Supporting Information

A Mixed-Valence Lanthanide Metal-Organic Framework Templated by 2,2'-Bipyridine Formed *In Situ* Reaction: Synthesis, Structure, and Luminescent Properties

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1. Synthesis of $\{(bpy)_{0.5}[Dy_3(ip)_4(phen)_4(H_2O)]\cdot 2H_2O\}_n$ (1)

All chemicals for the synthesis were commercially available and used without further purification. Elemental analyses(C, H and N) were performed on a Vario EL elemental analyzer.

A mixture of $Dy(NO_3)_3\cdot 6H_2O$(0.5mmol, 288mg), isophthalic acid(0.5 mmol, 83 mg), 1,10-phenanthroline (0.8 mmol, 144 mg), and distilled water(15 ml, 825 mmol), was stirred at room temperature for 20 min, and then was transferred into a 25 mL Teflon-lined stainless steel vessel. The reaction system was adjusted to pH = 6~7 using NaOH aqueous solution. The reaction mixture was heated at 160℃ for 72h under autogenous pressure. It was then cooled to room temperature at a rate of $5℃\cdot h^{-1}$. Light green block crystals were obtained and washed with distilled water and ethanol (Yield: 195 mg, 78% based on isophthalic acid). Elemental analysis of the air-dried sample (%) calcd. for $C_{85}H_{58}Dy_3N_9O_{19}$: C 51.12, H 2.93, N 6.31; found: C 51.05, H 2.84, N 6.27. IR (KBr pellet, cm^{-1}): 3406(br), 1630(s), 1547(s), 1393(s), 1150(w), 1094(w), 937(w), 889(w), 851(m), 816(w), 722(m), 652(w), 563(w), 430(w).

2. Single-crystal X-ray structure analysis

Single-crystal X-ray diffraction data were collected on a Rigaku RAXIS-RAPID diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and a CCD detector at 293 K. The primitive structure was solved by direct methods using the program SHELXS 97.[1] The difference Fourier maps based on these atomic positions yield the other non-hydrogen atoms. The final structure was refined by the full-matrix least-squares method on F^2 using the program SHELXL 97.[1] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbon atoms were generated geometrically.

