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COMMUNICATION

Cadmium metal–organic frameworks: Ln³⁺ ions functionalized assembly, fluorescence tuning and polymer film preparation

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Han Weng, Bing, Yan

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A series of lanthanide ions activated cadmium metal-organic framework Ln³⁺@Cd-MOF (Ln = Eu, Tb, Sm, Dy, Cd-MOF = {[Me₂NH₂]₂·[Cd₃(5-tbip)₄·2DMF]_n, 5-tbipH₂ = 5-tert-butylisophthalic acid) are prepared via cation exchange method and their photophysical properties are investigated. Dy³⁺@Cd-MOF exhibits white light output and especially, when two different lanthanide cations (Sm³⁺, Tb³⁺) are loaded into the Cd-MOF at the ratio of Sm³⁺_{0.98} / Tb³⁺_{0.02}, the luminescence color of it can be tuned into white. In addition, the luminescent properties of Eu³⁺ and Tb³⁺ coactivated Cd-MOF with varying ratios are also discussed. Simultaneously, we obtain size-reduced Cd-MOF (Cd-MOF-2) with the assistance of sodium acetate, while other conditions remain unchanged. Additionally, polymer film is prepared with the use of Ln³⁺@Cd-MOF-2 for further application.

Introduction

Metal-organic frameworks (MOFs), which are defined as a class of inorganic-organic hybrid materials formed by the self-assembly of central metal ions and polydentate bridging ligands, have attracted much attention for their characteristic of tunability, structural diversity, high specific surface area as well as special photoelectric and magnetic properties.¹ As previous reports, much work was carried out to extend their potential application, such as gas adsorption / separation,² catalysis,³ sensing,⁴ luminescent devices,⁵ drug delivery⁶ and so on. The various choices of central metal ions and organic ligands make it possible to provide MOFs with a variety of properties. However, the luminescent properties of MOFs are widely explored and applied. Allendorf's review published in 2009 once summarize several modes to generate luminescent in MOFs: (a) luminescence based on linkers, which includes ligand-localized emission and ligand-to-metal charge transfer (LMCT) as well as metal-to-ligand charge transfer; (b) emission based on coordinated metals; (c) weak luminescence enhanced by antenna effects; (d) luminophores bound to the porous of MOFs; (e) broad and featureless emission caused by the formation of exciplex and so on.⁷ Among the various coordinated metals, lanthanide ions exhibit unique photoactive properties, such as sharp characteristic emissions and wide range of fluorescence lifetime.⁸ Based on these, Lanthanide luminescent metal-organic frameworks draw a lot of attention in recent decades. It is worthy pointing out that lanthanide ions not only can behave as central coordinated metal

cations but also can be loaded into MOFs as active species in the formation of lanthanide luminescence MOFs.⁹ Unfortunately, the practical application of MOFs is greatly impeded by the low mechanical strength and poor physicochemistry stability. MOF thin films provide great opportunities for application of these fragile materials.¹⁰ Over the past years, several concepts have been developed for the fabrication of MOF thin films: (a) direct growth from solvothermal mother solutions; (b) immobilizing ideal MOFs in stable matrices such as silicon materials or polymers; (c) stepwise layer by layer growth on the substrate; (d) the electrochemical deposition on metal substrates; (e) the deposition of MOF thin films using a gel-layer approach.¹¹ However, The crystal size plays an important role in the preparation of MOF films, especially for immobilizing MOFs in stable matrices by polymerization reaction. Oversized particles are not suitable for polymerization. In recent years, considerable effort has been given to explore novel methods to control the size of MOFs. Fischer and co-workers realized successfully the size control of MOF-5 by the addition of ligand p-perfluoromethyl benzencarboxylate.¹² Kitagawa and his co-workers adjust the crystal size of carboxylate-based MOFs by changing the concentration of dodecanoic acid.¹³ In Lu's paper, a series of MOF-253 with different size (from 300 to 50 nm) were prepared by adjusting the content of base and acid in the reaction and the MOF in size of 50 nm can be successfully applied in the intracellular.¹⁴

