Metal–Organic Frameworks

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A Luminescent Metal–Organic Framework with Lewis Basic Pyridyl Sites for the Sensing of Metal Ions**

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The last two decades have witnessed significant progress in the design and synthesis of a new type of porous materials generally referred to as metal–organic frameworks (MOFs) and/or coordination polymers which can be readily self-assembled by the coordination of metal cations/clusters with organic linkers. Extensive efforts on such species have not only led to the creation of a huge number of MOFs of diverse topologies and aesthetic beauty, but also initiated a rational design strategy to construct porous materials with high surface areas, predictable structures, and tunable pore sizes to target some important applications, such as gas storage, separation, catalysis, magnetism, sensing, and imaging.[1–26] Such progress within this field allows us to rationally design and synthesize porous MOFs with functional sites for specific host–guest recognition and thus to tune their functional properties.

One of these extensively investigated methodologies is to immobilize unsaturated (open) Lewis acidic metal sites within porous MOFs for gas storage, catalysis, and sensing.[2–5] Immobilization of Lewis basic sites within porous MOFs, however, has been more challenging, as such Lewis basic sites tend to bind other metal ions to form condensed structures. The very few examples of porous MOFs with Lewis basic sites include POST-1 with pyridyl sites,[6] $[Cd(4\text{-btapa})_2(NO_3)_2]\cdot 6\,H_2O\cdot 2\,DMF$ (4-btapa = 1,3,5-benzenetricarboxylic acid tris[*N*-(4-pyridyl)amide]) with amide sites[7] and $[Zn_3(OH)_3(2\text{-stp})(bpy)_{1.5}(H_2O)]\cdot EtOH\cdot 2\,H_2O$ (2-stp = 2-sulfonylterephthalate; bpy = 4,4′- bipyridine) with anionic sulfonate sites.[8] Importantly, POST-1 and $[Cd(4\text{-btapa})_2(NO_3)_2]$ exhibit interesting catalytic activities for the transesterification and Knoevenagel condensation, attributed to pyridyl and amide sites, respectively, highlighting the significance of such Lewis basic sites within porous MOFs for their functional properties. To make use of the preferential binding of lanthanide ions (Ln^{3+}) to carboxylate oxygen atoms over pyridyl nitrogen atoms in Ln^{3+}-pyridinecarboxylate complexes,[9,27] herein we report a rare example of luminescent MOFs, $[Eu(pdc)_{1.5}(dmf)]\cdot(DMF)_{0.5}(H_2O)_{0.5}$ (**1**, pdc = pyridine-3,5-dicarboxylate), with Lewis basic pyridyl sites for the sensing of metal ions.

Compound **1** was synthesized by the solvothermal reaction of $[Eu(NO_3)_3]\cdot(H_2O)_6$ and H_2pdc in DMF at 120 °C over night. It was formulated as $[Eu(pdc)_{1.5}(dmf)]\cdot(DMF)_{0.5}(H_2O)_{0.5}$ by elemental microanalysis and single-crystal X-ray diffraction studies, and the phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD) and thermal gravimetric analysis (TGA) (see the Supporting Information, Figure S1-3).

Complex **1** is isostructural with $[Er(pdc)_{1.5}(dmf)]\cdot(solv)_n$ and $[Y(pdc)_{1.5}(dmf)]\cdot(solv)_n$, in which Eu atoms are bridged by pdc organic linkers to form a three-dimensional rod-packing structure.[9] Each europium atom is coordinated by six oxygen atoms from the carboxylate groups of pdc, and capped by one distorted DMF molecule. One-dimensional hexagonal channels of about 6.3 × 8.5 Å along the *a* axis are filled by the capping DMF molecule, as well as free DMF and water molecules (Figure 1).

TGA data indicated that **1** releases the free water and DMF, and terminal DMF molecules in the temperature range of 25–220 °C, to form a guest-free phase $[Eu(pdc)_{1.5}]$ (**1a**) which is thermally stable up to 450 °C. The powder X-ray diffraction (PXRD) pattern of the guest-free phase **1a** is almost identical with that of the as-synthesized **1**, and matches well with that of the anhydrous $[Er(pdc)_{1.5}]$, indicating that the basic 3D framework is retained and the in situ-generated open Eu sites are occupied by carboxylate oxygen atoms, thus the 1D hexagonal channels are accessible to guest molecules.[9] This shift of the carboxylate groups stabilizes the Eu sites and pores in **1a**, so, even re-immersed in DMF, no solvent molecules are coordinated.[10] Phase **1a** exhibits type I isotherm characteristic N_2 adsorption at 77 K with a Langmuir surface area of 537 m^2 g (see the Supporting Information, Figure S4). The most significant structural feature is the presence of free Lewis basic pyridyl sites within the pores, highlighting the potential for their recognition of metal ions and thus for sensing functions.

