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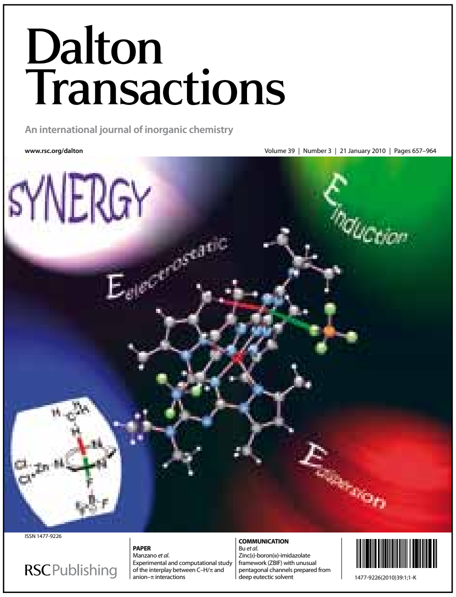

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ARTICLE TYPE

Tunable colors and white-light emission based on a microporous luminescent Zn(II)-MOF

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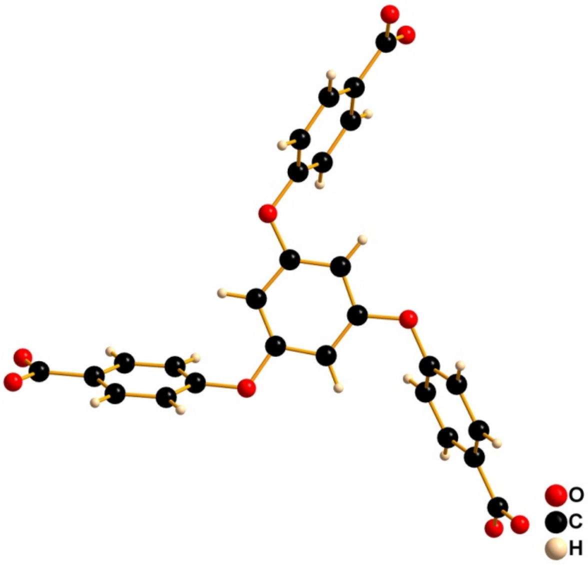
Metal-organic frameworks (MOFs) are a rapidly growing class of hybrid materials with many multifunctional properties. The permanent porosity plays a central role in the functional properties. Especially, the luminescent MOFs with permanent porosity have wide applications in guest species recognition and adsorption. In this contribution, we aim to develop tunable colors and white-light luminescence materials by the encapsulation of Ln^{3+} species in microporous luminescent MOFs. A semi-rigid trivalent carboxylic acid 1,3,5-tri(4-carboxyphenoxy)benzene (H_3TCPB) was selected as the organic building block, not only because it is suitable to construct microporous frameworks, but also by reason of its blue luminescent emission. Under solvothermal reactions, a microporous MOF material, $[Zn_3(TCPB)_2(H_2O)_2]\cdot 2H_2O\cdot 4DMF$ (JUC-113, JUC = Jilin University, China), was synthesized, which has permanent porosity and emits blue light. According to three-primary color, the guest luminescent species should be Tb^{3+} and Eu^{3+} owing to their distinctive colors (Tb^{3+}, green; Eu^{3+}, red). In addition, the luminescent properties of JUC-113 can be easily tuned by the different combination of the encapsulation amount of Tb^{3+} and Eu^{3+}, obtaining white-light emission materials.

