Metal–Organic Frameworks

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An In Situ One-Pot Synthetic Approach towards Multivariate Zirconium MOFs

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Abstract: *Chemically highly stable MOFs incorporating multiple functionalities are of great interest for applications under harsh environments. Herein, we presented a facile one-pot synthetic strategy to incorporate multiple functionalities into stable Zr-MOFs from mixed ligands of different geometry and connectivity. Via our strategy, tetratopic tetrakis(4-carboxyphenyl)porphyrin (TCPP) ligands were successfully integrated into UiO-66 while maintaining the crystal structure, morphology, and ultrahigh chemical stability of UiO-66. The amount of incorporated TCPP is controllable. Through various combinations of BDC derivatives and TCPP, 49 MOFs with multiple functionalities were obtained. Among them, MOFs modified with FeTCPPCl were demonstrated to be catalytically active for the oxidation of ABTS. We anticipate our strategy to provide a facile route to introduce multiple functionalities into stable Zr-MOFs for a wide variety of potential applications.*

Integrating multi-functionality into metal–organic frameworks (MOFs) has attracted growing attention as it plays a critical role in realizing the potential of MOFs for a wide range of applications.[1] To date, tremendous efforts have been made to develop strategies to incorporate multiple functionalities into MOFs.[2] Among them, mixed-ligand strategies have been extensively studied owing to the straightforward synthesis and preservation of the structural integrity of MOFs.[3] Remarkably, Yaghi and co-workers reported the synthesis of multifunctional MOFs, so-called multivariate (MTV)-MOFs by mixing ligands and successfully introduced up to eight functionalities into MOF-5.[4] However, mixed-ligand strategies generally require the use of ligands of the same geometry and connectivity (e.g. ligand derivatives) that are “indistinguishable” during the formation of MOFs to prevent generating mixed phases, which greatly limits the variety of ligand and functionality that can be incorporated into the MOF. In addition to the functionality, the excellent stability is another prerequisite for practical applications of MOFs, especially for those under harsh conditions, in order to guarantee the integrity of the framework. Although there have been a few reported examples of MOFs containing mixed ligands of different symmetry and connectivity, those MOFs are mostly based on M^{2+} metal species, which suffer from poor stability under harsh chemical conditions and thus their applications are severely restricted. Herein, we show that through one-pot thermodynamically controlled synthesis, multiple functionalities can be integrated into a Zr-MOF without forming separate domains even when mixing ligands of different size, symmetry, and connectivity. The multi-functionalized Zr-MOFs obtained maintain the crystal structure, morphology, and stability of the parent MOF. Owing to the excellent stability of the parent MOF, our multi-functionalized Zr-MOFs exhibit high stability under harsh chemical environments. Therefore, our strategy goes beyond the limit of conventional mixed-ligand strategies and expands the diversity of functionality for stable MOFs modification, holding great potentials for exploring the applications of MOFs extensively.

In recent years, Zr-MOFs have been intensively investigated owing to their considerably improved stability compared to common Zn/Cu/Cd-based MOFs.[5] The versatile symmetry and connectivity of the Zr_6 cluster make it compatible with many different kinds of organic ligands to form MOFs. However, the overwhelming majority of the reported Zr-MOFs obtained via de novo synthesis contain a single organic ligand, which is unfavorable for the incorporation of multi-functionality due to the limited modifiable sites. Despite of the topological feasibility, when a Zr-MOF can be constructed from a single organic ligand, it is very difficult to introduce a secondary ligand with different topology through one-pot synthesis unless the mixed-ligand product is thermodynamically highly preferred. So far, direct synthesis of Zr-MOFs from mixed ligands of different geometry or connectivity remains challenging.