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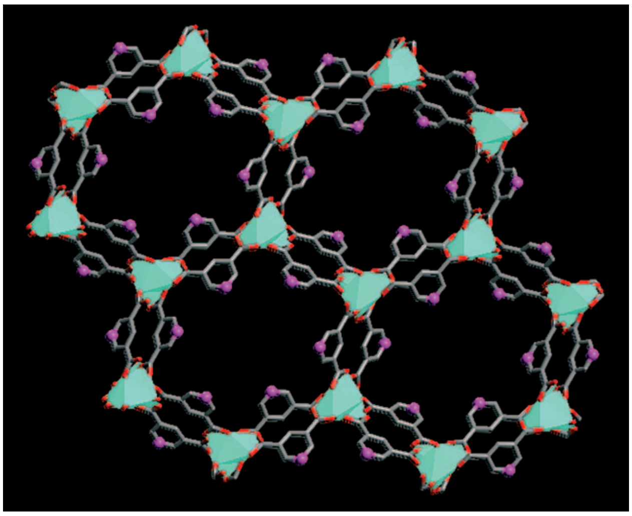

Figure 1. Crystal structure of **1**, viewed along *a* axis indicating immobilized Lewis basic pyridyl sites oriented towards pore centers. C gray, N purple, O red, Eu green polyhedra. Hydrogen atoms, terminal DMF molecules, and solvent molecules are omitted for clarity.

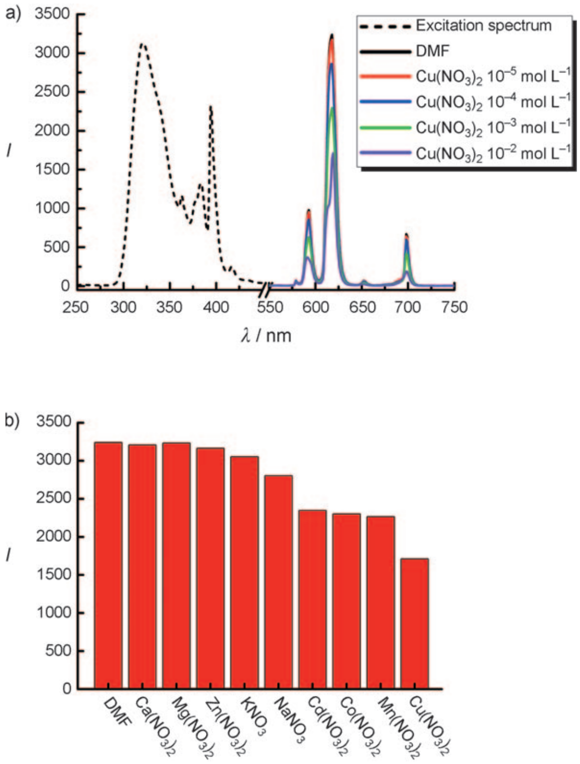

Figure 2. a) The excitation (-----) and PL spectra (——) of solid **1b** activated in DMF solutions of Cu$(NO_3)_2$ at different concentrations (excited and monitored at 321 nm and 618 nm, respectively); b) Comparison of the luminescence intensity of **1b** incorporating different metal ions, activated in 10 mm DMF solutions of M$(NO_3)_x$.

