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ARTICLE

Intercalation of lanthanide cations to a layer-like metal-organic framework for color tunable and white light emission

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One gallium carboxylates of MOF ($\text{Ga}_2(\text{OH})_4(\text{C}_9\text{O}_6\text{H}_4)$ or MIL-124) has been synthesized by a facile solvothermal approach, and tuned luminescence by encapsulating lanthanide(III)(Ln^{3+}) cations into the channels through the active-COOH group in MIL-124 by post-synthesis. PXRD, TEM, FTIR, and TGA were performed to determine the structure, thermal stability of the obtained products. The photophysical properties of these Ln^{3+} incorporated products are studied in detail, whose luminescent color can be tuned by controlling the composition of different Ln^{3+} cations in MOF. Furthermore, with careful adjustment of the excitation wavelength and concentration of the Ln^{3+} cations, the color of the luminescence can be modulated, and dichromatic (MIL-124@ Eu^{3+}) and trichromatic (MIL-124@ $\text{Eu}^{3+}/\text{Tb}^{3+}$) white-light-emission can indeed be achieved. One of the optimized chromaticity coordinates in white-light-emission is (0.3693, 0.3362) which is very close to the value for ideal white-light (0.333, 0.333). The versatile luminescence, good thermal stability, and compatibility with aqueous condition reveal these materials based on MOF may have some potential applications in luminescent devices for display or lighting.

Introduction

Materials capable of producing high-intensity white light have important application in solid-state lighting and displays¹. Comparison with mercury-containing fluorescent lights they are environment-friendly. Reported white-light-emitting materials include metal complexes, metal-doped or hybrid inorganic materials, small organic molecules, quantum dots or nanocrystals, and polymers²⁻⁵. Generally, white light can be obtained through three methods: (1) a single component emitting in the whole visible region from 400 to 700 nm; (2) a two-chromophore-containing component emitting blue and yellow or orange; (3) a three-chromophore-containing emitting primary colors^{1a, 6-10}. Different approaches have been reported to obtain efficient white-light-emitting materials in which single component materials capable of white light production are rare. The dichromatic and trichromatic white-light-emitting materials are typically superior to monochromatic and tetrachromatic counterparts in terms of their good color rendering properties and high luminous efficiency, and thus have attracted even more attention¹¹.

Recently, metal-organic frameworks (MOFs), crystalline materials with regular porous networks constructed from organic linker molecules and metal ions¹², have met with great interest owing to their enormous variety of interesting molecular topologies and a wide range of applications in the areas of gas storage/separation¹³,

catalysis¹⁴, magnetism¹⁵, and drug delivery¹⁶. Especially, luminescent MOFs have got more attention due to their potential applications in chemical sensors, light-emitting, and biomedicine¹⁷⁻¹⁹. A series of luminescent MOFs with the emission wavelengths ranging from 300 to 1500 nm in which not only the metal centers and organic linkers can produce luminescent emissive sources, the metal-organic charge transfer and the guest solvent molecules can also generate luminescent have been researched²⁰⁻²⁶. Lanthanide-based MOFs which are constructed by different organic linkers and various lanthanide (Ln^{3+}) cations are of particular interest among luminescent MOFs due to long lifetime, large Stokes shift, and narrow-band emission to give rise to pure light²⁷. However, despite the compelling recent developments, rational design and preparation of desired lanthanide-based MOFs still remain a great challenge, which is attributed to the high coordination number and variable nature of the Ln^{3+} sphere²⁸. Our group constructs series of photofunctional hybrid materials based with MOF through coordination bonding postsynthesis path²⁹.

Based on the above consideration, we chose MIL-124 ($\text{Ga}_2(\text{OH})_4(\text{C}_9\text{O}_6\text{H}_4)$) as a parent framework to load Ln^{3+} cations with the purpose of getting a new class of lanthanide luminescent MOFs. MIL-124, a layer-like network as reported, has a noncoordinating carboxyl group as well as the high thermal and chemical stabilities which can make it a good candidate to incorporate Ln^{3+} ions and sensitize the Ln^{3+} luminescence³⁰. In this

study, we demonstrate a facile solvothermal approach to prepare MIL-124 without using coordination modulators and surfactants. The photoluminescence (PL) spectra indicate that the ligand in MIL-124 not only can transfer absorbed energy to Ln^{3+} to emit their characteristic luminescence but also can maintain effective blue luminescent properties. So by careful adjustment of the excitation wavelength and concentration of the Ln^{3+} cations, we successfully obtained dichromatic (MIL-124@ Eu^{3+}) and trichromatic (MIL-124@ $\text{Eu}^{3+}/\text{Tb}^{3+}$) white-light-emitting materials with high luminescence, long lifetimes, and high quantum yields. The white-light emitter MIL-124@ Eu^{3+} and MIL-124@ $\text{Eu}^{3+}/\text{Tb}^{3+}$ show good thermal of luminescence that can open the way to practical application such as pellets, membranes, or sensors.