3. The coordination environments of Dy atoms

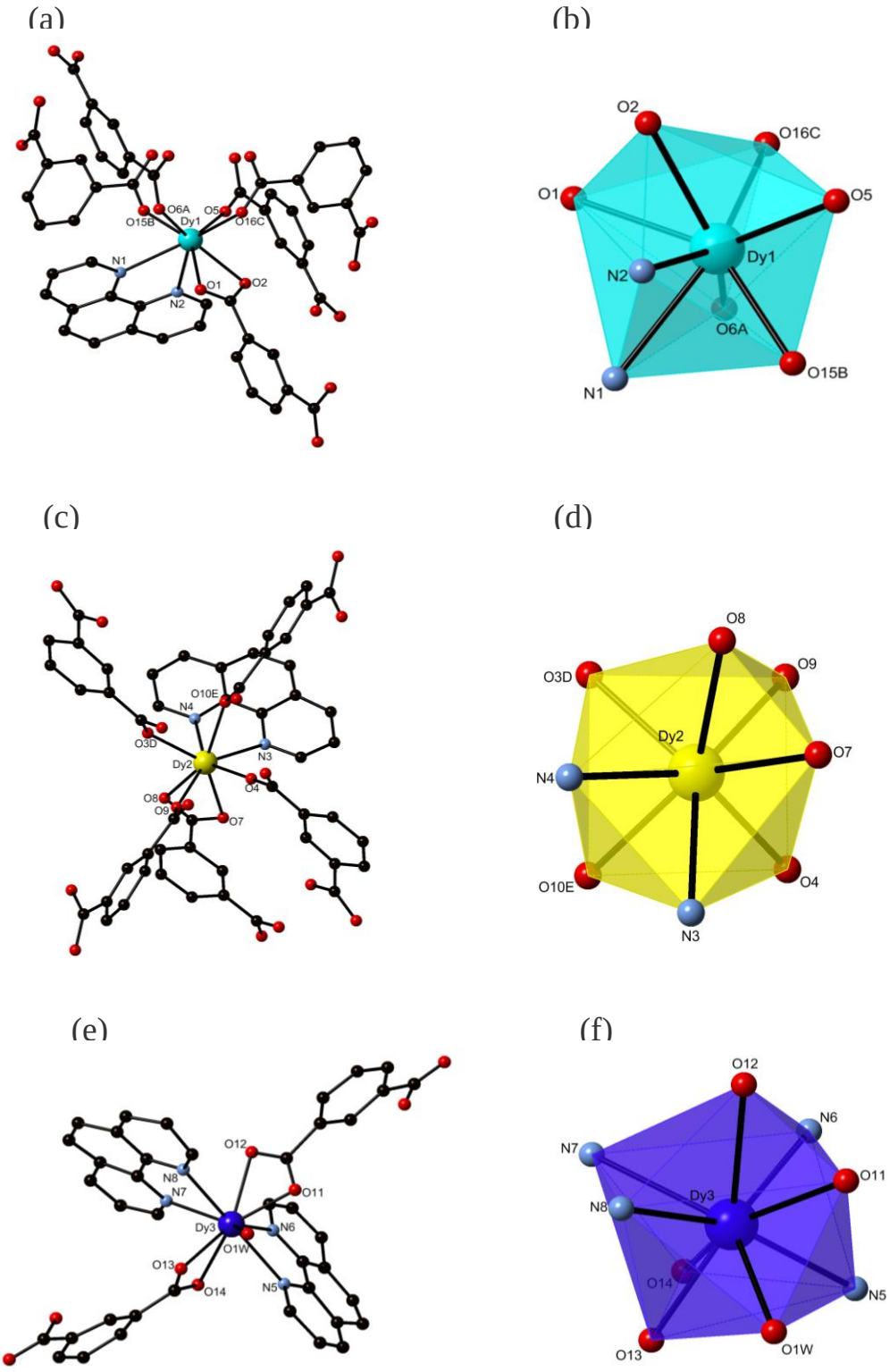


Figure S1. The coordination environments of Dy1 (a and b), Dy2 (c and d) and Dy3 (e and f) in **1**. (a, c and e) The ball-stick representation. (b, d

and f) The polyhedral representation. Atoms having “A”, “B”, “C”, “D” and “E” in their labels are symmetry-generated. Symmetry code: A: -x+2, -y+1, -z; B: -x+2, -y, -z; C: x, y+1, z; D: -x+1, -y+1, -z+1, E : -x+1, -y+1, -z+1(D=E). The colors of red, light blue, black, cyan, yellow and blue correspond to oxygen, nitrogen, carbon, Dy1, Dy2 and Dy3 atoms, respectively. Hydrogen atoms are omitted for clarity.

4. The coordination modes of isophthalate ligands in 1

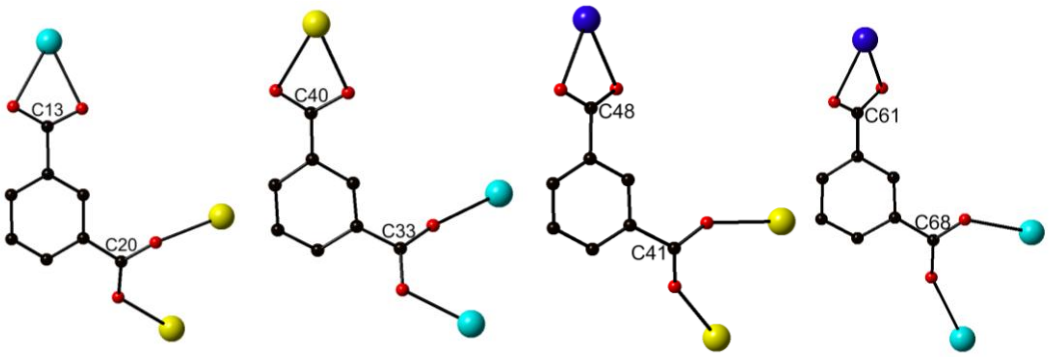


Figure S2. The coordination modes of isophthalate ligands in **1**. The colors of red, light blue, black, cyan, yellow and blue correspond to oxygen, nitrogen, carbon, Dy1, Dy2 and Dy3 atoms, respectively. Hydrogen atoms are omitted for clarity.

5. The X-ray photoelectron spectroscopy (XPS)

The XPS spectrum was obtained using a Kratos AXIS Ultra DLD XPS spectrometer using monochromated Al Kα X-rays. Figure S3 presents the XPS spectrum for Dy $4d_{5/2}$ of **1**. The peaks at 153.3eV and 156.7eV are attributed to Dy^{2+} and Dy^{3+}, respectively.

