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Pillared Porphyrin Homologous Series: Intergrowth in Metal−Organic Frameworks

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We report three new porphyrin-based, pillared paddle-wheel homologous series: porphyrin paddle-wheel frameworks PPF-3, -4, and -5. These compounds are assembled from free base or palladium tetrakis(4-carboxyphenyl)porphine, $M(NO_3)_2$ (M = Co and Zn), and 4,4′-bipyridine via solvothermal reactions. The resulting solids exhibit 3D metal−organic frameworks, where 2D layers are pillared by bipyridine with three different packing arrangements.

The topological control of metal−organic frameworks (MOFs) has become one of the most active areas in inorganic materials chemistry because of potential applications of MOFs in gas storage, molecular recognition, and catalysis.[1] A daunting challenge has been how to create designed and predictable topologies with desired physical properties.[2] A key advantage of such isorecticular MOFs is their tunability: the final topology is easily tunable by the choice of organic linkers and metal components, known as secondary building units (SBUs), as demonstrated by a series of pillared paddle-wheel frameworks.[3−6] The 3D pillared paddle-wheel frameworks previously demonstrated are assembled from three independent structural components [i.e., $M_2(COO)_4$ paddle-wheel SBUs (M = Mn, Co, Ni, Cu, Zn, and Cd), dicarboxylate linkers, and dipyridyl pillars], making the size and shape of the channels easily tunable. However, even in these series, alteration of the interlayer stacking sequence has not been established.[3−6] Recently, we have become particularly interested in a new synthetic strategy to build frameworks with multiple ligand binding sites.[7−9] To this end, porphyrins are promising ligands because a metal center can be incorporated in the center of the porphyrin ring, providing an additional binding site to control the framework topology. In this Communication, we present a new pillared homologous series that allows us to control the stacking sequence

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(1) (a) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (b) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (c) Kitagawa, S.; Kitaura, R.; Noro, S.-I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.

(2) Delgado-Friedrich, O.; O'Keeffe, M.; Yaghi, O. M. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1035.

(3) (a) Chun, H.; Dybtsev, D. N.; Kim, H.; Kim, K. *Chem.—Eur. J.* **2005**, *11*, 3521. (b) Dybtsev, D. N.; Chun, H.; Kim, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5033. (c) Kitaura, R.; Iwahori, F.; Matsuda, R.; Kitagawa, S.; Kubota, Y.; Takata, M.; Kobayashi, T. C. *Inorg. Chem.* **2004**, *43*, 6522. (d) Liu, B.; Xu, L. *Inorg. Chem. Commun.* **2006**, *9*, 364. (e) Dybtsev, D. N.; Yutkin, M. P.; Peresypkina, E. V.; Virovets, A. V.; Serre, C.; Férey, G.; Fedin, V. P. *Inorg. Chem.* **2007**, *46*, 6843. (f) Fu, Z.; Yi, J.; Chen, Y.; Liao, S.; Guo, N.; Dai, J.; Yang, G.; Lian, Y.; Wu, X. *Eur. J. Inorg. Chem.* **2008**, 628. (g) Chen, B.; Zhao, X.; Putkham, A.; Hong, K.; Lobkovsky, E. B.; Hurtado, E. J.; Fletcher, A. J.; Thomas, K. M. *J. Am. Chem. Soc.* **2008**, *130*, 6411. (h) Chen, B.; Ji, Y.; Xue, M.; Fronczek, F. R.; Hurtado, E. J.; Mondal, J. U.; Liang, C.; Dai, S. *Inorg. Chem.* **2008**, *47*, 5543. (i) Tanaka, D.; Horike, S.; Kitagawa, S.; Ohba, M.; Hasegawa, M.; Ozawa, Y.; Toriumi, K. *Chem. Commun.* **2007**, 3142. (j) Rather, B.; Zaworotko, M. J. *Chem. Commun.* **2003**, 830. (k) Yuen, T.; Danilovic, D.; Li, K.; Li, J. *J. Appl. Phys.* **2008**, *103*, 07B725. (l) Seki, K.; Mori, W. *J. Phys. Chem. B* **2002**, *106*, 1380. (m) Seki, K.; Takamizawa, S.; Mori, W. *Chem. Lett.* **2001**, 332.