Experimental section

Starting Materials

All the starting materials were available commercially and used without further purification. Gallium nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 99.9 %) and 1,2,4-benzenetricarboxylic acid (noted 1,2,4- H_3btc , $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$, 99 %) were bought from Aldrich. Four lanthanide chloride $\text{LnCl}_3 \cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}, \text{Tb}, \text{Sm}, \text{Dy}$) were prepared by dissolving their oxides (Eu_2O_3 , Tb_4O_7 , Sm_2O_3 , Dy_2O_3) into the concentrated hydrochloric acid (37 %) and followed by solvation in ethanol, respectively.

Synthesis of MIL-124 ($\text{Ga}_2(\text{OH})_4(\text{C}_9\text{O}_6\text{H}_4)$)²⁹

MIL-124 was synthesized according to the synthesis method and conditions (molar ratio, time and temperature) in the literature. 0.6 g $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (2.4 mmol), 0.37 g 1,2,4- H_3btc (1.8 mmol) and 5 mL H_2O (227.8 mmol) were stirred a few minutes before transferring the resulting suspension to a Teflon-lined steel autoclave, which was heated at 210 °C for 24 h. The powered solid were separated by centrifugation at 13000 rpm for 5 min, then washed three times with deionized water and dried at 100 °C for 24 h.

Synthesis of Ln^{3+} -doped MIL-124 (MIL-124@ Ln^{3+} , $\text{Ln} = \text{Eu}, \text{Tb}, \text{Sm}, \text{Dy}, \text{Eu}/\text{Tb}$)

Doping of MIL-124 in LnCl_3 ethanol solution. MIL-124 (100 mg) was immersed in ethanol solution of chlorate salts of Eu^{3+} , Tb^{3+} , Sm^{3+} , Dy^{3+} , $\text{Eu}^{3+}/\text{Tb}^{3+}$ (10 mL, 1 mmol) at room temperature. The products were collected after 24 h and washed three times with ethanol to remove residual Ln^{3+} on the surface and dried under vacuum.

Doping of MIL-124 in EuCl_3 ethanol solution with different concentrations. MIL-124 (100 mg) was immersed in EuCl_3 ethanol solution with different concentrations: 10^{-3} , 10^{-4} and 10^{-5} (mol/L). After 24 h stirring, the products were washed three times with ethanol to remove residual Eu^{3+} on the surface and then dried under vacuum.

Physical characterization

PXRD patterns were obtained on a Bruker D8 diffractometer using $\text{Cu K}\alpha$ radiation with 40 mA and 40 kV and the dates were collected within the 2θ range of 5-50 °. Measurement of metal ions was performed on an X-7 series inductively coupled plasma-mass spectrometer (ICPMS) (Thermo Elemental, Cheshire, UK). For MIL-124@ Ln^{3+} products, 10 mg samples were dissolved by HNO_3 and the dried for 3 times. Finally, the worked samples were diluting

with water to 20 mL for ICPMS measurement. Scanning electronic microscope (SEM) images were recorded with a Hitachi S-4800. Fourier transform infrared (FTIR) samples were prepared as KBr pellets and the spectra were obtained in 4000 cm^{-1} – 400 cm^{-1} range using Nexus 912 AO446 infrared spectrum radiometer. Thermogravimetric analysis (TG) was carried out on a Netzsch STA 449C system at a heating rate of 5 K min^{-1} from 30 °C temperature to 1000 °C under nitrogen atmosphere in the Al_2O_3 crucibles. Nitrogen adsorption/desorption isotherms were measured at liquid nitrogen temperature using a Nova 1000 analyzer. Samples were outgassed for 3 h at 200 °C before measurements. Surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. Excitation and emission spectra and luminescence lifetime (τ) of the solid samples were recorded on Edinburgh FL920 spectrophotometer using a 450 W xenon lamp as excitation source. The outer luminescent quantum efficiency was measured by an integrating sphere (150 mm diameter, BaSO_4 coating) from Edinburgh FL920 phosphorimeter. The luminescence spectra were corrected for variations in the output of excitation source and for variations in the detector response. The quantum yield can be defined as the integrated intensity of the luminescence signal divided by the integrated intensity of the absorption signal. The absorption intensity was calculated by subtracting the integrated intensity of the light source with the sample in the integrating sphere from the integrated intensity of the light source with a blank sample in the integrating sphere.

