Photocatalytic and Ferric Ion Sensing Properties of a New Three-Dimensional Metal–Organic Framework Based on Cuboctahedral Secondary Building Units

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* Supporting Information

ABSTRACT: A new three-dimensional microporous metal–organic framework based on Zn(II) clusters with the formula \([\text{Zn}_4\text{(NDC)}_3(\mu_4-\text{OH})_3] \cdot 7\text{DMF}\) \(_n\) (1) (H\(_2\text{NDC}\) = 1,4-naphthalenedicarboxylic acid) had been synthesized and characterized. The MOF 1 displays an uncommon bsn topology, which is based on a unique heptanuclear Zn\(_7\)(OH)\(_3\)(CO\(_2\))\(_{11}\) cluster as a secondary building unit. The MOF had been employed as a photocatalyst for the photodegradation of model organic dyes rhodamine B and methyl violet in light. The results of photocatalytic experiments showed that 1 can successfully be employed as the photocatalyst for the benign decomposition of these dyes. A mechanism for the photolysis exhibited by 1 had been proposed using the results of density of states (DOS) and partial DOS calculations. The fluorescence properties of the MOF have been investigated, which revealed that 1 could be exploited as the luminescent sensor to recognize Fe\(^{3+}\) ions with perceptible quenching (\(K_{sv} = 6.55 \times 10^4 \text{ M}^{-1}\)) and a limit of detection of 1.16 ppm.

INTRODUCTION

Recently, as a subclass of coordination polymers, metal–organic frameworks (MOFs) with porous structures have been considered to be capable of absorbing light radiation, because of which these systems behave as promising photocatalysts.1,2 The preliminary investigation on such systems was focused on the photocatalytic activity associated with MOF-5 for the degradation of phenol in ultraviolet (UV) light.3 Later, the usage of MOFs as a photocatalyst have been focused on the safe and sustainable degradation of organic contaminants, for example, a porous MOF, UTSA-38, with \([\text{Zn}_2\text{O}(2,6-\text{nrdc})_3(\text{DMF})_3(\text{H}_2\text{O})_{0.3}]\) units had been utilized in photodegrading methyl orange (MO) in aqueous medium.4 In addition, a stable material, UiO-66(\(\text{NH}_2\)), displayed visible-light-responsive photocatalysis for decomposing organic dyes.5 Numerous examples have confirmed that the optical properties of MOFs can be tuned to improve their light-harvesting properties, and hence they can act as hosts for other photosensitive molecules.5,6 Duan and co-workers have suggested that MOF-based photocatalysts on the basis of their active fragments can be classified into three categories: (i) the 0D inorganic cluster nodes containing MOFs, which behave like semiconductor dot photocatalysts, usually described as isolated semiconductor dots; (ii) the functional dye-based photocatalysts composed of linkers, which are alternatively termed as heterogeneous dye-based photocatalysts; and (iii) the photocatalytic MOFs that contain different pores that are taken as regularly distributed supramolecular systems.5,6,7 Despite many interesting reports, this research field is still considered to be an emerging area as many important concerns associated with the MOFs, viz. activity, efficiency, and stability, need additional exhaustive investigation.5,6

The luminescent MOFs (LMOFs) have been considered as outstanding sensors due to their intriguing structural feature and detectable fluorescence properties, which can be clearly altered.5 Li and co-workers first reported an LMOF that was capable of detecting traces of explosives in the vapor phase.7 To obtain an efficient sensor to detect various analytes, the rational design and syntheses of targeted MOFs have been

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creating interest among chemists involved in the syntheses of coordination polymers/MOFs. A general strategy that is utilized to make targeted MOF-based materials is the careful designing of the ligands, which can give rise to desired metal clusters. In this context, some simple organic aromatic carboxylic ligands (e.g., 1,4-naphthalenedicarboxylic acid) are appropriate candidates for the preparation of new LMOFs. Some recent reports have indicated that the luminescent behavior in LMOFs usually arises due to different electronic transitions, viz. ligand-to-ligand charge transfer (LLCT), ligand-to-metal charge transfer (LMCT), metal-to-ligand charge transfer (MLCT), and metal-to-metal charge transfer (MMCT). Also, the luminescent sensing of the analytes by LMOFs arises because of the Förster resonance energy transfer (FRET), Dexter electron exchange (DEE), and photoinduced electron transfer (PET). Although examples of MOFs with diversified topological properties are numerous, but MOFs composed of microporous voids and possessing good thermal stability with strong luminescent properties, which are based on host–guest chemistry, are less reported.7

