Metal–Organic Frameworks

DOI: 10.1002/anie.201207610

A Luminescent Metal–Organic Framework as a Turn-On Sensor for DMF Vapor**

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Metal–organic framework (MOF) materials, crystalline materials constructed from metal ions and organic ligands, have been an active research area since the beginning of this century. Various MOF systems have been established for the purpose of gas storage,[1] gas separation,[2] heterogeneous catalysis,[3] and small-molecule sensing.[4] Other possible applications of MOF materials are also emerging as researchers explore new metal–ligand combinations, such as proton-conducting MOFs for fuel cells[5] and MOF thermometers.[6] Of all the MOF applications, sensing has been largely unexplored until recently. Several groups have reported their discoveries on MOF sensors aimed at the convenient detection of explosives,[4h] chemical vapors,[4k,l] and O_2 gas.[4i,j]

For sensing applications lanthanide MOFs (LnMOFs) are more attractive candidates than transition-metal MOFs, because many LnMOFs have sharp and characteristic emissions; these can be modulated by both analyte–metal and analyte–ligand interactions since the unique luminescence mechanism involves ligand-to-metal energy transfer (LMET). While modulations of the lanthanide luminescent signal caused by analyte–metal interactions have found use in LnMOF sensors,[4a] those triggered by analyte–ligand interactions have not been exploited. In transition-metal MOF systems, only ligand-based emission may change upon ligand–analyte interactions.[4l]

Herein we report a new luminescent LnMOF displaying efficient turn-on triggered by solvent vapors, with excellent selectivity for DMF vapor. While luminescence turn-on upon exposure to liquid solvents has been demonstrated for MOFs,[4a,g,m,n] to the best of our knowledge, no LnMOF sensor and only one transition-metal counterpart displaying luminescence turn-on towards gaseous analytes has been reported.[4l] Recent studies have suggested that serious health concerns are associated with DMF exposure both through skin contact and inhalation in various industries, such as the production of synthetic fibers, films, and coatings, and leather tanning. Studies of exposed workers[7] and animal experiments[8] have confirmed the hepatotoxicity of DMF; other toxic effects have been suggested including embryotoxicity[9] and carcinogenesis.[10] Because of the large population at risk and the widespread use in industry, DMF has been prioritized for field studies. The standard sampling and detection method[11] for DMF vapor in air requires lengthy procedures involving physical absorption/desorption of air samples and the use of gas chromatography. A reusable, selective, and easy-to-use sensor for DMF vapor is desirable.

Needle-shaped crystals of $[Eu_2L_3(H_2O)_4]\cdot 3\,DMF$ (**1**) (L = 2′,5′-bis(methoxymethyl)-[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylate) can be obtained in high yield by heating a solution of $Eu(NO_3)_3$ and H_2L in DMF/H_2O (4:1 v/v) in a sealed scintillation vial at 80 °C for three days. The crystal structure of **1** is shown in Figure 1.[12] Each Eu center adopts a bicapped trigonal-prismatic geometry with six oxygen donors from carboxylate groups and two from coordinated water molecules occupying the eight coordination sites. Adjacent pairs of Eu centers are quadruply bridged by carboxylates to form one-dimensional (1D) chains along the *a*-axis. Each 1D chain is linked to four adjacent chains through L ligands, extending the structure into a 3D framework with solvent channels along the *a*-axis, where DMF molecules are located. The channel DMF molecules can be replaced by soaking the

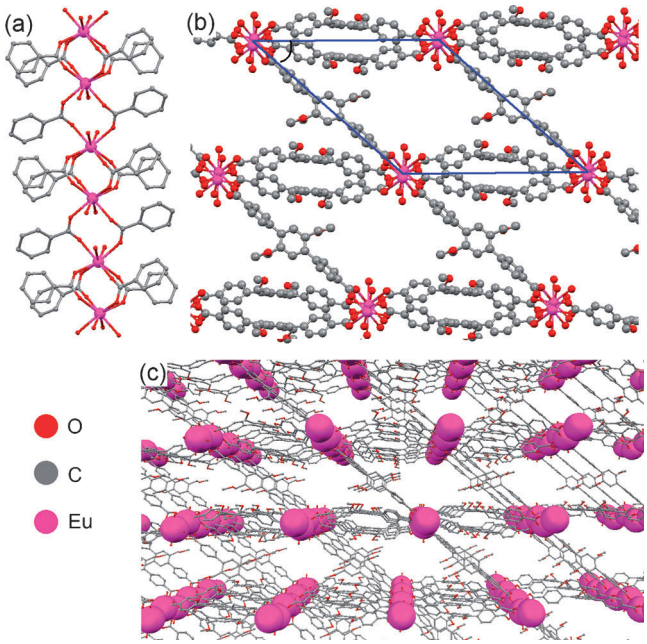

Figure 1. Crystal structure of 1: a) 1D chain with bridging carboxylate groups; b) extended structure showing connectivity; c) perspective view of 1D chains and open channels. All hydrogen atoms and channel solvent molecules are omitted for clarity.

