DOI: 10.1002/asia.201301531

A Stable Porous Anionic Metal–Organic Framework for Luminescence Sensing of Ln^{3+} Ions and Detection of Nitrobenzene

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Abstract: A hexagonal channel-based porous anionic metal–organic framework was successfully constructed. **IFMC-3** is stable in air and acidic/basic aqueous solutions at room temperature, and constitutes a selective luminescent sensing material for Ln^{3+} ions and a recyclable probe for the sensitive detection of nitrobenzene.

Because of their significant potential roles in a wide range of gas/liquid sorption and separations, associated research on metal–organic frameworks (MOFs) with tunable structures and functions has been a very active topic.[1,2] MOFs with well-defined pore sizes ranging from non-pores, micropores to mesopores are regarded to bridge the gap between zeolites and mesoporous silica.[3] In the last decade, much effort has been dedicated to the development of MOFs with large and tunable pores through various synthetic strategies.[4] In most cases, the application of MOFs is related to porous functionality (surface characteristic, pore size and shape) as well as the stability, toxicity, and biodegradability of MOF materials.[5]

Recently, continuous endeavors have been devoted to the design and preparation of various luminescent materials because they might have some potential applications, for instance in nonlinear optics, bioimaging, and sensing.[6] Among the reported luminescent MOF materials, lanthanide (Ln^{3+})-containing MOFs are attracting increasing attention because they can be designed in such a way that they possess narrow-band and fine-tuned luminescence.[7] As for Ln^{3+}-based luminescent MOF materials, two forms exist: 1) Ln^{3+} ions are directly part of the frameworks of MOFs,[8] and 2) Ln^{3+} ions reside within the pores of MOFs.[9] Intensive studies on Ln^{3+}-based luminescent MOF materials revealed that the post-synthetic encapsulation of Ln^{3+} ions provides a promising method to achieve tunable luminescence and prepare luminescence sensing materials towards Ln^{3+} ions. This procedure provides not only a new platform for the preparation of Ln^{3+}-doped luminescent MOF materials but also for obtaining Ln^{3+} probes. However, as luminescent materials, the stability of MOFs is crucial, especially their stability in air and water. MOFs with an anionic network are likely useful for exchange with Ln^{3+} cations, and thus approaches to obtain stable anionic MOFs for Ln^{3+} probe materials are worth studying.[10]

In addition, the sensing behaviors of luminescent MOFs for small organic molecules, ions, and explosives have been carried out over the past years.[11] As most of the organic species are volatile, their detection is an issue of international concern and crucial for security, environmental, and military matters. For instance, Kitagawa and co-workers reported a novel sensing method for distinguishing small structural differences using a molecular decoding.[11a] This simple yet sophisticated decoding method will like find novel applications of crystalline porous MOF materials as portable solid-state sensor devices. However, only a few works are related to the detection of small organic molecules or even explosives, and thus the preparation of novel porous MOF materials with high chemical stability and recyclability for fluorescence detection is a hot topic.

Given the above considerations, it is a significant challenge to obtain dual functional materials with high chemical stability that not only act as a fluorescent probe for different Ln^{3+} ions but can also detect nitrobenzene. In the present study we selected a tetrazole ligand and H_3PO_3 for the following reasons:[12] 1) zeolite materials formed on the basis of phosphate salts possess a relatively high chemical stability and tetrazole ligands are commonly used to construct zeolite-like materials that exhibit a high stability; 2) a phosphite ion and tetrazole moiety can take part in the coordination with metal ions in an anionic form, thereby resulting in neutral or even anionic frameworks; and 3) nitrobenzene is a good electron acceptor owing to the electron-deficient NO_2 group, and the tetrazole ligand is a N-rich linker with

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201301531.

lone pair electrons and an aromatic π-ring, which could adjust the position of ligands to provide intraligand interactions and promote the luminescent character. Fortunately, we could isolate solvothermically a microporous anionic MOF, $[Zn_2L_3(HPO_3)_{2/3}]\cdot(H_3O)_{1/3}\cdot H_2O$ (**IFMC-3**, HL = 5-methyl-1*H*-tetrazole, IFMC = Institute of Functional Material Chemistry). **IFMC-3** was structurally characterized, and the luminescence of Ln^{3+}-loaded **IFMC-3** as well as the luminescence behavior towards a series of organic solvents was investigated. Furthermore, **IFMC-3** was used as a sensor for the detection of nitrobenzene through fluorescence quenching.

