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M = Co, Ni, Cu, Zn

Development of Isostructural Porphyrin–Salen Chiral Metal–Organic Frameworks through Postsynthetic Metalation Based on Single-**Crystal to Single-Crystal Transformation**

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Supporting Information

ABSTRACT: The development of well-defined multimetallic porous metal-organic frameworks (MOFs) will add a new dimension to the application of MOF catalysis. From this perspective, the understanding and tailoring of the catalytic metal sites in MOFs are key fundamental challenges that could reveal the intrinsic potential of these materials. In this work, a series of porphyrin-salen chiral MOFs (ps-CMOFs 2-7) have been synthesized through postsynthetic metalation (PSMet) of the parent ps-CMOF via single-crystal to singlecrystal transformation. Crystal structures of these ps-CMOF analogues revealed the same topological structure but varied



INTRODUCTION

Metal-organic frameworks (MOFs) are some of the most widely studied hybrid materials because of their highly permanent porosity coupled with extraordinarily broad chemical and topological diversities, which in turn brings a multitude of potential for utility in gas storage,¹ heterogeneous catalysis,² chemical sensing,³ and other applications.⁴ In particular, the understanding and tailoring of inorganic metal nodes and organic linkers in MOFs are key fundamental challenges that could reveal the intrinsic potential of these materials for heterogeneous catalysis. Generally, three main approaches are used to identify active sites in MOFs: (i) using the unsaturated coordinative sites of the secondary building units (SBUs) after removal of coordinated solvent molecules, (ii) loading active species (e.g., noble metal nanoparticles) in MOF cavities through postsynthetic modification (PSM), and (iii) directly introducing metalloligands for MOF construction. Compared to the first two approaches, the latter is intriguing because it not only can incorporate different metal species into the framework for specific purposes by rationally tuning the

metalloligand cores but also enables the construction of a stable network with permanent porosity due to the general rigidity of the metalloligands.

Catalytic sites tuning

Metalloporphyrin and metallosalen are perceived as very profound molecular catalysts because of their diversities in structures and constitutions. Unlike their homogeneous counterparts, the immobilization of these complexes into MOFs can effectively enhance catalytic performance by eliminating multimolecular catalyst deactivation pathways owing to the confinement effect of MOFs and thus provides well-defined catalytic centers in the structures of MOFs that are capable of catalyzing more advanced reactions. Although large amounts of porphyrin- or salen-based MOFs have been synthesized and applied in different heterogeneous catalyses, most of these MOF catalysts are constrained to specific reactions because the catalytic metal sites in these cases are usually determined and inert for further modification.⁵ Thus,



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engineering an isostructural catalytic platform that can be utilized in a broad range of reactions is quite fascinating as it can maximize spatial and temporal productivity with minimal immobilized resources. Hupp et al. have shown the successful construction of a series of robust porphyrinic MOFs by incorporating two kinds of metalloporphyrin derivatives into one skeleton.⁶ The two types of metalloporphyrin cores can be judiciously tuned with different metal ion combinations and work cooperatively for tandem catalysis. In comparison, examples of chiral MOF catalytic platforms are extremely scarce.⁷ Cui et al. developed the chiral multivariate MOFs though do novo fabrication of multiple metallosalen analogues into one skeleton, and the obtained MOFs can be used as efficient and recyclable heterogeneous catalysts for a variety of asymmetric sequential alkene epoxidation/epoxide ring-opening reactions.^{7d} Apart from the porphyrin-porphyrin and salen-salen catalytic systems mentioned above, we recently reported the first porphyrin-salen-based chiral MOF (ps-CMOF 1) as an effective and recyclable heterogeneous catalyst for the asymmetric cyanosilylation of aldehydes.⁸ The high efficiency and enantioselectivity are induced by the cooperative function between Lewis acid activation (from metalloporphyrin) and chiral induction (from metallosalen). It is noteworthy that the crystal structure of 1 reveals two kinds of different interpenetrated frameworks; in one, the porphyrin core is occupied by an out-of-plane Cd²⁺ ion, and the other is metalfree porphyrin. This structural character enables the facile preparation of other ps-CMOF analogues by incorporation of various active metal sites into 1 though PSM, which can serve as a chiral catalytic platform for more enriched asymmetric catalyses.

