

Metal-Cation-Directed *de Novo* Assembly of a Functionalized Guest Molecule in the Nanospace of a Metal–Organic Framework

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Supporting Information

ABSTRACT: In this work, a new strategy is developed to encapsulate a metal-functionalized guest molecule into a metal–organic framework (MOF) via metal-cation-directed *de novo* assembly from the component fragments of the guest molecule. This strategy, as illustrated in proof-of-principle studies on the *de novo* assembly of metal(II) phthalocyanine molecules into bio-MOF-1, can circumvent some drawbacks of existing approaches for encapsulating guest molecules into MOFs, such as inaccessibility for larger guest molecules due to limitations of the MOF window size and disruption of the MOF framework structure by functionalized guest molecules. Overall, this work provides a general yet versatile approach for encapsulating a broader range of metal-functionalized guest molecules into MOFs for various applications.

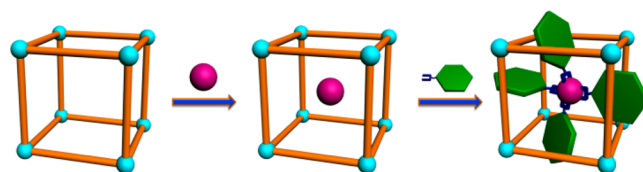
Metal–organic frameworks (MOFs),¹ as a new type of porous materials, have attracted tremendous attention from both academia and industry over the past decade. One of the most striking features of MOFs lies in their tunable and functionalizable nanospace,² which not only can be decorated with targeted functional groups on the framework³ but also can provide ideal room to accommodate gas molecule⁴ or guest species.⁵ This renders MOFs potentially useful for a plethora of applications such as gas storage/separation,⁶ CO₂ capture,⁷ catalysis,⁸ proton and electrical conductivity,⁹ and small-molecule recognition.¹⁰

Recently, there has been an escalating interest in encapsulating metal-functionalized guest molecules (e.g., metal-organic molecules,¹¹ organometallic complexes¹²) into the nanospace of MOFs, and the resulting guest@MOFs can serve as platforms for host–guest chemistry studies¹³ and particularly heterogeneous catalysis.^{8d,14} In existing guest@MOF systems, the functionalized guest molecule is incorporated as an entity into the nanospace of the MOF via impregnation,^{8d,15} chemical vapor deposition,¹⁶ cation exchange,¹⁷ or coassembly.^{11,18} The former three approaches are often limited by the window size of the MOF, which leads to inaccessibility for larger sized molecules and possible leaching for smaller sized molecules. For the fourth approach, the addition of metal-functionalized guest molecules would probably disrupt the formation of the expected MOF framework due to the coordination or template effect. In this Communication, we describe a new approach to

encapsulate a functionalized guest molecule into a MOF via a metal-cation-directed *de novo* assembly (or termed “ship-in-a-bottle” synthesis)¹⁹ strategy, which is based upon the formation of a functional guest molecule from its component fragments in the nanospace of the MOF under the direction of a metal cation. Compared with the aforementioned four approaches, the *de novo* assembly approach not only can allow the encapsulation of functional guest molecules with a larger size range but also can afford the desired functionalized guest molecule@MOF system without guest molecule/framework structure disruption. Therefore, it represents a versatile approach and provides new opportunities to encapsulate a broader range of metallorganic compounds and organometallic complexes into MOFs for various applications.

Our *de novo* assembly strategy typically includes two steps: (1) acquiring the metal-cation-containing MOF via presynthesis or post metal ion exchange and (2) assembling small component fragments under the direction of a metal cation to form the functional guest molecule in the nanospace of the MOF (Scheme 1).

Scheme 1. Procedure for Encapsulating a Functionalized Guest Molecule into a Metal–Organic Framework via the Metal-Cation-Directed *de Novo* Assembly Strategy^a



^aKey: turquoise ball, metal ion or metal cluster-based node; orange bar, organic linker; pink ball, metal cation in the pore; green hexagon, component fragment of guest molecule.