The reaction of $Zn(NO_3)_2\cdot 6H_2O$, HL, and H_3PO_3 in DMF at 85 °C for 72 hours resulted in the formation of colorless crystals of **IFMC-3**. X-ray crystallographic analysis revealed that **IFMC-3** crystallizes in the trigonal space group $P\bar{3}$ (147) and possesses a 3D open anionic framework (Table S1, Supporting Information). In the asymmetric unit of **IFMC-3** (Figure 1 a), two crystallographically unique

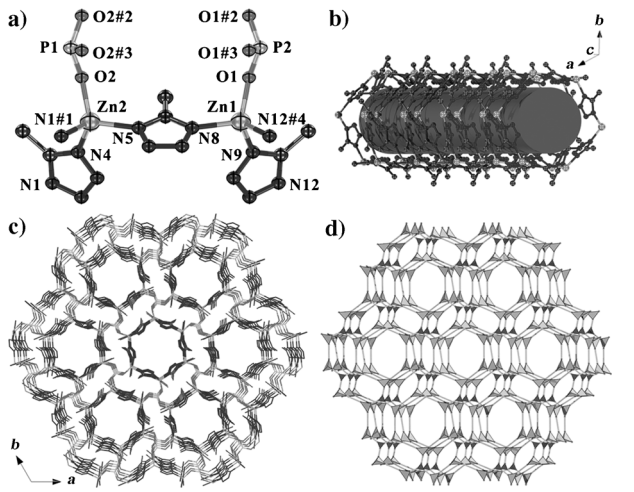

Figure 1. The structure of **IFMC-3**: a) the asymmetric unit, #1 $1+y$, $1-x+y$, $2-z$; #2 $1-x+y$, $1-x$, z; #3 $1-y$, $x-y$, z; #4 $1+y$, $1-x+y$, $1-z$; b) the 1D channel running along the *c* axis, c) the wireframe representation of 3D open framework, and d) the (3,4)-connected topology.

Zn^{2+} cations, a HPO_3^{2-} ion with 2/3 occupancy, three deprotonated L^- fragments, a protonated H_2O with 1/3 occupancy, and one water molecule are present. Each Zn^{2+} center is completed by three nitrogen atoms from three distinct L^- ligands and one oxygen atom from HPO_3^{2-} anions, thus leading to a distorted tetrahedral geometry. All Zn–N and Zn–O distances are within normal range.[13] Every L^- fragment adopts a linear coordination mode with bridged Zn^{2+} ions to give rise to a 1D hexagonal channel running parallel to the *c* axis (Figure 1 b). The side length of the hexagonal channel (distance of Zn···Zn) is about 6 Å, and the corresponding diameter of the window size is about 12 Å (Figure S1, Supporting Information). Furthermore, the 1D channels are connected to each other by HPO_3^{2-} ions, thereby resulting in a 3D open microporous framework with a honeycomb shape (Figure 1 c and Figure S2, Supporting Information). As a consequence, the solvent-accessible voids, as calculated by using PLATON[14] for **IFMC-3** without the contribution of disordered water molecules, amount to a value of 953.7 $Å^3$ and represent 29.7 % of the total volume of the structure. From a topological viewpoint, if L^- ligands are regarded as linkers, and HPO_3^{2-} and Zn^{2+} ions as 3- and 4-connected nodes, respectively, the structure of **IFMC-3** can be described as a (3,4)-connected topology (Figure 1 d). It should be noted that this topological type is different from the (3,4)-connected topology documented previously (ctn, bor, and ofp).[15]

The phase purity of **IFMC-3** was confirmed by the agreement between the experimental X-ray powder diffraction (XRD) pattern and the simulated data on the basis of structural analysis (Figure S3, Supporting Information). As **IFMC-3** was generated in DMF, we studied its stability in air and aqueous media. **IFMC-3** is stable in air, as confirmed by the XRD patterns and IR spectra (Figures S3 and S4, Supporting Information). Surprisingly, it was also found that it is stable in acidic and basic aqueous solution in the pH range of 2–12 at room temperature, as confirmed by subsequent XRD and FTIR measurements (Figures S5 and S6, Supporting Information). Only a few MOFs that are stable in both acidic and basic solutions have been reported.[16] Furthermore, the thermogravimetric analysis (TGA) of **IFMC-3** suggests that it exhibits a continuous weight-loss step from room temperature to about 400 °C, which corresponds to the loss of all water and organic ligand molecules (Figure S7, Supporting Information).