As an archetype of Zr-MOF, UiO-66 is constructed from Zr_6 clusters and commercially available 1,4-benzenedicarboxylate (BDC), which has a decomposition temperature above 500 °C and maintains good crystallinity under harsh chemical conditions and high external pressures.[5a,6] Ideally, UiO-66 has a 2,12-connected network with **fcu-a** topology, the high connectivity of which allows for several sub-networks (e.g. **bcu-a**, **reo-a**, and **hxg-a** network[7]) or highly defected frameworks[8] upon connectivity reduction. Moreover, accompanied with the reduced connectivity, available coordination sites on Zr_6 clusters can be generated, which is favorable for

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incorporating other functional moieties. Therefore, these features provide great possibilities for UiO-66 to tolerate diverse ligands of different topology and functionality, which makes UiO-66 a promising candidate to implement our strategy to incorporate multi-functionalities into stable MOFs.

Herein, we show that tetratopic porphyrin ligands can be incorporated, rather than simply encapsulated,[9] into UiO-66 through one-pot synthesis, which is of great significance due to combination of desired functionality and exceptional stability of the MOF (Figure 1). Porphyrins possess versatile functional properties that have been extensively exploited in both natural and artificial systems for various vital processes.[10] During the last two decades, tremendous efforts have been made to explore the potential of porphyrins towards practical applications including biomimetic catalysis,[11] sensors,[12] and solar cells[13] taking advantage of their ultrastability, ease of synthesis, and possibility of modifying physical and chemical properties at the molecular level. In particular, immobilization of porphyrins on MOFs is of great value in such applications since MOFs can prevent porphyrins from aggregation and formation of catalytically inactive dimers, thus enhancing the lifetime of porphyrin catalysts.[3d,14]

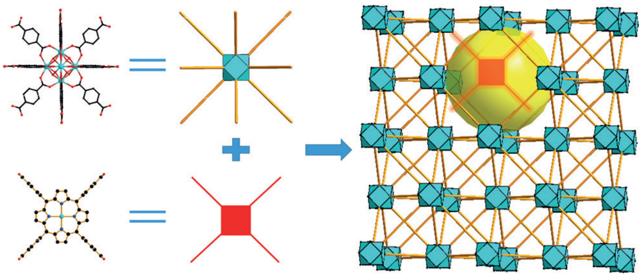

Figure 1. Schematic illustration of UiO-66 incorporating TCPP (red) as well as the usual Zr_6 cluster (blue). Yellow sphere indicates the pore cavity.

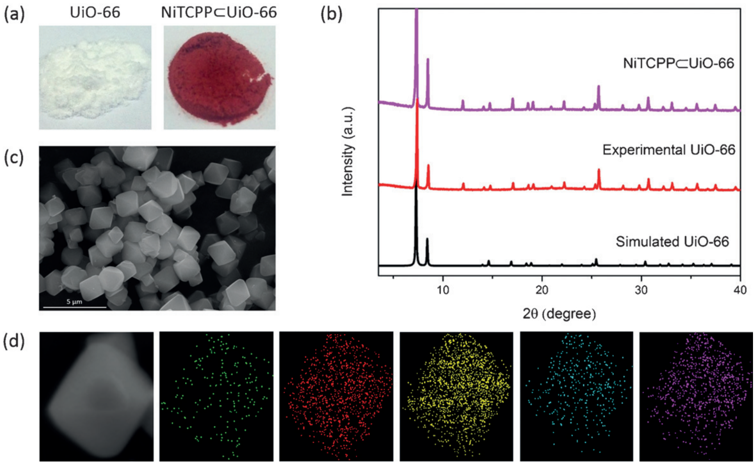

Figure 2. a) Photographs of UiO-66 and NiTCPP⊂UiO-66. b) The PXRD patterns for UiO-66 and NiTCPP⊂UiO-66. c) Representative SEM image of NiTCPP⊂UiO-66. Scale bar: 5 μm. d) SEM image of NiTCPP⊂UiO-66 single crystal and corresponding EDS-mappings of Ni, Zr, C, N, O from left to right.