To illustrate our strategy, we selected an anionic MOF, Zn₈(ad)₄(BPDC)₆O·2Me₂NH₂ (known as bio-MOF-1; ad = adeninate; BPDC = biphenyldicarboxylate),²⁰ for proof of principle. Bio-MOF-1 consists of 1D channels in which Me₂NH₂⁺ cations reside as counterions (Figure 1a). These Me₂NH₂⁺ cations can be readily exchanged with metal ions.^{10c}

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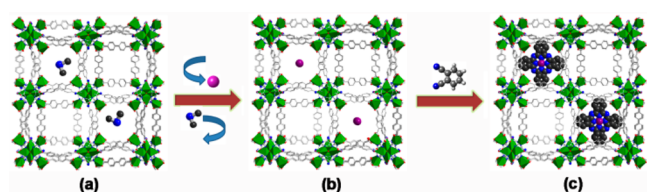


Figure 1. Schematic presentation of *de novo* assembly of Co-Pc@bio-MOF-1.

Cobalt(II)-ion-exchanged bio-MOF-1 (hereafter designated as Co@bio-MOF-1) was achieved by first immersing bio-MOF-1 crystals in a 0.1 M methanol solution of Co(Ac)₂ for 3 weeks (Figure 1b), with ~85% Me₂NH₂⁺ ions exchanged into Co(II), based upon inductively coupled plasma mass spectrometry (ICP-MS) analysis. The obtained Co@bio-MOF-1 was then placed in a formamide solution of 1,2-dicyanobenzene (DCB) at 190 °C for ~10 min, and the cobalt(II) phthalocyanine (Co-Pc) was successfully assembled in bio-MOF-1 (hereafter designated as Co-Pc@bio-MOF-1), as indicated by the crystal color change from pink to deep green (Figure 1c).

Powder X-ray diffraction (PXRD) studies showed that bio-MOF-1 retained its structural integrity during the *de novo* assembly processes, as evidenced by the consistence in the PXRD patterns of Co-Pc@bio-MOF-1 and the parent bio-MOF-1 (Figure S1). Successful formation of Co-Pc in bio-MOF-1 was confirmed by crystal optical images and UV-vis spectroscopy. The Co-Pc@bio-MOF-1 crystals are blue green, as compared to the colorless bio-MOF-1 crystals (Figure 2a), strongly indicating the association of Co-Pc molecules with

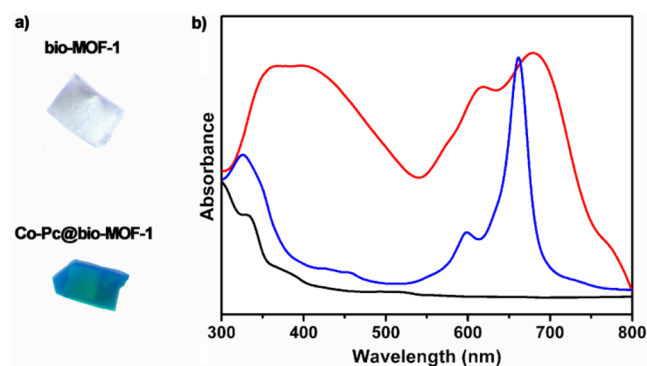


Figure 2. (a) Optical images of bio-MOF-1 and Co-Pc@bio-MOF-1. (b) UV-vis absorption spectra of bio-MOF-1 (black), Co-Pc@bio-MOF-1 (red), and Co-Pc (blue) in DMF solution.