The anionic framework and porosity of **IFMC-3** encouraged us to use it as a host to encapsulate Ln^{3+} cations for the preparation of tunable fluorescent materials. Ln^{3+} ions were introduced into the channels of **IFMC-3** by immersion of the freshly prepared samples in solutions of nitrate salts of Ln^{3+} ($Ln^{3+} = Sm^{3+}$, Eu^{3+}, Tb^{3+}, or Dy^{3+}) in DMF for 48 hours. Subsequently, the resulting samples were filtered off, washed several times with ethanol until no characteristic emission was observed upon excitation, and then dried in air. The crystalline integrity of **IFMC-3** was retained after the encapsulation of Ln^{3+} ions, as verified by analysis of the XRD patterns (Figure S8, Supporting Information). Judging from the IR spectra and XRD patterns, we consider that the basic framework of **IFMC-3** was maintained (Figure S9, Supporting Information). Furthermore, similar amounts of Ln^{3+} (Sm^{3+}, Eu^{3+}, Tb^{3+} or Dy^{3+}) ions were absorbed in fresh **IFMC-3**, as measured by inductively coupled plasma (ICP) for the **Ln^{3+}@IFMC-3** samples. The molar ratio of Zn^{2+}/Ln^{3+} was about 2.0:0.11, thus suggesting that the samples after cationic exchange can be formulated as $[Zn_2L_3(HPO_3)_{2/3}]\cdot Ln_{1/9}\cdot H_2O$ ($Ln^{3+} = Sm^{3+}$, Eu^{3+}, Tb^{3+}, or Dy^{3+}).

Next, luminescence studies were carried out on **IFMC-3** and **Ln^{3+}@IFMC-3**. Upon excitation at 336 nm, **IFMC-3** displays a strong emission with a maximum at about 398 nm (Figure 2 a). The **Ln^{3+}@IFMC-3** ($Ln^{3+} = Sm^{3+}$, Eu^{3+}, Tb^{3+}, and Dy^{3+}) samples display a similar emission in the region