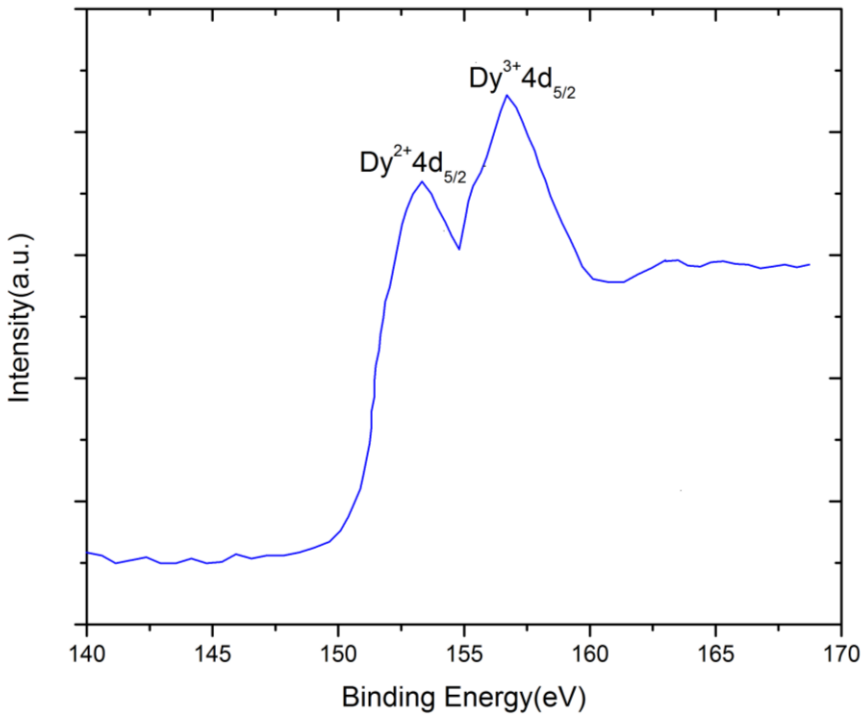
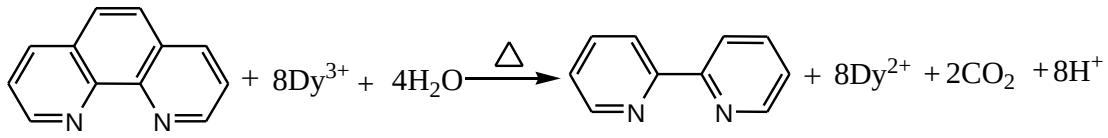
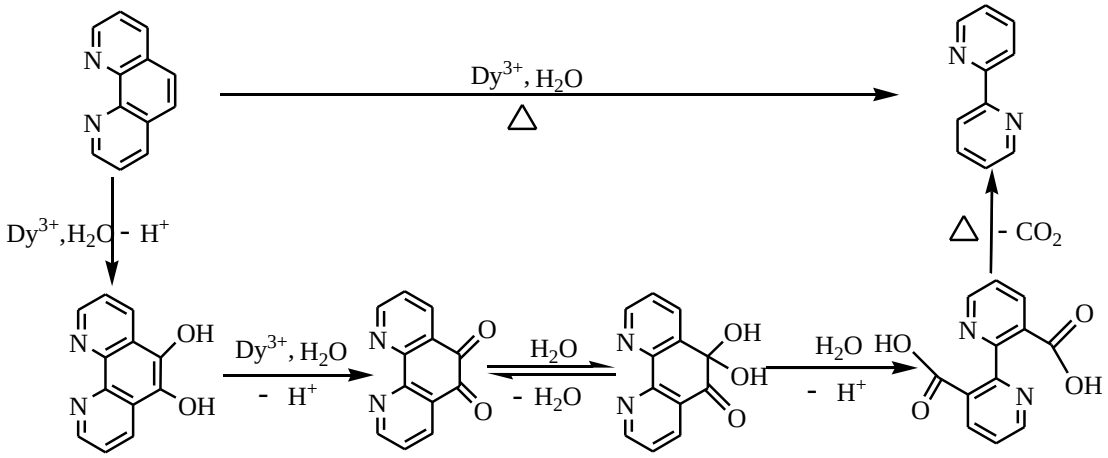


Figure S3. The XPS spectrum for Dy $4d_{5/2}$ of **1**.

