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Electronic Supplementary information

Temperature-induced self-assembly of two kinds Zn(II)-based coordination polymers with different properties in luminescence, sensing and adsorption

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Materials and physical measurements

All materials were purchased commercially and used without further purification. Single-crystal X-ray diffraction data were collected on a Bruker SMART 1000 CCD diffractometer operating at 48 kV and 30 mA by using a graphite-monochromated Mo-K α radiation source (λ = 0.71073 Å). The structures were solved by direct methods using SHELXTL-97¹ and refined by full-matrix least-squares cycles on F^2 . X-ray powder diffraction data were collected on a PAN alytical X'Pert Pro diffractometer operated at 40 kV and 40 mA with Cu K α radiation (λ =1.5406 Å). ICP data were collected on Agilent-725-ES ICP-OES. Fluorescence spectra were measured on an Edinburgh Instruments FSL920 fluorescence spectrometer. UV-vis spectra were measured on an Agilent Technologies Cary 5000 spectrophotometer. IR spectra were recorded on a Burker VERTEX 70 FTIR spectrometer using KBr pellets in the range 4000–400 cm⁻¹.

Synthesis of 4, 4'-(trans-cyclohexane-1,2-diyl)bis(azanediyl))bis(carbonyl))dibenzoic acid (H₂L)



Scheme S1 Synthetic procedure for H₂L.

H₂L (4,4'-(trans-cyclohexane-1,2-diyl)bis(azanediyl))bis(carbonyl))dibenzoic acid) was synthesised according to literature.²⁻³ 0.998 g (5 mmol) methyl 4-(chlorocarbonyl)benzoate were dissolved in 40 mL dried, distilled chloroform at 0 °C. Then, 0.2855 g (2.5 mmol) (\pm)-trans-1,2-diaminocyclohexane was added slowly to above solution with stirring. After about ten minutes, 0.5060 g (5 mmol) triethylamine dissolved in 10 mL dry chloroform were added dropwise to above mixture. Then the reactant were warmed to room temperature followed by white precipitates formed. The mixture was stirred overnight. After cooling to room temperature, solvent were removed under vacuum. The crude production was washed with water, saturated sodium bicarbonate solution and water again recrystallized from methanol giving white powder yield of 1.26 g (57.2 %). ¹H NMR((400 MHz, DMSO- d₆) δ 8.5 (s, 1 H), δ 7.9 (d, 2 H), δ 4.0 (s, 2 H), δ 1.9 (d, 2 H), δ 1.7(d, 2 H), δ 1.5 (d, 2 H), δ 1.3 (m, 2 H) ppm; ¹³C NMR((101MHz, DMSO- d₆) δ 168.71, 167.60, 140.70, 134.70, 131.05, 129.33 ppm (**Fig. S15, S16**).

Compound	1	2
Empirical formula	C ₂₅ H ₂₇ N ₃ O ₇ Zn·3(DMF)	$C_{22}H_{20}N_2O_6Zn$
Formula weight	766.17	473.77
Crystal system	triclinic	monoclinic
Space group	P-1	P2 ₁ /c
<i>a</i> (Å)	9.9976(17)	12.8920(18)
<i>b</i> (Å)	13.561(2)	5.1084(7)
<i>c</i> (Å)	14.593(3)	36.447(7)
α(°)	89.719(4)	90
<i>θ</i> (°)	71.759(4)	109.440
γ(°)	80.909(4)	90
V(ų)	1853.36	2267.33(66)
Ζ	2	4
<i>Dcalc</i> (Mg/m ³)	0.932013	1.38783
R _(int)	0.069	0.094
Data/restraints/parameters	7223/0/468	5223/18/289
Goodness-of-fit on F ²	1.00	1.158
R ₁ , wR ₂ [I>2sigma(I)]	0.069,0.184	0.23, 0.53

Table. S1 Crystal data and structure refinement parameters for 1 and 2.

 $w = 1/[\sigma^2(F_o^2) + (0.078P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$

Ratio of Eu ³⁺ /Tb ³⁺ added to ZnL	Ratio of Eu ³⁺ /Tb ³⁺ determined by ICP in	
	Eu _x Tb _(1-x) @ZnL	
0.01:0.99	0.01:0.99	
0.02:0.98	0.02:0.98	
0.05:0.95	0.049:0.95	
0.1:0.9	0.1:0.9	
0.15:0.85	0.153:0.847	

Table. **S2** ICP data for **Eu**_x**Tb**_(1-x)**@ZnL** materials.

Table **S3** ICP data for Zn²⁺ content in **Eu³⁺@ZnL** and **ZnL** supernate.

	Eu ³⁺ @ZnL (supernate)	ZnL (supernate)
Zn ²⁺ mg/L	257.17 mg/L	7.749 mg/L



Fig. S2 Solid-state emission spectra of $Nd^{3+}@ZnL$ at room temperature (λ_{ex} =577nm).



Fig. S3 a) Emission spectra of $Eu_x Tb_{(1-x)} @ZnL$ (X = 0, 0.01, 0.02, 0.05, 0.1, 0.15, 1) at solid-state at room temperature (λ_{ex} = 365 nm). b) CIE chromaticity diagram of $Eu_x Tb_{(1-x)} @ZnL$ (λ_{ex} = 365 nm).



Fig. S4 a) Emission spectra of $Eu_{0.02}Tb_{0.98}$ @ZnL at room temperature excited at 355 - 310 nm (λ_{ex} = 365 nm). b) CIE chromaticity diagram of $Eu_{0.02}Tb_{0.98}$ @ZnL at 355 - 310 nm.



Fig. S5 PXRD patterns of MB@ZnL



Acetonitrile EtOH THF Relative Intensity / a.u. Chloroform MeOH Ph-Me DMF Acetone Dichloro CP 2 Simulated 2Theta ³⁰ 20 10 40 50

Fig. S6 PXRD patterns of Eu_xTb_(1-x)@ZnL material.

Fig. S7 PXRD patterns of Tb³⁺@ZnL in different solvents.





Fig. S10 a) UV-vis spectra of acetone in n-hexane. b) Excitation spectra of Tb³⁺@ZnL at room temperature (λ_{em} = 544 nm).



Scheme S2 The structures of dyes.



Fig. S11 a) UV-vis spectra of MB calibration solutions. b) Working curve of MB calibration solutions.



Fig. S12 UV-Vis spectra of dyes adsorption (R6g and MB). The Insert: color change of the mixed dye solutions before (left) and after (right).



Fig. S13 UV-Vis spectra of dyes adsorption (AR and MB). The Insert: color change of the mixed dye solutions before (left) and after (right).



Fig. S14 UV-Vis spectra of dyes adsorption (MO and MB). The Insert: color change of the mixed dye solutions before (left) and after (right).



Fig. S15 ¹H NMR spectrum of H₂L in DMSO-d₆.



Fig. S16 ¹³C NMR spectrum of H₂L in DMSO-d₆

References

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