Introduction

Solid state light emitting materials are currently a very active topic because of their diverse applications in lighting, display, sensing and optical devices.[1-5] In the past, the rare-earth ions play a significant role in traditional inorganic luminescent materials.[2, 3] However, organic luminescent materials have been emerged as very promising light emissive materials in the evolution of efficient organic light-emitting diodes (OLEDs) in recent years.[4, 5] Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are an interesting class of microporous hybrid materials that are built from metal ions and organic bridging ligands.[6] They have been attracted wide attention for their superior functional properties and applications in gas storage, separation and sensors in the last two decades.[7-11] The permanent porosity plays a central role in the functional properties, typically in guest species recognition and adsorption. They are also very promising as multifunctional luminescent materials, attributing to the generation of luminescence from the inorganic and the organic moieties. At the same time, the metal-organic charge transfer and guest molecules also affect the luminescent functionalities.[12-14] The lanthanide MOFs are the most active filed in luminescent MOFs because of their unique fluorescent properties, such as long lifetime, sharp and intense luminescence and emission in the primary colors range (red, blue and green).[15-17]

Among luminescent materials, white-light-emitting diodes have been considered as the most active topic for solid state lighting as a result of their long operation lifetime and energy-saving.[18-19] However, the emission of most inorganic and organic luminescent materials can only cover part of the visible spectrum. Most of the white-light emission materials have been produced by the approaches of combining monochromatic emissions.[20] In order to achieve the white-light emission materials, facile methods are required for the effective tuning and controlling of the emission colors. Recently, it is attracted more interests to tune the emissive performance of luminescent MOFs by encapsulated Ln^{3+}.[21-23] However, it is not easy to realize tunable luminescence and multiband emissions for lanthanide MOFs, which generally consist of only one kind of lanthanide cationic node and one kind of organic spacers.[24] On the other hand, the synthesis of hetero-lanthanide MOFs are hard due to specific recognition requirements by the different lanthanide cations.[25-27] Moreover, higher coordination number and more flexible coordination geometry of lanthanide ions make it even harder to obtain stable lanthanide MOFs with pores, which is a key feature for tuning luminescence by guests reversibly.[16] Another strategy is the encapsulation of Ln^{3+} species in microporous luminescent MOFs constructed from transit metals. 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 cocktail.[25, 28-31] However, up to now, it is still a big challenge to obtain white-light emission MOFs, because there are several limitations, such as judicious selection of MOFs and guests with intense emissions in different colors, suitable permanent pores for encapsulation and stability of the framework in solvents. As far as we known, it is easy to generate all colors based on three-primary color (green, red and blue). And especially, it is preferable to the host framework with blue emission to generate white-light emission materials by introducing Eu^{3+} (red) and Tb^{3+} (green).

In this contribution, we aim to develop new tunable colors and white-light luminescence materials by the encapsulation of Ln^{3+} species in microporous luminescent MOFs. According to three-primary color, the guest luminescent species should be Eu^{3+} and Tb^{3+} owing to their distinctive colors (Tb^{3+}, green; Eu^{3+}, red), which could be readily observed with naked eyes. A semi-rigid trivalent carboxylic acid 1,3,5-tri(4-carboxyphenoxy)benzene (Scheme 1, H_3TCPB) was selected as the organic building block, not only because it is suitable to construct microporous frameworks, but also by reason of its blue luminescent emissions. Under solvothermal reactions with $Zn(NO_3)_2•6H_2O$, H_3TCPB was combined with Zn(II) to form a microporous MOF material, $[Zn_3(TCPB)_2(H_2O)_2]·2H_2O·4DMF$ (JUC-113, JUC = Jilin University, China), which has permanent porosity and emits blue light. As expected, the luminescent properties of JUC-113 can be easily tuned by the different combination of the encapsulated amount of Tb^{3+} and Eu^{3+}.[32]



Scheme 1 The structure of ligand H_3TCPB.

