

Electronic Supplementary Information

Hydrothermal in situ bifunctional hydrazine-carboxylate ligands synthesis for creating 3D rare earth metal-organic frameworks

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Table S1 Crystal data and structural refinements for the **REMOFs**

Identification code	Nd@NO₃	Sm@NO₃	Eu@NO₃	Gd@NO₃	Tb@NO₃
CCDC no.	2504410	2504411	2504412	2504413	2504414
Formula	C ₁₆ H ₁₄ N ₅ O ₉ Nd	C ₁₆ H ₁₄ N ₅ O ₉ Sm	C ₁₆ H ₁₄ N ₅ O ₉ Eu	C ₁₆ H ₁₄ N ₅ O ₉ Gd	C ₁₆ H ₁₄ N ₅ O ₉ Tb
Formula weight	564.56	570.67	572.28	577.57	579.24
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Pccn</i>	<i>Pccn</i>	<i>Pccn</i>	<i>Pccn</i>	<i>Pccn</i>
<i>a</i> (Å)	10.964(2)	10.7439(4)	10.7995(4)	10.6935(11)	10.7616(3)
<i>b</i> (Å)	18.593(3)	18.6500(6)	18.5967(6)	18.5976(19)	18.5730(5)
<i>c</i> (Å)	9.6771(18)	9.6663(3)	9.6571(4)	9.6661(10)	9.6815(2)
<i>V</i> (Å ³)	1972.6(6)	1936.87(11)	1939.48(12)	1922.3(3)	1935.09(8)
<i>Z</i>	4	4	4	4	4
ρ_{calcd} (g cm ⁻³)	1.901	1.957	1.960	1.996	1.988
μ (mm ⁻¹)	2.694	3.094	3.296	3.513	3.717
<i>F</i> (000)	1108.0	1116.0	1120.0	1124.0	1128.0
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Reflections collected	8382	48752	36144	10381	44255
Independent reflections	1806	2783	2618	2206	2414
<i>R</i> _{int}	0.1571	0.0612	0.0884	0.0628	0.0555
Data/restraints/parameters	1806/49/159	2783/49/159	2618/49/159	2206/49/159	2414/49/159
GOF on <i>F</i> ² , <i>S</i>	1.022	1.121	1.120	1.064	1.065
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0560, 0.1194	0.0482, 0.1062	0.0555, 0.1117	0.0501, 0.1052	0.0369, 0.0889
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	1.03, -1.86	1.41, -1.26	1.35, -1.75	1.19, -1.48	1.12, -1.10

Table S1 (Continued)

Identification code	Dy@NO₃	Er@NO₃	Tm@NO₃	Yb@NO₃	Lu@NO₃
CCDC no.	2504415	2504416	2504417	2504418	2504419
Formula	C ₁₆ H ₁₄ N ₅ O ₉ Dy	C ₁₆ H ₁₄ N ₅ O ₉ Er	C ₁₆ H ₁₄ N ₅ O ₉ Tm	C ₁₆ H ₁₄ N ₅ O ₉ Yb	C ₁₆ H ₁₄ N ₅ O ₉ Lu
Formula weight	582.82	587.58	589.25	593.36	595.29
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Pccn</i>	<i>Pccn</i>	<i>Pccn</i>	<i>Pccn</i>	<i>Pccn</i>
<i>a</i> (Å)	10.7485(7)	10.7291(10)	10.5281(6)	10.5822(5)	10.4729(3)
<i>b</i> (Å)	18.5423(12)	18.4792(16)	18.5264(10)	18.4772(8)	18.4880(5)
<i>c</i> (Å)	9.6571(6)	9.6486(9)	9.6725(5)	9.6572(5)	9.6615(3)
<i>V</i> (Å ³)	1924.7(2)	1913.0(3)	1886.60(18)	1888.27(16)	1870.69(9)
<i>Z</i>	4	4	4	4	4
ρ_{calcd} (g cm ⁻³)	2.011	2.040	2.075	2.087	2.114
μ (mm ⁻¹)	3.945	4.450	4.767	5.017	5.342
<i>F</i> (000)	1132.0	1140.0	1144.0	1148.0	1152.0
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Reflections collected	11657	10402	38129	40145	47919
Independent reflections	2390	1954	2557	2351	3343
<i>R</i> _{int}	0.0694	0.0809	0.1293	0.0714	0.0538
Data/restraints/parameters	2390/49/159	1954/49/159	2557/49/159	2351/49/159	3343/49/159
GOF on <i>F</i> ² , <i>S</i>	1.055	1.047	1.059	1.179	1.075
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0381, 0.0840	0.0409, 0.1027	0.0463, 0.0979	0.0449, 0.0907	0.0522, 0.1098
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.99, -1.11	1.11, -1.71	1.23, -1.03	1.73, -2.74	1.79, -2.25