Results and discussion

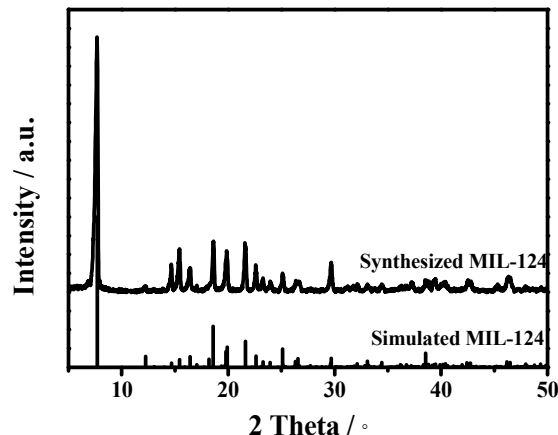


Figure 1 PXRD pattern of synthesized MIL-124

MIL-124 was hydrothermally synthesized from $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 1,2,4- H_3btc and H_2O as described as reported²⁹. In MIL-124, adjacent chains are linked to each other through the carboxylate functions in 1,2 position of 1,2,4- H_3btc , with a bidentate mode bridging the two gallium atoms Ga1 and Ga2 . It results in the formation a layer-like network developing in the (a,c) plane. The third carboxylate function (4 position) points toward to the b axis, which is not bonded to gallium cations and up and down to the gallium hydroxide trimellitate sheets (Figure S1, Supporting Information). The hydrogen bond interactions between the terminal carboxylic acid from one gallium hydroxide trimellitate layer with the bridging hydroxy groups from an adjacent one leads to the three-

dimensional cohesion of the MIL-124 structure. The experimental PXRD pattern of the synthesized MIL-124 was in good agreement with the simulated one generated on the basis of the single-crystal structure analysis, showing the successful preparation of MIL-124 (Figure 1). The SEM image of the MIL-124 phase (Figure S2, Supporting Information) shows large platelet-shaped crystals with the dimension in the range of 100-250 μm .

After introducing Ln^{3+} ($\text{Ln} = \text{Eu, Tb, Sm, Dy, Eu/Tb}$) into the pores of MIL-124, the compounds can maintain the crystalline integrity, as shown by the PXRD patterns (Figure 2), revealing that the framework topology of all the five compounds are isostructural with MIL-124. Besides, the morphology of these compounds do not change upon encapsulation of Ln^{3+} ($\text{Ln} = \text{Eu, Tb, Eu/Tb}$) showing in SEM. (Figure S3, Supporting Information). The loaded concentrations of Ln^{3+} ($\text{Ln} = \text{Eu, Tb, Eu/Tb}$) were determined by ICPMS. The molar ratio of Ln^{3+} and Ga^{3+} is close to 1: 60.

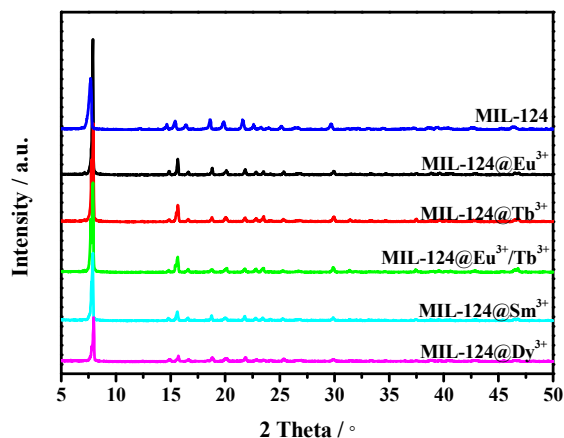


Figure 2 The PXRD pattern of MIL-124@ Ln^{3+} ($\text{Ln} = \text{Eu, Tb, Sm, Dy, Eu/Tb}$).

The thermal stability of MIL-124 and MIL-124@ Ln^{3+} ($\text{Ln} = \text{Eu, Tb, Sm, Dy, Eu/Tb}$) has been studied by thermal gravimetric analysis (TGA) from 40 to 800 $^{\circ}\text{C}$ (Figure 3), which was performed under air with a heating rate of 5 Kmin^{-1} under N_2 atmosphere. The TGA of MIL-124 exhibits two events of weight losses. The first step (10 % wt) occurs in the range of 250-350 $^{\circ}\text{C}$ which assigns to the partial decomposition of the organic ligand with the removal of the nonbonded CO_2 species (calcd 10.6 %). The second weight loss between 450 and 600 $^{\circ}\text{C}$ is attributed to the departure of the remaining organic part together with H_2O coming from the dehydroxylation (obs 38.1 %; calcd 44.3 %). The final plateau from 600 $^{\circ}\text{C}$ corresponds to amorphous gallium oxide (Ga_2O_3 obs 40.8 %; calcd 45.1 %). Incorporation of Ln^{3+} does not influence the thermal stability of the parent framework, as evidenced by TGA studies shown in Figure 3. Obviously, the MIL-124@ Ln^{3+} luminescent materials show better thermal stability in comparison with the lanthanide complexes and lanthanide hybrid materials. Figure S4 Supporting Information depicts the FTIR spectra of 1,2,4- H_3btc , MIL-124 and MIL-124@ Ln^{3+} ($\text{Ln} = \text{Eu, Tb, Sm, Dy, Eu/Tb}$). In the a, the broad band at 3000-2500 cm^{-1} is ascribed to the characteristic stretching vibrations of O-H in carboxylic acid two dimer. The stretching vibrations of the carboxylate groups are easily visible, ν at 1700 cm^{-1} and 1564 cm^{-1} . The FTIR of MIL-124@ Ln^{3+} ($\text{Ln} = \text{Eu, Tb, Sm, Dy, Eu/Tb}$) (Figure S4b, Supporting Information) are similar, further confirming their isostructuralism. The broad band at 3000 - 2500 cm^{-1} originating from $\nu(\text{OH})$ is not observed in the spectra. Compared with the free carboxyl groups in MIL-124, the lower wavenumber at 1690 cm^{-1} and 1524 cm^{-1} of $\nu(\text{C}=\text{O})$ indicates the coordination between carboxyl group and Ln^{3+} .

