Electronic Supplementary Information

Four series of lanthanide coordination polymers based on the tetrabromobenzene-1,4-dicarboxylate ligand: structural diversity and multifunctional properties

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Table S1 Crystal data and structural refinements for compounds in series $\mathbf{1}_{Ln}$ and $\mathbf{2}_{Ln}$.

Identification code (CCDC no.)	$\mathbf{1}_{Ce}$ (1940034)	$\mathbf{1}_{Pr}$ (1940036)	$\mathbf{1}_{Nd}$ (1940037)	$\mathbf{1}_{Sm}$ (1940038)
Formula	$C_{15}H_{12}Br_6CeO_9$	$C_{15}H_{12}Br_6O_9Pr$	$C_{15}H_{12}Br_6NdO_9$	$C_{15}H_{12}Br_6O_9Sm$
Formula weigh	955.83	956.56	959.95	966.01
Temperature (K)	296(2)	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	20.482(5)	20.4250(15)	20.3900(4)	20.281(3)
b (Å)	10.656(3)	10.6255(7)	10.6244(2)	10.5811(16)
c (Å)	22.090(6)	22.0706(15)	22.1112(5)	22.039(4)
β (°)	94.658(9)	94.676(3)	94.8930(10)	94.821(5)
V (Å)	4806(2)	4773.9(6)	4772.53(17)	4712.7(13)
Z	8	8	8	8
ρ_{calcd} (g cm^{-3})	2.642	2.662	2.672	2.723
GOF on F^2, *S*	1.041	1.036	1.122	1.062
R_1, $wR_2[I > 2\sigma(I)]$	0.0221, 0.0435	0.0231, 0.0459	0.0211, 0.0450	0.0261, 0.0499
Δ_{pmax}, Δ_{pmin} (e Å^{-3})	0.56, −0.59	0.65, −0.56	0.51, − 0.88	0.94, −0.65
Identification code (CCDC no.)	$\mathbf{1}_{Eu}$ (1940039)	$\mathbf{1}_{Gd}$ (1940040)	$\mathbf{1}_{Tb}$ (1940041)	$\mathbf{1}_{Dy}$ (2130091)
Formula	$C_{15}H_{12}Br_6EuO_9$	$C_{15}H_{12}Br_6GdO_9$	$C_{15}H_{12}Br_6O_9Tb$	$C_{15}H_{12}Br_6DyO_9$
Formula weigh	967.62	972.90	974.58	978.21
Temperature (K)	296(2)	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	20.2349(12)	20.2230(11)	20.1546(15)	20.140(3)
b (Å)	10.5715(6)	10.5573(6)	10.5416(8)	10.5370(11)
c (Å)	22.0267(15)	22.0212(12)	22.0160(17)	21.997(3)
β (°)	94.846(2)	94.884(2)	94.940(3)	94.896(5)
V (Å)	4695.0(5)	4684.5(4)	4660.2(6)	4650.9(10)
Z	8	8	8	8
ρ_{calcd} (g cm^{-3})	2.738	2.759	2.778	2.794
GOF on F^2, *S*	1.031	1.040	1.019	1.056
R_1, $wR_2[I > 2\sigma(I)]$	0.0237, 0.0470	0.0207, 0.0417	0.0279, 0.0480	0.0250, 0.0541
Δ_{pmax}, Δ_{pmin} (e Å^{-3})	0.89, −0.66	0.69, −0.55	0.69, −0.68	0.82, −0.76
Identification code (CCDC no.)	$\mathbf{2}_{Ce}$ (1940063)	$\mathbf{2}_{Pr}$ (1940047)	$\mathbf{2}_{Nd}$ (1940048)	$\mathbf{2}_{Sm}$ (1940091)
Formula	$C_{20}H_{16}Br_8Ce_2N_2O_{18}$	$C_{20}H_{16}Br_8N_2O_{18}Pr_2$	$C_{20}H_{16}Br_8N_2Nd_2O_{18}$	$C_{20}H_{16}Br_8N_2O_{18}Sm_2$
Formula weigh	1491.87	1493.45	1500.11	1512.27
Temperature (K)	296(2)	296(2)	296(2)	296(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a (Å)	10.4200(10)	10.3657(7)	10.3427(12)	10.2732(7)
b (Å)	12.6555(12)	12.6197(8)	12.6185(16)	12.5854(7)
c (Å)	16.2502(18)	16.2172(9)	16.2191(18)	16.1710(9)
α (°)	77.141(4)	77.345(2)	77.419(4)	77.559(2)
β (°)	72.822(3)	72.943(2)	72.879(4)	72.835(2)
γ (°)	68.507(3)	68.733(2)	68.729(5)	68.6920(10)
V (Å)	1889.1(3)	1874.8(2)	1870.4(4)	1847.30(19)
Z	2	2	2	2
ρ_{calcd} (g cm^{-3})	2.623	2.646	2.664	2.719
GOF on F^2, *S*	1.066	1.047	1.039	1.019
R_1, $wR_2[I > 2\sigma(I)]$	0.0361, 0.0826	0.0284, 0.0565	0.0358, 0.0915	0.0349, 0.0751
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.48, −0.84	0.99, −0.86	1.60, −1.76	0.88, −1.07

Table S2 Crystal data and structural refinements for compounds in series $\mathbf{3_{Ln}}$ and $\mathbf{4_{Ln}}$.

Identification code (CCDC no.)	$\mathbf{3_{Gd}}$ (1940055)	$\mathbf{3_{Tb}}$ (1940056)	$\mathbf{3_{Dy}}$ (1940057)
Formula	$C_9H_4Br_4GdNO_8$	$C_9H_4Br_4NO_8Tb$	$C_9H_4Br_4DyNO_8$
Formula weigh	730.98	732.69	736.23
Temperature (K)	296(2)	296(2)	296(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
a (Å)	9.165(2)	9.1698(3)	9.1555(7)
b (Å)	9.216(2)	9.1909(3)	9.1608(7)
c (Å)	10.039(2)	10.0385(2)	10.0141(8)
α (°)	104.271(8)	104.2990(10)	104.319(2)
β (°)	93.426(8)	93.4920(10)	93.375(3)
γ (°)	99.634(9)	99.6490(10)	99.769(3)
V (Å)	805.6(3)	803.58(4)	797.52(11)
Z	2	2	2
ρ_{calcd} (g cm^{-3})	3.013	3.028	3.066
GOF on F^2, *S*	1.025	1.069	1.178
R_1, $wR_2[I > 2\sigma(I)]$	0.0242, 0.0496	0.0246, 0.0472	0.0321, 0.0842
$\Delta\rho_{max}$, $\Delta_{\rho min}$ (e Å^{-3})	1.20, −1.02	1.11, −0.81	1.63, −1.12
Compound (CCDC No.)	$\mathbf{4_{Gd}}$ (1940050)	$\mathbf{4_{Tb}}$ (1940051)	$\mathbf{4_{Dy}}$ (1940054)
Formula	$C_{26.7}H_{15.4}Br_{12}Gd_2O_{17}$	$C_{26.7}H_{15.4}Br_{12}O_{17}Tb_2$	$C_{26.7}H_{15.4}Br_{12}Dy_2O_{17}$
Formula weigh	1881.49	1884.85	1891.99
Temperature (K)	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	11.587(5)	11.634(6)	11.550(4)
b (Å)	18.133(7)	18.038(8)	17.970(5)
c (Å)	21.632(9)	21.569(12)	21.577(6)
β (°)	97.686(15)	98.005(19)	97.910(10)
V (Å)	4504(3)	4482(4)	4436(2)
Z	4	4	4
ρ_{calcd} (g cm^{-3})	2.775	2.793	2.833
GOF on F^2, *S*	1.012	1.062	1.066
R_1, $wR_2[I > 2\sigma(I)]$	0.0326, 0.0619	0.0322, 0.0614	0.0435, 0.0772
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.29, −0.82	1.22, −0.63	1.39, −0.95

Table S3 Selected bond lengths (Å) and bond angles (°) for $\mathbf{1}_{Ln}$.

	$\mathbf{1}_{Ce}$	$\mathbf{2}_{Pr}$	$\mathbf{3}_{Nd}$	$\mathbf{4}_{Sm}$	$\mathbf{5}_{Eu}$	$\mathbf{6}_{Gd}$	$\mathbf{7}_{Tb}$	$\mathbf{8}_{Dy}$
Ln1−O1	2.382(2)	2.362(2)	2.3619(18)	2.337(3)	2.334(3)	2.327(2)	2.312(3)	2.308(2)
Ln1−O3^{i}	2.551(2)	2.533(2)	2.5222(19)	2.490(3)	2.479(3)	2.478(2)	2.457(3)	2.449(2)
Ln1−O4^{i}	2.616(2)	2.599(2)	2.5792(18)	2.548(3)	2.537(3)	2.520(2)	2.504(3)	2.500(2)
Ln1−O5	2.484(2)	2.464(2)	2.4513(18)	2.420(3)	2.406(3)	2.396(2)	2.378(3)	2.364(2)
Ln1−O6^{ii}	2.378(2)	2.363(3)	2.3509(19)	2.317(3)	2.306(3)	2.291(2)	2.275(3)	2.261(2)
Ln1−O7	2.487(3)	2.471(3)	2.457(2)	2.418(3)	2.404(3)	2.389(3)	2.372(3)	2.359(3)
Ln1−O8	2.537(2)	2.517(3)	2.499(2)	2.466(3)	2.451(3)	2.441(2)	2.421(3)	2.414(3)
Ln1−O9	2.482(2)	2.465(3)	2.446(2)	2.412(3)	2.403(3)	2.389(2)	2.371(3)	2.364(3)
O1−Ln1−O3^{i}	155.50(9)	155.35(9)	155.05(7)	154.47(10)	154.27(9)	153.84(8)	153.71(11)	153.40(9)
O1−Ln1−O4^{i}	125.36(8)	125.25(9)	125.14(7)	125.22(10)	125.25(10)	125.16(8)	125.26(11)	125.12(9)
O1−Ln1−O5	134.55(9)	134.55(9)	134.79(7)	135.18(10)	135.29(9)	135.57(8)	135.76(11)	135.82(9)
O1−Ln1−O7	74.60(9)	74.39(10)	74.04(7)	73.99(11)	74.01(10)	73.91(9)	73.85(12)	73.78(9)
O1−Ln1−O8	73.16(9)	73.00(9)	73.10(7)	72.90(11)	72.80(10)	72.99(9)	72.83(12)	72.98(9)
O1−Ln1−O9	78.29(9)	78.34(10)	78.05(8)	77.81(11)	77.61(10)	77.28(9)	77.26(12)	76.97(9)
O3^{i}−Ln1−O4^{i}	50.19(7)	50.72(8)	51.09(6)	51.62(10)	51.96(9)	52.05(8)	52.34(10)	52.55(8)
O5−Ln1−O3^{i}	69.94(8)	70.08(8)	70.13(7)	70.29(10)	70.36(9)	70.51(8)	70.42(11)	70.66(9)
O5−Ln1−O4^{i}	78.88(8)	78.79(8)	78.65(6)	78.34(10)	78.27(9)	78.31(8)	78.00(11)	78.18(8)
O5−Ln1−O7	78.71(9)	78.75(9)	79.16(7)	79.38(11)	79.38(10)	79.65(9)	79.67(12)	79.91(9)
O5−Ln1−O8	72.95(8)	72.99(9)	72.90(7)	72.82(10)	72.82(9)	72.67(8)	72.79(11)	72.53(9)
O6^{ii}−Ln1−O1	94.27(9)	94.15(9)	93.60(7)	92.66(11)	92.32(10)	91.84(9)	91.43(11)	91.14(9)
O6^{ii}−Ln1−O3^{i}	74.61(8)	74.45(8)	74.73(6)	75.07(10)	74.99(9)	75.34(8)	75.36(11)	75.53(8)
O6^{ii}−Ln1−O4^{i}	119.93(8)	120.42(8)	121.15(6)	122.24(10)	122.50(9)	123.04(8)	123.32(11)	123.80(8)
O6^{ii}−Ln1−O5	105.49(8)	105.46(9)	105.60(7)	105.73(11)	105.88(10)	105.84(9)	106.17(11)	106.05(9)
O6^{ii}−Ln1−O7	166.86(9)	166.37(10)	165.46(7)	164.23(11)	163.87(10)	163.14(9)	162.70(12)	162.26(10)
O6^{ii}−Ln1−O8	75.44(9)	75.46(9)	75.38(7)	75.55(11)	75.72(10)	75.49 9)	75.85(12)	75.63(9)
O6^{ii}−Ln1−O9	81.84(9)	81.90(10)	82.11(8)	82.25(12)	82.39(11)	82.60(9)	82.39(13)	82.77(10)
O7−Ln1−O3^{i}	118.34(9)	118.96(9)	119.62(7)	120.49(11)	120.93(10)	121.31(9)	121.74(12)	122.02(9)
O7−Ln1−O4^{i}	72.91(9)	72.94(9)	73.04(7)	73.18(11)	73.27(10)	73.45(9)	73.56(11)	73.50(9)
O7−Ln1−O8	94.35(9)	93.83(10)	93.37(7)	92.20(12)	91.77(11)	91.44(9)	90.84(13)	90.75(10)
O8−Ln1−O3^{i}	122.91(8)	122.97(8)	123.01(7)	123.43(10)	123.47(10)	123.61(8)	123.72(11)	123.76(9)
O8−Ln1−O4^{i}	150.93(8)	150.74(8)	150.37(7)	149.66(10)	149.49(9)	149.30(8)	148.94(11)	148.80(9)
O9−Ln1−O3^{i}	78.55(9)	78.45(9)	78.54(7)	78.39(11)	78.56(10)	78.50(9)	78.50(12)	78.56(10)
O9−Ln1−O4^{i}	67.38(8)	67.55(9)	67.77(7)	68.21(10)	68.27(9)	68.40(8)	68.59(11)	68.62(9)
O9−Ln1−O5	143.92(8)	143.90(9)	143.95(7)	143.94(11)	144.00(10)	144.13(9)	143.97(11)	144.21(9)
O9−Ln1−O7	102.23(10)	102.48(10)	102.26(8)	102.54(12)	102.46(11)	102.44(10)	102.61(14)	102.31(10)
O9−Ln1−O8	141.67(9)	141.68(9)	141.81(7)	141.99(11)	142.05(10)	142.09(9)	142.20(12)	142.27(9)

