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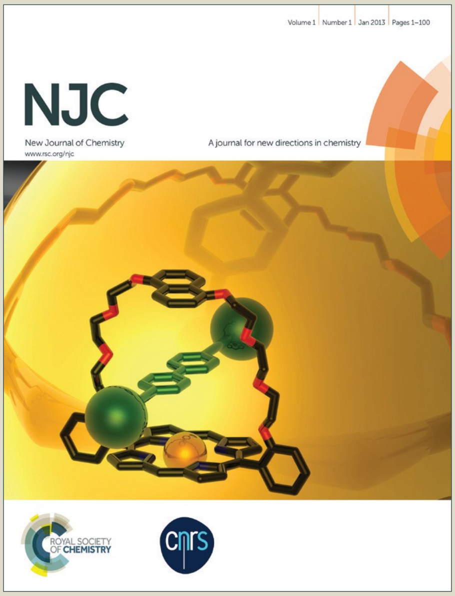

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Ln^{3+} post-functionalized metal-organic frameworks for color tunable emission and highly-sensitivity sensing of toxic anions and small molecules

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A facile strategy was put forward to fabricate highly luminescent metal-organic frameworks (MOFs) with tunable and white-light emission by incorporating lanthanide cations (Ln^{3+}) into the channels of MIL-121 ($Al(OH)(H_2btec){\cdot}H_2O$) whose uncoordinated carboxyl groups can act as postsynthetic modification sites. The intense luminescence of Ln^{3+} doped MIL-121 indicates that the framework with rigid, permanently porous structure and non-coordinated carboxyl can serve as both a scaffold and an antenna for hosting and sensitizing the luminescence of Ln^{3+} cations. Moreover, a fine-tuning of the emitted color luminescence can be easily achieved by simply modulating the doping ratio or adjusting the excitation wavelength. Notably, the Red-Green-Blue-based white light emitting Ln-MOFs can be realized by simultaneously doping Eu^{3+} and Tb^{3+} into the host framework. In addition, because of the excellent luminescence and the structural stability of Ln^{3+} functioanized MIL-121 (Ln^{3+}@MIL-121) in water or solvents, the Eu^{3+}@MIL-121 was developed as a luminescent probe for sensing of anions in aqueous solutions and small organic molecules. Luminescent studies reveal that Eu^{3+}@MIL-121 not only display a high-sensitivity sensing function with respect to fluoride and dichromate ions but also exhibit significant solvent-dependent luminescent response to small-molecule pollutants, such as chloroform and acetone.

Introduction

Metal-organic frameworks (MOFs) composed of metal ions and multitopic organic ligands are a new family of hybrid inorganic-organic porous materials, and have received tremendous attention in the past decades.[1] Among the hundreds of MOFs reported, lanthanide-organic frameworks (Ln-MOFs) are undoubtedly the most promising since they possess unique advantages for luminescence-based applications.[2] On one hand, the emergency of Ln-MOFs has brought bright promise to the development of new functional luminescent materials, especially white-light materials. Previously, efforts have been made in the design of visible color tunable and white-light emitting Ln-MOFs.[3] Typically, Rao *et al*. reported isostructural Tb^{3+}- and Eu^{3+}-codoped ligand-based luminous La^{3+} MOFs whose colors can be easily tuned by the different combination of the doped Tb^{3+} and Eu^{3+} concentrations, generating white light emitting materials.[4] Zhang *et al*. realized white-light emission by a single component Sm(III) framework and the two-component approach, Eu(III) ions doped into the Gd(III) framework, respectively.[5] However, it is still very challenging and difficult to develop suitable Ln-MOF materials capable of producing color tunable and white-light emission because the blue (400 to 490 nm) and yellow (570 to 600 nm) light emitters, and blue (400 to 490 nm), green (510 to 570 nm) and red (600 to 720 nm) light emitters should compensate exactly through the dichromatic and trichromatic approaches, respectively.[6] Moreover, a higher coordination number and more flexible coordination geometry of lanthanide ions make it even harder to obtain stable lanthanide MOFs with pores.[7] Postsynthetic modification (PSM) of MOFs[8] provides an alternative to the conventional introduction of Ln^{3+} species into the channels of MOFs. According to the host-guest system, it will offer a new possibility to realize the multiband emissions originated from different Ln^{3+} and tune the luminescent properties by adjusting the stoichiometry of the hetero-lanthanide ions.

On the other hand, Ln-MOFs can be considered as promising luminescent sensing materials because their inorganic and organic components can provide platforms to generate visible luminescence when induced by UV light. Increasing interest was found in the recognition and sensing of inorganic ions and small organic molecules using Ln-MOFs as luminescent systems.[9] With the development of modern society and industry, environmental pollutants, like toxic ions (heavy metals and anions) and organic small molecules, are increasing released from industrial facilities and other anthropogenic activities, which cause adverse effects on human health and consequently lead to heart attacks, lung cancer, hepatosis, and other serious diseases.[10] Thus, it is of considerable importance for the environment and human health to indentify and monitor these hazardous chemicals. Considering the intense luminescent signal and visible luminescent colors, Ln-MOFs could be good candidates as luminescent sensing materials for environmental pollutants.

Herein, we demonstrate a facile approach to prepare lanthanide-based MOFs with tunable and white-light luminescence by encapsulating the Ln^{3+} cations into MIL-121 crystals. MIL-121[11] ($Al(OH)(H_2btec){\cdot}H_2O$) was chosen as a typical PSM of MOF due to its rigid, permanently porous structure, and the presence of non-coordinating carboxylate groups on the H_4btec linker, which are amenable to post-synthetic modification by reaction with Ln^{3+} ions. The intense luminescence of Ln^{3+} in Ln^{3+} doped MIL-121 implies that the framework was an efficient scaffold for sensitizing Ln^{3+} cations. A fine-tuning of the emission color can be easily achieved by simply adjusting the doped Ln^{3+} concentration or excitation wavelength and the RGB-based white light emitting Ln-MOFs have been realized by simultaneously doping Eu^{3+} and Tb^{3+} into the host framework. In addition, since the excellent luminescence and the structural stability of Ln^{3+}@MIL-121 in water or solvents, the study on the potential of the Eu^{3+}@MIL-121 as a fluorescence probe for toxic anions and organic small molecule pollutants was also carried out.

Experimental section

Materials and instrumentation. Lanthanide chlorides were obtained from the corresponding oxides in HCl (37 %). All the other chemicals were commercially available and used without further purification. Powder X-ray diffraction (PXRD) were performed on a a Rigaku D/max-Rb diffractometer with Cu-Kα radiation. Fourier transform infrared spectra (FTIR) were recorded in the range 4000 – 400 cm^{-1} on a Nexus 912 AO446 infrared spectrum radiometer using KBr pellets. Nitrogen adsorption/desorption isotherms were measured at liquid nitrogen temperature using a Tristar 3000 analyzer. Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. Thermogravimetric analysis (TG) was measured using a Netzsch STA 449C system at a heating rate of 5 K min^{-1} under the nitrogen protection. Measurement of Ln^{3+} and Al^{3+} was performed on an X-7 series inductively coupled plasma-mass spectrometer (ICPMS) (Thermo Elemental, Cheshire, UK). Luminescence spectra and emission lifetimes (τ) were examined by an Edinburgh FLS920 phosphorimeter. The outer absolute luminescent quantum efficiency (η) was determined using an integrating sphere (150 mm diameter, $BaSO_4$ coating) from an Edinburgh FLS920 phosphorimeter.

