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Luminescent lanthanide barcodes based on postsynthetic modified nanoscale metal-organic frameworks

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A new method for luminescent barcode based on nanoscale MOFs (MOF-253) is displayed, which the barcoding is realized by postsynthetic method (PSM) to introduce lanthanide ion (Eu\textsuperscript{3+}, Tb\textsuperscript{3+} and Sm\textsuperscript{3+}). The framework does not preferentially include either lanthanide ion, and then any desired lanthanide composition in the result product can be achieved by controlling the stoichiometry of the reactant. The emission intensity of each of lanthanide ion is proportional to its amount in the MOF, resulting in unique luminescent barcodes that depend on the lanthanide ion ratios and compositions. The synthesized barcoded material is successfully applied in marking functional ionic liquid and preparing luminescent thin film.

Introduction

Barcoded material has been achieved considerable attention as labels for multiplexed assays in biological species and anticounterfeiting application.\textsuperscript{1} An ideal barcoded material must meet some requirement: it should be stable and available in large scale, its synthesis method should be simple and highly reproducible, its spectral signature should be easily acquired and unique interpreted.\textsuperscript{2} Many encoding strategies have been proposed for barcoded materials, including incorporation of segmented nanowires\textsuperscript{3} and photopatterning,\textsuperscript{4} as well as the use of photonic crystals,\textsuperscript{5} conjugated polymer,\textsuperscript{7} fluorescent silica colloids,\textsuperscript{8} alumina\textsuperscript{9} and semiconductor quantum dots (QDs).\textsuperscript{10} But some flaw still remains, for example, although QDs or silica colloids barcoded materials have size-dependent multispectral emissions and superior photostability, their preparation with well-defined size is difficult and complicated;\textsuperscript{7a, 10d, 11} the emission of QDs or organic polymer generally is broad band which is prone to be overlapped.\textsuperscript{12}

Recently, a new conceptual approach have been reported by White and coworker, which is luminescent barcoded systems based on metal-organic frameworks (MOFs) that contain multiple near-IR emitting lanthanides ion as the framework node.\textsuperscript{2} Lanthanide ion has inherent advantages on building luminescent barcoded materials, such as sharp emission spectra and various emission bands.\textsuperscript{13} In addition, the emission wavelengths of lanthanide ion are fixed and not impacted by environment, not like some organic fluorophores.\textsuperscript{14} Moreover, the lanthanide MOFs is able to generate simultaneous emission of several wavelengths using one excitation wavelength for the common antenna; the defined structure of MOFs could determine the precise location of lanthanide ion.\textsuperscript{15} But this field still leaves much to be desired. For example, the nanoscale size is important for biomarker and functional thin film,\textsuperscript{16} the ligand could have some selectivity to lanthanide ion (as framework node) for different atomic radius so that affect the number and variety of barcode;\textsuperscript{2, 17} moreover, the synthesis method should be simplified as far as possible for mass produce.

Postsynthetic method (PSM) maybe is a new choice to solve these problems, whose chemical modification can be performed on the fabricated material rather than on the molecule precursors.\textsuperscript{10} Using PSM, the introduction of lanthanide ion could be occurred in fabricated MOFs rather than in precursors. This provides a new possibility for building lanthanide MOFs barcode that barcoding occur on prepared MOFs instead of the process of synthesizing MOFs (Figure 1).

Results and discussion

Preparation of MOF-253-Ln (Ln= Eu, Tb and Sm)