A previous report indicated that the photocaltactic properties in MOFs are arising due to their structures, which include their topological features, pore size, and structural stability.8 To prepare targeted MOFs with desired topology, pore size, and stability, an aromatic dicarboxylate ligand, 1,4-naphthalenedicarboxylate (NDC), is usually selected as a possible ligand system. This is because the rodlike NDC ligand possesses an interesting feature that favors the versatility of its application (Scheme 1). Moreover, the metal ions are coordinated through polytopic multicarboxylate linkages, which thereby results in M–O–C-type clusters in which the carboxylate carbon groups are capable of modulating the shape of the secondary building unit (SBU). Yaghi et al. proposed such strategy and successfully synthesized two three-dimen-

![Scheme 1. Chemical Structure of the H2NDC Ligand and Perspective View of the Two Coordination Modes of NDC Ligands in the Zn(II) MOF Presented in This Study](image)

sional (3D) metal carboxylate frameworks constructed by linking Zn(II) centers to the NDC ligand and m-benzene dicarboxylate ligand to yield MOF-48 and MOF-49, respectively.10 The two MOFs exhibited pentagonal antiprismatic and cuboctahedral SBUs.9 Later, it has been found that the Zn(II) assemblies composed of multicarboxylate ligands are suitable in producing various types of clusters, viz. Zn2, Zn3, Zn4, Zn5, Zn6, Zn7, Zn8, and Zn9.8–10

As part of our continuous effort in this direction,12 in the presented work, NDC was selected as the ligand to coordinate with Zn(II) ions to construct a new MOF with the formula \([\{\text{Zn}_7(\text{NDC})_{5.5}(\mu_4\text{OH})\}_7\text{DMF}\}_n\) (1) within an appropriate template reagent. The newly synthesized MOF possesses a heptanuclear \(\text{Zn}_7(\text{OH})_3(\text{CO}_2)_11\) cluster as the SBU. The MOF 1 not only possesses interesting sensing activity but also displayed photocatalytic activity against organic dye degradation and sensing properties for ferric ions. The results of these investigations are presented in this report.