(4) (a) Chen, B.; Ma, S.; Hurtado, E. J.; Lobkovsky, E. B.; Liang, C.; Zhu, H.; Dai, S. *Inorg. Chem.* **2007**, *46*, 8705. (b) Ma, B.-Q.; Mulfort, K. L.; Hupp, J. T. *Inorg. Chem.* **2005**, *44*, 4912. (c) Chen, B.; Ma, S.; Zapata, F.; Fronczek, F. R.; Lobkovsky, E. B.; Zhou, H.-C. *Inorg. Chem.* **2007**, *46*, 1233. (d) Dalai, S.; Mukherjee, P. S.; Zangrando, E.; Lloret, F.; Chaudhuri, N. R. *Dalton Trans.* **2002**, 822. (e) Chen, B.; Ma, S.; Zapata, F.; Lobkovsky, E. B.; Yang, J. *Inorg. Chem.* **2006**, *45*, 5718. (f) Chen, B.; Fronczek, F. R.; Courtney, B. H.; Zapata, F. *Cryst. Growth Des.* **2006**, *6*, 825. (g) Pichon, A.; Fierro, C. M.; Nieuwenhuyzen, M.; James, S. L. *CrystEngComm* **2007**, *9*, 449. (h) Cho, S.-H.; Ma, B.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Chem. Commun.* **2006**, 2563.

(5) (a) Wang, R.; Han, L.; Jiang, F.; Zhou, Y.; Yuan, D.; Hong, M. *Cryst. Growth Des.* **2005**, *5*, 129. (b) Chen, B.; Ma, S.; Hurtado, E. J.; Lobkovsky, E. B.; Zhou, H.-C. *Inorg. Chem.* **2007**, *46*, 8490. (c) Choi, E.-Y.; Park, K.; Yang, C.-H.; Kim, H.; Son, J.-H.; Lee, S. W.; Lee, Y. H.; Min, D.; Kwon, Y.-U. *Chem.—Eur. J.* **2004**, *10*, 5535. (d) Lee, S. W.; Kim, H. J.; Lee, Y. K.; Park, K.; Son, J.-H.; Kwon, Y.-U. *Inorg. Chim. Acta* **2003**, *353*, 151. (e) Hsu, L.-P.; Wu, J.-Y.; Lu, K.-L. *J. Inorg. Organomet. Polym. Mater.* **2007**, *17*, 259. (f) Xue, M.; Ma, S.; Jin, Z.; Schaffino, R. M.; Zhu, G.-S.; Lobkovsky, E. B.; Qiu, S.-L.; Chen, B. *Inorg. Chem.* **2008**, *47*, 6825.

(6) For a review on Zn-based paddle-wheel frameworks, see: Vagin, S. I.; Ott, A. K.; Rieger, B. *Chem. Ing. Tech.* **2007**, *79*, 767.

(7) For an example of a 1D porphyrin tape, see: Choi, E.-Y.; Barron, P. M.; Novotny, R. W.; Hu, C.; Kwon, Y.-U.; Choe, W. *CrystEngComm* **2008**, *10*, 824.

(8) Porphyrin-based linkers are examples of metalloligands. See: Kitagawa, S.; Noro, S.-I.; Nakamura, T. *Chem. Commun.* **2006**, 701.

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by the introduction of metallotetrakis(4-carboxyphenyl)porphyrin (MTCPP) linkers, providing an additional recognition site for the organic pillar molecule. We report three distinct stacking arrangements (AA, ABBA, and AB), where the ABBA stacking pattern represents an intergrowth of AA and AB patterns. The stacking sequence of 2D paddle-wheel layers can be systematically varied depending on stereochemical preferences of the metal center in the porphyrin linkers. This simple synthetic strategy is useful for controlling 3D pillaring of 2D-layered materials. To the best of our knowledge, this pillared framework series is the first example of MOFs that exhibit an intergrowth pattern via multiple metal recognition sites.

Porphyrin paddle-wheel frameworks (PPFs) were synthesized by solvothermal reaction of tetrakis(4-carboxyphenyl)porphine (TCPP) or metalated TCPP (MTCPP), metal nitrates, and 4,4′-bipyridine (bpy) in *N*,*N*-dimethylformamide (DMF)/ethanol at 80 °C.[10] The samples were characterized by elemental analysis, single-crystal X-ray diffraction, powder X-ray diffraction, and thermogravimetric analysis (TGA).[10−12]

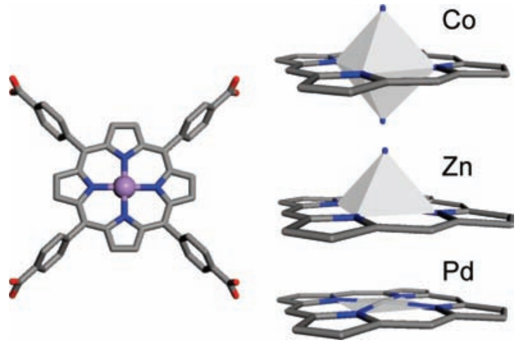

Figure 1. Left: Porphyrin building unit, MTCPP. Right: Coordination geometry of the metal centers found in PPF-3 (Co), PPF-4 (Zn), and PPF-5 (Pd).

