



## White-light emission by selectively encapsulating single lanthanide metal ions into alkaline earth metal-organic coordination polymers



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### ABSTRACT

An effective method to obtain white-light emitters by encapsulating a single lanthanide metal ion into an alkaline earth metal-organic coordination polymers is presented. Two novel complexes SrL(H<sub>2</sub>O) and BaL(DMF) (L = 1,1',1''-(benzene-1,3,5-triyl)tripiperidine-4-carboxylic acid) were synthesized, and lanthanide metal ions were encapsulated by coordination with their active sites. The CIE coordinates of the modified complexes are tuned along two separate trajectories by regulating the content of either Eu<sup>3+</sup> or Tb<sup>3+</sup>. The trajectories of the complexes containing Eu<sup>3+</sup> pass through the white region in the CIE diagram. Different from the traditional idea of overlaying three emission colors, white-light emission of the modified complexes is explored by encapsulating only Eu<sup>3+</sup> into the blue-light emission coordination polymers to decrease the number of unmanageable variables. Luminescence measurements show that the complexes can specifically identify Fe<sup>3+</sup> with almost complete emission quenching, which is not observed in the presence of other metal ions.

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### 1. Introduction

Metal-organic coordination polymers with a three-dimensional ordered microporous structure have been elaborated in fruitful researches for gas storage [1], separation [2], catalysis [3], drug delivery [4], biomedical imaging [5], magnetism [6] and luminescence performance [7]. Accounting for about ten percent of all reported coordination polymers [8], luminescent coordination polymers have aroused tremendous interest because of their potential applications in displays [9], optical devices [10], sensing [11] and lighting [12]. Owing to the fact that the luminescence of coordination polymers can be subversively influenced by the guest, some luminescent coordination polymers have been used as sensors to identify target molecules and ions [13], while others have been modified to optimize their luminescence performance [14].

Most reported luminescent coordination polymers contain lanthanide [15] or transition metals [16]; alkaline earth metals are inactive because of their poor coordination ability. However,

alkaline earth metals may be used in luminescent coordination polymers and become more economical substitutes when coordinated with a specific luminescent ligand. This ligand should possess active sites that can interact with guests and influence the luminescence performance, and also play vital roles in postsynthetic modification (PSM) to expand the functionality of coordination polymers.

Since coordination polymers with PSM were first reported by Robson [17], modified coordination polymers for many potential applications have been produced [18]. The PSM of alkaline earth luminescent coordination polymers for functional properties is still relatively unexplored. Coordination polymers must be sufficiently stable during a chemical transformation, dense and porous to allow access to the interior of the lattice. In addition, most have to provide an available active site to interact with the guest.

The luminescence of coordination polymers can be affected by the guest, which makes them attractive for sensing. Simultaneously, to optimize luminescence properties including white-light emission, some luminescent coordination polymers with more than one lanthanide metal ion were prepared. However, coordination polymers based on alkaline earth ions with multiple functions of sensing, tunable color and white-light emission have not been studied.

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White-light emission coordination polymers have attracted considerable interest recently [19]. It has been suggested that white-light emission could be realized by adjusting the molar ratios of  $Tb^{3+}$  and  $Eu^{3+}$  within blue-light emission coordination polymers based on the three-primary colors principle [20]. However, this strategy introduced more variables, which made color tuning difficult, especially when energy transfer occurred between  $Tb^{3+}$  and  $Eu^{3+}$  [21]. Therefore, it is important to decrease the number of variabilities and determine the possibility of white-light emission by incorporating a single  $Ln^{3+}$ , which requires a ligand with flexible luminescent properties.

Herein, we report two stable microporous luminescent coordination polymers composed of alkaline earth metal ions ( $Sr^{2+}$  and  $Ba^{2+}$ ) and a  $\pi$ -conjugated ligand with heterocyclic rings and carboxylate groups. Remarkably, multiple active sites in the pores of the coordination polymers can interact with guest metal ions, allowing the luminescence of the host framework to be tuned. The luminescence mechanisms are and demonstrated by the photoluminescence measurements, diffuse reflectance ultraviolet–visible (DR UV–Vis) analysis and electrospray mass spectrometry (ESI–MS) analysis.

## 2. Experimental section

### 2.1. Materials and general methods

$H_3BTPCA$  (1,1',1''-(benzene-1,3,5-triyl)tripiperidine-4-carboxylic acid) was synthesized according to the method in literature [22]. All other reagents were readily available from commercial sources and used as received without further purification. The IR spectra in KBr pellets were recorded in the range 400–4000  $cm^{-1}$  with an Alpha Centaur FT/IR spectrophotometer. Elemental analysis (C, N, and H) were performed on a Perkin–Elmer 2400 CHN elemental analyzer. Elemental analysis for Eu and Tb were obtained using a PLASMA-SPEC(I) ICP atomic emission spectrometer. Powder X-ray diffraction measurements are performed on a Rigaku D/MAX-3 instrument with Cu-K $\alpha$  radiation in the angular range  $2\theta = 3$ – $60^\circ$  at 293 K. Thermogravimetric analysis was carried out by using a Perkin–Elmer TGA7 instrument, with a heating rate of 10  $^\circ C/min$ , under a nitrogen atmosphere. Diffuse-reflectance ultraviolet–visible (DR UV–Vis) absorption spectra of polycrystalline samples were obtained using a Cary 500 UV–Vis–NIR spectrophotometer at room temperature. Electrospray ionization mass spectrometry was carried out with a Bruker Micro TOF-QII instrument. Photoluminescence spectra were measured using a FLSP 920 Edinburgh instrument (Eng) with 450 W Xenon lamp monochromatized by double grating.