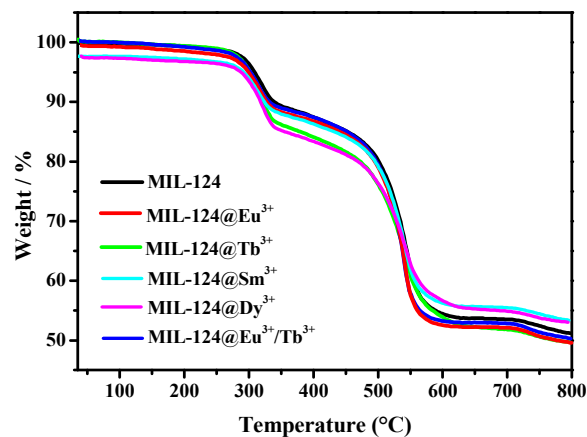


Figure 3 Thermal gravimetric analysis of MIL-124 and MIL-124@ Ln^{3+} ($\text{Ln} = \text{Eu, Tb, Sm, Dy, Eu/Tb}$).

Photoluminescent Properties

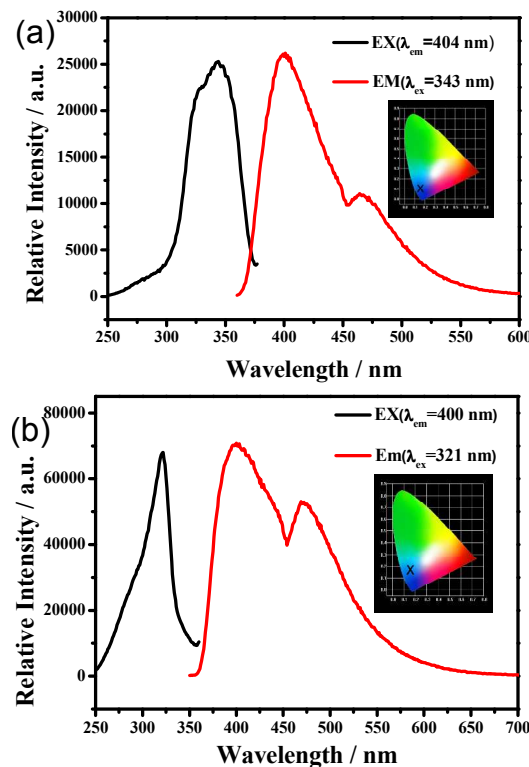


Figure 4 Excitation (black line) and emission (red line) spectra of 1,2,4- H_3btc and MIL-124 and the inset shows the corresponding CIE chromaticity diagram.

The emission and excitation spectra measured at room temperature for the power sample of 1,2,4- H_3btc and MIL-124 are displayed in Figure 4. The free 1,2,4- H_3btc ligand exhibits a weak emission at 404 nm presumably due to $\pi \rightarrow \pi^*$ transitions under 343 nm UV light excitation. The excitation spectra of MIL-124 collected

at an emission wavelength of 400 nm in the range of 250–350 nm with a maximum at 321 nm. With the excitation wavelength at 321 nm, MIL-124 exhibits much enhanced blue light emission at 400 nm. Compared with the free organic linker, the large enhancement of emission intensity and slight blue shifting of the emission in MIL-124 may be attributed to metal-to-ligand charge transfer (MLCT) and the coordination effects of the ligand to Ga^{3+} cations which increases the ligand conformational rigidity and reduces the non-radiative decay³¹. The CIE coordinates for the blue emission of MIL-124 was calculated to be (0.1707, 0.1083), which close to that of saturated blue emitter with CIE coordinates of (0.14, 0.08)³². The quantum yield of MIL-124 was 8.26 % measured under $\lambda_{\text{ex}} = 321$ nm at room temperature. These data demonstrate that MIL-124 is an efficient blue-light emitter.