Initially, solvothermal reactions of $ZrCl_4$, BDC, [5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinato]nickel(II) (NiTCPP), and benzoic acid (BA) in DMF yielded red powders of NiTCPP⊂UiO-66 (Supporting Information, Section S2). The products remained red after washing with DMF and acetone (Figure 2a), implying the presence of NiTCPP, and displayed powder X-ray diffraction (PXRD) patterns consistent with that of phase-pure UiO-66 (Figure 2b). Phase purity was also confirmed by scanning electron microscopy (SEM), which showed that the powders were octahedral microcrystals with an even distribution in size (Figure 2c). The elemental mappings of a single crystal obtained from energy dispersive X-ray spectroscopy (EDS) demonstrated an even distribution of all the elements, especially Ni and Zr (Figure 2d), implying the integration of NiTCPP into the framework.

To understand the chemistry behind our approach, we attempted to explain our experimental results from both thermodynamic and kinetic perspectives. Under our synthetic conditions, the nucleation of UiO-66 is probably dominating due to much higher concentration of BDC than NiTCPP (Figure S66). However, as NiTCPP also exists in the system, it can competitively coordinate to the Zr_6 cluster during the nucleation process of UiO-66 and therefore participate in its growing process. Owing to high symmetry and connectivity of Zr_6 cluster, UiO-66 can still preserve its three-dimensional (3D) framework even when the coordination sites of Zr_6 cluster is partially occupied by NiTCPP to create some defects in the 3D space. On the other hand, owing to much lower concentration of NiTCPP in the system, the initial nucleation process of possible impurity phases will take longer time. Whereas faster nucleation of UiO-66 consumes Zr continuously and further inhibits the formation of porphyrin-based MOFs. Consequently, phase-pure UiO-66 can be obtained with NiTCPP participating in the coordination to Zr_6 clusters.

EDS and ^{1}H NMR analyses were performed to quantify the amount of incorporated NiTCPP (Supporting Information, Section S10 and S11). As shown in Figure 3a, the amount of NiTCPP incorporated into UiO-66 can be gradually tuned by varying the synthetic condition (Section S8), which provides another dimension for optimizing the performance of installed functional moiety where its concentration matters. It is notable that impurity phase began to form when NiTCPP increased up to 20 mg (0.024 mmol; Figure S37), which suggests "saturation" of NiTCPP in the framework and reveals that UiO-66 has certain tolerance for NiTCPP ligands.

Since the parent MOF UiO-66 exhibits excellent chemical stability, we expect that NiTCPP⊂UiO-66 shows similar stability. To carry out the stability test, we immersed the sample in aqueous solutions with different conditions for 12 h (Section S7). The solutions stayed colorless after these treatments, suggesting no leaching of NiTCPP. In addition, the PXRD patterns (Figure 3b) indicated that no framework collapse or phase transition occurred during the experiment. N_2 adsorption isotherms (Figure S33) showed that the porosity was preserved. These results confirmed that NiTCPP⊂UiO-66 maintained the stability of UiO-66 after incorpo-

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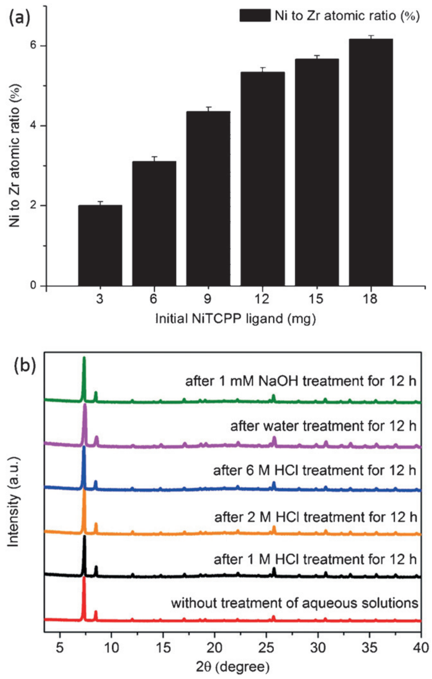

