Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

Assembly of chainlike polyoxometalate-based lanthanide complexes in one-pot reaction system

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Contents

1. Orthogonal experiments for optimizing the synthetic conditions of compounds 1-3

Table S1a Orthogonal experiments for optimizing the synthetic conditions of **1-3**[a,b]

T **(70 °C),** ***t*** **(1.0 h), pH (1.0)**	***T*** **(90 °C),** ***t*** **(1.5 h), pH (1.0)**	***T*** **(80 °C),** ***t*** **(2.0 h), pH (1.0)**
T **(80 °C),** ***t*** **(1.0 h), pH (1.5)**[c]	***T*** (70 °C), ***t*** (1.5 h), **pH** (1.5)[c]	***T*** (90 °C), ***t*** (2.0 h), **pH** (1.5)[c]
T **(90 °C),** ***t*** **(1.0 h), pH (2.0)**	***T*** (80 °C), ***t*** (1.5 h), **pH** (2.0)	***T*** (70 °C), ***t*** (2.0 h), **pH** (2.0)

[a] In this experimental group, the three reaction solutions were fixed as follows: solution A ({As_2W_{19}} 1.0 mmol), solution B ({Ln^{3+}+Pro} 1.0 mmol), solution C ({NaCl aq.} 1 M).
[b] ***T*** = temperature, ***t*** = time, pH means the final pH of the reaction system.
[c] The experimental groups with blue background represent the isolation of crystalline compounds **1-3.**

Table S1b Orthogonal experiments for optimizing the components in three solutions[a,b]

A (1.0 mmol), B (1.0 mmol), C (1.0M)	**A (2.0 mmol), B (1.5 mmol), C (1.0M)**	**A (1.5 mmol), B (2.0 mmol), C (1.0M)**
A (1.5 mmol), B (1.0 mmol), C (2.0M)	**A (1.0 mmol), B (1.5 mmol), (2.0M)**[c]	**A (2.0 mmol), B (2.0 mmol), C (2.0M)**
A (2.0 mmol), B (1.0 mmol), C (3.0M)	**A (1.5 mmol), B (1.5 mmol), C (3.0M)**	**A (1.0 mmol), B (2.0 mmol), C (3.0M)**

[a] In this experimental group, the reaction solutions were fixed as follows: T = 80 °C, t = 1.5 h, pH = 1.5.
[b] **A** = {As_2W_{19}} in 10 mL aqueous solution A (pH = 1.5); **B** = {Ln^{3+}+Pro} in 5 mL aqueous solution B; **C** = {NaCl aq.} in 10 mL aqueous solution C.
[c] The experimental groups with blue background exhibits the best yield for crystalline compounds **1-3.**

2. Additional structural figures for compounds 1 - 3

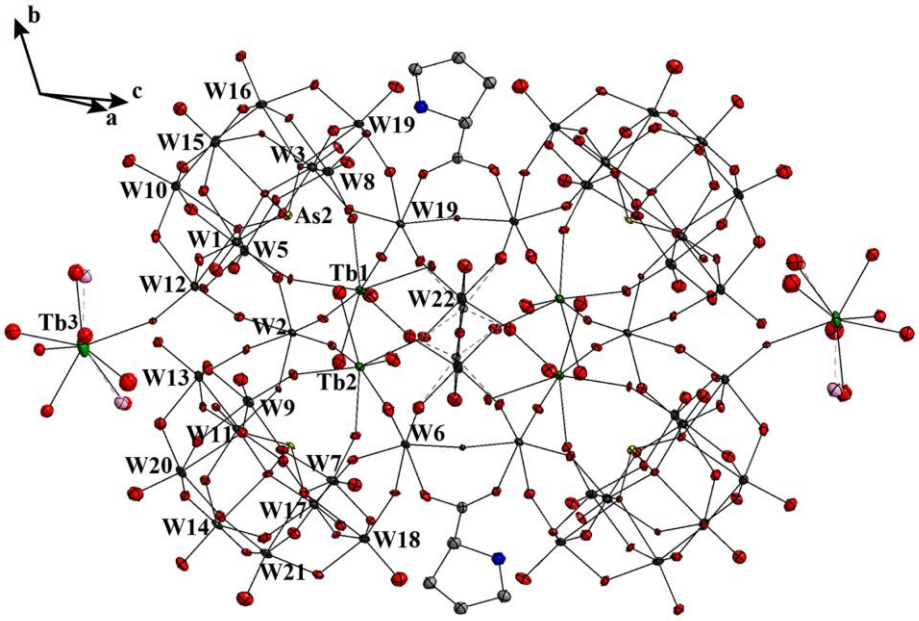

Fig. S1 ORTEP diagram of the basic structural unit in **1** with thermal ellipsoids at 30% probability. Hydrogen atoms, Na cations and crystalline water molecules are omitted for clarity. The disordered oxygen atoms in the polyoxoanion are shown with pink color and broken lines and the disordered W atoms and W-O bonds are shown with grey color and broken lines, respectively.

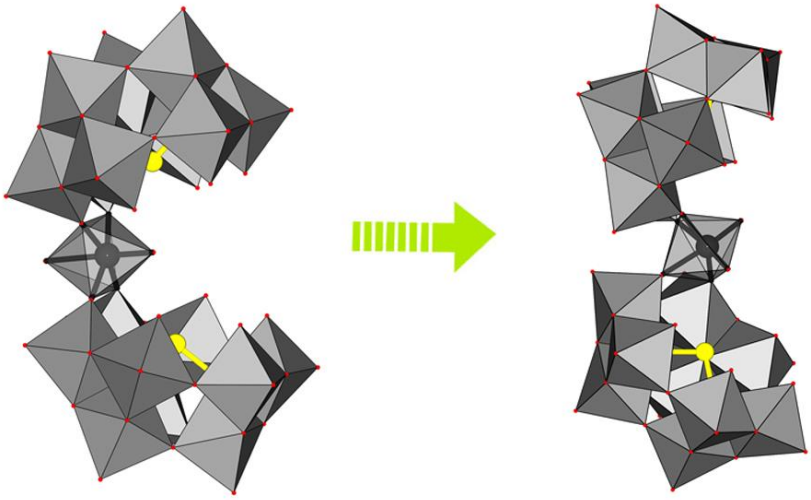

Fig. S2 Structural comparison of the $\{As_2W_{19}O_{67}(H_2O)\}$ precursor (left) and the $\{As_2W_{19}O_{68}\}$ building block in compound **1** (right).

