

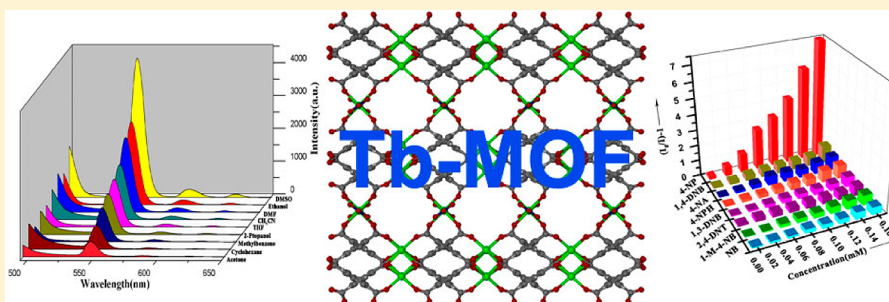
Luminescent Terbium–Organic Framework Exhibiting Selective Sensing of Nitroaromatic Compounds (NACs)

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S Supporting Information



ABSTRACT: An open terbium–organic framework (UPC-11) based on a rigid tetracarboxylate ligand was successfully assembled, which exhibits excellent solvent-dependent photoluminescence (PL). Moreover, UPC-11 displays rapid and selective sensing of nitroaromatic compounds (NACs), especially for 4-nitrophenol (4-NP), which represents the first Tb MOF that can be used as fluorescence detection of 4-NP.

Nitroaromatic compounds (NACs) have become serious pollution sources of groundwater, soils, and other security applications due to their explosivity and high toxicity.^{1,2} Hence, the convenient and high-efficiency detective technologies based on the NACs have received much attention from chemists. Although some traditional detective methods bear high selectivity such as metal detectors, gas chromatography, surface-enhanced Raman spectroscopy, electron capture detection, and cyclic voltammetry,^{3–6} they are usually expensive, inconvenient, and not very good for manipulation. Therefore, new technologies need to be developed so that we may cheaply and rapidly complete detection. The fluorescence-based sensing materials have recently been considered as one of the most excellent and promising techniques in the detection of NACs,^{7–9} because this kind of technique possesses several advantages such as high selectivity, simplicity, portability, and the ability to be applied in both solution and solid phases.^{10–13} In the past decade, some oligomeric, polymeric, or nanoscale fluorescent materials have been prepared and used in the detection of NACs.^{14–16} However, it is still a great challenge for chemists to develop novel fluorescent materials for the detection of NACs because it is not facile to introduce chromophores into the above-mentioned materials as fluorescence sensor.

Metal–organic frameworks are a new class of crystalline materials, which are built from metal cations or clusters and organic ligands.^{17–19} The fluorescent behavior of a MOF is highly dependent on the organic ligands and metal ion/cluster; thus, it is facile to construct fluorescent MOFs by using either

organic ligands with chromophores or metal ions such as Zn²⁺, Cd²⁺, or Ln³⁺, or utilizing the combination of these two parts.^{20–23} Li et al. pioneered the application of fluorescent MOFs on the detection of NACs. In 2009, they first reported a Zn MOF exhibiting fast and reversible detection of high explosives based on mixed ligands.²⁴ Following that, a series of fluorescent MOFs containing Zn²⁺ and Cd²⁺ ions were documented for the rapid fluorescence detection of NACs.^{25–29} For example, Su et al. reported a two-dimensional Cd MOF that can recognize NACs with different numbers of nitro groups.³⁰ Moon et al. directly observed the interaction sites between NACs and the framework by a luminescent Li-based MOF.³¹ Surprisingly, fluorescence detection of NACs based on Ln MOFs was seldom explored, although Ln MOFs show characteristic emission properties and have been considered a class of popular luminescent materials that possess potential applications in bioassays, time-resolved luminescence measurement, and other practical areas.^{32–36} Very recently, Zhang and co-workers reported a porous Eu MOF used as a fluorescent sensor for 2,4,6-trinitrophenol (TNP).³⁷ Mahata et al. reported a three-dimensional Eu-Doped Y-Based MOF used as a fluorescent sensor for 2,4,6-trinitrophenol (TNP).³⁸ However, Tb MOF have seldom been explored.^{39–41} In this Communication, we describe a

