Electronic Supplementary Information

A luminescent terbium coordination polymer for sensing methanol

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Luminescent Sensing Measurements

The finely ground powder of $\{[Tb(aip)(H_2O)_5]\cdot 0.5(bdc)\cdot 3H_2O\}_n$ (3 mg) was immersed in organic solvent (4 mL) and the mixture was well stirred for one hour at room temperature. The steady state luminescent emission of each sample was measured after three days of aging and stirred vigorously before testing.

Table S1 Crystal data and structure refinement parameters for complex **1**

Complex	**1**
Empirical formula	$C_{12}H_{23}EuNO_{14}$
Formula weight	557.27
Crystal system	Monoclinic
Space group	P 21/c
a / Å	10.2389(7)
b / Å	10.3829(6)
c / Å	17.8300(6)
α (°)	90
β (°)	97.856(5)
γ (°)	90
V /Å^3	1877.71(18)
Z	4
Calculated density / mg·m^{-3}	1.971
Absorption coefficient/ mm^{-1}	3.414
Crystal size / mm	0.30 x 0.20 x 0.05
Reflections collected / unique	9623 / 4327
GOF	1.050
R_1[a] / wR_2[b][$I > 2\sigma(I)$]	0.0596/0.1365
R_1, wR_2 (all data)	0.0869/0.1613

[a] $R_1 = \Sigma||F_o| - |F_c||/|F_o|$. [b] $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

Table S2 Selected bond lengths (Å) and angles (°) for **1**

Eu(1)-O(3w)	2.361(6)	Eu(1)-O(2w)	2.396(6)
Eu(1)-O(4)#1	2.427(6)	Eu(1)-O(5w)	2.440(6)
Eu(1)-O(1w)	2.462(6)	Eu(1)-O(2)	2.470(6)
Eu(1)-O(1)	2.510(6)	Eu(1)-O(4w)	2.526(6)
Eu(1)-O(3)#1	2.546(6)	O(3)-Eu(1)#2	2.546(6)
O(3w)-Eu(1)-O(2w)	77.7(2)	O(3w)-Eu(1)-O(4)#1	140.6(2)
O(2w)-Eu(1)-O(4)#1	140.9(2)	O(3w)-Eu(1)-O(5w)	138.0(2)
O(2w)-Eu(1)-O(5w)	69.5(2)	O(4)#1-Eu(1)-O(5w)	73.0(2)
O(3w)-Eu(1)-O(1w)	76.0(2)	O(2w)-Eu(1)-O(1w)	74.5(2)
O(4)#1-Eu(1)-O(1w)	103.3(2)	O(5w)-Eu(1)-O(1w)	70.6(2)
O(3w)-Eu(1)-O(2)	126.8(2)	O(2w)-Eu(1)-O(2)	82.2(2)
O(4)#1-Eu(1)-O(2)	77.3(2)	O(5w)-Eu(1)-O(2)	74.4(2)
O(1w)-Eu(1)-O(2)	143.0(2)	O(3w)-Eu(1)-O(1)	117.4(2)
O(2w)-Eu(1)-O(1)	71.8(2)	O(4)#1-Eu(1)-O(1)	78.74(18)
O(5w)-Eu(1)-O(1)	116.7(2)	O(1w)-Eu(1)-O(1)	139.1(2)
O(2)-Eu(1)-O(1)	52.2(2)	O(3w)-Eu(1)-O(4w)	79.0(2)
O(2w)-Eu(1)-O(4w)	136.8(2)	O(4)#1-Eu(1)-O(4w)	73.4(2)
O(5w)-Eu(1)-O(4w)	143.0(2)	O(1w)-Eu(1)-O(4w)	132.9(2)
O(2)-Eu(1)-O(4w)	83.4(2)	O(1)-Eu(1)-O(4w)	67.2(2)
O(3w)-Eu(1)-O(3)#1	92.0(2)	O(2w)-Eu(1)-O(3)#1	145.9(2)
O(4)#1-Eu(1)-O(3)#1	52.56(19)	O(5w)-Eu(1)-O(3)#1	100.5(2)
O(1)-Eu(1)-O(3)#1	137.1(2)	O(4w)-Eu(1)-O(3)#1	70.3(2)

[a] Symmetry codes for 2: #1 x,-y+1/2,z-1/2; #2 x,-y+1/2,z+1/2; #3 -x,-y,-z.