## RESULTS AND DISCUSSION

### Crystal Structure Description. \([\{\text{Zn}_7(\text{NDC})_{5.5}(\mu_4\text{OH})\}_7\text{DMF}\}_n\) (1)

The single-crystal X-ray diffraction (XRD) studies indicated that 1 displays a 3D framework, which encompasses 1D channels along the [010] direction. These 1D channels are occupied by free dimethylformamide (DMF) molecules. The MOF is composed of a heptazinc secondary building unit (SBU) with 11 peripheral carboxylates, which is different from the SBU existing in the \(\text{Zn}_7(\text{m-BDC})_n(\text{OH})_3(\text{H}_2\text{O})_2\)·6DMF·4H2O (MOF-49) \((\text{m-BDC} = 1,3\text{-benzenedicarboxylate})\) entity containing 10 carboxylic acids. Additionally, the SBU for 1 is different in comparison to other heptazinc SBUs, viz. \([(\text{CH}_3)_2\text{NH})_2\text{Zn}_7(\mu_4\text{OH})_5(\text{NDC})_4\] and \{(\text{EMIM})_2[\text{Zn}_7(\mu_3\text{O})(\text{NDC})]_6\}^{11}\text{DMF}\) as both the previously reported SBUs had been assembled by utilizing two equivalent oxygen-centered \(\text{Zn}_n(\mu_3\text{O})\) tetrahedrons with 10 NDC ligands. In MOF 1, the seven Zn(II) centers are connected together by two \(\mu_4\text{-OH}\) groups and capped by 11 carboxylate groups from 11 NDC ligands (Figure S1). The NDC ligands exhibit \(\mu_4\text{-OH}\) and \(\mu_4\text{-OH}^\text{–}\text{N}^\text{–OH}\) modes in 1 (Scheme 1), which is similar with that of the previous reports (Table 1).11 In addition, there is one terminal –OH group coordinated with one Zn(II) as a charge balanced part of \(\text{Zn}_n(\mu_4\text{OH})_5(\text{CO}_2)_11\) (Figure 1a,b). After carefully analyzing the SBU, it can be inferred that in addition to the five Zn(II) centers with a tetrahedral geometry \((\text{Zn}_5, \text{Zn}_6, \text{Zn}_7, \text{Zn}_8, \text{and Zn}_9)\), one five-coordinated Zn(II) with a trigonal bipyramidal geometry \((\text{Zn}_4)\) and another Zn(II) with an octahedral geometry \((\text{Zn}_3)\) also exist in the SBU (Figure 1b and Figure S1). The \(\text{Zn}--\text{Zn}\) distance in the SBU is in the range 3.13–3.27 Å, indicating no significant interactions between Zn(II) centers. The capping hydroxyl oxygen centers are lying slightly above (0.62 Å) and below the Zn cluster plane with ca. 338° sum of angles around O2. The 11 peripheral NDC ligands around the SBU in 1 can be divided into six groups; 10 NDC ligands are classified into five groups of two ligands each, while the eleventh NDC ligand is classified as a separate group as it is disordered over two positions. Each group bridges the SBU with another SBU, so the \(\text{Zn}_n(\text{OH})_3(\text{CO}_2)_11\) SBU extended out to six other SBUs through these ligands (Figure 1c). In this manner, a 3D three-periodic MOF with bsn topology is constructed with these six-connected SBU and NDC ligands (Figure 1d–f and Figure S2). The face-to-face and centroid–centroid distances between lateral and middle rings are \(\sim 3.58\) and 3.81 Å, respectively.
Table 1. Representative MOFs Composed of the NDC Ligand

| formula                                      | bridging mode | motif            | application                                      | refs  |
|----------------------------------------------|---------------|------------------|-------------------------------------------------|-------|
| [Zn₆(4-ppt)₃(NDC)₆]₉⁺                          | µ₄-η¹'η¹'η⁴     | 3D (6.87,7)     | fluorescent sensor                               | 11a   |
| [Eu₃(Zn₂⁺(µ₃-OH)₃(NDC)₃(H₂O)₆]₉⁺              | µ₄-η¹'η¹'η¹     | 3D pcc topology | detection of antibiotics in aqueous solution     | 11b   |
| [Zn₆(µ₃-OH)₂(NDC)₆(dpp)₁₂]₁⁺                   | µ₄-η¹'η¹'η¹     | 3D (3.4,5,6)    | photoluminescence property                       | 11c   |
| ([Zn₆(NDC)₂(3-abpt)₂2DMF]₁⁺                   | µ₄-η¹'η¹     | 2D (4°⁰)       | multifunctional sensors (Fe⁺³ and TNP)          | 11d   |
| ([Zn₆(H₂O)(NDC)₆(ipcb)]₁⁺                     | µ₄-η¹'η¹'η¹     | 3D (10-12):(10-12) | photocatalytic activity of methyl orange and methyl blue | 11e   |
| [Co₆(µ₃-H₂O)₃(NDC)₆(dpbb)₁₂]₁⁺                | µ₄-η¹'η¹'η¹     | 3D (3.11,5,6)   | antiferromagnetic coupling                      | 11f   |
| ([Co₆(µ₃-OH)₃(NDC)₆(btp)]₁⁺                   | µ₄-η¹'η¹'η¹     | 3D self-penetrating (4°⁰,6°) | antiferromagnetic exchanges                  | 11g   |
| ([CH₃₂NH₂]₂[Ni₄-O]₆(NDC)₆]₁⁺                   | µ₄-η¹'η¹'η¹     | 3D bcu topological net | sensors for acetone and chloroform              | 11h   |
| [Zn₆(µ₃-OH)₂(NDC)₆(1,4-bix)]₁₂                | µ₄-η¹'η¹'η¹     | 3D (3.4,5,6)    | photoluminescence property                      | 11i   |
| [Zn₆(btz)₆(NDC)₆(H₂O)]₁₂                     | µ₄-η¹'η¹'η¹     | 3D mdi topology | sensors for metal ions and small molecules      | 11j   |
| ([EMIM]₁[Zn₆(µ₃-O)₂(NDC)₆]₁⁺                  | µ₄-η¹'η¹'η¹     | 3D bcu (4°³)    | photoluminescence property                      | 11k   |
| ([Zn₆(µ₃-O)₂(NDC)₆(DMF)]₁⁺                   | µ₄-η¹'η¹'η¹     | 3D (4°³)       | photoluminescence property                      | 11l   |
| 1                                               | µ₄-η¹'η¹'η¹     | 3D bsn topology | sensors for metal ions and photocatalytic activity | this work |