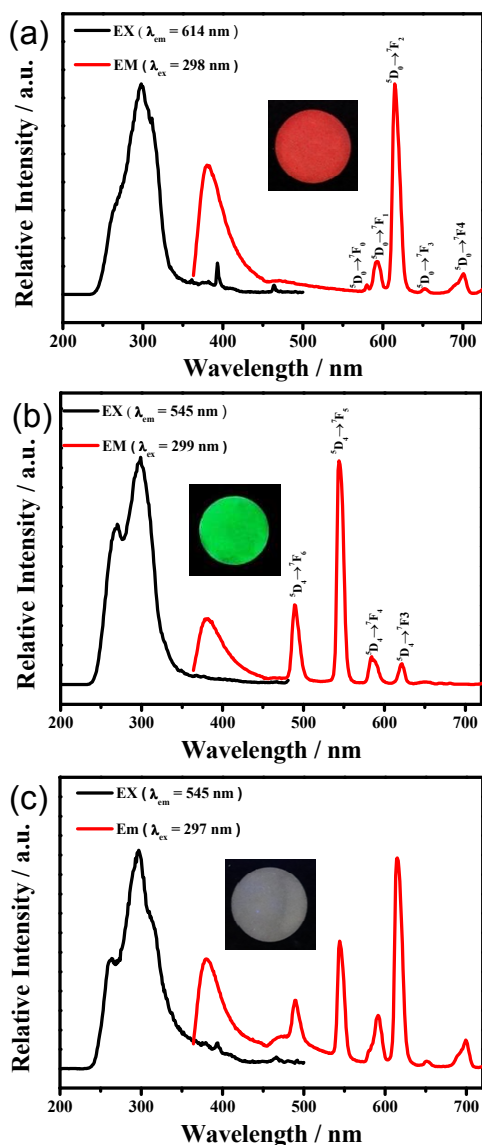


Figure 5 Excitation (black line) and emission (red line) spectra of MIL-124@ Ln^{3+} ($\text{Ln} = \text{Eu}, \text{Tb}, \text{Eu/Tb}$). The insets are the corresponding luminescence pictures under UV-light irradiation of 254 nm.

The luminescent properties of the five complexes in the solid state were investigated at room temperature. As expected, after

postsynthetic functionalization of Ln^{3+} ($\text{Ln} = \text{Eu}, \text{Tb}, \text{Eu/Tb}$), the products yield their corresponding emissions, while emission intensities from 1,2,4- H_3btc still remains. Compared to the emission band of the free ligand (404 nm for Figure 4a), the blue-shift of the ligand emission can be attributed to the coordination between the ligand and lanthanide cations. The MIL-124@ Eu^{3+} exhibits the characteristic transitions of Eu^{3+} excited at 298 nm, which can be assigned to $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0-4$) transitions at 580, 593, 614, 650 and 697 nm for Eu^{3+} in addition to the emission at 387 nm from the ligand (Figure 5a). Under UV-light irradiation, MIL-124@ Eu^{3+} shows strong red luminescence which can be readily observed by naked eye, as shown in the inset of Figure 5a. The emission spectra of MIL-124@ Tb^{3+} exhibit four emission band at 489, 545, 582 and 619 nm, which assigned to $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6, 5, 4, 3$) transition and the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ emission at 545 nm is the strongest one in the green region as shown in the Figure 5b. The multiband doped MIL-124@ $\text{Eu}^{3+}/\text{Tb}^{3+}$ shows the characteristic emission of Eu^{3+} and Tb^{3+} excited at 545 nm (Figure 5c), performing the potential of barcoded materials³⁰. Exciting the MIL-124@ $\text{Eu}^{3+}/\text{Tb}^{3+}$ at 297 nm yields a strong red band at 614 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), minor green band at 545 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_5$) and weaker blue broad band at 350–450 nm from the ligand, suggesting the energy transfer from Tb^{3+} to Eu^{3+} (Figure 5c). Lanthanide-centered excitation spectra recorded for MIL-124@ Eu^{3+} , MIL-124@ Tb^{3+} , MIL-124@ $\text{Eu}^{3+}/\text{Tb}^{3+}$ all display a strong band centered at ~ 298 nm, which suggest that energy transfers through the same electronic levels located in the chromophoric structure of the parent framework for all three products.

Table 1 Luminescence Lifetimes (τ) and Absolute Quantum Yields (η) of MIL-124@ Ln^{3+} ($\text{Ln}^{3+} = \text{Eu}^{3+}, \text{Tb}^{3+}, \text{Eu}^{3+}/\text{Tb}^{3+}$).