Table S3 Hydrogen bonding geometry (Å and deg.) for **1**

D–H	*d*(D–H)	*d*(H…A)	d(D…A)	∠D–H…A	A(Symmetry Codes)
O(1w)–H(1w1)	0.84	2.43	2.806(8)	108	O(3) [1–*x, 1/2+y, 1/2–z*]
O(1w)–H(1w2)	0.84	2.10	2.848(11)	149	O(7w)
O(2w)–H(2w1)	0.84	2.10	2.804(11)	141	O(6w)
O(2w)–H(2w2)	0.84	2.56	3.172(9)	130	O(2) [1–*x, 1/2+y, 1/2–z*]
O(3w)–H(3w1)	0.84	2.22	2.725(10)	118	N(1) [*x, 3/2–y, -1/2+z*]
O(3w)–H(3w2)	0.84	1.94	2.767(9)	166	O(2) [1-*x, 1/2+y, 1/2–z*]
O(4w)–H(4w1)	0.84	2.56	2.989(10)	113	O(5) [1+*x, y, z*]
O(4w)–H(4w2)	0.84	2.30	2.972(10)	137	O(6) [1–*x, 1/2+y, 1/2–z*]
O(5w)–H(5w1)	0.84	2.09	2.852(9)	150	O(8w) [1-*x, 1-y, 1-z*]
O(5w)–H(5w2)	0.84	1.93	2.686(9)	148	O(1) [1–*x, -1/2+y, 1/2–z*]
O(6w)–H(6w1)	0.84	1.95	2.782(11)	172	O(6) [–*x, 1/2+y, 1/2–z*]
N(1) –H(12)	0.88	2.20	2.995(10)	151	O(8w)
O(6w)–H(6w2)	0.84	2.08	2.835(12)	149	O(7w)
O(8w)–H(8w1)	0.84	2.00	2.777(10)	153	O(6) [1+*x, 1/2-y, 1/2+z*]
O(8w)–H(8w2)	0.84	2.23	2.844(10)	130	O(5) [1-*x, 1-y, 1-z*]

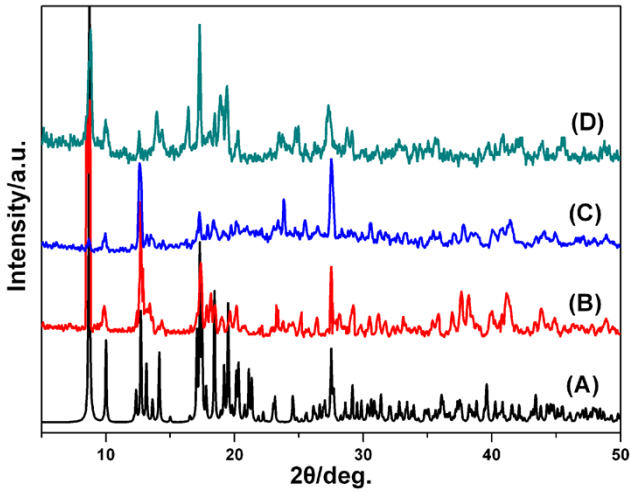

Fig. S1 Powder X-ray diffraction patterns of simulated **1** (A), as-synthesized **1** (B), as-synthesized **2** (C) and the solid sample of **2** obtained after immersion in acetonitrile and 7% methanol (D).

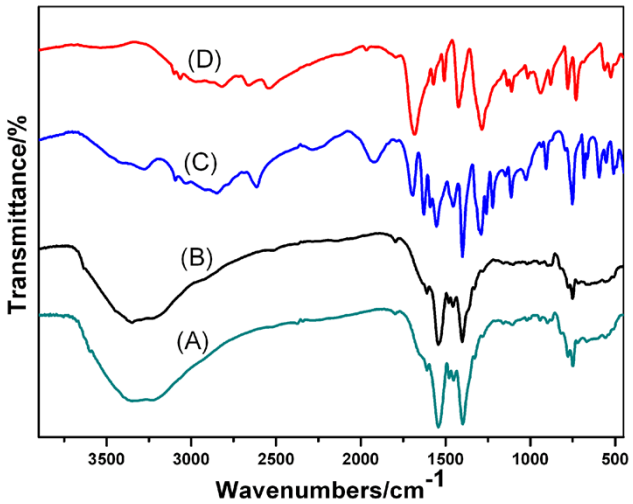

Fig. S2 FT-IR spectra of complex **1** (A), complex **2** (B), H_2aip (C) and H_2bdc (D).

