Supporting Information for

Stepwise Pillar Insertion into Metal-Organic Frameworks: A Sequential–Assembly Approach

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1. Experimental

1.1 General Considerations

Materials. 5,10,15,20-tetrakis(4-carboxyphenyl)-21H,23H-porphyrin (TCPP) (Frontier Scientific), Zn(NO$_3$)$_2$·6H$_2$O (Sigma-Aldrich), Pyrazine (Sigma-Aldrich), 4,4'-bipyridine (BPY) (Sigma-Aldrich), 3,6-di-(4-pyridyl)-1,2,4,5-tetrazine (DPT) (TCI America), and \( N,N' \)-diethylformamide (DEF) (TCI America) were all obtained from commercial sources and used without further purification. \( N,N' \)-di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide (DPNI) was synthesized according to published procedure.$^1$

Instrumentation. X-ray diffraction data were taken using a spinning capillary method$^2$ with a Bruker AXS DA x-ray diffractometer with a GADDS area detector and a conventional copper target x-ray tube set to 40 KV and 40 mA. The resulting patterns were compared to the simulated patterns obtained by Mercury.$^3$ Thermogravimetric Analysis (TGA) was performed on a Perkin Elmer STA 6000 Termogravimetric Analyzer, heated from 25°C to 600°C at a rate of 5°C/minute under N$_2$ atmosphere. $^1$H NMR was performed on a Bruker FT-NMR spectrometer (300 MHz).

1.2 Syntheses. For all structures, TGA and Elemental Analysis revealed the amount of solvent in the crystals and were taken into account to calculate the yield.

**PPF-1[Zn$_2$(ZnTCPP)].** TCPP (55.3 mg, 0.07 mmol), Zn(NO$_3$)$_2$·6H$_2$O (62.3 mg, 0.21 mmol), and pyrazine (11.2 mg, 0.14 mmol) were added to a mixture of DEF (10.5 mL) and ethanol (3.5 mL) in a capped pressure vessel, sonicated to mix, and heated to 80°C for 24 h, followed by slow cooling to room temperature over 9 h. Yield: 73.3 mg (71% based on porphyrin). Anal. Calcd. for [C$_{48}$H$_{42}$N$_4$O$_8$Zn$_3$] 3.3 DEF · 1.5 H$_2$O · ethanol · 0.4 pyrazine: C, 57.7; H, 5.0; N, 8.9%. Found: C, 57.8; H, 5.0; N, 9.0%.

**PPF-27 [Zn$_2$(ZnTCPP)(BPY)] from PPF-1.** Filtered PPF-1 (44.1 mg, 0.03 mmol) and BPY (3.2 mg, 0.02 mmol) were added to a mixture of DEF (4.5 mL) and ethanol (1.5mL) in a capped vial, swirled by hand to mix, and left to react at room temperature for ~ 2 hr. Yield: 45.1 mg (95%). Anal. Calcd. for [C$_{58}$H$_{32}$N$_6$O$_8$Zn$_3$] 3DEF · 2 H$_2$O · 1 ethanol · 0.2 BPY: C, 59.5; H, 5.0; N, 9.0%. Found: C, 59.4; H, 5.0; N, 9.0%.

**PPF-18 [Zn$_2$(ZnTCPP)(DPNI)] from PPF-1.** Filtered PPF-1 (14.7 mg, 0.01 mmol) and DPNI (8.5 mg, 0.02 mmol) were added to a mixture of DEF (1.5 mL) and ethanol (0.5 mL) in a capped vial, swirled by hand to mix, and left to react at room temperature for ~ 2 hr. Yield: 21.2 mg (86%). Anal. Calcd. for [C$_{72}$H$_{36}$N$_8$O$_{12}$Zn$_3$] 3.6 DEF · 0.5 H$_2$O · 3.0 ethanol · 0.2 pyrazine: C, 59.0; H, 4.9; N, 9.0%. Found: C, 59.0; H, 4.9; N, 9.0%.

**PPF-21 [Zn$_2$(ZnTCPP)(DPT)] from PPF-1.** Filtered PPF-1 (14.7 mg, 0.01 mmol) and DPT (4.6 mg, 0.02 mmol) were added to a mixture of DEF (1.5 mL) and ethanol (0.5 mL) in a
capped vial, swirled by hand to mix, and left to react at room temperature for ~2 hr. Yield: 16.8 mg (89%). Anal. Calcd. for \([C_{60}H_{32}N_{10}O_{8}Zn_{3}]\) 1.7 DEF · 2.8 ethanol: C, 58.6; H, 4.49; N, 10.8%. Found: C, 58.8; H, 4.52; N, 10.7%.