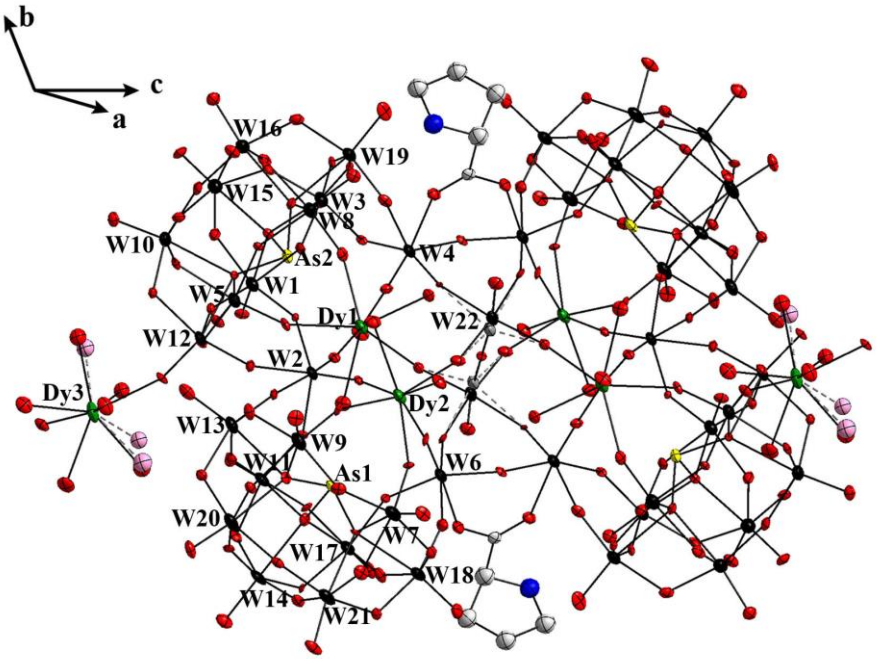

Fig. S3 ORTEP diagram of the basic structural unit in **2** with thermal ellipsoids at 30% probability. Hydrogen atoms, Na cations and crystalline water molecules are omitted for clarity. The disordered oxygen atoms in the polyoxoanion are shown with pink color and broken lines and the disordered W atoms and W-O bonds are shown with grey color and broken lines, respectively.

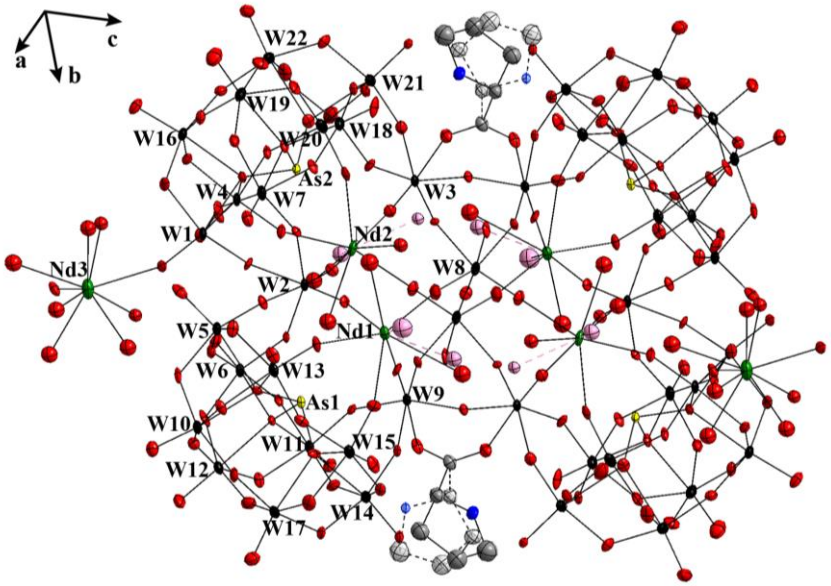

Fig. S4. ORTEP diagram of the basic structural unit in **3** with thermal ellipsoids at 30% probability. Hydrogen atoms, Na cations and crystalline water molecules are omitted for clarity. The disordered oxygen atoms in the polyoxoanion are shown with pink color and broken lines and the disordered W atoms and W-O bonds are shown with grey color and broken lines, respectively.

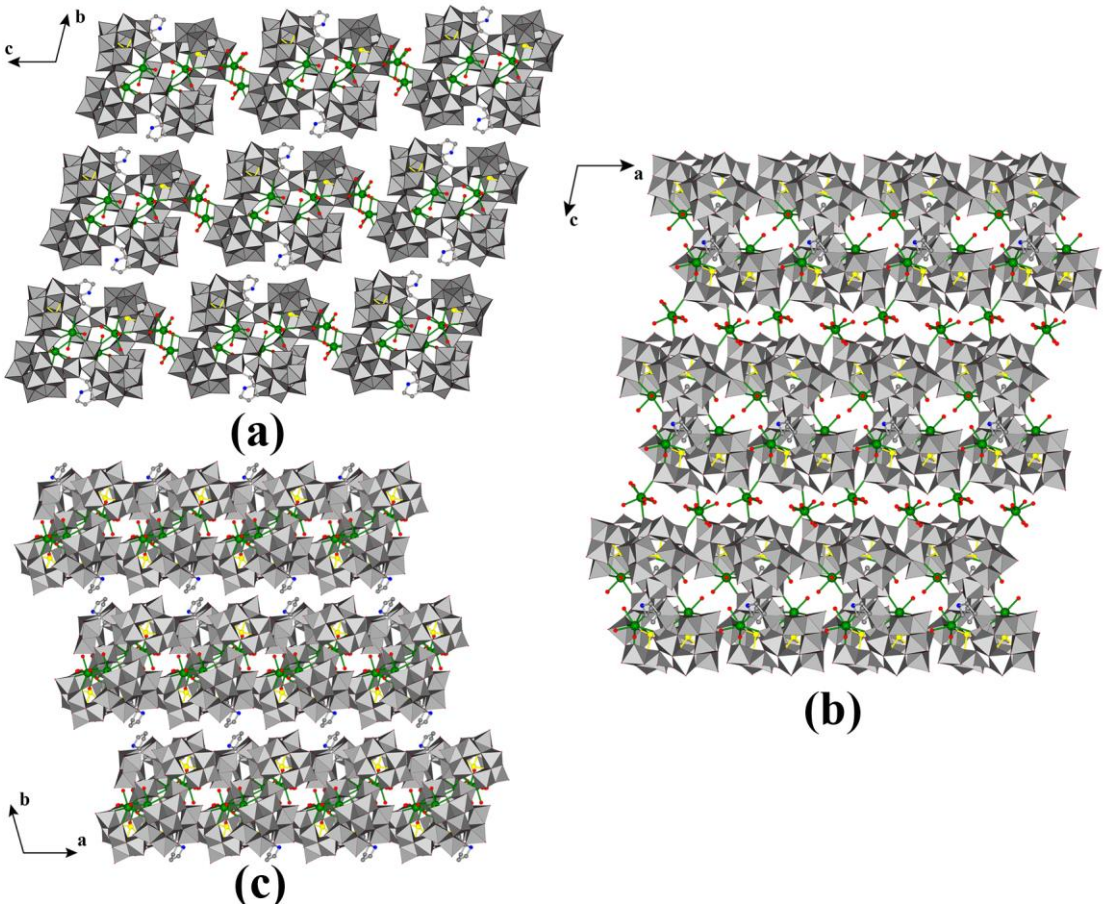

Fig. S5 (a) 3-D packing arrangement of **1** viewed along the *a* axis; **(b)** 3-D packing arrangement of **1** viewed along the *b* axis. **(c)** 3-D packing arrangement of **1** viewed along the *c* axis. The polyoxoanions are represented with polyhedra; Na ions and solvent water molecules are omitted for clarity.