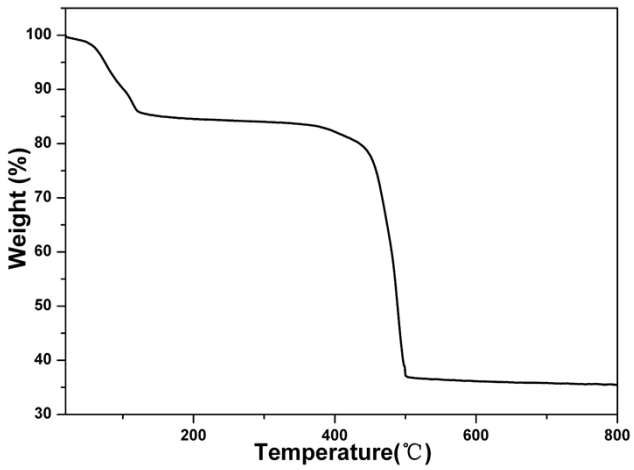

Fig. S3 TGA curves of **2** in air atmosphere.

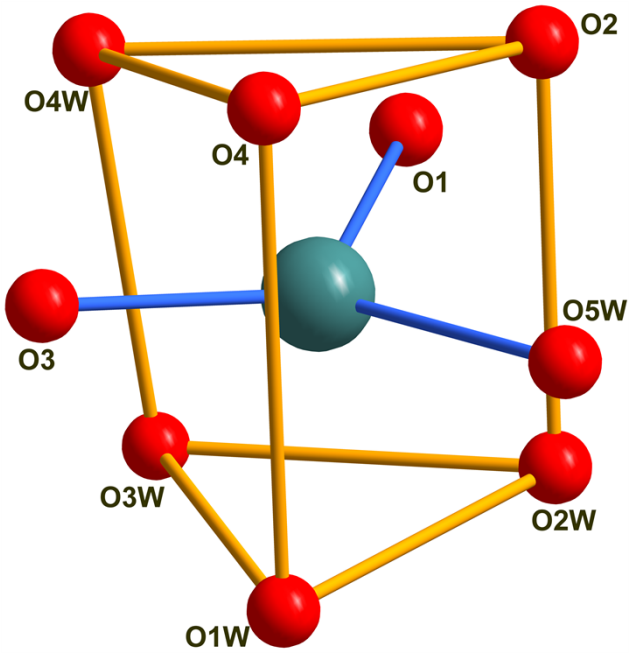

Fig. S4 The distorted tricapped trigonal prism coordination polyhedron of Eu^{3+} in **1**.

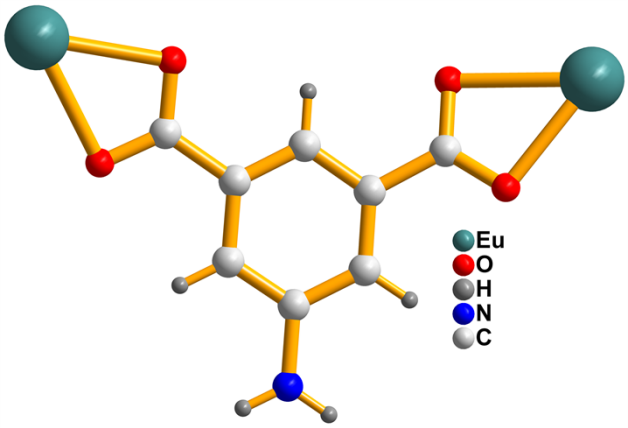

Fig. S5 Coordination modes of ligand in **1**.

