

An efficient strategy for improving the water stability of a near-infrared-emissive lanthanide MOF

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Abstract. Near-Infrared-emissive materials have attracted substantial attention due to their unique properties. To solve the urgent requirements of high-water stability materials can be widely used in practical engineering. Hence, a novel near infrared luminescent and highly water-stable lanthanide-organic frameworks (namely Yb-MOF-Y) was synthesized under hydrothermal method by anchoring functionalized, rigid ligands 2,3,5,6-tetrafluoroterephthalic acid and 1,10-phenanthroline onto its skeleton. It is notable that the Yb-MOF-Y possess high structural stability in water for 28 days, in different acid-base solutions (pH = 4-10) for 3 days and the thermal stability in water (-20 °C to 60 °C) for 3 days. Remarkably, luminescent studies reveal that the Yb-MOF-Y can be used as a potential material in near infrared field.

1 Introduction

Lanthanide metal-organic frameworks (Ln-MOFs) as a unique class of crystalline materials comprised of organic ligands and lanthanide ions, have demonstrated a wide range of application prospects. Ln-MOFs possess unique characteristics of large Stokes shift, wide emission range from ultraviolet-visible to near-infrared (NIR) as well as long luminescent lifetime [1-3]. So far, many UV-visible luminescent Ln-MOFs have been successfully constructed, while there are few reports on the use of NIR luminescent lanthanide complexes. Simultaneously, the near-infrared emitting materials which are of great interest for a variety of applications ranging from optical thermometry, telecommunications, sensing, anticounterfeiting to bioimaging [4-5]. However, they still suffer from some obvious shortcomings such as the presence of high-energy chemical bonds (such as O-H, N-H, and C-H) can largely act as an oscillator to significantly inhibit the near-infrared emission of lanthanide ions and the weak water-stability limits its application in the actual biological environment [6-7].

Hence, by anchoring functionalized ligands (1,10-phenanthroline and 2,3,5,6-tetrafluoroterephthalic acid) and ytterbium ion onto its skeleton, we successfully synthesized a novel Yb-MOF-Y with high water stability and strong near-infrared emission mainly attributed to I) the selection of hydrophobic group -F and pyridine nitrogen can effectively improve water stability[8]. II) Choosing Yb ions as metal sites which can obtain the effect of near infrared emission [9-10]. III) The existence of multiple fluorine atoms and nitrogen atoms largely avoids high-energy bonds and guarantees strong near-infrared emission [11].

2 Experimental Section

2.1 Materials and Methods

Yb(NO₃)₃·5H₂O, 2,3,5,6-tetrafluoroterephthalic acid (H₂tfBDC), 1,10-phenanthroline (phen) and other reagents involved in this article were purchased and applied to the experiments directly. Single-crystal X-ray diffraction data for Yb-MOF-Y were recorded on a Bruker Apex CCD II area-detector diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 293(2) K. Absorption corrections were applied using the multi-scan technique. Their structures were solved by the direct methods of SHELXS-97 and refined by the full-matrix least-squares technique with the SHELXL-97 program. Non-hydrogen atoms were refined with anisotropic temperature parameters. The CCDC number of Yb-MOF-Y is 2016122.

2.2 Synthesis of Yb-MOF-Y

Under hydrothermal method, Yb(NO₃)₃·5H₂O (44.9 mg, 0.1 mmol), phen (35.7 mg, 0.15 mmol), and H₂tfBDC (29.7 mg, 0.15 mmol) was dissolved in deionized water (8 mL). The fully mixed solution was then ultrasound for 12 minutes at room temperature and heated at 110 °C for 2.5 days in 23 mL Teflon-lined autoclave. Then, the resulted colorless transparent block crystals (namely Yb-MOF-Y) were obtained. Elemental analysis Calculated (%) for Yb-MOF-Y [Yb(tfBDC)_{1.5}(phen)(H₂O)]_n

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C₂₄H₁₀F₆N₂O₇Yb: C, 39.72; H, 1.38; N, 3.86. Found (%): C, 40.01; H, 1.39; N, 3.91.

2.3 Water Stability Experiments

Yb-MOF-Y (5mg) were dispersed in 5mL of deionized water for 30 days; Yb-MOF-Y (5mg) were immersed in 5 mL of different pH-value (3-11) aqueous solutions for 3 days, and Yb-MOF-Y (5mg) immersed in deionized water then heated them at 60 °C and frozen at -20 °C for 3days; subsequently, the PXRDs were detected.