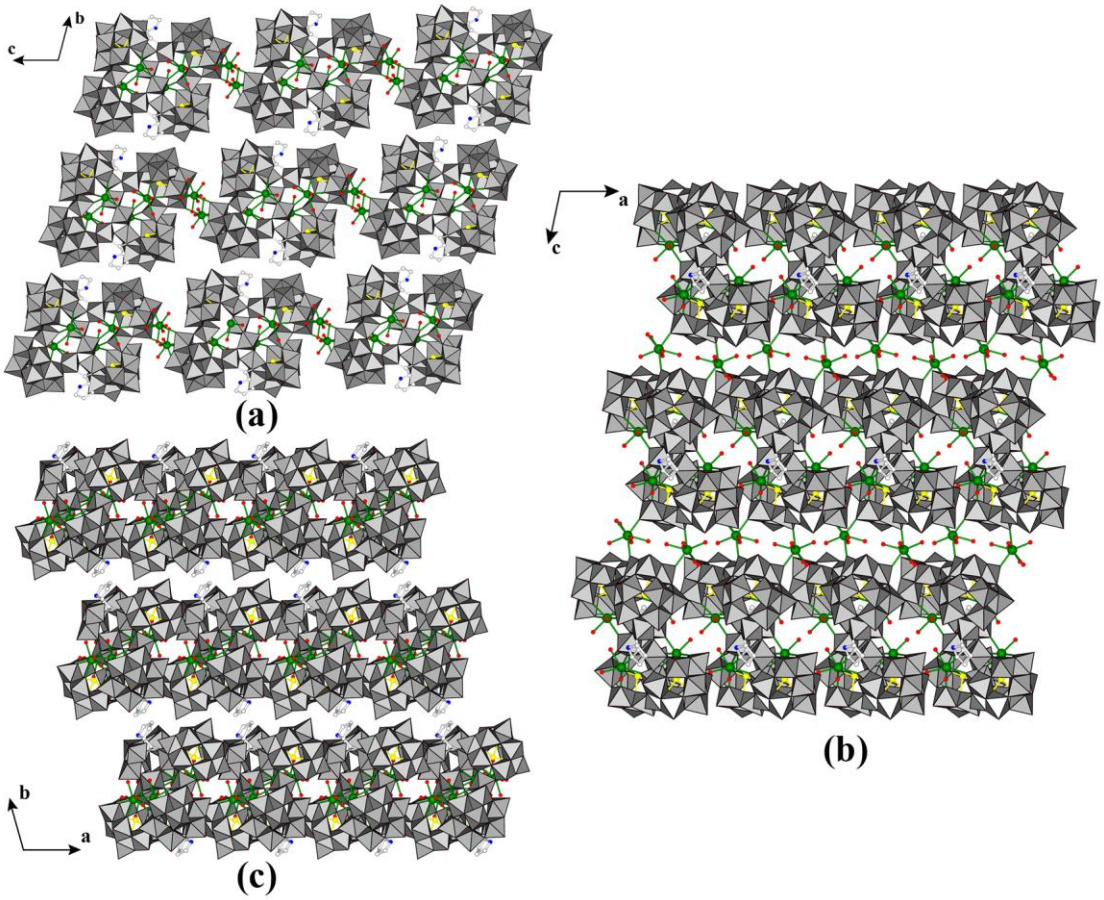

Fig. S6 (a) 3-D packing arrangement of **2** viewed along the *a* axis. **(b)** 3-D packing arrangement of **2** viewed along the *b* axis. **(c)** 3-D packing arrangement of **2** viewed along the *c* axis. The polyoxoanions are represented with polyhedra; Na ions and solvent water molecules are omitted for clarity.

