

Short communication

Photofunctional hybrid based lanthanide functionalized metal-organic frameworks by ion exchange and coordination modification for luminescent sensing



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ABSTRACT

In this paper, bio-MOF-1 ($Zn_8(ad)_4(BPDC)_6O \cdot 2Me_2NH_2$, ad = adeninate, BPDC = biphenyldicarboxylate) is modified to afford series of luminescent lanthanide hybrid material systems through both ion exchange of Ln^{3+} (Ln = Eu, Sm, Nd and Yb), and coordination modification of HBN (6-hydroxybenz[de]anthracen-7-one) ligand. The resulted hybrids formulated as HBN-Ln-bio-MOF-1 show the characteristic luminescence to Ln^{3+} in both visible (for Eu^{3+} , Sm^{3+}) and near infra-red region (for Nd^{3+} and Yb^{3+}), respectively. Furthermore, HBN-Eu-bio-MOF-1 is selected for sensing metal ions and small molecules. Interestingly, it shows highly sensitive sensing for both Fe^{3+} and Fe^{2+} ions, and especially for Fe^{3+} , which can be expected to have potential application for recognizing iron ion species. Besides, it also shows the sensitive sensing for acetone molecules. The results are benefit for the further application of functionalized bio-MOFs in practical fields.

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Photofunctional hybrid materials have been extensively investigated for their advantages that both provide the versatile choice for composition units and improve the photo-stability [1]. Among the chemically bonded hybrids are assembled through all kinds of strong interactions consisting of covalent, coordination, ion-covalent and Lewis acid/base bonds, etc. [2,3], which attracts great interest of researchers. The building units to construct the hybrid materials involve a lot of species, such as silica or mesoporous silica, polymer or polymer composites, microporous zeolite or metal coordination polymers and so on [4–6]. It needs to be referred that the crystalline building units is important for hybrid systems for they can show the luminescence behaviors of both inorganic phosphors and molecular materials [7,8]. On the other hand, it can be expected to realize the photofunctional integration to be favorable for practical application in optical devices for display or lighting. Besides, it is also attractive to explore the application of luminescent sensing in biomedicine or environmental fields [9,10].

Besides traditional zeolite molecular sieve, metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) are another important crystal materials and have been developed in many areas [11], whose versatile choice of metal ions and organic linkers can readily control the composition, structure and function of the framework [12]. Besides, MOFs or PCPs display a wide range of luminescent performance,

involving both an organic linker and a metal ion within the special porous structure [13] to produce all kinds of luminescence nature such as linker or ligand-based luminescence, the coordinated metal ions based luminescence, antenna effects for energy transfer and sensitization luminescence from linker or ligand to metal ions, excimer and exciplex formation emission, etc. [14]. Lanthanide ions is noteworthy for their abundant luminescent behavior, which not only form the luminescent MOFs as central ions but also modify the other metal centered MOFs through the ion substitution or coordination [15,16]. The introduction of lanthanide ions in MOFs endows the new luminescent character of Ln^{3+} , which can compensate with MOFs or ligands as the luminescent species for their different luminescent region. Therefore, it can easily to tune the luminescence color and even to obtain the white color emission [17].

Bio-MOFs is interesting for their basic bio-molecule building units in the frameworks [18] and among which bio-MOF-1 ($Zn_8(ad)_4(BPDC)_6O \cdot 2Me_2NH_2$, ad = adeninate, BPDC = biphenyldicarboxylate) is most popular for it can be further easily functionalized via post-synthetic cation exchange of luminescent lanthanide ions [18,19]. We have also introduced the organic ligands to realize the luminescence integration and further to try to develop their applications [20–23]. In this paper, we further assemble the hybrid material system based bio-MOF-1 as host using the special ligand to link lanthanide ions exchanged to bio-MOF-1 framework. Some visible (Eu^{3+} , Sm^{3+}) and near infrared (Nd^{3+} , Yb^{3+}) luminescent lanthanide ions

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are used to modify bio-MOF-1 and then a new ligand HBN (6-hydroxybenz[de]anthracen-7-one, Fig. S1) is then to coordinate to Ln^{3+} . At the basis of the research on the luminescence properties of these hybrid materials, we put emphasis on the checking the sensing of them.