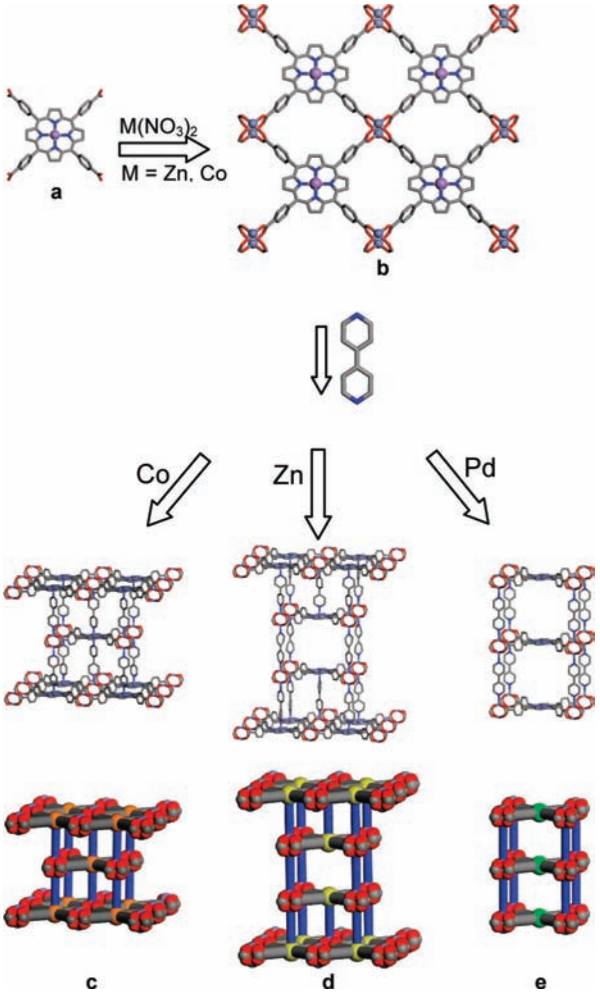

Figure 2. PPF frameworks constructed from (a) porphyrin ligands, which can be TCPP or PdTCPP. Using metal nitrates, the 2D infinite sheets (b) are constructed with paddle-wheel SBUs and the MTCPPs. The 2D sheets are pillared with bpy to give (c) PPF-3 (Co, orange), (d) PPF-4 (Zn, yellow), and (e) PPF-5 (Pd, green). The resulting stacking arrangements are dependent on the preferred coordination geometry of the porphyrin metal centers.

Figure 1 shows the three tetratopic metalloporphyrin linkers ($MTCPP^n$; M = Co^{3+}, Zn^{2+}, and Pd^{2+}; $n = 1+$ for Co^{3+} and $n = 0$ for Zn^{2+} and Pd^{2+}) used in this study, each representing six- (octahedral), five- (square-pyramidal), and four- (square-planar) coordination environments. These porphyrin linkers and $M_2(COO)_4$ SBUs (M = Zn or Co) form a 2D "checkerboard" pattern with approximately 11.8 Å between the porphyrin metal center and the paddle-wheel SBU, as shown in Figure 2b. The resulting 2D layers are pillared by bpy molecules. Interestingly, the 2D layers in PPFs can be pillared in two different ways: homogeneously or heterogeneously. Homogeneous pillaring is commonly observed in paddle-wheel frameworks when a dipyridyl pillar connects two $M_2(COO)_4$ SBUs.[3−6] A new type of hetero-

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(9) For porphyrin frameworks, see: (a) Suslick, K. S.; Bhyrappa, P.; Chou, J. H.; Kosal, M. E.; Nakagaki, S.; Smithenry, D. W.; Wilson, S. R. *Acc. Chem. Res.* **2005**, *38*, 283. (b) Kosal, M. E.; Chou, J. H.; Wilson, S. R.; Suslick, K. S. *Nat. Mater.* **2002**, *1*, 118. (c) Drain, C. M.; Goldberg, I.; Sylvain, I.; Falber, A. *Top. Curr. Chem.* **2005**, *245*, 55. (d) Goldberg, I. *Chem. Commun.* **2005**, *10*, 1243. The PIZA structures developed by Suslick et al. contain MTCPP building units connected by inorganic SBUs. Similar to PPF-4 and -5, these PIZA structures have Zn and Co porphyrin metal centers decorating the pore channels.