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

Table S4 Hydrogen bond geometry (Å, °) for $\mathbf{1}_{\mathbf{Ln}}$.

	[D−H···A]	*d*[D−H]	*d*[H···A]	*d*[D···A]	∠[D−H···A]
$\mathbf{1}_{\mathbf{Ce}}$	O7−H7···O2	0.81(1)	2.57(4)	3.062(4)	121(4)
	O7−H7···O4^{i}	0.81(1)	2.14(2)	2.904(4)	156(4)
	O8−H8···O3^{ii}	0.82(1)	1.92(1)	2.728(4)	173(5)
	O9−H9···O2^{iii}	0.82(1)	1.84(1)	2.643(4)	168(4)
$\mathbf{1}_{\mathbf{Pr}}$	O7−H7···O2	0.82(1)	2.56(4)	3.033(4)	119(4)
	O7−H7···O4^{i}	0.82(1)	2.15(2)	2.922(4)	158(5)
	O8−H8···O3^{ii}	0.82(1)	1.91(1)	2.731(4)	178(5)
	O9−H9···O2^{iii}	0.82(1)	1.85(2)	2.645(4)	164(5)
$\mathbf{1}_{\mathbf{Nd}}$	O7−H7···O2	0.81(1)	2.39(4)	2.976(3)	129(4)
	O7−H7···O4^{iii}	0.81(1)	2.26(3)	2.975(3)	147(4)
	O8−H8···O3^{i}	0.82(1)	1.91(1)	2.727(3)	175(4)
	O9−H9···O2^{ii}	0.82(1)	1.84(1)	2.645(3)	168(4)
$\mathbf{1}_{\mathbf{Sm}}$	O7−H7···O2	0.81(1)	2.43(5)	2.928(5)	120(4)
	O7−H7···O4^{iii}	0.81(1)	2.26(2)	3.022(5)	157(5)
	O8−H8···O3^{i}	0.82(1)	1.93(2)	2.736(5)	171(6)
	O9−H9···O2^{ii}	0.82(1)	1.84(2)	2.647(5)	167(6)
$\mathbf{1}_{\mathbf{Eu}}$	O7−H7···O2	0.82(1)	2.35(5)	2.904(4)	126(5)
	O7−H7···O4^{i}	0.82(1)	2.31(3)	3.050(4)	151(5)
	O8−H8···O3^{ii}	0.82(1)	1.91(1)	2.732(4)	176(5)
	O9−H9···O2^{iii}	0.82(1)	1.85(2)	2.648(4)	165(6)
$\mathbf{1}_{\mathbf{Gd}}$	O7−H7···O2	0.82(1)	2.22(4)	2.877(4)	138(5)
	O7−H7···O4^{iii}	0.82(1)	2.43(4)	3.082(4)	137(5)
	O8−H8···O3^{i}	0.82(1)	1.91(1)	2.728(4)	175(5)
	O9−H9···O2^{ii}	0.82(1)	1.85(1)	2.655(4)	167(4)
$\mathbf{1}_{\mathbf{Tb}}$	O7−H7···O2	0.82(1)	2.24(5)	2.850(5)	132(6)
	O7−H7···O4^{iii}	0.82(1)	2.42(4)	3.125(5)	144(6)
	O8−H8···O3i	0.82(1)	1.93(1)	2.735(5)	173(6)
	O9−H9···O2ii	0.82(1)	1.85(2)	2.660(5)	169(6)
$\mathbf{1}_{\mathbf{Dy}}$	O7−H7···O2	0.82(1)	2.22(5)	2.834(4)	131(5)
	O7−H7···O4^{i}	0.82(1)	2.44(4)	3.131(4)	143(5)
	O8−H8···O3^{ii}	0.82(1)	1.91(1)	2.731(4)	175(5)
	O9−H9···O2^{iii}	0.82(1)	1.88(2)	2.663(4)	160(4)

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

Table S5 Selected bond lengths (Å) and bond angles (°) for $\mathbf{2_{Ln}}$.

	$\mathbf{2_{Ce}}$	$\mathbf{2_{Pr}}$	$\mathbf{2_{Nd}}$	$\mathbf{2_{Sm}}$
Ln1−O1	2.382(4)	2.363(3)	2.347(4)	2.340(4)
Ln1−O3	2.393(4)	2.376(3)	2.372(4)	2.342(5)
Ln1−O5^{i}	2.383(4)	2.361(3)	2.347(4)	2.324(5)
Ln1−O7	2.665(5)	2.647(3)	2.626(4)	2.617(5)
Ln1−O8	2.602(5)	2.578(3)	2.561(4)	2.534(5)
Ln1−O10	2.510(5)	2.494(3)	2.490(4)	2.450(5)
Ln1−O11	2.531(6)	2.514(4)	2.503(5)	2.473(5)
Ln1−O13^{i}	2.422(4)	2.400(3)	2.390(3)	2.372(4)
Ln2−O2	2.386(4)	2.365(3)	2.351(4)	2.331(5)
Ln2−O4	2.412(4)	2.389(3)	2.373(4)	2.357(4)
Ln2−O6^{ii}	2.409(4)	2.389(3)	2.382(4)	2.368(5)
Ln2−O12	2.371(4)	2.351(3)	2.338(4)	2.315(5)
Ln2−O14	2.586(5)	2.560(3)	2.546(4)	2.518(5)
Ln2−O15	2.671(5)	2.653(3)	2.632(4)	2.617(5)
Ln2−O17	2.546(6)	2.535(4)	2.522(5)	2.486(5)
Ln2−O18	2.526(5)	2.504(3)	2.486(4)	2.456(5)
O1−Ln1−O7	78.34(15)	77.85(10)	77.47(14)	77.43(16)
O1−Ln1−O8	126.16(15)	125.97(10)	126.15(13)	126.74(16)
O1−Ln1−O10	76.04(16)	76.19(11)	76.30(15)	76.38(17)
O1−Ln1−O11	95.1(2)	94.18(13)	93.79(18)	92.54(19)
O1−Ln1−O13^{i}	155.77(17)	156.31(11)	156.49(15)	157.19(17)
O3−Ln1−O1	89.63(16)	89.83(11)	89.74(15)	89.47(17)
O3−Ln1−O7	133.45(16)	133.54(11)	133.67(15)	133.91(16)
O3−Ln1−O8	130.70(16)	130.40(11)	130.07(15)	129.92(17)
O3−Ln1−O10	76.67(16)	76.53(11)	76.09(15)	75.69(17)
O3−Ln1−O11	71.44(18)	71.15(12)	71.26(16)	71.17(19)
O3−Ln1−O13^{i}	81.36(16)	81.01(11)	80.73(14)	80.78(16)
O5−Ln1−O1	86.33(16)	86.36(11)	86.54(15)	87.09(17)
O5−Ln1−O3	151.32(17)	151.39(12)	151.05(16)	150.65(18)
O5−Ln1−O7	73.30(16)	73.14(11)	73.28(15)	73.48(17)
O5−Ln1−O8	72.38(17)	72.58(12)	73.14(15)	73.30(17)
O5−Ln1−O10	74.80(16)	75.02(11)	75.13(15)	75.17(17)
O5−Ln1−O11	137.19(18)	137.38(12)	137.62(16)	138.09(19)
O5−Ln1−O13^{i}	90.88(16)	91.30(11)	91.47(15)	91.38(17)
O8−Ln1−O7	48.53(14)	48.73(9)	49.19(12)	49.76(15)
O10−Ln1−O7	139.94(16)	139.76(10)	139.72(14)	139.74(17)
O10−Ln1−O8	138.13(15)	138.55(11)	139.06(14)	139.03(16)
O10−Ln1−O11	146.98(19)	146.31(13)	145.90(16)	145.11(19)
O11−Ln1−O7	65.24(17)	65.44(11)	65.53(15)	65.62(17)
O11−Ln1−O8	72.5(2)	72.93(13)	72.75(17)	73.65(19)