**PPF-4 [Zn_2(ZnTCPP)(BPY)]_{1.5} from PPF-27.** Filtered PPF-27 (15.8 mg, 0.01 mmol) and BPY (8.0 mg, 0.05 mmol) were added to a mixture of DEF (1.5 mL) and ethanol (0.5 mL) in a capped vial, swirled by hand to mix, and left to react at room temperature for ~2 hr. Yield: 15.0 mg (92%). Anal. Calcd. for \([C_{63}H_{36}N_7O_8Zn_3]\) 3.3 DEF · 1.5 H_2O · 1 ethanol: C, 60.3; H, 5.1; N, 8.9%. Found: C, 61.0; H, 5.4; N, 8.9%.

**PPF-4 from PPF-1.** Filtered PPF-1 (14.7 mg, 0.01 mmol) and BPY (8.0 mg, 0.05 mmol) were added to a mixture of DEF (1.5 mL) and ethanol (0.5 mL) in a capped vial, swirled by hand to mix, and left to react at room temperature for ~2 hr. Purity of PPF-4 was confirmed by PXRD.

**PPF-27 from PPF-18.** Filtered PPF-18 (24.5 mg, 0.01 mmol) and BPY (3.2 mg, 0.02 mmol) were added to a mixture of DEF (1.5 mL) and ethanol (0.5 mL) in a capped vial, swirled by hand to mix, and left to react at room temperature for ~2 hr. Purity of PPF-27 was confirmed by PXRD.

**PPF-27 from PPF-21.** Filtered PPF-21 (18.9 mg, 0.01 mmol) and BPY (3.2 mg, 0.02 mmol) were added to a mixture of DEF (1.5 mL) and ethanol (0.5 mL) in a capped vial, swirled by hand to mix, and left to react at room temperature for ~2 hr. Purity of PPF-27 was confirmed by PXRD.
2. Structure Analysis

2.1 Analysis of PPF-1

PPF-1 is synthesized using pyrazine as a directing agent, aiding in the AB stacking pattern observed by powder and single crystal X-ray diffraction spectrum. Without pyrazine in the experimental procedure, a different phase is observed in the powder X-ray diffraction spectrum. Thus it is believed that pyrazine is needed for the construction of the AB stacked PPF-1 structure. Pyrazine, however was not observed in the single crystal structure and elemental analysis indicates only 0.4 pyrazine molecules per unit cell indicating it being a guest molecule instead of a coordinated linker. To quantitatively find how much pyrazine was in PPF-1 structure, we digested samples of PPF-1 in acid according to the method reported by Cohen.4 Approximately 5 mg of PPF-1 crystals were filtered, washed ≥ 3 times with 5 mL of DMF to rid the crystals of any free (unbound) ligands, and dried under vacuum at 90°C overnight. The dried crystals were then digested with sonication in 500 μL of dilute DCl (10 μL of 35% DC1 in D2O diluted with 500 μL of DMSO-d6). 1H NMR spectra was obtained from the resulting solution (Figure S3). Analysis of the integration of porphyrin signals to pyrazine signals indicate a porphyrin to pyrazine ratio of 1:0.3 which supports the conclusion that pyrazine is a guest and not a coordinated linker which would yield a porphyrin to pyrazine ratio of 1:1.

Figure S1. Representation of single crystal of PPF-1.
Figure S2. The simulated (black) and as synthesized (red) X-ray powder diffraction patterns for PPF-1.
Figure S3. $^1$H NMR spectra of digested PPF-1. Red squares and blue circles represent signals of pyrazine and ZnTCPP respectively.
2.2 Analysis of PPF-27 synthesized from PPF-1

Powder X-ray diffraction shows full conversion from PPF-1 to PPF-27 and no other products formed (Figure S5). To quantitatively find the occupation of BPY linker in PPF-27, we digested samples of PPF-27 in acid following the same method described above. Analysis of the $^1$H NMR spectra shows 93% occupation of BPY linker in PPF-27 (Figure S6).