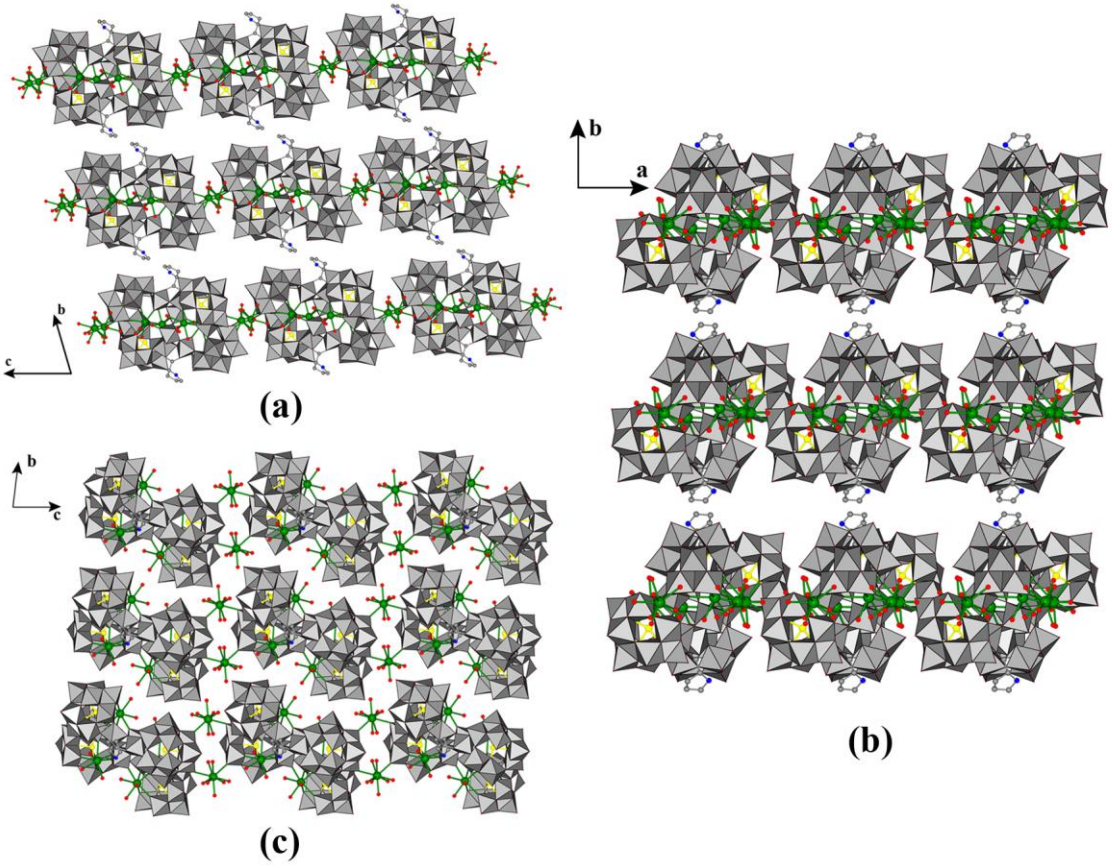

Fig. S7 (a) 3-D packing arrangement of **3** viewed along the *a* axis. **(b)** 3-D packing arrangement of **3** viewed along the *b* axis. **(c)** 3-D packing arrangement of **3** viewed along the *c* axis. The polyoxoanions are represented with polyhedra; Na ions and solvent water molecules are omitted for clarity.

3. Selected bond lengths and angles for compounds 1-3

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

Tb(1)-O(53)	2.31(2)	Tb(1)-O(75)	2.35(2)	Tb(1)-O(2W)	2.44(3)
Tb(1)-O(50)#1	2.34(2)	Tb(1)-O(41)	2.35(2)	Tb(1)-O(1W)	2.46(3)
Tb(1)-O(40)	2.34(2)	Tb(1)-O(3W)	2.44(2)	Tb(2)-O(4W)	2.45(3)
Tb(2)-O(66)	2.25(2)	Tb(2)-O(12)	2.32(2)	Tb(2)-O(30)#1	2.30(3)
Tb(2)-O(1)	2.27(2)	Tb(2)-O(5W)	2.36(3)	Tb(2)-O(15)	2.39(3)
Tb(3)-O(12W)	2.26(9)	Tb(3)-O(7W)	2.35(5)	Tb(3)-O(9W)	2.39(4)
Tb(3)-O(10W)	2.35(8)	Tb(3)-O(2)	2.37(3)	Tb(3)-O(11W)	2.53(10)
Tb(3)-O(8W)	2.36(4)	Tb(3)-O(4)#3	2.42(2)		
W(6)-O(66)	1.76(2)	W(6)-O(47)	1.88(2)	W(6)-O(8)	2.01(2)
W(6)-O(6)	1.79(3)	W(6)-O(19)	1.90(3)	W(6)-O(79)	2.22(2)
W(19)-O(72)	1.68(3)	W(19)-O(38)	1.91(2)	W(19)-O(62)	1.960(19)
W(19)-O(57)#1	1.84(2)	W(19)-O(58)	1.92(2)	W(19)-O(61)	2.41(2)
W(22)-O(74)	1.74(3)	W(22)-O(53)	1.83(2)	W(22)-O(6)	2.08(3)
W(22)-O(30)	1.76(3)	W(22)-O(10)	2.01(2)	W(22)-O(26)	2.349(5)
O(53)-Tb(1)-O(40)	70.3(9)	O(66)-Tb(2)-O(1)	73.9(8)	O(12W)-Tb(3)-O(10W)	148(4)
O(53)-Tb(1)-O(50)#1	76.0(8)	O(66)-Tb(2)-O(30)#1	74.7(9)	O(12W)-Tb(3)-O(8W)	108(3)
O(53)-Tb(1)-O(75)	139.9(9)	O(66)-Tb(2)-O(12)	126.1(10)	O(12W)-Tb(3)-O(7W)	67(3)
O(53)-Tb(1)-O(41)	148.2(10)	O(66)-Tb(2)-O(5W)	120.5(10)	O(12W)-Tb(3)-O(2)	98(3)
O(53)-Tb(1)-O(3W)	104.9(8)	O(66)-Tb(2)-O(15)	76.1(9)	O(12W)-Tb(3)-O(11W)	84(3)
O(53)-Tb(1)-O(2W)	69.9(9)	O(66)-Tb(2)-O(4W)	139.4(11)	O(12W)-Tb(3)-O(9W)	139(3)
O(53)-Tb(1)-O(1W)	73.9(9)			O(12W)-Tb(3)-O(4)#3	77(3)
O(66)-W(6)-O(6)	100.7(13)	O(72)-W(19)-O(57)#1	99.3(12)	O(74)-W(22)-O(30)	102.2(13)
O(66)-W(6)-O(47)	97.8(11)	O(72)-W(19)-O(38)	102.3(11)	O(74)-W(22)-O(53)	98.2(12)
O(66)-W(6)-O(19)	100.9(11)	O(72)-W(19)-O(58)	97.0(12)	O(74)-W(22)-O(6)	90.9(13)
O(66)-W(6)-O(8)	89.0(12)	O(72)-W(19)-O(62)	101.4(11)	O(74)-W(22)-O(10)	94.2(12)
O(66)-W(6)-O(79)	171.8(12)	O(72)-W(19)-O(61)	169.0(10)	O(74)-W(22)-O(26)	170.9(11)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+2, #3 -x+1,-y,-z+1

