Supplementary Information

Achieving Stable Photoluminescence by Double Thiacalix[4]arene-Capping: the Lanthanide-Oxo Cluster Core Matters

Zixiu Lu,[ab] Shujian Wang,[ab] Guo-Ling Li,[cd] Zhu Zhuo,[cd] Haomiao Zhu,[cd] Wei Wang,[cd*] You-Gui Huang,[cde*] and Maochun Hong[abd]

[a] School of Rare Earth, University of Science and Technology of China, Ganzhou, China.

[b] Ganjiang Innovation Academy, Chinese Academy of Sciences, Ganzhou 341000, China

[c] CAS Key Laboratory of Design and Assembly of Functional Nanostructures, and Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, China

[d] Xiamen Key Laboratory of Rare Earth Photoelectric Functional Materials, Xiamen Institute of Rare Earth Materials, Haixi Institutes, Chinese Academy of Sciences, Xiamen, Fujian 361021, China;

[e] Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou, 350108

*Corresponding author: wangwei@fjirsm.ac.cn; yghuang@fjirsm.ac.cn

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1. Supplementary Tables.

Table S1. Crystallographic Data and Structure Refinements for **1**−**5**.

	1	**2**	**3**
formula	$\{Eu_4(\mu_4\text{-}OH)(TC4A)_2(DMF)_6(CH_3OH)_3(HCOO)Cl_2\}\cdot 0.33CH_3OH$	$\{Tb_4(\mu_4\text{-}OH)(TC4A)_2(DMF)_6(CH_3OH)_3(HCOO)Cl_2\}\cdot 0.66\ CH_3OH$	$\{Gd_9(\mu_5\text{-}OH)_2(\mu_3\text{-}OH)_8(CH_3OH)_2(TC4A)_2(H_2O)_{24}Cl_9\}\cdot 3.36DMF$
fw	2572.80	2618.24	3759.68
crystal system	Triclinic	Triclinic	Tetragonal
space group	$P\bar{1}$	$P\bar{1}$	*P*4/*nnc*
a, Å	12.2472(3)	12.2571(3)	13.3613(4)
b, Å	20.8833(5)	20.9533(5)	13.3613(4)
c, Å	22.7770(5)	22.9088(6)	46.1864(17)
α, deg	69.3320(10)	69.3000(10)	90
β, deg	83.0420(10)	83.0000(10)	90
γ, deg	86.5600(10)	86.5820(10)	90
V, Å^3	5409.5(2)	5461.9(2)	8245.4(6)
Z	2	2	2
D_c / g cm^{-3}	1.573	1.575	1.411
T, K	200.00	200.00	200.00
F(000)	2582	2598	3380
reflections collected	114643	104934	325276
/ unique	/24852	/ 22162	/ 4793
R_{int}	0.0398	0.0364	0.0611
GOF on F^2	1.159	1.177	1.060
R_1, wR_2 $I>2\sigma(I)$[a]	0.0350, 0.0975	0.0351, 0.1001	0.0454, 0.1267
R_1, wR_2 (all data)	0.0427, 0.1098	0.0415, 0.1120	0.0537, 0.1350
	4	**5**	
formula	$\{Tb_9(\mu_5\text{-}OH)_2(\mu_3\text{-}OH)_8(OCH_3)(TC4A)_2(H_2O)_{24}Cl_9\}\cdot 2.6DMF$	$\{Tb_9(\mu_5\text{-}OH)_2(\mu_3\text{-}OH)_8(OCH_3)(TC4A)_2(H_2O)_{24}Cl_9\}\cdot 5.36DMF$	

fw	3703.03	3722.45
crystal system	Tetragonal	Tetragonal
space group	*P*4/*nnc*	*P*4/*nnc*
a, Å	13.3479(4)	13.2526(4)
b, Å	13.3479(4)	13.2526(4)
c, Å	46.0809(18)	46.0114(19)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
V, Å^3	8210.1(6)	8081.0(6)
Z	2	2
D_c / g cm^{-3}	1.423	1.459
T, K	200.00	200.00
F(000)	3398	3416
Reflectionscolleced/	102383	322222
unique	/4747	/4681
R_{int}	0.0566	0.0590
GOF on F^2	1.107	1.058
R_1, wR_2 $I>2\sigma(I)$[a]	0.0628, 0.1582	0.0498, 0.1338
R_1, wR_2 (all data)	0.0787, 0.1731	0.0572, 0.1411