MOF-253 with a bipyridine derivative in the ligand is famous in the inherent advantage of postsynthetic method (PSM).\textsuperscript{19} In the structure of MOF-253, a one-dimensional infinite chains of AlO\textsubscript{6}...
corner-sharing octahedral is built by connecting bpydc (bpydc = 2,2’-bipyridine-5,5’-dicarboxylic) linkers to construct rhombic shaped pores. The bipyridine group plays two roles, the first is to fix the lanthanide ion, and the second is to sensitize lanthanide ion. The representative structure of MOF-253 has been isolated by PXRD and a Pawley refinement using the Al(OH)3@bpydc (bpydc2− = 4,4-biphenyldicarboxylate) unit cell parameters in the reported work. As-synthesized MOF-253 is confirmed by PXRD (Figure S1), elemental analysis (see experiment details), nitrogen adsorption/desorption isotherms (Figure S2) and FT-IR spectroscopy (Figure S3). The corresponding transmission electron microscopy (TEM) image is shown in Figure S4, the size of MOF-253 particles is almost less than 100 nm, although the size distribution is not very satisfactory. MOF-253-Ln is prepared by introducing Ln3+ ion (Ln = Eu, Tb and Sm) to MOF-253 through PSM. For reacting completely, the amount of MOF-253 slightly exceed to lanthanide ion, and then the molar ratio of Al3+/Ln3+ ion in MOF-253-Eu is really very close to feed ratio, which is determined by inductively coupled plasma (ICP) analysis (details see ESI). After PSM, the crystallization degree is weakened, but the framework is not ruined (Figure S1). The FT-IR spectroscopy also can prove this point (Figure S3).

The FT-IR spectroscopy analysis is also solidly proved the coordination effect between lanthanide ion and bipyridine for antenna effect. There is a shoulder band at about 380 nm in the excitation spectra of MOF-253-Ln. This is due to the luminescence of matrix. The excitation spectra of MOF-253 are obtained by monitoring the emission at 550 nm and are dominated by a broad band centred at about 380 nm, and the emission of MOF-253 display broad band centred at about 525-625 nm under excitation at 380 nm (Figure S6). Using MOF-253 as the luminescent centre, the emission of MOF-253 could be clearly observed in the luminescent spectra of MOF-253-Ln, which obtained by exciting MOF-253-Ln at 380 nm (Figure S7).

The lifetime of 3D4(Eu3+) for MOF-253-Eu, 3D4(Tb3+) for MOF-253-Tb and 4G7/2(Sm3+) for MOF-253-Sm is 347.47 µs, 122.29 µs and 20.76 µs, respectively, which is shown in the Figure S8 and listed in the Table S1. The MOF-253-Ln also displays satisfactory photostability. The integrated intensity loss of 3D4→4F transitions for MOF-253-Eu, 3D4→4F transitions for MOF-253-Tb and 4G7/2→4F transitions for MOF-253-Sm is only 8.21 %, 8.28 % and 8.86 %, respectively, after 24 hrs exposure under UV (λ = 365 nm) (Figure S9).

Preparation of MOF-253-Tb,Eu1-x,Smx

After successfully introducing lanthanide ion to MOF-253, we use the same method to yield barcoded MOF-253 with varying Tb3+ ion and Eu3+ ion stoichiometries: MOF-253-Tb0.09Eu0.01, MOF-253-Tb0.09Eu0.005 and MOF-253-Tb0.09Eu0.01 (see experiment details). The lanthanide compositions in the resulting products were determined by ICP, and directly correlated to the feed ratio of each lanthanide salt (Table S2). This result indicates that the MOF structure does not preferentially include either lanthanide ion, and then any desired lanthanide composition in the result product can be achieved by controlling the stoichiometry of the reactant.

Luminescence studies demonstrate the different lanthanide compositions could result in unique and discernible barcoded signals. The emission of MOF-253-Tb,Eu1-x displays the characteristic transition of Eu3+ ion and Tb3+ ion with excitation at 330 nm (Figure 3a). With an increase in the amount of Eu3+ ion and a decrease in the amount of Tb3+ ion, their characteristic emission intensities increase and decrease accordingly. That means we can quantitatively control the luminescent intensities of the two emitting lanthanide ion by controlling the lanthanide composition. A plot of the ratio of the integrated intensities of the transition of 4G9/2→5F2 (Eu3+ ion) and the transition of 4H9/2→5L6 (Tb3+ ion) reveals a linear relationship between 1: 99 and 0.1: 99.9 Eu3+/Tb3+ (molar ratio) (Figure S10). Their relative intensities could be reflected as unique and visible colour which is corresponding with three distinct barcodes. The points of emission of MOF-253-Tb0.09Eu0.01, MOF-253-Tb0.09Eu0.01 and MOF-253-Tb0.09Eu0.005 in CIE chromaticity diagram is green (X = 0.2876, Y = 0.4915), yellow (X = 0.3630, Y = 0.4698) and red (X = 0.5276, Y = 0.3980), respectively (Figure 3b).