6. The possible reaction and mechanism

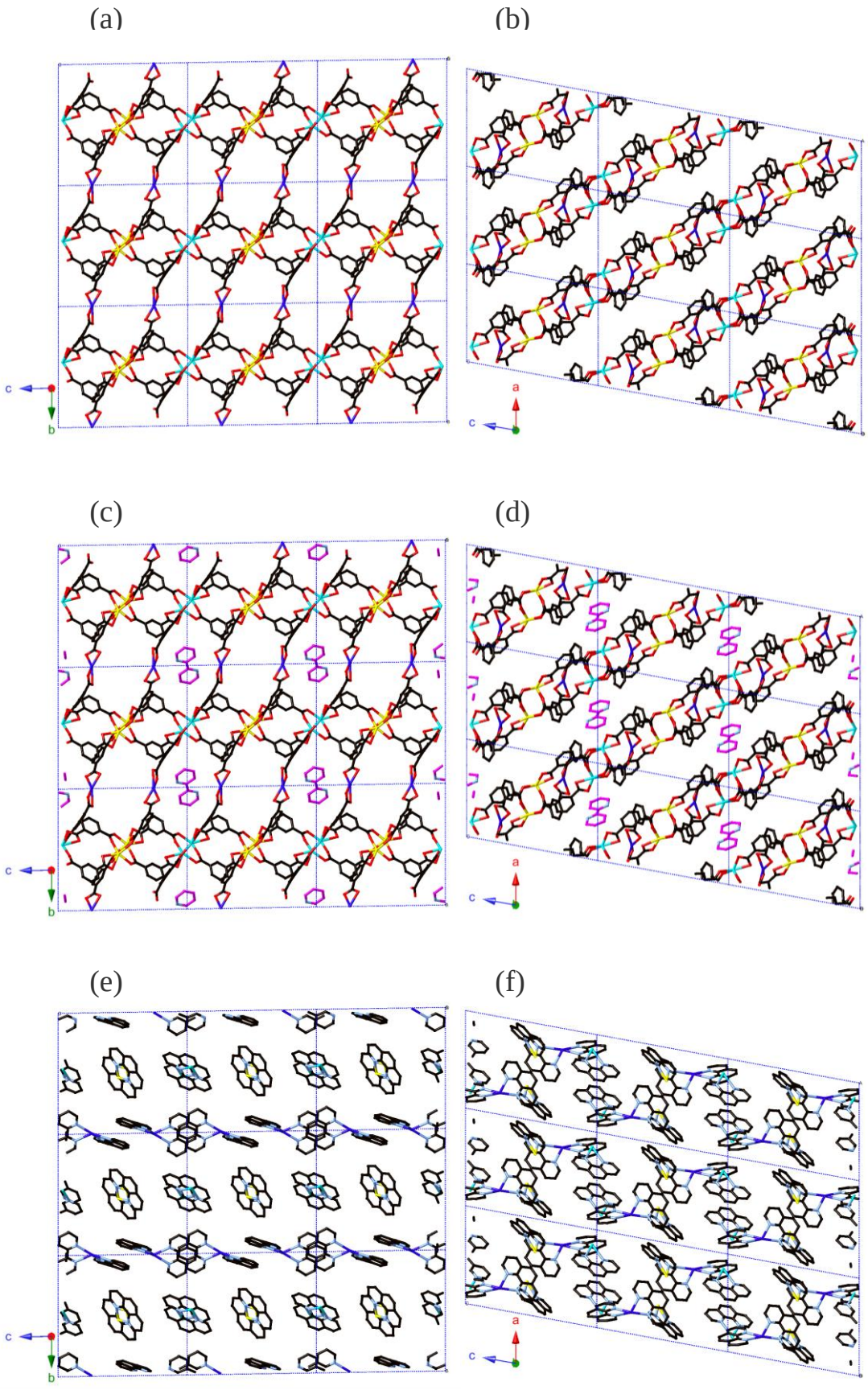


Scheme S1. The possible reaction of 1,10-phenanthroline and Dy^{3+}.



Scheme S2. Schematic representation of the possible transformation mechanism of 1,10-phenanthroline to 2,2′-bipyridine.

7. **The construction of 1**



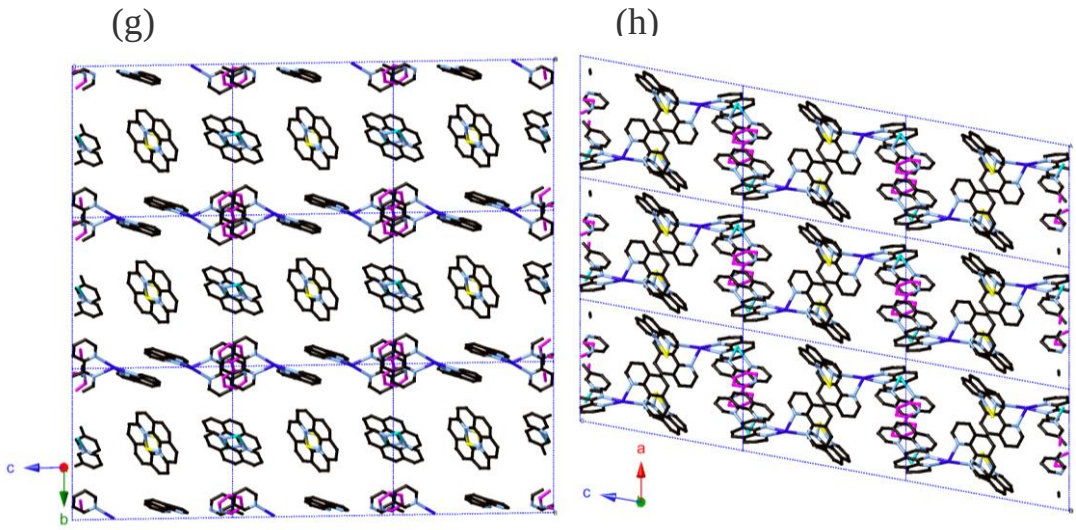


Figure S4. The diagrams showing the construction of **1**. (a, b) The layers structure constructed by Dy(Ⅱ, Ⅲ) and isophthalate ligands. Other ligands and guest molecules are omitted. (c, d) The diagrams showing the guest-template 2,2′-bipyridine molecules are situated in the spaces between layers. 1,10-phenanthroline ligands and water molecules are omitted. (e, f) 1,10-phenanthroline molecules are lined along the a, b and *c* axis, chelating Dy(Ⅱ, Ⅲ) ions. Other ligands and guest molecules are omitted. (g, h) The diagrams showing the guest-template 2,2′-bipyridine molecules are located among the 1,10-phenanthroline ligands. Isophthalate ligands and water molecules are omitted. (a, c, e, g) The views along the a-axis. (b, d, f, h) The views along the *b*-axis. The colors of red, light blue, black (or magenta), cyan, yellow and blue correspond to oxygen, nitrogen, carbon, Dy1, Dy2 and Dy3 atoms, respectively. Hydrogen atoms are omitted for clarity.