[a] $R_1 = \Sigma||F_o| - |F|| / \Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2. Selected bond lengths [Å] for **2** and **4.**

2			
Tb(1)-Cl(2)	2.7288(14)	Tb(3)-O(4)	2.368(3)
Tb(1)-S(5)	2.9516(13)	Tb(3)-O(6)#1	2.376(3)
Tb(1)-S(7)#2	2.9416(13)	Tb(3)-O(8)#1	2.373(3)
Tb(1)-O(3)#2	2.374(3)	Tb(3)-O(10)	2.366(3)
Tb(1)-O(7)	2.5438(2)	Tb(3)-O(12)	2.416(4)
Tb(1)-O(11)#2	2.377(3)	Tb(3)-O(14)	2.4740(2)
Tb(1)-O(13)	2.414(3)	Tb(3)-O(16)	2.376(4)
Tb(1)-O(18)	2.378(3)	Tb(4)-Cl(1)	2.7474(15)
Tb(1)-O(19)	2.422(4)	Tb(4)-S(1)#1	2.9330(12)
Tb(2)-S(2)#2	2.9416(13)	Tb(4)-S(4)	2.9364(13)
Tb(2)-S(3)	2.9551(13)	Tb(4)-O(1)	2.336(4)
Tb(2)-O(3)	2.385(3)	Tb(4)-O(4)	2.410(3)
Tb(2)-O(5)	2.343(4)	Tb(4)-O(6)	2.379(3)
Tb(2)-O(7)	2.5582(2)	Tb(4)-O(8)#1	2.397(3)
Tb(2)-O(11)#2	2.385(3)	Tb(4)-O(10)#1	2.389(3)

Tb(2)-O(13)	2.371(3)	Tb(4)-O(14)	2.6205(2
Tb(2)-O(15)	2.398(4)	Tb(1)-Tb(2)	3.6144(3)
Tb(2)-O(18)#2	2.386(3)	Tb(1)-Tb(2)#2	3.6010(3)
Tb(3)-S(6)	2.9547(12)	Tb(3)-Tb(4)	3.5983(3)
Tb(3)-S(8)#1	2.9762(12)	Tb(3)-Tb(4)#1	3.6094(3)
4			
Tb(1)-O(6)#2	2.426(6)	Tb(2)-O(2)#1	2.404(7)
Tb(1)-O(6)#3	2.426(6)	Tb(2)-O(3)	2.402(10)
Tb(1)-O(6)#4	2.426(6)	Tb(2)-O(4)	2.414(9)
Tb(1)-O(6)#1	2.426(6)	Tb(2)-O(5)	2.494(7)
Tb(1)-O(6)#5	2.426(6)	Tb(2)-O(6)	2.324(5)
Tb(1)-O(6)#6	2.426(6)	Tb(2)-O(6)#5	2.342(6)
Tb(1)-O(6)#7	2.426(6)	Tb(2)-O(7)	2.5554(7)
Tb(1)-O(6)	2.426(6)	Tb(1)-Tb(2)#1	3.7367(4)
Tb(1)-O(7)	2.874(10)	Tb(1)-Tb(2)	3.7366(4)
Tb(1)-O(7)#2	2.874(10)	Tb(2)-Tb(2)#5	3.6081(6)
Tb(2)-S(1)#1	2.965(2)	Tb(2)-Tb(2)#1	3.6081(6)
Tb(2)-O(2)	2.384(6)		

Symmetry transformations used to generate equivalent atoms:

2: #1 –x+2, −y+2, −z+1 #2 −x+1, −y+1, −z+2

4: #1 –y+3/2, X, z #2 –x+3/2, y, –z+1/2 #3 x, –y+3/2, –z+1/2 #4 –y+3/2, –x+3/2, –z+1/2 #5 y, x, –z+1/2 #6 y, x, z+1/2 #7 –x+3/2, –y+3/2, z

Table S3. Selected bond valence analysis for **2** and **4**.