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[**] This research is supported by grants to D.S. from the Natural Science and Engineering Research Council (NSERC) of Canada and the Ontario Ministry of Research and Innovation.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201207610.

crystals of **1** in distilled water for three days, resulting in the water-exchanged framework **2**.[13]

Compound **1** displays characteristic Eu emissions at 578, 590, 616, 698 nm in the emission spectrum (see Figure S5 in the Supporting Information), corresponding to $^5D_0$–$^7F_0$, $^5D_0$–$^7F_1$, $^5D_0$–$^7F_2$, and $^5D_0$–$^7F_4$ transitions of Eu, respectively. In the excitation spectrum, only a broad band of ligand-based excitation is observed around 341 nm. The water-exchanged framework **2** displays a much weaker luminescence under UV irradiation (Figure S6). This finding prompted us to examine the sensing ability of **2** for various solvents. The luminescence response of **2** after incubation for 24 h under various solvent vapors were measured and the results are plotted in Figure 2.[14] The histogram clearly shows that while most

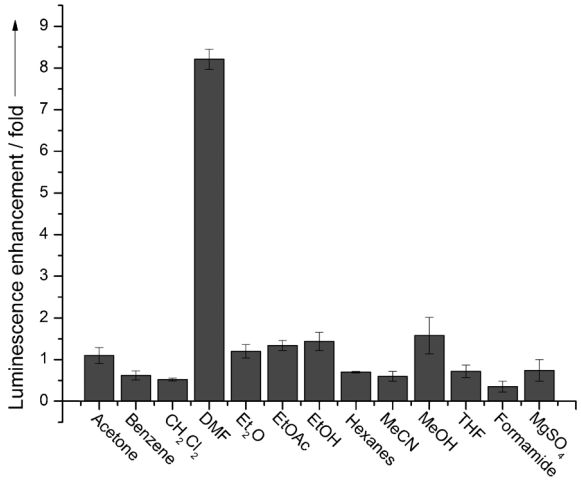

Figure 2. Increase in Eu emission intensity of **2** ($I_{after}/I_{before}-1$) after incubation for 24 h under various solvent vapors and with anhydrous $MgSO_4$. The intensity is measured at 616 nm. Error bars indicate the standard deviations of three or four parallel experiments.

solvents give around onefold enhancement, DMF triggers a superior turn-on (Figure S16), that is, more than eightfold enhancement of luminescence (Figure 3). The used powder of **2** can be regenerated by soaking in water and reused in the aforementioned experiments without notable loss of the selectivity (see Figure S10 in the Supporting Information).

Interactions with the O–H bond of coordinating H_2O is known to quench Eu luminescence.[15] We reason that when the channel H_2O molecules are partially replaced by other solvent molecules, the equilibrium between coordinated and channel H_2O will shift, leaving fewer O–H bonds around the Eu centers and thus triggering enhancement of Eu emission. Such a hypothesis is consistent with the fact that anhydrous $MgSO_4$, which may remotely remove water from **2**, can enhance the emission as well (Figure 2). Our NMR experiments also confirmed the uptake of various solvents and the decrease of water content in **2** after 24 h incubation (see the Supporting Information for more details). However, such a decrease in water content might only reflect the "exchangeable" water (or channel water). To investigate the change in coordinated water during the turn-on event, we measured the lifetime of Eu emission, before and after exposure to DMF

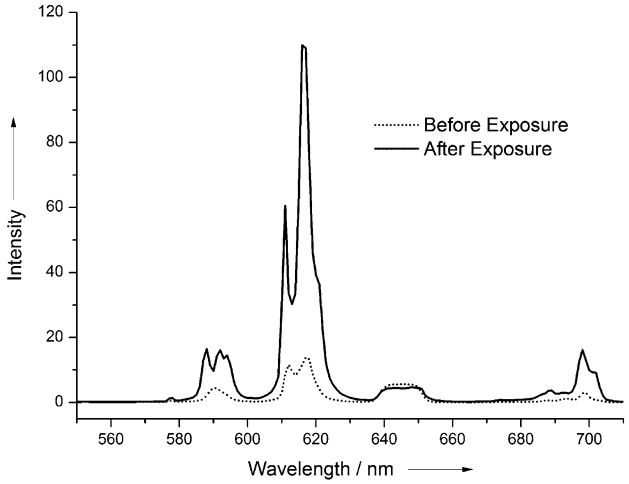

Figure 3. Emission spectra of **2** before and after exposure to DMF vapor (excitation at 323 nm). The broad peak around 640 nm arises from scattering.

