



A flexible Tb(III) functionalized cadmium metal organic framework as fluorescent probe for highly selectively sensing ions and organic small molecules



Han Weng, Bing Yan*

Department of Chemistry, Tongji University, Shanghai 200092, China

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ABSTRACT

A luminescent terbium functionalized cadmium metal-organic framework Tb³⁺@Cd-MOF (Cd-MOF = {[Me₂NH₂]₂}[Cd₃(5-tbip)₄·2DMF]_n, (5-tbipH₂ = 5-tert-butylisophthalic acid)) has been prepared via postsynthetic cation exchange. Subsequently, Tb³⁺@Cd-MOF is chosen as probe for sensing metal cations, anions and small organic molecules because of its high luminescent intensity and robust framework. The detailed study reveals that Tb³⁺@Cd-MOF has the potential to be highly selectively and sensitive probe for detection of Fe³⁺ (detection limit, 0.010 mM), Cr₂O₇²⁻ (detection limit, 0.012 mM) and acetone through its fluorescence quenching. However, the crystal structures of Tb³⁺@Cd-MOF with different solutions or organic solvents are in good stability, except for pyridine solvent. As a flexible MOF, a single-crystal-to-single-crystal (SCSC) transformation appears when the complex is immersed into pyridine. Furthermore, the study on fluorescence shows selective pyridine recognition through luminescent quenching. Nevertheless, the structure and luminescent intensity can be restored when we remove pyridine solvent and introduce DMF solvent into the complex.

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1. Introduction

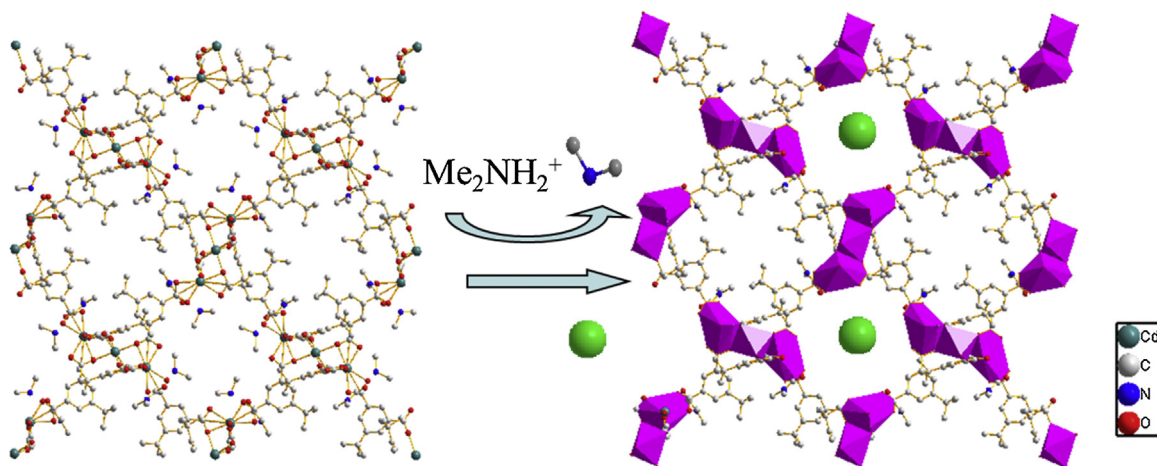
Metal-organic frameworks (MOFs), or porous coordination polymers (PCPs) behave as a class of hybrid materials formed by the self-assembly of polydentate bridging ligands and central metals [1]. They have attracted much attention for their potential applications such as chemical sensors [2], lighting devices [3–5], gas sorption [6], catalysis [7,8] and so on. As previous reports, there are several modes for generating luminescence in MOFs: emission directly from the linker or charge transfer with the coordinated metal ions and clusters can generate luminescence; lanthanide ions can emit sharp but weak luminescence, while the luminescent intensity can be enhanced by antenna effect; pores of MOFs make it possible to entrap luminophores so as to emit luminescence; and exciplex formation caused by π - π interactions exhibits broad, featureless luminescence. However, luminophores bound to the surface of MOFs can also create luminescence [9]. It is worthy pointing out that lanthanide ions can form luminescent MOFs, which not only behave as the central metal cations [10] but also be encapsulated into MOFs as active species [11–14].