2											
Atom	Cl2	S5	S7	O3	O7	O11	O13	O18	O19	—	Σcation
Tb1	0.44	0.30	0.31	0.38	0.24	0.37	0.34	0.37	0.33	—	3.09
Atom	S2	S3	O3	O5	O7	O11	O13	O15	O18	—	Σcation
Tb2	0.31	0.30	0.37	0.41	0.23	0.36	0.38	0.35	0.36	—	3.08
Atom	S6	S8	O4	O6	O8	O10	O12	O14	O16	—	Σcation
Tb3	0.30	0.28	0.38	0.37	0.38	0.38	0.34	0.29	0.38	—	3.11
Atom	Cl1	S1	S4	O1	O4	O6	O8	O10	O14	—	Σcation
Tb3	0.42	0.32	0.32	0.42	0.34	0.37	0.35	0.36	0.19	—	3.10
Atom	Tb1	Tb1	Tb2	Tb	—	—	—	—	—	—	Σion
O7	0.24	0.24	0.23	0.23	—	—	—	—	—	—	0.94
Atom	Tb1	Tb1	Tb2	Tb	—	—	—	—	—	—	Σion
O14	0.29	0.29	0.19	0.19	—	—	—	—	—	—	0.97
4											
Atom	O7	O7	O6	O6	O6	O6	O6	O6	O6	O6	Σcation
Tb1	0.10	0.10	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	3.00
Atom	S1	O2	O2	O3	O4	O5	O5	O6	O7	—	Σcation
Tb2	0.28	0.39	0.37	0.37	0.36	0.39	0.45	0.43	0.24	—	3.08
Atom	Tb1	Tb2	Tb2	—	—	—	—	—	—	—	Σion
O6(μ_3)	0.45	0.43	0.34	—	—	—	—	—	—	—	1.22
Atom	Tb1	Tb2	Tb2	Tb2	Tb2	—	—	—	—	—	Σion
O5(μ_5)	0.10	0.23	0.23	0.23	0.23	—	—	—	—	—	1.02

The bond valence was calculated by the equation: $S = \exp((R_0 - R)/b)$ where where S is

the experimental bond valence, R the observed bond length, and R_0 and b are fitted bond valence parameters. R_0 of Tb–O, Tb–S are 2.032, 2.510 and b = 0.37.

Table S4. Decay analysis data of **1**, **2**, and **4**.

Compound	Corresponding lifetime lifetime (ns)		Contributing amplitude		Average decay time (ns)[a]
	τ_1	τ_2	A_1	A_2	τ^*
1	$6.36*10^4$	$2.59*10^5$	0.49	0.52	$5.22*10^4$
2	$4.98*10^5$	$1.36*10^6$	0.07	1.04	$1.34*10^6$
4	$4.92*10^5$	$1.01*10^6$	0.03	0.75	$1.00*10^6$