Experimental

Materials and synthesis

All the chemical reagents were obtained from commercial sources and used without further purification. The organic ligand H_3TCPB was prepared according to literature procedures.[33] Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240 analyzer. Powder X-ray-diffraction (PXRD) patterns were acquired on a Scintag X1 diffractometer with Cu-Kα (λ =1.5418 Å) at 50 kV, 200 mA. Thermogravimetric analyses (TGA) were performed with a Perkin-Elmer TGA thermogravimetric analyzer in the range of 30-800 °C under air flow at a heating rate of 10 °C/min for all measurements. Inductively Coupled Plasma (ICP) were measured by OPTIMA 3300DV. Fourier-transform infrared spectra (FT-IR) were obtained as KBr pellets in the 4000-400 cm^{-1} range using a Nicolet Impact 410 FT-IR spectrometer. All fluorescence measurements were recorded on a Fluoromax-4 Spectrofluorometer at room temperature. Gas sorption-desorption measurements were performed using an Autosorb-iQ_2-MP-AG machine. The Commission International de I'Eclairage (CIE) color coordinates were calculated on the basis of the international CIE standards.[34]

Synthesis of $[Zn_3(TCPB)_2(H_2O)_2]·2H_2O·4DMF$ (JUC-113)

A mixture of $Zn(NO_3)_2•6H_2O$ (30 mg, 0.1 mmol), H_3TCPB (25 mg, 0.05 mmol), DMF(5 ml) and 4 drops of aqueous HNO_3 solution (2.0 mol/L) was sealed into a 20 ml capped vessel. The vessel was heated at 85 °C. The crystals were obtained after 3 days and washed with DMF and dried in air. Yellow crystals were collected. Yield: 28 mg (70% based on the ligand); FT-IR (KBr): 3392 (br), 1670 (m), 1594 (s), 1502 (s), 1463 (s), 1401(m), 1224 (s), 1160 (s), 1121 (m), 1009 (s), 854 (m), 815 (w), 783 (w), 707 (w), 650 (m), 458 cm^{-1} (s). Anal. calcd for $C_{66}H_{66}N_4O_{26}Zn_3$: C 51.93, H 4.36, N 3.67%; found: C 52.36, H 3.98, N 3.59%.

Encapsulation of Tb^{3+} in JUC-113 (JUC-113⊃Tb1, JUC-113⊃Tb2)

The dried JUC-113 (100 mg) was soaked in a DMF solution (5 ml) of $TbCl_3$ (20 and 180 mg for JUC-113⊃Tb1 and JUC-113⊃Tb2 respectively) in a 20 mL capped vessel with parafilm at 75 °C. The crystals were obtained after 4 h, which were washed with DMF carefully to make sure no Tb^{3+} on the external surface.

Encapsulation of Eu^{3+} in JUC-113 (JUC-113⊃Eu1, JUC-113⊃Eu2)

The procedure was the same as that for encapsulation of Tb^{3+} in JUC-113 except that $EuCl_3$ (150 and 180 mg for JUC-113⊃Eu1 and JUC-113⊃Eu2 respectively) instead of $TbCl_3$ and soaked 15 h.

Encapsulation of Tb^{3+} and Eu^{3+} in JUC-113 (JUC-113⊃Ln1, JUC-113⊃Ln2)

The dried JUC-113 (100 mg) was soaked in a DMF solution (5 ml) of $EuCl_3$ (150 and 180 mg for JUC-113⊃Ln1 and JUC-113⊃Ln2 respectively) in a 20 mL capped vessel with parafilm at 75 °C. The crystals were collected after 5 h and 12 h for JUC-113⊃Ln1 and JUC-113⊃Ln2 respectively and then put into a DMF solution (5 ml) of $TbCl_3$ (50 mg) in a 20 ml capped vessel with parafilm at 75 °C. The resultant crystals were obtained after 5 h and 8 h for JUC-113⊃Ln1 and JUC-113⊃Ln2 respectively. The crystals were washed with DMF to remove the residual lanthanide(III) cations on the surface.

X-ray structure determination and structure refinement

X-ray intensity data of JUC-113 was collected at 298K on Bruker SMART APEX II CCD-based diffractometer using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). The structure was solved with direct methods. All non-hydrogen atoms were located successfully from Fourier maps and were refined anisotropic thermal parameters. All calculations performed using the SHELEXTL program package.[35] Crystallographic data for the structure are reported in Table 1 and the selected bond lengths and bond angles are listed in Table S2.