Materials	$\lambda_{\text{ex}}/\lambda_{\text{em}}$ (nm)	τ (μs)	η (%)
MIL-124@ Eu^{3+}	298/614	395	8.3
MIL-124@ Tb^{3+}	299/545	559	15.7
MIL-124@ $\text{Eu}^{3+}/\text{Tb}^{3+}$	297/545	550	21.6
	297/614	547	22.8

However, for MIL-124@ Sm^{3+} and MIL-124@ Dy^{3+} , unlike Eu, Tb or Eu/Tb-MOF the distinctive colors under UV-light were all blue corresponding to the emission of ligand (Figure 5, Supporting Information). The emission spectrum of Dy^{3+} is comparatively weaker and shows a much weaker characteristic emission of Dy^{3+} ion at 480 nm and 575 nm corresponding to the $^7\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ and $^7\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transition, as shown in Figure S5a, Supporting Information. There was no characteristic emission of Sm^{3+} can be observed in the emission spectra (Figure S5b, Supporting Information). The emissions line in the Dy and Sm compound indicate that the selected ligand is not suitable for sensitizing their emitters.

In order to discuss the photophysical properties of the MIL-124@ Ln^{3+} , the luminescent lifetimes were measured at room

temperature under the excitation wavelength that maximizes the emission of lanthanide cations and the results are given in Table 1. The decay curves can be well fitted into biexponential function, revealing the presence of two distinct lanthanide environments within in the MOF. The luminescent decay test shows that the $\text{Eu}^{3+}/\text{Tb}^{3+}$ -doped MOF have a shorter $^5\text{D}_4$ (Tb^{3+}) lifetime than MIL-124@ Tb^{3+} and a longer $^5\text{D}_0$ (Eu^{3+}) lifetime than MIL-124@ Eu^{3+} , which further approves the phenomenon of Tb^{3+} -to- Eu^{3+} energy transfer mainly controlled by the phonon-assisted Forster transfer mechanism³³. Besides, the quantum yields which are an important parameter for evaluation of the efficiency of the emission process in luminescent materials were determined with integrated sphere instruments (Table 1). Comparatively high quantum yields of these samples may be attributed to efficient energy transfer from the sensitizer embedded in the MOF to the incorporated Ln^{3+} cations.

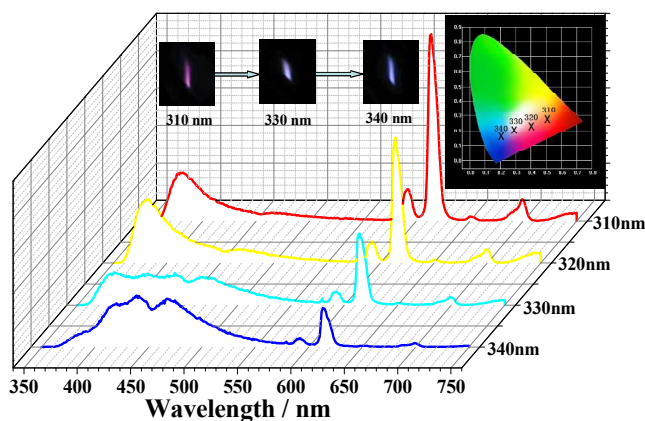


Figure 6 Emission spectra of MIL-124@ Eu^{3+} collected at different excitation wavelengths. The insets are the corresponding CIE chromaticity diagram and photographs.

It is expected that MIL-124 is a promising system for developing high performance of white-light emitting compounds attracted much attention due to their important applications in general lighting sources. Considering that MIL-124 provides blue light, by means of the Eu^{3+} ion (red emission) singly doped in to the MIL-124 framework, it will therefore be possible to construct white emitting material. As depicted in Figure 6, MIL-124@ Eu^{3+} was excited with excitation wavelength from 310 nm to 340 nm. The intensity of shape band from Eu^{3+} decreases by degrees with excitation wavelength varying from 310 nm to 340 nm, while the broad band from the framework increases in the meantime. The corresponding CIE chromaticity diagram is depicted inset in Figure 6, which shows a tunable chromaticity of emission from red to white to blue by varying the excitation wavelength from 310 nm to 340 nm. The color change can be further confirmed by the photographs irradiated under 299 nm (the inset in Figure 6). This verifies that the white-light emitting from MIL-124@ Eu^{3+} is caused by the broad blue emission of MIL-124 and red emission of incorporated Eu^{3+} simultaneously, because the excitations at different wavelengths will definitely give rise to different emission intensity relativity of these two kinds of luminescence, thus leading to a shift of the chromaticity coordinate in the CIE diagram. The CIE coordinates for the emission of MIL-124@ Eu^{3+} under 330nm excitation are determined as $x=0.2905$, $y=0.2083$, which locates in the white-light emission by two-

chromophore-containing compound. MIL-124 was immersed in EuCl_3 ethanol solution with concentrations in the range of 10^{-5} - 10^{-3} mol L^{-1} . Figure 7a shows the emission spectra of the as-obtained samples collected at the excitation wavelength of 298 nm. As the concentration of EuCl_3 ethanol solution increasing from 10^{-5} to 10^{-3} mol L^{-1} , the characteristic emission of Eu^{3+} strengthens sharply. The Eu^{3+} emission continually improved when further raising the concentration of Eu^{3+} . In contract, the ligand-centered emission decreases with increasing Eu^{3+} concentration due to the enhancement of the energy transfer probability from organic linkers to Eu^{3+} . Figure 7b demonstrates the corresponding chromaticity diagram calculated from the luminescent from blue to red. The chromaticity coordinates of the product with concentrations from 10^{-5} to 10^{-3} mol L^{-1} EuCl_3 solutions are shown in Table S1, which locates in the region of red-blue.