Figs. S2 and S3 show the selected X-ray diffraction patterns of bio-MOF-1, Ln-bio-MOF-1 and HBN-Ln-bio-MOF-1 hybrids (Ln = Eu, Nd, Sm, Yb). From the XRD results, it can be found that after the long time exchange treatment, the Ln^{3+} loaded bio-MOF-1 and further HBN coordinated hybrid materials (Ln-bio-MOF-1 and HBN-Ln-bio-MOF-1 hybrids) still maintain the crystal framework of bio-MOF-1 and the incorporation of lanthanide ions or coordinated ligands can't destroy on the framework structure of it. So the pore structure of the functionalized bio-MOF should be also maintained, suggesting that bio-MOF-1 is stable crystal framework host materials benefit for the further application. Fig. S4 shows the selected SEM image of bio-MOF-1, Eu-bio-MOF-1 and HBN-Eu-bio-MOF-1 hybrids, which presents the similar irregular schistose morphology. In the hybrid materials, bio-MOF-1 crystal phase and framework are maintained well. Figs. S5 and S6 show the selected FT-IR spectra of bio-MOF-1, Ln-bio-MOF-1 and HBN-Ln-bio-MOF-1 hybrids (Ln = Eu, Sm, Nd, Yb). Both of them show the similar bands. The bands at 1540 and 1385 cm^{-1} are stretching vibration of benzene and carboxylate anion, respectively. The inset of the zoom bands at range of 1350 to 1700 cm^{-1} further clearly show the IR spectra of bio-MOF-1 and Ln^{3+} @bio-MOF-1 are almost identical. This means that the loading Ln^{3+} into the bio-MOF-1 framework have not change the chemical linking modes of bio-MOF-1, which takes agreement with the result of XRD.

Fig. S7 presents the luminescent excitation and emission spectra of bio-MOF-1 (a) and HBN ligands (b). For Fig. S7(b), HBN show the wide emission ranging in 450 – 650 nm , whose excitation extends to visible region of around 460 nm . For Fig. S7(a), the excitation spectrum shows a similar broad excitation band ranged in 250 – 400 nm , corresponding to the absorption of organic linker BPDC in the framework of bio-MOF-1. Its emission spectrum presents a broad band covering 350 – 550 nm with maximum peak at around 400 nm , which belonging to a high energy level near ultraviolet emission with deep blue color. Fig. 1 presents the luminescent excitation and emission spectra of hybrid systems HBN-Eu-bio-MOF-1 (a) and HBN-Sm-bio-MOF-1 (b), both of them show a similar broad excitation band ranged in 250 – 400 nm originating from the absorption of BPDC in the framework of bio-MOF-1. So this suggests that the energy derives from the absorption of bio-MOF-1. After the incorporation of Eu^{3+} , its characteristic luminescent spectrum bands appear, and the luminescence band for bio-MOF-1 still exists. For HBN-Eu-bio-MOF-1 hybrids in Fig. 1(a), five strong emission bands at around 578 , 589 , 615 , 649 and 698 nm can be found for the characteristic ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($j = 0$ – 5) transition of Eu^{3+} . For HBN-Sm-bio-MOF-1 hybrids in Fig. 1(b), four weak emission bands at around 560 , 598 , 643 and 722 nm appear for the characteristic ${}^4\text{G}_{5/2} \rightarrow {}^6\text{F}_j$ ($j = 5/2, 7/2, 9/2, 11/2$) transition of Sm^{3+} . Sm^{3+} @bio-MOF-1 hybrids still show the strong emission of bio-MOF-1, resulting in the deep blue color luminescence, like bio-MOF-1 itself. While Eu^{3+} @bio-MOF-1 hybrid system only shows very weak emission of bio-MOF-1, suggesting that the effective energy transfer take place between bio-MOF-1 and HBN Eu^{3+} and Sm^{3+} . Fig. 1(c) shows the picture of the luminescent bio-MOF-1, HBN-Eu-bio-MOF-1 and HBN-Sm-bio-MOF-2 hybrids under the xenon lamp, which shows the blue, red and orange-red color.