Table S1 (Continued)

Identification code	Tb@Cl	Tb@Br	Tb@I	TDH
CCDC no.	2504420	2504421	2504422	2540949
Formula	C ₁₆ H ₁₈ ClN ₄ O ₈ Tb	C ₁₆ H ₁₈ BrN ₄ O ₈ Tb	C ₁₆ H ₁₄ IN ₄ O ₆ Tb	C ₈ H ₁₀ N ₄ O ₂
Formula weight	588.71	633.17	644.13	194.20
Temperature (K)	296(2)	296(2)	296(2)	296(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>Pccn</i>	<i>Pccn</i>	<i>Pccn</i>	<i>P2₁/n</i>
<i>a</i> (Å)	11.3067(6)	11.5900(3)	11.0634(8)	10.1609(5)
<i>b</i> (Å)	18.2380(9)	18.1145(5)	18.3996(13)	3.8194(2)
<i>c</i> (Å)	9.6785(5)	9.7232(3)	9.7113(7)	12.1924(7)
	90	90	90	90
	90	90	90	113.042(2)
	90	90	90	90
<i>V</i> (Å ³)	1995.82(18)	2041.36(10)	1976.9(2)	435.42(4)
<i>Z</i>	4	4	4	2
ρ_{calcd} (g cm ⁻³)	1.959	2.060	2.164	1.481
μ (mm ⁻¹)	3.730	5.474	5.179	0.111
<i>F</i> (000)	1152.0	1224.0	1216.0	204
λ (Å)	0.71073	0.71073	0.71073	0.71073
Reflections collected	45148	52025	45101	11279
Independent reflections	2587	2756	3030	1081
<i>R</i> _{int}	0.0772	0.0383	0.0661	0.0467
Data/restraints/parameters	2587/12/152	2756/6/152	3030/12/142	1081/2/72
GOF on <i>F</i> ² , <i>S</i>	1.147	1.137	1.059	1.139
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0384, 0.0822	0.0595, 0.1626	0.0408, 0.0933	0.0592, 0.1491
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.95, -1.29	1.92, -3.81	1.16, -1.40	0.30, -0.29