In this paper, an anionic MOF {[Me₂NH₂]₂·[Cd₃(5-tbip)₄·2DMF]_n was chosen as host materials.¹⁵ The existence of (Me₂NH₂)⁺ in porous makes it possible to encapsulate lanthanide ions into the MOF via cation exchange method. As the introduction of different lanthanide ions into the MOF, it will show different photoluminescence properties, therefore we can modulate and optimize the emission colors by adjusting the kind and content of loaded lanthanide ions, changing the experimental temperature, so

Department of Chemistry, Tongji University, Shanghai 200092, P. R. China.
E-mail: byan@tongji.edu.cn; Tel: (+86) 21-65984663

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that it can be further employed for luminescent devices, chemical sensing and so on. Size-reduced Cd-MOF (denoted by Cd-MOF-2) was obtained by the addition of a certain amount of sodium acetate, subsequently, Ln^{3+} ions are introduced into the Cd-MOF-2 via cation exchange. Polymer film is also prepared with the use of as-synthesized Ln^{3+} @Cd-MOF-2.

Experimental Section

Materials and instrumentation

$\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was prepared by dissolving lanthanide oxide in concentrated nitric acid followed by evaporation and vacuum drying. Other reagents (A. R.) were obtained commercially and used without further purification. A Bruker D8 diffractometer using Cu $\text{K}\alpha$ radiation with 40 mA and 40kV was employed to obtain the PXRD patterns within the 2θ range of 5–30°. FTIR spectra were collected on a Nexus 912 AO446 spectrophotometer using KBr pellets in the range of 4000–400 cm^{-1} . Thermogravimetric analysis (TGA) was performed using a Netzsch STA 449C system with a heating rate of 5 $^\circ\text{C}/\text{min}$. The morphology of the samples were obtained on a Philips XL-30 scanning electron microscope (SEM). Excitation and emission spectra of the samples were recorded on a Edinburgh FLS920 spectrophotometer using a 450 W xenon lamp as excitation source. Luminescent lifetime was also inspected in the equipment using a microsecond lamp (100 mW). The luminescent quantum efficiency was measured by an integrating sphere (150 mm diameter, BaSO_4 coating) from Edinburgh FL920 phosphorimeter.

Syntheses

Cd-MOF and Ln^{3+} @Cd-MOF

Anionic MOF $\{[(\text{Me}_2\text{NH}_2)_2] \cdot [\text{Cd}_3(5\text{-tbip})_4] \cdot 2\text{DMF}\}_n$ was solvothermally synthesized as previous report.¹⁵ $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (1 mmol, 0.3084 g) and 5-tbip ligand (1 mmol, 0.2222 g) were dissolved in 6 mL of dimethylformamide (DMF) in a glass vial which volume is 15 mL. The mixture was heated to 90 $^\circ\text{C}$ for 3 days and then cooled down to room temperature. After washing with DMF for several times, the yield was dried under vacuum at 80 $^\circ\text{C}$ for 6h. Ln^{3+} @Cd-MOF was prepared via a cation exchange method: 30 mg of Cd-MOF was soaked into the DMF solution of $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (5 mL, 1 mmol) for 24 h. The product was collected by centrifugation and washed with DMF for several times to remove the residual Ln^{3+} . After drying under vacuum at 80 $^\circ\text{C}$ for 6 h, the Ln^{3+} enspulsated Cd-MOF was obtained.

Cd-MOF-2 and Ln^{3+} @Cd-MOF-2

At the first, Cd-MOF-2 was prepared as follows: $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (1 mmol, 0.3084 g), 5-tbip ligand (1 mmol, 0.2222 g) and $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (2 mmol, 0.2722 g) were dissolved in 6 mL of DMF in a 15 mL of glass vial. The mixture was then heated to 90 $^\circ\text{C}$ for 3 days and then cooled down to room temperature. After washed with DMF for several times, the product was dried under a vacuum at 80 $^\circ\text{C}$ for 6 hours. Ln^{3+} @Cd-MOF-2 was obtained as a similar way with Ln^{3+} @Cd-MOF. 30 mg of Cd-MOF-2 was soaked into the DMF solution of $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (5 mL, 1 mmol) for 24 hours. The product was collected by centrifugation and washed with DMF for several times to remove the residual Ln^{3+} . After drying under a vacuum at 80 $^\circ\text{C}$ for 6 h, the target product was obtained.

