

## Anthracene Dicarboxylate-Based Metal-Organic Framework Gel with $\text{Zn}^{2+}$ as a TNT Sensor

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Organogels and hydrogels composed from small molecules or 'low molecular weight gelators' (LMWGs), which are linked into fibers by supramolecular interactions are current topics of great interest. Supramolecular gels have been studied as soft materials for use in applications such as drug-delivery systems, tissue engineering, sensing devices, separation and optoelectronic devices.<sup>1-17</sup> The incorporation of labile metals or anions within these supramolecular gels is of particular importance because metallogels and coordination polymer gels with metal-organic framework structures have widespread applications in areas such as redox responsiveness,<sup>18,19</sup> catalytic action,<sup>20,21</sup> absorption,<sup>22,23</sup> emission,<sup>24-27</sup> magnetism,<sup>23</sup> and electron emission.<sup>21</sup> In addition, the gels composed of a metal-organic framework (MOF) structure can be rapidly, efficiently, and easily prepared under mild conditions in comparison to a typical crystalline MOF with similar properties.<sup>28</sup>

To date, the literature has contained little information regarding the photoluminescence properties and the sensing ability of MOF-based gels, including switching of the emission color, field emission and light emitting properties.<sup>24-27</sup> In view of the high photoluminescence quantum efficiencies of anthracene derivatives used as fluorescent dyes,<sup>28</sup> such compounds may be expected to exhibit interesting spectroscopic and sensing properties for specific guest molecules. In particular, the sterically hindered ligand in the MOF may force unusual coordination geometry around the metal atoms, which are crucial for a number of applications. We chose an anthracene-based ligand as the framework for the attachment of the ligand. Herein, we describe an approach for the preparation of a MOF gel with  $\text{Zn}^{2+}$  ion and its sensing ability for the TNT molecule. Interestingly, its fluorescence intensity is enhanced upon the formation of MOF gel **1** with  $\text{Zn}^{2+}$ , relative to sol **1** in organic solvents. The MOF gel **1** with  $\text{Zn}^{2+}$  selectively recognized the TNT molecule.

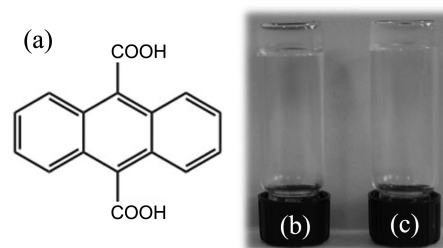
Ligand **1** was conveniently prepared in a one-pot synthesis according to methods described previously.<sup>29</sup> The MOF gel based on **1** was prepared by dissolving 3% (by weight) of **1** in organic solvents in a final volume of 100-500  $\mu\text{L}$ .

To this solution was added a small volume (100-500  $\mu\text{L}$ ) of metal ions in water in concentrations varying from 1.0-3.0 equivalents with respect to the ligand concentration. The

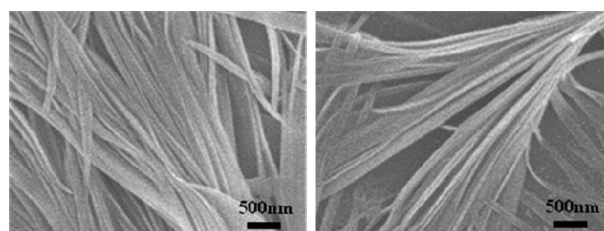
samples were then left to stand for a week at room temperature. Tables S1 summarize the results of a gelation test of **1** in the presence of transition metal ions (3.0 equivalents) with several organic solvents. Opaque gel **1** was obtained only with  $\text{Zn}(\text{ClO}_4)_2$  in DMSO and DMSO/*p*-xylene (1:1 v/v) (Figure 1).

The effect of anions other than  $\text{ClO}_4^-$  on the gelation ability of **1** was examined under the same conditions. In the presence of the halide counter ions  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ , **1** could not gelate (Figure S1). This outcome reflects the stronger Hofmeister effect of  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ , as opposed to that for  $\text{ClO}_4^-$ . The strong Hofmeister effect of the halide anions prevented gelation due to high solubility in organic solvents. Thus, the MOF gel formation of **1** is strongly dependent on the nature of the anion in the zinc salt.

The morphology of xerogel **1** obtained with  $\text{Zn}(\text{ClO}_4)_2$  was investigated by scanning electron microscopy (SEM). The SEM image of MOF gel **1** with  $\text{Zn}^{2+}$  clearly displayed the fiber structure with diameter of 100-200 nm and lengths of several micrometers (Figure 2).