[a] $\tau^* = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$

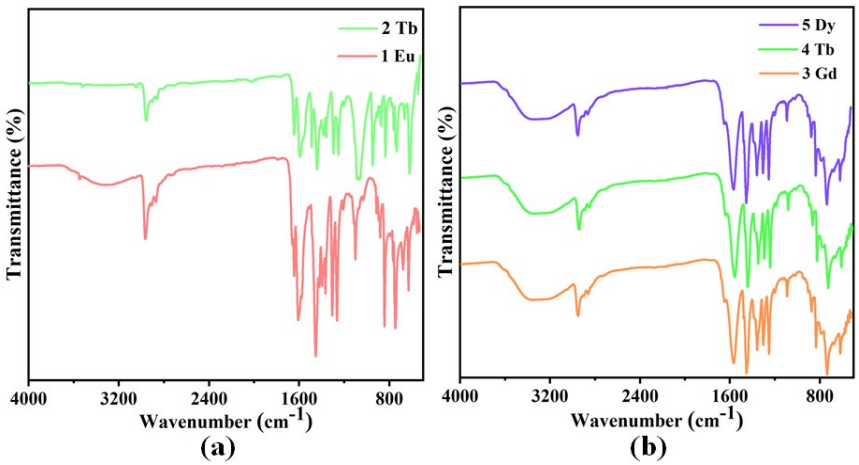

Fig. S1 (a) FTIR spectra of **1**−**2**; (b) FTIR spectra of **3**−**5**.

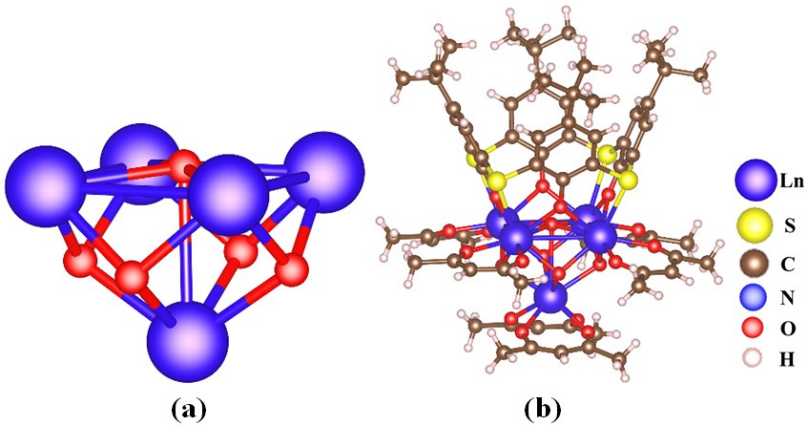

Fig. S2 (a) Pyramid core [$Ln_5(\mu_5\text{-}O)(\mu_3\text{-}O)_4$]; (b) Pentanuclear structure of H_4TC4A-support {Ln_5} cluster.

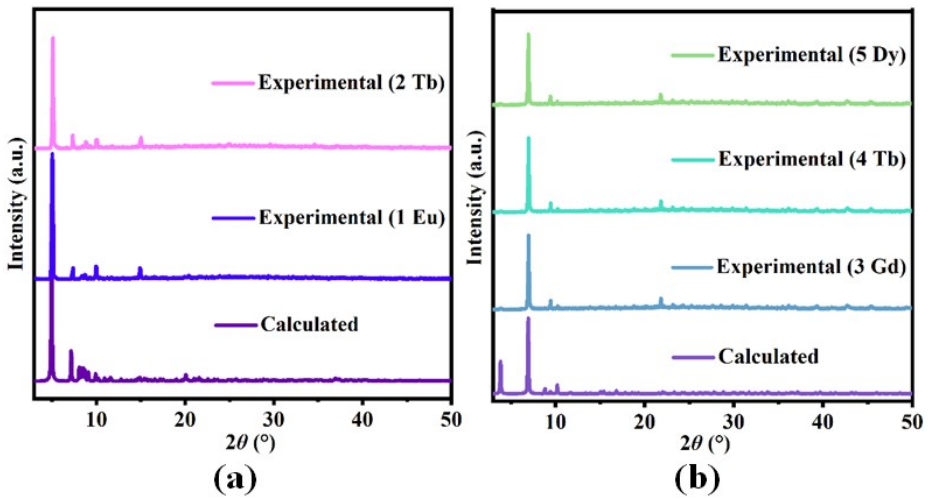

Fig. S3 Calculated and experimental XRD patterns for **1**−**5**. The purple curve is the calculated one obtained from single-crystal X-ray structure analysis.