Table 1 Crystal data and structure refinement for JUC-113

Empirical formula	$C_{54}H_{30}O_{26}Zn_3$
Formula weight	1290.95
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	Trigonal
space group	*P*-31c
a [Å]	16.6504(16)
b [Å]	16.6504(16)
c [Å]	14.521(3)
α [°]	90
β [°]	90
γ [°]	120
Volume [$Å^3$]	3486.4(9)
Z	2
Calculated density/ mg/m^3	1.230
μ/ mm^{-1}	1.094
F(000)	1304.0
Nref	2060
Reflections collected / unique	17148/2060 [R(int) = 0.0291]
GOF	1.101
Final R indices [I>2sigma(I)]	$R_1 = 0.0658$, $wR_2 = 0.2014$
R indices (all data)	$R_1 = 0.0792$, $wR_2 = 0.2227$

Results and discussion

Structure description

Single crystal X-ray crystallography reveals that JUC-113 consists of a two-dimensional (2D) framework with double-(6, 3)-layers in the trigonal *P*-31c space group. In the asymmetric unit, there is one sixth Zn1 ion, one third Zn2 ion, one third $TCPB^{3-}$ ligand, one third terminal H_2O. As shown in Fig. 1a, the crystallographically independent two Zn(II) centers (Zn1 and Zn2) are linked by carboxylate in the sequence of Zn2-Zn1-Zn2 to form a trinuclear $[Zn_3(COO)_6]$ unit. Zn1 is octahedrally coordinated by six oxygen atoms from six different ligands (Zn1-O, 2.073 Å), while Zn2 is four-coordinated by three carboxylate oxygen atoms from two different ligands and one oxygen atom from terminal H_2O (Zn2-O, 1.900-1.979 Å). Each $[Zn_3(COO)_6]$ units is connected by six $TCPB^{3-}$ to form a double-(6, 3)-layer. The double-layers (Fig. 1b) are packed together with AB fashion by aromatic π-π stacking and weak intermolecular van der Waals interactions to form a 3D supermolecular architecture (Fig. 1c). There are one-dimensional (1D) channels about 4.0 × 4.0 $Å^2$ in the three-dimensional (3D) framework along *c* direction (shortest aromatic C···C distance). The solvent accessible volume of JUC-113 is 40% calculated by PLATON analysis.[36]

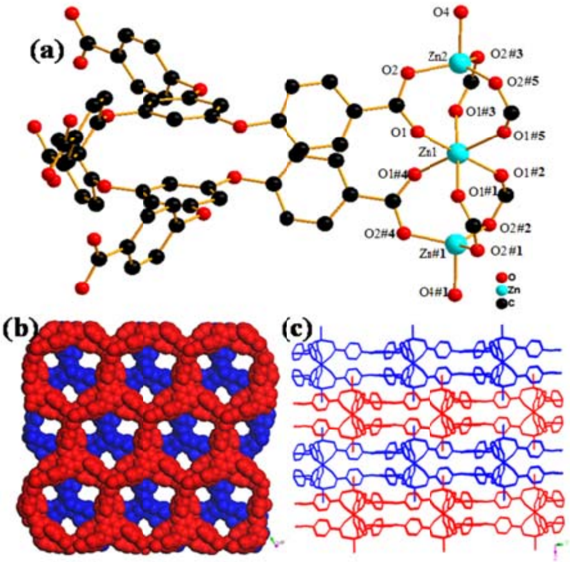


Fig. 1 (a) Coordination environments of Zn (II) atoms (symmetry code: #1: -y+1, -x+1, -z+1/2; #2: x, x-y+1, -z+1/2; #3: -y+1, x-y+1, z; #4: -x+y, y, -z+1/2; #5: -x+y, -x+1, z;). (b) The packed double-layers of JUC-113 view along c axis. (c) View along a axis.