Table S3 Selected bond lengths (Å) and angles (°) of compound **2**

Dy(1)-O(53)	2.265(17)	Dy(1)-O(41)	2.364(17)	Dy(1)-O(2W)	2.44(2)
Dy(1)-O(50)#1	2.336(18)	Dy(1)-O(75)	2.38(2)	Dy(1)-O(1W)	2.47(2)
Dy(1)-O(40)	2.354(18)	Dy(1)-O(3W)	2.410(17)	Dy(2)-O(12)	2.333(18)
Dy(2)-O(1)	2.236(15)	Dy(2)-O(30)#1	2.25(2)	Dy(2)-O(15)	2.367(18)
Dy(2)-O(66)	2.252(18)	Dy(2)-O(5W)	2.318(18)	Dy(2)-O(4W)	2.45(2)
Dy(3)-O(8W)	2.29(2)	Dy(3)-O(12W)	2.34(6)	Dy(3)-O(7W)	2.41(3)
Dy(3)-O(2)	2.326(18)	Dy(3)-O(4)#3	2.380(19)	Dy(3)-O(11W)	2.46(5)
Dy(3)-O(10W)	2.33(5)	Dy(3)-O(9W)	2.38(2)		
W(4)-O(50)	1.72(2)	W(4)-O(9)	1.828(16)	W(4)-O(57)	2.050(18)
W(4)-O(10)	1.786(14)	W(4)-O(47)	1.931(18)	W(4)-O(77)	2.240(19)
W(6)-O(66)	1.757(18)	W(6)-O(47)	1.869(17)	W(6)-O(8)	1.99(2)
W(6)-O(6)	1.804(17)	W(6)-O(19)	1.89(2)	W(6)-O(78)	2.203(19)
W(22)-O(74)	1.69(2)	W(22)-O(30)	1.81(2)	W(22)-O(10)	2.072(15)
W(22)-O(53)	1.786(18)	W(22)-O(6)	2.068(19)	W(22)-O(26)	2.393(4)
O(53)-Dy(1)-O(50)#1	77.2(7)	O(1)-Dy(2)-O(66)	75.2(6)	O(8W)-Dy(3)-O(2)	146.7(8)
O(53)-Dy(1)-O(40)	78.3(6)	O(1)-Dy(2)-O(12)	92.1(6)	O(8W)-Dy(3)-O(12W)	96.5(15)
O(53)-Dy(1)-O(41)	146.5(7)	O(1)-Dy(2)-O(30)#1	92.8(7)	O(8W)-Dy(3)-O(9W)	72.1(8)
O(53)-Dy(1)-O(75)	141.6(7)	O(1)-Dy(2)-O(15)	127.6(7)	O(8W)-Dy(3)-O(10W)	89.0(12)
O(53)-Dy(1)-O(3W)	105.6(7)	O(1)-Dy(2)-O(4W)	74.0(6)	O(8W)-Dy(3)-O(11W)	142.6(14)
O(53)-Dy(1)-O(2W)	70.6(7)	O(1)-Dy(2)-O(5W)	156.1(7)	O(8W)-Dy(3)-O(7W)	87.6(10)
O(53)-Dy(1)-O(1W)	73.8(7)			O(8W)-Dy(3)-O(4)#3	74.5(8)
O(50)-W(4)-O(10)	102.3(8)	O(66)-W(6)-O(6)	100.9(9)	O(74)-W(22)-O(30)	101.3(10)
O(50)-W(4)-O(9)	98.7(9)	O(66)-W(6)-O(47)	98.4(8)	O(74)-W(22)-O(10)	91.4(8)
O(50)-W(4)-O(47)	97.6(8)	O(66)-W(6)-O(19)	100.1(8)	O(74)-W(22)-O(6)	92.7(9)
O(50)-W(4)-O(57)	90.9(8)	O(66)-W(6)-O(8)	90.5(9)	O(74)-W(22)-O(26)	169.3(7)
O(50)-W(4)-O(77)	171.5(7)	O(66)-W(6)-O(78)	172.7(9)	O(74)-W(22)-O(53)	102.7(9)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+2; #3 -x+1,-y,-z+1

Table S4 Selected bond lengths (Å) and angles (°) of compound **3**

Nd(1)-O(18)	2.403(17)	Nd(1)-O(2)	2.448(12)	Nd(1)-O(5W)	2.84(4)
Nd(1)-O(76)#1	2.431(14)	Nd(1)-O(3W)	2.46(3)	Nd(1)-O(40)#1	2.462(13)
Nd(1)-O(46)	2.444(14)	Nd(2)-O(6)#1	2.390(14)	Nd(2)-O(8W)	2.50(2)
Nd(2)-O(29)	2.364(17)	Nd(2)-O(55)	2.457(13)	Nd(2)-O(2W)	2.54(3)
Nd(2)-O(7)	2.368(13)	Nd(2)-O(33)	2.469(14)	Nd(2)-O(4W)	2.60(3)
Nd(3)-O(10W)	2.446(16)	Nd(3)-O(6W)	2.484(18)	Nd(3)-O(12W)	2.541(16)
Nd(3)-O(62)#2	2.455(15)	Nd(3)-O(1W)	2.524(16)	Nd(3)-O(9W)	2.581(14)
Nd(3)-O(7W)	2.474(18)	Nd(3)-O(41)	2.531(15)	Nd(3)-O(11W)	2.586(15)
W(3)-O(29)	1.761(17)	W(3)-O(58)	1.906(14)	W(3)-O(45)	2.024(14)
W(3)-O(70)	1.807(14)	W(3)-O(74)	1.952(13)	W(3)-O(77)	2.255(16)
W(8)-O(76)	1.746(14)	W(8)-O(73)	1.9213(12)	W(8)-O(60)	2.081(12)
W(8)-O(6)	1.746(14)	W(8)-O(70)	2.065(13)	W(8)-O(14)	2.103(18)
W(9)-O(18)	1.719(17)	W(9)-O(74)	1.884(13)	W(9)-O(21)	2.004(14)
W(9)-O(60)	1.805(12)	W(9)-O(28)	1.911(14)	W(9)-O(78)	2.203(15)
O(18)-Nd(1)-O(76)#1	73.9(6)	O(55)-Nd(2)-O(4W)	118.9(7)	O(12W)-Nd(3)-O(9W)	84.3(5)
O(18)-Nd(1)-O(46)	75.4(5)	O(55)-Nd(2)-O(33)	115.9(5)	O(12W)-Nd(3)-O(11W)	133.2(5)
O(18)-Nd(1)-O(2)	115.5(5)	O(55)-Nd(2)-O(8W)	67.7(6)	O(10W)-Nd(3)-O(12W)	138.1(5)
O(18)-Nd(1)-O(40)#1	69.5(5)	O(55)-Nd(2)-O(2W)	155.1(7)	O(62)#2-Nd(3)-O(12W)	66.7(5)
O(18)-Nd(1)-O(13W)	140.1(7)	O(6)#1-Nd(2)-O(55)	82.7(5)	O(7W)-Nd(3)-O(12W)	79.2(6)
O(18)-Nd(1)-O(5W)	66.1(10)	O(29)-Nd(2)-O(55)	69.3(5)	O(6W)-Nd(3)-O(12W)	74.4(6)
O(18)-Nd(1)-O(3W)	140.4(7)	O(7)-Nd(2)-O(55)	82.0(5)	O(1W)-Nd(3)-O(12W)	71.9(5)
				O(41)-Nd(3)-O(12W)	142.2(6)
O(29)-W(3)-O(70)	100.1(7)	O(76)-W(8)-O(6)	103.0(7)	O(18)-W(9)-O(60)	103.0(7)
O(29)-W(3)-O(58)	102.2(7)	O(76)-W(8)-O(73)	99.4(6)	O(18)-W(9)-O(74)	97.9(6)
O(29)-W(3)-O(45)	92.0(7)	O(76)-W(8)-O(70)	88.1(6)	O(18)-W(9)-O(28)	100.5(7)
O(29)-W(3)-O(77)	173.0(6)	O(76)-W(8)-O(60)	162.1(7)	O(18)-W(9)-O(21)	90.0(7)
O(29)-W(3)-O(74)	96.3(6)	O(76)-W(8)-O(14)	88.6(7)	O(18)-W(9)-O(78)	171.8(6)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+2; #2 -x+1,-y,-z+1