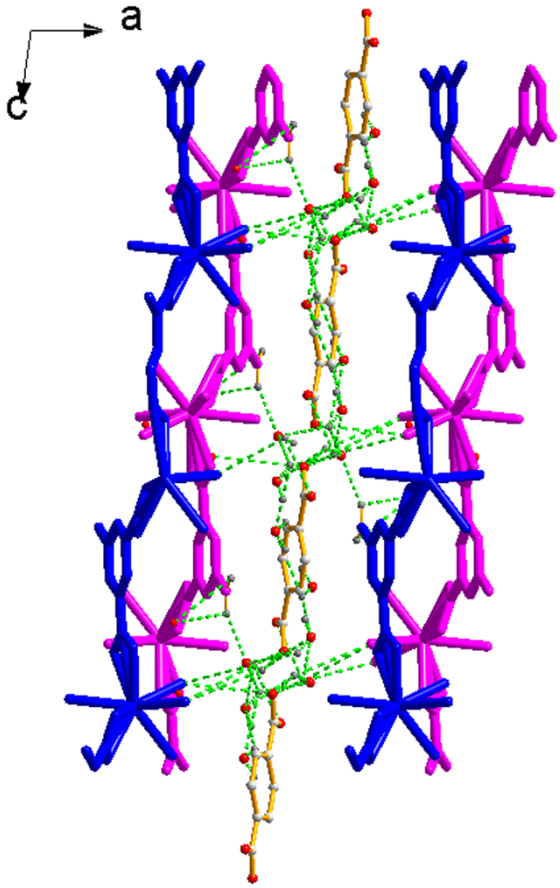

Fig. S6 Hydrogen bonds between two double-chain motifs viewed in the *ac* plane. Hydrogen bonds are shown as a green dashed line.

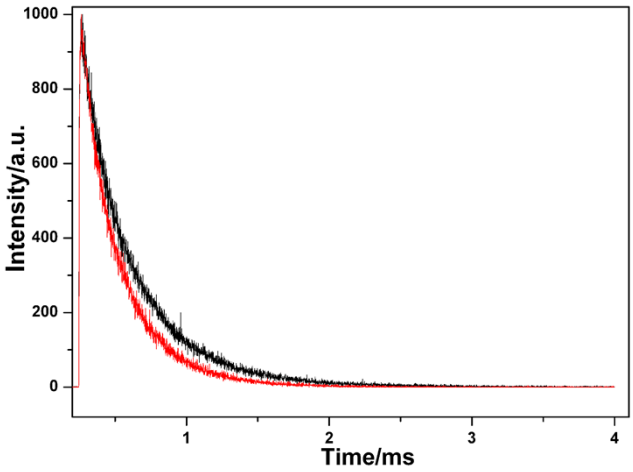

Fig. S7 Luminescence decay profiles of **2** in solid state (black) and in acetonitrile (red).

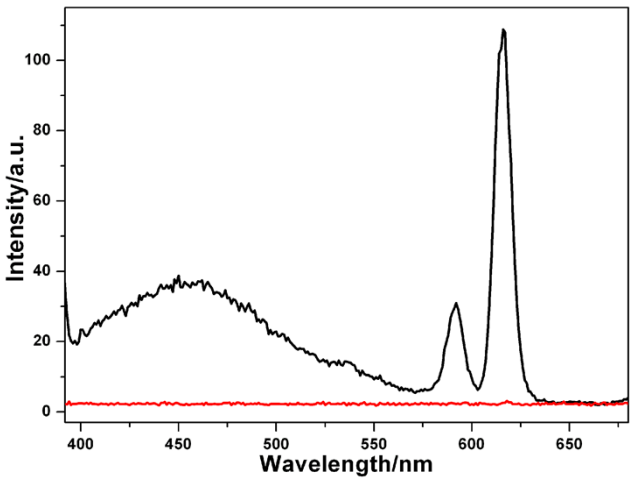

Fig. S8 Emission spectra of **1**, excited at 358 nm. The excitation and emission slits were 3/3 nm (red) and 10/10 nm (black), respectively.