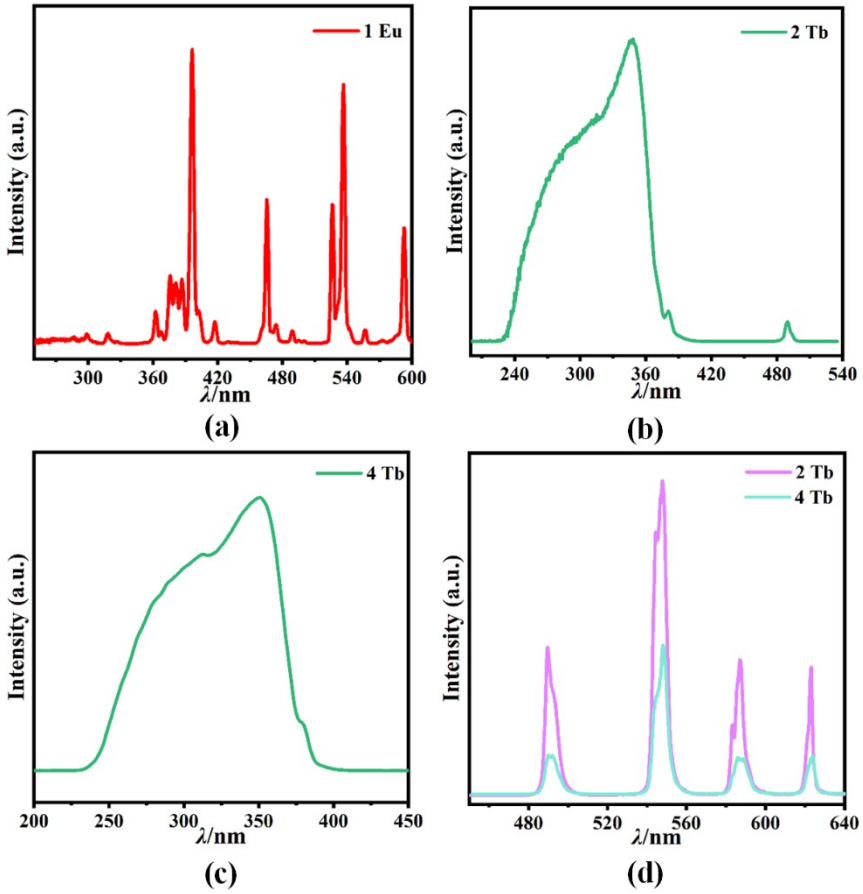

Fig. S4 (a) Excitation spectra of **1**; (b) Excitation spectra of **2**; (c) Excitation spectra of **4**; (d) the contrasting emission spectra of **2** and **4** in the solid state at room temperature.

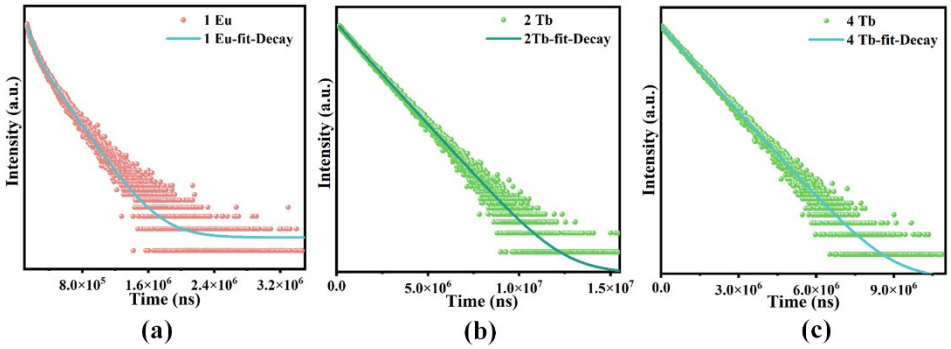

Fig. S5 Decay curves of **1** (a), **2** (b), and **4** (c).

