Exposed Equatorial Positions of Metal Centers via Sequential Ligand Elimination and Installation in MOFs

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ABSTRACT: Metal−organic frameworks (MOFs) provide highly designable platforms to construct complex coordination architectures for targeted applications. Herein, we demonstrate that trans-coordinated metal centers with exposed equatorial positions can be placed in a MOF matrix. A Zr-based MOF, namely, PCN-160, was initially synthesized as a scaffold structure. Postsynthetic linker labilization was subsequently implemented to partially remove the original dicarboxylate linkers and incorporate pyridinecarboxylates. A pair of neighboring pyridyl groups was arranged at proper proximity within the framework to form trans-binding sites that accommodate different metal cations including Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, and Pd²⁺. Furthermore, the trans-coordinated Ni²⁺ sites in porous frameworks can be readily accessed by substrates along the equatorial plane, facilitating the catalysis as manifested by the superior activity in ethylene dimerization over that observed for a cis-chelated catalyst.

INTRODUCTION

Metal−organic frameworks (MOFs) are an emerging class of crystalline porous materials constructed from metal-containing nodes and organic linkers.¹ The structures and structure-related properties of MOFs can be precisely controlled at atomic precision by judicious design of both constituents.² Most recently, our group proposed the concept of postsynthetic strategies.⁶b Along this line, we seek to use molecular elaborations to preformed Zr-MOFs using a series of postsynthetic linker labilization (PSM) methods were developed.⁸ Functional groups and metal complexes have been postsynthetically anchored on the organic linkers through covalent or coordinative bonds, giving rise to topologically identical MOFs with diverse functionalities.⁹ Furthermore, metal cations and organic linkers can be exchanged by virtue of the framework dynamics. This allows the formation of metastable MOFs that cannot be synthesized in a “one-pot” reaction.¹⁰ Recent developments of stable MOFs bring new opportunities to perform a wider range of PSM reactions while maintaining the framework’s structural integrity.¹¹ For example, as stable and versatile platforms, Zr-MOFs allow the incorporation of terminal linkers,¹² dicarboxylate linkers,¹³ metal cations,¹⁴ and metal−organic complexes onto the coordinatively unsaturated Zr₆ clusters. Most recently, our group proposed the concept of “MOF retrosynthesis” to construct complex MOFs by “layer-on” molecular elaborations to preformed Zr-MOFs using a series of postsynthetic strategies.⁶b Along this line, we seek to use MOFs as the matrix to assemble coordination structures that...
are difficult to synthesize in other systems, such as the trans-coordinated metal complexes.

Trans-chelating or trans-spanning ligands are bidentate ligands that bind the opposite sites of a complex with square-planar geometry at or near a 180° angle.15 Although a far larger number and variety of cis-chelating ligands than trans-chelating ones have been developed for catalysis and their chemistry is more thoroughly explored, catalysts containing trans-chelating ligands may display alternative chemistry, activity, and selectivity in various catalytic processes. However, many attempts to generate trans-chelating complexes have led to the formation of coordination polymers in which bidentate ligands act as bridging linkers. Although this problem can be addressed by tuning the ligand rigidity and bulkiness,16 ligand synthesis remains a challenge. Herein, we show that trans-coordinated metal centers with exposed equatorial positions can be created in three dimensions using MOFs as the matrix.

■ RESULTS AND DISCUSSION

Creating trans-Coordination Sites in MOFs. In the literature, trans-chelating bis-pyridyl ligands are usually constructed by connecting two 2-pyridyl groups by judiciously designed spacers such as 1,2-dialkynylbenzene (Figure S1a).16a−c We hypothesized that MOFs can act as three-dimensional spacers for the alignment of two pyridyl moieties in the trans-position (Figure S1b). For this purpose, we used a previously reported Zr-based MOF, Zr6-AZDC or PCN-160, as the matrix.17 It is noteworthy that Zr-AZDC based MOFs were first reported in 2012 and reproduced using different synthetic methods in many other studies.17 By replacing the azobenzene-4,4′-dicarboxylate linker (AZDC) with a pair of 4-pyridinecarboxylates (also known as isonicotinate, or INA), a bis-pyridyl site at the trans-position will be formed (Figure 1a,b). Direct exchange of AZDC by INA or M-INA2 was unsuccessful because of the inertness of the AZDC linker. Our previous works have shown that AZDC can be labilized by the exchange of an imine-based linker with identical length, denoted as CBAB (4-carboxybenzylidene-4-aminobenzoate, Figure 1c,d).18 The CBAB can be dissociated into 4-aminobenzoic acid and 4-formylbenzoic acid through hydrolysis by acetic acid/N,N-dimethylformamide (DMF) solution to create missing-linker defects (Figure 1e). Since isonicotinic acid (pK_a = 4.96) exhibits similar acidity to acetic acid (pK_a = 4.76), we hypothesized that it would replace the CBAB linker and form trans-binding sites (Figure 1f). In fact, metalloligands with similar trans-coordinated geometries have been adopted in MOF synthesis.19 Therefore, we expect that the proposed structure is feasible.