4. Additional physical measurements for compounds 1-3

4.1 IR spectra of compound 1-3

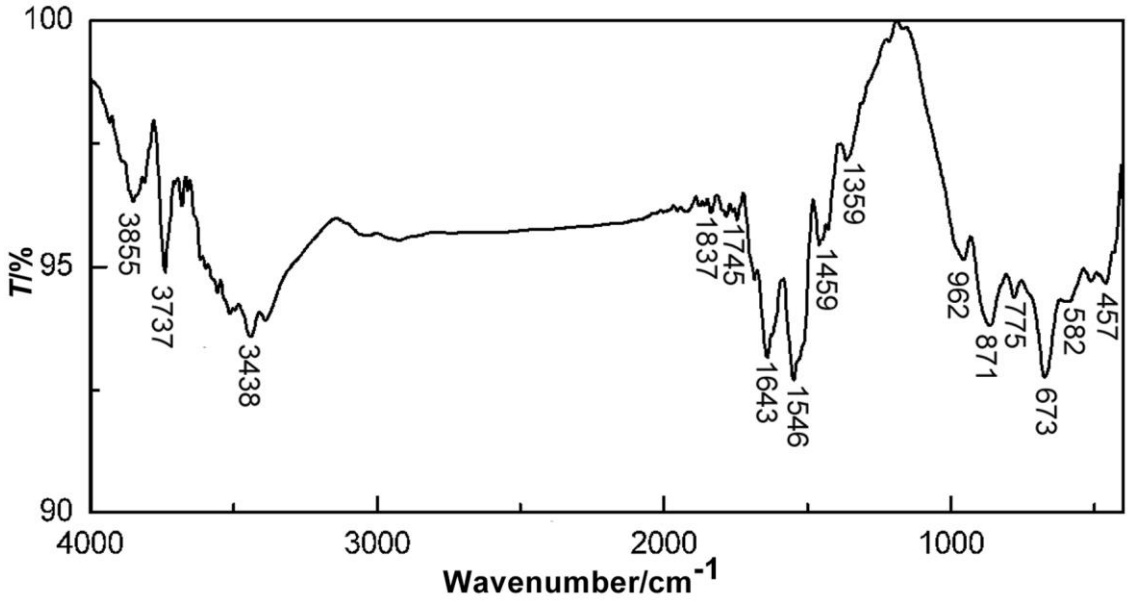

Fig. S8 FT-IR spectrum of compound **1** measured at room temperature

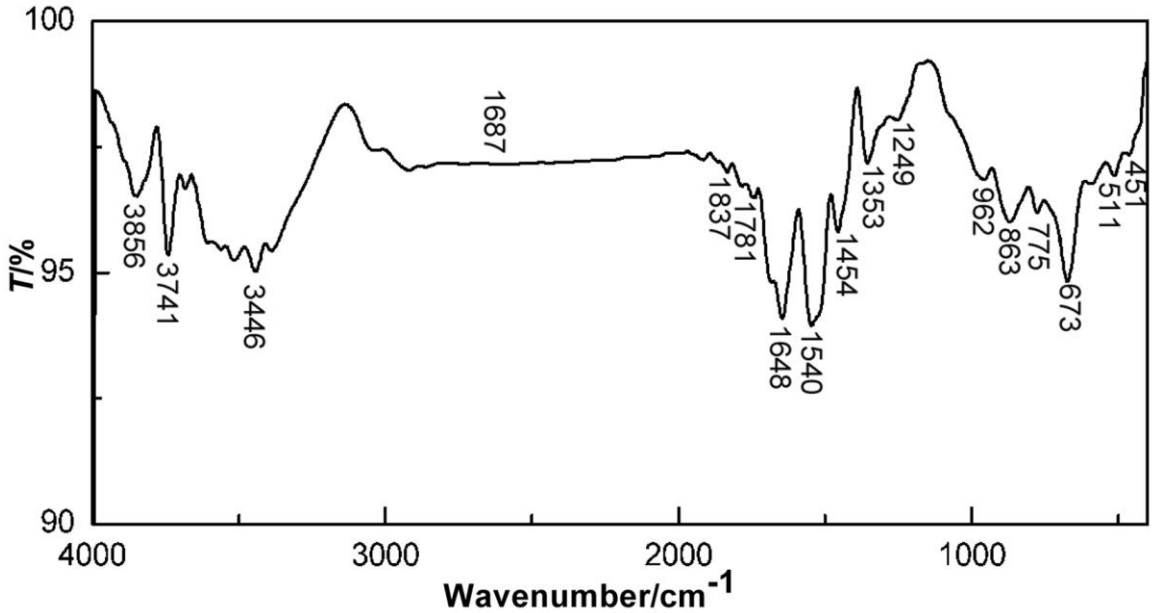

Fig. S9 FT-IR spectrum of compound **2** measured at room temperature

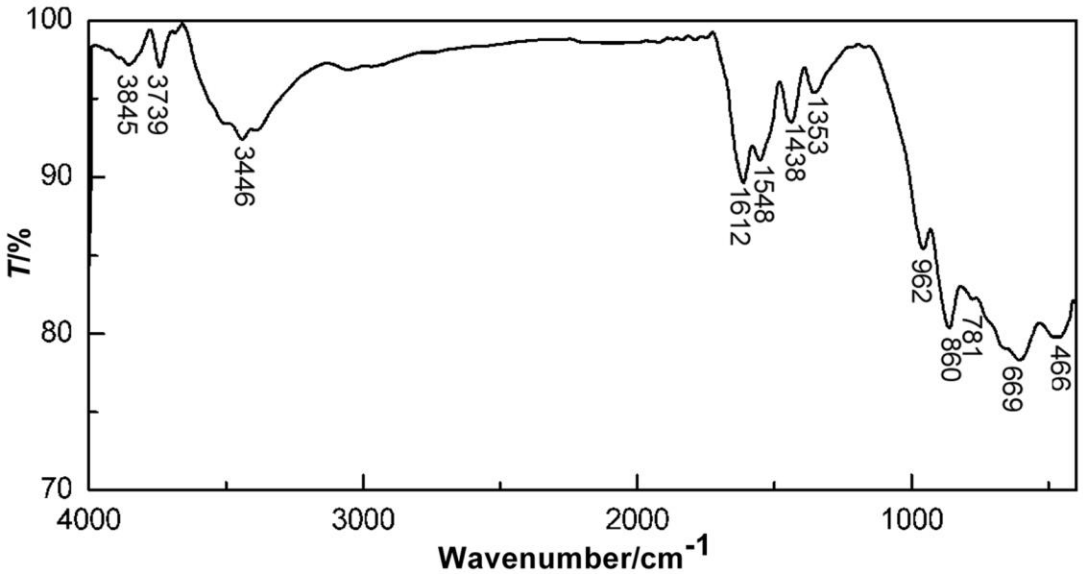

Fig. S10 FT-IR spectrum of compound **3** measured at room temperature

IR spectra

In the IR spectrum of compounds **1-3** (Fig. S8-S10), four characteristic peaks in the range of 1000-700 cm^{-1} are ascribed to the vibrations of ν(As-O), ν(W=O_t) and ν(W–$O_{b/c}$–W) of POM clusters, respectively. The strong and broad peak near 3440 cm^{-1} is attributed to extending vibrations of crystalline lattice water molecules. The strong peaks close to 3850 cm^{-1} and 1640 cm^{-1} are attributed to the ν(C=O) vibration of proline ligands. The peaks close to3740 cm^{-1} and 1545 cm^{-1} correspond to the vibration of the NH_2^+ group, and the peak near 1355 cm^{-1} corresponds to ν(C–N) of proline ligands.