Stability and porosity

Powder X-ray diffraction (PXRD, Fig. 2a) of JUC-113 confirmed the phase purity of the bulk crystalline materials. To determine whether the frameworks could be retained upon heating, the crystals of JUC-113 were retained at different temperatures under air atmosphere. According to the powder X-ray diffraction, it shows the framework can be stable up to 165 °C (Fig. S1). Additionally, the framework could retain its crystalline integrity after the encapsulation of Ln^{3+} species, as demonstrated by PXRD profiles (Fig. 2b). Thermogravimetric analysis (Fig. 2c) under air atmosphere was measured. It is found that there was a weight loss of 22.59% before 300 °C, which could be attributable to the loss of guest and terminal molecules (calculated 22.67%). The residue was ZnO (experimental: 16.54% and calculated: 16.46%). In order to verify its porosity, gas sorption isotherms of JUC-113 were measured. Before the measurement, JUC-113 was activated at 100 °C under vacuum for 12 h. The PXRD patterns of the activated sample and the as-synthesized samples are shown in Fig. 2d, which shows the activated framework was almost containing its structure. The typical type-I N_2 adsorption isotherm at 77 K reveals that JUC-113 is a microporous material corresponding to a Langmuir surface area of 132.6 $m^2 \cdot g^{-1}$ (Fig. S2). JUC-113 also has selective sorption capabilities for CO_2 over CH_4 at 273 K, which is likely attributed to the molecular sieving effect of the narrow apertures (kinetic diameters: CH_4 (3.76 Å), CO_2 (3.30 Å)) and host-guest interactions between significant quadrupole moment CO_2 molecules and the unsaturated Zn^{2+} sites (Fig. S3).[37]

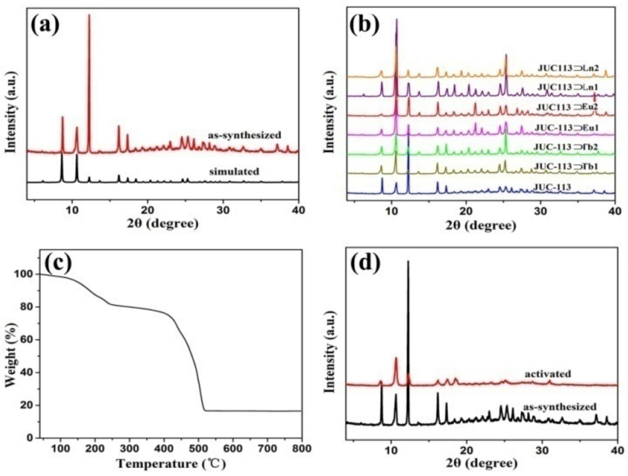


Fig. 2 (a) The simulated and as-synthesized powder X-ray diffraction of JUC-113. (b) The PXRD patterns of JUC-113 and Ln^{3+}-encapsulated JUC-113. (c) The TGA curve of JUC-113. (d) The PXRD patterns of activated and as-synthesized samples.

Tunable colors and white-light emission

As shown in Fig. 3a, it is worth to note that JUC-113 yields blue light, corresponding to the transitions emissions from 400 to 500 nm. It also can be seen in the excitation spectra that the blue luminescence of JUC-113 could be excited from 250 to 400 nm and the peak of excitation spectra is at 347 nm. Compared to the excitation and emission spectra of the ligand H_3TCPB, the luminescence spectrum of JUC-113 is similar, which indicates that the luminescent property of JUC-113 is mostly attributed to the emission of the organic linker.