Under such low doping ratio of Eu3+ ion, the characteristic emission intensity of Eu3+ ion is still satisfied. Except for inherent factor (the emission intensity of Eu3+ ion emission is generally stronger than Tb3+ ion), there may be some energy transfer from Tb3+ ion to Eu3+ ion. For further explaining the energy transfer, MOF-253-Eu1-x is prepared which have the same Eu3+ content to MOF-253-Tb0.09Eu0.01 and have not Tb3+ ion. The intensity of characteristic Eu3+ emission is obviously enhanced after adding Tb3+ ion (Figure S11). This indicates the energy transfer from Tb3+ to Eu3+. Meanwhile, the lifetime of MOF-253-Tb,Eu1-x could also observe the energy transfer. The 3D0(Eu3+) and 3D4(Tb3+) lifetime of MOF-253-Tb,Eu1-x is shown in the Figure S12 and listed in Table S1. The 3D0(Eu3+) lifetime of MOF-253-Tb0.09Eu0.01 is 84.80 µs which is increased by almost 2.5 times in comparison to MOF-253-Eu; meanwhile the 3D4(Tb3+) lifetime of MOF-253-Tb0.09Eu0.01 is 39.07 µs.
µs which is plunged by about 70 percent in comparison to MOF-253-Tb. The similar situation also occurs on MOF-253-Tb0.995Eu0.005 and MOF-253-Tb0.999Eu0.001 (Figure S12 and Table S1). The observed change in lifetimes of the Tb3⁺ and Eu3⁺ emission in MOF-253-TbEu1.4, compared to that of pure Tb3⁺ and Eu3⁺ emission (MOF-253-Tb and MOF-253-Eu), further proves that the energy transfer between Tb3⁺ and Eu3⁺ indeed exists.

The excitation which monitored Tb3⁺ characteristic emission is 50: 0.5: 49.5 for MOF-253-Ln-1 and 70: 0.7: 29.3 for MOF-253-Ln-2. The lanthanide compositions in the resulting products are directly correlated to the feed ratio of each lanthanide salt which is determined by ICP (Table S3). The different of atomic radius have not influenced the coordination between lanthanide ion and ligand. The emission spectra of MOF-253-Ln-1 and MOF-253-Ln-2 are normalized to the Eu3⁺ ion signal in Figure 5a, which is obtained by excitation at 330 nm and located at red area in CIE chromaticity diagram (Figure S15). For the same doping ratio of Eu3⁺ ion and Tb3⁺ ion, the emission intensity ratio of Eu3⁺ ion and Tb3⁺ ion is the same in the MOF-253-Ln-1 and MOF-253-Ln-2. This again demonstrates the excellent reproducibility of the barcoded signal based on PSM. With decrease the amount of Sm³⁺ ion, the emission of characteristic Sm³⁺ ion obviously weak from MOF-253-Ln-1 to MOF-253-Ln-2. As expected, it displays a more sophisticated barcode signal from three component lanthanide ion. The excitation of MOF-253-Ln-1 and MOF-253-Ln-2 is obtained by monitoring the characteristic lanthanide ion emission (Figure 5b and 5c). The 5D0 (Eu³⁺), 5D2 (Tb³⁺) and 4G2 (Sm³⁺) lifetime of MOF-253-Ln-1 is 551.15 µs, 75.38 µs and 31.02 µs, respectively; and the 5D0 (Eu³⁺), 5D4 (Tb³⁺) and 4G2 (Sm³⁺) lifetime of MOF-253-Ln2 is 613.32 µs, 98.52 µs and 32.89 µs, respectively. Those are all shown in the Figure S16 and listed in the Table S1.