Table S2 The selected bond lengths (Å) and bond angles (°) for REMOFs

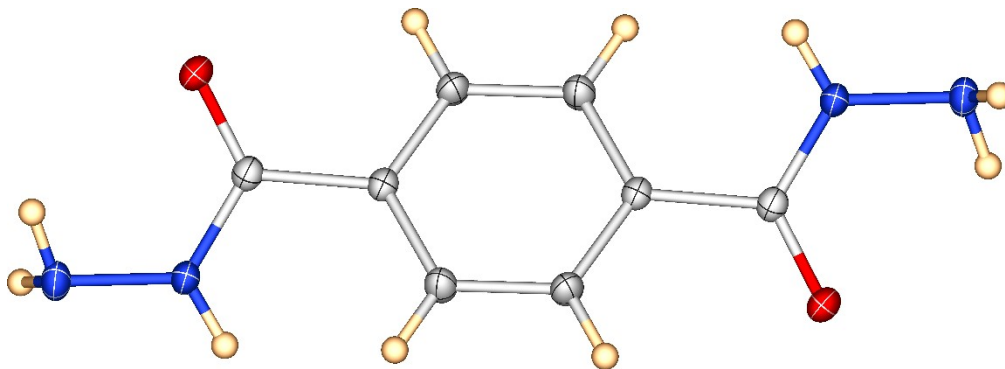
	Nd@NO ₃	Sm@NO ₃	Eu@NO ₃	Gd@NO ₃	Tb@NO ₃	Dy@NO ₃	Er@NO ₃	Tm@NO ₃	Yb@NO ₃	Lu@NO ₃
RE1–O1	2.452(7)	2.431(5)	2.420(5)	2.408(6)	2.403(4)	2.395(4)	2.368(5)	2.364(5)	2.361(5)	2.358(6)
RE1–O2 ⁱⁱ	2.345(7)	2.305(4)	2.306(5)	2.286(5)	2.279(4)	2.270(4)	2.251(5)	2.237(5)	2.232(4)	2.216(5)
RE1–O3 ^{iv}	2.413(8)	2.369(5)	2.356(5)	2.334(6)	2.328(4)	2.309(4)	2.279(5)	2.276(5)	2.255(5)	2.248(6)
RE1–N1	2.667(9)	2.614(7)	2.616(7)	2.566(8)	2.584(6)	2.569(6)	2.532(7)	2.510(8)	2.505(7)	2.483(8)
O1–RE1–O1 ⁱ	134.8(4)	134.7(2)	135.5(2)	134.9(3)	134.80(19)	134.83(19)	135.3(2)	134.5(3)	134.7(2)	134.2(3)
O1–RE1–N1 ⁱ	142.2(3)	141.40(18)	140.60(18)	140.6(2)	140.19(15)	139.88(15)	139.26(18)	138.7(2)	138.49(19)	138.6(2)
O1–RE1–N1	60.9(3)	61.24(18)	61.51(18)	61.9(2)	62.36(15)	62.65(15)	62.99(19)	63.8(2)	63.87(19)	64.1(2)
O2 ⁱⁱ –RE1–O1	80.4(3)	80.28(17)	79.78(18)	80.1(2)	79.92(14)	79.56(14)	79.10(17)	79.3(2)	78.81(18)	79.2(2)
O2 ⁱⁱⁱ –RE1–O1	135.8(3)	135.35(18)	135.15(19)	135.2(2)	135.29(15)	135.63(15)	135.53(19)	136.1(2)	136.4(2)	136.4(2)
O2 ⁱⁱ –RE1–O2 ⁱⁱⁱ	88.4(4)	90.3(3)	90.8(3)	90.7(3)	91.6(2)	92.0(2)	92.8(3)	92.5(3)	92.9(3)	92.9(3)
O2 ⁱⁱ –RE1–O3 ^{iv}	145.8(3)	148.0(2)	148.8(2)	148.6(2)	149.49(16)	149.29(16)	149.8(2)	86.1(2)	86.5(2)	86.4(2)
O2 ⁱⁱ –RE1–O3 ^v	83.1(3)	83.2(2)	83.9(2)	84.2(2)	84.48(17)	84.94(16)	85.1(2)	149.3(2)	149.7(2)	149.6(2)
O2 ⁱⁱ –RE1–N1	72.1(3)	73.9(2)	74.5(2)	74.5(2)	74.95(17)	74.89(17)	75.4(2)	75.4(2)	75.3(2)	75.4(3)
O2 ⁱⁱⁱ –RE1–N1	75.0(3)	74.19(19)	73.7(2)	73.4(2)	73.01(15)	73.06(16)	72.62(19)	72.4(2)	72.6(2)	72.3(2)
O3 ^v –RE1–O1	75.3(3)	74.46(18)	74.18(19)	74.4(2)	73.84(15)	73.87(16)	73.7(2)	73.7(2)	73.19(19)	73.3(2)
O3 ^{iv} –RE1–O1	82.9(3)	82.50(17)	82.45(19)	81.9(2)	81.74(15)	81.45(16)	81.5(2)	80.7(2)	80.89(18)	80.5(2)
O3 ^{iv} –RE1–O3 ^v	120.9(4)	117.6(3)	115.5(3)	115.3(3)	113.4(2)	112.5(2)	111.3(3)	110.1(3)	108.9(3)	109.0(3)
O3 ^v –RE1–N1	132.1(3)	132.57(18)	133.16(19)	133.6(2)	133.94(15)	134.43(16)	134.91(19)	135.9(2)	135.67(19)	136.0(2)
O3 ^{iv} –RE1–N1	73.7(3)	74.19(19)	74.5(2)	74.4(2)	74.98(17)	75.00(17)	75.2(2)	75.1(2)	75.6(2)	75.5(2)
N1–RE1–N1 ⁱ	133.5(4)	134.1(3)	134.0(3)	133.7(4)	133.4(3)	133.2(3)	132.9(4)	132.6(4)	132.8(3)	132.4(4)