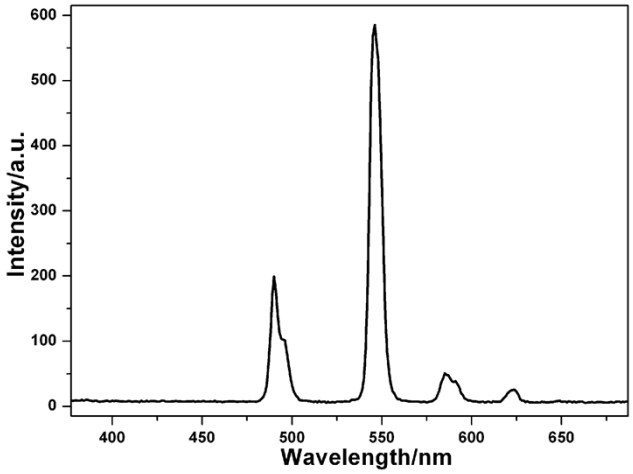

Fig. S9 Emission spectrum of **2** in 375-685 nm, excited at 354 nm. The excitation and emission slits were 3/3 nm.

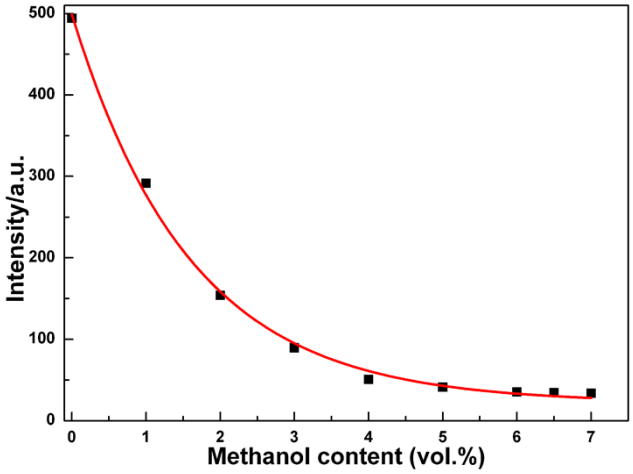

Fig. S10 The emission intensity of **2**/ acetonitrile emulsion as a function of methanol content (excited at 341 nm).

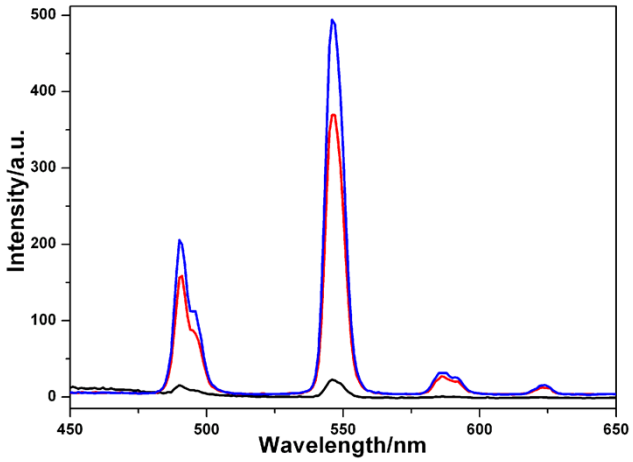

Fig. S11 The PL spectra of **2**/acetonitrile emulsion. The blue line represents the emission in pure acetonitrile. The red line represents the emission in the presence of many other organics including ethanol, 1-propanol, 2-propanol, 1-butanol, acetone, chloroform, ethylacetate and THF (7.0 vol%, respectively). The black line represents the emission in the presence of many other organics and methanol (7.0 vol%, respectively).

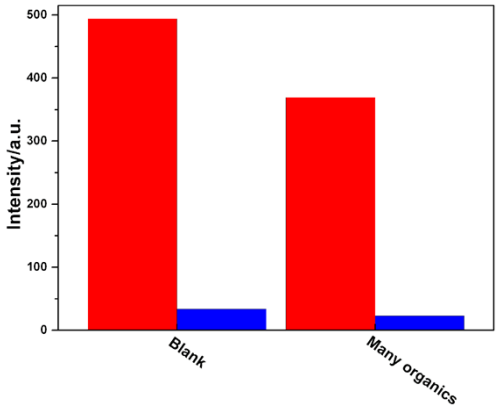

Fig. S12 The $^5D_4 \rightarrow {}^7F_5$ transition intensities of **2** dispersed into acetonitrile on the addition of many organics (7.0 vol%, respectively, red) and subsequent addition of methanol (7.0 vol%, blue) when excited at 341 nm.