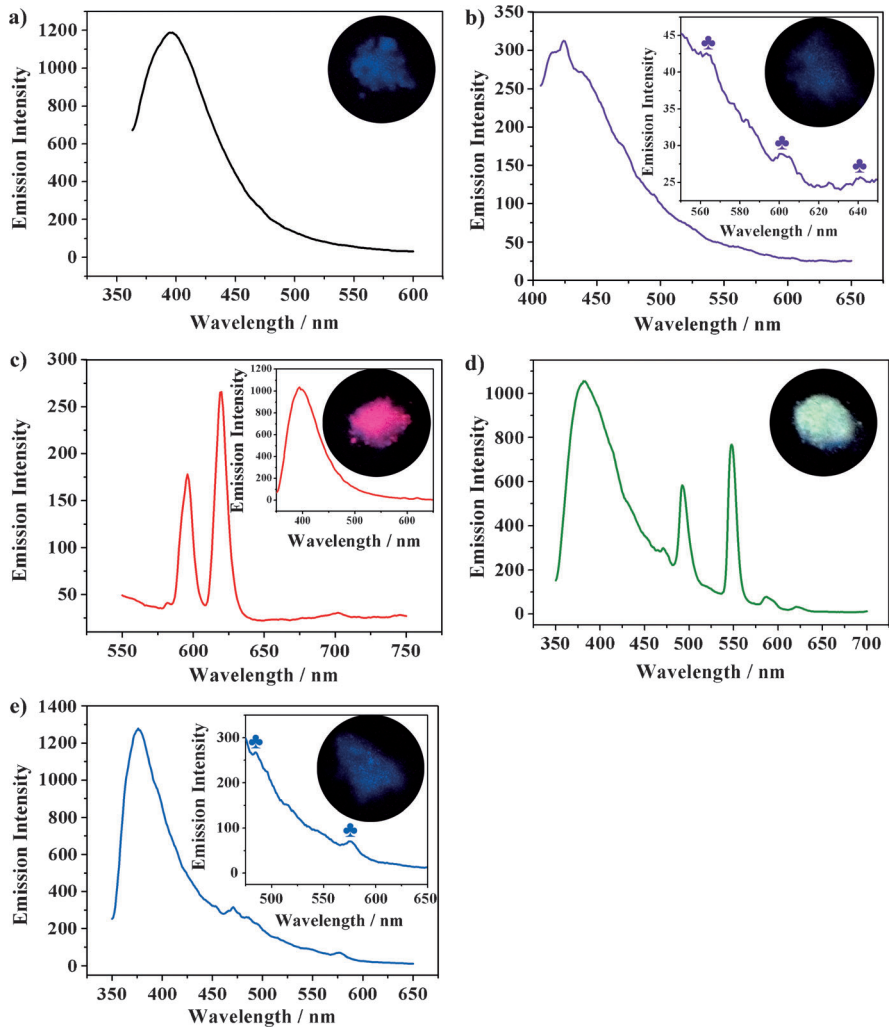

Figure 2. Emission spectra of a) **IFMC-3** ($\lambda_{ex}=336$ nm), b) **Sm^{3+}@IFMC-3** ($\lambda_{ex}=374$ nm), c) **Eu^{3+}@IFMC-3** ($\lambda_{ex}=395$ nm; inset: $\lambda_{ex}=336$ nm), d) **Tb^{3+}@ IFMC-3** ($\lambda_{ex}=276$ nm), and e) **Dy^{3+}@IFMC-3** ($\lambda_{ex}=274$ nm). Insets: Photos of the respective samples illuminated with UV light (365 nm).

of 350–450 nm but with different intensities than that of **IFMC-3** (Figure 2b–e). Under excitation at 374 nm, **Sm^{3+}@IFMC-3** shows a weak characteristic emission at 563, 600, and 641 nm, which can be assigned to the $^4G_{5/2}\rightarrow{}^6H_J$ ($J=5/2$, 7/2, and 9/2) emission transitions (Figure 2b).[17a] The **Eu^{3+}@IFMC-3** sample emits a distinctive red color in the solid state at room temperature upon excitation at 395 nm (Figure 2c). The four emission bands observed at 582, 596, 619, and 702 nm correspond to the characteristic $^5D_0\rightarrow{}^7F_0$, $^5D_0\rightarrow{}^7F_1$, $^5D_0\rightarrow{}^7F_2$, and $^5D_0\rightarrow{}^7F_4$ emission transitions, respectively.[17] The $^5D_0\rightarrow{}^7F_3$ transitions were too weak to be observed. As for **Tb^{3+}@IFMC-3**, an intense green luminescence was clearly observed upon excitation at 276 nm, which was assigned to the characteristic $^5D_4\rightarrow{}^7F_J$ ($J=3$–6) transitions of the Tb^{3+} ions.[18] The two intense emission bands at 492 and 548 nm originate from $^5D_4\rightarrow{}^7F_6$ and $^5D_4\rightarrow{}^7F_5$ transitions, while the weak emission bands at 587 and 620 nm correspond to $^5D_4\rightarrow{}^7F_4$ and $^5D_4\rightarrow{}^7F_3$ transitions (Figure 2d). This kind of visible emission phenomenon has been commonly observed in the published literature. As for **Dy^{3+}@IFMC-3**, two relatively weak emissions at 484 and 576 nm were observed ($\lambda_{ex}=274$ nm, Figure 2e), which can be assigned to the characteristic $^4F_{9/2}\rightarrow{}^6H_J$ ($J=15/2$ and 13/2) transitions of the Dy^{3+} ions. Although the encapsulation amounts of Ln^{3+} ions are similar for **Sm^{3+}@IFMC-3**, **Eu^{3+}@IFMC-3**, **Tb^{3+}@IFMC-3**, and **Dy^{3+}@IFMC-3**, the characteristic emission intensities are very different. Moreover, the microporous **IFMC-3** is suitable for sensitization of Eu^{3+} and Tb^{3+} rather than Sm^{3+} and Dy^{3+} emission. The results indicate that **IFMC-3** can serve as a host for encapsulating different Ln^{3+} ions to exhibit luminescent sensing of Eu^{3+} and Tb^{3+} ions. The successful encapsulation of Eu^{3+} and Tb^{3+} ions can be observed directly by the naked eye through the characteristic red and green color upon excitation with a standard UV lamp ($\lambda_{ex}=365$ nm) of the Eu^{3+} and Tb^{3+}-doped samples, respectively (Figure 2, insert).