Application of the nanoscale barcoded material based on MOF-253 in functional ion liquid and luminescent thin film

Two systems which have been extensively applied in luminescent material are used to prove the advantage of the nanoscale barcoded material based on MOF-253, one is functional ion liquid, and the other one is ITO glass-supported luminescent thin film.16 A common ionic liquid, 1-(2-hydroxyethyl)-3-methylimidazolium bromide (IL), is been choose as the matrix to disperse MOF-253-Ln1, record as IL-MOF-Ln. The synthesis method of IL-MOF-Ln is similar with preparing functional ionic liquid incorporated semiconductor nanoparticle (details see supporting information).26 The IL-MOF-Ln is clear (about 70 °C) and could emit the luminescence barcoded signal under 330 nm (Figure 6b and 6c). The
luminescent spectra of IL-MOF-Ln are the same to MOF-253-Ln-1 (Figure S17). This means the luminescent barcoded signal is successfully marked on ionic liquid. Meantime, the integrity of MOF-253-Ln-1 is also proved for excitation spectra (Figure S18). ITO glass-supported luminescent thin films of MOF-253-Ln-1 are prepared by direct spin-coating, like the thin films constructed by nanoscale MOF-76. In the photograph, the thin film is transparent (Figure 6d) and emits the luminescent barcoded signal under 330 nm (Figures 6e). From SEM images (Figure 6a), the surface of thin film is continuous and defect-free over a large area. The similarity of emission spectra of the thin film and powder demonstrate the ITO glass have been successfully marked by MOF-253-Ln-1 (Figure S18).

**Figure 6** (a) The emission spectra of MOF-253-Ln-1(black) and MOF-253-Ln-2 (red) ($\lambda_{em}$ = 330 nm), the excitation spectra of MOF-253-Ln-1 (b) and MOF-253-Ln-2 (c).

Conclusions

In conclusion, we present a new method for luminescent lanthanide barcode based on postsynthetic modified nanoscale MOFs that simultaneously emit several independent visible signals arising from different lanthanide ion. This method is not only simple and straightforward, but also suitable to almost all lanthanide ions. Furthermore, the barcoded materials have been successfully used to mark ionic liquid and prepare spin coating thin film ITO glass. The nanoscale of matrix (MOF-253) endows the barcoded materials with greater advantage in the practical application.

**Experiment**

**Chemicals.** Chemicals were purchased from commercial sources. All solvents were analytical grade and without further purification. Eu(NO$_3$)$_3$·xH$_2$O, Tb(NO$_3$)$_3$·xH$_2$O and Sm(NO$_3$)$_3$·xH$_2$O were prepared by dissolving oxides (Eu$_2$O$_3$, Tb$_2$O$_3$ or Sm$_2$O$_3$) in concentrated nitric acid (HNO$_3$).

**Physical characterization.** The elemental analyses are measured with a Vario EL III elemental analyser. X-ray diffraction patterns are recorded on a Rigaku D/ max-Rb diffractometer equipped with a Cu anode in a 20 range from 5 to 45°. Scanning electronic microscope (SEM) was measured on Hitachi S-4800. Transmission electron microscope (TEM) experiments were conducted on a JEOL2101 microscope operated at 200 kV. Nitrogen adsorption/desorption isotherms are measured by using a Nova 1000 analyser under the liquid nitrogen temperature. Luminescence excitation and emission spectra of samples are obtained on Edinburgh FLS920 spectrophotometer. Luminescence lifetime measurements are carried out on an Edinburgh FS920 phosphorimeter using a microsecond pulse lamp as excitation source. The data of life time is achieved from fitting the experiment luminescent decay. UV-visible diffuse reflectance spectrum was taken with BWS003. The measurement of metal ion was performed on Agilent 7700X inductively coupled plasma-mass spectrometer (ICPMS).

**MOF-253.** MOF-253 (Al(OH)(bpydc)) is synthesized according to the references. MOF-253 was prepared from hydrothermal reaction of AlCl$_3$, 6H$_2$O (151 mg, 0.625 mmol), 2,2’-bipyridine-5,5’-dicarboxylic acid (153 mg, 0.625 mmol) and 10 mL N,N’-dimethylformamide (DMF) at 120 °C for 24 hrs. The resulting white microcrystalline powder was then collected with centrifugation and washed with DMF. The solid products were washed with methanol via Soxhlet extraction for 24 hrs, and then was collected by filtration and finally dried at 200 °C under vacuum for 12 hrs to give [Al(bpydc)(OH)], MOF-253 (165 mg, 90 %). Anal. Calcd for C$_{31}$H$_{47}$N$_{12}$O$_{6}$: C, 55.47; H, 6.79; N, 28.57. Found: C, 55.37; H, 6.68; N, 28.49.