8. The π-π stacking interactions in 1

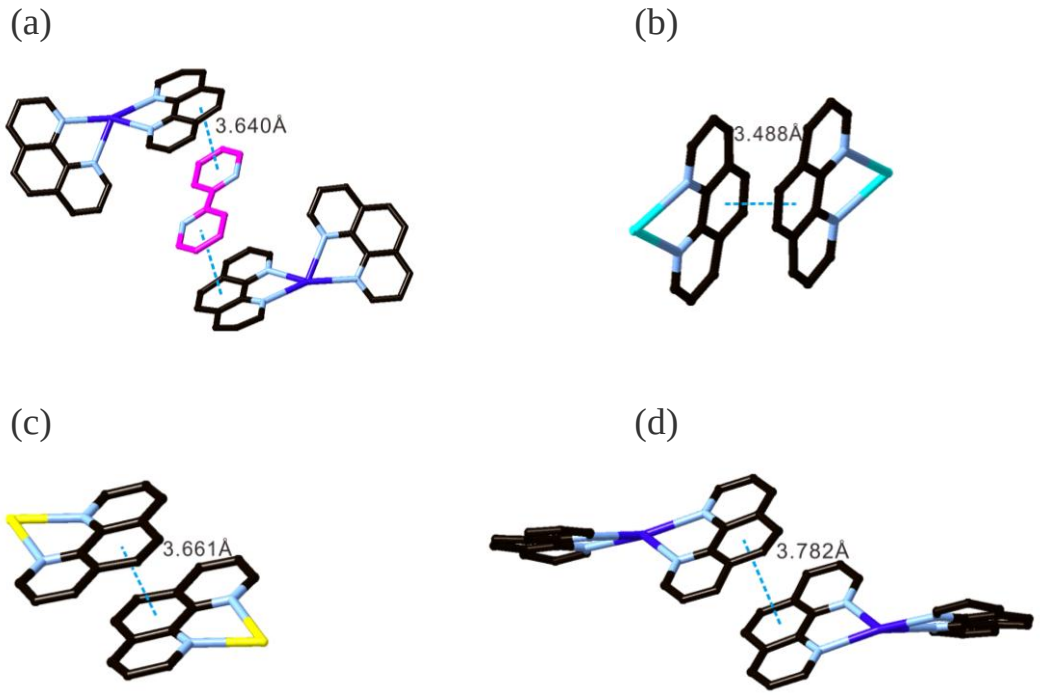


Figure S5. The π-π stacking interactions in **1**. (a) The π-π stacking interactions between a guest-template 2,2′-bipyridine molecule and two 1,10-phenanthroline molecules. The angle between two benzene rings is 12.78°. (b) The π-π stacking interactions between two 1,10-phenanthroline molecules coordinated to Dy1. (c) The π-π stacking interactions between two 1,10-phenanthroline molecules coordinated to Dy2. (d) The π-π stacking interactions between two 1,10-phenanthroline molecules coordinated to Dy3. (b, c, d) Each pair of coordinated 1,10-phenanthroline molecules are parallel. The colors of red, light blue, black (or magenta), cyan, yellow and blue correspond to oxygen, nitrogen, carbon, Dy1, Dy2 and Dy3 atoms, respectively. Hydrogen atoms are omitted for clarity.

9. The thermogravimetric(TG) curve of the framework 1

The thermogravimetric(TG) curve of the framework **1** was measured using a SDT Q600 thermogravimetric analyzer.

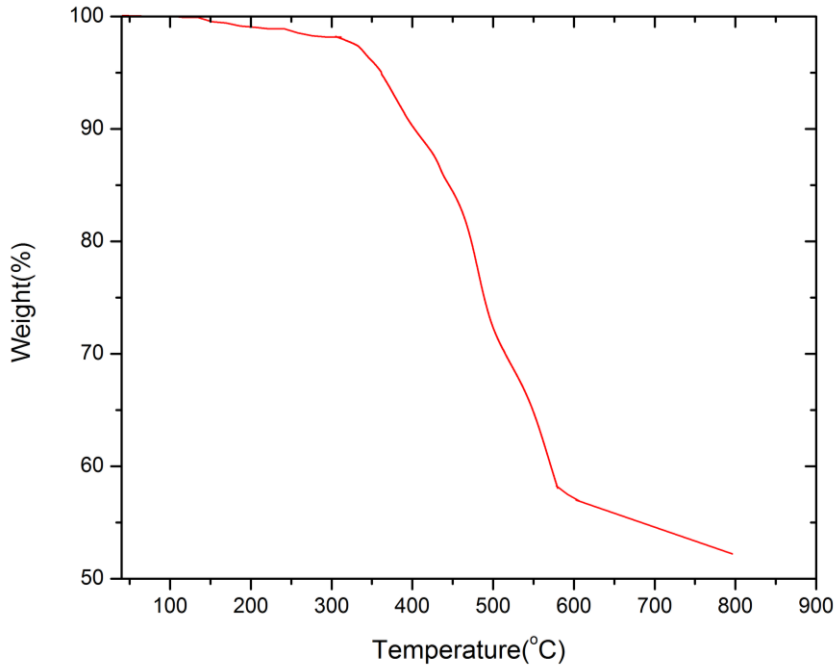


Figure S6. The TG curve of **1** under N_2 atmosphere (10 ºC/min).