Polymer films

The polymer films were prepared as follows: 10 mg of Ln^{3+} @Cd-MOF-2 was added into the mixed solution of 1 mL of PEMA (Polyethoxyethyl methacrylate) and 10 mL of THF (tetrahydrofuran). The mixture was further stirred for 30min at 80 $^\circ\text{C}$, 0.0125 g of BPO (benzoyl peroxide) dissolved in 2 mL of THF was then added into the mixture and reacted for 6 h under refluxing. The radical PEMA and sample monomer was occurred in this process. THF was removed by rotary evaporation. The film was finally obtained by a directly spin-coating method.

Results and discussion

Characterization of Cd-MOF and Ln^{3+} @Cd-MOF

Cd-MOF is solvothermally synthesized with a mixture of 5-tbip and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in DMF. As previous reports, there are $(\text{Me}_2\text{NH}_2)^+$ cations in the pores generating from the in-situ hydrolysis of DMF, which balance the anionic $[\text{Cd}_3(5\text{-tbip})_4]^{2-}$ framework (Scheme S1). Based on this, a series of luminescent Ln^{3+} @Cd-MOF are collected via postsynthetic cation exchange while Ln^{3+} ions substitute $(\text{Me}_2\text{NH}_2)^+$ cations in the porous. The PXRD patterns (Fig. 1) show that the as-synthesized Cd-MOF and Ln^{3+} @Cd-MOF match well with the simulated one, which suggests that we have prepared target compounds and the structures remain unchanged after the introduction of lanthanide ions. ICP-OES analysis indicates successful Ln^{3+} cations incorporation into Cd-MOF (Table S1).

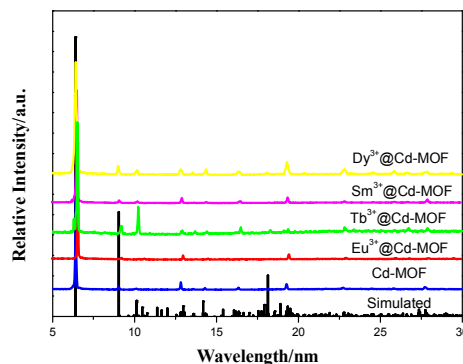


Fig. 1 PXRD patterns of as-synthesized Cd-MOF and Ln^{3+} @Cd-MOF (Ln = Eu, Tb, Sm, Dy).

The FTIR spectra of Ln^{3+} @Cd-MOF are similar to Cd-MOF (Fig. S1). The peak appears at $\sim 3440 \text{ cm}^{-1}$ can be assigned to the stretching vibrations of N-H, the absorption band at $\sim 2960 \text{ cm}^{-1}$ is ascribed to the stretching vibration of $-\text{CH}_3$, while the absorption band located at $\sim 1660 \text{ cm}^{-1}$ is assigned to the asymmetric stretching vibrations of C=O. Comparing with the free carboxyl groups whose absorption band of C=O is at $\sim 1700 \text{ cm}^{-1}$, the lower wavenumber indicates the coordination between carboxyl groups and Cd^{2+} . The peak at $\sim 1370 \text{ cm}^{-1}$ may result from C-N stretch of amino. The absorptions at 1050 and 780 cm^{-1} can be ascribed to the C-H deformation vibrations of the aromatic ring.

The TGA diagram of Cd-MOF (Fig. S2) exhibits two main weight losses in the curves. The first weight loss is about in the temperature range of 200 – 300 $^\circ\text{C}$, which may be ascribed to the decomposition of DMF and dimethylammonium cations in the

channels. The second weight loss occurs about 380 to 600 °C, assigned to the decomposition of the framework. However, when it comes to $\text{Eu}^{3+}@ \text{Cd-MOF}$, we can find that the weight loss from 200 to 300 °C is hardly to observe, but the thermo-stability of the framework is influenced in a certain degree, corresponding to the cation exchange of $(\text{Me}_2\text{NH}_2)^+$ and Eu^{3+} .¹⁶