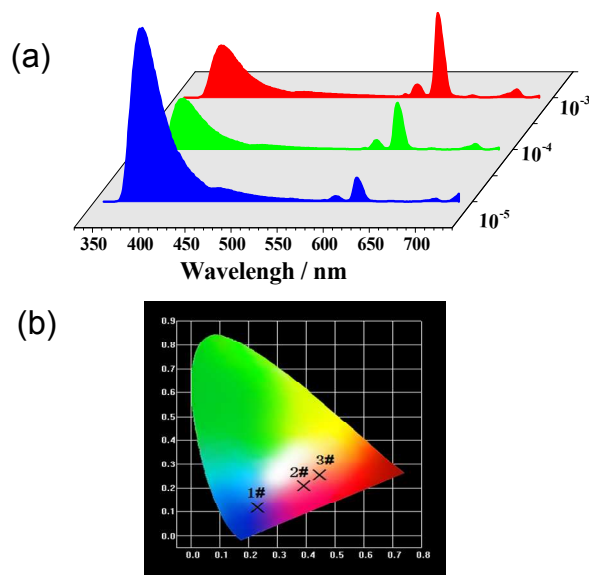


Figure 7 Emission spectra ($\lambda_{\text{ex}} = 298$ nm) (a) and CIE chromaticity (b) of MIL-124@ Eu^{3+} products resulting from EuCl_3 ethanol solutions with concentrations in the range of 10^{-5} - 10^{-3} mol/L.

The tunable colors from doped MIL-124@ Eu^{3+} and MIL-124@ Tb^{3+} have provided the basis for us to compensate the blue color from H_3btc ligand, red color from Eu^{3+} and green color from Tb^{3+} in the doped MIL-124@ $\text{Eu}^{3+}/\text{Tb}^{3+}$ by adjusting different excitation wavelength. The emission spectra of the MIL-124@ $\text{Eu}^{3+}/\text{Tb}^{3+}$ sample excited between 297 nm and 320 nm are shown in Figure 8a. Several narrow-band emission peaks from Eu^{3+} , Tb^{3+} and broad-band emission from MIL-124 are seen and can be tuned by varying the excitation wavelength when Eu^{3+} and Tb^{3+} were codoped in the molar ratio of 1:1. The CIE chromaticity diagram of these codoped materials is shown in Figure 8b and corresponding CIE coordinates is listed in Table S1. The results show that when exciting from 297 nm to 315 nm the calculated chromaticity coordinated of light emission fall within the white-light region of the CIE chromaticity diagram. The optimized chromaticity coordinates can be tuned to (0.3693, 0.3362) when exciting at 297 nm, which is very close to the value for ideal white-light (0.333, 0.333). As expected the codoped material can produce white light at a reasonably broad excitation wavelength. The white luminescence

can be further confirmed by the photograph irradiated under 297 nm (the inset in Figure 8a).

On the basis of the above discussion, the white-light luminescence of MIL-124@Eu³⁺/Tb³⁺ is generated from a three-chromophore-containing emitting pathway, as demonstrated in Scheme 1. There are three kinds of luminescent centers in MIL-124@Eu³⁺/Tb³⁺. Excepting the ligand-centered emission of the framework, others are the characteristic f-f emission of Eu³⁺ and Tb³⁺ coming from the antenna effect. The excitation wavelengths have a strong impact on the relative luminescence intensity between the emission of Ln³⁺ and MIL-124, thus playing an important role to come up white luminescence from MIL-124@Eu³⁺/Tb³⁺. Meanwhile, dichromatic (MIL-124@Eu³⁺) white light-emission has the same mechanism with MIL-124@Eu³⁺/Tb³⁺ including two luminescent centers. Obviously, incorporation of Ln³⁺ into MOFs can pave the way to novel white-light luminescent materials.