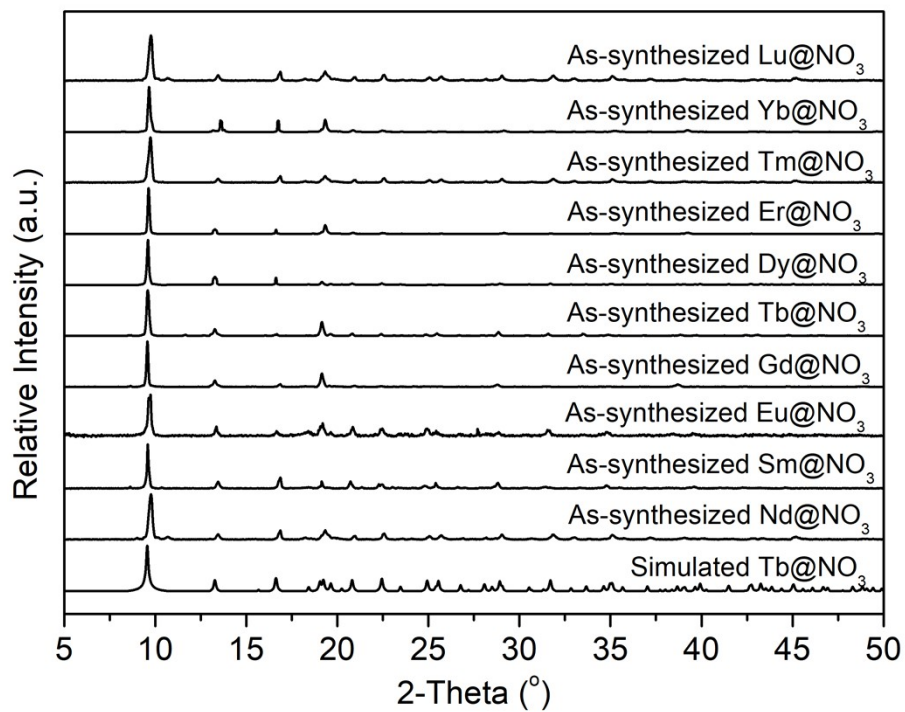
Symmetry codes: (i) $-x + 1/2, -y + 3/2, z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x - 1/2, y + 1/2, -z + 1$; (iv) $-x + 1, y + 1/2, -z + 3/2$; (v) $x - 1/2, -y + 1, -z + 3/2$.

Table S2 (Continued)