Photoluminescent properties of $\text{Ln}^{3+}@ \text{Cd-MOF}$

The luminescence of the four Ln^{3+} modified complexes in solid state are investigated at room temperature. As is shown in Fig. 2, all the excitation spectrums are located at about 293 nm, which indicates that the complex can absorb ultraviolet light and sensitize the emission of Lanthanides by energy transfer efficiently. The emission spectra of $\text{Ln}^{3+}@ \text{Cd-MOF}$ exhibit characteristic transitions of different lanthanide ions when excited at 293 nm. For $\text{Eu}^{3+}@ \text{Cd-MOF}$ (Fig. 2a), when excited at 293 nm, it exhibits sharp lines located at about 580, 593, 614, 650, 702 nm respectively, which can be ascribed to $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($J = 0-4$) transitions of Eu^{3+} .¹⁷ The KBr pellet of $\text{Eu}^{3+}@ \text{Cd-MOF}$ shows a bright red light under UV-light when it is excited at 254 nm, which can be easily observed by naked eye, as is shown in the inset of Fig. 2a, the emission colour can be further proved by Fig. S3a. The emission spectrum of $\text{Tb}^{3+}@ \text{Cd-MOF}$ is demonstrated in Fig. 2b, which can also exhibit characteristic emission lines of Tb^{3+} when excited at 293 nm. The emission lines located at about 488, 547, 582, and 625 nm respectively can be assigned to $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($J = 6, 5, 4, 3$) transitions of Tb^{3+} ,¹⁸ resulting in the green color under the UV light when it is excited at 254 nm, as is presented in the inset of Fig. 2b, CIE diagram (Figure S3b) also present the green color. For both $\text{Eu}^{3+}@ \text{Cd-MOF}$ and $\text{Tb}^{3+}@ \text{Cd-MOF}$, the emission of ligand is hardly detected when excited at 293 nm, which suggests the efficient energy transfer between ligand and $\text{Eu}^{3+}/\text{Tb}^{3+}$.

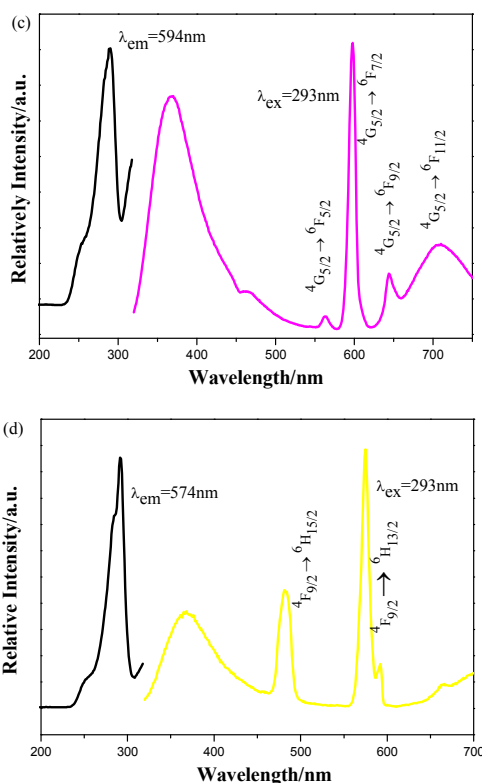
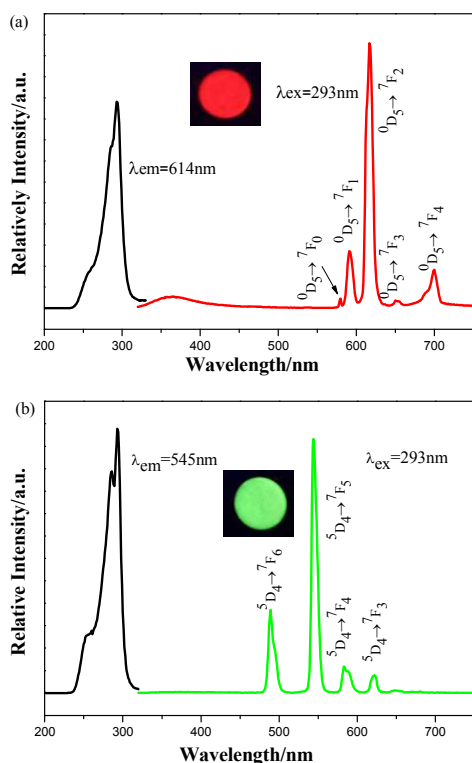


Fig. 2 Room temperature excitation and emission spectra of $\text{Ln}^{3+}@ \text{Cd-MOF}$ (a) $\text{Ln} = \text{Eu}$; (b) $\text{Ln} = \text{Tb}$; (c) $\text{Ln} = \text{Sm}$; (d) $\text{Ln} = \text{Dy}$.

