



# Series of resorcin[4]arene-based lanthanide coordination polymers and selective luminescent sensing properties



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## ABSTRACT

By using tetracarboxylatoresorcin[4]arene 2,8,14,20-tetrapentyl-6,12,18,23-tetra-methoxy-4,10,16,22-tetracarboxymethoxy-resorcin[4]arene (H<sub>4</sub>L), eight lanthanide-based coordination polymers (CPs), [M(HL)(DMF)(H<sub>2</sub>O)<sub>2</sub>]:3H<sub>2</sub>O (M = Tb 1, Eu 2, Gd 3, Yb 4 and Sm 5) and [M(HL)(DMF)(H<sub>2</sub>O)] (M = Ce 6, Pr 7 and La 8), have been constructed. Isostructural CPs 1–5 exhibit charming ribbons built with rare earth cations and cup-like HL<sup>3-</sup> anions. The ribbons are lengthened by hydrogen bonds to constitute supramolecular layers, respectively. CPs 6–8 are isostructural and show unique layer networks. The luminescent properties of 1 and 2 in solid states were studied. The detection of CPs 1 and 2 towards metal cations, polyoxometalates (POMs) and organic small molecules by luminescent quenching and enhancement process has been systematically investigated.

## 1. Introduction

Resorcin[4]arene polymers have caused considerable concerns because of their potential utilization in such as catalysis, magnetic properties and chemical sensing [1–3]. Many attempts have been made to the functionalized resorcin[4]arene, such as carboxylato, tert-butyl and sulfonato [4–10]. Among them, carboxylate acid has attracted particularly attractive due to its versatile coordination fashions and multiple binding sites with metal ions [11,12].

Fluorescent detection is significant for it is highly critical and necessary in the domain of environmental monitoring, separation and biotechnology [13–16]. As a class of luminescent materials, lanthanide CPs, especially Tb-CPs and Eu-CPs have been successfully employed for molecular sensing with quenching process [17–25]. However, much less progress has been achieved in the enhancement effect of Ln-CP sensors to probe organic small molecules [26,27].

Recently, our group embarked upon a study in synthesizing of three transition metal CPs based on 2,8,14,20-tetra-pentyl-6,12,18,23-tetramethoxy-4,10,16,22-tetra-carboxymethoxy-resorcin[4]arene (H<sub>4</sub>L) (Scheme 1) [12]. As an extension of our study, a series of lanthanide CPs, [M(HL)(DMF)(H<sub>2</sub>O)<sub>2</sub>]:3H<sub>2</sub>O (M = Tb 1, Eu 2, Gd 3, Yb 4 and Sm 5) and [M(HL)(DMF)(H<sub>2</sub>O)] (M = Ce 6, Pr 7 and La 8) have been synthesized. We measured the luminescent properties of 1 and 2. Their detection abilities to metal cations, POMs and small organic molecules have been investigated systematically.

## 2. Experimental

*Synthesis of [M(HL)(DMF)(H<sub>2</sub>O)<sub>2</sub>]:3H<sub>2</sub>O (M = Tb 1, Eu 2, Gd 3, Yb 4 and Sm 5) and [M(HL)(DMF)(H<sub>2</sub>O)] (M = Ce 6, Pr 7 and La 8).*

A mixture of TbCl<sub>3</sub>·6H<sub>2</sub>O (22 mg, 0.06 mmol), H<sub>4</sub>L (21 mg, 0.02 mmol), DMF/H<sub>2</sub>O (3/3 mL) was put into a autoclave with Teflon core, kept for 3 days at 90 °C, set a cooling rate of 4 °C h<sup>-1</sup> to rt, and obtained the colorless crystals of 1 by filtration (yield = 35%). Anal. Calcd for C<sub>63</sub>H<sub>94</sub>TbNO<sub>22</sub> (Mr = 1369.35): C, 55.21; H, 6.86; N, 1.02. Found: C, 55.06; H, 6.78; N, 1.14.