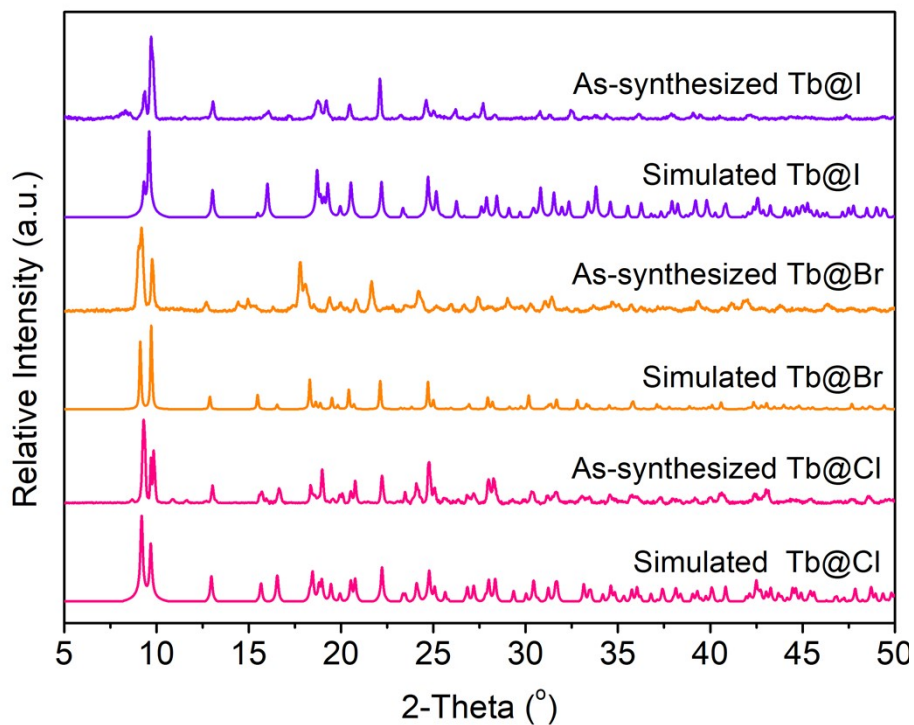
	Tb@Cl	Tb@Br	Tb@I
RE1–O1	2.405(4)	2.410(5)	2.404(4)
RE1–O2 ⁱⁱ	2.285(4)	2.288(5)	2.279(4)
RE1–O3 ^{iv}	2.327(4)	2.325(5)	2.309(5)
RE1–N1	2.569(5)	2.572(7)	2.570(7)
O1–RE1–O1 ⁱ	135.28(18)	136.0(2)	135.7(2)
O1 ⁱ –RE1–N1	140.22(14)	140.1(2)	139.79(17)
O1–RE1–N1	62.49(14)	62.43(19)	62.40(17)
O2 ⁱⁱ –RE1–O1	79.68(13)	79.58(18)	79.13(17)
O2 ⁱⁱ –RE1–O1 ⁱ	134.86(15)	134.31(18)	135.21(18)
O2 ⁱⁱ –RE1–O2 ⁱⁱⁱ	92.5(2)	92.6(3)	92.6(2)
O2 ⁱⁱ –RE1–O3 ^v	84.01(15)	84.4(2)	85.32(18)
O2 ⁱⁱⁱ –RE1–O3 ^v	149.63(16)	149.9(2)	149.64(19)
O2 ⁱⁱ –RE1–N1	75.13(16)	75.5(2)	75.17(19)
O2 ⁱⁱⁱ –RE1–N1	72.50(15)	72.0(2)	72.90(18)
O3 ^v –RE1–O1	74.25(15)	74.64(18)	74.16(18)
O3 ^{iv} –RE1–O1	81.63(15)	81.3(2)	81.17(17)
O3 ^{iv} –RE1–O3 ^v	113.5(2)	112.4(3)	111.1(3)
O3 ^v –RE1–N1	134.39(15)	135.0(2)	134.76(18)
O3 ^{iv} –RE1–N1	75.05(16)	75.2(2)	75.29(19)
N1–RE1–N ¹ⁱ	132.5(2)	132.2(3)	133.1(3)

Symmetry codes: (i) $-x + 1/2, -y + 3/2, z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x - 1/2, y + 1/2, -z + 1$; (iv) $-x + 1, y + 1/2, -z + 3/2$; (v) $x - 1/2, -y + 1, -z + 3/2$.

**Fig. S1** Crystal structure of the TDH compound.



(a)



(b)

Fig. S2 Comparison of the simulated and as-synthesized PXRD patterns for (a) **RE@NO₃** and (b) **Tb@X** (X = Cl, Br, I).