Figure 1. (a, b) Zn₆(µ₃-OH)₂(CO₂)₁₁ SBU. (c) Six-connected SBU extended out with 11 NDC ligands. (d) Simplified bsn topology. (e) Pore surface of the MOF simulated by Material Studio. (f) Tiling of the bsn topology.

which indicates substantial π···π interaction. It has been observed the assemblies of Zn(II)/Co(II) with the NDC ligand are suitable to form a variety of cluster systems, viz. Zn₂, Zn₃, Zn₄, Zn₅, Zn₆, Zn₇, and Zn₈ (Table 1), and such MOFs have been used as photocatalysts, sensors, and magnetic materials.¹¹ It should be noted that some complexes possessing the heptanuclear [Zn₆(µ₃-O)(µ₃-COO)]₁₀ SBU with one octahedral and six tetrahedral zinc centers had been constructed using mixed coligands. The sites of the heptanuclear cores are occupied by a terminal and/or bridging nitrogen center containing ligands.¹¹k The MOF 1 is composed of a window of channels along the a direction with a diameter of 3.75 Å. In addition, a cavity with a diameter of about 6.7 Å can be found in these channels (Figure 1e). Also, 1 exhibits 33.8% porosity when calculated with a probe radius of 1.8 Å. The MOF was activated using high vacuum at 80 °C for 12 h before nitrogen sorption isotherm test was executed at 77 K. The adsorption isotherm for the MOF 1 demonstrated typical type I sorption characteristics (Figure S6). The small uptake of nitrogen at 77 K and at atmospheric pressure indicated that the pore channels in the MOF are pre-occupied because of the orientation of the naphthalene ring toward the inward direction of the pores.¹¹k,¹²

FTIR, Powder X-Ray Diffraction, and Thermal Stability Analyses. The FTIR spectrum for 1 display bands at 1666, 1557, 1421, 1366, and 1256 cm⁻¹, which corresponds to the NDC ligand (Figure S3). The band around 3200 cm⁻¹ can be attributed to the hydroxyl groups. In the powder X-ray diffraction (PXRD) pattern for 1, the main peak positions are almost consistent with the simulated pattern. However, the additional peaks in the PXRD pattern at 2θ = 12° and 21° did not exist in the simulated PXRD pattern, which indicates that 1 is mixed with other crystalline phases (Figure S4). The intensity differences in the PXRD pattern may be arising because of the differences in the orientations of the microcrystalline material in the finely divided powder. The thermogravimetric analysis (TGA) for MOF 1 exhibited weight loss in three distinct steps (Figure S5). The first weight
loss commenced at room temperature and ended at 205 °C, which agrees well with the loss of free DMF molecules (24.1%; calcd 23.3%). The second weight loss from 230−290 °C can be ascribed to the decomposition of the hydroxyl groups and two NDC ligands, and finally the third weight loss can be attributed to the remaining NDC ligands, leading to the formation of ZnO (28.6%; calcd 26.5%).