Synthetic Procedures.

Typical synthesis of MIL-121. The compound MIL-121 was synthesized according to the synthesis method and conditions (molar ration, time and temperature) described in the literature.[11] A mixture of $Al(NO_3)_3{\cdot}9H_2O$ (1.2 g, 3.2 mmol), pyromellitic acid (noted H_4btec, 0.4 g, 1.6mmol), and H_2O (5 mL) was sealed in a 50 mL Teflon-lined stainless steel autoclave which was heated under autogenous pressure at 210 °C for 24 h, then slowly cooled to room temperature. A white powdered product was filtered off, washed with deionized water and dried at 80 °C for 12 h in vacuum. To remove the organic species encapsulated within the pores of the open framework, the resulting product was activated by Soxhlet extraction in methanol for 24 h and then dried at 80 °C under vacuum overnight.

Eu^{3+}@MIL-121 preparation. MIL-121 (100 mg) was soaked in ethanol solutions of $EuCl_3{\cdot}6H_2O$ (10 mL, 2 mmol) for 2 days at 60 °C. The solid was then separated from the mixed dispersion by centrifugation, and extensively washed with ethanol to remove residual Ln^{3+} cations on the surface. Subsequently, the resulted white powder was dried under vacuum at 80 °C for 12 h.

Tb^{3+}@MIL-121preparation. The synthetic procedure for Tb^{3+}@MIL-121 was the same as that for Eu^{3+}@MIL-121 except that $EuCl_3{\cdot}6H_2O$ was replaced by $TbCl_3{\cdot}6H_2O$.

Eu^{3+}/Tb^{3+}@MIL-121preparation. A similar process was employed to prepare Eu^{3+} and Tb^{3+} co-doped MIL-121 by adding a certain amount of $EuCl_3{\cdot}6H_2O$ and $TbCl_3{\cdot}6H_2O$ (total molar amounts: 2 mmol, molar ratio: 1: 2).

Soakage of MIL-121 in $EuCl_3{\cdot}6H_2O$ ethanol solutions with different concentrations. Compound MIL-121 was soaked in 10 mL of ethanol solution of $EuCl_3{\cdot}6H_2O$ with different concentrations: 0.2, 0.1, 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5} (mol/L). After 2 days of soakage at 60 °C, the product was extensively washed with ethanol and dried at 80 °C under vacuum at 12 h.

Luminescent sensing experiments. For the experiments of sensing anions, 3 mg of Eu^{3+}@MIL-121 were simply immersed in the aqueous solutions of anion (10 mM, 3 mL) at room temperature (anions = F^-, Cl^-, Br^-, I^-, NO_3^-, CO_3^{2-}, $Cr_2O_7^{2-}$). For sensing properties with respect to small molecules, 3 mg of Eu^{3+}@MIL-121 powder were introduced into 3 mL of chloroform, acetonitrile, THF, toluene, methanol, ethanediol, ethylether, formaldehyde, acetone, or DMF. The PL spectra of the suspensions were measured after 24 h and stirred vigorously before testing.[9c]

Results and discussion

Characterization of MIL-121 and Ln^{3+}@MIL-121

A series of Ln^{3+} (Ln^{3+} = Eu, Tb and Eu/Tb) functionalized MOFs (MIL-121) were sysntesized by immersing MIL-121 into the ethanol solutions of lanthanide chloride to form Ln^{3+}@MIL-121. The compound MIL-121 was obtained as a white powdered product generated from a carboxyl-rich ligand of benzene-1,2,4,5-tetracarboxylic acid (H_4btec) and $Al(NO_3)_3{\cdot}9H_2O$ under hydrothermal conditions. The PXRD pattern (Figure 1a) of the as-synthesized MIL-121 is in good agreement with that of the previously reported one.[11] MIL-121 is built up from the connection of infinite chains of $AlO_4(OH)_2$ octahedra with the pyromellitate ligand, creating a three-dimensional (3D) framework with one-dimensional pore channels. In the structure of MIL-121, only two carboxylate arms (1,4 positions) of the pyromellitate play the role of linker while the two remaining (2,5 positions) are non-bonded (Figure 1b). Infrared spectroscopy (Figure S1) confirms this point since the bands observed at 1718 cm^{-1} are assigned to the non-coordinating –COOH functions. The N_2 adsorption-desorption studies demonstrated MIL-121 maintains its permanent pore after guest removal, which shows a BET surface area of 165 m^2 g^{-1} (Figure S2). This value is in reasonable agreement with the result reported by Christophe

Volkringer *et al.*[11] Due to the reactive nature of the uncoordinated carboxyl groups and the permanent porosity of MIL-121, Ln^{3+} cations were introduced into the pores of MIL-121 via postsynthetic modification (PSM), and the properties of the resulting host-guest materials (Ln^{3+}@MIL-121) were investigated. After the modification, the IR absorption band of free C=O in MIL-121 becomes weaker, indicating the successful coordination of Ln^{3+} to the free carboxyl in the MIL-121. The incorporation of Ln^{3+} cations does not impact the crystalline integrity and the thermostability of MIL-121, as confirmed by PXRD (Figure 1a) and TGA (Figure S3), respectively. The Ln^{3+}@MIL-121 samples exhibit similar N_2 sorption behavior with MIL-121 (Figure S2), but the BET surface area of Ln^{3+}@MIL-121, as we expected, shows reduced values of 102 (Eu^{3+}@MIL-121), 119 (Tb^{3+}@MIL-121), and 108 (Eu^{3+}/Tb^{3+}@MIL-121) $m^2\ g^{-1}$. Besides, ICP-MS measurements were conducted on the resulting hybrid materials to analyze the skeleton metal (Al) and the loaded Ln components. The results, which are listed in Table S1, reveal that the ratio of Al^{3+} and Ln^{3+} is close to 2:1.