PSM has now been utilized as a powerful alternative tool to prepare topologically identical but functionally diverse frameworks when traditional direct synthesis suffers from vagaries such as the incompatibility of functional groups, the low solubility of reagents, and the formation of undesired topologies.⁹ As one subset of PSM, postsynthetic metalation (PSMet) refers to the fabrication of metal ions within the frameworks. To date, plenty of new analogues of MOFs that could not be synthesized de novo have been successfully obtained in the assistance of PSMet,¹⁰ which also offers better control of structural diversities over traditional hydro- or solvothermal reactions.¹¹ In principle, four main PSMet methods are utilized to incorporate extraneous metal ions into MOF structures: (i) addition to the empty coordination sites within MOFs, (ii) cation exchange at metal nodes, (iii) cation exchange at linkers, and (iv) encapsulation of nanoparticles into the cavity of MOFs. Herein, we report the preparation of six ps-CMOF analogues (2-7) using the PSMet method based on the single-crystal to single-crystal (SC-SC) transformation. The whole process involves three different PSMet methods, cation exchange at the Cd-Cd paddle-wheel node, addition of extraneous metal ions to the free porphyrin, and cation exchange at the Cd-porphyrin, which result in four sets of bimetallic paddle-wheel M-Cd (M = Cu, Zn, Ni, or Co) clusters that are characterized by single-crystal X-ray diffraction for the first time. In addition, the cation exchange process in the porphyrin core proved to be dynamically faster than the addition process, providing the possibility of tuning the content of catalytic metal sites in ps-CMOF catalysts. For CO₂ adsorption, all ps-CMOF analogues showed enhanced adsorption capacities and Q_{st} values compared to those of the original 1. As a representative example of the ps-CMOF

catalytic platform, **5** was used as an efficient and recyclable heterogeneous catalyst for the asymmetric addition reaction of CO_2 with epoxides under mild conditions and exhibited substrate size-dependent enantioselectivity.

EXPERIMENTAL SECTION

Materials and Methods. All of the reagents were commercially available and were used without further purification. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 powder diffractometer at 40 kV and 40 mA with Cu K α radiation (λ = 1.5406 Å), with a step size of 0.0131° (2 θ). Solid-state circular dichroism (CD) spectra were recorded on a J-800 spectropolarimeter (Jasco). Thermogravimetric analyses (TGA) were performed on a Q600 SDT instrument under a flow of N_2 at a heating rate of 10 °C/min. Gas chromatography-mass spectroscopy (GC-MS) data were recorded on a Shimadzu model GCMS-QP5050A system that was equipped with a 0.25 mm \times 30 m DB-WAX capillary column. The content of metal ions was determined with an atomic absorption spectrometer (AAS, Z-2000, Hitachi). The gas adsorption measurements were performed on a MicroActive ASAP 2460 system under N₂ (77 K) and CO₂ (273 and 298 K). The X-ray photoelectron spectroscopy (XPS) experiment was conducted using a spectrometer with an Al K α radiation source. Enantiomeric excess (ee) values were determined by high-performance liquid chromatography (HPLC) performed on an Agilent 1200 series system with an Analytical CHIRALCEL OD-H chiral column or by GC performed on an Agilent 7820A series system with an Agilent 19091J-413 capillary column.

Synthesis. ps-CMOF **1** was synthesized according to the reported procedure.⁸ After being thoroughly washed with dimethylformamide (DMF), the single crystals of **1** were soaked in a DMF solution containing 0.04 M MCl₂ (M = Cu, Zn, Ni, or Co) for 7 days (for **2**–**5**) or 30 days (for **6** and **7**) at room temperature. The metal salts were refreshed every other day during the soaking process. Then, the exchanged crystals of **2**–**7** were thoroughly washed with DMF to remove excess metal salts.

Catalytic Experiments. Epoxides (10 mmol), **5** (0.5 mol %), and *n*-tetrabutylammonium bromide (TBAB) (1 mol %) were mixed in a Schlenk flask with a magnetic bar. The mixture was outgassed completely and then purged with CO_2 . This operation was repeated three times before the mixture was stirred at 0 °C for 24 h with a CO_2 balloon. Upon completion, the mixture was filtered to remove the solid phase and the filtrate was analyzed via GC–MS to give the conversion.

Recycle Experiments. The recyclability of **5** was tested with five consecutive runs. After the reaction, the solid phase was filtered and collected. By being washed three times with DMF, catalyst **5** was dried at 150 $^{\circ}$ C for 6 h under vacuum pressure before it was used for another run.