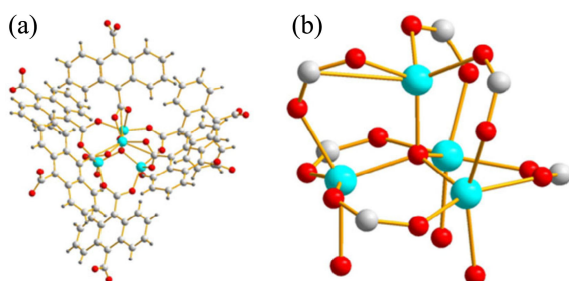
**Figure 1.** (a) Chemical structure **1** and photograph of MOF gel **1** with  $\text{Zn}^{2+}$  in; (b) DMSO, (c) DMSO: *p*-xylene (1:1 v/v).



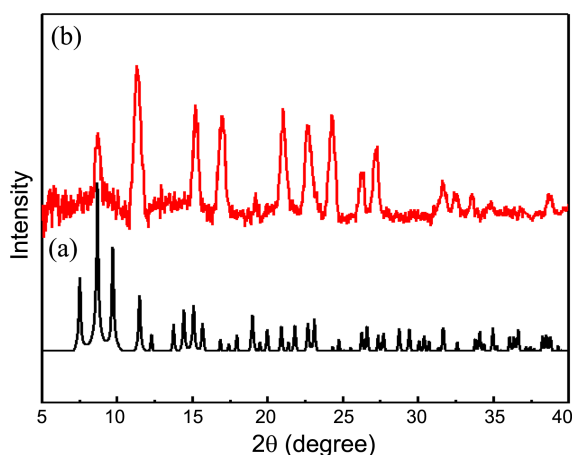
**Figure 2.** SEM images of MOF gel **1** with 3.0 equivalents of  $\text{Zn}(\text{ClO}_4)_2$ .

We examined the absorption and fluorescence emission properties of sol **1** and MOF gel **1** with  $Zn^{2+}$  ion. The UV-vis absorption bands of MOF gel **1** with  $Zn^{2+}$  and sol **1** appeared at 369 nm (Figure S2), indicating that ligand **1** in the gel state does not undergo the  $\pi$ - $\pi^*$  transition. The fluorescence intensity of the MOF gel **1** with  $Zn^{2+}$  was enhanced compared to sol **1** (Figure S3). The planar conformation of **1** may be induced in the gel state due to the strong intermolecular forces, which tend to optimize close packing between molecules. This aggregation-induced planarization extends the effective aromatic groups in ligand **1** molecule. Furthermore, in the gel state, the MOF structure of **1** with  $Zn^{2+}$  plays the important role of favoring J-type aggregation, which restricts the formation of the excimer complex.<sup>30</sup>

Detailed crystallographic data of ligand **1** in complex with  $Zn^{2+}$  ion was reported by Zhou group.<sup>31</sup> Analysis of the crystal structure of the Zn(II) complex revealed a 3D structure of formula  $[Zn_4O(H_2O)_3(1)_3 \cdot 2(C_3H_7NO)]_n$  that is built up from six molecules of ligand **1** connecting with the distorted  $Zn_4O(COO)_6$  cluster (Figure 3). Wide-angle X-ray diffraction (WAXD) was used to probe the molecular packing between the gel **1** with zinc ion and the single crystal **1**- $Zn^{2+}$  complex. Powder XRD patterns of ligand **1** with  $Zn(ClO_4)_2$  in a single crystal had the same diffraction pattern as that of the xerogel **1** with  $Zn(ClO_4)_2$ , suggesting that the molecular packing of the gel **1** with  $Zn^{2+}$  was the same as the



**Figure 3.** (a) Six adc ligands connecting with the distorted  $Zn_4O(COO)_6$  cluster and (b)  $Zn_4O(H_2O)_3(COO)_6$  SUB (carbon, gray, oxygen, red, zinc, turquoise).



**Figure 4.** Powder X-ray diffraction patterns of (a) single crystal **1**- $Zn^{2+}$  and (b) xerogel **1** with  $Zn(ClO_4)_2$ .

molecular packing of the single crystal **1** with  $Zn^{2+}$  (Figure 4). To garner insight into the thermally promoted stability of the MOF gel **1** with  $Zn^{2+}$ , the transition temperature ( $T_{sol-gel}$ ) of the MOF gel **1** with  $Zn^{2+}$  was measured by differential scanning calorimetry (DSC) (Figure S5). The MOF gel **1** with  $Zn^{2+}$  showed a sharp phase transition at 141 °C, an endothermic reaction. This endothermic thermogram is due to the transition of the MOF gel **1** with  $Zn^{2+}$  into a solution phase as observed in Figure S5.