Monitoring Sequential Ligand Elimination and Installation. As anticipated, Ni-INA2 moieties were successfully incorporated into PCN-160 by CBAB exchange and subsequent treatment with a solution of INA and NiCl2. The final product was verified by single-crystal X-ray crystallography (Figure 1f, Table S1), powder X-ray diffraction (PXRD), inductively coupled plasma mass spectrometry (ICP-MS), and 1H NMR digestion experiments (Table S3). The effect of CBAB linker and reaction time on the level of incorporation of M-INA2 to the PCN-160 structure was systematically studied. For this purpose, first, a series of PCN-160 samples with variable CBAB linker content were synthesized through a linker exchange procedure reported in the literature (Figures S2–S4). These samples are denoted as PCN-160-R%, where R % stands for the percentage of the CBAB linker to the total amount of linkers in the sample (Table S2). Crystals of PCN-160-R% were subsequently incubated in DMF solution with an excess amount of INA and NiCl2 at 75 °C. Incorporation of the INA linker to the PCN-160 structure was monitored by ultraviolet–visible (UV–vis) spectroscopy, as both AZDC and INA linkers possess distinctive UV–vis absorption peaks at 432 and 264 nm, respectively. The Ni-INA2 exchange ratio in PCN-160, defined as the amount of Ni-INA2 divided by the total amount of all the linkers (CBAB + AZDC + Ni-INA2), was calculated based on the UV–vis data of the digested MOFs. As shown in Figure 2a, the Ni-INA2 content in the samples increased with time and leveled off after 4 h, indicating that a dynamic equilibrium was reached between the MOF scaffold and the solution. The CBAB ligands are important for the incorporation of Ni-INA2 as manifested by the low exchange ratio and slow reaction kinetics of PCN-160. After the treatment by INA and NiCl2, the CBAB linker was completely replaced by Ni-INA2 according to UV–vis and 1H NMR data. The maximum Ni-INA2 exchange ratios were roughly equal to the CBAB content in the initial sample (Table S3). The size and morphology of the MOF particles were maintained throughout the postsynthetic modification, suggesting a single crystal to single crystal transformation process. It is important to note that the direct synthesis of MOFs using CBAB (PCN-160-R%) or Ni-INA2 (PCN-160-R%Ni) as starting materials was not successful due to the labile imine bonds or Ni-pyridyl bonds that tend to be destroyed by the harsh solvothermal synthesis necessary for Zr-MOF synthesis (Figure S5).

As revealed by the PXRD patterns (Figure 2b), PCN-160-R%Ni samples maintained crystallinity. They showed similar PXRD patterns to that of the parent PCN-160 with slight changes of the peak intensities and some shifting of the peak...
positions. The peak intensity at 6.0 degrees decreased while the peaks at 10.4 degrees increased with the incorporation of Ni-INA2, which matched well with simulations. The peaks of PCN-160-R%Ni were slightly shifted to a lower angle as compared to that of the parent PCN-160 (Figure S6), corresponding to a unit cell expansion, which resulted from the replacement of the shorter AZDC linkers (13.1 Å) with longer Ni-INA2 linkers (13.7 Å). After the incorporation of the Ni-INA2 linkers, the PCN-160-R%Ni were still porous, although the total N2 uptake and BET surface area decreased (Figure 2c). This is attributed to the increased material density and decreased pore size after the Ni-INA2 ligand incorporation. In addition, the partial decomposition of the framework after solvent removal also accounts for the decreased surface area.

Indeed, PCN-160-R%Ni samples showed decreased mechanical stability due to the relatively weak Ni-pyridyl bonds.

**Versatility of M-INA2.** The method for incorporating Ni-INA2 linkers to the PCN-160 structure can also be used to incorporate a series of M2+ transition metals including Mn2+, Fe2+, Co2+, Ni2+, Cu2+, and Pd2+ into the structure of a MOF. The successful incorporation of different metals into the framework can be directly observed by microscope images of the respective single crystals (Figure 3). The compositions of PCN-160-65%M (M = Mn, Fe, Co, Ni, Cu, and Pd) were further determined by ICP-MS and 1H NMR. Although the amount of incorporated M-INA2 varied for different samples, the metal to INA ligand ratio was approximately 1:2 (Table S4). The PXRD patterns and N2 sorption isotherms further verified the maintained crystallinity and porosity (Figures S7 and S8). Although different metal sizes can affect the length of M-INA2 linkers, the framework of PCN-160 possesses a certain flexibility that can tolerate the change caused by different metals. X-ray photoelectron spectroscopy (XPS) showed that all the metals incorporated into MOFs are in +2 oxidation states (Figures S9−S13).