10. The optical properties of the framework 1

The absorption spectrum of the framework **1** was measured using a Hitachi U-3010 UV-Vis spectrophotometer. The luminescence spectra of the framework **1** were recorded on a Hitachi F-4500 fluorescence spectrophotometer.

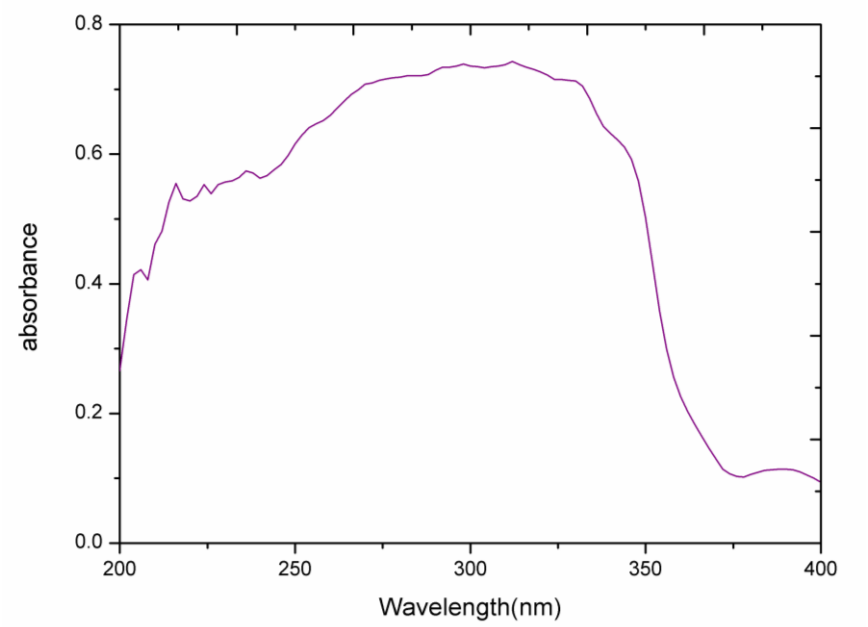


Figure S7. The absorption spectrum of the framework **1** in the solid state at room temperature.

11. IR spectroscopy

The FT-IR spectrum was recorded on a BRUKER TENSOR 27 infrared spectrometer in 4000–400 cm^{-1} region using a KBr pellet. Figure S8 presents the IR spectrum of **1**. The IR spectrum of **1** shows the asymmetric stretching vibration for the COO^- groups at 1630.37cm^{-1} and the symmetric stretching vibration at 1393.44cm^{-1}.

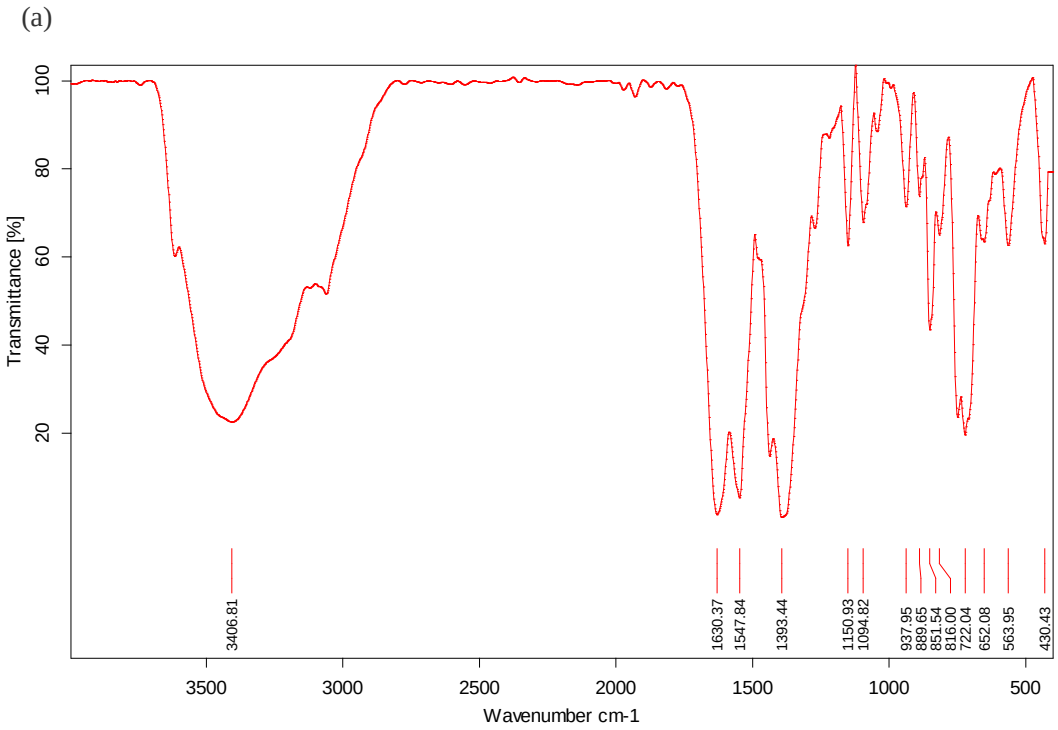


Figure S8. The FT-IR spectrum of **1**.