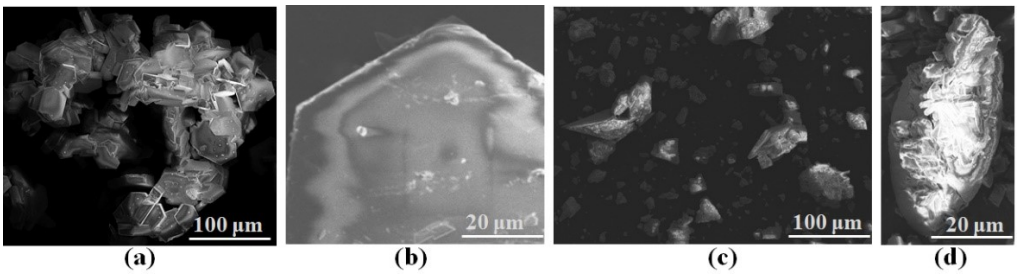

Fig. S6 SEM images of a piece of **2** crystals after soaking in water for two weeks (a) and (b); SEM images of a piece of **4** crystals after soaking in water for two weeks (c) and (d).

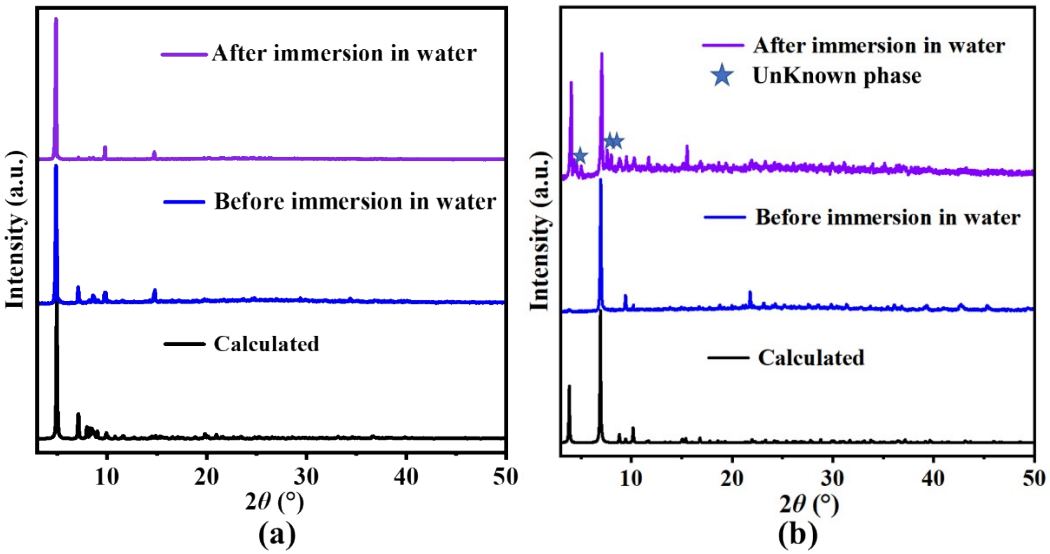

Fig. S7 (a) XRD patterns of **2** before and after soaking in water; (b) XRD patterns of **4** before and after soaking in water.