The preparations of 2–8 were similar to that of 1 except that 0.06 mmol EuCl<sub>3</sub>·6H<sub>2</sub>O, GdCl<sub>3</sub>·6H<sub>2</sub>O, YdCl<sub>3</sub>·6H<sub>2</sub>O, SmCl<sub>3</sub>·7H<sub>2</sub>O, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, PrCl<sub>3</sub>·7H<sub>2</sub>O and LaCl<sub>3</sub>·7H<sub>2</sub>O were used instead of TbCl<sub>3</sub>·6H<sub>2</sub>O. The crystals of 2–8 were obtained in 38%, 30%, 27%, 29%, 28%, 31% and 30%, respectively. Anal. Calcd for 2 C<sub>63</sub>H<sub>94</sub>EuNO<sub>22</sub> (Mr = 1376.31): C, 54.93; H, 6.83; N, 1.02. Found: C, 54.79; H, 6.98; N, 1.06. Anal. Calcd for 3 C<sub>63</sub>H<sub>94</sub>GdNO<sub>22</sub> (Mr = 1374.64): C, 55.00; H, 6.84; N, 1.02. Found: C, 55.24; H, 6.92; N, 1.07. Anal. Calcd for 4 C<sub>63</sub>H<sub>94</sub>YbNO<sub>22</sub> (Mr = 1390.43): C, 54.37; H, 6.76; N, 1.01. Found: C, 54.49; H, 6.59; N, 1.08. Anal. Calcd for 5 C<sub>63</sub>H<sub>94</sub>SmNO<sub>22</sub> (Mr = 1367.74): C, 55.27; H, 6.87; N, 1.02. Found: C, 55.38; H, 6.73; N, 1.11. Anal. Calcd for 6 C<sub>66</sub>H<sub>93</sub>CeN<sub>2</sub>O<sub>19</sub> (Mr = 1358.54): C, 55.65; H, 6.85; N, 2.06. Found: C, 55.73; H, 6.71; N, 2.11. Anal. Calcd for 7 C<sub>66</sub>H<sub>93</sub>PrN<sub>2</sub>O<sub>19</sub> (Mr = 1359.33): C, 58.26; H, 6.84; N, 2.06. Found: C, 58.39; H, 6.95; N, 2.13. Anal. Calcd for 8 C<sub>66</sub>H<sub>93</sub>LaN<sub>2</sub>O<sub>19</sub> (Mr =

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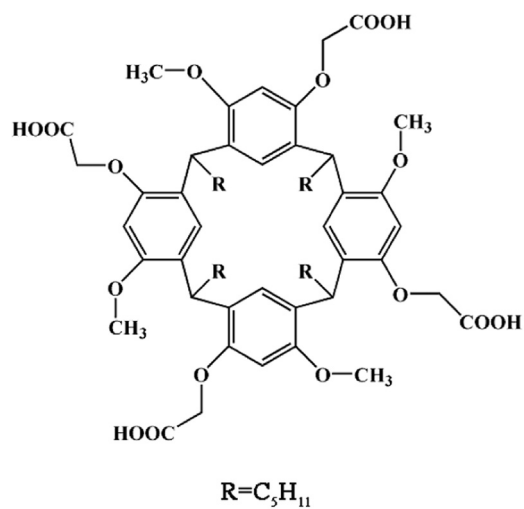
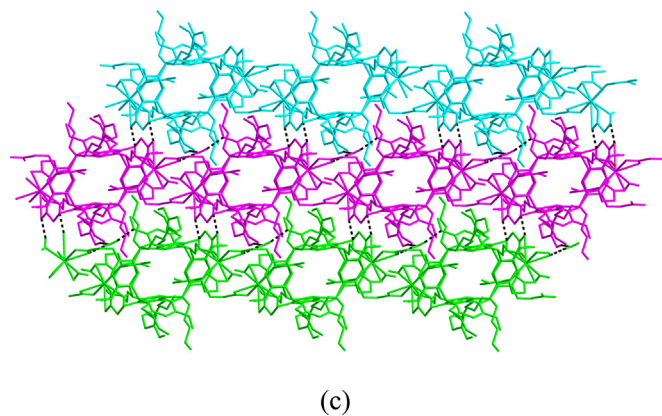
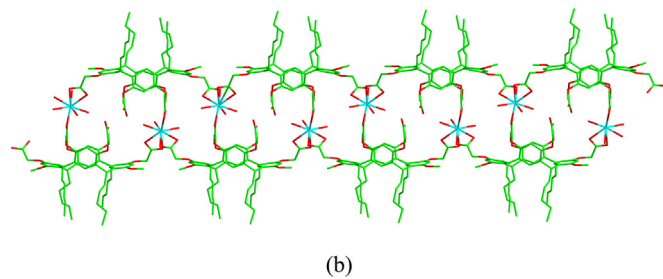
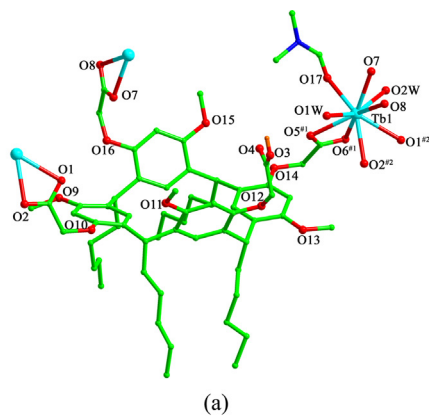
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Scheme 1. The structure of  $H_4L$ .Fig. 1. (a) Coordination sphere of the Tb(III) cation in **1**. (b) The Tb-HL ribbon. (c) The supramolecular layer of **1**.