12. Crystallographic data and structural refinements for 1

Table S1. Crystallographic data and structural refinements for **1**

Compound	**1**
Chemical formula	$C_{85}H_{58}Dy_3N_9O_{19}$
Formula Mass	1996.90
Crystal system	Triclinic
a/Å	13.576(3)
b/Å	17.145(3)
c/Å	18.090(4)
α/°	86.72(3)
β/°	79.10(3)
γ/°	77.04(3)
Unit cell volume/Å^3	4028.8(14)
Temperature/K	293(2)
Space group	$P\bar{1}$
No. of formula units per unit cell, *Z*	2
Absorption coefficient, μ/mm^{-1}	2.830
No. of reflections measured	30959
No. of independent reflections	18206
R_{int}	0.0455
Final R_1 values ($I > 2\sigma(I)$)	0.0803
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1323
Final R_1 values (all data)	0.0842
Final $wR(F^2)$ values (all data)	0.1350
Goodness of fit on F^2	1.078

13. Selected bond lengths (Å) for 1

Table S2. Selected bond lengths (Å) for **1**[a]

Dy(1)-O(15)#1	2.284(12)	Dy(1)-O(5)	2.301(11)
Dy(1)-O(6)#2	2.326(12)	Dy(1)-O(16)#3	2.344(12)
Dy(1)-O(1)	2.422(13)	Dy(1)-O(2)	2.435(13)
Dy(1)-N(2)	2.550(14)	Dy(1)-N(1)	2.643(16)
Dy(2)-O(4)	2.271(10)	Dy(2)-O(9)	2.283(12)
Dy(2)-O(3)#4	2.300(13)	Dy(2)-O(10)#4	2.331(11)
Dy(2)-O(7)	2.370(13)	Dy(2)-O(8)	2.488(14)
Dy(2)-N(4)	2.519(14)	Dy(2)-N(3)	2.575(15)
Dy(3)-O(13)	2.318(14)	Dy(3)-O(11)	2.342(14)
Dy(3)-O(1W)	2.433(18)	Dy(3)-O(14)	2.486(12)
Dy(3)-N(6)	2.499(16)	Dy(3)-O(12)	2.520(15)
Dy(3)-N(5)	2.527(17)	Dy(3)-N(7)	2.558(19)
Dy(3)-N(8)	2.569(16)		

[a]Symmetry transformations used to generate equivalent atoms:

#1 -x+2, -y, -z #2 -x+2, -y+1, -z #3 x, y+1, z

#4 -x+1, -y+1, -z+1

14. The hydrogen bonds for the framework 1

Table S3. The hydrogen bonds for the framework **1** [Å and deg.]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1W-H1WA...O11	0.85	2.11	2.71(2)	127.0
O1W-H1WA...O2W	0.85	2.14	2.86(3)	142.3
O1W-H1WB...O13	0.84	2.29	2.78(2)	117.8
O1W-H1WB...N8	0.84	2.37	3.14(3)	153.6
O2W-H2WA...O11	0.84	2.17	2.83(2)	135.2
O2W-H2WB...O8	0.84	2.22	2.79(2)	125.5

15. Selected angles [deg.] for 1

Table S4. Selected angles [deg.] for **1**[a]