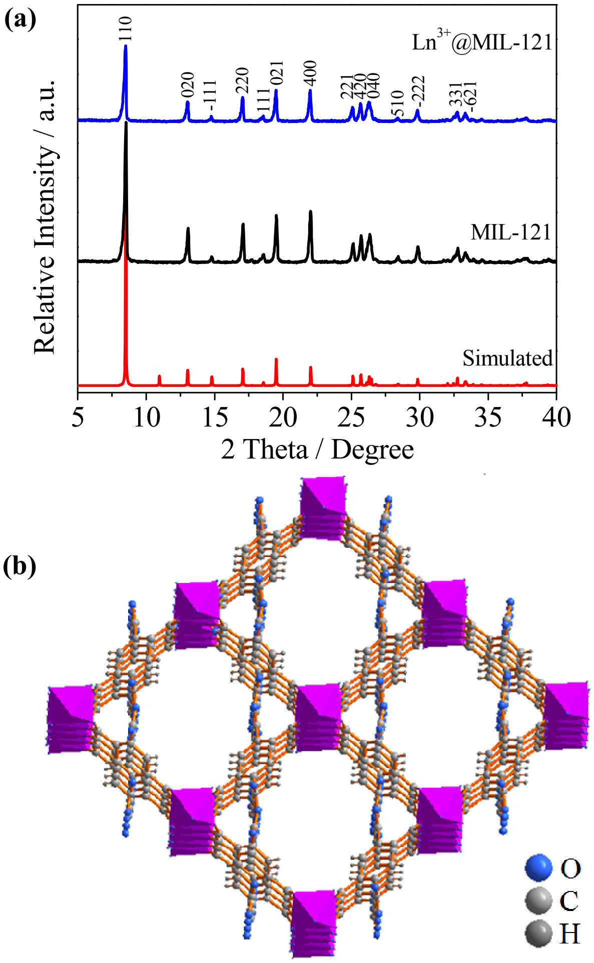
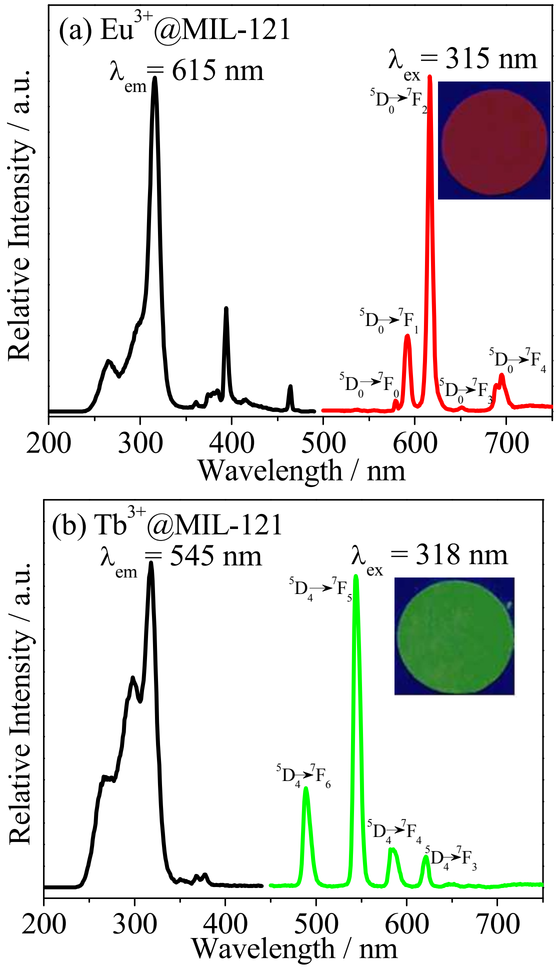


Figure 1 (a) PXRD of MIL-121 (black line) and Ln^{3+}@MIL-121 (blue line); (b) Representative structure of MIL-121, with open non-coordinated –COOH sites for the subsequent incorporation of Ln^{3+} cations.

Luminescence Properties of Ln^{3+}@MIL-121

Photoluminescence studies were performed on each sample of MIL-121 (Figure S4), Eu^{3+}@MIL-121 (Figure 2a), Tb^{3+}@MIL-121 (Figure 2b), and Eu^{3+}/Tb^{3+}@MIL-121 (Figure 2c). Compound MIL-121 displays a wide emission band centered at 350 nm located at the blue region, which arise from π→π* transitions of the ligands. After incorporating Ln^{3+} cations, the resuting samples exhibit their respective strong sharp emission bands (Figure 2) and emit their distinctive colors under UV-light irradiation (insets in Figure 2) (Eu^{3+}@MIL-121, red; Tb^{3+}@MIL-121, green; Eu^{3+}/Tb^{3+}@MIL-121, yellow). This indicates the successful encapsulation of lanthanide ions. Upon excitation at 315 nm, the Eu^{3+} doped MIL-121 (Eu^{3+}@MIL-121) displays narrow luminescence originating from the Eu(III) lowest emitting state $^5D_0$ to $^7F_0$ (578 nm), $^7F_1$ (591 nm), $^7F_2$ (615 nm), $^7F_3$ (650 nm) and $^7F_4$ (695 nm) levels. The most intense emission at 615 nm corresponds to the $^5D_0 \rightarrow {}^7F_2$ transition, yielding an intense red color output. Similarly, for Tb^{3+}@MIL-121, when excited at 318 nm, four sharp distinctive peaks at 489, 545, 585, and620 nm are observed in the visible region coming from $^5D_4 \rightarrow {}^7F_J$ (J = 6 – 3) transitions of Tb^{3+} ion, respectively, and the hypersensitive green color is dominated by the emission of $^5D_4 \rightarrow {}^7F_5$ at 545 nm. When the Eu^{3+}/Tb^{3+} co-doped MIL-121 are excited at 317 nm, the characteristic sharp emission bands of Eu^{3+} (615 nm, $^5D_0 \rightarrow {}^7F_2$; 650 nm, $^5D_0 \rightarrow {}^7F_3$; 695 nm, $^5D_0 \rightarrow {}^7F_4$) and Tb^{3+} (489 nm, $^5D_4 \rightarrow {}^7F_6$; 545 nm, $^5D_4 \rightarrow {}^7F_5$) ions simultaneously exist. The multiband emissions from the Eu^{3+}/Tb^{3+} co-doped sample have the potential to be applied as barcoded materials.[2d, 8e,12]



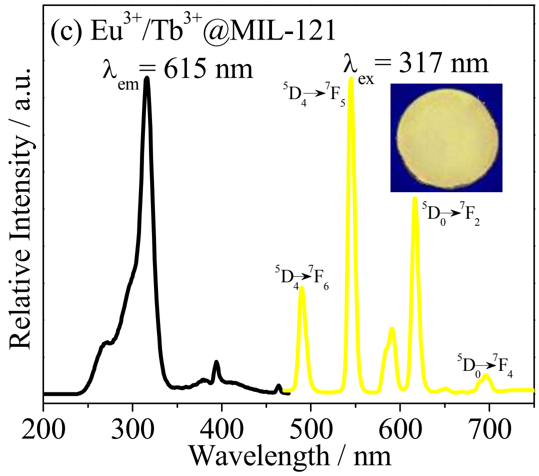


Figure 2 Photoluminescence spectra of Eu^{3+}@MIL-121 (a), Tb^{3+}@MIL-121 (b), and Eu^{3+}/Tb^{3+}@MIL-121 (c). The insets are their corresponding photographs irradiated under a UV lamp.