Compound **1a** was immersed in DMF solutions containing different concentrations of M$(NO_3)_x$ (M = Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, or Cd^{2+}) to form metal-ion-incorporated $[Eu(pdc)_{1.5}]\cdot$DMF (**1b**) as microcrystalline solids for luminescence studies. The excitation and photoluminescence (PL) spectra of Cu^{2+}-incorporated **1b** are shown in Figure 2a. The excitation peaks around 321 nm are ascribed to the absorption of pdc ligands, and those from 350 nm to 420 nm are from the absorption of Eu^{3+} ion. The emission spectra of **1b** excited at 321 nm reveals well-resolved magnified luminescence of the f–f transitions, attributed to the energy transfer from pdc ligands to Eu^{3+} ions. Characteristic transitions of the Eu^{3+} ion are also evident for **1b**, at 590, 616, and 698 nm, which are ascribed to the $^5D_0\rightarrow{}^7F_1$, $^5D_0\rightarrow{}^7F_2$ and $^5D_0\rightarrow{}^7F_4$ transitions, respectively. Most interestingly, the luminescence intensity of the metal-ion-incorporated **1b** is heavily dependent on the identity of the metal ion: alkali metal ions and alkaline-earth metal ions have a negligible effect on the luminescence intensity, whereas others effect varying degrees of quenching on the luminescence intensity. Cu^{2+} has the most significant effect (Figure 2b). The luminescence intensity of the Cu^{2+}-incorporated **1b** from a 10 mm DMF solution of Cu$(NO_3)_2$ is about half that of metal-ion-free **1b**·DMF, indicating the potential of **1b** for the sensing of metal ions. The emitted visible red light from Cu^{2+}-incorporated **1b** is noticeably less intense than that from **1b**·DMF under UV light (see the Supporting Information, Figure S7). The quenching effect of Cu^{2+} on the luminescence intensity of **1b** has been further examined by fluorescence lifetime studies of Eu^{3+}. The fluorescence lifetime of 898.86 μs in the **1b**·DMF is significantly reduced to 494.6 μs in the presence of 10 mm Cu^{2+} (see the Supporting Information, Figure S8).

To elucidate the possible mechanism for such luminescence quenching by metal cations, N1s X-ray photoelectron spectroscopy (XPS) studies were carried out on **1b**·DMF and M^{2+}-incorporated **1b** ($M^{2+} = Cu^{2+}$ or Co^{2+}). The N1s peak from free pyridyl nitrogen atoms at 398.5 eV in **1b**·DMF is shifted to 399.2 eV on the addition of Cu^{2+} or Co^{2+} (Figure 3 and Figure S9 in the Supporting Information), indicating the weak binding of pyridyl nitrogen atoms to M^{2+} in M^{2+}-incorporated **1b** ($M^{2+} = Cu^{2+}$ and Co^{2+}). A peak at 406.1 eV in the N1s XPS spectra for Cu^{2+}- or Co^{2+}-incorporated **1b** is attributed to NO_3^- counterions. Such binding of the pyridyl nitrogen atoms to Cu^{2+} or Co^{2+} reduces the antenna efficiency of the pdc organic linkers to magnify the f–f transitions of Eu^{3+}, resulting in quenching of the luminescence. As alkali

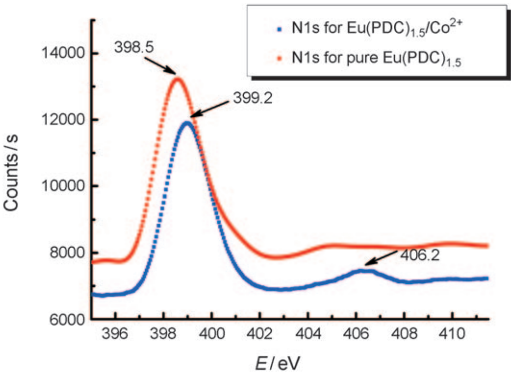

Figure 3. XPS spectra of the original **1b**·DMF (red) and Co^{2+}-incorporated **1b** (blue) activated in 10 mm DMF solution of Co$(NO_3)_2$.

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and alkaline-earth metal ions are not bound to the pyridyl nitrogen atoms, their effects on the luminescence are negligible.

Quantitatively, this quenching effect can be rationalized by the Stern-Volmer equation: $\frac{I_0}{I} = 1 + K_{sv}\,[M]$. The values I_0 and I are the luminescence intensity of metal-ion-free **1b**·DMF and metal-ion-incorporated **1b**, respectively, $[M]$ is the molar concentration of the metal ion, and K_{SV} is the quenching effect coefficient of the metal ion. It is thus expected that the reduction in luminescence intensity is proportional to the concentration of the metal ion. K_{sv} was calculated from the experimental data for the examined ions (Table 1). The largest K_{sv} value is 89.4 M^{-1} for Cu^{2+}, indicating that it has the strongest quenching effect on the luminescence intensity of **1b**.

Table 1: Quenching effect coefficients (K_{sv}) of different metal ions on the luminescence intensity of metal-ion-incorporated **1b**.