Inspired by the reported solvent-dependent luminescence of aromatic ligand-based MOF materials with porosity,[11] the luminescent behavior of **IFMC-3** was investigated by suspending fresh samples into different pure organic solvents. It can be clearly seen from the spectra shown in Figure 3 that its luminescent behavior is strongly dependent on the solvent used. The emission of **IFMC-3** in different solvents is blue-shifted compared with that of the powder sample, which perhaps can be attributed to a solvent effect. The luminescent intensity is significantly enhanced in benzene, while a quenching effect is observed in nitrobenzene. Thus, **IFMC-3** might be a potential luminescent probe for the detection of explosives containing nitrobenzene.

Furthermore, fluorescence detection experiments were performed in order to examine the sensing sensitivity towards nitrobenzene in more detail. A batch of suspensions of **IFMC-3** in *N*,*N*-dimethylacetamide (DMA) with gradually increasing nitrobenzene concentration was prepared and the corresponding emission spectra were recorded. As shown in Figure 4a, the emission intensity was significantly

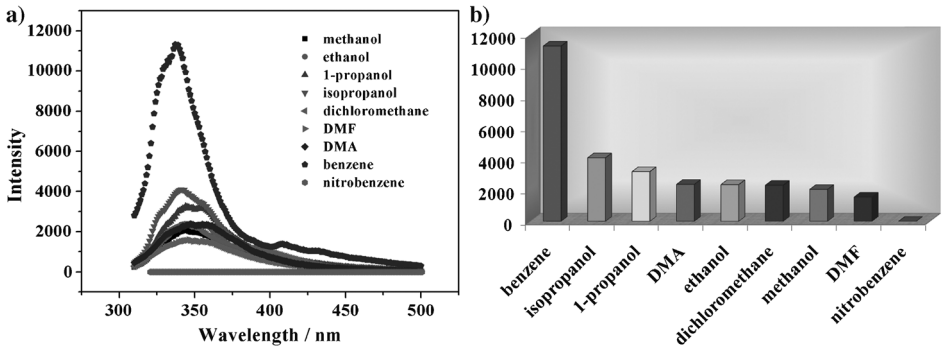

Figure 3. a) Luminescence spectra and b) emission intensities of **IFMC-3** powders suspended in various pure organic solvents upon excitation at 282 nm.

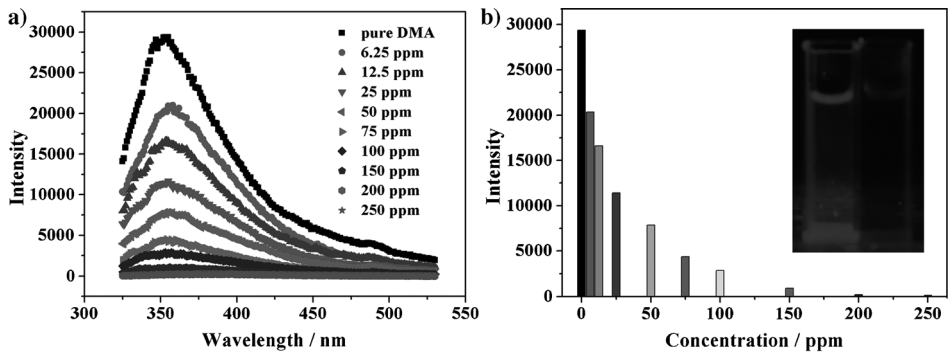

Figure 4. a) Emission spectra and b) emission intensities of **IFMC-3** at different concentrations of nitrobenzene in DMA ($\lambda_{ex}=292$ nm). Inset: Photograph showing the fluorescence quenching upon the addition of nitrobenzene under illumination with UV light (365 nm).