However, the ligand-centered emission bands located at about 365 nm of $\text{Sm}^{3+}@ \text{Cd-MOF}$ and $\text{Dy}^{3+}@ \text{Cd-MOF}$ are obvious, which means the energy transfer between ligand and Sm^{3+} or Dy^{3+} is not as strong as Eu^{3+} and Tb^{3+} . The luminescent emissions of KBr pellet of $\text{Sm}^{3+}@ \text{Cd-MOF}$ and $\text{Dy}^{3+}@ \text{Cd-MOF}$ are hardly to observe under UV-light. As is shown in Fig. 2c, $\text{Sm}^{3+}@ \text{Cd-MOF}$ exhibits characteristic emission of Sm^{3+} centered at 563, 594, 645, 705 nm respectively, which can be ascribed to $^4\text{D}_{5/2} \rightarrow ^6\text{F}_j$ ($J = 5/2, 7/2, 9/2, 11/2$) transitions of Sm^{3+} .¹⁹ CIE diagram (Fig. S3c) shows that it presents the pink, which is nearly to white. For $\text{Dy}^{3+}@ \text{Cd-MOF}$ (Figure 2d), we can observe the emission bands located at about 480 and 574 nm respectively, which can be ascribed to $^4\text{F}_{9/2} \rightarrow ^6\text{F}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{F}_{13/2}$ transitions of Dy^{3+} . Interestingly, CIE diagram (Fig. S3d) shows it exhibits white color, which makes it can be further employed such as LED. Comparing to the emission of pure ligand (5 tbip, 410 nm), which is drawn in Fig. S4, there is a blue shift about 45 nm, which can be attributed to the coordination of ligand white central metals Cd^{2+} .

Table 1 The luminescent efficiencies and lifetimes of $\text{Ln}^{3+}@ \text{Cd-MOF}$

Materials	$\tau/\mu\text{s}$	$\eta /(\%)$
$\text{Eu}^{3+}@ \text{Cd-MOF}$	1323	11.8%
$\text{Tb}^{3+}@ \text{Cd-MOF}$	1873	47.0%
$\text{Sm}^{3+}@ \text{Cd-MOF}$	28	2.3%
$\text{Dy}^{3+}@ \text{Cd-MOF}$	21	6.0%

According to the phenomenon above, we can see that ligand 5-tbip can effectively sensitize the luminescence of Eu^{3+} , Tb^{3+} and Dy^{3+} , especially for Tb^{3+} ions. To further investigate the luminescence properties, luminescence lifetimes and quantum efficiencies are

measured. As is displayed in Table 1, Tb^{3+} @Cd-MOF possesses the highest quantum efficiencies, which is much higher than Eu^{3+} @Cd-MOF, Dy^{3+} @Cd-MOF and Sm^{3+} @Cd-MOF.

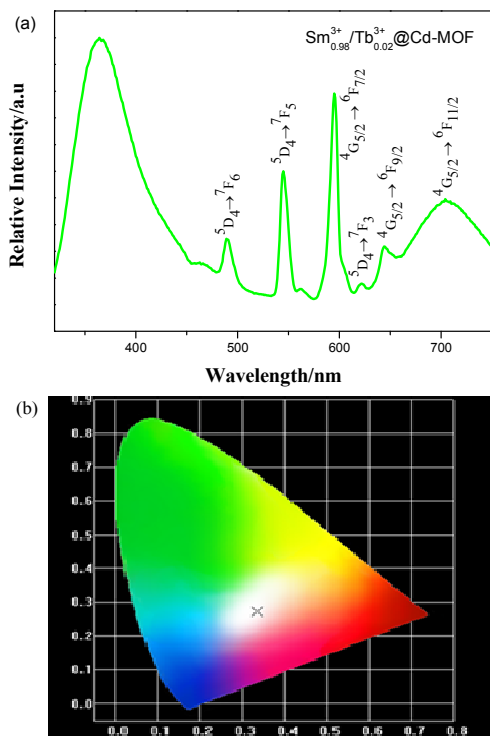


Fig. 3 (a) Emission spectra of Sm^{3+} and Tb^{3+} co-activated Cd-MOF when excited at 293 nm; (b) CIE diagram of Sm^{3+} and Tb^{3+} co-activated Cd-MOF.