X-ray Crystallography. Single-crystal XRD analysis of 2-5 was performed on an Xcalibur Onyx Nova four-circle diffractometer using Cu K α radiation (λ = 1.54184 Å) at 100 K. The empirical absorption correction was performed using the CrystalClear program. The structures were determined by the direct method and refined on F^2 by the full-matrix least-squares technique using the SHELX-97 program package.¹² The metal atoms in the asymmetric unit were located first from the difference Fourier map and refined anisotropically. The other atoms (O, C, and N) in the salen and porphyrin rings were then located from the difference Fourier map and partly refined isotropically, as a result of the relatively weak diffraction (which is not uncommon for this kind of framework with large solvent accessible void space). Restraints (DELU and SIMU) on displacement parameters and DFIX for bond lengths of salen framework were applied, and all phenyl rings of 1,2-diphenylethylenediimine on the salen ligand were constrained to ideal six-membered rings. The SQUEEZE subroutine of the PLATON software suite¹³ was applied to remove the scattering from the highly disordered guest molecules. The resulting new HKL files were used to further refine the structures. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. CCDC 1579011

Table 1. Structural Details of the Crystal Structures of ps-CMOFs 1-5



Figure 1. (a) Simplest network of **3** (diphenyl groups on the salen ligand have been omitted for the sake of clarity). (b) Topological structure of the 3D network of **3** (green and red rods represent porphyrin linkers, and gray rods represent salen linkers; lavender spheres represent the paddle-wheel cluster). (c) Space-filling view of the 2-fold interpenetrated network of **3** along the *b* axis.

(for 2), 1579012 (for 3), 1579013 (for 4), and 1579014 (for 5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

PSMet and Crystal Structures. As reported in our previous work,⁸ 1 consists of two kinds of different interpenetrated frameworks; in one, the porphyrin core is occupied by an out-of-plane Cd^{2+} ion with a ΔC_{β} (the average deviation of β -carbon atoms from the porphyrin plane) of 0.82 Å, and the other is a metal-free porphyrin. These highly tunable porphyrin cores together with the highly twisted $Cd_2(COO)_4$ paddle-

wheel cluster prompted us to explore the possibility of using PSMet to synthesize ps-CMOF analogues. Immersing the crystals of 1 in a DMF solution containing 0.04 M MCl₂ (M = Cu, Zn, Ni, or Co) for 7 days at room temperature afforded the corresponding ps-CMOFs 2-5 that are suitable for single-crystal XRD. The unit cell parameters of 2-5 agree well with those of 1 with only slight deviations (Table 1). Crystal structures of 2-5 revealed the same topological structure but varied metal entities as compared to those of the parent framework. Here, we discuss the structure of 3 only for detail. 3 crystallizes in the chiral P1 space group. The simplest network is based on a highly twisted $ZnCd(COO)_4$ paddle-wheel SBU, which is bridged by four bidentate carboxylate groups from four

porphyrin linkers and pillared by two salen linkers at the axial positions (Figure 1a). This connection to other orientations leads to the final three-dimensional (3D) framework with 2-fold interpenetration (Figure 1b). Similar to the parent framework, notable one-dimensional (1D) channels ($6.5 \text{ Å} \times 10.5 \text{ Å}$) still exist in the 2-fold interpenetrated framework of 3 (Figure 1c). On the basis of structural analysis, there are three different methods involving cation exchange at the Cd–Cd paddle-wheel cluster, cation exchange at the Cd–porphyrin species, and addition at the free porphyrin.