quenched (ca. 99.2%) at 200 ppm nitrobenzene. It can be clearly observed that the fluorescence intensity is decreasing with increasing nitrobenzene concentration in the range of 0–250 ppm (Figure 4b). The blue luminescence of the dispersed solution of ground **IFMC-3** powders under irradiation with UV light completely disappeared upon addition of nitrobenzene solution (inset in Figure 4b). The ground powders could be dispersed well in the analyte solution, which enables nitrobenzene to be adsorbed on the surface of **IFMC-3** particles, thereby facilitating possible host–guest interactions. Hence, electron transfer from the electron-donating framework to the electron-deficient analyte can take place upon excitation, thus leading to fluorescence quenching. Similar quenching phenomena were reported previously.[19] **IFMC-3** can be recycled by centrifuging the solution after use, followed by washing several times with DMA. The quenching efficiencies in cycles 1–6 were basically unchanged at around 99% (200 ppm), demonstrating the good recyclability and stability of **IFMC-3** for detection applications (Figure S10, Supporting Information). Analysis of the XRD pattern and FTIR spectrum recorded after the detection of nitrobenzene (Figures S11 and S12, Supporting Information) confirmed that the framework of **IFMC-3** was unaffected. The detection sensitivity of **IFMC-3** towards nitrobenzene was found to be comparable or superior to other coordination polymers as platform.[20]

In conclusion, a microporous anionic MOF with a honeycomb shape and a new (3,4)-connected topology, **IFMC-3**, was successfully constructed. **IFMC-3** is stable in air as well as in acidic/basic aqueous solution in the pH range of 2–12 at ambient temperature. **IFMC-3** can serve as a host for the encapsulation of Ln^{3+} ions, exhibiting luminescent sensing with preference toward Eu^{3+} and Tb^{3+} over Sm^{3+} and Dy^{3+} ions. In addition, a significant quenching effect of **IFMC-3** is observed in the presence of trace amounts of nitrobenzene, which suggests that it is a potential luminescent probe for the detection of nitrobenzene. This study thus presents a promising example of dual functional materials with high chemical stability for sensing different Ln^{3+} ions and detecting nitrobenzene. Extension of the tetrazole-based ligand and phosphite ion to MOFs that have channels larger in size and studies on their potential functional applications are currently underway.

Experimental Section

*Preparation of **IFMC-3***

Three drops of aqueous H_3PO_3 (50%) were added to a mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.12 g, 0.40 mmol) and HL (0.05 g, 0.60 mmol) in DMF (5 mL) with stirring. The mixture was heated at 85 °C for 72 h and then cooled to room temperature. Colorless crystals (0.07 g) were collected and dried in air (80% yield based on $Zn(NO_3)_2{\cdot}6H_2O$). IR (KBr, Figure S4, Supporting Information): $\tilde{\nu}=3503$ (w), 2373 (w), 1621 (m), 1505 (s), 1400 (s), 1283 (w), 1119 (s), 1020 (s), 695 (m), 563 (m), and 413 cm^{-1} (s); elemental anal. calcd (%) for $C_6H_{12.67}N_{12}O_{3.33}P_{0.67}Zn_2$ (457.67): C 15.75, H 2.79, N 36.73; found: C 15.63, H 2.85, N 36.59.

Acknowledgements

This work was financially supported by Pre-973 Program (2010CB635114), the National Natural Science Foundation of China (No. 21001020 and 21371099), Key Project of Science and Technology Department of Jilin Province (No. 20126019), the Jiangsu Specially-Appointed Professor, the Natural Science Research of Jiangsu Higher Education Institutions of China (No. 13KJB150021), the Priority Academic Program

Development of Jiangsu Higher Education Institutions, the Foundation of Jiangsu Collaborative Innovation Center of Biomedical Functional Materials and Graduate Innovation Fund of Jilin University (No. 20121048), and the Science and Technology Development Planning of Jilin Province (No. 20140520089JH).

Keywords: lanthanides · luminescence · metal–organic frameworks · nitrobenzene · sensors

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Received: November 14, 2013
Revised: November 30, 2013
Published online: January 8, 2014