O13^{i}–Ln1–O7	123.79(15)	123.92(10)	124.29(13)	123.85(16)
O13^{i}–Ln1–O8	75.27(15)	75.20(10)	75.13(13)	74.10(16)
O13^{i}–Ln1–O10	79.99(16)	80.43(11)	80.55(14)	81.22(16)
O13^{i}–Ln1–O11	103.09(18)	103.30(12)	103.26(16)	103.57(18)
O2–Ln2–O4	91.34(16)	91.72(11)	91.49(15)	91.57(17)
O2–Ln2–O6^{ii}	81.21(16)	80.66(11)	80.42(15)	80.31(17)
O2–Ln2–O14	73.89(15)	74.02(10)	73.94(14)	73.67(16)
O2–Ln2–O15	122.44(15)	122.77(11)	123.15(14)	123.25(16)
O2–Ln2–O17	107.57(19)	107.93(13)	108.29(17)	108.72(19)
O2–Ln2–O18	76.69(16)	77.09(11)	77.13(14)	77.88(17)
O4–Ln2–O14	73.42(16)	73.62(11)	73.89(15)	74.09(16)
O4–Ln2–O15	70.96(16)	70.87(11)	71.16(15)	71.00(16)
O4–Ln2–O17	134.34(17)	134.57(12)	134.95(16)	135.51(18)
O4–Ln2–O18	76.02(16)	76.16(11)	76.23(15)	76.17(17)
O6^{ii}–Ln2–O4	155.51(18)	155.63(12)	155.24(16)	154.56(17)
O6^{ii}–Ln2–O14	125.59(16)	125.17(11)	124.95(15)	125.27(17)
O6^{ii}–Ln2–O15	132.41(17)	132.44(11)	132.57(15)	133.30(17)
O6^{ii}–Ln2–O17	69.98(18)	69.61(12)	69.63(16)	69.67(19)
O6^{ii}–Ln2–O18	79.56(17)	79.57(11)	79.16(15)	78.56(17)
O12–Ln2–O2	151.66(17)	152.15(11)	152.59(15)	153.34(17)
O12–Ln2–O4	84.18(16)	84.45(11)	84.87(15)	85.78(16)
O12–Ln2–O6^{ii}	91.37(16)	91.55(11)	91.62(15)	90.81(17)
O12–Ln2–O14	130.44(15)	130.26(10)	130.15(14)	130.28(16)
O12–Ln2–O15	82.47(16)	81.97(11)	81.30(14)	80.85(16)
O12–Ln2–O17	95.2(2)	93.98(14)	93.06(18)	91.3(2)
O12–Ln2–O18	75.07(16)	75.21(11)	75.62(15)	75.73(17)
O14–Ln2–O15	48.71(14)	48.91(10)	49.38(13)	49.79(15)
O17–Ln2–O14	72.8(2)	73.28(14)	73.56(18)	74.5(2)
O17–Ln2–O15	63.76(16)	63.99(11)	64.08(15)	64.72(17)
O18–Ln2–O14	136.52(16)	137.00(11)	137.32(14)	137.75(16)
O18–Ln2–O15	141.57(16)	141.35(11)	141.36(14)	140.71(17)
O18–Ln2–O17	147.87(19)	147.11(13)	146.52(17)	145.49(19)

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

Table S6 Hydrogens bond geometry (Å, °) for $\mathbf{2_{Ln}}$.

[D−H···A]	*d*[D−H]				*d*[H···A]				*d*[D···A]				∠[D−H···A]			
	$\mathbf{2_{Ce}}$	$\mathbf{2_{Pr}}$	$\mathbf{2_{Nd}}$	$\mathbf{2_{Sm}}$	$\mathbf{2_{Ce}}$	$\mathbf{2_{Pr}}$	$\mathbf{2_{Nd}}$	$\mathbf{2_{Sm}}$	$\mathbf{2_{Ce}}$	$\mathbf{2_{Pr}}$	$\mathbf{2_{Nd}}$	$\mathbf{2_{Sm}}$	$\mathbf{2_{Ce}}$	$\mathbf{2_{Pr}}$	$\mathbf{2_{Nd}}$	$\mathbf{2_{Sm}}$
O10−H10···O14	0.85(1)	0.85(1)	0.86(1)	0.86(1)	1.99(2)	1.98(1)	1.98(1)	2.04(3)	2.827(7)	2.830(5)	2.830(6)	2.870(7)	169(8)	175(4)	175(5)	163(8)
O11−H11···O9^{i}	0.85(1)	0.85(1)	0.85(1)	0.86(1)	2.04(3)	2.00(2)	2.01(3)	2.01(3)	2.862(8)	2.832(5)	2.841(7)	2.833(8)	164(10)	165(7)	163(9)	163(9)
O17−H17···O15^{ii}	0.85(1)	0.85(1)	0.85(1)	0.86(1)	2.29(5)	2.33(3)	2.41(5)	2.55(6)	3.076(7)	3.120(5)	3.167(6)	3.237(7)	155(10)	155(5)	148(8)	138(8)
O17−H17···O16^{ii}	0.85(1)	0.85(1)	0.85(1)	0.86(1)	2.19(6)	2.19(5)	2.11(5)	2.01(3)	2.945(8)	2.911(6)	2.882(7)	2.844(8)	148(10)	142(7)	150(9)	164(10)
O18−H18···O8^{iii}	0.85(1)	0.85(1)	0.86(1)	0.86(1)	2.00(2)	1.99(1)	2.00(1)	2.02(2)	2.840(7)	2.838(5)	2.850(6)	2.867(7)	173(8)	177(5)	175(6)	171(7)

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

Table S7 The Br···X halogen bond geometry (Å, °) for $\mathbf{2_{Ln}}$.

[C−Br···X]	*d*[Br···X]				∠[C−Br···X]			
	$\mathbf{2_{Ce}}$	$\mathbf{2_{Pr}}$	$\mathbf{2_{Nd}}$	$\mathbf{2_{Sm}}$	$\mathbf{2_{Ce}}$	$\mathbf{2_{Pr}}$	$\mathbf{2_{Nd}}$	$\mathbf{2_{Sm}}$
C3−Br1···O9^{i} (Type I)	3.134(5)	3.118(4)	3.113(5)	3.113(5)	149.1(2)	149.4(11)	150.3(16)	150.7(2)
C3−Br1···Br7^{ii} (Type II)	3.745(9)	3.751(7)	3.759(9)	3.756(10)	121.4(19)	121.4(10)	121.0(15)	120.7(19)
C4−Br2···Br7^{ii} (Type I)	3.681(10)	3.674(7)	3.670(9)	3.658(9)	124.2(18)	124.1(11)	124.3(14)	124.1(18)
C4−Br2···Br8^{ii} (Type II)	3.731(9)	3.737(7)	3.743(8)	3.744(10)	175.7(2)	175.5(13)	175.8(18)	176.0(3)
C7−Br3···Br6^{i} (Type I)	3.917(10)	3.904(7)	3.897(10)	3.878(1)	130.7(16)	130.9(9)	131.3(12)	131.2(17)
C8−Br4···O13^{iii} (Type I)	3.683(5)	3.687(3)	3.694(4)	3.728(5)	91.1(2)	90.7(12)	90.5(16)	89.7(2)
C11−Br5···Br1^{iv} (Type I)	3.816(13)	3.803(8)	3.800(12)	3.812(13)	127.1(2)	126.9(16)	126.6(2)	126.1(3)
C12−Br6···Br2^{iv} (Type I)	3.783(14)	3.765(7)	3.759(13)	3.762(15)	123.5(2)	123.2(13)	123.1(15)	123.0(2)
C17−Br7···Br1^{ii} (Type II)	3.745(9)	3.751(7)	3.759(9)	3.756(10)	174.0(18)	174.9(12)	173.7(12)	173.7(2)
C17−Br7···Br2^{ii} (Type I)	3.681(10)	3.737(7)	3.670(9)	3.658(9)	123.9(17)	121.7(10)	124.0(14)	123.7(18)
C17−Br7···O8^{v} (Type I)	3.359(5)	3.358(3)	3.347(5)	3.355(5)	121.5(19)	121.1(12)	121.0(16)	120.4(2)
C18−Br8···Br2^{ii} (Type II)	3.731(9)	3.737(7)	3.743(8)	3.744(10)	122.1(19)	121.7(10)	121.4(14)	121.3(19)
C18−Br8···O16^{iv} (Type I)	3.070(5)	3.066(4)	3.063(5)	3.056(5)	147.3(2)	148.0(12)	148.4(18)	148.5(2)

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

Table S8 Selected bond lengths (Å) and bond angles (°) for $\mathbf{3}_{\mathbf{Ln}}$.

	$\mathbf{3}_{\mathbf{Gd}}$	$\mathbf{3}_{\mathbf{Tb}}$	$\mathbf{3}_{\mathbf{Dy}}$
Ln1−O1	2.272(3)	2.254(3)	2.249(5)
Ln1−O2^{i}	2.351(3)	2.339(2)	2.319(5)
Ln1−O3^{ii}	2.455(3)	2.440(3)	2.420(5)
Ln1−O4^{iii}	2.356(3)	2.341(2)	2.326(5)
Ln1−O4^{ii}	2.560(3)	2.556(2)	2.543(5)
Ln1−O5	2.421(3)	2.403(3)	2.396(6)
Ln1−O6	2.445(3)	2.436(3)	2.427(7)
Ln1−O8	2.359(3)	2.347(3)	2.328(6)
O1−Ln1−O2^{i}	89.65(10)	89.17(9)	89.13(18)
O1−Ln1−O3^{ii}	75.42(10)	75.48(9)	75.01(18)
O1−Ln1−O4^{ii}	121.01(10)	121.26(9)	121.28(17)
O1−Ln1−O4^{iii}	158.46(11)	158.35(10)	158.3(2)
O1−Ln1−O5	124.78(12)	125.12(11)	124.6(2)
O1−Ln1−O6	82.87(12)	82.41(12)	82.1(2)
O1−Ln1−O8	81.44(11)	81.45(11)	81.7(2)
O2^{i}–Ln1−O3^{ii}	164.57(9)	164.14(9)	163.69(18)
O2^{i}–Ln1−O4^{iii}	77.94(10)	77.99(8)	78.20(17)
O2^{i}–Ln1−O4^{ii}	143.51(9)	143.68(8)	143.92(17)
O2^{i}–Ln1−O5	109.21(12)	109.05(11)	109.4(2)
O2^{i}–Ln1−O6	80.69(12)	80.54(12)	80.6(2)
O2^{i}–Ln1−O8	88.46(12)	88.46(11)	88.3(2)
O3^{ii}–Ln1−O4^{ii}	51.45(9)	51.68(8)	51.85(17)
O4^{iii}–Ln1−O3^{ii}	117.46(9)	117.83(8)	118.06(17)
O4^{iii}–Ln1−O4^{ii}	66.53(11)	66.69(9)	66.63(19)
O4^{iii}–Ln1−O5	76.34(11)	76.00(10)	76.6(2)
O4^{iii}–Ln1−O6	111.88(12)	112.04(11)	112.5(2)
O4^{iii}–Ln1−O8	80.70(11)	80.85(10)	80.5(2)
O5−Ln1−O3^{ii}	77.26(12)	77.65(11)	77.7(2)
O5−Ln1−O4^{ii}	71.08(10)	71.21(9)	70.95(19)
O5−Ln1−O6	52.04(10)	52.47(10)	52.5(2)
O6−Ln1−O3^{ii}	93.40(12)	93.30(12)	93.3(2)
O6−Ln1−O4^{ii}	119.46(10)	119.82(10)	119.59(19)
O8−Ln1−O3^{ii}	93.04(12)	93.07(11)	93.0(2)
O8−Ln1−O4^{ii}	78.21(10)	78.15(9)	78.49(19)
O8−Ln1−O5	147.02(10)	146.97(10)	147.1(2)
O8−Ln1−O6	160.94(11)	160.56(10)	160.4(2)

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

Table S9 Hydrogen bond geometry (Å, °) for $\mathbf{3_{Ln}}$.