O(15)#1-Dy(1)-O(5)	75.0(5)	O(15)#1-Dy(1)-O(6)#2	83.2(5)
O(5)-Dy(1)-O(6)#2	124.9(5)	O(15)#1-Dy(1)-O(16)#3	127.2(5)
O(5)-Dy(1)-O(16)#3	79.2(5)	O(6)#2-Dy(1)-O(16)#3	75.1(5)
O(15)#1-Dy(1)-O(1)	143.5(5)	O(5)-Dy(1)-O(1)	137.3(4)
O(6)#2-Dy(1)-O(1)	86.3(4)	O(16)#3-Dy(1)-O(1)	82.9(4)
O(15)#1-Dy(1)-O(2)	144.5(5)	O(5)-Dy(1)-O(2)	83.3(4)
O(6)#2-Dy(1)-O(2)	132.2(5)	O(16)#3-Dy(1)-O(2)	74.0(5)
O(1)-Dy(1)-O(2)	54.5(4)	O(15)#1-Dy(1)-N(2)	82.1(5)
O(5)-Dy(1)-N(2)	87.0(5)	O(6)#2-Dy(1)-N(2)	139.4(5)
O(16)#3-Dy(1)-N(2)	141.6(5)	O(1)-Dy(1)-N(2)	83.5(5)
O(2)-Dy(1)-N(2)	68.9(5)	O(15)#1-Dy(1)-N(1)	66.9(5)
O(5)-Dy(1)-N(1)	132.9(4)	O(6)#2-Dy(1)-N(1)	77.5(5)
O(16)#3-Dy(1)-N(1)	146.7(4)	O(1)-Dy(1)-N(1)	76.8(4)
O(2)-Dy(1)-N(1)	112.9(5)	N(2)-Dy(1)-N(1)	61.9(4)
O(4)-Dy(2)-O(9)	75.4(4)	O(4)-Dy(2)-O(3)#4	125.2(4)
O(9)-Dy(2)-O(3)#4	78.4(5)	O(4)-Dy(2)-O(10)#4	80.0(5)
O(9)-Dy(2)-O(10)#4	125.9(4)	O(3)#4-Dy(2)-O(10)#4	77.9(5)
O(4)-Dy(2)-O(7)	87.5(5)	O(9)-Dy(2)-O(7)	81.7(5)
O(3)#4-Dy(2)-O(7)	134.6(4)	O(10)#4-Dy(2)-O(7)	144.4(4)
O(4)-Dy(2)-O(8)	135.0(4)	O(9)-Dy(2)-O(8)	77.7(5)
O(3)#4-Dy(2)-O(8)	82.8(4)	O(10)#4-Dy(2)-O(8)	144.6(4)
O(7)-Dy(2)-O(8)	53.1(4)	O(4)-Dy(2)-N(4)	140.4(4)
O(9)-Dy(2)-N(4)	144.2(4)	O(3)#4-Dy(2)-N(4)	77.5(5)
O(10)#4-Dy(2)-N(4)	73.7(5)	O(7)-Dy(2)-N(4)	97.0(5)
O(8)-Dy(2)-N(4)	73.3(5)	O(4)-Dy(2)-N(3)	81.4(4)
O(9)-Dy(2)-N(3)	146.3(5)	O(3)#4-Dy(2)-N(3)	135.3(5)
O(10)#4-Dy(2)-N(3)	72.1(5)	O(7)-Dy(2)-N(3)	73.2(5)
O(8)-Dy(2)-N(3)	103.3(5)	N(4)-Dy(2)-N(3)	62.8(4)
O(13)-Dy(3)-O(11)	140.5(5)	O(13)-Dy(3)-O(1W)	71.5(6)
O(11)-Dy(3)-O(1W)	69.3(6)	O(13)-Dy(3)-O(14)	53.9(4)
O(11)-Dy(3)-O(14)	146.5(4)	O(1W)-Dy(3)-O(14)	115.7(6)
O(13)-Dy(3)-N(6)	129.7(5)	O(11)-Dy(3)-N(6)	78.6(5)
O(1W)-Dy(3)-N(6)	135.0(7)	O(14)-Dy(3)-N(6)	76.4(5)
O(13)-Dy(3)-O(12)	149.2(5)	O(11)-Dy(3)-O(12)	55.1(5)
O(1W)-Dy(3)-O(12)	110.7(6)	O(14)-Dy(3)-O(12)	133.6(5)
N(6)-Dy(3)-O(12)	71.7(5)	O(13)-Dy(3)-N(5)	89.2(4)
O(11)-Dy(3)-N(5)	79.2(4)	O(1W)-Dy(3)-N(5)	78.7(5)
O(14)-Dy(3)-N(5)	70.1(4)	N(6)-Dy(3)-N(5)	64.7(5)
O(12)-Dy(3)-N(5)	121.6(5)	O(13)-Dy(3)-N(7)	81.2(5)
O(11)-Dy(3)-N(7)	131.8(5)	O(1W)-Dy(3)-N(7)	135.4(6)

O(14)-Dy(3)-N(7)	70.0(5)	N(6)-Dy(3)-N(7)	89.5(5)
O(12)-Dy(3)-N(7)	76.8(5)	N(5)-Dy(3)-N(7)	136.5(4)
O(13)-Dy(3)-N(8)	81.8(4)	O(11)-Dy(3)-N(8)	93.9(4)
O(1W)-Dy(3)-N(8)	77.7(6)	O(14)-Dy(3)-N(8)	119.6(4)
N(6)-Dy(3)-N(8)	136.6(4)	O(12)-Dy(3)-N(8)	69.3(5)
N(5)-Dy(3)-N(8)	156.3(4)	N(7)-Dy(3)-N(8)	63.7(5)
O(13)-Dy(3)-H(1WB)	65.1	O(11)-Dy(3)-H(1WB)	78.2
O(1W)-Dy(3)-H(1WB)	16.8	O(14)-Dy(3)-H(1WB)	116.4
N(6)-Dy(3)-H(1WB)	151.3	O(12)-Dy(3)-H(1WB)	107.7
N(5)-Dy(3)-H(1WB)	94.3	N(7)-Dy(3)-H(1WB)	118.7
N(8)-Dy(3)-H(1WB)	62.0		

[a]Symmetry transformations used to generate equivalent atoms:

#1 -x+2, -y, -z #2 -x+2, -y+1, -z #3 x, y+1, z

#4 -x+1, -y+1, -z+1

Reference

(1) Sheldrick G M. SHELX-97, Program for X-ray Crystal Structure Solution and Refinement. University of Gottingen, Germany, 1997