vapor, with MOF samples **3**-H_2O and **3**-D_2O,[16] which are prepared by soaking compound **1** in H_2O and D_2O, respectively, and subsequently drying under vacuum (see the Supporting Information for more details). The completeness of the deuteriation has been confirmed by NMR experiments. According to an early study,[17] the luminescence quenching rate attributed to O–H bonds is proportional to the number of coordinating water molecules in the first coordination sphere of Eu, and this quenching rate displays such a strong isotope effect that the O–D bond essentially has no quenching effect. The average number of coordinated water molecules per Eu center can be calculated using Equation (1)

$$n_{H_2O} = 1.05\left(\tau_{H_2O}^{-1} - \tau_{D_2O}^{-1}\right) \quad (1)$$

where τ_{H_2O} and τ_{D_2O} are the lifetimes of Eu emission in microseconds, for H_2O- and D_2O-containing samples, respectively. The numbers of coordinated water molecules were calculated for **3** before and after DMF exposure and the results are shown in Table 1, together with the intensity of Eu emission at 616 nm for comparison. Because of the presence of H_2O in **3**-H_2O, the lifetime of **3**-H_2O is much shorter than that of **3**-D_2O; this corresponds to around 0.5 water molecules on each Eu center. After exposure to DMF vapor, the difference in lifetime between **3**-H_2O and **3**-D_2O is much smaller and almost all of the water molecules on the Eu centers have been removed. As a result, the Eu emission intensity is greater for **3**-D_2O than for **3**-H_2O before exposure to DMF vapor, and both increase to similar levels after the exposure. These observations are consistent with our hypothesis of the "water effect" that removal of coordinated water contributes to the turn-on.

However, the water effect does not account for all the luminescence turn-on after **3** is exposed to DMF vapor. If we ascribe the difference in emission intensity between **3**-H_2O and **3**-D_2O before exposure to DMF vapor (243 and 342, respectively, top half of Table 1) to the water effect, the much

Table 1: Emission lifetime (τ) and intensity (Int) measured with ligand-based excitation and direct Eu excitation.

	τ_{H_2O}@ 616 nm [μs][a]	τ_{D_2O}@ 616 nm [μs][a]	No. coord. water molecules	Int_{H_2O}@ 616 nm	Int_{D_2O}@ 616 nm
Ligand-based excitation (@323 nm):					
before DMF[b]	748	1134	0.48	243	342
after DMF[b]	1244	1310	0.04	972	1037
Direct Eu-based excitation (@466 nm):					
before DMF[b]	688	1087	0.56	92	114
after DMF[b]	1090	1140	0.04	111	132

[a] τ_{H_2O} and τ_{D_2O} are the luminescence lifetime for **3**-H_2O and **3**-D_2O, respectively, with emission measured at 616 nm. Int_{H_2O} and Int_{D_2O} are the emission intensities at 616 nm for **3**-H_2O and **3**-D_2O, respectively, and are given in arbitrary units. [b] Before or after exposure to DMF vapor.

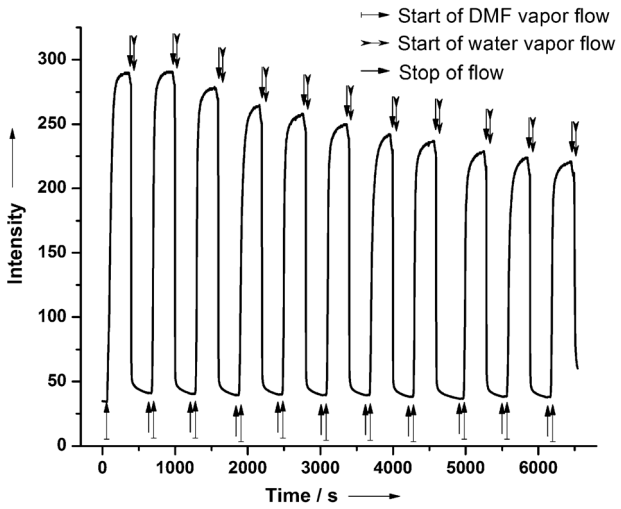

Figure 4. On–off cycles of the sensor with alternating treatment with DMF and with water vapor. The intensity is measured at 616 nm with the excitation wavelength of 323 nm.