[D−H···A]	*d*[D−H]			*d*[H···A]			*d*[D···A]			∠[D−H···A]		
	$\mathbf{3_{Gd}}$	$\mathbf{3_{Tb}}$	$\mathbf{3_{Dy}}$	$\mathbf{3_{Gd}}$	$\mathbf{3_{Tb}}$	$\mathbf{3_{Dy}}$	$\mathbf{3_{Gd}}$	$\mathbf{3_{Tb}}$	$\mathbf{3_{Dy}}$	$\mathbf{3_{Gd}}$	$\mathbf{3_{Tb}}$	$\mathbf{3_{Dy}}$
O8−H8···O5^{i}	0.85(1)	0.85(1)	0.86(1)	2.03(2)	2.01(2)	2.01(4)	2.789(4)	2.772(4)	2.763(8)	148(3)	149(3)	146(6)
O8−H8···O7^{ii}	0.85(1)	0.85(1)	0.86(1)	2.58(3)	2.62(3)	2.60(5)	3.158(5)	3.182(5)	3.197(10)	126(3)	125(3)	128(6)

Symmetry codes: (i) $-x+1, -y, -z+2$; (ii) $x+1, y, z$.

Table S10 The Br···X halogen bond geometry (Å, °) in $\mathbf{3_{Ln}}$.

[C−Br···X]	*d*[Br···X]			∠[C−Br···X]		
	$\mathbf{3_{Gd}}$	$\mathbf{3_{Tb}}$	$\mathbf{3_{Dy}}$	$\mathbf{3_{Gd}}$	$\mathbf{3_{Tb}}$	$\mathbf{3_{Dy}}$
C3−Br1···Br3^{i} (type I)	3.876(10)	3.872(6)	3.867(13)	120.8(12)	120.9(11)	120.4(2)
C3−Br1···Br4^{i} (type II)	3.923(11)	3.922(8)	3.916(15)	159.8(15)	159.8(13)	159.2(3)
C4−Br2···Br3^{i} (type II)	3.900(10)	3.902(7)	3.895(14)	119.7(13)	119.7(12)	119.7(2)
C4−Br2···O7^{ii} (type I)	3.034(4)	3.032(4)	3.017(7)	163.7(16)	164.0(15)	163.9(3)
C7−Br3···Br1^{iii} (type I)	3.876(10)	3.872(6)	3.867(13)	121.1(19)	121.2(11)	121.2(2)
C7−Br3···Br2^{iii} (type II)	3.900(10)	3.902(7)	3.895(14)	162.5(12)	162.3(13)	162.3(3)
C8−Br4···Br1^{iii} (type I)	3.923(11)	3.922(8)	3.916(15)	119.6(13)	119.7(12)	119.5(2)

Symmetry code: (i) $-1+x, y, z$; (ii) $-x, -y, 1-z$; (iii) $1+x, y, z$.

Table S11 Selected bond lengths (Å) and bond angles (°) for $\mathbf{4_{Ln}}$.

	$\mathbf{4_{Gd}}$	$\mathbf{4_{Tb}}$	$\mathbf{4_{Dy}}$
Ln1−O1	2.287(4)	2.279(4)	2.259(6)
Ln1−O4^{i}	2.310(4)	2.289(4)	2.265(5)
Ln1−O5	2.267(4)	2.246(4)	2.230(5)
Ln1−O7^{ii}	2.311(4)	2.290(4)	2.281(6)
Ln1−O9	2.247(4)	2.227(4)	2.206(6)
Ln1−O11	2.243(4)	2.226(4)	2.205(6)
Ln2−O2^{iii}	2.358(4)	2.344(4)	2.326(6)
Ln2−O3	2.326(4)	2.307(4)	2.293(6)
Ln2−O8^{iv}	2.315(4)	2.305(4)	2.278(6)
Ln2−O13	2.455(7)	2.441(7)	2.428(9)
Ln2−O14	2.445(5)	2.431(5)	2.425(7)
Ln2−O15	2.334(5)	2.335(5)	2.301(7)
Ln2−O16	2.447(5)	2.429(5)	2.415(7)
Ln2−O17	2.487(7)	2.469(7)	2.454(8)
Ln2−O18	2.356(11)	2.350(11)	2.310(12)
O1−Ln1−O4^{i}	91.91(16)	91.39(16)	91.7(2)
O1−Ln1−O7^{ii}	86.52(16)	86.18(16)	86.7(2)
O4^{i}−Ln1−O7^{ii}	89.15(15)	88.81(15)	89.4(2)
O5−Ln1−O1	86.49(16)	86.93(17)	86.5(2)
O5−Ln1−O4^{i}	88.19(16)	88.33(16)	87.8(2)
O5−Ln1−O7^{ii}	172.43(16)	172.48(16)	172.6(2)
O9−Ln1−O1	90.42(17)	90.78(16)	90.6(2)
O9−Ln1−O4^{i}	176.83(15)	177.00(15)	177.1(2)
O9−Ln1−O5	94.11(16)	93.85(16)	94.1(2)
O9−Ln1−O7^{ii}	88.85(15)	89.27(16)	89.0(2)
O11−Ln1−O1	177.73(15)	177.82(16)	178.0(2)
O11−Ln1−O4^{i}	87.53(15)	88.02(15)	87.6(2)
O11−Ln1−O5	95.69(16)	95.15(17)	95.4(2)
O11−Ln1−O7^{ii}	91.27(16)	91.70(16)	91.4(2)
O11−Ln1−O9	90.06(16)	89.74(16)	90.0(2)
O2^{iii}−Ln2−O13	146.9(3)	146.9(3)	147.6(4)
O2^{iii}−Ln2−O14	143.57(18)	143.62(18)	143.2(3)
O2^{iii}−Ln2−O16	73.07(16)	73.21(16)	73.1(2)
O2^{iii}−Ln2−O17	77.1(3)	77.4(4)	76.5(5)
O3−Ln2−O2^{iii}	85.79(15)	85.18(15)	85.5(2)
O3−Ln2−O13	70.8(3)	71.2(3)	70.7(4)
O3−Ln2−O14	117.0(2)	117.6(2)	117.9(3)
O3−Ln2−O15	136.73(17)	136.93(16)	136.6(2)
O3−Ln2−O16	151.38(15)	150.70(15)	150.8(2)
O3−Ln2−O17	74.6(4)	75.4(4)	74.6(5)

O3−Ln2−O18	80.4(11)	78.6(12)	80.0(17)
O8^{iv}−Ln2−O2^{iii}	83.44(15)	83.06(16)	83.6(2)
O8^{iv}−Ln2−O3	82.49(15)	81.67(15)	81.8(2)
O8^{iv}−Ln2−O13	115.0(3)	114.9(4)	113.2(5)
O8^{iv}−Ln2−O14	72.82(17)	73.58(17)	73.2(2)
O8^{iv}−Ln2−O15	137.34(17)	138.27(16)	138.1(2)
O8^{iv}−Ln2−O16	76.24(18)	76.38(17)	76.3(2)
O8^{iv}−Ln2−O17	150.8(4)	150.9(4)	150.1(5)
O8^{iv}−Ln2−O18	149.5(12)	148.4(14)	150.0(19)
O14−Ln2−O13	69.4(3)	69.4(3)	69.2(4)
O14−Ln2−O16	74.7(2)	74.4(2)	73.9(3)
O14−Ln2−O17	134.1(4)	133.3(4)	134.6(5)
O15−Ln2−O2^{iii}	110.4(2)	110.4(2)	110.5(3)
O15−Ln2−O13	75.4(3)	75.6(4)	76.2(5)
O15−Ln2−O14	73.3(2)	73.4(2)	73.0(3)
O15−Ln2−O16	70.37(18)	70.75(17)	71.1(3)
O15−Ln2−O17	70.8(4)	69.7(4)	70.8(5)
O15−Ln2−O18	69.1(13)	70.0(14)	68.6(19)
O16−Ln2−O13	135.9(3)	136.1(3)	136.2(4)
O16−Ln2−O17	117.5(3)	117.3(3)	117.6(4)
O18−Ln2−O2^{iii}	70.3(9)	71.0(11)	71.4(15)
O18−Ln2−O13	82.7(8)	81.5(9)	82.8(13)
O18−Ln2−O14	137.7(12)	137.7(13)	136.7(19)
O18−Ln2−O16	109.2(8)	111.4(9)	110.5(13)

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

Table S12 Hydrogen bond geometry (Å, °) in $\mathbf{4_{Ln}}$.

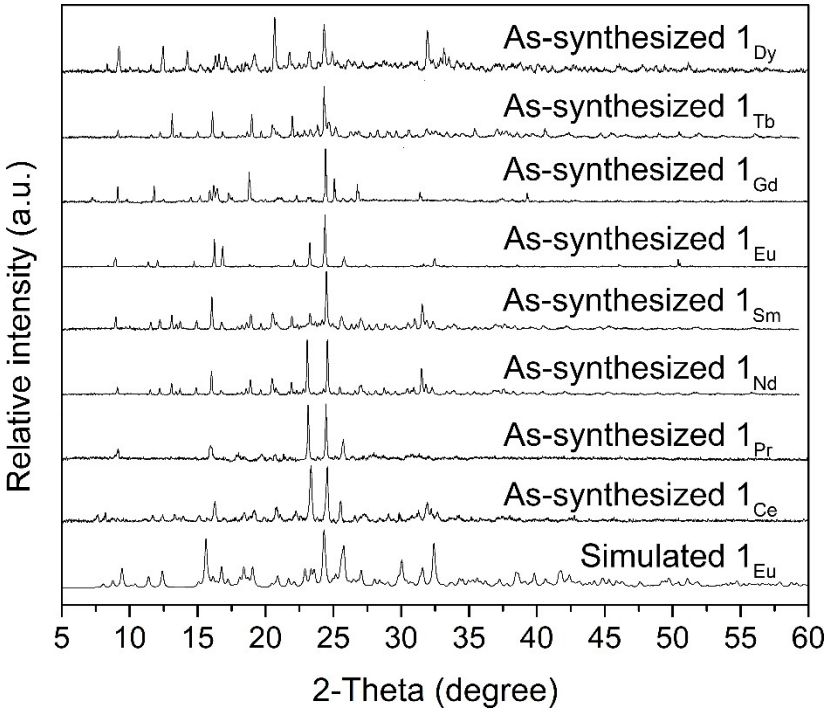
[D−H···A]	*d*[D−H]			*d*[H···A]			*d*[D···A]			∠[D−H···A]		
	$\mathbf{4_{Gd}}$	$\mathbf{4_{Tb}}$	$\mathbf{4_{Dy}}$	$\mathbf{4_{Gd}}$	$\mathbf{4_{Tb}}$	$\mathbf{4_{Dy}}$	$\mathbf{4_{Gd}}$	$\mathbf{4_{Tb}}$	$\mathbf{4_{Dy}}$	$\mathbf{4_{Gd}}$	$\mathbf{4_{Tb}}$	$\mathbf{4_{Dy}}$
O13−H13···O12^{i}	0.85(1)	0.86(1)	0.85(1)	1.92(7)	1.84(3)	2.03(13)	2.655(10)	2.660(11)	2.653(16)	143(10)	160(7)	129(14)
O13*A*−H13*A*···O6^{i}	0.85(1)	0.85(1)	0.85(1)	2.33(3)	2.39(8)	2.49(16)	3.09(3)	3.14(2)	3.14(3)	150(2)	147(11)	134(19)
O14−H14···O12^{i}	0.85(1)	0.86(1)	0.86(1)	1.92(2)	1.92(2)	1.92(3)	2.733(7)	2.731(7)	2.732(10)	158(6)	157(6)	158(7)
O15−H15*B*···O6^{i}	0.85(2)	0.85(2)	0.84(2)	1.82(3)	1.86(4)	1.85(4)	2.643(7)	2.647(7)	2.653(10)	163(6)	154(9)	162(11)
O16−H16*B*···O10^{i}	0.86(2)	0.86(2)	0.85(2)	1.95(3)	1.99(3)	2.03(5)	2.740(7)	2.777(6)	2.771(9)	151(4)	151(4)	146(8)

Symmetry codes: (i) $-x+3/2, y-1/2, -z+3/2$.