Cation Exchange at the Cd-Cd Paddle-Wheel Cluster. Generally, four main aspects have to be taken into consideration for a successful metal node exchange. (i) The exchangeable metal sites are coordinated unsaturated or coordinated by at least one solvent molecule or coordinated by a ligand with a weak binding energy. (ii) The thermodynamic stability of the daughter SBU has to be higher than that of the parent SBU. (iii) The incoming metal ions can assume a coordination state similar to that of the outgoing one. (iv) The incoming metal ions can freely enter the interior of the framework. In 1, the axial positions of the Cd^{2+} ion of nodes are weakly coordinated by pyridyl groups from salen linkers, and thus, this Cd^{2+} ion may be labile for exchange. In addition, the $Cd_2(COO)_4$ cluster is highly distorted and thermodynamically inclined to transfer to a more regular paddle wheel with enhanced thermal stability. Furthermore, the relatively large pore openings (10.5 Å) of 1 facilitate free access of the incoming metal ions to the framework interior. These structural characteristics of 1 described above suggested feasible metal node exchange. Therefore, we select divalent Cu²⁺, Zn²⁺, Ni²⁺, and Co²⁺ ions with smaller radii for operating PSMet as these cations tend to form a regular paddle-wheel cluster and successful metal exchange in other complexes has been realized utilizing these cations.^{11b,14} Interestingly, crystal structure analyses showed that four sets of bimetallic Cd-M (M = Cu, Zn, Ni, or Co) paddle-wheel clusters are found in 2-5 (Table 1). The obvious changes lie in the differences in bond distances between M-O and M-N and between Cd-O and Cd-N (Table 1 and Table S1). In theory, complete cation exchanges are prone to occur from a less thermodynamically stable paddle-wheel cluster to a more stable one, as found in many cases.¹⁵ In addition, exchange of larger-radius metal ions with smaller ones is also favored kinetically. Therefore, we envisioned complete metal exchanges might be achieved by extending the soaking time (3 months), increasing the metal salt concentration (0.1 M), increasing the exchange temperature (60 °C), or switching to other exchange solvents with smaller solvation spheres (methanol and acetone). As the Irving-Williams series established the thermodynamic stability in MOF metal nodes following the order Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+} , we chose 2 to perform the attempt described above. Unfortunately, all efforts led to the same structure with an unaltered Cd-Cu bimetallic paddle-wheel cluster, as revealed by single-crystal XRD. Although numerous factors such as reaction kinetics, ionic radii, solution concentrations, and solvent effects may limit full metal node exchange, none of these seems to be responsible for the partial exchange in ps-CMOFs. We consider that the framework flexibility determines the exchange process and prevents it from fully exchanging. As mentioned previously,⁸ porphyrin and salen linkers having bulky molecular sizes are quite able to form large pore openings in the corresponding ps-CMOFs. The irregular $Cd_2(COO)_4$ paddle-wheel cluster endows 1 with a triclinic crystal system,

which not only favors a series of supramolecular interactions between pillar metallosalen linkers and lamellar metalloporphyrin planes but also maximally diminishes the pore openings and thus enhances the stability of the frameworks. Conversely, in an attempt to completely transfer the irregular $Cd_2(COO)_4$ to a regular $M_2(COO)_4$ (M = Cu, Zn, Ni, or Co) paddle-wheel cluster, the triclinic crystal system of the framework has to change into a monoclinic or orthorhombic crystal system, which is thermodynamically unfavored or, if possible, requires large amounts of energy. In other words, the lattice of ps-CMOF limits the geometrical distortion available for a full metal node exchange. In addition, there is another possible reason that the two Cd centers in the 1D channel have different accessibilities for the incoming solvated metal ions. To date, much effort has been devoted to synthesize bimetallic paddlewheel cluster-based MOFs for their unique properties relative to their homometallic counterparts.^{11d,16} However, most of them lack direct evidence for the detailed structures in the paddle-wheel clusters. To the best of our knowledge, this is the first example of bimetallic paddle-wheel clusters (Cd-Cu, Cd-Zn, Cd-Ni, and Cd-Co) concisely characterized by singlecrystal XRD.

Cation Exchange at Cd–Porphyrin. As mentioned above, in one framework of 1, the porphyrin core is occupied by an outof-plane Cd²⁺ ion, indicating a weak bonding of the Cd²⁺ ion within porphyrin, and the exchange of the Cd²⁺ ion with divalent metal ions possessing smaller radii is thus preferred. Indeed, structural analysis showed that all Cd²⁺ ions within porphyrin cores are replaced by the incoming cations in 2-5and are all well located in the porphyrin core with a ΔC_{β} of ~0. It should be noted that Cu^{2+} , Ni^{2+} , and Co^{2+} are coordinated in a nearly square-planar geometry with four nitrogen atoms from porphyrin, while the Zn^{2+} ion is further linked by a water molecule at the axial position, adopting a square-pyramidal geometry (Table 1). The $M{-}N_{porphyrin}$ distances range from 1.988 to 2.040 Å for Cu^{2+} , from 2.010 to 2.074 Å for Zn^{2+} , from 1.999 to 2.026 Å for Ni²⁺, and from 1.969 to 2.048 Å for Co²⁺, all of which are obviously shorter than the average Cd- $N_{porphyrin}$ bond distance (2.260 Å) and within the range of reported Cu (Zn, Ni, or Co)-porphyrin-based MOFs.^{5c,1}