Among the various particular characteristics of MOFs, the flexibility of the framework has aroused much attention. Flexible MOFs, or soft porous crystals (SPCs) are defined as porous solids which possess both highly ordered networks and structural transformability [15]. The diverse structures of flexible MOFs exhibit multitudinous dynamic behaviors, such as the opening/closing of pores [16,17], the expansion/shrinkage of the framework [18–20] and reversible physicochemical properties, etc. [21,22] Based on these facts, flexible MOFs show great potential in many fields, which appears different character with normal MOFs [23–30]. The mechanisms of these characteristic structural flexibility are various and complicated. Bond rotations of organic linkers, weak intermolecular bonding interactions and bond angles change of the coordination complexes within the network; any of these can cause the formation of flexible MOFs [31]. However, these changes may be subtle, involving small shifts in the position of functional groups. On the other hand, these changes may be quite significant that we can examine the transformation of crystal structures [32–37].

Comparing with the investigated applications of flexible MOFs in storage and separation, their investigations as sensors are relatively limited. In this paper, an anionic MOF {[Me₂NH₂]₂}[Cd₃(5-tbip)₄·2DMF]_n is chosen as host material [38], in which Tb³⁺ ions can be incorporated into the framework via cation exchange method since the existence of residual

* Corresponding author.

E-mail address: byan@tongji.edu.cn (B. Yan).



Scheme 1. The coordination environment of central Cd^{2+} and the structure of $\text{Tb}^{3+}@$ Cd-MOF.

$[(\text{NH}_3)_2\text{Me}_2]^+$ in the pore. For the host material Cd-MOF, it is successfully synthesized using a semi-rigid ligand 5-tbip as a linker, which makes it possible to present the characteristic of flexible. The luminescent $\text{Tb}^{3+}@$ Cd-MOF is used for the detection of metal cations, anions and small organic molecules. When the $\text{Tb}^{3+}@$ Cd-MOF is immersed into the pyridine solvent, it exhibits crystal structure transformation and luminescent quenching, while the structure of $\text{Tb}^{3+}@$ Cd-MOF soaked into other solvent remains unchanged. However, the structure and luminescent intensity can be reversible when we remove the pyridine solvent and introduce DMF solvent to it. We also find the luminescent $\text{Tb}^{3+}@$ Cd-MOF can highly selectively recognizes acetone solvent through luminescent quenching. Obviously, the mechanisms of the above-mentioned quenching effects are different, which are further discussed hereinafter. In addition, the $\text{Tb}^{3+}@$ Cd-MOF has also been chosen as fluorescence probe for the sensing of metal cations and anions. The experimental results reveal that both metal cations and anions have fluorescence quenching effects to a certain degree, especially in the case of Fe^{3+} and $\text{Cr}_2\text{O}_7^{2-}$. The color changing can be observed by naked eyes under UV light. As we known, pyridine and acetone can both anesthetize the central nervous system, Fe^{3+} is one of the elements for humans and living organisms, $\text{Cr}_2\text{O}_7^{2-}$ is a highly toxic hexavalent chromium ion which can lead to gastrointestinal disease and skin lesions even cancer. Therefore, identifications of these solvents and ions are of great importance. (see Scheme 1).

2. Experimental

2.1. Synthesis of Cd-MOF

Cd-MOF was synthesized as is reported by Chaudhari, et al. [38]. 1 mmol of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.3084 g) and 1 mmol of 5-tbip ligand (0.2222 g) were dissolved in 6 mL of DMF in a glass vial. The mixture was heated to 90°C for 3 days and then cooled down to room temperature. After washing with DMF for several times, the yield was dried under a vacuum at 80°C for 6 h.