For application as a portable chemosensor kit, the sensing ability of gel **1** with  $Zn^{2+}$  was studied in the film state by exposing film to explosive trinitrotoluene (TNT) and dinitrotoluene (DNT) vapors (Figure S6). Films of the MOF gel **1** with  $Zn^{2+}$  were drop casted from water and, when monitored at 454 nm, the film showed 70% fluorescence quenching after one min of exposure to saturated TNT vapors. Nearly 90% quenching was observed upon continuous exposure for 10 min (Figure S6). As expected, the MOF gel **1** with  $Zn^{2+}$  exhibited a gradual decrease in the fluorescence intensity upon the addition of TNT, which is attributed to charge-transfer interactions occurring between the electron-deficient aromatic ring of TNT and the electron-rich aromatic group of gel **1** with  $Zn^{2+}$ . The use of MOF gel **1** with  $Zn^{2+}$  for the detection of DNT vapors was also studied. A film of gel **1** with  $Zn^{2+}$  showed a fluorescence quenching effect when exposed to saturated DNT vapors under the same conditions; however, the quenching efficiency was found to be much less as compared to that with TNT vapors. After exposure for 10 min, only 20% quenching was observed in the presence of DNT compared to 90% quenching for the case of TNT.

In conclusion, we report the formation of a simple  $Zn^{2+}$ -based MOF gel. The anthracene-based ligand was shown to efficiently produce the organogel by simple mixing with  $Zn^{2+}$ . Upon the formation of the MOF gel, the complex shows a pronounced fluorescence enhancement, as compared to the ligand alone. The anthracene-based ligand **1** in complex with  $Zn^{2+}$  was influenced by the concentration of metal ions to form the 3D coordination polymer structure. In addition, the metal-organic framework gel can act as a chemosensor, such illustrated by the detection of the TNT molecule. MOF gels provide a powerful strategy for developing new molecularly defined materials in the areas of biology, medicine, and materials science. We believe this new MOF gel could possibly provide a model system for the development of novel sensors, catalysis, and delivery.

## Experimental

**General.** The optical absorption spectra of the samples were obtained at 278-77 K using a UV-vis spectrophotometer (Hitachi U-2900). All fluorescence spectra were recorded in RF-5301PC spectrophotometer.

**SEM Observation.** For Scanning electron micrographs of the samples were taken with a field emission scanning electron microscope (FE-SEM, Philips XL30 S FEG). The accelerating voltage of SEM was 5-15 kV and the emission

current was 15  $\mu$ A.

**Photophysical Studies.** UV-Vis absorption and emission spectra of the gel at room temperature and dispersed in DMSO in the range of 200-800 nm. The absorption properties of MOF gel **1** were studied extensively. UV/vis absorption spectra of MOF gel **1** ([1] = 20 mM) were observed in the presence of  $\text{Zn}^{2+}$  (0-5 equiv).

**DSC Measurement.** Differential scanning calorimetry (DSC) was performed on a Seiko DSC6100 high-sensitivity differential scanning calorimeter equipped with a liquid nitrogen cooling unit. Samples of  $\text{Zn}^{2+}$  coordination polymer gels were hermetically sealed in a silver pan and measured against a pan containing alumina as the reference. The thermograms were recorded at a heating rate of 0.5  $^{\circ}\text{C}/\text{min}$ .

**Preparation of MOF Gel.** In a vial, the solution of Metal salt [150  $\mu\text{L}$ , 3 equiv in DMSO] was added to solution of gelator [150  $\mu\text{L}$ , 1-5 wt % in DMSO]. The metal coordination polymeric gel is formed immediately upon standing in ambient temperature. The resulting reaction mixture was allowed to sonicate. The gelation state of the material was evaluated by "stable-to-inversion" of the test tube.

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**Supporting Information.** Gelation test, UV-vis and fluorescence spectra of gel **1** with  $\text{Zn}^{2+}$ , DSC thermogram of gel **1** with  $\text{Zn}(\text{ClO}_4)_2$ , and Fluorescence spectra of gel **1** with  $\text{Zn}^{2+}$  after exposure with DNT and TNT.

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