Meanwhile, we also try to obtain white light by introducing two kinds of lanthanide ions into the Cd-MOF. After immersing 30 mg of Cd-MOF into the mixed solution of Sm^{3+} and Tb^{3+} with the ratio of 98: 2 for 24 hours, we monitored the photoluminescence spectra (Fig. 3a), which indicates the successful introduction of both Sm^{3+} and Tb^{3+} since we can observe the characteristic peaks of them. To our surprise, the luminescent Ln^{3+} @Cd-MOF can emit white light, as is demonstrated in Fig. 3b.

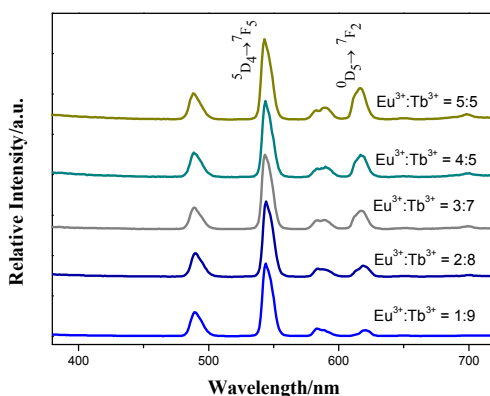


Fig. 4 Emission spectra of Eu^{3+} and Tb^{3+} co-activated MOF with a series of ratio.

A series of Eu^{3+} and Tb^{3+} co-activated Ln^{3+} @Cd-MOF are prepared by immersing 30 mg of Cd-MOF in the mixed DMF solution of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ for 24 hours. As is shown in

Figure S5, The emission colour presents a change from green to yellow gradually as the ratio of $\text{Eu}^{3+}:\text{Tb}^{3+}$ is 1: 9, 2: 8, 3: 7, 4: 5, 5: 5, while the intensity ratio of $\text{Tb}^{3+}:\text{Eu}^{3+}$ = 34.17, 10.35, 5.21, 4.09 and 2.94, respectively (Fig. 4). Obviously, the sensitization of ligand to Eu^{3+} and Tb^{3+} is different, which is in conformity with analysis above.

Characterization of Cd-MOF-2 and Ln^{3+} @Cd-MOF-2

Cd-MOF-2 is prepared by the addition of sodium acetate while other synthesis condition remain unchanged. The morphology of Cd-MOF-2 is studied by SEM. As is shown in Fig. 5, we get the rod-like crystals with the size of $0.5 \times 0.5 \times 2 \mu\text{m}$, which is much smaller than previous ($0.18 \times 0.15 \times 0.12 \text{mm}^3$), as it is reported.¹⁵ PXRD patterns of the resulting Cd-MOF-2 is nearly identical with Cd-MOF, indicating the unchanged crystal structure (Fig. S6). The decrease of the particle size may be due to that the introduction of sodium acetate can lead to competition coordination, which can affect the growth of crystal. However, we also get the Ln^{3+} @Cd-MOF-2 by immersing 30 mg of Cd-MOF-2 into the DMF solution of $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ for 3 days. Therefore, the photoluminescence properties are investigated, as is shown in Fig. S7. ICP-OES analysis indicates that Ln^{3+} cations is introduced into Cd-MOF-2 successfully (Table S1).