**Coordination Environment of Metal Sites.** Single-crystal structures of PCN-160-47%Ni and PCN-160-47%Pd were successfully obtained, providing direct structural evidence of the M-INA2 moieties in a trans-geometry (Table S1). The existence of Ni and Pd was clearly refined with an occupancy of 50%, consistent with the ICP-MS results. However, the terminal ligands cannot be precisely refined because of the disorder within the structure. To gain a better understanding of the structure of the M-INA2 moieties, single crystals of molecular M-INA2 complexes were isolated by slow cooling of saturated solutions containing the corresponding MCl2 salts and INA ligands. Both Ni-INA2 and Cu-INA2 show a six-
coordinate octahedral metal center surrounded by two INA ligands, two Cl⁻ ions, and two DMSO molecules in a trans orientation (Figure S14). By adding 30% water to precipitate the Ni-INA₂ and Cu-INA₂ crystals, the Cl⁻ and DMSO ligands could be replaced by OH⁻ and H₂O, respectively. The identity of the coordinated solvent on the metal center was further confirmed by thermogravimetric analysis/mass spectrometry (TGA-MS) plots, which revealed the loss of coordinated solvent molecules before 250 °C (Figure S15). The coordination environment of Ni in PCN-160-47%Ni was further studied by extended X-ray absorption fine structure (EXAFS) at the Ni K-edge. EXAFS fitting confirms the presence of four direct O/N ligands and two Cl in the PCN-160-47%Ni MOF sample (Table S5 and Figure S16a). The EXAFS technique does not have the sensitivity to separate N from O; hence both ligands are treated with the same single scattering path. For comparison, a complementary fitting was performed on PCN-160-47%Ni assuming only six O/N ligands without Cl coordination; however, the unsuitability of that model was clear (Figure S16b and Table S6). Furthermore, the pre-edge of the X-ray absorption near edge structure (XANES) spectra also indicates an octahedral local geometry (see comparison of the reference standards NiO and NiCl₂·6H₂O with PCN-160-47%Ni in Figure S18). The single-crystal structures, TGA-MS, XANES, and EXAFS manifest that the Ni center is six coordinated to INA ligands, two Cl⁻ ions, and two solvent molecules in octahedral geometry. In contrast to the first-row transition metals, Pd was determined to be four coordinated with two INA ligands and two Cl⁻ ions, leading to a square-planar geometry. Strictly speaking, only PCN-160-R%Ni Pd can be named as a trans-chelating complex, because the trans-chelating ligands are defined as bidentate ligands that span the trans-positions of square-planar complexes.

Very recently, the Rosi group also reported Zr-MOFs built from a Cu-(2-methyl-INA)₂ complex as a supramolecular linear dicarboxylate linker.⁵⁶ This work is in line with our hypothesis that M-INA₂ can act as a linker fragment to support the MOF structure. Compared with our stepwise synthetic method, the one-pot strategy by the Rosi group allows facile preparation of heterometallic MOFs with various structures. However, these structures are supported by M-INA₂ ligands exclusively, resulting in relatively labile frameworks. PCN-160-R%M contains both stable AZDC linkers to form a robust matrix and M-INA₂ ligands as catalytic sites, which is more suitable for catalysis. Since the stability and porosity of PCN-160-R%M decrease as R% escalates, the exchange ratio was controlled up to 47% for catalytic applications.