4.2 TG analysis of compounds 1-3

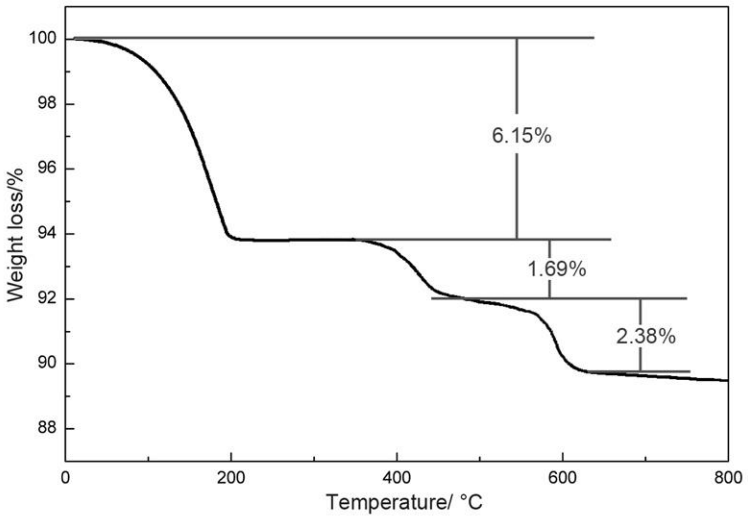

Fig. S11 TG curve for compound **1**

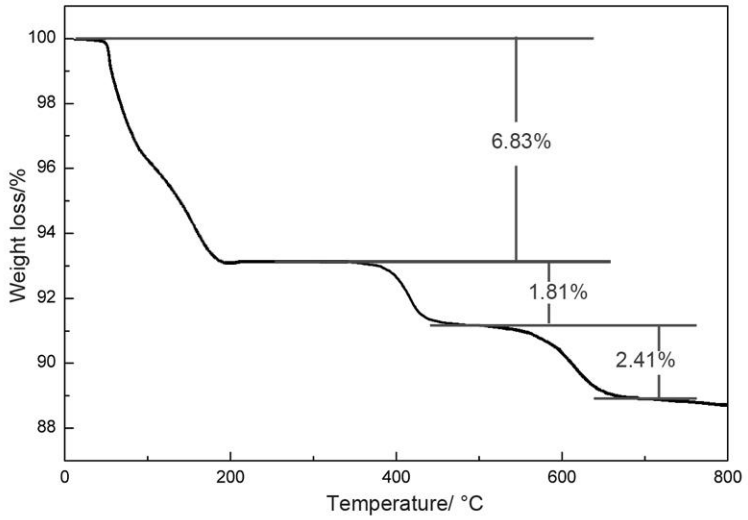

Fig. S12 TG curve for compound **2**

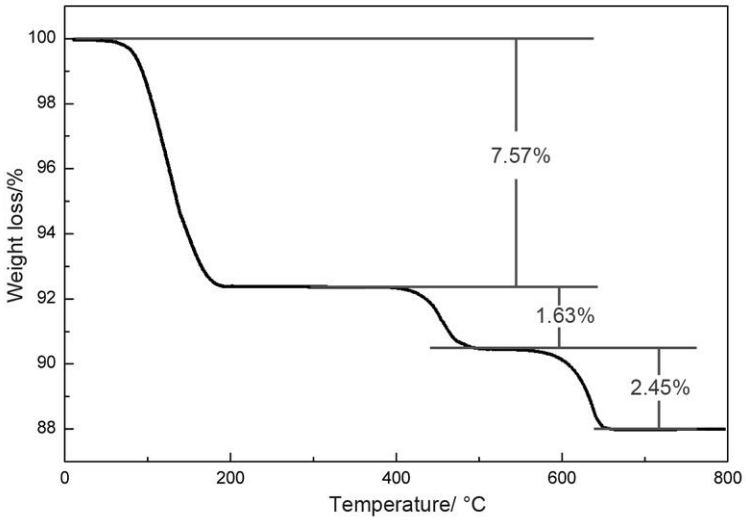

Fig. S13 TG curve for compound **3**

TG analysis

The TG curve of **1** shows a total weight loss of 10.22 % in the range of 44-617 °C, in agreement with the calculated value of 10.36 %. The weight loss of 6.15% at 44-207 °C corresponds to the loss of all crystalline and coordinated water molecules (calc. 6.07%). The weight loss of 1.77% at 375-435 °C is attributed to the decomposition and loss of proline ligands. The weight loss of 2.38% occurs between 440–600 ◦C, probably due to the loss of partial arsenic oxide and composition water molecules (calc. 2.53%).

The TG curve of **2** gives a total weight loss of 11.05 % in the range of 52-671 °C, which agrees with the calculated value of 10.72%. The weight loss of 6.83 % at 52-194 °C corresponds to the loss of all crystalline and coordinated water molecules (calc. 6.45%). The weight loss of 1.81% at 385-461 °C is attributed to the decomposition and loss of proline ligands. The weight loss of 2.41% occurs between 538–673 ◦C, probably due to the loss of partial arsenic oxide and composition water molecules (calc. 2.52%).

The TG curve of **3** shows a total weight loss of 11.65 % in the range of 53-642 °C, in agreement with the calculated value of 12.04%. The weight loss of 7.57% at 53-195 °C corresponds to the loss of all crystalline and coordinated water molecules (calc. 7.78%). The weight loss of 1.63% at 419-495 °C is attributed to the decomposition and loss of proline ligands. The weight loss of 2.45% occurs between 565–639 ◦C, probably due to the loss of partial arsenic oxide and composition water molecules (calc. 2.52%).