(10) Syntheses: (a) **PPF-3.** 5,10,15,20-Tetrakis(4-carboxyl)-21*H*,23*H*-porphine (7.9 mg, 0.01 mmol), cobalt nitrate hexahydrate (8.7 mg, 0.03 mmol), and bpy (3.1 mg, 0.02 mmol) were added to a mixture of DMF (1.5 mL) and ethanol (0.5 mL) in a small capped vial and heated to 80 °C for 24 h, followed by slow cooling to room temperature over 9 h. Yield: 10.4 mg (82% based on porphyrin). Anal. Calcd for $[C_{68}H_{40}N_8O_8Co_3]NO_3 \cdot 7H_2O \cdot 14DMF$: C, 53.2; H, 6.2; N, 13.0. Found: C, 53.0; H, 6.2; N, 13.0. (b) **PPF-4.** 5,10,15,20-Tetrakis(4-carboxyl)-21*H*,23*H*-porphine (7.9 mg, 0.01 mmol), zinc nitrate hexahydrate (8.2 mg, 0.03 mmol), and bpy (3.3 mg, 0.02 mmol) were added to a mixture of DEF (1.5 mL) and ethanol (0.5 mL) in a small capped vial and heated to 80 °C for 24 h, followed by slow cooling to room temperature over 9 h. Yield: 9.0 mg (74% based on porphyrin). Anal. Calcd for $C_{63}H_{36}N_7O_8Zn_3 \cdot 3.7H_2O$: C, 59.0; H, 3.4; N, 7.7. Found: C, 58.9; H, 3.4; N, 7.9. (c) **PPF-5.** Palladium(II) 5,10,15,20-tetrakis(4-carboxyl)porphine (9.2 mg, 0.01 mmol), cobalt nitrate hexahydrate (8.8mg, 0.03 mmol), and bpy (2.8 mg, 0.02 mmol) were added to a mixture of DEF (1.5 mL) and ethanol (0.5 mL) in a small capped vial and heated to 80 °C for 24 h, followed by slow cooling to room temperature over 9 h. Yield: 8.8 mg (70% based on porphyrin). Anal. Calcd for $C_{58}H_{32}N_6O_8Co_2Pd \cdot 2CH_3CH_2OH$: C, 60.2; H, 3.6; N, 6.5. Found: C, 59.2; H, 3.5; N, 6.7.

(11) Crystallographic data. (a) **PPF-3**: $C_{68}H_{40}N_9O_{11}Co_3$, tetragonal, *I*4/*mmm* (No. 139), $a = 16.6007(2)$ Å, $c = 24.6892(5)$ Å, $V = 6803.93(18)$ Å^3, $Z = 2$, R1 = 0.0801, wR2 = 0.2432 ($I > 2\sigma$, after SQUEEZE). (b) **PPF-4**: $C_{63}H_{36}N_7O_8Zn_3$, tetragonal, *I*4/*mmm* (No. 139), $a = 16.7122(2)$ Å, $c = 54.2436(14)$ Å, $V = 15150.1(5)$ Å^3, $Z = 4$, R1 = 0.0332, wR2 = 0.0854 ($I > 2\sigma$, after SQUEEZE). (c) **PPF-5**: $C_{58}H_{32}N_6O_8Co_2Pd$, tetragonal, *I*4/*mmm* (No. 139), $a = 16.7123(1)$ Å, $c = 13.9165(2)$ Å, $V = 3889.89(6)$ Å^3, $Z = 1$, R1 = 0.0305, wR2 = 0.0836 ($I > 2\sigma$, after SQUEEZE).

(12) See the Supporting Information.

geneous pillaring can be seen in PPF-3, [Co_2(CoTCPP)-$(bpy)_2$](NO_3). In this structure, the bpy pillars connect $Co_2(COO)_4$ clusters and CoTCPP linkers. As shown in Figure 2, this type of pillaring saturates all available Co metal sites; consequently, the resulting stacking pattern becomes AB.