The diminished LC emissions in the spectra of Ln^{3+}@MIL-121 and their intense luminescence under UV-light irradiation, as well as their long lifetimes and the reasonable high quantum yields (Table S2), indicate the efficient energy transfer from the ligand to the Ln^{3+} cations.

As both the parent structure and the incorporated Ln^{3+} ions contribute to the compound's luminescence properties, a fine-tuning of the emitted color luminescence can be easily achieved by modulating the doping ratio or adjusting the excitation wavelength, Figure 3a shows the emission spectra of the as-obtained samples collected at the excitation wavelength of 315 nm. As the concentration of $EuCl_3$ ethanol solution decreases from 0.2 to 10^{-5} M, the characteristic emission of Eu^{3+} recedes gradually, meanwhile, the broad ligand-centered band in the range of 350 – 450 nm arising from the MIL-121 framework appears. As a result, a tunable chromaticity of visible emission from red to purple could be realized, as depicted by the CIE diagram in Figure 3b.

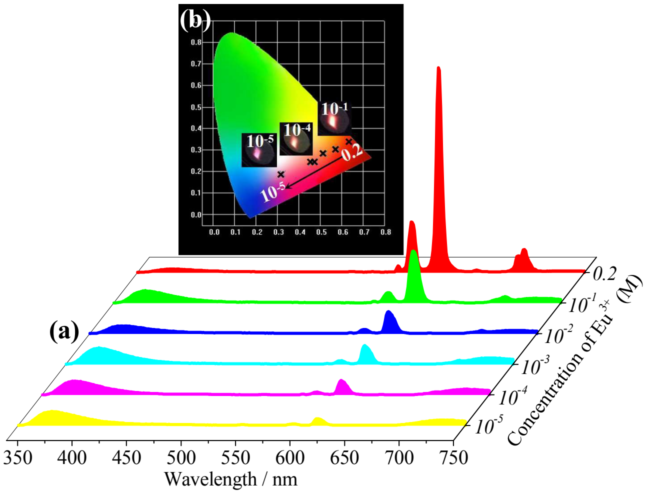


Figure 3 Emission spectra (λ_{ex}=315 nm) (a) and CIE chromaticity (b) of Eu^{3+}@MIL-121 products resulting from $EuCl_3$ ethanol solutions with concentrations in the range of 10^{-5} – 0.2 M. The insets in (b) are the optical photographs excited under 315 nm Xe lamp.

Figure 4a presents the emission spectra of Eu^{3+}/Tb^{3+}@MIL-121 recorded at different excitation wavelength. It was found that the emission color of Eu^{3+}/Tb^{3+}@MIL-121 can be tuned from yellow to white by varying the excitation wavelength. The representative emission photos excited at varied wavelength with a Xenon lamp, as well as the corresponding 1931 CIE diagram showing the chromaticity coordinates are illustrated in Figure 4b. Notably, when excited at 265 or 300 nm, the PL emission spectra feature in observation of three kinds of luminescence. One is the broad LC emission centered at 400 nm, and the others are the characteristic Eu^{3+} and Tb^{3+} sharp emissions. A striking feature is that the combination of these three kinds of luminescence leads to the overall white light emission. This verifies that the white-light emitting from Eu^{3+}/Tb^{3+}@MIL-121 is balanced on synergetic contributions from Eu^{3+}, Tb^{3+} and ligand emissions, because the excitations at different wavelengths will definitely give rise to different emission intensity relativity of these three kinds of luminescence, thus causing shift of the chromaticity coordinate in the 1931 CIE diagram. As a consequence, the luminescent colors are depending on the excitation wavelength, enabling an approach to regulate the white-light property.

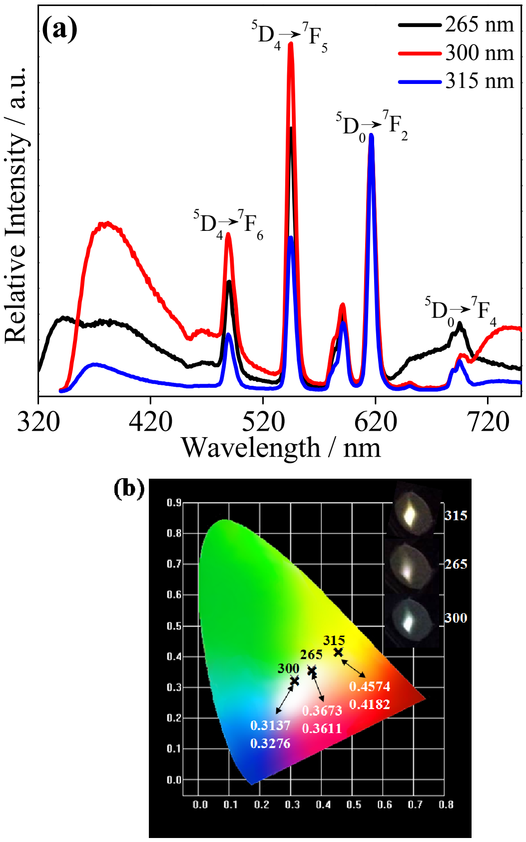


Figure 4 Emission spectra (a) and CIE chromaticity diagram (b) of Eu^{3+}/Tb^{3+}@MIL-121 collected at different excitation wavelengths. Insert in Figure (b): the optical photographs with UV excitation using a Xe lamp as the excitation source.

Anions Sensing

In order to investigate anion recognition of the Eu^{3+}@MIL-121, the suspension-state luminescent experiments were performed. Different kinds of anions (F^-, Cl^-, Br^-, I^-, NO_3^-, CO_3^{2-}, and $Cr_2O_7^{2-}$) have been introduced to the system of Eu^{3+}@MIL-121, and the

Eu^{3+}@MIL-121 is insoluble and stable in anion aqueous solutions, confirmed by the PXRD (Figure S5). The luminescent measurements (Figure 5) illustrate that the intensity of Eu^{3+}@MIL-121 shows the quenching effect for most anions, but the quenching degree is heavily dependent on the species of anions. Among the anions studied, the quenching effects of F^- and $Cr_2O_7^{2-}$ are very pronounced, especially for $Cr_2O_7^{2-}$ ion. After $Cr_2O_7^{2-}$ introduced, the luminescent intensity of Eu^{3+} reduces to 0 from 26250. Although both F^- and $Cr_2O_7^{2-}$ can seriously quench the emission of Eu^{3+}, they can be distinguishable by Eu^{3+}@MIL-121. This is because F^- ion only has quenching effect on the Eu-luminescence but not on the LC emission, while $Cr_2O_7^{2-}$ can not only quench the emission of Eu^{3+}, but also have quenching effect on the emission of ligand, as shown in the inset of Figure 5a. As a result, in the presence of $Cr_2O_7^{2-}$ and F^-, the luminescence color of Eu^{3+}@MIL-121 changes from red to blue and dark, respectively.