**MOF-253-Ln (Ln = Eu, Tb and Sm).** The preparation of MOF-253-Eu was carried out as follows: The compound Al(OH)(bpydc) (31.7 mg, 0.11 mmol), solution of Eu(NO$_3$)$_3$·xH$_2$O in the acetonitrile (10 mL, 10 mmol/L) and acetonitrile (5 mL) were added to a methanol via Soxhlet extraction for 24 hrs, and then was collected by filtration and finally dried at 200 °C under vacuum for 12 hrs to give [Al(bpydc)(OH)]MOF-253 (165 mg, 90 %). Anal. Calcd for C$_{31}$H$_{47}$AlN$_{12}$O$_{6}$: C, 24.01; H, 1.18; N, 11.04. Found: C, 24.00; H, 1.17; N, 11.04. ICP analysis showed that the molar ration of Al$^{3+}$/Eu$^{3+}$ was 10.99:9.98. MOF-253-Tb and MOF-253-Sm was prepared in a similar manner to MOF-253-Eu. **MOF-253-Tb$_{x}$Eu$_{y}$ (x = 0.99, 0.995 and 0.999).** The preparation of MOF-253-Tb$_{0.99}$Eu$_{0.01}$ was carried out as follows: The compound Al(OH)(bpydc) (31.7 mg, 0.11 mmol), solution of Tb(NO$_3$)$_3$·xH$_2$O in the acetonitrile (9.9 mL, 10 mmol/L), Eu(NO$_3$)$_3$·xH$_2$O in the
acetonitrile (1 mL, 0.01 mmol/L) and acetonitrile (5 mL) were added to a Teflon-capped 20 mL scintillation vial and heated on a hotplate at 65 °C for 24 hrs. The resulting white solid product was washed with acetonitrile by ultrasonic three times and dried at 65 °C under vacuum for 12 hrs to give Al(bpyn)(OH)(Tb(NO₃)₃)ₓₑₒ₀₀₀(Eu(NO₃)₃)ₓₒ₀₀₀). MOF-253-Tbₓₑₒ₀₀₀ (639, 95 %). Anal. Calcd for C₁₂₇H₂₆AlTbₓₑₒ₀₀₀N₄₁₇O₁₂₇₁: C, 23.90; H, 1.17; N, 11.03. Found: C, 23.89; H, 1.18; N, 11.04. ICP analysis showed that the molar ratio of Al²⁺/Tb³⁺/Eu³⁺ was 10:99:99. 0.10. MOF-253-Tbₓₑₒ₀₀₀ and MOF-253-Tbₓₑₒ₀₀₀ were prepared in a similar manner to MOF-253-Tbₓₑₒ₀₀₀.

0.5-MOF-253-Tbₓₑₒ₁₅ (x = 0.99, 0.995 and 0.999). 0.5-MOF-253-Tbₓₑₒ₁₅ (x = 0.99, 0.995 and 0.999) is prepared by the same method, the amount and ratio of lanthanide ion keep the same as before, but the amount of matrix, MOF-253, is double.

MOF-253-Ln-1 and MOF-253-Ln-2. MOF-253-Ln-1 and MOF-253-Ln-2 is prepared by the same method, except for different ratio of lanthanide ion.

1-(2-Hydroxyethyl)-3-methylimidazolium bromide (IL). IL is synthesized according to the references. Tolueno as a solvent, the 1-methylimidazolium was mixed with bromoeathanol (1:1 equiv.), the mixture was stirred at 110 °C for 24 hrs under nitrogen atmosphere. Then, the pale-yellow viscous product was washed with ethyl acetate at least 3 times. Yield: 90 %.

Notes and references

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