Fig. 5 SEM image of low magnification (A) and high magnification (a) of as-synthesized Cd-MOF-2

Characterization of Ln^{3+} @Cd-MOF-2 polymer film

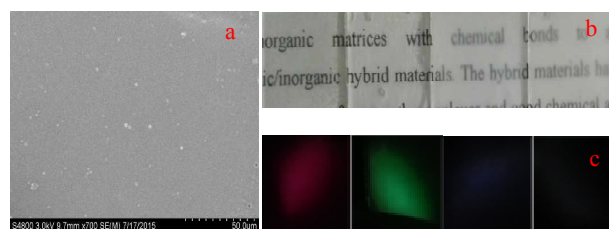


Fig. 6 (a) SEM image of Eu^{3+} @Cd-MOF-2; (b) images of Ln^{3+} @Cd-MOF-2 polymer films under sunlight; (c) images of Ln^{3+} @Cd-MOF-2 polymer films under xenon lamp when excited at 293 nm.

The Ln^{3+} @Cd-MOF-2 polymer film was prepared with the assistance of PEMA and BPO. The SEM image of Eu^{3+} fabricated polymer is shown in Fig. 6. The surface of the film is smooth and defect-free over a large area. The emission spectra of the Ln^{3+} @Cd-MOF-2 polymer are similar to pure Ln^{3+} @Cd-MOF-2, as is demonstrated in Fig. S8, all the MOF fabricated polymer films show similar luminescent emission with powder. However, the

luminescence mechanism may not change since PEMA acts as a physical matrix in the form of the film. As we can see, all the Lanthanide ions encapsulated films can exhibit their characteristic emission bands when excited at 293 nm, especially for Tb³⁺@Cd-MOF-2, Eu³⁺@Cd-MOF-2. The Lanthanide fabricated polymer films are transparent under sunlight, while showing red, green, blue and white when excited at 293 nm under Xenon lamp.

Conclusions

A series of lanthanide ions encapsulated $\{[(Me_2NH_2)_2] \cdot [Cd_3(5-tbip)_4] \cdot 2DMF\}_n$ are prepared via cation exchange method. All the luminescent compounds as-prepared can emit their characteristic bands under the excitation of 293 nm and Dy³⁺ doped $\{[(Me_2NH_2)_2] \cdot [Cd_3(5-tbip)_4] \cdot 2DMF\}_n$ can emit white colour. Furtherly, we try to introduce two kinds of lanthanides into the $\{[(Me_2NH_2)_2] \cdot [Cd_3(5-tbip)_4] \cdot 2DMF\}_n$. When excited at 293 nm, Sm³⁺ and Tb³⁺ co-activated $\{[(Me_2NH_2)_2] \cdot [Cd_3(5-tbip)_4] \cdot 2DMF\}_n$ can present white emission as the ratio of Sm³⁺ and Tb³⁺ was 98: 2. The emission of a series of Eu³⁺ and Tb³⁺ co-activated $\{[(Me_2NH_2)_2] \cdot [Cd_3(5-tbip)_4] \cdot 2DMF\}_n$ at the ratio of 1:9, 2:8, 3:7, 4:5, 5:5 (Eu:Tb) are studied. The emission color transits from green to yellow gradually with the increase of the ratio of Eu³⁺. Meanwhile, we also explore the influence of temperature to the Eu³⁺ and Tb³⁺ co-activated luminescent MOF in the range of 300 to 375 K. With the raise of temperature, the emission intensity of Tb³⁺ at 545 nm decreases while the intensity of Eu³⁺ at 614 nm increases. Moreover, polymer films are prepared by embedding lanthanide ions fabricated $\{[(Me_2NH_2)_2] \cdot [Cd_3(5-tbip)_4] \cdot 2DMF\}_n$ of reduced volume into polyethyl methacrylate. The transparent luminescent polymer films can be further used in many fields.

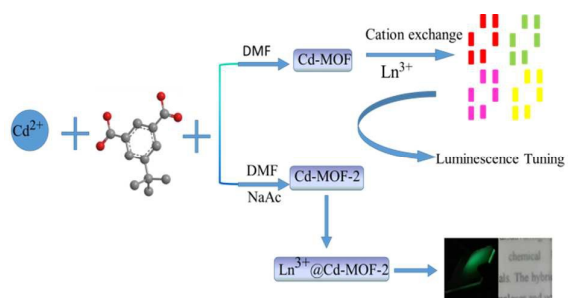
Acknowledgements

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We obtain size-reduced Cd-MOF with the assistance of sodium acetate, with the use of it, luminescent and transparent polymer films are prepared for further application.