In order to introduce luminescent lanthanide ions into the pores of JUC-113, the crystals were immersed in a DMF solution of $LnCl_3$ (Ln = Tb or Eu) for several hours, then washed with DMF to make sure no Ln^{3+} on the external surface. The encapsulated weight amounts of Ln^{3+} were found to be relative to the concentration of $LnCl_3$ solution, which were confirmed by ICP measurement (Table S1). It is worth to mention that the additional lines of Tb^{3+} and Eu^{3+} become more intense along with the increasing of the encapsulated amount of Tb^{3+} or Eu^{3+}. The encapsulated amount of Tb^{3+} could be up to 9.59% (JUC-113⊃Tb2) and the highest encapsulated weight fraction of Eu^{3+} was 5.91% (JUC-113⊃Eu2). Fig. 3b shows the excitation and emission spectra of the most intense emission of Tb^{3+} (green, 543 nm) and Eu^{3+} (red, 612 nm) in JUC-113⊃Ln. It is demonstrated that 283 nm is the optimum to the JUC-113⊃Ln, which is beneficial to yield green (λ_{em} = 543 nm) and red lights (λ_{em} = 612 nm) respectively. Similarly, in order to introduce Eu^{3+} and Tb^{3+} into the framework, JUC-113 was soaked in a DMF solution of $EuCl_3$, then soaked in a DMF solution of $TbCl_3$. As shown in Fig. 3c, when irradiated at 283 nm, the blue emission from JUC-113 is still existed although it should decrease from the as-synthesized sample under 347 nm. Fig. 3d-f show the luminescent spectrum of the air-dried Ln^{3+}-encapsulated samples excited at 283 nm in the solid-state at room temperature, respectively. It can be seen clearly that the characteristic transitions of Tb^{3+} from $^5D_4$ to ^7F_J (J = 6, 5, 4 and 3): 488, 543, 582, 621 nm respectively in Fig. 3d and those of Eu^{3+}, corresponding to the transitions from $^5D_0$ to ^7F_J (J = 0-4): 578, 590, 612, 650 and 699 nm respectively in Fig. 3e. Fig. 3f shows that the luminescent spectrum of Eu^{3+}- and Tb^{3+}-encapsulated JUC-113 (JUC-113⊃Ln1, JUC-113⊃Ln2) with the additional characteristic transitions of Tb^{3+} and Eu^{3+}. Similarly, the luminescent intensity of Eu^{3+}- and Tb^{3+}-encapsulated JUC-113 increase with the increasing of the encapsulated amount of Tb^{3+} and Eu^{3+}, which indicates that the color of JUC-113 crystals could be changed by the adjustment of the encapsulated amount of Ln^{3+} ions.[38] As shown in Fig. 4a, the CIE chromaticity coordinates of JUC-113 is in the blue region. With the encapsulation of Tb^{3+} or Eu^{3+} in JUC-113, JUC-113⊃Tb1, JUC-113⊃Tb2, JUC-113⊃Eu1, JUC-113⊃Eu2, JUC-113⊃Ln1 and JUC-113⊃Ln2 can be tuned colors from blue to other colors and the optical photographs of JUC-113, JUC-113⊃Tb2 and JUC-113⊃Eu2 under the UV 254 nm lamp exhibiting the blue, red and green respectively.