Figure 3. a) Ni to Zr atomic ratio in NiTCPP$\subset$UiO-66 with different amounts of initial NiTCPP ligand. b) The PXRD patterns for NiTCPP$\subset$UiO-66 after treatment with different aqueous solutions.

ration of porphyrin ligand, which is promising for porphyrin-related applications. To further demonstrate the advantages of our strategy, we tested the chemical stability of two representative porphyrin MOFs, namely PCN-222 and PPF-5. For pillared-layer PPF-5, a secondary functionality can be readily introduced through pillars, which makes PPF-5 a handy platform to explore the advanced applications of porphyrin species.[3b] On the other hand, catalytically active PCN-222 contains single porphyrinic linker and exhibits relatively high chemical stability.[15] However, the PXRD patterns demonstrated loss of crystallinity after immersing PPF-5 in 0.1 mM NaOH and PCN-222 in 1 mM NaOH for 12 h, respectively (Figure S35). In contrast, NiTCPP$\subset$UiO-66 was stable under these conditions. Consequently, our strategy provides a facile route to introduce desired functionality into stable MOFs, which can extensively promote the potential of MOFs for practical applications.

We designed several control experiments to demonstrate that NiTCPP is not only attached on the outer surface of UiO-66 and to differentiate our strategy from post-synthetic modification (PSM) of the available coordination sites of Zr$_6$ clusters.[16] Firstly, we synthesized UiO-66 under the same conditions as NiTCPP$\subset$UiO-66 in the absence of NiTCPP. Then UiO-66 was mixed together with NiTCPP (10 mg, 0.012 mmol) in 10 mL DMF and stirred at room temperature and 85 °C, respectively. After 12 h, the products were thoroughly washed to remove remaining NiTCPP. The obtained powders both showed very light pink color despite of varied reaction temperature (Figure 4a). ^{1}H NMR spectra of the digested products did not show the resonance signals of NiTCPP (Figure S49), suggesting that the light pink color results from the attachment of NiTCPP on the outer surface of UiO-66. The PXRD patterns of these powders were identical to that of UiO-66 (Figure S48), demonstrating that the framework was well preserved during this post-synthetic modification process and excluding the possibility that integration of NiTCPP was hampered by the collapse of internal framework. Compared with the post-synthetic modification approach, our method involves incorporation of NiTCPP during the growth of UiO-66, which largely avoids the size limitation imposed by the pore windows in UiO-66 on NiTCPP diffusion during the post-synthetic modification process (Figure S50). Moreover, once NiTCPP is incorporated, the small pore windows of UiO-66 will in turn prohibit its leaking, much like a “ship-in-a-bottle”.