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terbium-organic framework, $[\text{Tb}_3(\text{NO}_3)(\text{BPTA})_2(\text{H}_2\text{O})_6] \cdot 3\text{Diox} \cdot 8\text{H}_2\text{O}$ (UPC-11, $\text{H}_4\text{BPTA} = [1,1'\text{-biphenyl}] \cdot 2,2',5,5'$ -tetracarboxylic acid, $\text{Diox} = 1,4\text{-dioxane}$), based on a tetracarboxylate ligand, which shows rapid and selective fluorescent sensing properties of NACs, especially for 4-nitrophenol (NP).

UPC-11 was synthesized by solvothermal reaction of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and H_4BPTA in the mixed solvents of 1,4-dioxane and water. The formula of $[\text{Tb}_3(\text{NO}_3)(\text{BPTA})_2(\text{H}_2\text{O})_6] \cdot 3\text{Diox} \cdot 8\text{H}_2\text{O}$ was further confirmed by elemental analysis and TGA. Single crystal X-ray diffraction reveals that UPC-11 bears a three-dimensional open framework and contains three types of central Tb ions with similar coordination environments: both Tb^1 and Tb^2 are eight-coordinated by six oxygen atoms from four different BPTA ligands and two coordinated water molecules; Tb^3 is also eight-coordinated by four oxygen atoms from two different BPTA ligands, two oxygen atoms from one chelating NO_3^- groups, and two coordinated water molecules. All the carboxylic groups of BPTA ligand were deprotonated during the reaction, two of which adopt bidentate bridging mode to link two Tb ions and the remaining two adopt chelating mode to connect one Tb ion (Figure 1a). Thus, Tb^1 and Tb^2 ions are first connected by

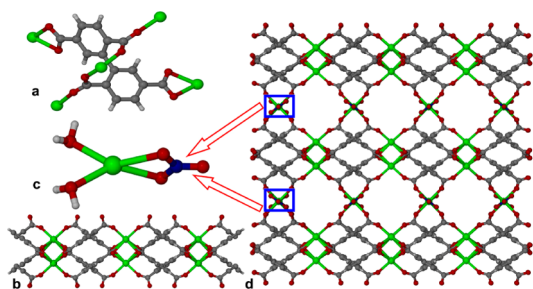


Figure 1. (a) Coordination mode of BPTA in UPC-11. (b) 2D layer generated by BPTA ligands connecting Tb^1 ions. (c) $[\text{Tb}^2(\text{NO}_3)_2]$ unit. (d) 3D open framework of UPC-11 along a axis.

BPTA ligands to generate a two-dimensional wave-like layer framework with the nearest Tb–Tb distance being 6.512 Å. The layers are further linked by the $[\text{Tb}^3(\text{NO}_3)(\text{H}_2\text{O})_2]$ units (Figure 1c) to generate a three-dimensional open framework, in which a large amount of uncoordinated 1,4-dioxane and water molecules reside (Figure 1).

The luminescence spectra of ligand and UPC-11 are shown in Figure S4. UPC-11 exhibits luminescent emissions at $\lambda_{\text{max}} = 490, 545, 584, 622$ nm, upon excitation at 330 nm. The spectrum of UPC-11 show the characteristic transitions of Tb^{3+} ion, which are tentatively assigned to $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$, $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transitions,^{42,43} respectively. On the basis of the luminescent property of UPC-11, its fluorescence sensing was carried out for metal ions and NACs. Usually, provided that MOFs are used as sensing material, they should be dispersed in some organic solvent. To achieve optimal analytic effect and make the results easier to distinguish, the material should have strong emission in the selected solvent. Thus, the photoluminescence (PL) properties of UPC-11 were investigated by dispersing in different solvents. As shown in Figure 2, the PL intensities of UPC-11 are highly dependent on the solvent molecules. Clearly, UPC-11 possesses the strongest emission when it is dispersed in dimethyl sulfoxide (DMSO), and the weakest emission when it is dispersed in nitrobenzene (NB). Accordingly, UPC-11 was dispersed in DMSO to form