**Ethylene Dimerization Reaction.** With a series of trans-coordinated metal complexes with exposed equatorial positions incorporated into MOFs, we further explored their catalytic properties. The Ni-catalyzed ethylene dimerization reaction was selected as a model reaction in this study. The ethylene dimerization reactions were carried out in a 25 mL stainless steel reactor under 40 bar of ethylene in toluene at 25 °C with diethylaluminum chloride (Et₂AlCl) as the activator (Table 1, Table S7, and Figure S19). Both PCN-160 and the activator Et₂AlCl showed no catalytic activity for ethylene dimerization as controls, thus ruling out the possibility of any background reaction in the absence of Ni²⁺ (entries 1 and 2). To eliminate the influence of Ni²⁺ trapped in the MOF cavity, PCN-160 was incubated in NiCl₂ solution without INA ligands (NiCl₂@PCN-160). It showed very low catalytic activity (entry 3). The molecular Ni-INA₂ and (bpy)NiCl₂ (bpy = 2,2′-bipyridy-) complexes displayed poor catalytic activity, due to the low solubility and limited surface area, which prevent the exposure of active sites (entries 4 and 5). For comparison, the catalytic performance of Uio-67-50%Ni with cis-chelating Ni₂⁺-bipyridyl centers was also tested.⁵⁷ Notably, we found that PCN-160-47%Ni has an intrinsic activity of 3360 h⁻¹ for ethylene dimerization reaction, which is ~7 times higher than that of Uio-67-50%Ni. The PCN-160-47%Ni and Uio-67-50%Ni showed butene selectivity comparable to other previously reported catalysts (entries 6 and 7).²¹ Since PCN-160-47%Ni and Uio-67-50%Ni have similar Ni content, pore size, and BET surface area (Figure S20), the superior catalytic activity of PCN-160-47%Ni was attributed to its unique trans-coordination environment of the Ni. The trans-coordinated Ni sites in PCN-160-47%Ni are more sterically accessible than those of the Ni₂⁺-bipyridyl sites in Uio-67-50%Ni. As such, substrates can more readily reach the trans-coordinated Ni center from any direction within the equatorial plane, facilitating the ethylene binding and accelerating the reaction. Moreover, PCN-160-47%Ni can be recycled for at least three runs by separation from the reaction mixture through centrifugation at the end of each reaction without significant loss of Ni content and crystallinity (Figure S21). Elemental mapping at the microstructural level by scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX) shows uniform distribution of Ni throughout the crystal (Figure S22). The catalytic activity evaluated by the amount of generated C₄ only reduced by 14% after three cycles (Table S7).

<table>
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aReactions were performed in toluene under 40 bar of ethylene at 25 °C. Et₂AlCl (Al/Ni = 300) was used as activator, and reaction time was 1 h. bCatalysts containing 5 μmol of Ni were used unless otherwise noted. cCalculated based on the moles of butenes generated and the Ni content in the catalyst. Standard deviations were calculated based on three runs. dMOF catalysts (5 mg) were used. The Ni loading in NiCl₂@PCN-160 is 0.4 wt %, as determined by ICP-MS. eEt₂AlCl (1.5 mmol) was added. fThe first cycle of PCN-160-47%Ni catalyst.

### CONCLUSIONS

In conclusion, trans-coordinated metal centers were created in MOFs by sequential ligand elimination and installation of M-INA₂ moieties. This method enables the convenient incorporation of different M²⁺ transition metals of various ratios into trans-binding sites within a porous framework. Furthermore, we have shown that the trans-coordinated metal complexes displayed poor catalytic activity, due to the low solubility and limited surface area, which prevent the exposure of active sites (entries 4 and 5). For comparison, the catalytic performance of Uio-67-50%Ni with cis-chelating Ni₂⁺-bipyridyl centers was also tested. Notably, we found that PCN-160-47%Ni has an intrinsic activity of 3360 h⁻¹ for ethylene dimerization reaction, which is ~7 times higher than that of Uio-67-50%Ni. The PCN-160-47%Ni and Uio-67-50%Ni showed butene selectivity comparable to other previously reported catalysts (entries 6 and 7). Since PCN-160-47%Ni and Uio-67-50%Ni have similar Ni content, pore size, and BET surface area (Figure S20), the superior catalytic activity of PCN-160-47%Ni was attributed to its unique trans-coordination environment of the Ni. The trans-coordinated Ni sites in PCN-160-47%Ni are more sterically accessible than those of the Ni₂⁺-bipyridyl sites in Uio-67-50%Ni. As such, substrates can more readily reach the trans-coordinated Ni center from any direction within the equatorial plane, facilitating the ethylene binding and accelerating the reaction. Moreover, PCN-160-47%Ni can be recycled for at least three runs by separation from the reaction mixture through centrifugation at the end of each reaction without significant loss of Ni content and crystallinity (Figure S21). Elemental mapping at the microstructural level by scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX) shows uniform distribution of Ni throughout the crystal (Figure S22). The catalytic activity evaluated by the amount of generated C₄ only reduced by 14% after three cycles (Table S7).
sites in MOFs have intriguing properties in catalytic processes due to the exposed equatorial positions, as demonstrated by the remarkably improved activity of PCN-160-47%Ni in catalytic ethylene dimerization. Considering the versatility of this method and the unlimited tunability of MOFs, many more trans-coordinated metal complexes are envisioned. Apart from providing a method to construct trans-coordinated complexes, this work also highlights the vast opportunities of using a MOF matrix to assemble coordination architectures that are otherwise difficult or impossible to realize.

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**Author Contributions**

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**Notes**

The authors declare no competing financial interest.

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