### 2.2. Synthesis

#### 2.2.1. $[Sr(HBTPCA)(H_2O)]$ (**1**)

A mixture of  $SrCO_3$  (0.015 g, 0.10 mmol),  $H_3BTPCA$  (0.047 g, 0.10 mmol), DMF (6 mL), EtOH (3 mL) was sealed in a Teflon-lined stainless steel vessel (15 mL), which was heated at 140  $^\circ C$  for 12 h and cooled to room temperature at a rate of 5  $^\circ C h^{-1}$ . Colorless lamellar crystals of **1** were collected in 73% yield (0.041 g, based on BTPCA). Anal. Calcd for  $C_{21}H_{27}N_6O_7Sr$ : C, 44.79%; H, 4.83%; N, 14.92%. Found: C, 44.73%; H, 4.90%; N, 14.83%. IR (KBr disks): 3442 (m), 2939 (m), 1941 (m), 1531(s), 1415 (m), 1371 (m), 1187 (m), 945 (s), 804 (s), 666 (w), 511 (m).

#### 2.2.2. $[Ba(HBTPCA)(DMF)]$ (**2**)

A mixture of  $BaCO_3$  (0.020 g, 0.10 mmol),  $H_3BTPCA$  (0.047 g, 0.10 mmol), DMF (6 mL), EtOH (3 mL) was sealed in a Teflon-lined stainless steel vessel (15 mL), which was heated at 120  $^\circ C$  for 8 h

and cooled to room temperature at a rate of 5  $^\circ C h^{-1}$ . Colorless petal-like crystals of **2** were collected in 76% yield (0.053 g, based on BTPCA). Anal. Calcd for  $C_{24}H_{34}N_7O_7Ba$ : C, 43.03%; H, 5.12%; N, 14.64%. Found: C, 42.98%; H, 5.15%; N, 14.58%. IR (KBr disks): 3445 (m), 2918 (m), 1941 (m), 1686 (m), 1525(s), 1409 (m), 1234 (m), 1097 (m), 930 (s), 806 (s), 663 (w), 511 (m).

#### 2.2.3. The encapsulation of transition metal ions of **1** and **2** (**1** $\supset M$ and **2** $\supset M$ )

Dried samples of **1** or **2** (0.035 mmol) were soaked in EtOH (10 mL) solutions containing different concentrations of  $MCl_x$  ( $M = Co^{2+}, Mn^{2+}, Cr^{3+}, Ni^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+},$  or  $Sn^{2+}$ ) for 24 h to form metal-ion-incorporated **1** $\supset M$  or **2** $\supset M$ . The microcrystalline solids were collected by centrifugation, rinsed with multiple aliquots of pure EtOH, and dried in a desiccator maintained at 50  $^\circ C$  for 8 h, then used for physical and chemical characterizations.

#### 2.2.4. The encapsulation of lanthanide metal ions of **1** (**1** $\supset Eu$ and **1** $\supset Tb$ )

The operation was the same as the encapsulation of transition metal ions, except that the lanthanide metal ions were used instead of the transition metal ions.

### 2.3. Single-crystal X-ray crystallography

Single-crystal diffraction was conducted on a Bruker Smart Apex CCD diffractometer with Mo Kr monochromated radiation ( $\lambda = 0.71073$  Å) at room temperature. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [23]. Empirical absorption corrections were applied. The structures were solved by using the direct method and refined through the fullmatrix least-squares method on  $F^2$  using SHELXS-97 [24]. The crystal data and structure refinement results of **1** and **2** are summarized in Table 1.

## 3. Results and discussion

### 3.1. Synthetic processes

To synthesize the coordination polymers, in addition to adjusting the solvent (the DMF was added for the protonation of the ligand), temperature and filling degree, we used sulfates, nitrates and chlorides as the metal source in the reaction system. However, good quality crystals were not obtained because of the rapid release of metal ions, which limited formation of single crystals. The white precipitates formed using these metal salts were microcrystals of the target products. To slow the release of metal ions, carbonate was used as a starting material to synthesize **1** and **2**. Fortunately, the low solubility of the carbonate salts slowed the release of metal ions to give single crystals.

### 3.2. Crystal structure descriptions

Single-crystal X-ray diffraction analysis revealed that **1** and **2** crystallized in the orthorhombic space group Pbca. Their framework structures are isostructural, the asymmetric unit of them contains one crystallographically independent Sr (Ba) cation, one  $H_3BTPCA^{2-}$  anion and one coordination  $H_2O$  (DMF) molecule. The coordinated solvent molecules of alkaline earth metals are different, and the IR spectra confirmed the absence or presence of a peak at 1679  $cm^{-1}$  in **1** or **2**, which is attributable to the C=O (DMF) bond, as shown in Fig. S1.

The  $Sr^{2+}$  ions of **1** are each nonacoordinate and situated in a coordination sphere composed of eight O atoms from six different

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