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Short communication

A luminescent Li(I)-based metal–organic framework showing selective Fe(III) ion and nitro explosive sensing

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ABSTRACT

A new Li(I)-based metal–organic framework (MOF), namely $\{(Me_2NH_2)_2[Li(NTB)](H_2O)_3(DMF)_2\}_n$ (**1**, NTB = 4.4′,4″-nitrilotrisbenzoate; DMF = *N*,*N*-dimethylformamide), has been successfully achieved by solvothermal reaction of a C_3-symmetric tricarboxytriphenylamine based ligand and Li(I) ion. The resulting framework features a binuclear Li(I) secondary building unit (SBU) and a rare 3.6-connected **ant** topology. Luminescence properties of **1** towards different metal ions and solvents have also been investigated systematically, with emission intensities significantly quenched towards Fe(III) ion and nitrobenzene (NB). The quenching mechanism has also been investigated in detail.

As a kind of promising solid crystalline materials for practical applications, metal–organic frameworks (MOFs) has attracted considerable interest in various scientific areas that include gas storage/separation, sensing, catalysis, and luminescent materials [1–9]. In order to achieve these applications, various efforts have been made in the development of appropriate materials such as the introduction open metal sites (OMSs) and the design of functionalized organic ligands [10–12]. In particular, the organic ligand plays an important role in the function of the resulting MOFs because it could not only determine the final framework structure, but also alter the electronic structures and surface functionalities of MOFs [13]. Recent research reveals that the ligand-centered luminescence of MOFs has shown great promise in the luminescent sensor [14–18]. The rich delocalized π-electron and rigidified framework natures of MOFs allow them to act as fast, reversible, and highly sensitive chemical sensors, especially in the detection of small molecules. Additionally, calculations regarding the electronic structure of prototypical porous 3-D MOFs have suggested that the band gaps of these materials can be altered by changing the degree of conjugation in the ligand [19]. Such factors are important for the practical application of these materials. On the other hand, the choice of lithium ion as the metal center might afford lightweight luminescent framework materials featuring strong binding interaction and highly thermal stability for its ionic nature [20]. With these in mind, in this study, a new luminescent Li(I)-based MOF was successfully fabricated by employment of a π-electron rich ligand 4.4′,4″-nitrilotrisbenzoic acid (H_3NTB) and a binuclear Li SBU. This luminescent MOF was studied as a detector for toxic nitrobenzene and Fe(III) ion in solution. Furthermore, the detection mechanism has also been investigated in detail.

Block-like pale yellow crystals of **1** were obtained by solvothermal reaction of $LiNO_3$ and H_3NTB in DMF solution at 130 °C. X-ray structural determination indicates that complex **1** crystallizes in the monoclinic space group *C*2/*c* and each asymmetric unit contains one crystallographically independent Li(I) ion, one fully deprotonated NTB^{3-} ligand, three water, two Me_2NH_2 cations, and two DMF molecules. The lattice guests were not well resolved because they are highly disordered. As shown in Fig 1a, Li(I) ion is four-coordinated by four carboxylate O atoms from four different NTB^{3-} ligands to furnish a slightly distorted tetrahedral geometry. Two such Li(I) ions are bridged by two carboxyl groups to form a binuclear Li secondary building unit. The intrametallic distance between adjacent Li(I) ions is 3.449 Å. The three carboxylate acid groups on the NTB^{3-} ligands exhibit two coordination modes: one is bidentate chelating and the other two are monodentate coordinating (Fig. 1b). Each NTB^{3-} ligand connects with three binuclear Li(I) SBUs resulting in a three-dimensional framework with 1D channels which are filled with highly disordered $(CH_3)_2NH_2$ cations (Fig. 1c). To simplify the whole framework, the binuclear Li SBU could be viewed as a six-connected node and the NTB^{3-} ligand as a three-connected node. The whole framework could be simplified to a 3.6-connected anatase (**ant**) net with the Schlafli symbol of $\{4^2.6\}_2\{4^4.6^2.8^8.10\}$ (Fig. 1d and Fig. S1 in the Supplementary information). To the best of our knowledge, the 3.6-connected **ant** nets are seldom observed in MOF chemistry and **1** represents the first example of Li-based MOF showing the **ant** topology [20,21].

The TGA curve shows a continuous weight loss of 29.5% from 25 to 320 °C (Fig. S2 in the Supplementary information), corresponding to the loss of three water and two DMF molecules (calced 29.7%). The