**UV−vis and Diffuse Reflectance Spectroscopy.** The UV−vis spectroscopy for 1 had been performed in the solid state at room temperature (Figure S7). The UV−vis spectrum indicated a band at 316 nm, which may be arising because of the π → π* transition taking place in the NDC ligand. Additionally, diffuse reflectance spectroscopy for 1 was also performed. The Kubelka−Munk equation had been used to correlate the absorption coefficients of the allowed band gap in 1. The band gap energy ($E_g$) of 3.5 eV for MOF 1 had been calculated by extrapolating the linear region of absorption edge (Figure S7b). Therefore, the diffuse reflectance spectroscopy indicates that MOF 1 possesses potential to act as a photocatalyst for photodegradation.13−17

**Photocatalysis.** Crystals can be seen as a small bulk that grew in a spherical pattern in few micrometer (2−30 μm) sizes (Figure S7). On the basis of the band gap energy, it can be inferred that 1 can behave as a semiconductor on exposure to light and therefore can act as a photocatalyst.18,19 Therefore, to assess the suitability of 1 as a photocatalyst to photodegrade aromatic dyes, two model organic dyes (MV and Rh B) were selected as model aromatic dyes (MV and Rh B) were selected as model aromatic dyes (MV and Rh B) were selected as model aromatic dyes (MV and Rh B) were selected as model aromatic dyes (MV and Rh B). In the typical photocatalytic process, 2 mg of the photocatalyst (MOF 1) was suspended in 250 mL aqueous solutions of MV or Rh B with a concentration of 1.5 × 10−4 M. Thereafter, the mixture was stirred in the dark for ~30 min to establish an adsorption/desorption equilibrium. Thereafter, these mixtures were then exposed to UV light by using a 400 W Hg lamp with continuous stirring of the solution. After every 5 min time intervals, aliquots of 5 mL were taken out from the reaction mixture, and their UV−vis spectra were recorded. Also, the photodegradation of MV and Rh B without adding photocatalyst 1 was also studied for comparison under identical reaction conditions. The results of photocatalysis displayed by 1 are presented in Figure 2. The plots between $C_t/C_0$ for MV and Rh B versus reaction time (wherein $C_0$ is the initial concentration of the MV or Rh B and $C_t$ is t time’s concentration of the dye) have been constructed (Figure 2b,d), which indicate that under strong illumination by a 400 W Hg lamp, the model organic dyes MV and Rh B underwent decomposition to some extent even in the absence of photocatalyst 1. However, in the presence of 1, the shortened photodegradation time indicates that 1 is an effective catalyst that can be used to decompose MV and Rh B under UV light irradiation. A control experiment on the photodegradation of MV and Rh B was conducted in the same condition without light irradiation (Figure S9). There is no obvious change in the degradation of dyes without light irradiation, which indicated that the presence of light irradiation is important for the efficient degradation of dyes. Some MOFs were examined as photocatalysts to degrade organic pollutants under UV, visible, or UV−vis light. Table S2 lists some of these MOFs, which showed good photocatalytic performances for the degradation of organic pollutants. After photocatalysis experiments, 1 was filtered and characterized using PXRD (Figure S4) and IR (Figure S3). The results of PXRD and IR indicated nearly identical PXRD pattern and IR bands as can be obtained for the as-synthesized 1. Based on
current results, the repeated photocatalytic degradation of MV was explored, and the degradation rates of 1 exhibited no significant decrease when the photocatalyst was used five times in the same condition, which indicated that the photocatalytic activities have well reproducibility (Figure S10).

The photocatalytic mechanism is complicated, which usually involves the generation of OH radical in the reaction mixture for photodegradation. Hence, to check whether there is involvement of OH radical in the degradation process or not, the photocatalytic reactions were carried under the same reaction conditions using 1 along with thiourea, which is considered to be a good OH scavenger. The results of this experiment indicated that the catalytic activity associated with 1 disappeared (Figure S11). Therefore, it had been inferred that OH radicals play a key role for the degradation of aromatic dyes. During photocatalysis, in the presence of UV−vis light, the electronic excitation take place from HOMO → LUMO in photocatalyst 1 to produce oxygen−metal charge transfer. This excited state gets deactivated by oxidizing the pollutants and/or oxidizing the water molecules to OH radicals to accomplish the photocatalytic process (Scheme S1).