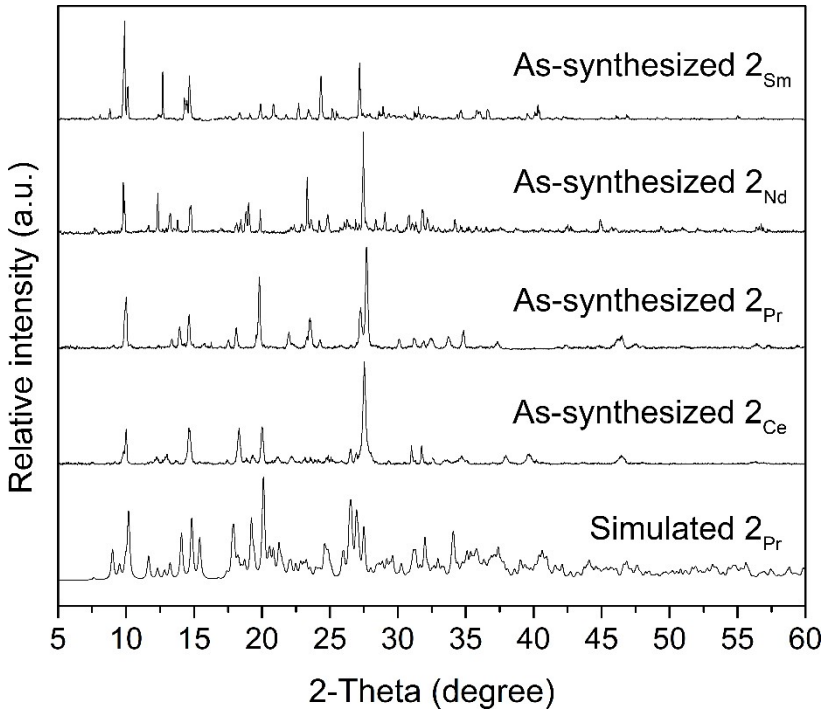
Table S13 The Br···X halogen bond geometry (Å, °) in $\mathbf{4_{Ln}}$.

[C−Br···X]	*d*[Br···X]			∠[C−Br···X]		
	$\mathbf{4_{Gd}}$	$\mathbf{4_{Tb}}$	$\mathbf{4_{Dy}}$	$\mathbf{4_{Gd}}$	$\mathbf{4_{Tb}}$	$\mathbf{4_{Dy}}$
C3−Br1···Br3^{i} (type II)	3.538(15)	3.508(16)	3.492(16)	130.6(19)	130.3(19)	130.2(3)
C3−Br1···Br11^{ii} (type I)	3.851(19)	3.872(2)	3.858(2)	80.4(19)	80.5(19)	80.9(3)
C4−Br2···Br7^{iii} (type II)	3.622(14)	3.601(16)	3.581(16)	128.25(17)	128.3(17)	128.7(2)
C4−Br2···O12^{iv} (type I)	3.696(5)	3.712(5)	3.717(7)	125.57(19)	125.76(19)	125.9(3)
C6−Br3···Br1^{v} (type II)	3.538(15)	3.508(16)	3.492(16)	171.81(18)	171.5(18)	171.7(3)
C7−Br4···Br6^{vi} (type II)	3.434(16)	3.409(2)	3.406(15)	169.1(17)	168.5(17)	169.6(2)
C11−Br5···Br12^{vii} (type II)	3.567(17)	3.543(2)	3.541(16)	124.7(2)	124.5(2)	124.8(2)
C12−Br6···Br4^{viii} (type II)	3.434(16)	3.409(2)	3.406(15)	131.9(18)	132,2(18)	132.2(2)
C14−Br7···Br2^{iii} (type II)	3.622(14)	3.601(16)	3.581(16)	164.9(2)	164.2(2)	164.5(3)
C19−Br9···Br11 (type II)	3.719(16)	3.682(18)	3.660(17)	164.8(18)	165.1(18)	165.0(3)
C20−Br10···Br5^{vi} (type I)	3.849(2)	3.865(2)	3.844(2)	107.9(2)	107.3(19)	107.4(3)

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

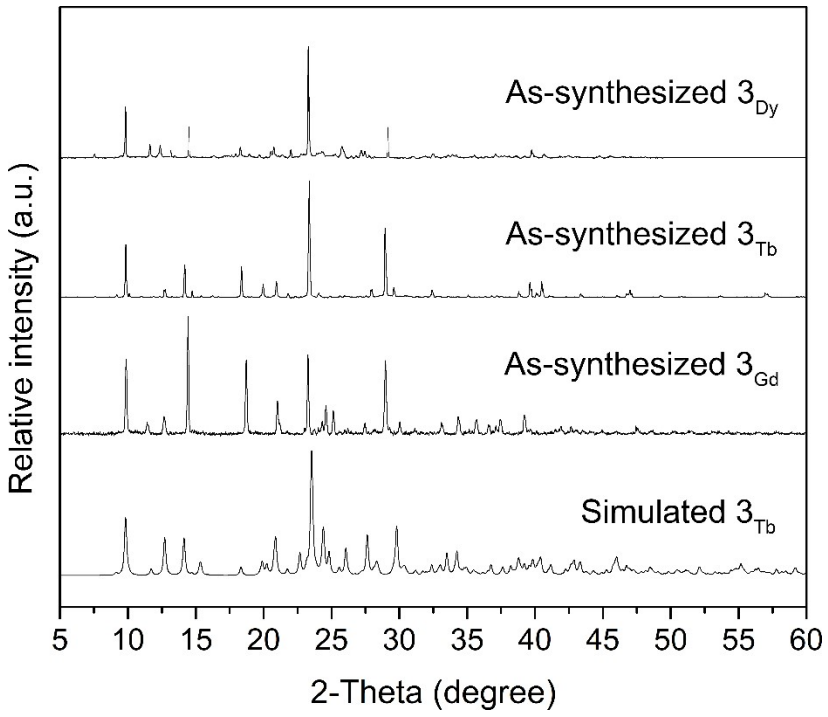


(a)

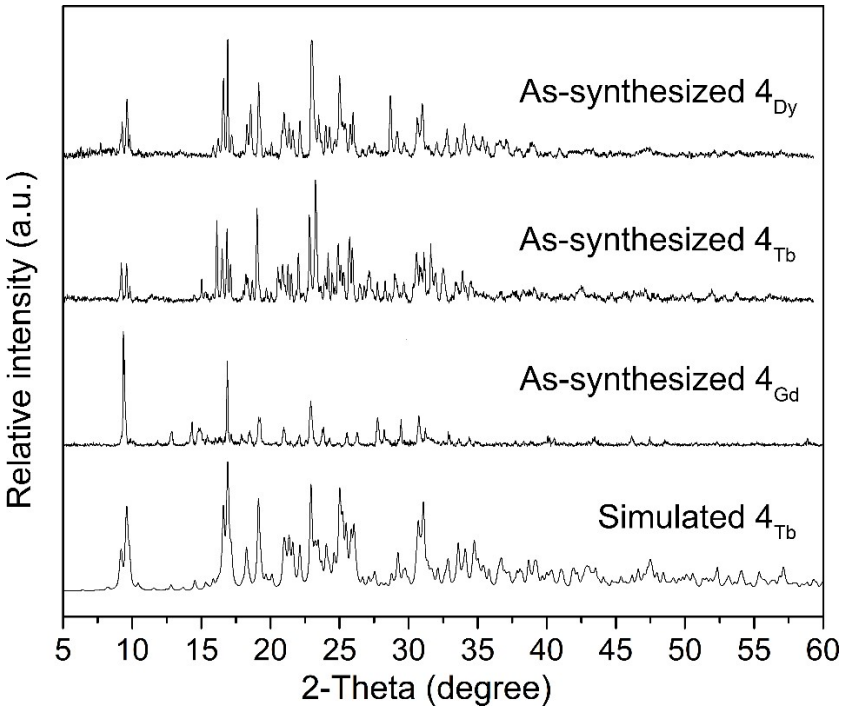


(b)

Figure S1. Comparison of the simulated and as-synthesized PXRD patterns of compounds in series $\mathbf{1}_{\mathbf{Ln}}$ (a), $\mathbf{2}_{\mathbf{Ln}}$ (b), $\mathbf{3}_{\mathbf{Ln}}$ (c), and $\mathbf{4}_{\mathbf{Ln}}$ (d).

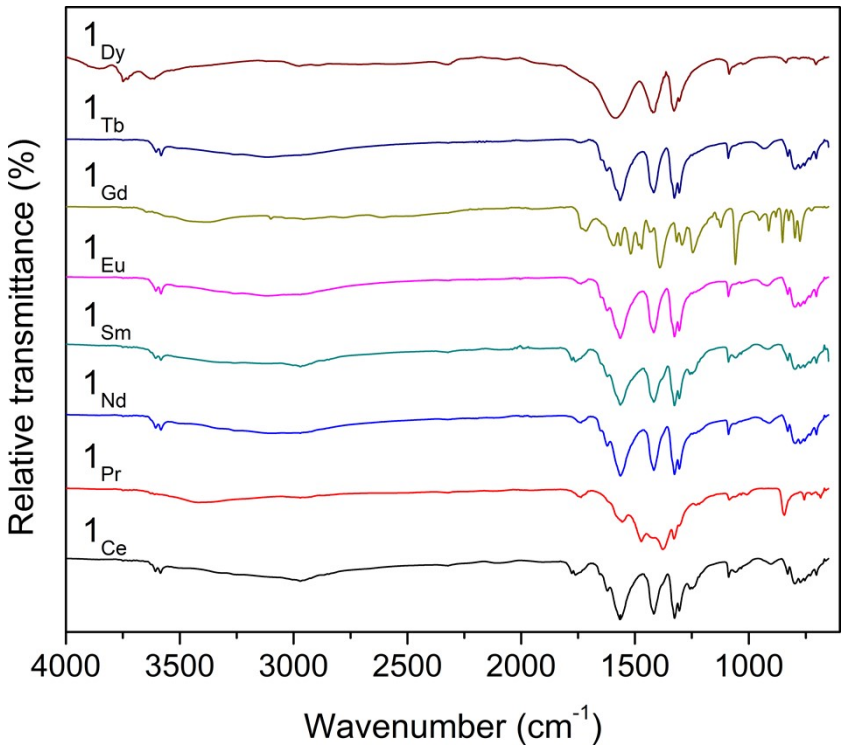


(c)