The luminescent spectra of HBN-Nd-bio-MOF-1 and HBN-Yb-bio-MOF-1 hybrids are shown in Fig. 2. For HBN-Nd-bio-MOF-1, its excitation spectrum is obtained by monitoring the strongest emission of the Nd^{3+} ion at 1059 nm , which exhibits a broad excitation band in ultraviolet region at the rage of 250 to 400 nm . Following the photoexcitation at 327 nm , the characteristic emission of Nd^{3+} ions is obtained, whose emission spectrum consists of three bands, peaking at about 905 , 1064 , and 1330 nm . They are derived from the Nd^{3+} 's f-f transitions

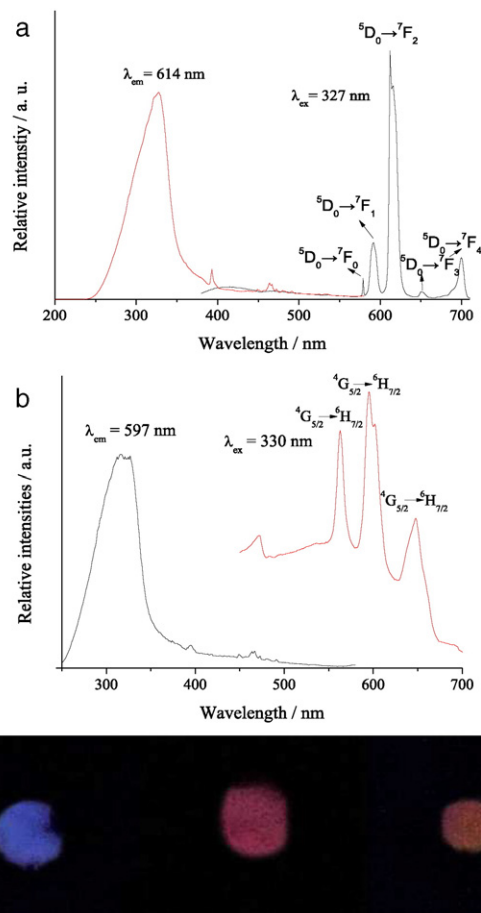


Fig. 1. The excitation (red) and emission spectra (black) of (a) HBN-Eu-bio-MOF-1 ($\lambda_{\text{em}} = 614\text{ nm}$, $\lambda_{\text{ex}} = 327\text{ nm}$) and (b) HBN-Sm-bio-MOF-1 hybrids ($\lambda_{\text{em}} = 597\text{ nm}$, $\lambda_{\text{ex}} = 330\text{ nm}$) and (c) photos of bio-MOF-1, HBN-Eu-bio-MOF-1 and HBN-Sm-bio-MOF-1 hybrids at 254 nm under UV lamp.

of ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$, ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$, and ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{13/2}$, respectively. Among the three emission bands of these emission spectra, the bands centered at 1059 nm exhibit the strongest intensity, which is potentially applicable for the laser system [22]. Fig. 2(b) shows the excitation and emission spectra of HBN-Yb-bio-MOF-1 hybrids. The excitation spectrum measured by monitoring 980 nm emission are composed of a broad band in the ultraviolet/visible spectral range from 250 to 400 nm , which are attributed to the light absorption by the bio-MOF-1 and HBN ligand. The excitation spectrum extends to the visible range, which enables photoexcitation of them by visible sources. After ligand-mediated excitation at around 327 nm , the emission spectra of both complexes and hybrid materials show the characteristic emission of the Yb^{3+} ion, a band in the 910 – 1180 nm range with the main and strongest peak at 1015 nm . This is assigned to the ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition of Yb^{3+} [23].

Firstly we examine the potential of HBN-Eu-bio-MOF-1 hybrids for the sensing of organic small molecules. As shown in Figs. S8 and 3(a), the PL spectra are significantly dependent on the solvent molecules, particularly in the case of acetone, which exhibit clearly quenching effects. When immersing different quantities (6 – 2 mg) of HBN-Eu-bio-MOF-1 in 2 mL acetone, the emission of Eu^{3+} results in a dramatic decreased luminescence intensity. The luminescent signal induced by organic small molecules can be partially attributed to the UV-vis absorption. The result indicates that the absorption band of acetone partially overlaps with the absorption band of HBN-Eu-bio-MOF-1 which has reduced the absorption of light by organic ligand and affected the energy transformation from MOF to Eu^{3+} .

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