To establish the mechanism for MOF 1 assisted degradation of dyes under irradiation, the density of states calculations based on DFT (density functional theory) have been performed to assess the band structure of 1 (Figure 3). As indicated in Figure 3, the aromatic carbon centers and oxygen centers of the carboxylate groups are the major contributors in the valence band of the MOF. In addition, the band is also having meagre contribution from zinc centers. The conduction band of the MOF in the range of −0.97 to −0.44 eV is again having contribution from carbon centers in major and with minor contribution coming from oxygen. Hence, density of states plots indicate that electronic transitions in the MOF is operating from one naphthalene center to other naphthalene centers of the carboxylate groups are the major contributors in electronic transitions of the MOF in the range of −1.16 to −0.44 eV.

In other words, during photoexcitation, there is an occurrence of charge transfer from HOMO → LUMO to generate a hole at the HOMO. The electron-deficient HOMO will now strongly require an electron to revert back to the ground state. Therefore, an electron is captured by the photocexcited MOF from the water molecule, which therefore produces the OH radical. These OH radicals are capable of decomposing the organic dye efficiently to accomplish the photocatalytic decomposition. The plausible mechanistic pathway that may be operating during the photodecomposition of dyes in the presence of 1 can be presented as follows:

\[
\begin{align*}
1 \rightarrow & \ 1^* \ \text{i.e., } 1(h^+ + e^-) \quad (1) \\
1(h^+ + e^-) + H_2O \rightarrow & \ 1(e^-) + HO + H^+ \quad (2) \\
HO + MV \rightarrow & \ \text{oxygen products} \rightarrow CO_2 + H_2O \quad (3) \\
1(e^-) + O_2 \rightarrow & \ 1(O_2^-) \quad (4) \\
O_2^-/HO_2 + S \rightarrow & \ \text{oxygen products} \quad (5)
\end{align*}
\]

**Luminescence Sensing.** The LMOFs are attracting research interest as luminescent materials as they offer application as ion sensors. With this aspect in mind, the suspension of MOF 1 was treated with different metal nitrate solutions with concentrations of 10−2 M, and thereafter luminescence intensity measurements for all the M+n@1 suspensions were done (Figure 4a and Figure S12). The experiments revealed that the luminescence intensity of M+n@1 vary with the change in the nature of the M+n. In most of the M+n@1 suspensions (especially Pb2+ and Cd2+), the luminescence intensity of 1 was almost unaltered, while in Fe3+@1, the quenching in the luminescence intensity was observed. Alternatively, it can be stated that Fe3+ ions displayed a maximum alleviating effect on the luminescent intensity of the MOF 1, which almost lead to quenching in emission (Figure 4a).

The luminescent intensity of 1 declined to the maximum extent in the presence of Fe3+ ions. Hence, luminescent intensity measurements for MOF 1 on incremental addition of Fe3+ (in parts per million (ppm)) have been executed (Figure 4b), and using this titration experiment, the Stern−Volmer (S−V) curve had been plotted (Figure 4c). The S-V plot for Fe3+ is almost linear when the Fe3+ concentration is low with the Ksv value of 6.55 × 104 M−1 (Figure 4c). The Ksv value of Fe3+ reported in the presented work is as good as those previously reported for LMOFs (Table S1). On the basis of the S-V plot, the limit of detection (LOD) for Fe3+ is 1.16 ppm. It had been documented that the Fe3+ cations compete to absorb light radiation with organic molecules and hence can decrease the extent of energy transfer that is taking place from the ligand toward the ions. To validate this, the electronic absorption spectrum for the H2NDC ligand was recorded, which displayed λmax at 256 nm. This band is largely overlapped by the electronic absorption band of Fe3+ (Figure S13). Hence, on excitation, there will be competitive absorption of radiation between Fe3+ and the NDC ligand in between 250 and 350 nm. On the basis of this spectral overlap analyses, the quenching behavior in Fe3+@1 may be ascribed to be arising because of the photoinduced electron transfer. Furthermore, the luminescence lifetime of 8.36 ns in 1 was reduced to 3.81 ns when 1.0 mM Fe3+ solution was added to it (Figure S14). Therefore, the lifetime measurements further suggest that Fe3+ ions are incorporated into the defect sites in 1.