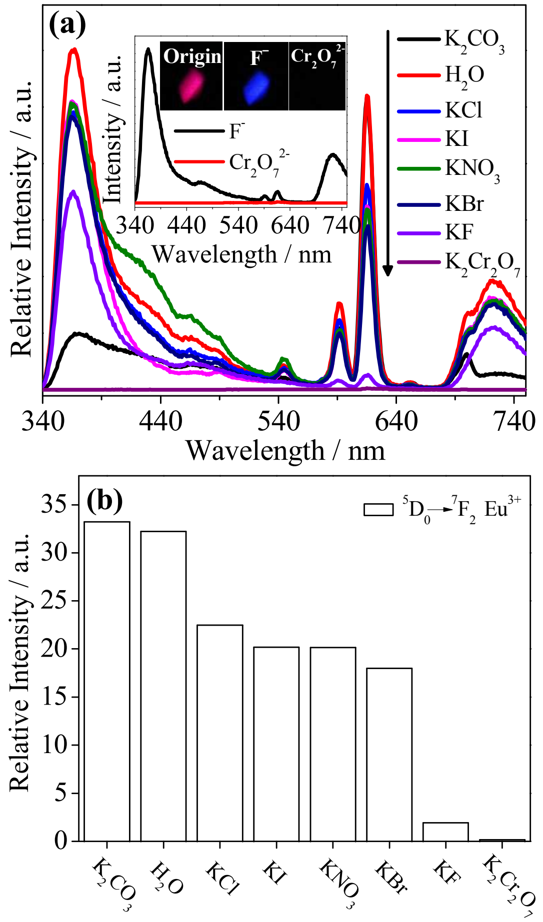


Figure 5 (a) Suspension-state PL spectra and (b) the relative intensities of $^5D_0 \rightarrow {}^7F_2$ at 614 nm for Eu^{3+}@MIL-121 dispersed in aqueous solutions containing different anion ions (10 mM) when excited at 315 nm.

To clearly illustrate the different degrees of quenching effects on the ligand emission by the F^- and $Cr_2O_7^{2-}$ ions, the pure ligands were immersed in the aqueous solutions containing F^- and $Cr_2O_7^{2-}$, respectively. The luminescent properties of pure ligand in the two kinds of anions aqueous solutions were recorded and compared in Figure S6. As expected, $Cr_2O_7^{2-}$ totally quenches the emission of pure ligands while F^- has no significantly quenching effect. These results imply that the Eu^{3+}@MIL-121 can selectively sense F^- and $Cr_2O_7^{2-}$ ions. To further examine the quenching effect of F^- and $Cr_2O_7^{2-}$ on the luminescence intensity of Eu^{3+}@MIL-121, the fluorescence lifetimes were also measured. The luminescence of lifetime (τ) of the Eu^{3+} is shortened from 237.6 μs into 50.9 μs after F^- addition (Table S3), and that is undetectable in the case of $Cr_2O_7^{2-}$, which is in good agreement with the reduction of the PL intensity.

For better understanding the response of fluorescence of Eu^{3+}@MIL-121 to F^- and $Cr_2O_7^{2-}$, concentration-dependent luminescence measurements were also performed. Figure 6 shows the PL spectra of Eu^{3+}@MIL-121 in aqueous solutions containing different concentrations of $Cr_2O_7^{2-}$. With the increase of $Cr_2O_7^{2-}$ concentration from 0 to 500 μM, the luminescence intensity decreases gradually. Quantitatively, this quenching effect can be rationalized by the Stern-Volmer equation:

$$I_0/I = 1 + K_{sv} \times [Q]$$

Where K_{sv} is the Stern-Volmer constant, [Q] is the anion molar concentration, and I_0 and I are the luminescent intensity before and after anion addition, respectively.[13] The linear correlation coefficients of the fluorescence intensity vs $[Cr_2O_7^{2-}]$ plot is 0.99904 (inset of Figure 6), suggesting the quenching effect of anion on the luminescence of Eu^{3+}@MIL-121 fits the Stern-Volmer model well. Similarly, with the increasing concentration of F^-, the luminescence intensity of $^5D_0 \rightarrow {}^7F_2$ at 615 nm of Eu^{3+}@MIL-121 suspension is also showed linear quenching in experiment (Figure S7). The Stern-Volmer constant, K_{sv}, is calculated as 4.34×10^{-3} M^{-1} and 2.07×10^{-3} M^{-1}, for $Cr_2O_7^{2-}$ and F-, respectively, which reveals that $Cr_2O_7^{2-}$ has a stronger quenching effect on the Eu^{3+}@MIL-121 luminescence than F^-. From these data, we have estimated the detection limit of Eu^{3+}@MIL-121 for $Cr_2O_7^{2-}$ and F^- to be 0.054 μM and 0.063 μM, respectively, and this detection limit meets the requirement for the pollutant sensing.

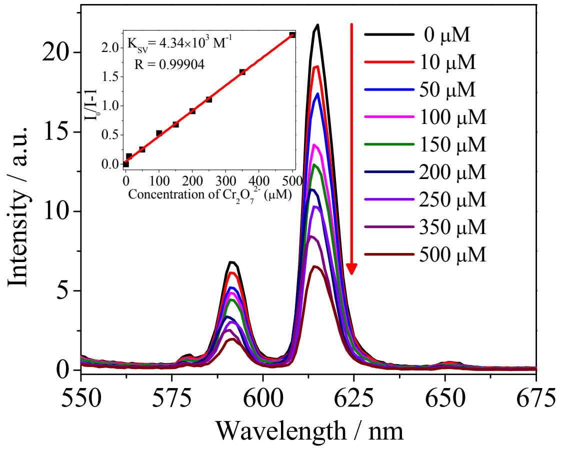


Figure 6 Fluorescence intensity of Eu^{3+}@MIL-121 at 615 nm as a function of $Cr_2O_7^{2-}$ concentration in aqueous solution (λ_{ex}=315nm). Insert: linear relationship of Eu^{3+}@MIL-121 quenched by $Cr_2O_7^{2-}$ aqueous solution.

Organic Small Molecule Sensing.

Organic pollutants are increasingly concerned because of their environmental biological hazards.[14] As a promising new type of sensing materials, luminescent MOFs have been explored to detect organic small pollutants in the environment and biological system, in view of the obvious change of luminescent signals induced by additional organic small molecules.[35-37,40-43] To examine the potential of Eu^{3+}@MIL-121 for the sensing of organic small molecules, their luminescent recognition and selectivity in different solvent suspensions were investigated. Before the solvent-suspension luminescent measurements, the stability and insolubility of the frameworks in common organic solvents, such as chloroform, acetonitrile, THF, toluene, methanol, ethanediol, ethylether, formaldehyde, acetone, and DMF were confirmed by PXRD (Figure S8).