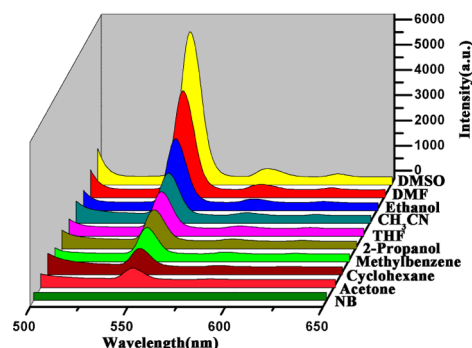


Figure 2. PL spectra of UPC-11 that was dispersed in different solvents.

suspension in the following measurements, into which the analyte in DMSO was gradually added.

To examine the potential of UPC-11 for the sensing of metal ions, DMSO solution containing different metal ions (Li^+ , Ag^+ , Mg^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} , Fe^{3+}) was gradually added into the DMSO emulsions of UPC-11. The PL properties are recorded and listed in Figure 3. Most of metal ions have quenching

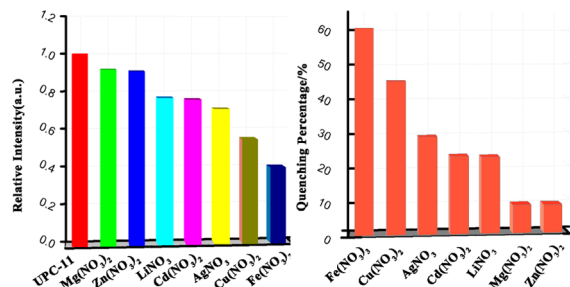


Figure 3. (Left) photoluminescence intensity of the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition (545 nm) and (Right) percentage of fluorescence quenching, obtained for introducing different metal ions into the DMSO-emulsion of UPC-11.

effects on the luminescence intensity of original suspension to some extent. Specifically, the luminescence intensity of UPC-11 at 545 nm decreases slightly when Li^+ , Ag^+ , Mg^{2+} , Zn^{2+} , Cd^{2+} ions are added, but decreases significantly when Cu^{2+} and Fe^{3+} ions are added (Figure 3). This result indicates that UPC-11 can sense Cu^{2+} and Fe^{3+} ions through fluorescence quenching, although the selectivity is moderate.^{44,45}

As mentioned above, rapid and selective detection of benzene compounds, especially for nitroaromatic compounds (NACs), is very important. Hence, different benzene compounds in DMSO (1 mM) were gradually added into the DMSO-suspensions of UPC-11 to determine its sensing properties. We first selected some general solvents, such as benzene (BZ), toluene (TO), chlorobenzene (CB), and nitrobenzene (NB), as the analyte. The results show that nitrobenzene can slightly quench the emission of UPC-11, as shown in Figure 4a. The quenching mechanism is likely derived from the electron transfer from the BPTA ligands to the electron-deficient NB molecules.³⁰ In order to further explore the sensing potential of UPC-11 for other NACs, various analogues, such as 1,3-dinitrobenzene (1,3-DNB), 2,4-dinitrotoluene (2,4-DNT), 1,4-dinitrobenzene (1,4-DNB), 4-nitrophenol (4-NP), 4-nitroaniline (4-NA), 1-methyl-4-nitrobenzene (1-M-4-NB), and (4-nitrophenyl)-hydrazine (4-NPH)