Metal ion	K_{sv} [M^{-1}]
Na^+	15.6
K^+	6.1
Mg^{2+}	0.2
Ca^{2+}	1.0
Mn^{2+}	43.0
Co^{2+}	40.8
Cu^{2+}	89.4
Zn^{2+}	2.5
Cd^{2+}	38.0

Lewis basic sites within porous MOFs are expected to play very important roles for their recognition of small Lewis acidic molecules and metal ions, and thus to find functionalities in chemical transformation and sensing. Further efforts will be focused on the construction of porous luminescent MOFs with tuned micropores to enhance their recognition selectivity and a variety of immobilized Lewis basic sites to induce preferential binding with respect to different metal ions, leading to highly selective luminescent MOF probes, which might be exploited for the sensing of metal ions in the near future.

Experimental Section

Synthesis of **1**: A solution of $[Eu(NO_3)_3]\cdot(H_2O)_6$ (1.120 g, 2.617 mmol) and H_2pdc (0.614 g, 3.674 mmol) in DMF (200 mL) was heated in a sealed vial (400 mL) at 115 °C for 24 h, forming **1** as light-yellow needle-shaped crystals (1.187 g, 87 %). Elemental analysis calcd (%) for $[Eu(pdc)_{1.5}(dmf)]\cdot(DMF)_{0.5}(H_2O)_{0.5}$: $C_{15}H_{16}EuN_3O_8$: C 34.56, H 3.67, N 8.06; found: C 34.72, H 3.55, N 7.98. TGA: weight loss calcd (%) for (1.5 DMF + 0.5 H_2O): 22.38 %; found: 21.73. **1a**: A sample of **1** was heated at 150 °C under reduced pressure for 24 h to afford **1a**.

Single-crystal X-ray Crystallography: Intensity data for the MOF **1** were collected using graphite monochromated Mo radiation on a Nonius Kappa-CCD diffractometer fitted with an Oxford Cryostream cooler. Data reduction included absorption corrections by the multiscan method. Structures were solved by direct methods and refined by full-matrix least squares using SHELXL97. All non-hydrogen atoms were refined anisotropically. Crystallographic data for **1**: $[Eu(pdc)_{1.5}(dmf)]\cdot(DMF)_{0.5}(H_2O)_{0.5}$; $T = 90$ K; orthorhombic; space group *Pnma*; $a = 8.0154(9)$, $b = 30.175(3)$, $c = 15.322(2)$ Å; $V = 3705.9.2(7)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.922$ g cm^{-3}; $\mu(Mo_{K\alpha}) = 3.44$ mm^{-1}; $2\theta_{max} = 45°$; 2322 reflections measured ($R_{int} = 0.046$); $R_1 = 0.044$; wR_2 (all data) = 0.120; GOF = 1.07; 290 parameters. CCDC-699468 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Photoluminescence of **1b** was investigated in the solid state at room temperature. Compound **1b** was prepared as a powder by introducing **1a** powder (10 mg) into DMF solutions (2.00 mL) of $M(NO_3)_x$ ($M = Na^+, K^+, Mg^{2+}, Ca^{2+}; Mn^{2+}; Co^{2+}, Cu^{2+}, Zn^{2+}$, or Cd^{2+}) at various concentrations (10^{-5}–10^{-2} mol L^{-1}). Metal-ion-incorporated **1b** was isolated by filtration and drying at 50 °C for 24 h. PL spectra were measured using a Hitachi F4500 fluorescence spectrometer, with a PMT voltage of 950 V, a scan speed of 240 nm min^{-1}, and a slit width of 2.5 nm. The fluorescence lifetime was measured using an Edinburgh Instruments FLS920 Fluorescence Spectrometer, excited by an UF920 flash Xe lamp with a pulse width of 2.5 µs.

Powder XRD diffraction was carried out using a Siemens D5005 X-ray diffractometer with $Cu_{K\alpha}$ line ($\lambda = 1.54178$ Å) as the incident beam. A Gobel mirror was employed as a monochromator. The sample powder was loaded into a glass holder and leveled with a glass slide before mounting it on the sample chamber. The specimens were scanned at 4–40°. The scan step-width was set to 0.01° and the scan rate to 0.01° s^{-1}. XPS data were obtained using an ESCALAB 250 X-ray photoelectron spectroscopy. TGA/DSC data were obtained on a TGA G500 V5.3 Build 171 instrument with a heating rate of 10 °C min^{-1} under N_2 atmosphere. N_2 adsorption isotherm at 77 K was measured using an ASAP 2020 apparatus.

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