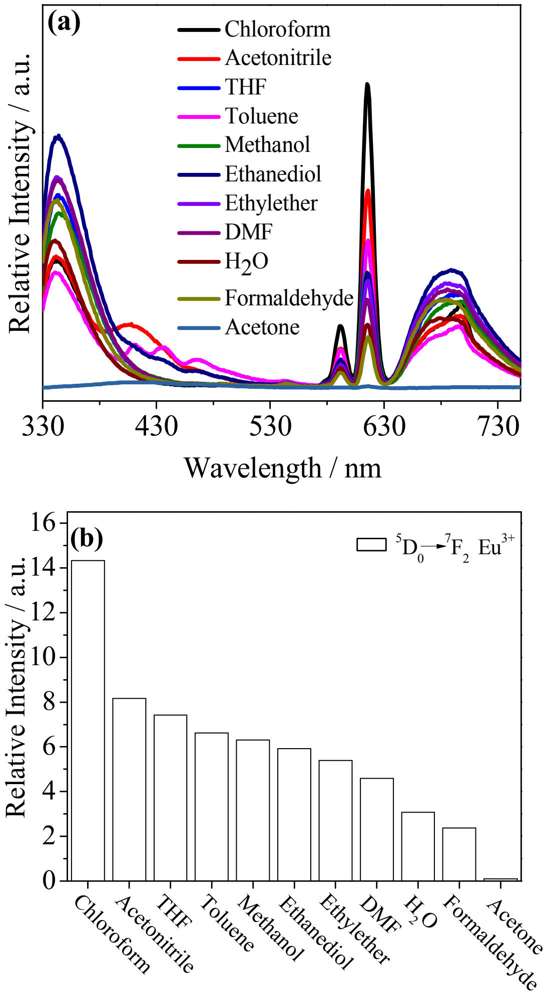


Figure 7 (a) PL spectra and (b) the $^5D_0 \rightarrow {}^7F_2$ transition intensities of Eu^{3+}@MIL-121 dispersed into various pure solvents when excited at 315 nm.

Figure 7 shows the emission spectra of Eu^{3+}@MIL-121 treated by different solvents, and it reveals the luminescence of Eu^{3+} is significantly dependent on the solvent molecules, particularly in the case of chloroform and acetone, which exhibit the most noticeable enhancing and quenching effects, respectively. Such solvent-dependent luminescent properties are of interest for the sensing of chloroform and acetone, which are very harmful to human beings. Therefore, the effects of chloroform and acetone on the luminescent intensities of the compound have been examined in detail further.

The Eu^{3+}@MIL-121 was dispersed in DMF as the standard suspension, while the content of chloroform/acetone was gradually increased to monitor the emissive intensities. It was noticeable that the luminescent intensity of the suspension of Eu^{3+}@MIL-121 increased with the addition of chloroform, as shown in Figure 8A, and the enhancement was nearly proportional to the content of chloroform (inset of Figure 8A). Conversely, addition of acetone into the standard suspension of Eu^{3+}@MIL-121 led to a significant decrease of the fluorescence intensity, which almost disappeared at an acetone content of 8 vol% (Figure 8B). This decreasing trend of the largest luminescent intensities of Eu^{3+} at 615 nm versus the volume ratio of acetone could be well fitted with a first-order exponential decay (insert of Figure 8B), implying that luminescence quenching of Eu^{3+}@MIL-121 by acetone is diffusion-controlled.[36] The above results indicate that the Eu^{3+}@MIL-121 is a promising chemical sensor for small molecule pollutants.

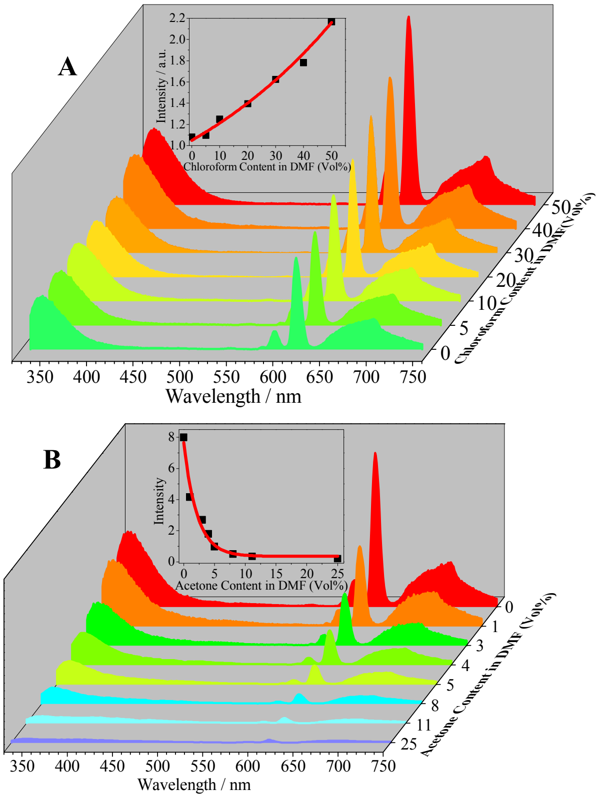


Figure 8 The PL spectra of Eu^{3+}@MIL-121 DMF suspension in the presence of various content of (A) chloroform and (B) acetone solvent, respectively (excited at 315 nm). The insets in Figures (A) and (B) show the $^5D_0 \rightarrow {}^7F_2$ transition intensity of Eu^{3+} for DMF suspension of Eu^{3+}@MIL-121 as a function of chloroform and acetone content, respectively.

The Mechanism of Luminescent Response.

It is well known that the fluorescence intensity of lanthanide ions depends crucially on the efficiency of energy transfer from the ligand to Ln^{3+}.[15] If there is efficient intramolecular energy transfer, Ln^{3+} can be excited more effectively, producing an enhanced luminescence of lanthanides, otherwise, producing a decreased luminescence. It is expected that the addition of certain anions or small organic molecules influence the efficiency of ligand-metal energy transformation (LMET), leading to the luminescent enhancing and quenching, respectively.[9a-d] To deeply understand the luminescent response induced by organic molecules and anions, the UV-vis spectra were measured. As shown in Figure 9A, among the solvents we used, only acetone have a strong absorption ranging from 250 to 350 nm, while other solvents have no significant absorption in this range. The absorption band of ligand (H_4btec) within Eu^{3+}@MIL-121 is located in the range of 260 – 350 nm, which is partially overlaps with the absorption band of acetone. When Eu^{3+}@MIL-121/acetone suspensions are excited at 315 nm, there is competition of the absorption of the light source energy between acetone molecules and H_4btec in the range of 250 to 350 nm, thus affecting the absorption of H_4btec and reducing the efficiency of LMET. Consequently, the luminescence of Eu^{3+}@MIL-121 is reduced by acetone. Besides, from the emission spectra of Eu^{3+}@MIL-121 treated by acetone (Figure 7a), we can see that the ligand-centered emission is also quenched by acetone, indicating that the energy transfer happened between ligands and acetone. Due to physical interaction between ligands and acetone, the energy absorbed by ligands H_4btec is transferred to acetone molecules, resulting in the quenching luminescence of Eu^{3+}@MIL-121. The two above-mentioned factors contribute to the quenching luminescence of Eu^{3+}@MIL-121 induced by acetone.[9b-c] Up to date, the mechanism for the enhancing effects of chloroform is still not very clear. Nevertheless, the influence of chloroform on LMET definitely plays an important role. Considering its opposite effect on the luminescence with acetone, it can be speculated that the energy absorbed by chloroform is transferred to ligands, which will increase in the efficiency of LMET and enhance the luminescence of Eu^{3+}@MIL-121.