Addition at the Free Porphyrin. With respect to the addition of extraneous metal ions to the free porphyrin, the results differ for Cu^{2+} , Zn^{2+} , Ni^{2+} , and Co^{2+} ions. As shown in Table 1, Cu^{2+} and Zn^{2+} ions in 2 and 3 are successfully trapped in the free porphyrin with Cu-N bond lengths ranging from 1.982 to 2.010 Å and Zn-N bond lengths ranging from 2.059 to 2.106 Å. Similarly, the Cu²⁺ ion is coordinated in porphyrin with a square-planar geometry, and the Zn^{2+} ion is also axially coordinated by a water molecule. In 4 and 5, the porphyrin remains uncoordinated during the soaking process. These structural differences between 2 (or 3) and 4 (or 5) offer two insights for illustrating the exchange course. (i) The reaction kinetic rates of Cu2+ and Zn2+ ions in the complexation of porphyrin are faster than those of Ni²⁺ and Co²⁺ ions, and (ii) the metal ion exchange in porphyrin proceeds faster than the complexation of metal ions into free porphyrin. The first result is ascribed to the affinity of Cu^{2+} and Zn^{2+} ions for nitrogenous linkers being higher than that of Ni²⁺ and Co²⁺ ions. Second, we suggested that the labile Cd²⁺ ion in porphyrin provides the driving force for cation exchange, while in the course of complexation, the necessity of dissociating two N-H bonds makes the reaction proceed slower than exchange. This finding provides good structural evidence for the study of the



Figure 2. (a and b) PXRD patterns of ps-CMOF analogues. (c and d) N_2 adsorption/desorption isotherms at 77 K and pore size distributions (insets) of 1–4 and 5–7, respectively.

coordination kinetics substitution reaction demonstrated by Berezin.¹⁸ Next, when the reaction time is extended to 30 days, complexation of Ni²⁺ and Co²⁺ ions to the free porphyrin was observed in **6** and **7**, respectively. Although the structural determination of **6** and **7** by single-crystal XRD was unsuccessful because of the relatively poor quality of the single crystals, the PXRD patterns evidence the stability of the framework (Figure 2a). In addition, AAS results revealed Cd:Ni and Cd:Co ratios of 1:2.96 and 1:1.98 for **6** and **7**, respectively, which are in accordance with the stoichoimetric ratios of 1:3 and 1:2 predicted for **6** and **7**, respectively.

The different selectivity of the porphyrin cores for the incoming metal ion of the two network structures might be attributed to the framework interpenetration, in which the network of Cd–porphyrin imparts certain steric hindrance to the other network of free porphyrin, blocking the entry of the second Cd²⁺ ion into the free porphyrin core, as shown in **1**. For **2**, **3**, **6**, and 7, owing to the smaller ion radii of Cu²⁺, Zn²⁺, Ni²⁺, and Co²⁺ compared to that of Cd²⁺, the free porphyrin could coordinate the incoming metal ions during PSMet processes. Note that the Ni²⁺ ions in salen linkers were not exchanged during PSMet processes, probably because the four-coordinated planar geometry of the Ni²⁺ ion in the salen scaffold is extremely thermodynamically stable and thus inert for further modification.

PXRD, CD, TG, and Gas Adsorption. The ps-CMOF analogues after PSMet processes retain the crystalline nature of the parent framework, as also evidenced by comparing their simulated PXRD patterns from crystal data. To confirm that no new phase is formed during the PSMet process, the bulky samples of 2–7 were filtered and then characterized by PXRD

measurement. As revealed in Figure 2a, all ps-CMOF analogues showed almost the same PXRD pattern, unambiguously suggesting their phase purity. The solid-state CD spectra (Figure S1) of 2-7 made from R and S enantiomers of the salen linker showed curves similar to those of 1, which are all mirror image of each other, confirming the chiral nature of the bulk materials. Then TGA were performed to evaluate the thermal stability of 2-7 (Figure S2). The TG curves showed first weight losses of approximately 17.6, 19.4, 20.4, 22.4, 18.2, and 20.6% for 2-7, respectively, corresponding to the loss of disordered guest molecules from the channels. The sharp weight losses after 390, 377, 388, 387, 383, and 381 °C for 2-7, respectively, indicate the collapse of the framework. All TG curves showed trends similar to that of the parent framework, further suggesting the maintenance of the thermal stability of the framework after PSMet processes. The N₂ adsorption measurements at 77 K were then performed to confirm the permanent porosity of 2-7. The samples were outgassed at 150 °C under vacuum for 12 h before tests. As shown in panels c and d of Figure 2, the N2 adsorption isotherms of 2-7 are similar to that of the parent framework and present type I behavior, an indication of microporous materials. It is noteworthy that the rates of uptake of N_2 by these ps-CMOF analogues are slightly higher than that of the parent framework. We proposed this might result from the removal of some unknown species that were trapped inside the parent framework during the soaking of metal salt solutions, thus causing a slight increase in the surface area of 2-7. However, the pore size distributions of 2-7 calculated on the basis of the N2 sorption isotherms at 77 K reveal almost the same peaks at \sim 11 Å, which are quite consistent with the observations of their



