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Short communication

A new bimetallic lanthanide metal-organic framework as a self-calibrating sensor for formaldehyde

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ABSTRACT

We have designed and synthesized a new material of bimetallic lanthanide metal–organic framework [$Eu_{3.2}Gd_{0.8}(NDC)_6(H_2O)_5]\cdot 3H_2O$($Eu_8Gd_2$-NDC NDC = Naphthalene-2,6-dicarboxylic acid) with dual emission. The structure, composition and morphology of the Eu_8Gd_2-NDC were characterized by XRD, SEM and FT-IR respectively. The Eu_8Gd_2-NDC exhibits a highly detectable luminescence in response to formaldehyde (HCHO). The luminescence intensity (I_{453}/I_{616}) increases linearly with increasing HCHO content in the range from 0.05 to 2.5%. The sensing mechanism was also discussed. A paper strip coated with Eu_8Gd_2-NDC material was also shown to be highly selective for formaldehyde. This is the first demonstrated self-calibrating luminescent sensor for small molecules based on the bimetallic lanthanide metal-organic framework.

1. Introduction

Metal organic frameworks (MOFs) are a relatively new type of porous and crystalline materials consisting of an assembly of metal-containing units coordinated to organic ligands and promising multifunctional materials [1, 2]. Luminescence is one of the most interesting properties of the MOFs. Particularly, luminescent lanthanide MOFs have captured widespread research interests due to the unique optical properties of lanthanide ions and are becoming very promising functional materials for sensing applications [3–7]. In the past decade, research on luminescent Ln-MOFs for sensing metal ions [8], anions [9,10], small molecules [11–14] and temperature [15–17] have been widely reported.

In most of the Ln-MOFs, the sensing function is performed based on the luminescence quenching in a single emission, which is generally influenced by environmental interference like light source intensity, sensor concentration, etc. This could lead to inaccuracy in quantification [18, 19]. The ratiometric sensing approach is one of the breakthroughs because it can provide a self-calibrating mechanism by comparing the luminescence intensities of different luminescent center without requiring any external reference [20–22]. Meanwhile, Lanthanide ions like terbium and europium could emit the characteristic luminescence via antenna effect [23, 24]. Naphthalic derivatives can sensitize the luminescent lanthanide ions effectively and exhibit interesting optical properties [25,26]. Investigations on MOF sensors with dual luminescent centers have been very limited [20]. In this paper, lanthanide metal organic frameworks with dual emission signals is designed and utilized as a sensor for detection of analytes analytes via interaction between analyte and ligand.

Detection of aldehydes has been under the spotlight for a long time due to their biological and genetic toxicity. Among aldehydes, formaldehyde is widely used in construction, furniture and particle board [27–28], however, it is very dangerous to human being and could result in asthma, dermatitis, respiratory irritation, and pulmonary edema [29–31]. Thus, it is very meaningful to monitor and control exposure from formaldehyde in both industrial and other environments. Formaldehyde detection is usually performed by high performance liquid chromatography (HPLC) or gas chromatography, etc. Nevertheless, sophisticated instruments and complicated sample preparation have restricted the development of the techniques. Therefore it is necessary to develop simple, highly sensitive and low-cost luminescent probes. The wide variety of luminescent Ln-MOFs and their inherent synthetic versatility make them ideal for small molecular recognition. However, in recent years, there have been few reports about lanthanide MOFs used on the detection of formaldehyde [32].

Herein, we designed and synthesized a new luminescent material Eu_8Gd_2-NDC with dual-emission signal by simple hydrothermal method. The material can be used as a self-calibrating luminescent sensor targeting formaldehyde in aqueous solution, which exhibited excellent ratiometric luminescence response to HCHO (0.05–2.5%). The advantages of this sensor include high selectivity and sensibility, water stability, low-cost and the application convenience which renders potential in biological system.

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Powder X-ray diffraction (PXRD) patterns of Eu_8Gd_2-NDC were in agreement with simulation [33] (Fig. 1). The field emission scanning electron microscopy (FE-SEM) results revealed that the material consists of homogeneous particles with crystal sizes in the range of 100–250 nm (Supporting information Fig. S1a and b). Thermogravimetric analysis of Eu_8Gd_2-NDC was performed in Fig. S1c.

As seen in Fig. 2(a), the emission intensity of the mixed Ln-MOFs can be fine-tuned by adjusting the Eu^{3+}/Gd^{3+} ratios. In mixed Ln-MOFs, when the ratio of Eu^{3+}/Gd^{3+} is 9;1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, luminescence intensity of the mixed Ln-MOF changes little, when the ratio of Eu^{3+}/Gd^{3+} is 8:2, luminescence intensity reached the maximum. The enhanced luminescence efficiencies of Eu^{3+} ions in the doped complexes might result from the decrease of the self-quench of the Eu^{3+} ions induced by the doped lanthanide ions [34]. As shown in Fig. 2(b), Eu_8Gd_2-NDC exhibits characteristic emission of the Eu^{3+} ion upon excitation at 360 nm. Eu_8Gd_2-NDC exhibits the characteristic peaks at 590, 612, 700 nm, which are attributed to $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 4) transitions of the Eu^{3+} ion, respectively. The photoluminescence spectra of NDC^{2-} (before and after treatment with formaldehyde) and Eu_8Gd_2-NDC (after treatment with formaldehyde) were examined at room temperature. a free NDC^{2-} ligand treated with HCHO (40%) showed maximum emission at 453 nm. The emission spectrum of Eu_8Gd_2-NDC (after treated with formaldehyde) is rather analogous to that of the NDC^{2-} (after treated with formaldehyde) indicating that the luminescence of the framework can be regarded as ligand-centered emission (Supporting information Fig. S2).