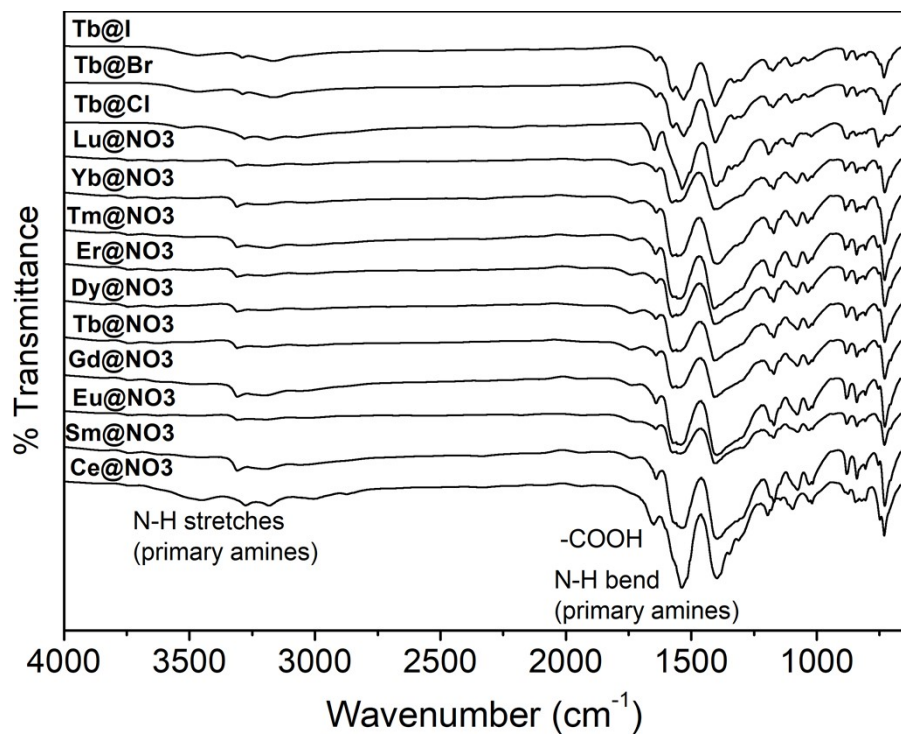


Fig. S3 IR spectra for RE@NO_3 and Tb@X ($X = \text{Cl}, \text{Br}, \text{I}$).