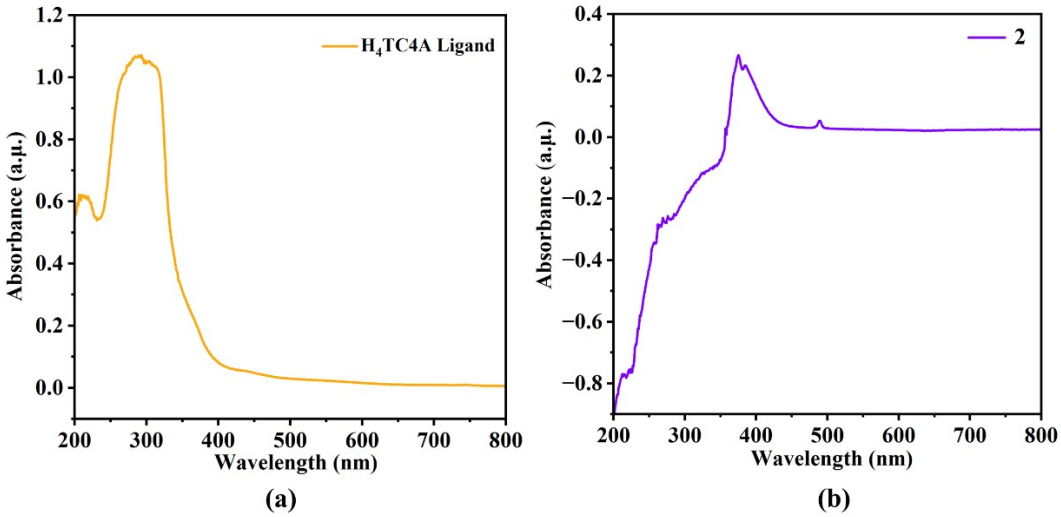

Fig. S8 (a) Absorption spectra of **H_4TC4A** ligand; (b) Absorption spectra of **2**.

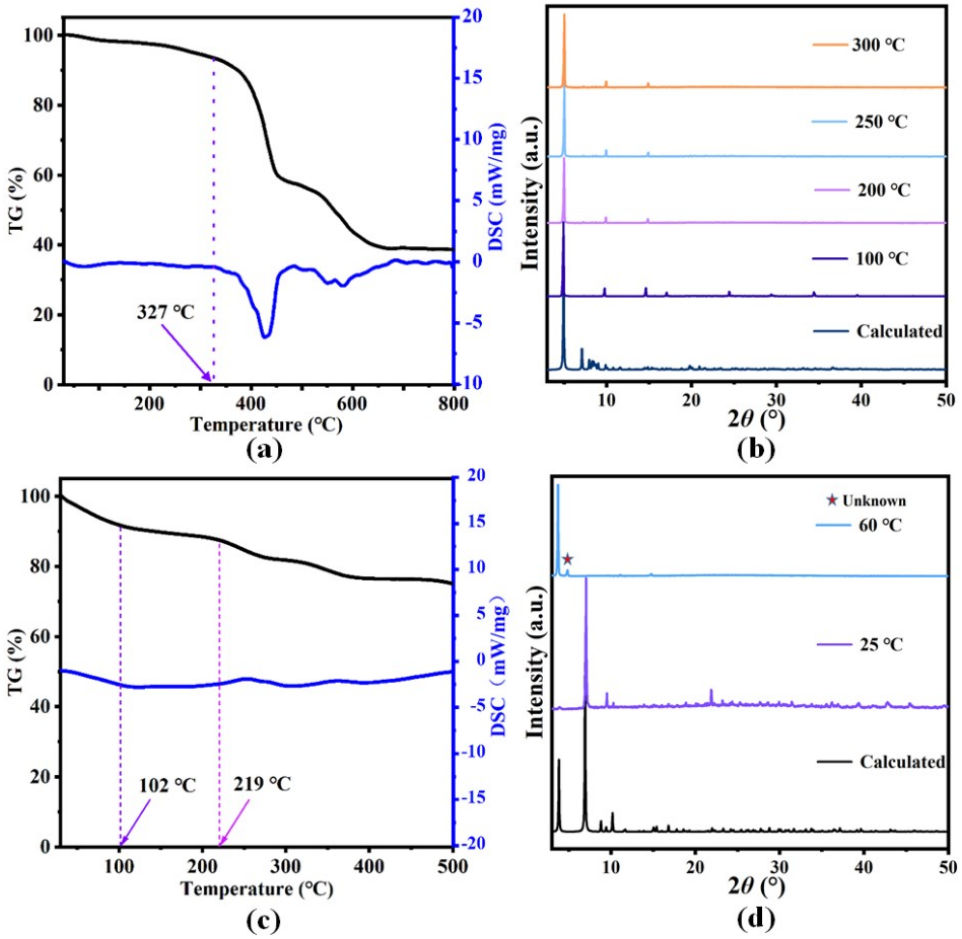

Fig. S9 (a) The thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) curve of **2**; (b) Powder XRD patterns of **2** at 100, 200, 250, and 300 °C; (c) The thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) curve of **4**; (d) Powder XRD patterns of **4** at 25 and 60 °C.