Additionally, to explicate the plausible mechanism for the observed quenching in the luminescence of 1 by Fe3+ ions, O 1s X-ray photoelectron spectroscopy (XPS) studies were performed on 1 and Fe3+@1 (Figure S15). The O 1s peaks for the oxygen centers observed at 530.79 eV in 1 shifted to

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**Figure 3.** Density of states (DOS) and partial DOS plots for MOF.
531.66 eV for Fe³⁺@1 (Figure S15b). These results indicate the Fe³⁺ ions may bind with the bridging hydroxyl groups and the carboxylate oxygens, which may also be responsible for the emission quenching in 1.

■ CONCLUSIONS

A new Zn(II)-based 3D metal–organic framework with bsn topology embracing cuboctahedral secondary building units had been derived from 1,4-naphthalenedicarboxylic acid (H₂NDC). The MOF 1 displayed photocatalytic properties to photodecompose model organic dyes MV and Rh B under UV irradiation. In addition, the MOF is a selective and sensitive sensor for ferric ions with reasonably good $K_v$ values and low limits of detection. Our investigation indicated that by changing the stoichiometric ratio between same metal salts and ligands and also altering the reaction conditions, a new 3D architecture in MOFs can be obtained, which possess various topologies and different kinds of channels. Such strategy is useful in developing MOFs that offers tunable luminescence properties and thus can be used as sensors for the detection of ions/molecules and also be utilized as a heterogeneous photocatalyst for the decomposition of organic dyes.

■ MATERIALS AND METHODS

The crystallographic and other computational details are reported in the Supporting Information.

Synthesis of $\{[	ext{Zn}_7(\text{NDC})_{5.5} (\mu_4-\text{OH})_3] \cdot 7 \text{DMF}\}_{n}$ (1). A mixture containing H₂NDC (0.10 mmol), 2,5-bis(3′,5′-dicarboxyphenyl)benzoic acid (0.05 mmol), and Zn(NO₃)₂·4H₂O (0.15 mmol) in 15 mL of DMF was stirred for 30 min. The obtained reaction mixture was thereafter transferred to a 25 mL Teflon-lined reactor, sealed, and then heated to 100 °C for 72 h. Then, the reaction mixture was cooled down to room temperature with a cooling rate of 5 °C/h. The crystals of MOF 1 were obtained in 30% yield on the basis of Zn. IR (cm⁻¹): 3320 (m), 2352 (m), 1666 (m), 1557 (vs), 1421 (v), 1366 (m), 1256 (vs), 1073 (m), 809 (v), 654(m). Analysis calculated for C₈₇H₈₂O₃₂N₇Zn₇: C 47.59, H 3.76, N 4.47%; found: C 47.01, H 3.33, N 4.02%.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01008.

Materials and methods, characterization data, X-ray crystallography, computational details, photocatalytic methods, photoluminescence measurement methods, gas adsorption analysis, SEM, UV–vis, XPS, photocatalytic mechanism, tables presenting comparative detection sensitivity for Fe³⁺, and comparison of performances of some MOFs as photocatalysts for the degradation of organic pollutants in aqueous medium (PDF)

X-ray crystal details for MOF 1 (CIF)

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Figure 4. (a) Photoluminescence intensity of suspension of 1 in the presence of different $10^{-2}$ M metal ion solutions ($\lambda_{ex} = 320$ nm). (b) Emissive response of 1 when variable concentrations of Fe³⁺ solutions were added. (c) Stern–Volmer plot for Fe³⁺@1.
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Notes
The authors declare no competing financial interest.

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