Figure 3. (a) CO_2 adsorption isotherms of 2 at 273 and 298 K. (b) CO_2 adsorption isotherms of 3 at 273 and 298 K. (c) CO_2 adsorption isotherms of 4 and 6 at 273 and 298 K. (d) CO_2 adsorption isotherms of 5 and 7 at 273 and 298 K.

crystal structures. As unsaturated coordinative metal sites have been proven to be highly responsible for the interaction with CO_2 , the CO_2 adsorption isotherms of 2–7 at 273 and 298 K were recorded to evaluate the properties of different metal ions with respect to the CO_2 uptake performance. It can be seen from Figure 3 that the rates of uptake of CO_2 by 2–7 obviously outperformed that of the parent framework, which implied an affinity of Cu^{2+} , Zn^{2+} , Ni^{2+} , and Co^{2+} ions for CO_2 that is higher than that of the Cd^{2+} ion. To gain more insights into the CO_2 adsorption capacity, we calculated the Q_{st} values for 2–7 from the CO_2 isotherms by using the Clausius–Clapeyron equation. The Q_{st} values at low coverages are calculated to be 25.7, 20.4, 38.9, 48.1, 37.1, and 41.5 kJ/mol for 2–7, respectively, all of which overwhelmed that of the parent framework (16.7 kJ/ mol) (Table 2). More specifically, 2, 3, 6, and 7 with the fully

Table 2. CO₂ Adsorption Properties of ps-CMOF Analogues

	1	2	3	4	5	6	7
CO ₂ uptake (cm ³ /g) at 273 K	32.1	51.8	44.3	54.4	63.9	63.21	92.4
CO ₂ uptake (cm ³ /g) at 298 K	21.8	36.7	24.8	25.0	23.5	47.8	30.5
initial Q _{st} of CO ₂ (kJ/mol)	16.7	25.7	20.4	38.9	48.1	37.1	41.5

metalated porphyrin cores showed distinctly varied Q_{st} values that decreased in the following order: $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+} >$ Zn^{2+} . These results illustrate the stronger interaction between the Co^{2+} ion and CO_2 in ps-CMOF analogues, which has been previously observed in other MOFs.¹⁹ Furthermore, both 4 and 5, whose porphyrin cores are partially metalated, showed approximate Q_{st} values compared to those of their fully metalated counterparts **6** and 7, indicating the free porphyrin might also contribute to the interaction with CO₂, because the introduction of amine groups into the framework has been identified as an effective method for improving CO₂ adsorption behavior.²⁰

Catalytic Performance. On the basis of the results presented above, the PSMet of 1 successfully provides a family of ps-CMOF analogues with different catalytic sites and inherent chiral groups, which might serve as a superior catalytic platform for varieties of asymmetric catalyses. With our continuing interest in CO₂ fixation,^{5e} herein 5 was selected as a representative catalyst to evaluate the asymmetric catalytic performance for the synthesis of cyclic carbonates using CO₂ and epoxides, owing to its high CO_2 adsorption capacity. This reaction not only provides a 100% atom-economical route to cyclic carbonates widely used as electrolytes for lithium ion batteries, monomers, and fine chemical intermediates but also develops an environmentally favored process with CO₂ as a nontoxic, nonflammable, and sustainable C1 feedstock. $^{\overline{2}1}$ To date, most reported homogeneous or heterogeneous catalysts were constrained to the synthesis of racemic cyclic carbonates, and little attention has been focused on the formation of the value-added optical active cyclic carbonates.²² For MOF catalysts, to the best of our knowledge, only two chiral MOFs have been utilized in the asymmetric cycloaddition of CO₂ with epoxides.²³ Among them, we constructed a Ni(saldpen)-based porous chiral MOF as the first example of a MOF catalyst used for this transformation,^{23b} and the results demonstrated that the potential high CO₂ adsorption capacity and stability of this MOF make it a highly active and recyclable catalyst for CO_2 fixation. On the other hand, the Co(II)-based MOFs have been utilized in the formation of cyclic carbonates