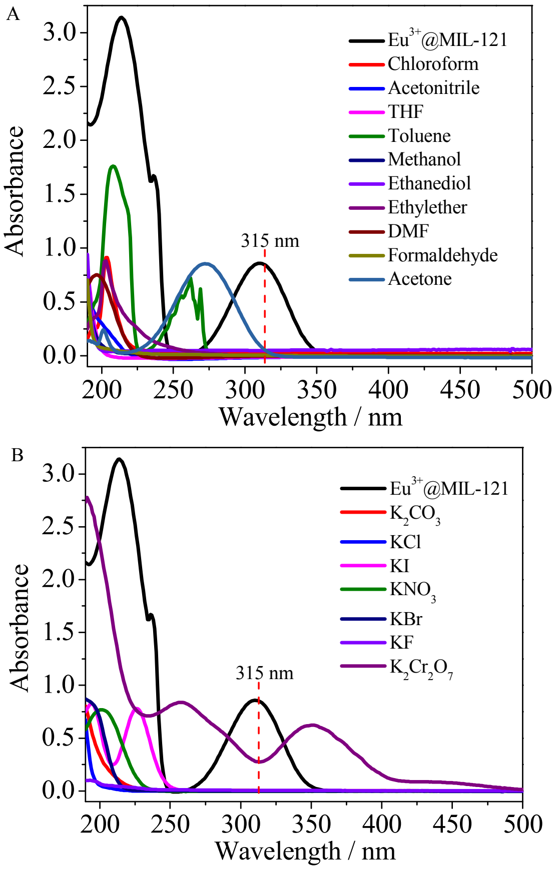


Figure 9 The UV-vis absorption spectra for Eu^{3+}@MIL-121 and target solvents (A) or various anions (B).

The quenching mechanism of Eu^{3+}@MIL-121 by $Cr_2O_7^{2-}$ is similar to that of acetone. As shown in Figure 9B, only $Cr_2O_7^{2-}$ have strong absorptions from 220 to 420 nm, which overlaps with the absorption bands of ligand (250 – 350 nm), thus directly hindering the absorption of ligands when excited at 315 nm and block the LMET process. As a result, $Cr_2O_7^{2-}$ totally quenched the luminescence of Eu^{3+}@MIL-121.

Conclusions

In summary, a facile method, post-synthesized method, was utilized to construct a new class of lanthanide-based MOFs with tunable color and white-light emission by encapsulating Ln^{3+} cations into MIL-121. The framework of MIL-121 possess uncoordinated carbonyl group that bind with the Ln^{3+} cations and are good chromophores for the efficient luminescent sensitization of Ln^{3+} cations. A fine-tuning of the emitted color luminescence can be easily achieved by modulating the doping ratio or adjusting the excitation wavelength. Notably, the Eu^{3+}/Tb^{3+} co-doped MOFs emit tunable three primary colors towards white light. In addition, the Eu^{3+}-doped MIL-121 was developed as a luminescent probe for sensing of toxic anions in aqueous solutions and small organic molecules. Luminescent studies reveal that Eu^{3+}@MIL-121 not only display a high-sensitivity sensing function with respect to fluoride and dichromate ions but also exhibit significant solvent-dependent luminescent response to small-molecule pollutants, such as chloroform and acetone. These results indicate the Ln-doped MIL-121 materials have potential applications in LED lamps, barcoded materials, and biological sensors.

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Notes and references

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1 (*a*) S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276; (*b*) S. T. Meek, J. A. Greathouse and M. D. Allendorf, *Adv. Mater.*, 2011, **23**, 249; (*c*) Y. Sakata, S. Furukawa, M. Kondo, K. Hirai, N. Horike, Y. Takashima, H. Uehara, N. Louvain, M. Meilikhov, T. Tsuruoka, S. Isoda, W. Kosaka, O. Sakata and S. Kitagawa, *Science*, 2013, **339**, 193; (*d*) Q. L. Zhu and Q. Xu, *Chem. Soc. Rev.*, 2014, **43**, 5468; (*e*) Y. J. Cui, Y. F. Yue, G. D. Qian and B. L. Chen, *Chem. Rev.*, 2012, **112**, 1126; (*f*) K. Khaletskaya, S. Turner, M. Tu, S. Wannapaiboon, A. Schneemann, R. Meyer, A. Ludwig, G. Van Tendeloo and R. A. Fischer, *Adv. Funct. Mater.*, 2014, **24**, 4804.

2 (*a*) J. Rocha, L. D. Carlos, F. A. A. Paz, D. Ananias, *Chem. Soc. Rev.*, 2011, **40**, 926; (*b*) Y. H. Han, C. B. Tian, Q. H. Li and S. W. Du, *J. Mater. Chem. C*, 2014, **2**, 8065; (*c*) S. R. Zhang, D. Y. Du, J. S. Qin, S. L. Li, W. W. He, Y. Q. Lan and Z. M. Su, *Inorg. Chem.*, 2014, **53**, 8105; (*d*) K. A. White, D. A. Chengelis, K. A. Gogick, J. Stehman, N. L. Rosi and S. Petoud, *J. Am. Chem. Soc.*, 2009, **131**, 18069; (*e*) Y. J. Cui, B. L. Chen and G. D. Qian, *Coord. Chem. Rev.*, 2014, **273–274**, 76.

3 (*a*) D. F. Sava, L. E. S. Rohwer, M. A. Rodriguez and T. M. Nenoff, *J. Am. Chem. Soc.*, 2012, **134**, 3983; (*b*) H. B. Zhang, X. C. Shan, Z. J. Ma, L. J. Zhou, M. J. Zhang, P. Lin, S. M. Hu, E. Ma, R. F. Li and S. W. Du, *J. Mater. Chem. C*, 2014, **2**, 1367; (*c*) Z. F. Liu, M. F. Wu, S. H. Wang, F. K. Zheng, G. E. Wang, J. Chen, Y. Xiao, A. Q. Wu, G. C. Guo and J. S. Huanga, *J. Mater. Chem. C*, 2013, **1**, 4634; (*d*) Y. Liu, M. Pan, Q. Y. Yang, L. Fu, K. Li, S. C. Wei and C. Y. Su, *Chem. Mater.*, 2012, **24**, 1954; (*e*) Y. Y. Liu, R. Decadt, T.