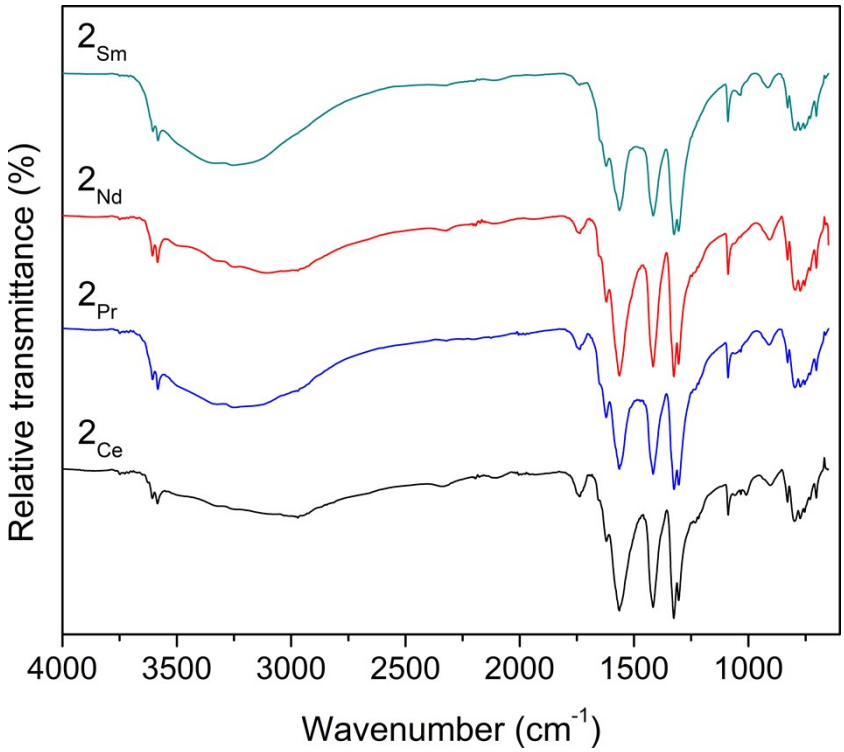


(d)

Figure S1. (Continued).

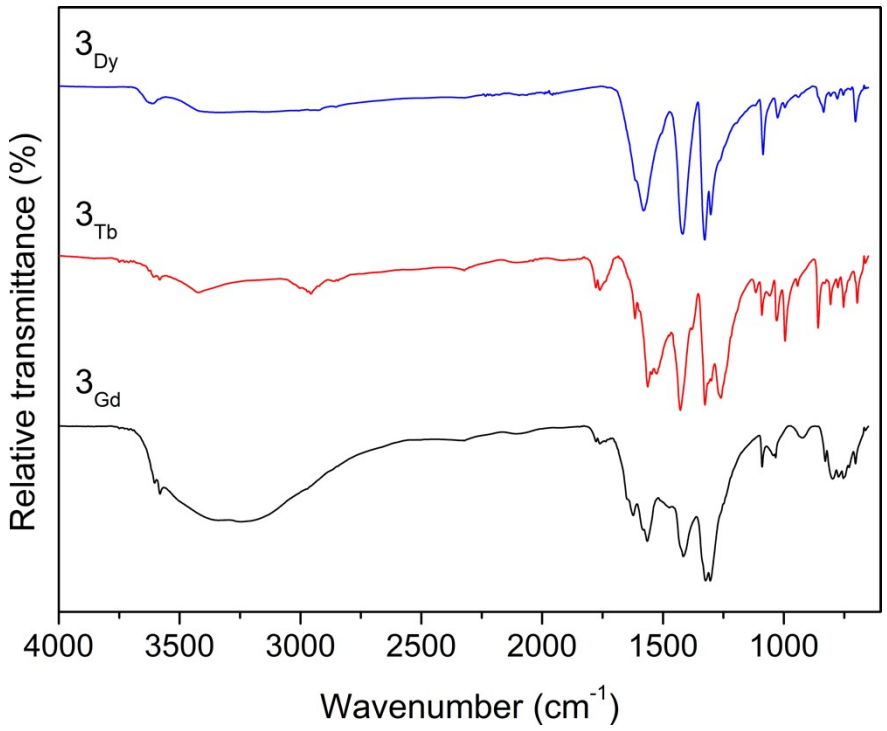


(a)

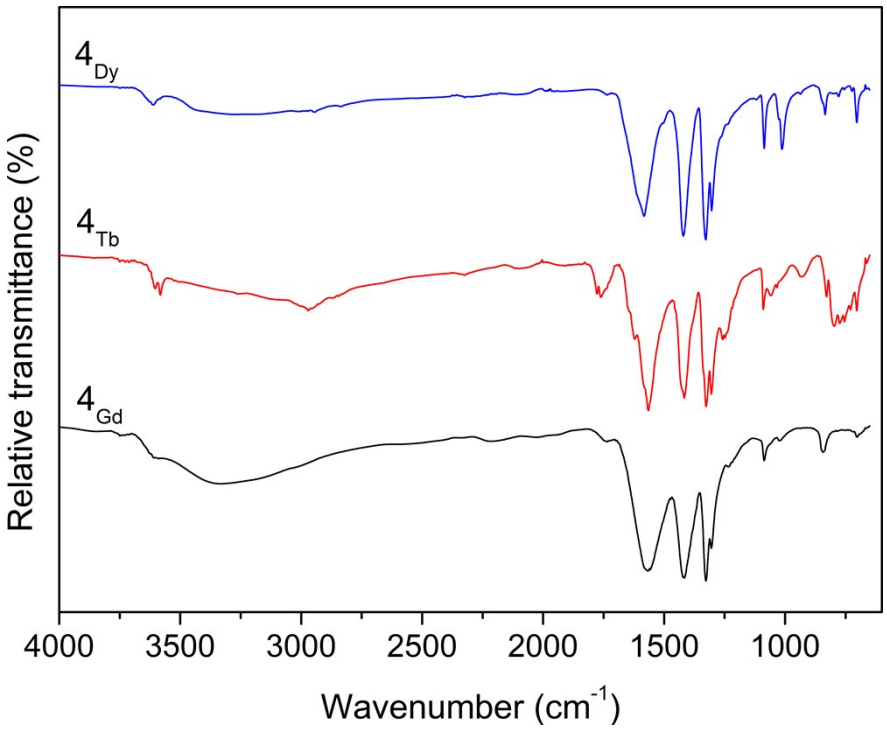


(b)

Figure S2. FT-IR spectra of compounds in series $\mathbf{1}_{Ln}$ (a), $\mathbf{2}_{Ln}$ (b), $\mathbf{3}_{Ln}$ (c), and $\mathbf{4}_{Ln}$ (d).



(c)



(d)

Figure S2. (Continued).

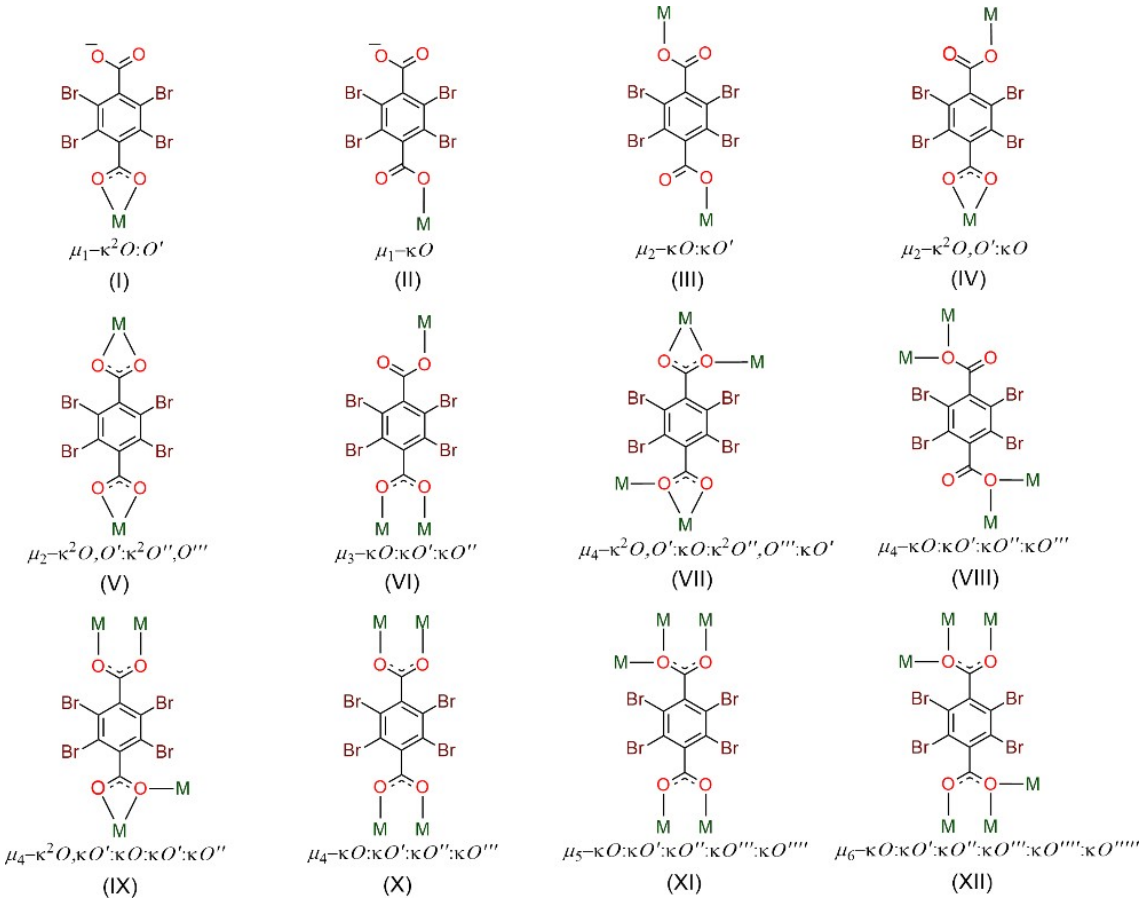


Figure S3. Coordination modes of the Br_4bdc^{2-} ligand observed in previous reports and the present study.

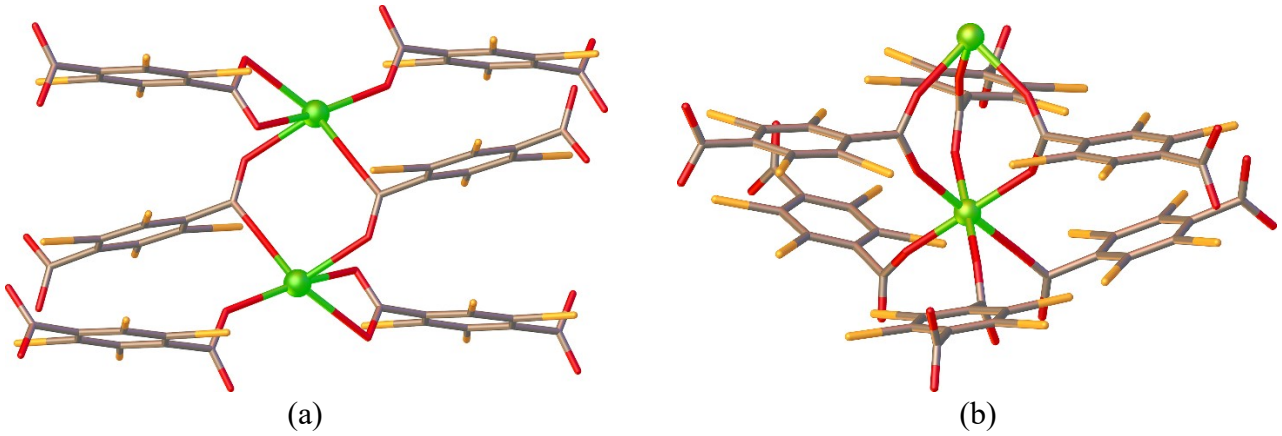


Figure S4. Secondary building unit (SBU) of $\mathbf{1_{Eu}}$ (a) and $\mathbf{4_{Tb}}$ (b). The coordinated H_2O and MeOH molecules are not shown for clarity.