Another interesting structural feature can be seen in PPF-4, [Zn_2(ZnTCPP)$(bpy)_{1.5}$]. In this structure, 2D porphyrin layers are connected by alternating homogeneous and heterogeneous pillaring. Because of this unique pillaring pattern, the stacking sequence found in PPF-4 becomes ABBA (Figure 2). This stacking pattern originates from the Zn coordination in porphyrin. Although examples of six-coordinate Zn are known, five-coordinate Zn is energetically favored by 14 kcal/mol in related compounds.[13] A notable feature of this stacking pattern is that the Zn center in ZnTCPP could accommodate an additional ligand without changing the overall framework connectivity. In this regard, the framework contains coordinatively unsaturated metal centers. It is noteworthy that such unsaturated metal centers created in MOFs are an important factor in hydrogen storage in terms of increasing hydrogen adsorption energies at ambient temperatures.[14] In both cases (i.e., PPF-3 and -4), the coordination environment of the metal center in the porphyrin governs the stacking pattern of the 3D pillared porphyrin network.

To extend the relationship between the stacking pattern and the coordination environment of the metals, we also synthesized a new compound, PPF-5, assembled from PdTCPP linkers, Co paddle-wheel SBUs, and bpy pillars under synthetic conditions similar to those used in PPF-3 and -4.[10c] As expected, the single-crystal structure reveals only homogeneous pillaring between paddle-wheels because the d^8 metal (Pd^{2+}) inside TCPP does not participate in coordination bonding with bpy pillars. PPF-5 has the lowest framework density (0.498 g/cm^3) in this series.[11c] The AA stacking pattern observed in PPF-5 is particularly interesting because the porphyrin metal centers are decorating the pore surface. Because the exposed metal centers in MOFs are attractive features in gas storage and catalysis, the AA stacking pattern found in PPF-5 would be interesting if it could be obtained with octahedral metals incorporated inside TCPP.

These three observed layered stacking patterns are closely related; one might consider that the ABBA stacking pattern found in PPF-4 is a 1:1 intergrowth of AB and AA stacking sequence in PPF-3 and -5, respectively. Although intergrowth is commonly observed in other types of inorganic extended solids,[15] to the best of our knowledge, this homologous series represents the first example of an intergrowth pattern observed in MOFs.

In order to distinguish between the three stacking patterns and optimize the synthetic conditions for PPFs, powder X-ray diffraction has been used.[12] Because all three structures have virtually identical unit cell lengths in the *a* and *b* directions,[11] reflections involving the *c* value were ideal for the structural characterization. The resulting crystal morphologies are square platelets, typically with the edge length five times greater than the thickness. This morphology results in a very strong preferred orientation.[12] The preferred orientation allows for easy indexing of the 00*l* reflections and, consequently, determination of the framework stacking patterns. This quick characterization of samples increases throughput and eventually leads to optimization of the synthetic conditions. The synthetic conditions for single-crystal growth have been determined by systematic variation of the following parameters: the concentrations of the ligands and metal nitrates, the amounts and types of solvents used, and the solvent ratio. In an attempt to remove the preferred orientation, the samples are ground. This procedure, however, results in an apparent loss of crystallinity, and the samples become amorphous. The 3D PPF samples (PPF-3 and -4) are not thermally robust and are only stable up to ~200 °C, becoming amorphous or unidentified phases upon heating.

In conclusion, this PPF series demonstrates a new level of tunability in MOFs. We have demonstrated that the stacking arrangement of 2D paddle-wheel porphyrin layers can be altered by the coordination geometry of the porphyrin linkers. Work is in progress to form AA stacking patterns with various transition metals and to create other stacking sequences.

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Supporting Information Available: Powder X-ray diffraction patterns, IR and TGA data, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Kleij, A. W.; Kuil, M.; Tooke, D. M.; Spek, A. L.; Reek, J. N. H. *Inorg. Chem.* **2005**, *44*, 7696.

(14) (a) Ma, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 11734. (b) Dinča, M.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 9376. (c) Dinča, M.; Yu, A. F.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 8904. (d) Dinča, M.; Han, W. S.; Liu, Y.; Dailly, A.; Brown, C. M.; Long, J. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 1419. (e) Dinča, M.; Dailly, A.; Liu, Y.; Brown, C. M.; Neumann, D. A.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 16876.

(15) Forster, P. M.; Eckert, J.; Heiken, B. D.; Parise, J. B.; Yoon, J. W.; Jhung, S. H.; Chang, J.-S.; Cheetham, A. K. *J. Am. Chem. Soc.* **2006**, *128*, 16846.