from CO_2 and epoxides for their high efficiency and selectivity. 24

First, **5** was activated at 150 °C under vacuum for 12 h to remove guest solvents in the channels, providing accessible Lewis acidic sites. The activated sample was measured by XPS to confirm whether the oxidation state of cobalt ion changed during the activating process. As shown in Figure S4, the peaks of Co $2p_{3/2}$ at 781.4 eV and Co $2p_{1/2}$ at 796.9 eV, together with two satellite peaks at 784.1 and 798.9 eV, indicate the oxidation state of the cobalt ion remains +2.²⁵ The coupling of CO₂ and styrene oxide was used as the model reaction to investigate the effect of various parameters on activity and enantioselectivity. Initially, the reaction proceeded with 0.1 mol % catalyst and 1 mol % TBAB under ambient conditions for 6 h to give a conversion of 11% and an enantioselectivity of 13% (entry 3, Table 3). It was found that both **5** and TBAB were

Table 3. Optimization of Reaction Parameters for the Cycloaddition of CO_2 with Styrene Oxide^a

entry	catalyst (loading)	additive	temp (°C)	$^{T}_{(h)}$	$(\%)^b$	ee (%) ^c
1	-	TBAB	25	6	2	-
2	5 (0.1 mol %)	-	25	6	_	_
3	5 (0.1 mol %)	TBAB	25	6	11	13
4	5 (0.5 mol %)	TBAB	25	6	23	15
5	5 (0.5 mol %)	TBAB ^d	25	6	26	9
6	5 (0.5 mol %)	TBAB	0	24	22	30
7	5 (0.5 mol %)	TBAB	-20	24	_	_
8	7 (0.5 mol %)	TBAB	0	24	21	27
^a React	tion conditions:	epoxide ((10 mmol).	TBA	B (1 mol %).	$CO_{2}(1)$

atm). ^bDetermined by GC–MS. ^cDetermined by chiral GC or HPLC. ^dTBAB (2.5 mol %).

indispensable to this reaction (entries 1 and 2, Table 3), which is quite consistent with other reported binary catalytic systems.²¹ When the catalyst loading was increased from 0.1 to 0.5 mol %, an increased conversion (23%) and a slightly increased enantioselectivity (15%) were obtained (entry 4, Table 3), but further increasing the catalyst loading to 1 mol % gave no observably improved catalytic behaviors. On the other hand, the augmentation of TBAB to 2.5 mol % resulted in a decreased enantioselectivity (9%), which might be due to the background reaction proceeding via the racemic pathway (entry 5, Table 3). In general, a low temperature favors higher chirality; therefore, we decreased the temperature to 0 °C, and an improved enantioselectivity (30%) was indeed achieved. However, prolonging the reaction time from 6 to 24 h is necessary to compensate for the decreased reaction rates (entry 6, Table 3). Further decreasing the temperature to -20 °C makes the reaction almost inert, which makes the determination of enantioselectivity impossible (entry 7, Table 3). Thus, the optimized reaction conditions involve 10 mmol of epoxide, 0.5 mol % catalyst, and 1 mol % TBAB under 1 atm of CO₂ at 0 °C for 24 h, with a conversion of 22% and an enantioselectivity of 30% (entry 6, Table 3). In comparison, 7, which exhibits a $Q_{\rm st}$ lower than that of 5, showed slightly decreased values of conversion (21%) and ee (27%) under identical conditions (entry 8, Table 3).

Upon examination of ps-CMOF **1** for asymmetric cyanosilylation of aldehydes,⁸ the porphyrin active sites proved to be responsible for the Lewis activation and the salen moieties that account for the induction of chirality. Thus, the control

experiment was conducted by combining the mixture of homogeneous porphyrin-Co(II) and salen-Ni linkers under identical reaction conditions. The catalytic results showed decreased conversion (14%) and negligible ee values (<3%) compared to those of 5. Therefore, the good catalytic performance of 5 originates from the framework confinement effect together with its well-positioned chiral induction environment. In the homogeneous system, the decreased chance of the two linkers meeting and their random spatial orientation resulted in poor enantioselectivity. The AAS of the supernatant after catalytic reaction was tested, and the result revealed negligible leaching of the metal ions (\sim 2.11 ppm for Co^{2+} and ~2.02 ppm for Ni²⁺) from the framework, which confirmed the heterogeneous nature of this catalytic reaction. After the end of the reaction, the catalyst can be recovered by filtration, washing with DMF, and drying at 150 °C under vacuum for 6 h. Recyclability tests showed 5 could be reused for five consecutive runs without any apparent loss of activity or enantioselectivity (Figure 4). The PXRD pattern of the



Figure 4. Recyclability tests of 5.

recovered catalyst after five catalytic runs remained almost unchanged (Figure 2b), demonstrating the stability of the framework during the catalytic reactions.