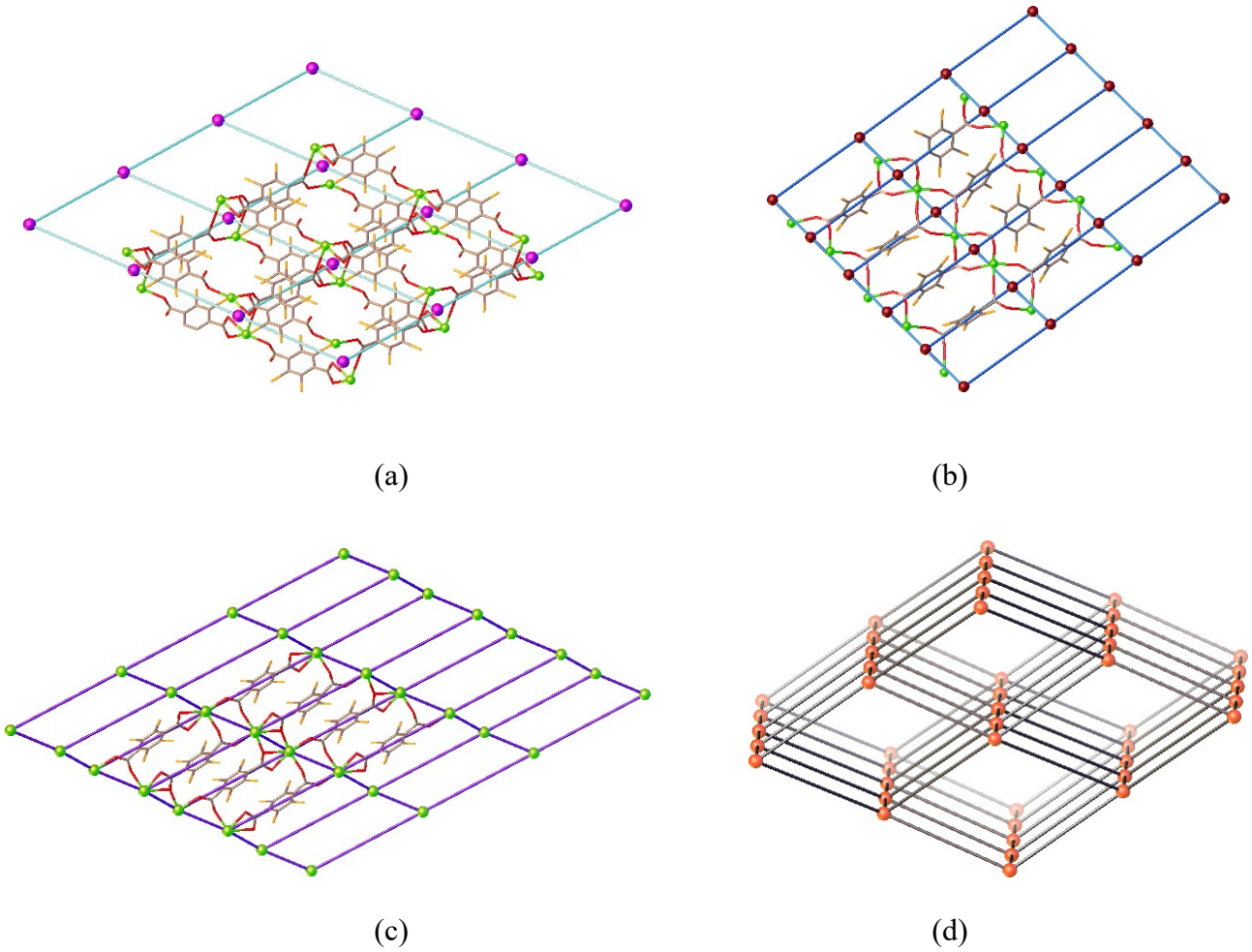


Figure S5. Topological representation of the *sql* net in $\mathbf{1}_{\mathbf{Eu}}$ (a), $\mathbf{2}_{\mathbf{Pr}}$ (b), and $\mathbf{3}_{\mathbf{Tb}}$ (c), and the *pcu* α-Po net in $\mathbf{4}_{\mathbf{Ln}}$ (d).

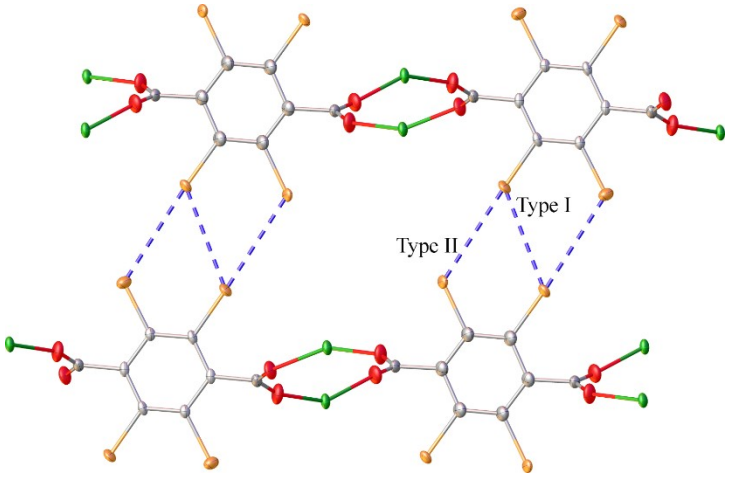


Figure S6. Partial view of types I and II Br···Br halogen bonds in $\mathbf{2_{Pr}}$.

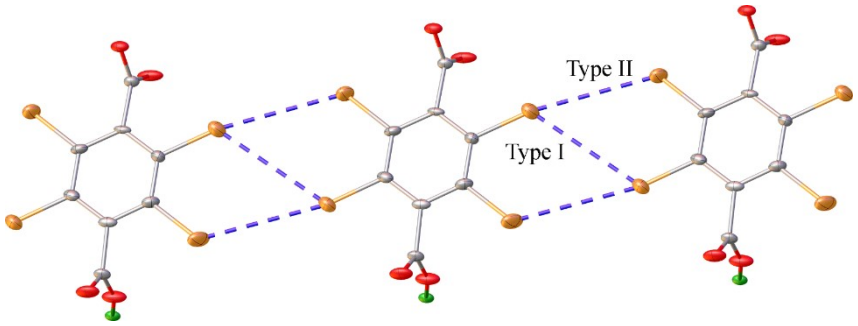


Figure S7. Partial view of types I and II Br···Br halogen bonds in $\mathbf{3_{Tb}}$.

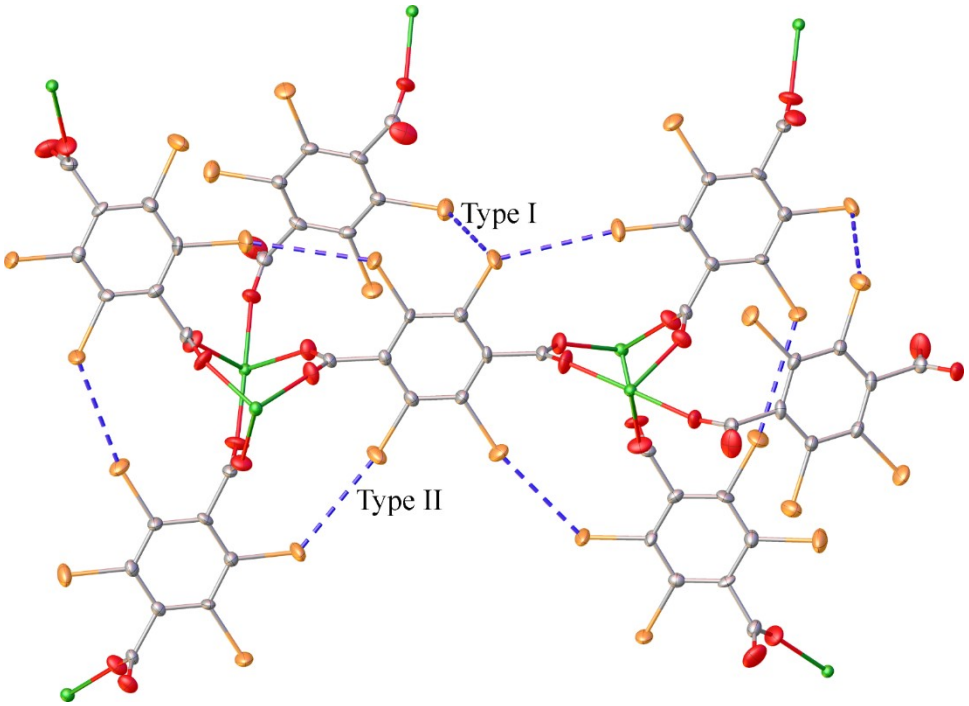


Figure S8. Partial view of types I and II Br···Br halogen bonds in $\mathbf{4_{Tb}}$.

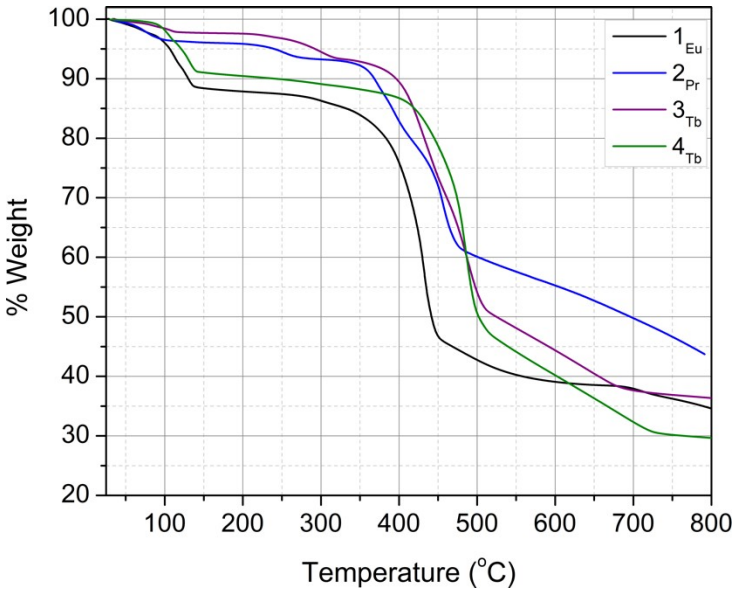


Figure S9. TGA curves of $\mathbf{1_{Eu}}$ (back line), $\mathbf{2_{Pr}}$ (blue line), $\mathbf{3_{Tb}}$ (purple line), and $\mathbf{4_{Tb}}$ (green line).