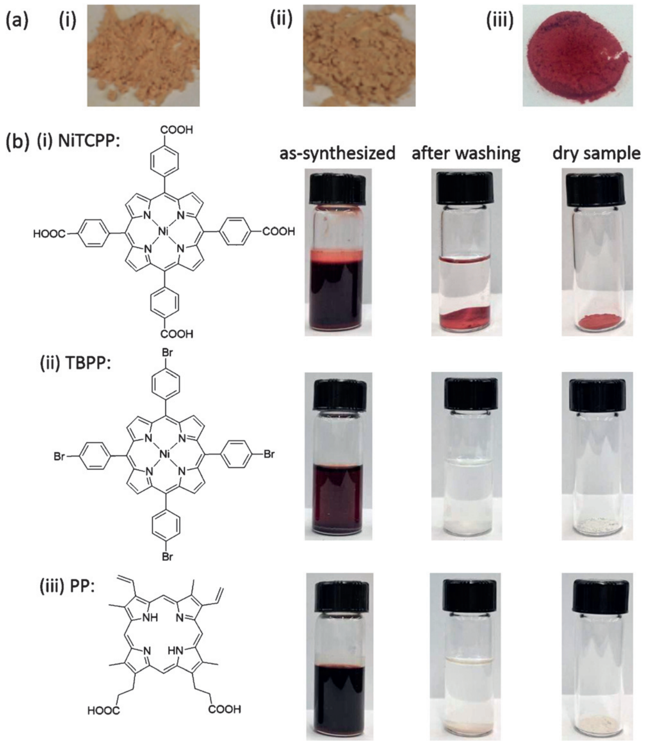

Figure 4. a) Photographs of the products obtained after stirring UiO-66 and NiTCPP in DMF for 12 h i) at room temperature and ii) at 85 °C. iii) Photographs of NiTCPP$\subset$UiO-66. b) Photographs of i) NiTCPP$\subset$UiO-66, ii) TBPP$\subset$UiO-66, and iii) PP$\subset$UiO-66.

To address the issue that in which ways NiTCPP incorporates into the framework, either through coordination to the Zr$_6$ clusters or just purely trapped in the pore,[9] we firstly replaced NiTCPP with tetrakis(4-bromophenyl)porphyrin (TBPP). White powders were obtained (Figure 4b) and characterized (Section S12). Although the size of TBPP is similar to NiTCPP, the difficulty in incorporating TBPP limits the possibility that NiTCPP is purely trapped in the pore, suggesting that carboxylates on NiTCPP participated the coordination during UiO-66 formation. However, when we used another carboxylate-containing porphyrin species, PP, the amount of incorporated PP is almost negligible. We reasoned that this is because two carboxylates of PP are too close for PP to serve as a bridging ligand. Therefore, PP tends to act similar to the monotopic modulating reagent (BA) during MOF formation. As a result, PP will be easily substituted by BDC even if it can coordinate to Zr$_6$ cluster during the nucleation process, which makes integration of PP through metal-ligand-fragment co-assembly[17] unattainable (Figure 4b). To exclude the possibility that incorporation of PP is impeded by higher pK_a of carboxylic acid, we adopted monotopic 4-bromobenzoic acid (BBA) that exhibits similar pK_a to NiTCPP. The results indicated that integration of BBA is unsuccessful (Section S12), suggesting that incorporation of multitopic linker is favored and possibly there is more than one carboxylate participating in the coordination to Zr_6 cluster. These experiments demonstrated that the number of carboxylic groups plays a vital role in integrating NiTCPP into UiO-66, very likely through coordination to more than one Zr_6 cluster during the synthesis, generating defects and larger pores to allow the residence of NiTCPP in the framework.