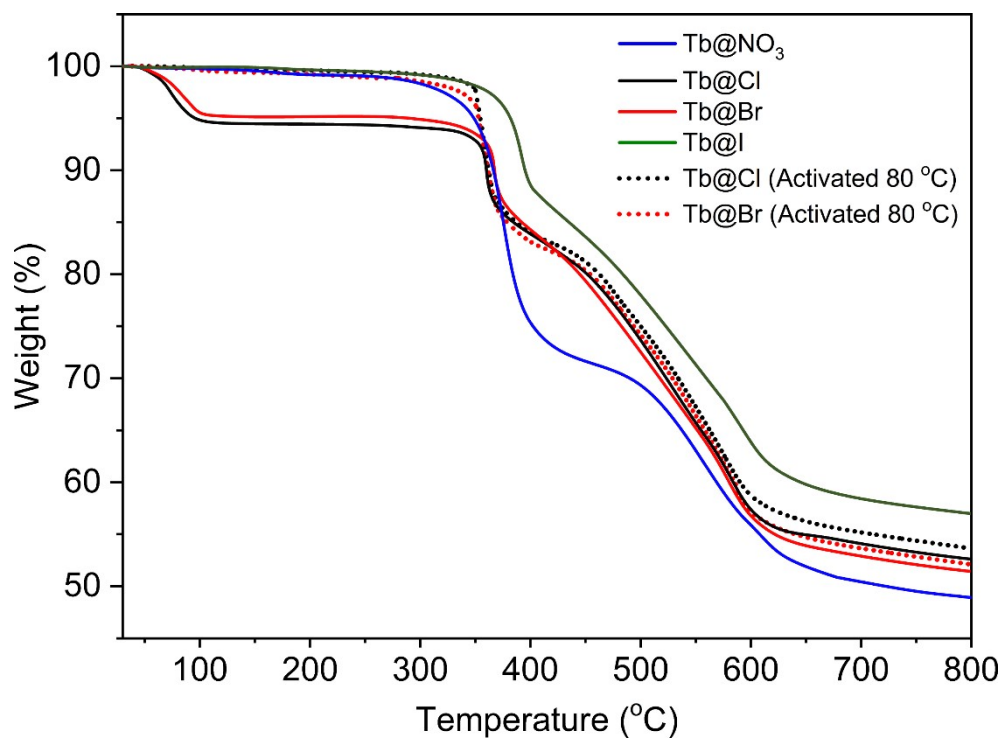


Fig. S4 TGA curves for the following Tb-based compounds: Tb@NO_3 , Tb@Cl , Tb@Br , Tb@I , activated Tb@Cl , and activated Tb@Br .

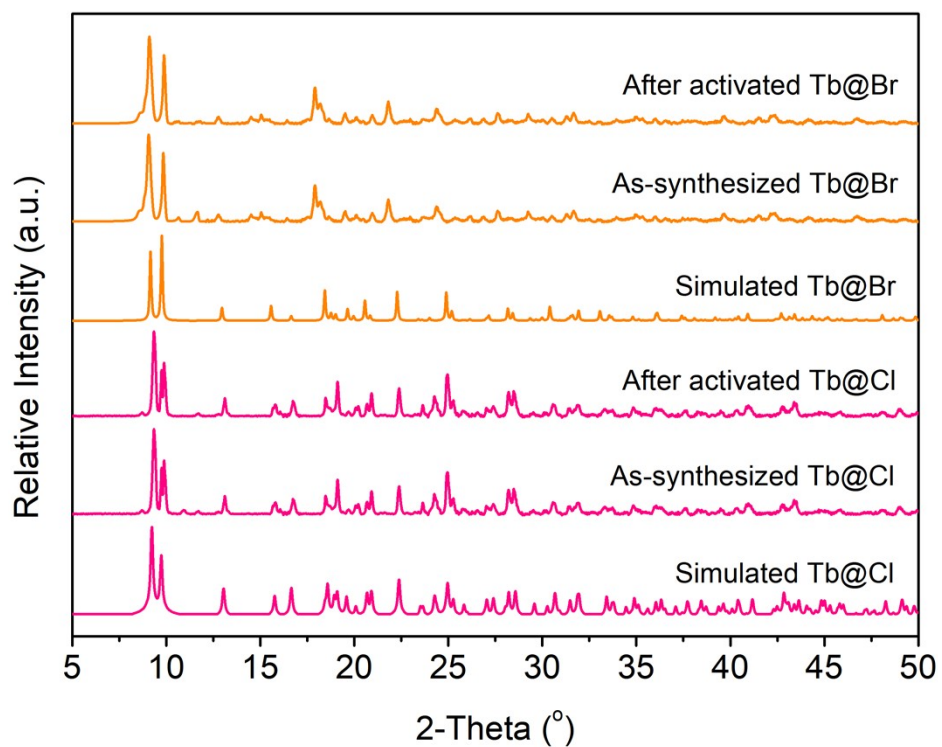


Fig. S5 The simulated PXRD patterns, as-synthesized and after thermal activation of **Tb@Cl** and **Tb@Br**