The cycloaddition reactions of CO₂ with other epoxides were then conducted to investigate the general applicability of 5. Note that propylene oxide and butylene oxide were found to be sluggish with respect to enantioslectivity (0 and 1% ee, respectively) (entries 1 and 2, respectively, Table 4), while hexylene oxide gave a significantly enhanced ee (53%) for the corresponding cyclic carbonate (entry 3, Table 4). The asymmetric catalytic performances of 5 for hexylene oxide and styrene oxide ($k_{\rm rel}$ values of 4.8 and 2, respectively) can compare to those of a bifunctional polymeric Co(III)-salen complex.^{22d} We attributed this substrate size-dependent enantioselectivity to the constrained chiral pocket within the framework. As revealed by the crystal structure of 5, the shortest distances between the Co²⁺ ion in porphyrin and the chiral diphenyl groups were calculated to be 5.141 Å (Figure S3); therefore, propylene oxide and butylene oxide, which possessed smaller or similar geometry dimensions of 4.35 Å \times $\overline{3.41}$ Å and $\overline{5.64}$ Å \times 3.39 Å, respectively, have greater difficulty effectively interacting with the chiral groups, leading to poor enantioselectivity. In contrast, bulky substrates such as styrene oxide (7.26 Å \times 4.28 Å) and hexylene oxide (8.19 Å \times 3.39 Å) might well position within the chiral pocket with an appropriate

Table 4. Asymmetric Synthesis of Various Cyclic Carbonates Catalyzed by 5^a



^{*a*}Reaction conditions: epoxide (10 mmol), **5** (0.5 mol %), TBAB (1 mol %), 0 °C, 24 h, CO₂ (1 atm). ^{*b*}Determined by GC–MS. ^{*c*}Determined by chiral GC or HPLC. ^{*d*}The k_{rel} is calculated as $\{\ln[1 - c(1 + ee)]\}/\{\ln[1 - c(1 - ee)]\}$, where *c* is conversion and ee is enantiomeric excess.

distance and an ideal spatial orientation, thus resulting in enhanced stereocontrol. Then, we selected the more bulky substrate phenyl glycidyl ether (9.91 Å \times 4.31 Å) to further investigate the influence of substrate size on enantioselectivity. However, phenyl glycidyl ether gave a much lower ee (entry 5, Table 4). It was likely that the steric repulsion effect largely inhibited effective chiral induction, consequently leading to insufficient transfer of chirality. To date, the substrate sizedependent enantioselectivity in the asymmetric carbonatation reactions has been witnessed in other catalytic systems,²⁶ but there is no evidence illustrating the intrinsic reason for this phenomenon. Here in the ps-CMOF catalytic platform, the crystal structures provide detailed structural evidence that improves our understanding of the interaction between the substrate and chirally induced groups. However, further evidence, including the steric repulsion effect, the chiral induction mode, and the detailed interaction pathway, is still needed to clarify this phenomenon.

CONCLUSIONS

In summary, we have successfully developed a family of isostructural ps-CMOF analogues through PSMet via SC-SC transformation, and four sets of heterometallic (Cd-Cu, Cd-Zn, Cd-Ni, and Cd-Co) paddle-wheel clusters were concisely characterized by single-crystal XRD for the first time. The results indicate that the increased surface areas, reserved porosity, rich adsorptive sites, and enhanced synergistic effects within multimetallic ps-CMOFs resulting from the incorporation of new paddle-wheel nodes, cation exchange, or addition at the porphyrin cores have strong influence on their intrinsic properties. For example, these daughter structures show CO₂ adsorption performances that are better than that of their parent network. As one representative of the ps-CMOF catalytic platform, 5 proved to be an effective recyclable heterogeneous catalyst for the substrate size-dependent enantioselective synthesis of cyclic carbonates from CO₂ and epoxides under mild conditions. Our research results not only pave a new way for building isomer MOF structures based on a bimetallic paddle-wheel cluster but also elucidate the possibility of porous ps-CMOFs with multifunctional sites to be applied in more enriched asymmetric catalyses. Relevant work involving incorporation of trivalent metal ions into porphyrin cores of the ps-CMOF skeleton is ongoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02631.

Selective average bond lengths, CD spectra, TG curves of ps-CMOFs, the chiral environment and XPS of 5, and HPLC or GC analysis of the synthesized cyclic carbonates (PDF)

Accession Codes

CCDC 1579011–1579014 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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