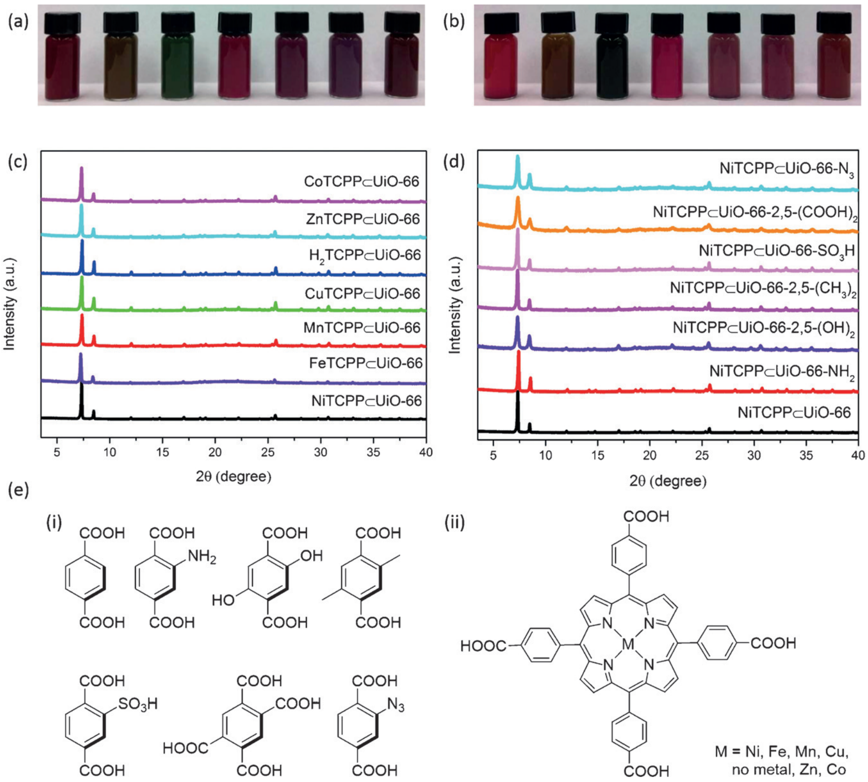

Figure 5. Photographs of a) X⊂UiO-66, b) X⊂UiO-66-NH_2 (X = NiTCPP, FeTCPPCl, MnTCPPCl, CuTCPP, H_2TCPP, ZnTCPP, and CoTCPP, from left to right). c),d) the PXRD patterns of some representative multifunctional porphyrin⊂UiO-66. e) Chemical structures of selected i) BDC derivatives and ii) TCPP ligands.

To introduce a secondary functionality, we replaced BDC with NH_2-BDC since MOFs with amino groups exhibit many attractive features.[18] Moreover, amino groups can undergo a wide variety of chemical transformations, which is useful for further adjusting chemical functionality of the MOF.[19] NiTCPP⊂UiO-66-NH_2 was synthesized and characterized (Supporting Information). The product was stable in aqueous solutions with conditions ranging from 6 M HCl to 10 mM NaOH (Section S7). One major advantage of MOFs over other conventional porous materials is the synthetic versatility from the design of diverse ligands. With that in mind, we sought to incorporate a broad scope of functionalities into the MOF through BDC and TCPP moieties (Figure 5e). BDC modified with hydroxy group, methyl group, sulfonic group, carboxy group, and azide group were selected because of their importance in adjusting the properties of MOFs.[20] Moreover, MOFs with these groups can be easily modified with additional functionality.[21] A series of multi-functionalized MOFs were obtained through various combinations of BDC derivatives and TCPP, including X⊂UiO-66-NH_2, X⊂UiO-66-2,5-$(OH)_2$, X⊂UiO-66-2,5-$(CH_3)_2$, X⊂UiO-66-SO_3H, X⊂UiO-66-2,5-$(COOH)_2$, and X⊂UiO-66-N_3 (X = NiTCPP, FeTCPPCl, MnTCPPCl, CuTCPP, H_2TCPP, ZnTCPP, and CoTCPP) (Figure 5a,b, and Section S14). The PXRD patterns of these products were identical to that of UiO-66 (Figure 5c,d and Section S3). Compared to UiO-66, MOFs modified with FeTCPPCl showed high catalytic activity for the oxidation of 2,2′-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) in the presence of H_2O_2, indicating the preservation of the functionality of TCPP species (Section S15). These results suggested that our strategy is promising to introduce multi-functionalities into stable MOFs by one-pot synthesis for a wide variety of applications.

In summary, we reported a facile one-pot synthetic strategy to incorporate multi-functionalities into stable Zr-MOFs through mixing ligands of different geometry and connectivity. Tetratopic TCPP ligands were successfully integrated into UiO-66, and the crystal structure, morphology, and stability of UiO-66 were well preserved, which is unachievable by post-synthetic modification or conventional mixed-ligand approaches. The amount of integrated TCPP is tunable. Through combinations of BDC derivatives and TCPP ligands, 49 MOFs with multi-functionalities were obtained. Combining the advantages of framework robustness and facile functionalization that allow further chemistry to be explored within the framework, we expect our strategy to provide a facile route to introduce multi-functionalities for an extensive variety of potential applications.

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