bio-MOF-1. UV-vis absorption spectroscopy studies (Figure 2b) revealed that Co-Pc@bio-MOF-1 exhibits the characteristic absorption bands of Co-Pc at 386 (B-band), 618 (Q-band), and 681 nm (Q-band), thus confirming the formation of Co-Pc in bio-MOF-1. Interestingly, the corresponding absorption bands of Co-Pc solution (in DMF) are at 326 (B-band), 599 (Q-band), and 661 nm (Q-band), respectively;²¹ the bathochromic shift of Co-Pc encapsulated in bio-MOF-1 is indicative of the interactions between the Co-Pc molecules and the MOF framework. In addition, the UV-vis spectra of Co-Pc digested from Co-Pc@bio-MOF-1 are consistent with those of the free Co-Pc, further confirming the formation of Co-Pc in bio-MOF-1 (Figure S2). Successful assembly of DCB into Pc under the direction of the Co(II) cation was also supported by Fourier transform infrared spectroscopy studies, which indicate

the disappearance of the -CN stretching peak at 2229 cm⁻¹ and the appearance of three characteristic absorption peaks of Co-Pc at 1116, 1086, and 1058 cm⁻¹ for Co-Pc@bio-MOF-1 compared with DCB-loaded Co@bio-MOF-1 and Co@bio-MOF-1 (Figure S3). The *de novo* formation of Co-Pc in bio-MOF-1 was further verified by X-ray photoelectron spectroscopy (XPS) and mass spectrometry (MS) studies. XPS analysis on Co-Pc@bio-MOF-1 shows a cobalt signal at a binding energy of 781.5 eV (Figure S4), which corresponds to the peak of Co2p_{3/2}, indicating the presence of Co(II) in Co-Pc@bio-MOF-1.²² MS analysis on Co-Pc@bio-MOF-1 digested by 2 M H₂SO₄ shows a peak at *m/z* = 571 (Figure S5), confirming the existence of a Co-Pc entity in bio-MOF-1. Fracturing the Co-Pc@bio-MOF-1 crystal revealed that the crystal interior also displayed optical images retaining the blue-green color of the Co-Pc (Figure S6), indicating formation of Co-Pc molecules in the interior pores of the bio-MOF-1 crystal. ICP-MS and elemental analysis studies indicate that ~30% Co(II) are metalated in the phthalocyanine rings during the *de novo* assembly process, which is consistent with the conversion of Co(II) to Co-Pc in bio-MOF-1 calculated from UV-vis analysis (Figure S7). This is also in reasonable agreement with the observed decrease in BET surface area from 1005 m²/g for bio-MOF-1 to 752 m²/g for Co-Pc@bio-MOF-1, as revealed by Ar sorption isotherms (Figure S8).

To verify that the exchanged metal cations play the critical role in directing the *de novo* formation of Pc, a control experiment was performed on parent bio-MOF-1. Immersing the bio-MOF-1 sample into the formamide solution of DCB followed by heating at 190 °C did not lead to color change in crystals, suggesting no formation of Pc in the parent Me₂NH₂⁺ cation-containing bio-MOF-1 (Figure S9).

To elaborate the advantages of our *de novo* assembly strategy compared to existing approaches, the encapsulation of Co-Pc molecules into bio-MOF-1 using coassembly and impregnation approaches was attempted. The attempt to encapsulate Co-Pc into bio-MOF-1 using a coassembly approach, adding Co-Pc during its synthesis, only afforded colorless crystals of bio-MOF-1, indicating the absence of Co-Pc (Figure S10). Employment of an impregnation approach, immersing bio-MOF-1 into Co-Pc solution (0.02 M in DMF) at room temperature for 24 h or at 190 °C for ~10 min, also did not succeed, as evidenced by the colorless immersed bio-MOF-1 crystals after being washed with DMF (Figures S11 and S12). This could be due to the relatively small windows of bio-MOF-1 (window size ~1.0 nm × 1.0 nm) compared to Co-Pc molecules (molecular dimensions ~1.3 nm × 1.3 nm). Therefore, these control experiments highlight the uniqueness of the metal-cation-directed *de novo* assembly strategy for encapsulating functionalized guest molecules, particularly large ones, into MOFs.