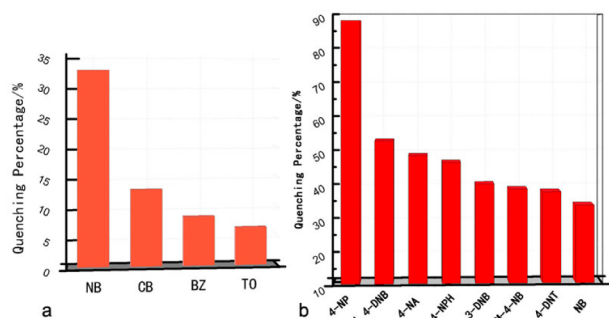


Figure 4. (a,b) Percentage of fluorescence quenching obtained for introducing different benzene compounds and NACs into the DMSO-emulsion of UPC-11.

were used as the investigated reagents. Similar to the above method, the DMSO solution (1 mM) containing NACs were gradually added into the DMSO-suspensions of UPC-11, and the fluorescence change was monitored by PL spectroscopy. The results that show all NACs can weaken the fluorescence intensity of UPC-11 suspension, but the quenching percentage exhibits a big difference (Figure 4b). Meanwhile, the addition of 1,3-DNB, 2,4-DNT, 1,4-DNB, 4-NA, 1-M-4-NB, and 4-NPH solution caused relatively little but similar fluorescent intensity change of suspension, but the introduction of 4-NP produced significant quenching of fluorescence intensity. As shown in Figure 5, the fluorescence quenching efficiency was calculated

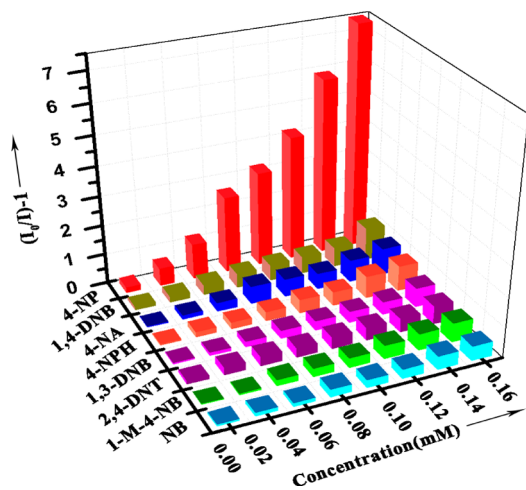


Figure 5. Corresponding Stern–Volmer plots of analytes.

using the Stern–Volmer (SV) equation,⁷ $(I_0/I) = K_{sv}[A] + 1$, where I_0 is the initial fluorescence intensity before the addition of analyte, I is the fluorescence intensity after adding the analyte, $[A]$ is the molar concentration of analyte, and K_{sv} is the quenching coefficient. According to the equation, the quenching efficiency for the NACs in DMSO was found to be the following order: 4-NP \gg 1,4-DNB > 4-NA > 4-NPH > 1,3-DNB > 1-M-4-NB > 2,4-NB > NB. The significant sensing of UPC-11 on 4-NP molecule in DMSO suspension prompted us to investigate its capabilities for the detection of 4-NP in vapor phase at room temperature. Unfortunately, the fluorescence quenching effect of 4-NP on UPC-11 is very slow. After exposing UPC-11 to the vapor of 4-NP for 7 days at room temperature, the emission of UPC-11 was completely

quenched as observed by naked eyes under UV light (Figure S17).

In summary, a terbium-organic framework (UPC-11) based on a tetracarboxylate ligand was synthesized and characterized. UPC-11 exhibits excellent photoluminescence properties with solvent-dependent fluorescent intensities, and the strongest emission intensity is observed in DMSO solvent. Moreover, UPC-11 can sense Fe^{3+} and Cu^{2+} ions in DMSO-suspension in a moderate selectivity. The most striking property of UPC-11 is its fast and selective detection for NACs, especially for 4-NP, which make it a promising NAC-selective luminescent probe. Further studies will focus on the synthesis of other fluorescent MOFs and their application in the detection of NACs.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis and selected crystallographic data (CIF) of UPC-11; PXRD, TGA, and PL experimental procedures; calculation details; and additional figures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.5b00381.

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Notes

The authors declare no competing financial interest.

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