Bogaerts, K. Hemelsoet, A. M. Kaczmarek, D. Poelman, M. Waroquier, V. Van Speybroeck, R. Van Deun and P. Van Der Voort, *J. Phys. Chem. C*, 2013, **117**, 11302; (*f*) H. M. He, F. X. Sun, T. Borjigin, N. Zhao and G. S. Zhu, *Dalton Trans.*, 2014, **43**, 3716; (*g*) L. L. da Luz, B. F. Lucena Viana, G. C. Oliveira da Silva, C. C. Gatto, A. M. Fontes, M. Malta, I. T. Weber, M. O. Rodrigues and S. A. Júnior, *CrystEngComm*, 2014, **16**, 6914.

4 X. T. Rao, Q. Huang, X. L. Yang, Y. J. Cui, Y. Yang, C. D. Wu, B. L. Chen and G. D. Qian, *J. Mater. Chem.*, 2012, **22**, 3210.

5 Y. H. Zhang, X. Li and S. Song, *Chem. Commun.*, 2013, **49**, 10397.

6 (*a*) E. F. Schubert and J. K. Kim, *Science*, 2005, **308**, 1274; (*b*) X. J. Zhang, M. A. Ballem, Z. J. Hu, P. Bergman and K. Uvdal, *Angew. Chem. Int. Ed.*, 2011, **50**, 5728; (*c*) M. S. Wang, S. P. Guo, Y. Li, L. Z. Cai, J. P. Zou, G. Xu, W. W. Zhou, F. K. Zheng and G. C. Guo, *J. Am. Chem. Soc.*, 2009, **131**, 13572.

7 (*a*) R. Decadt, K. Van Hecke, D. Depla, K. Leus, D. Weinberger, I. Van Driessche, P. Van der Voort and R. Van Deun, *Inorg. Chem.*, 2012, **51**, 11623; (*b*) M. Ji, X. Lan, Z. P. Han, C. Hao and J. S. Qiu, *Inorg. Chem.*, 2012, **51**, 12389.

8 (*a*) S. M. Cohen, *Chem. Rev.*, 2012, **112**, 970; (*b*) J. D. Evans, C. J. Sumby and C. J. Doonan, *Chem. Soc. Rev.*, 2014, **43**, 5933; (*c*) J. W. Cao, Y. F. Gao, Y. Q. Wang, C. F. Du and Z. L. Liu, *Chem. Commun.*, 2013, **49**, 6897; (*d*) R. M. Abdelhameed, L. D. Carlos, A. M. S. Silva and J. Rocha, *Chem. Commun.*, 2013, **49**, 5019; (*e*) Y. Lu and B. Yan, *J. Mater. Chem. C*, 2014, **2**, 7411; (*f*) J. An, C. M. Shade, D. A. Chengelis-Czegan, S. Petoud and N. L. Rosi, *J. Am. Chem. Soc.*, 2011, **133***,* 1220; (*g*) M. L. Ma, J. H. Qin, C. Ji, H. Xu, R. Wang, B. J. Li, S. Q. Zang, H. W. Hou and S. R. Batten, *J. Mater. Chem. C*, 2014, **2**, 1085.

9 (*a*) B. L. Chen, Y. Yang, F. Zapata, G. N. Lin, G. D. Qian and E. B. Lobkovsky, *Adv. Mater.*, 2007, **19**, 1693; (*b*) Z. M. Hao, X. Z. Song, M. Zhu, X. Meng, S. N. Zhao, S. Q. Su, W. T. Yang, S. Y. Song, H. J. Zhang, *J. Mater. Chem. A*, 2013, **1**, 11043; (*c*) J. N. Hao and B. Yan, *J. Mater. Chem. A*, 2015, **3**, 4788; (*d*) J. M. Zhou, W. Shi, N. Xu and P. Cheng, *Inorg. Chem.*, 2013, **52**, 8082; (*e*) Z. C. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815; (*f*) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105; (*g*) J. N. Hao and B. Yan, *J. Mater. Chem. A*, 2014, **2**, 18018; (*h*) Q. Tang, S. X. Liu, Y. W. Liu, J. Miao, S. J. Li, L. Zhang, Z. Shi and Z. P. Zheng, *Inorg. Chem.*, 2013, **52**, 2799; (*i*) M. Zheng, H. Q. Tan, Z. G. Xie, L. G. Zhang, X. B. Jing and Z. C. Sun, *ACS Appl. Mater. Interfaces*, 2013, **5**, 1078; (*j*) Z. Z. Lu, R. Zhang, Y. Z. Li, Z. J. Guo and H. G. Zheng, *J. Am. Chem. Soc.*, 2011, **133**, 4172; (*k*) Z. Y. Guo, H. Xu, S. Q. Su, J. F. Cai, S. Dang, S. C. Xiang, G. D. Qian, H. J. Zhang, M. O'Keeffed and B. L. Chen, *Chem. Commun.*, 2011, **47**, 5551; (*l*) J. N. Hao and B. Yan, *J. Mater. Chem. A*, 2015, 3, 4788.

10 (*a*) M. Harada, *Crit. Rev. Toxicol.*, 1995, **25**, 1; (*b*) A. J. Cohen, H. Ross Anderson, B. Ostro, K. D. Pandey, M. Krzyzanowski, N. Kunzli, K. Gutschmidt, A. Pope, I. Romieu, J. M. Samet and K. J. Smith, *J. Toxicol. Environ. Health, Part A*, 2005, **68**, 1301; (*c*) M. Kampa and E. Castanas, *Environ. Pollut.*, 2008, **151**, 362.

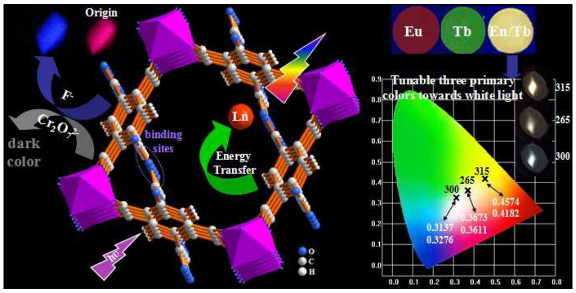
11 C. Volkringer, T. Loiseau, N. Guillou, G. Ferey, M. Haouas, F. Taulelle, E. Elkaim and N. Stock, *Inorg. Chem.*, 2010, **49**, 9852.

12 Y. Q. Lan, H. L. Jiang, S. L. Li and Q. Xu, *Adv. Mater.*, 2011, **23**, 5015.

13 S. W. Thomas, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339.

14 (*a*) R. W. Mcdonald, M. G. Ikonomou and D. W. Paton, *Environ. Sci. Technol.*, 1998, **32**, 331; (*b*) R. E. Alcock, K. C. Jones, M. S. McLachlan and A. E. Johonston, *Environ. Sci. Technol.*, 1999, **33**, 206; (*c*) K. C. Jones and P. de Voogt, *Environ. Pollut.*, 1999, **100**, 209.

15 (*a*) S. I. Weissman, *J. Chem. Phys.*, 1942, **10**, 214; (*b*) N. Arnaud, E. Vaquer and J. Georges, *Analyst*, 1998, **123**, 261.



Ln^{3+}-functionalized MOFs with tunable color and white-light emission were fabricated and developed as luminescent sensors for anions and small molecules.