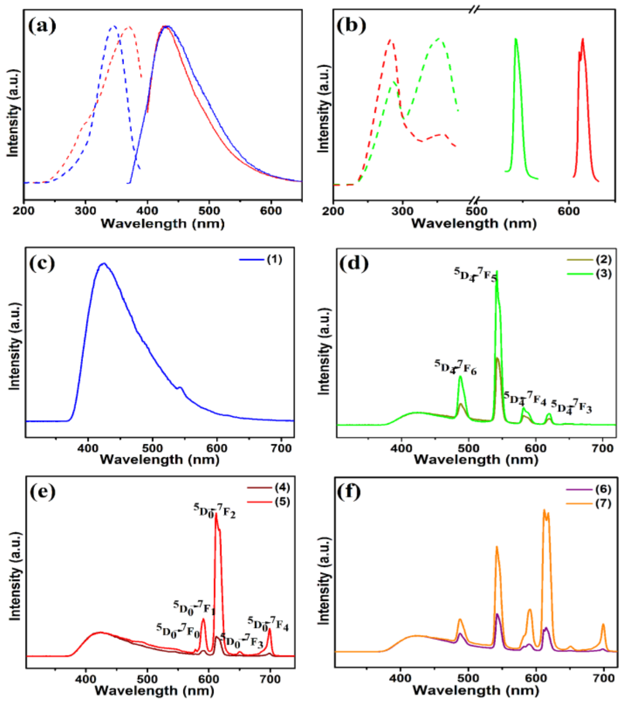


Fig. 3 (a) Excitation (dot lines) and emission (solid lines) spectra of free H_3TCPB ligand (blue) and JUC-113 (red). (b) The excitation (dot lines) and emission (solid lines) spectra of the most intense emission of Tb^{3+} (green, 543 nm) and Eu^{3+} (red, 612 nm) in JUC-113⊃Ln. (c) The emission spectra of JUC-113 excited at 283 nm. (d-f) JUC-113⊃Tb (d; 2, 3 for Tb1, Tb2, respectively), JUC-113⊃Eu (e; 4, 5 for Eu1, Eu2, respectively) and JUC-113⊃Ln (f; 6, 7 for Ln1, Ln2, respectively) excited at 283 nm.

The tunable luminescent properties of Ln^{3+}-encapsulated JUC-113 offer us an opportunity to tune the luminescent properties and obtain white-light emission. More interesting, JUC-113⊃Ln1 (1.05% Eu and 1.56% Tb) could emit white light under 254 nm UV lamps (Fig. 4b). The emission spectra shows the main emission peaks of Ln^{3+} and JUC-113 are comparable in intensity when excited at 254 nm, because the emission of the host is quenched more than the sharp characteristic peaks of Ln^{3+} luminescence. The corresponding CIE is (0.3292, 0.3543), which is very closed to the international pure white light CIE chromaticity coordinates (0.333, 0.333).

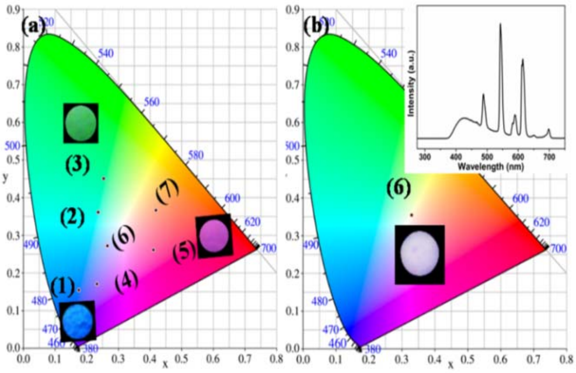


Fig. 4 (a) CIE chromaticity of JUC-113 (1), JUC-113⊃Tb1 (2), JUC-113⊃Tb2 (3), JUC-113⊃Eu1 (4), JUC-113⊃Eu2 (5), JUC-113⊃Ln1 (6) and JUC-113⊃Ln2 (7) excited at 283 nm. (insert: optical photographs of (1), (3) and (5) excited under 254 nm UV lamps) (b) CIE chromaticity of JUC-113⊃Ln1 under 254 nm UV lamps. (insert: the optical photograph and the emission spectra of JUC-113⊃Ln1 excited at 254 nm UV lamps)

Conclusion

In summary, we synthesized a microporous MOF material JUC-113, which has 1D microporous channels and emits blue light. The results demonstrate that the luminescent and porous MOFs have the ability to be solid state lighting materials in the future. It is expected that more extensive research to explore and develop the microporous luminescent MOFs as solid state light emitting materials.

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Notes and references

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† Electronic Supplementary Information (ESI) available: details of experimental results, PXRD, ICP, gas sorption-desorption. CCDC 971950. See DOI:10.1039/b000000x/

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