4.3 Photoluminescent propertie of compound 3

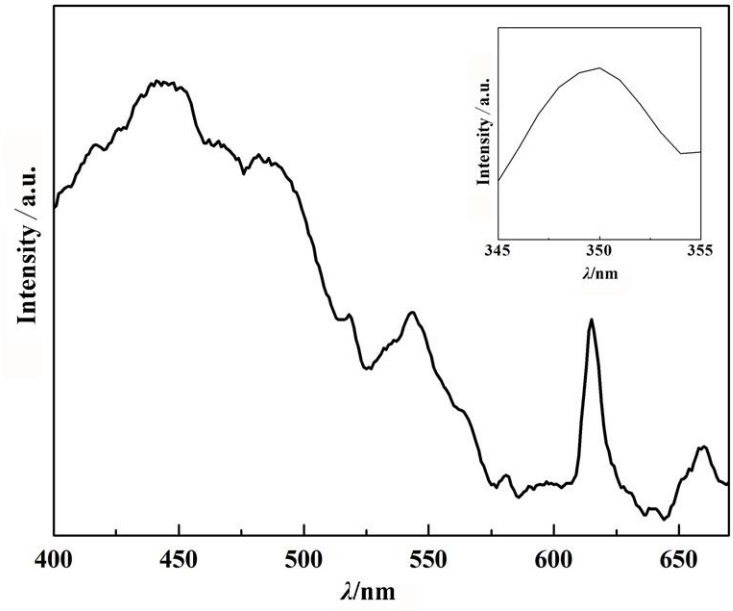

Fig. S14 The luminescence spectrum of Nd(III) in compound **3** excited at 350 nm.

4.4 Powder X-ray diffractions of compounds 1-3

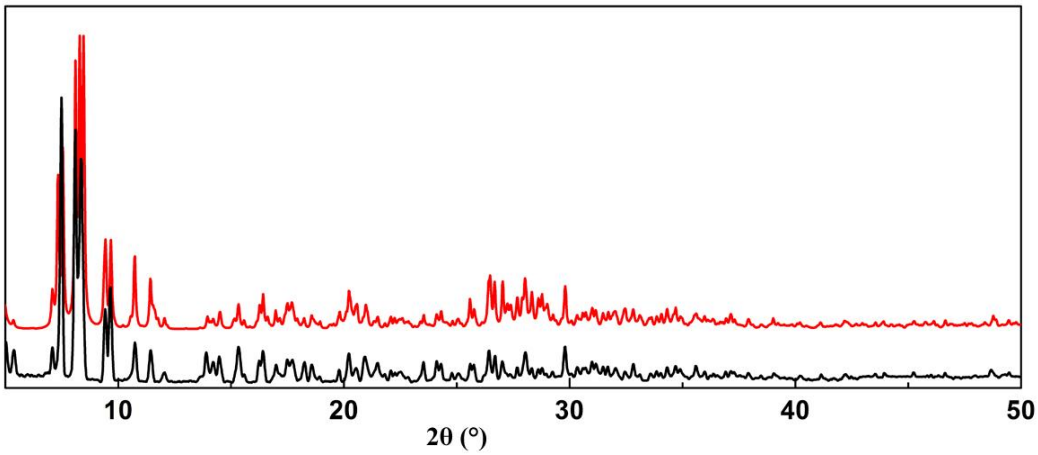

Fig. S15 Experimental powder X-ray diffraction pattern of **1** (black) and simulated PXRD pattern (from the single-crystal X-ray diffraction data) of **1** (red).

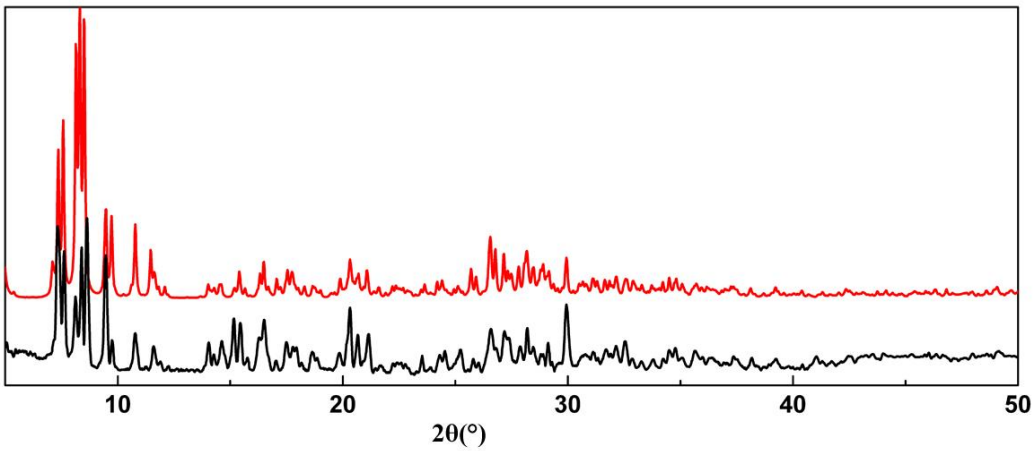

Fig. S16 Experimental powder X-ray diffraction pattern of **2** (black) and simulated PXRD pattern (from the single-crystal X-ray diffraction data) of **2** (red).

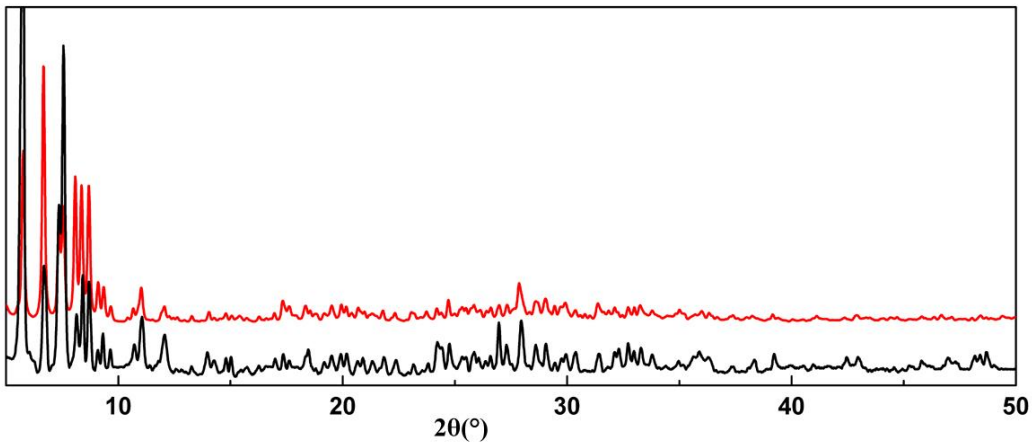

Fig. S17 Experimental powder X-ray diffraction pattern of **3** (black) and simulated PXRD pattern (from the single-crystal X-ray diffraction data) of **3** (red).

Discussion: Powder X-ray diffraction pattern of all compounds have been collected to confirm the phase purity of the bulk compounds (Figure S15-S17).