3 Results and discussion

3.1 Crystal structure of Yb-MOF-Y.

Single-crystal X-ray diffraction analyses demonstrate that Yb-MOF-Y crystallizes belongs to the monoclinic space group C2/c (Table 1). The asymmetric unit of Yb-MOF-Y is assembled one crystallographically unique Yb³⁺ ions, 1.5 deprotonated tfBDC²⁻ ligands, one phen ligand and one terminal water molecules (Fig. 1a). The eight-coordinated Yb atom is composed of two N atoms are from one phen ligand and five carboxylate, five O atoms are from 1.5 H₂tfBDC ligands and one oxygen atoms from coordination water molecules (Fig.1b). The adjacent Yb³⁺ ions are connected orderly by oxygen atoms of the H₂tfBDC ligands, forming a one-dimensional chain, eventually further connected ligands to form a three-dimensional porous architecture (Fig. 1c, 1d).

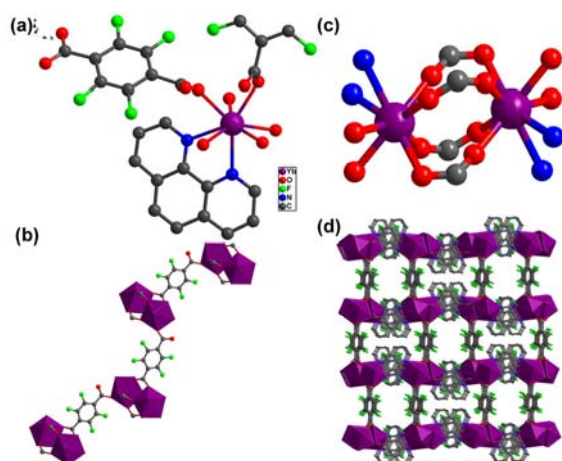


Fig. 1. (a) The asymmetric unit of Yb-MOF-Y. (b) Coordination of adjacent Yb³⁺ atoms. (c) 1D chain structure. (d) 3D structure. (Yb, purple; O, red; C, black; F, green; N, blue;)

Table 1. Crystal data and structure refinement details for Yb-MOF-Y.

	Yb-MOF-Y
empirical formula	C ₂₄ H ₁₀ F ₆ N ₂ O ₇ Yb
formula weight	725.38
crystal system	monoclinic
space group	C2/c
a	19.530(4) Å
b	21.121(5) Å
c	11.501(3) Å
α	90°
β	101.307(8) °
γ	90°
volume	4651.9(19) Å ³
z	48
ρ _{calc}	2.071 g/cm ³
μ/mm ⁻¹	4.120
F(000)	2784.0
2θ range for data collection	5.284 to 50.152
Independent reflections	4124 [R _{int} = 0.0614, R _{sigma} = 0.0320]
goodness-of-fit on F ²	1.029
R ₁ ^a [I ≥ 2σ (I)]	R ₁ ^a = 0.0253
wR ₂ ^b [all data]	wR ₂ ^b = 0.0518

$$R_1^a = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2^b = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right]^{1/2}$$

3.2 Characterization of Yb-MOF-Y

Fig. 2a obviously shown that a good matching relationship between the powder X-ray diffraction peaks of Yb-MOF-Y obtained from the experiments and simulated data from the CIF file (CCDC number: 2016122), manifesting the highly crystalline structure and high phase purity of the synthesized Yb-MOF-Y. The TGA result of Yb-MOF-Y was shown in the Fig. 2b, the Yb-MOF-Y demonstrates excellent thermal stability (about 329 °C), there is a 2.5% weight loss around 109 °C due to the release of one coordination water molecules. After exceeding 327 °C, the weight dropped significantly, indicating that its frame began to collapse.

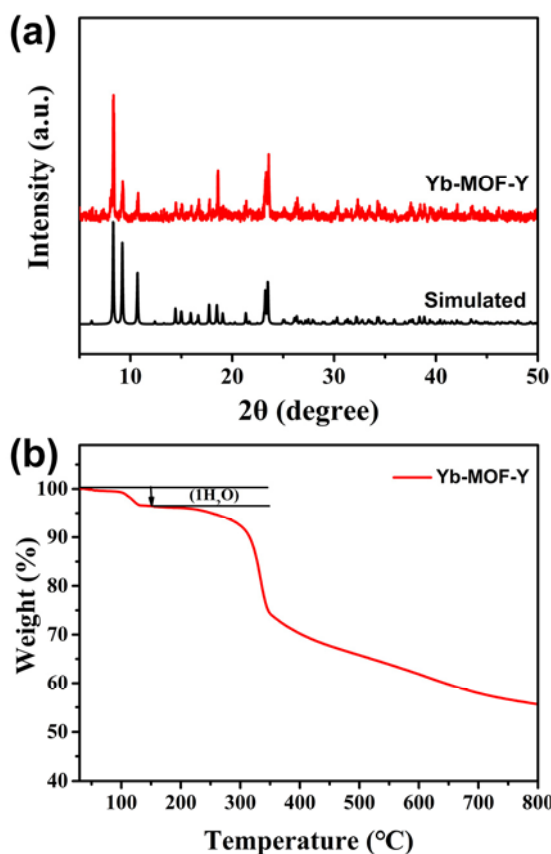


Fig. 2. (a) Simulated and experimental PXRD pattern of Yb-MOF-Y. (b) The TGA of Yb-MOF-Y.