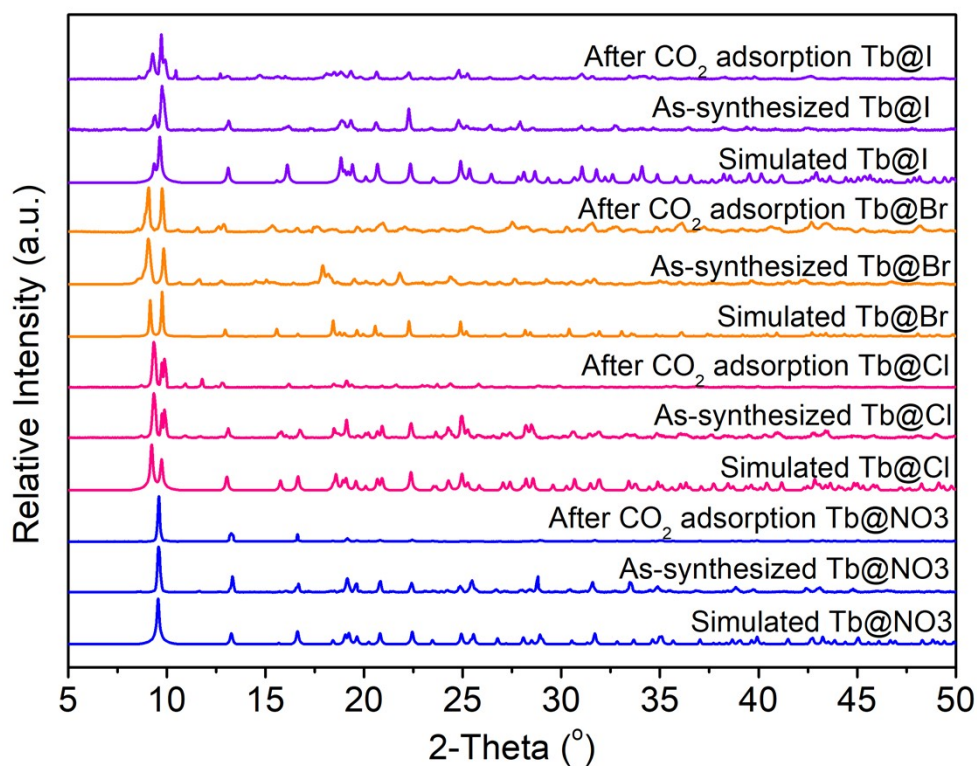


Fig. S6 PXRD patterns before and after gas sorption of **Tb@NO₃**, **Tb@Cl**, **Tb@Br**, and **Tb@I**.

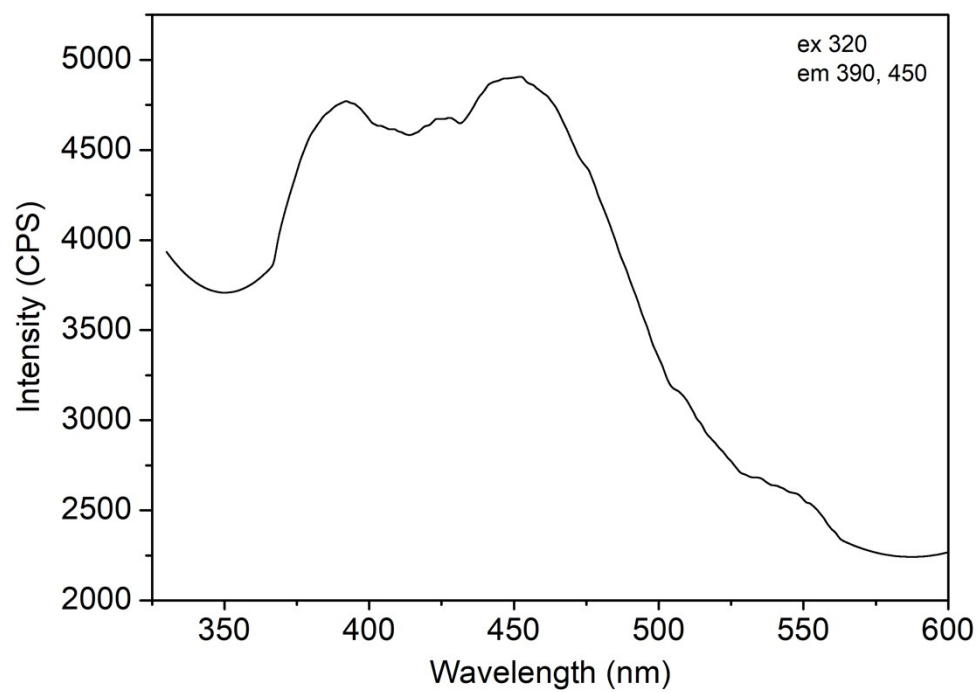


Fig. S7 The luminescence spectrum of the free TDH ligand in solid-state ($\lambda_{\text{excitation}} = 320$ nm).