In view of the excellent luminescence and good water stability of Eu_8Gd_2-NDC (Supporting information Fig. S3), we investigate small molecules recognition of the Eu_8Gd_2-NDC in aqueous solution. In Fig. 3(a), the powder of Eu_8Gd_2-NDC are immersed in various small molecules (MeOH, EtOH, acetone, H_2O, DMF and HCHO), The results reveal that most small molecules display slight quenching effects on the emission intensity of Eu_6Gd_3NDC at 616 nm and 453 nm, however, the addition of formaldehyde showed almost completely quench the emission at 616 nm, while the emission at 453 nm becomes conspicuous. The luminescence property of Eu_8Gd_2-NDC was investigated with increasing formaldehyde concentration. As seen in Fig. 3(b), with increasing concentration of formaldehyde, the intensity of the emission at 616 nm dramatically decreases, meanwhile the ligand-based emission at 453 nm becomes strong. Based on these results, it is obvious that the Eu_8Gd_2-NDC can detect HCHO in aqueous solution via a ratiometric luminescence approach. In Fig. 3(c), when the added formaldehyde concentration reaches 2.5%, the relative ratio of the luminescence intensities at 453 and 616 nm exhibit a 38-fold increase. The results reveal that a linear relationship between the luminescent intensity ratios (I_{453}/I_{616}) and the concentrations of HCHO in the range of 0.05–2.5%, suggesting that the analytical performance of Eu_8Gd_2-NDC is also potentially useful for the quantitative sensing of HCHO. In Fig. 3(d), the Eu_8Gd_2-NDC was also immersed in a solution containing HCHO and a series other analytes, including DMF, Acetone, EtOH, MeOH and MeCN respectively. Under the excitation of 360 nm light, compared to the original one, the luminescence intensity of the Eu_8Gd_2-NDC immersed in the other analyte (1% DMF, Acetone, EtOH, MeOH and MeCN respectively) changes slightly, However, when the Eu_8Gd_2-NDC is immersed in the mixed analytes (1% other analyte + 1% HCHO), the measurement of the luminescence intensity shows that the luminescence is quenched completely, indicating that the selectivity for HCHO is not interfered by the existence of other analytes.

As seen in Fig. 4(a), PXRD of the residues of suspensions (Eu-NDC and HCHO) is consistent with the pattern of NDC^{2-} (after treatment with formaldehyde). In Fig. 4(b), Fourier transform infrared spectra (FTIR) show that the vibration bands (1685, 1294 and 831 cm^{-1}) are assigned as NDC^{2-} (after treatment with formaldehyde). Compared to Eu_8Gd_2-NDC, infrared spectra of Eu_8Gd_2-NDC (after treatment with HCHO) showed new peaks at 1685 and 1294 cm^{-1} which are consistent with the peaks of NDC^{2-} (after treatment with formaldehyde). Moreover, electrospray ionization mass spectrometry spectra (the residues from Eu_8Gd_2-NDC treated with HCHO) showed an intense peak at *m/z* 215.3, which could be belonged to the NDC^{2-} (from Eu_8Gd_2-NDC) (Fig. 4c). The above results show that the detection of HCHO by Eu_8Gd_2-NDC was attributed to the collapse of the crystal structure of Eu_8Gd_2-NDC and regeneration of the NDC^{2-} after treatment with HCHO, thus leading to the disappearance of the emission at 616 nm and the emergence of the ligand emission at 453 nm.

To demonstrate potential applications of Eu_8Gd_2-NDC in the portable devices, a luminescent test paper was prepared by pouring a suspended aqueous solution of Eu_8Gd_2-NDC (0.5 mg/mL) on to filter paper and then dried in air. As shown in Fig. 4, these test papers were utilized to sense HCHO. The red luminescence of the test paper was completely and dramatically quenched when HCHO aqueous solution was dropped on the paper. Indoor HCHO detection is of great necessity and in huge demand for human health. The film was also applied to detect HCHO vapor (Supporting information Figs. S4 and S5). The results show that the film can detect HCHO vapor.

2. Conclusions

In summary, a new bimetallic lanthanide metal–organic framework (Eu_8Gd_2-NDC) with dual emission were designed and prepared via simple hydrothermal method. The material (Eu_8Gd_2-NDC) can be used as a

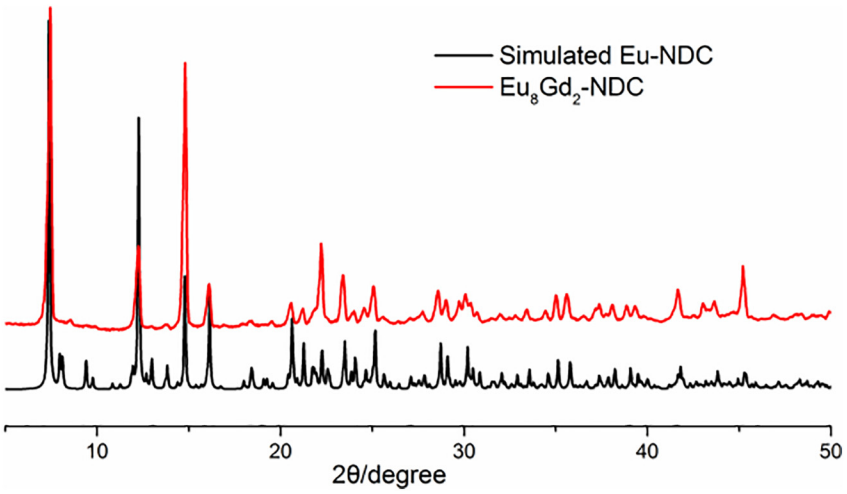

Fig. 1. PXRD patterns of the simulated Eu-NDC and Eu_8Gd_2-NDC.