Figure S4. Representation of single crystal structure of PPF-27.
Figure S5. The simulated (black) and as synthesized (red) X-ray powder diffraction patterns for PPF-27.
**Figure S6.** $^1$H NMR spectra of digested PPF-27. Red squares and blue circles represent signals of BPY and ZnTCPP respectively.
2.3 Analysis of PPF-18 synthesized from PPF-1

Powder X-ray diffraction shows full conversion from PPF-1 to PPF-18 and no other products formed (Figure S8). To quantitatively find the occupation of DPNI linker in PPF-18, we digested samples of PPF-18 in acid following the same method described above. Analysis of the $^1$H NMR spectra shows 89% occupation of DPNI linker in PPF-18 (Figure S9).

Figure S7. Representation of single crystal structure of PPF-18.
**Figure S8.** The simulated (black) and as synthesized (red) X-ray powder diffraction patterns for PPF-18.
**Figure S9.** $^1$H NMR spectra of digested PPF-18. Red squares and blue circles represent signals of DPNI and ZnTCPP respectively.
2.4 Analysis of PPF-21 synthesized from PPF-1

Powder X-ray diffraction shows full conversion from PPF-1 to PPF-21 and no other products formed (Figure S11). To quantitatively find the occupation of DPT linker in PPF-21, we digested samples of PPF-21 in acid following the same method described above. Analysis of the $^1$H NMR spectra shows 87% occupation of DPT linker in PPF-21 (Figure S12).

Figure S10. Representation of single crystal structure of PPF-21.
Figure S11. The simulated (black) and as synthesized (red) X-ray powder diffraction patterns for PPF-21.
Figure S12. $^1$H NMR spectra of digested PPF-21. Red squares and blue circles represent signals of DPT and ZnTCPP respectively.
2.5 Analysis of PPF-4 synthesized from PPF-27

Powder X-ray diffraction shows full conversion from PPF-27 to PPF-4 and no other products formed (Figure S14). To quantitatively find the occupation of BPY linker in PPF-4, we digested samples of PPF-4 in acid following the same method described above. Analysis of the \(^1\)H NMR spectra shows 95% occupation of BPY linker in PPF-4 (Figure S15).

Figure S13. Representation of single crystal structure of PPF-4.
Figure S14. The simulated (black) and as synthesized (red) X-ray powder diffraction patterns for PPF-4.
Figure S15. $^1$H NMR spectra of digested PPF-4. Red squares and blue circles represent signals of BPY and ZnTCPP respectively.
2.6 Analysis of PPF-4 synthesized by PPF-1

Powder X-ray diffraction shows full conversion from PPF-1 to PPF-4 and no other products formed (Figure S16). To quantitatively find the occupation of BPY linker in PPF-4, we digested samples of PPF-4 in acid following the same method described above. Analysis of the $^1$H NMR spectra shows 90% occupation of BPY linker in PPF-4 (Figure S17).

![X-ray powder diffraction patterns](image)

**Figure S16.** The simulated (black) and as synthesized (red) X-ray powder diffraction patterns for PPF-4.
**Figure S17.** $^1$H NMR spectra of digested PPF-4. Red squares and blue circles represent signals of BPY and ZnTCPP respectively.
**Table S1.** Amounts of reactants and resulting structures for the linker insertion investigation of PPFs.

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<th>Starting Structure</th>
<th>Pillar</th>
<th>Pillar Amt. (equivalents)</th>
<th>Phase(s) identified&lt;sup&gt;a&lt;/sup&gt;</th>
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<tr>
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<tr>
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<sup>a</sup> based upon powder XRD pattern analysis
Figure S18. The difference in linker insertion connectivity between frameworks with one single metal node and two different metal nodes.
**Figure S19.** Schematic representation of all attempted linker insertion reactions in PPFs. Red crosses denote reactions which were not successful. Grey arrows denote a linker replacement reaction which was previously reported by our group (see ref. 2a).
Figure S20. TGA data of PPF-1 (black), PPF-27 (red), PPF-18 (blue), PPF-21 (green), and PPF-4 (purple).
References


(2) (a) Burnett, B. J.; Barron, P. M.; Hu, C.; Choe, W. J. Am. Chem. Soc. 2011, 133, 9984.

(3) http://www.ccdc.cam.ac.uk/products/mercury/