3.3 Luminescence properties of Yb-MOF-Y.

As shown in the Fig.3, Upon exciting at 330 nm, Yb-MOF-Y displays the characteristic emission of Yb³⁺ at 980 nm which can be attributed to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition [12].

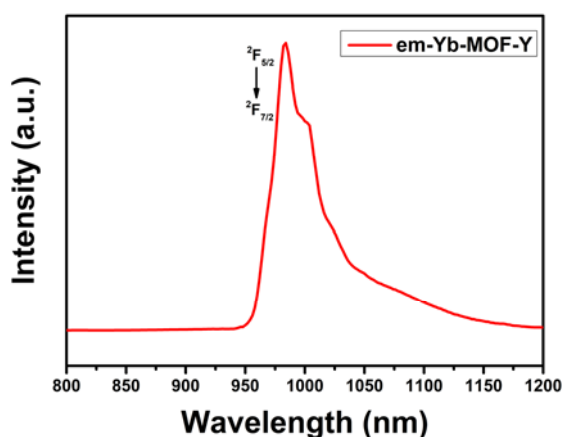


Fig. 3. Emission spectra of Yb-MOF-Y

The appearance of this strong near infrared emission peak is attributed to ligands with a much higher T1 triplet-state energy than the accepting level of metal ions, resulting in good energy transfer from the ligand to the Yb³⁺ metal site and the addition of multiple -F groups and pyridine nitrogen avoids the occurrence of high-

energy bonds to suppress the appearance of near-infrared emissions.

3.4 Water stability properties

The water stability of MOF is critical because water is present in most biological processes. Therefore, the water stability of Yb-MOF-Y in different water environments was carried out by Powder X-ray diffraction. Fig. 4a, 4b show that the diffraction peaks of Yb-MOF-Y after immersion in water for 30 days, heating at 60 °C, freezing at -20 °C for 3 days and immersed in aqueous solutions with different pH values (2-10) are in good agreement with the original Yb-MOF-Y, manifesting that Yb-MOF-Y has high water stability which may be due to the hydrophobic group and Ln-N coordination enhance the crystal's resistance to water molecules [13].

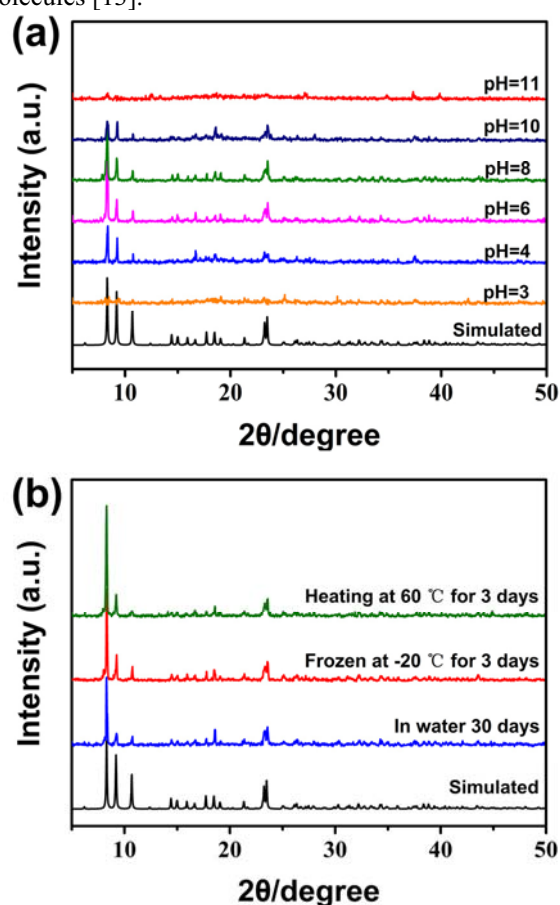


Fig. 4. (a) PXRD patterns of Yb-MOF-Y were immersed in water 30 days, frozen at -20 °C, heated at 60 °C in water for 3 days. (b) PXRD patterns of Yb-MOF-Y were treated by aqueous solutions with various pH values (3-11).

4 Conclusion

In summary, guided by the strategy for the purposeful selection of functional ligands 2,3,5,6-tetrafluoroterephthalic acid and 1,10-phenanthroline, a novel Ln-MOF-based near infrared luminescent materials (namely, Yb-MOF-Y) has been successfully prepared. The Yb-MOF-Y reveals high water stability, not only suitable for pure water, freezing and heating

environment, but also can apply to acid-base aqueous solution (pH=4-10). The fluorescence detection results manifest that has strong emission at 980 nm which can be used as potential materials in the near infrared field.

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