2.2. Preparation of $\text{Tb}^{3+}@$ Cd-MOF

$\text{Tb}^{3+}@$ Cd-MOF was prepared as a cation exchange method: 30 mg of Cd-MOF was soaked into the DMF solution of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (5 mL, 1 mmol) for 3 days. The product was collected by centrifugation and washed with DMF for several times to remove the residual Tb^{3+} . After drying under a vacuum at 80°C for 6 h, we can get the target compound.

2.3. Sensing for small organic molecules and ions

3 mg of $\text{Tb}^{3+}@$ Cd-MOF or pure Cd-MOF was immersed in the 3 mL of different organic solvents (pyridine, acetone, ethanol, chloroform, THF, toluene, cyclohexane, DMF, dichloromethane, acetonitrile, methylene chloride, methanol) at room temperature, respectively. For the sensing of metal cations and anions, $\text{Tb}^{3+}@$ Cd-MOF (3 mg) powder was immersed in the DMF solutions (3 mL, 10^{-4} mol/L) of $\text{M}(\text{NO}_3)_2$ ($\text{M}^{2+} = \text{Na}^+, \text{Ag}^+, \text{Cu}^{2+}, \text{Pb}^{2+}, \text{Hg}^{2+}, \text{Cd}^{2+}, \text{Mg}^{2+}, \text{Co}^{2+}, \text{Fe}^{2+}, \text{Cr}^{3+}, \text{Fe}^{3+}, \text{Al}^{3+}$) or anions (anions = $\text{Ac}^-, \text{Br}^-, \text{I}^-, \text{Cl}^-, \text{F}^-, \text{NO}_2^-, \text{NO}_3^-, \text{SO}_4^{2-}, \text{CO}_3^{2-}, \text{CrO}_4^{2-}, \text{Cr}_2\text{O}_7^{2-}, \text{PO}_4^{3-}, \text{MnO}_4^-$). After sonicating for 5 min to form the suspension, the mixture was then used for luminescent measurements immediately.

2.4. Recoverable structures of $\text{Tb}^{3+}@$ MOF

3 mL pyridine solvent was introduced into 3 mg $\text{Tb}^{3+}@$ Cd-MOF or pure Cd-MOF and sonicated for 5 min, then we got the compound by centrifugation. After washing with DMF for several times, the compound was immersed into 3 mL of DMF for 12 h and then dried for further study.

2.5. Materials and instrumentation

$\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was prepared by dissolving the corresponding lanthanide oxide in concentrated nitric acid followed by evaporation and vacuum drying. Other reagents (A.R.) were obtained commercially and used without further purification. Scanning within the 2θ range of $5\text{--}30^\circ$, a Bruker D8 diffractometer using $\text{Cu K}\alpha$ radiation with 40 mA and 40 kV was employed to obtain the PXRD patterns. FTIR spectra were collected in the range of $4000\text{--}400\text{ cm}^{-1}$ on a Nexus 912 AO446 spectrophotometer using KBr pellets. Excitation and emission spectrums of the samples were recorded on an Edinburgh FLS920 spectrophotometer using a 450 W xenon lamp as excitation source.

3. Results and discussion

3.1. Characterization of $\text{Tb}^{3+}@$ Cd-MOF

Cd-MOF was synthesized as reported. $\text{Tb}^{3+}@$ Cd-MOF was prepared via postsynthetic cation exchange by encapsulating Tb^{3+} ions into an anionic metal-organic framework. As is exhibited in Fig. 1, the experimental PXRD patterns of the synthesized Cd-MOF and $\text{Tb}^{3+}@$ Cd-MOF were in great agreement with the simulated one, which is necessary for the further study. FTIR spectra are col-

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