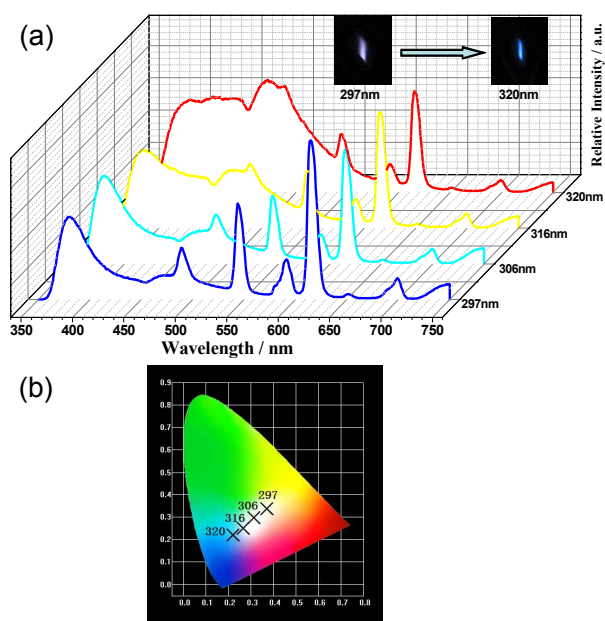
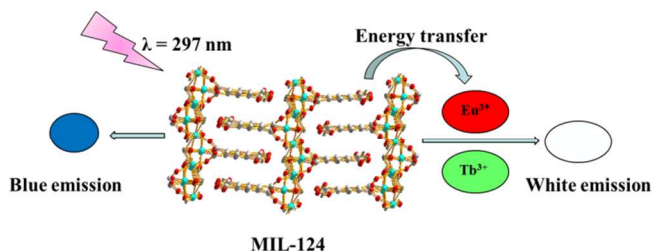


Figure 8 Emission spectra (a) and CIE chromaticity diagram (b) of MIL-124@Eu³⁺/Tb³⁺ collected at different excitation wavelengths.



Scheme 1 Representation of the Generation Mechanism of the White-Light Emission of MIL-124@Eu³⁺/Tb³⁺.

Conclusions

In summary, MIL-124 has been synthesized a facile solvothermal approach without using coordination modulators and surfactants. A versatile strategy was demonstrated for generating a new class of MOFs with tunable and white-light emission by encapsulating Ln³⁺

into the channels through the active-COOH groups in MIL-124. The framework can serve as an antenna that lead to the energy transfer from the organic linkers embedded in the MOF to Ln³⁺ (Ln = Eu, Tb, Eu/Tb) center to emit characteristic luminescence. However, the ligand cannot effectively sensitize the luminescence of Sm³⁺ and Dy³⁺. With careful adjustment of the excitation wavelength and concentration of the Ln³⁺ cations, the color of the luminescence can be modulated. Notably, when at a certain excited wavelength, the dichromatic (MIL-124@Eu³⁺) and trichromatic (MIL-124@Eu³⁺/Tb³⁺) white-light-emission involving emission from organic ligands and Eu³⁺, Tb³⁺ cations can indeed be achieved. One of the optimized chromaticity coordinates in these white-light-emission is (0.3693, 0.3362) which is very close to the value for ideal white-light (0.333, 0.333). The versatile luminescence, good thermal stability, and compatibility with aqueous condition reveal these materials based on MOF may have some potential applications in luminescent devices for display or lighting. It is expected that some more research endeavors to explore white-light-emitting MOF materials and develop their application in lighting, automobiles, transportation, communication, imaging, agriculture, and medicine will be carried out in the near future.

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Notes and references

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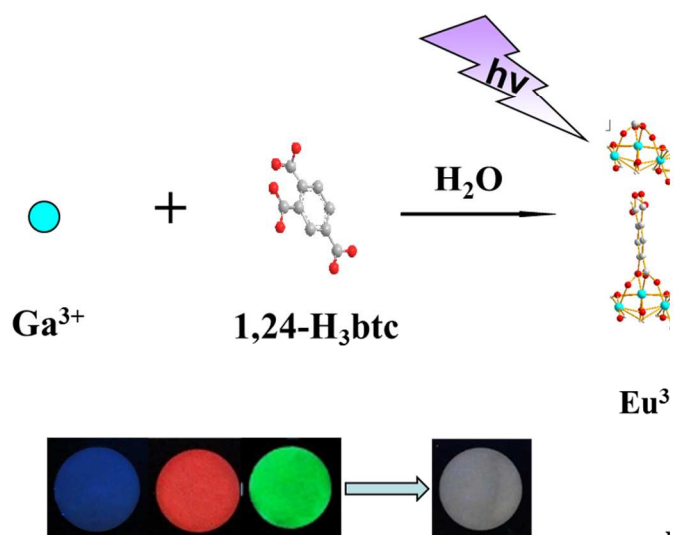
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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Graphical Abstract



One gallium carboxylates of MOF ($\text{Ga}_2(\text{OH})_4(\text{C}_9\text{O}_6\text{H}_4)$ or MIL-124) has been synthesized by a facile solvothermal approach, and tuned luminescence by encapsulating Ln^{3+} cations into the channels. With careful adjustment of the excitation wavelength and concentration of the Ln^{3+} cations, the color of the luminescence can be modulated, and dichromatic (MIL-124@ Eu^{3+}) and trichromatic (MIL-124@ $\text{Eu}^{3+}/\text{Tb}^{3+}$) white-light-emission can indeed be achieved.