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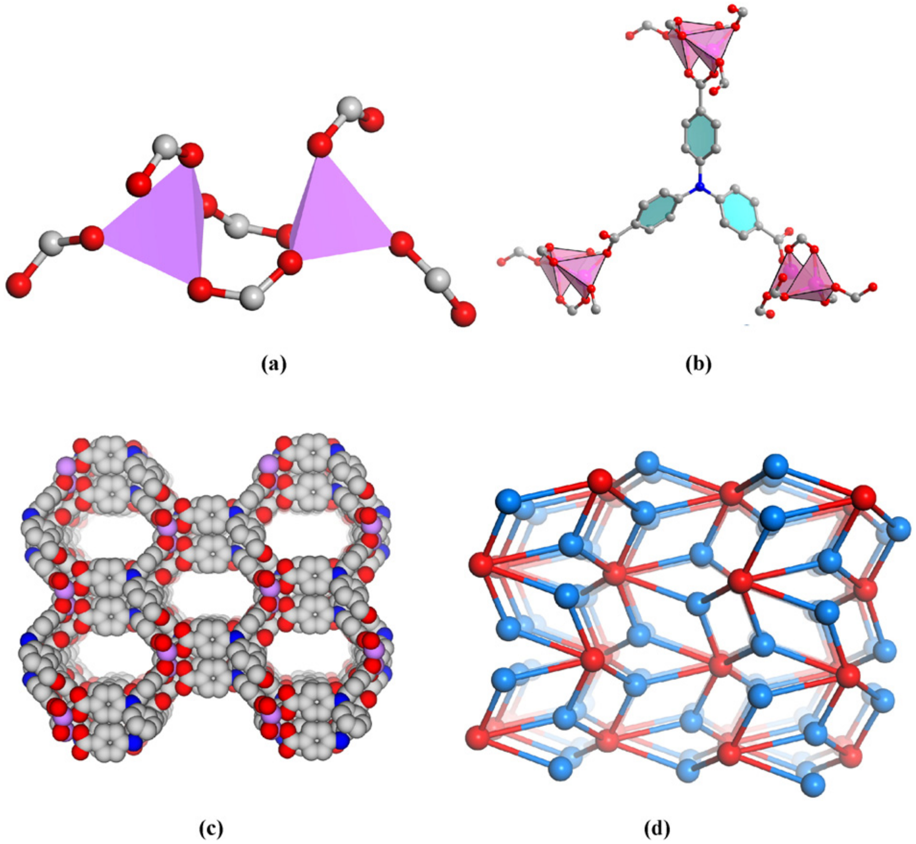

Fig. 1. Views of (a) the binuclear Li unit in 1, (b) the connection mode of NTB^{3-} ligand in 1, (c) space-filling representation of 1 viewed from *c* axis, and (d) the 3D net with 3.6-connected ant topology of 1.

remaining substance is stable to 510 °C, and further heating leads to the decomposition of the overall framework. The purity of the as-synthesized **1** was confirmed by PXRD, the measured patterns match well with the ones calculated from the single-crystal data, indicative of its high pure state (Fig. S3 in the Supplementary information).

The photoluminescence (PL) spectra of **1** and H_3NTB ligand in the solid state were studied at room temperature (Fig. S4 in the Supplementary Information). **1** exhibited an emission peak at 467 nm upon excitation at 360 nm. This emission band can be assigned to ligand-centered emission, because similar emission was observed at 458 nm for the free H_3NTB ligand [22]. The excellent luminescent property of **1** promotes us to investigate its potential application in detection of common metal ions. The luminescence spectra of **1** dispersed in the DMF solutions containing different metal ions (3 mL, 1×10^{-3} mol/L) were studied (Fig. 2), compared with other metal ions, only the Fe(III) ion can bring essentially complete quenching to the system. This result demonstrates that **1** can be highly effective and selective luminescent sensors for Fe(III) ions. We have also investigated the influence of coexisting metal ion (Fe(II)) on the quenching effect. The luminescent intensities display no evident changes in presence of coexisting Fe(II) with the same amount of Fe(III) ions, which confirms the high selectivity of **1** for detecting Fe(III) ions in a mixture of Fe(II)/Fe(III) solution. In order to elucidate the possible mechanism for such photoluminescence quenching by the Fe^{3+}, the PXRD of **1**-Fe(III) (**1** after Fe(III) detection) was carried out (Fig. S3 in the Supplementary information), which indicated that the crystalline structure of **1** was retained after Fe(III) detection and the luminescence quenching was not caused by collapse of the framework. According to the UV–Vis

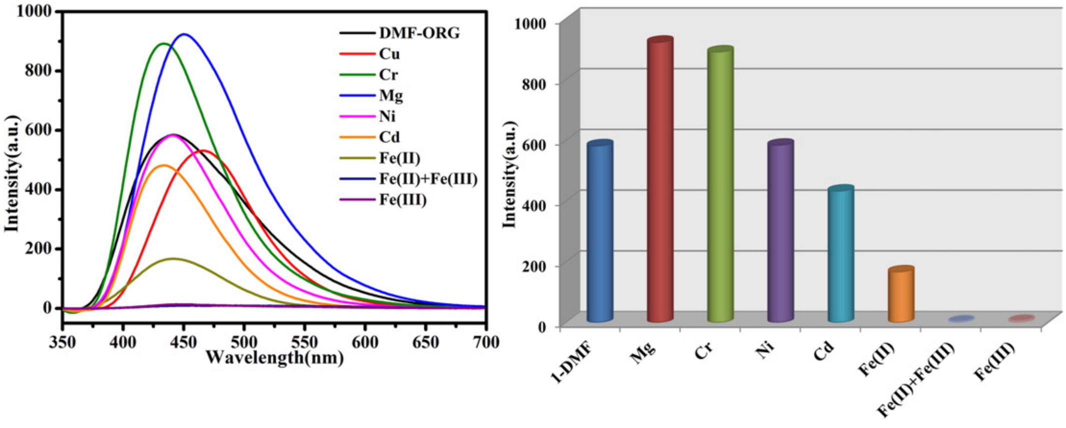

Fig. 2. Emission spectra of 1 towards different metal ions in DMF solution.