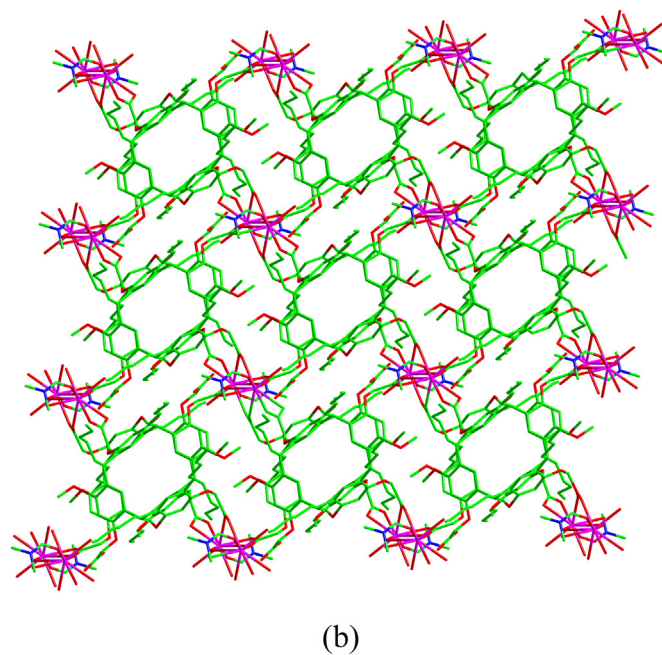
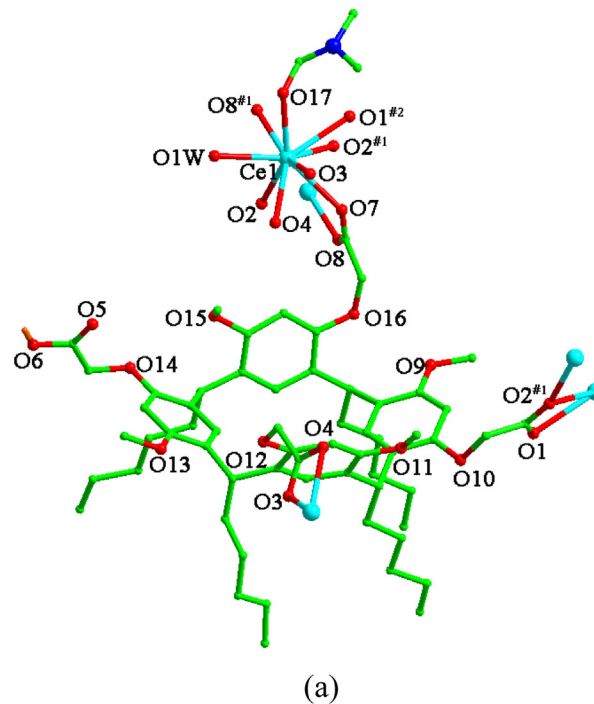
1357.33): C, 58.35; H, 6.85; N, 2.06. Found: C, 58.13; H, 6.79; N, 1.97.

### 3. Results and discussion

#### 3.1. Description of the structures

##### 3.1.1. Crystal structures of 1–5

CPs **1–5** are isostructural, and here we only describe the structure of **1** as a delegate. The independent unit of **1** embraces one Tb(III) ion, one  $HL^{3-}$  anion, one DMF, two coordinated and three free water molecules (Fig. 1a). The Tb(III) is nine-ligated by six O atoms from three  $HL^{3-}$

Fig. 2. (a) Coordination sphere of the Ce(III) cation in **6**. (b) The unique layer structure of **6**.

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