The applicability of the metal-cation-directed *de novo* assembly strategy to other metal ions was also demonstrated. Placing Ni(II)- and Cu(II)-ion-exchanged bio-MOF-1 (designated as Ni@bio-MOF-1 and Cu@bio-MOF-1, respectively) in the formamide solution of DCB followed by heating at 190 °C afforded Ni-Pc@bio-MOF-1 and Cu-Pc@bio-MOF-1, respectively (Figure 3), which were confirmed by PXRD, IR, XPS, MS, and Ar sorption studies (Figures S14–S23).

To illustrate that the metal-cation-directed *de novo* assembly strategy can stabilize and heterogenize homogeneous catalysts in MOFs, we examined the catalytic performance of Co-Pc@bio-MOF-1 in the context of styrene epoxidation, and control

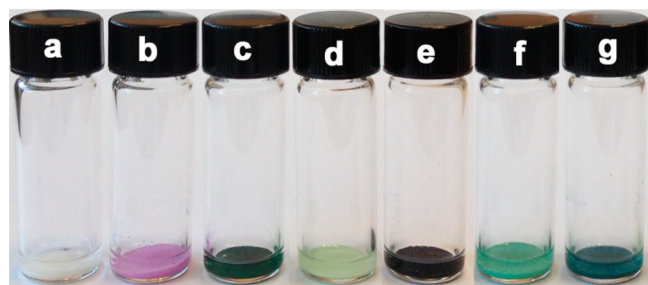


Figure 3. Optical photos of bio-MOF-1, M@bio-MOF-1, and M-Pc@bio-MOF-1: (a) bio-MOF-1, (b) Co@bio-MOF-1, (c) Co-Pc@bio-MOF-1, (d) Ni@bio-MOF-1, (e) Ni-Pc@bio-MOF-1, (f) Cu@bio-MOF-1, and (g) Cu-Pc@bio-MOF-1.

experiments were conducted for homogeneous Co-Pc and also the parent bio-MOF-1. Co-Pc@bio-MOF-1 can efficiently catalyze the styrene epoxidation reaction, with a conversion of 72% (styrene epoxide selectivity: 65%) observed after 16 h reaction at 60 °C (Table S1). In comparison, homogeneous Co-Pc exhibits a much lower conversion of 38% (styrene epoxide selectivity: 60%) under the same reaction conditions, which could be ascribed to the formation of Co-Pc oligomer through π - π stacking in solution.²³ A very poor performance of 8% conversion was observed for bio-MOF-1 under the same reaction conditions, indicating a negligible contribution from the bio-MOF-1 framework to the high activity of Co-Pc@bio-MOF-1. No detectable leaching of Co-Pc or Co(II) ion in the reaction solution was observed after removal of Co-Pc@bio-MOF-1 by filtration, and Co-Pc@bio-MOF-1 could be reused for three cycles without significant drop in its catalytic activity (Table S1). The accessibility of styrene to the catalytically active Co-Pc molecules residing inside the pores was proved by the control catalytic experiment on a larger substrate, *cis*-stilbene, which revealed a much lower conversion of 13.7% (Table S2), as compared to 72% conversion for styrene.

In summary, we have illustrated a metal-cation-directed *de novo* assembly strategy for the encapsulation of a functionalized guest molecule into a MOF, as exemplified by the *de novo* assembly of metal(II) phthalocyanine molecules into bio-MOF-1. The metal-cation-directed *de novo* assembly approach demonstrates unique advantages compared to existing approaches for encapsulating functionalized guest molecules into MOFs. It thus represents a general yet versatile approach to encapsulate a broader range of metallorganic compounds and organometallic complexes into MOFs for various applications. Ongoing work in our laboratory includes employing this strategy to encapsulate some other interesting functional metallorganic compounds and organometallic complexes into MOF systems for host-guest chemistry studies and heterogeneous catalysis investigations.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental and characterization details; additional figures and optical images; plots of PXRD patterns; gas sorption isotherms; and TGA, IR, XPS, MS, and catalysis data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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