greater luminescence enhancement of **3**-D_2O after exposure to DMF vapor (1037, comparing to 342 before exposure) can only be explained as the solvent-specific effect, since no O–H bond is present in the first coordination sphere of Eu in **3**-D_2O. When the Eu emission intensity and lifetime were measured using the direct Eu-based excitation at 466 nm to eliminate the involvement of ligand L via LMET (bottom half of Table 1), the observed emission enhancement of **3**-D_2O after exposure to DMF vapor is much weaker, suggesting that the major contributor of the strong turn-on effect is the more efficient LMET process rather than any local environment change at the metal sites. The selectivity for DMF could be attributed to the tailored solvent channels since the MOF channels are built around DMF as the solvent template. In fact, in the powder X-ray diffraction patterns of samples incubated in various solvent vapors (Figure S8 in the Supporting Information), a breathing effect[18] triggered by solvent adsorption was observed, with DMF causing the most significant change among all solvent vapors tested. These observations, along with the fact that DMF molecules are located only around the ligands rather than in the coordination sphere of the metal centers in the as-synthesized structure leads us to believe that the DMF–ligand interaction is the major contributor to the strong turn-on effect. The adsorption of a large amount of DMF into the solvent channel presumably provides the right combination of the solvent media as well as the rotational constraint for the phenyl rings on the ligands (see the Supporting Information for more details), leading to a change in ligand energy levels that are more favorable for the LMET process.

Besides good selectivity, fast response is also an important criterion for a good sensor. In order to test the response rate of **2**, we designed a prototype sensor setup (see Figure S14 in the Supporting Information). The sensor slide was prepared by attaching a powder of **2** on a glass slide with double-sided tape. DMF and water vapors were introduced to the sensor slide in an alternating manner, and the luminescence intensity at 616 nm was monitored continuously with excitation at 323 nm. The luminescence intensity versus time is plotted in Figure 4.[19] The response rate of the sensor slide is quite fast, with 95% of turn-on and -off achieved within a few minutes and 10–20 seconds,[20] respectively, rendering the MOF a potential sensor for practical application.

In summary, we have successfully synthesized a new luminescent lanthanide MOF that shows a selective luminescence turn-on response to DMF vapor. The XRD, NMR, and luminescence lifetime studies suggest that the majority of the turn-on in response to DMF vapor is caused by DMF–ligand interactions that presumably shift the excited state energy level of the ligand and thus facilitates the LMET process. Such a turn-on mechanism opens up the possibility to build lanthanide-based turn-on luminescent MOF sensors by proper ligand design, targeting analytes through ligand–analyte interactions. We also found that the removal of water ligands from the Eu centers adds to the turn-on effect as a minor contributor. Our prototype sensor showed fast response rates. Studies are underway in our laboratory to further improve the on–off contrast and to optimize the sensor setup.

Received: September 19, 2012
Published online: November 20, 2012

Keywords: DMF · luminescence · metal–organic frameworks · sensors

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[12] CCDC 855541 contain 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.

[13] The $\nu_{C=O}$ band of DMF at 1660 cm^{-1} was not longer evident in the FTIR spectrum of **2** (Figure S7) and nitrogen was no longer detected in elemental analysis. (Anal. calcd for $[Eu_2L_3(H_2O)_4]\cdot 13H_2O$: C, 47.43; H, 5.20; N, 0. Found: C, 47.26; H, 5.11; N, 0.) Powder X-ray diffraction shows that **2** is crystalline (Figure S8).

[14] All incubated samples except that with formamide reached maximum emission intensity within 24 h; the emission intensity of the formamide-incubated sample continued to increase slowly to 1.3-fold enhancement after 96 h, likely due to its low vapor pressure (11 Pa at 20 °C).

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[16] The difference between **2** and **3** is that **2** is air dried while **3** is dried under vacuum which is necessary before it can be transfered into the glovebox. Keeping in mind the two water molecules per Eu center in the crystal structure of **2**, the 0.5 coordinated water molecules per Eu found in **3**-H_2O/D_2O sample is likely the direct consequence of the drying process.

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[19] The decease in the intensity in "on" state is not observed for recycled powder samples (Figure S10), suggesting that the slight intensity decrease over many on–off cycles shown in Figure 4 is likely due to the short exposure time or instability of the sensor slides because of engineering problems.

[20] The response rate was found to be sensitive to the experimental setup. The typical ranges are reported here. Refer to the Supporting Information for details regarding the sensing experiments.

