. Soc.* **129**, 8552-8556 (2007).
- Côté, A. P., Benin, A. I., Ockwig, N. W., O'Keeffe, M., Matzger, A. J. & Yaghi, O. M. Porous, crystalline, covalent organic frameworks. *Science* 310, 1166-1170 (2005).
- 6. Spitler, E. L. & Dichtel, W. R. Lewis acid-catalysed formation of twodimensional phthalocyanine covalent organic frameworks. *Nat. Chem.* **2**, 672-677 (2010).
- 7. Levendorf, M. P., Ruiz-Vargas, C. S., Garg, S. & Park, J. Transfer-Free Batch Fabrication of Single Layer Graphene Transistors. *Nano Lett.* **9**, 4479-4483 (2009).
- 8. Materials Studio Release Notes v.5.0 (Accelrys Software, San Diego, 2009).