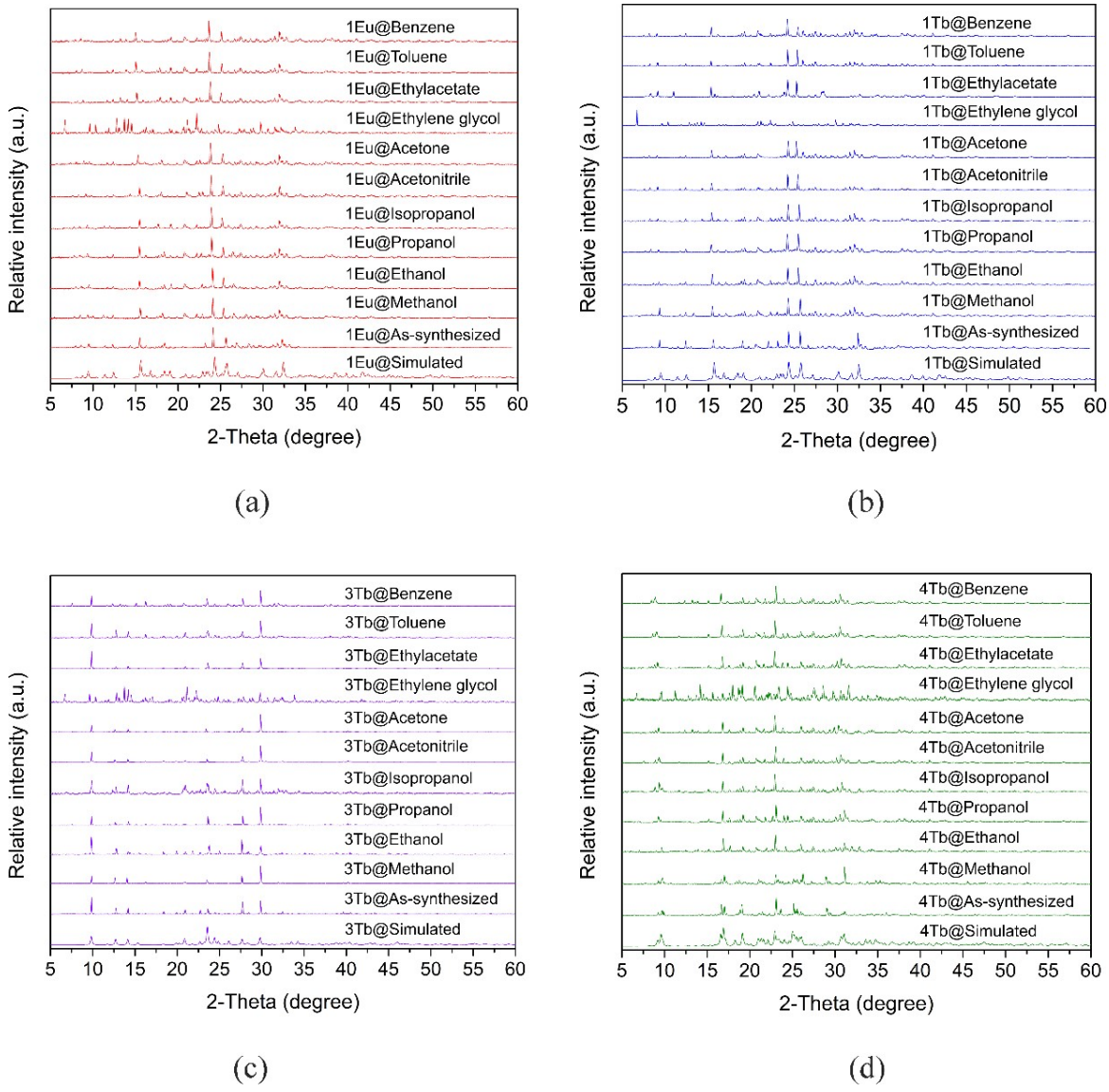
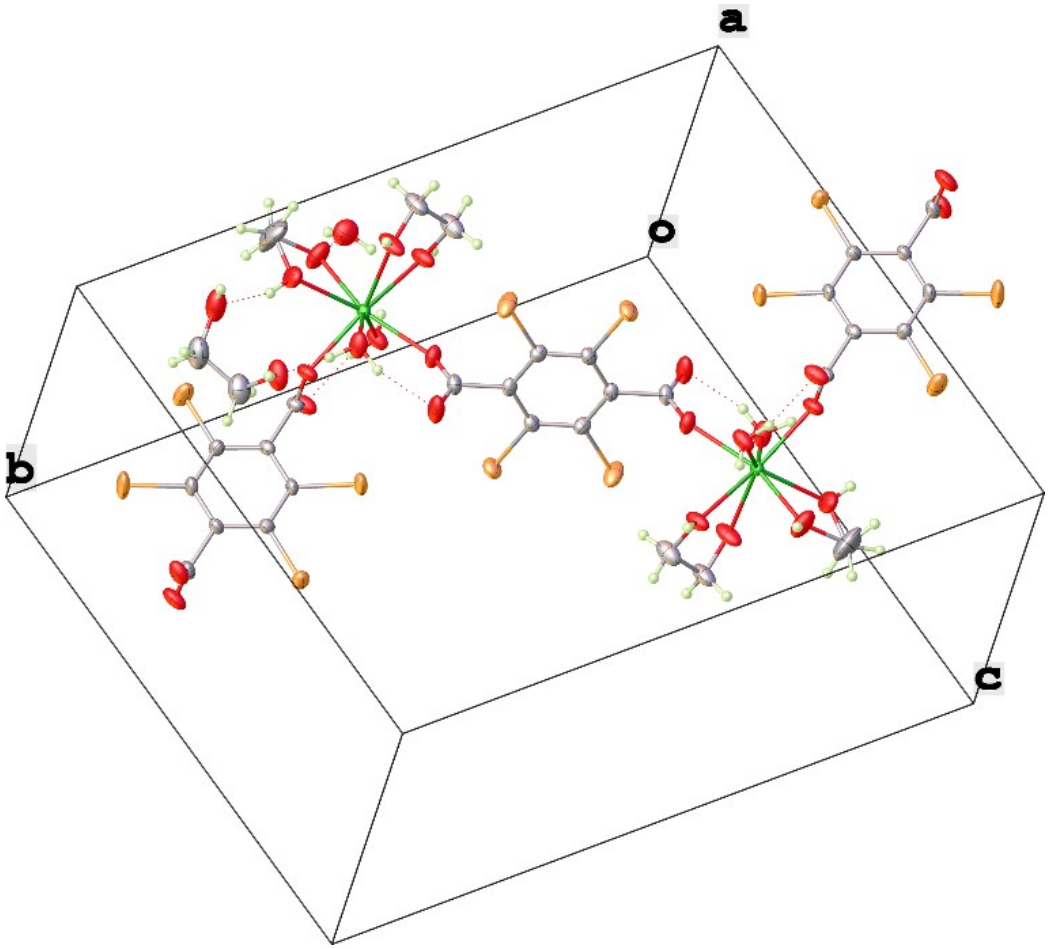
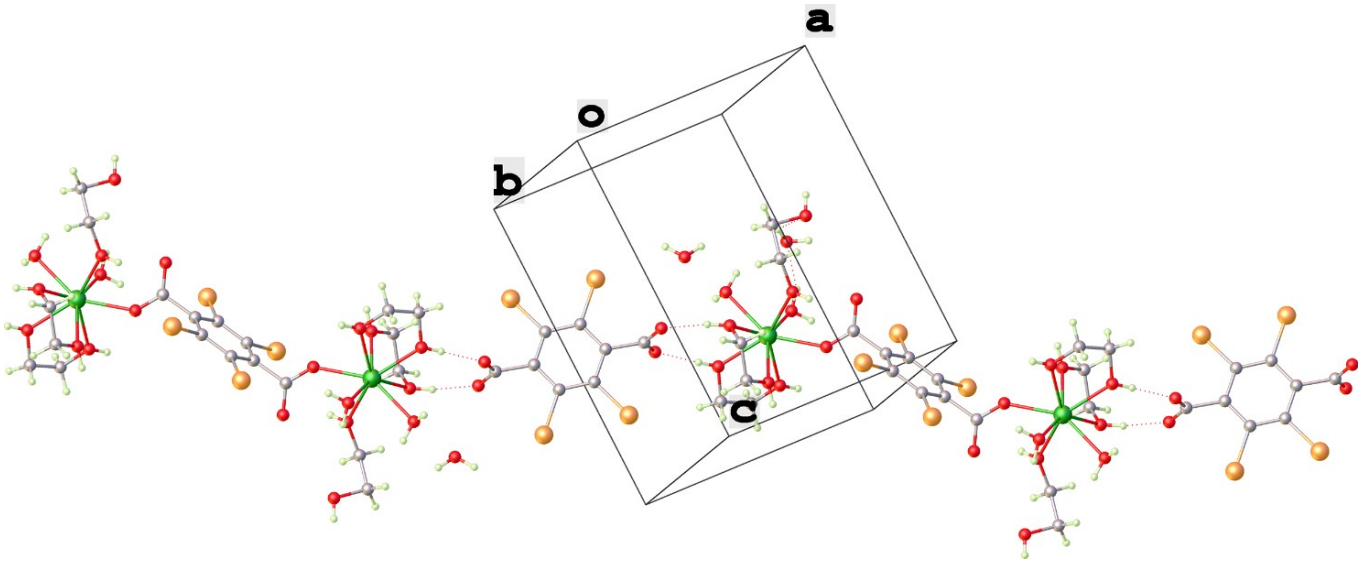


Figure S10. PXRD patterns of $\mathbf{1_{Eu}}$ (a), $\mathbf{1_{Tb}}$ (b), $\mathbf{3_{Tb}}$ (c), and $\mathbf{4_{Tb}}$ (d) after soaking in different solvents for 24 h.



CCDC no.	2130102	*a* (Å)	8.62280(10)	*V* (Å)	3157.09(9)
Formula	$C_{36}H_{48}Br_{12}O_{30}Tb_2$	*b* (Å)	22.3036(4)	*Z*	2
Formula weigh	2237.50	*c* (Å)	16.5045(3)	ρ_{calcd} (g cm^{-3})	2.354
Temperature (K)	296	*α* (°)	90	GOF on F^2, *S*	1.022
Crystal system	Monoclinic	*β* (°)	95.9410(10)	R_1, $wR_2[I > 2\sigma(I)]$	0.0235, 0.0505
Space group	$P2_1/c$	*γ* (°)	90	$\Delta_{\rho max}$, $\Delta_{\rho min}$ (e Å^{-3})	1.43, −1.13

(a)



CCDC no.	2130103	*a* (Å)	10.4965(3)	*V* (Å)	1606.23(7)
Formula	$C_{36}H_{52}Br_{12}O_{32}Tb_2$	*b* (Å)	12.3708(3)	*Z*	1
Formula weigh	2274.21	*c* (Å)	12.7873(3)	ρ_{calcd} (g cm^{-3})	2.351
Temperature (K)	296.15(2)	*α* (°)	78.8140(10)	GOF on F^2, *S*	1.023
Crystal system	Triclinic	*β* (°)	82.6170(10)	R_1, $wR_2[I > 2\sigma(I)]$	0.0268, 0.0550
Space group	*P*-1	*γ* (°)	82.6250(10)	$\Delta_{\rho max}$, $\Delta_{\rho min}$ (e Å^{-3})	0.92, −0.90

(b)

Figure S11. Views of 1D chain structures of compounds $\mathbf{3_{Tb'}}$ (a) and $\mathbf{4_{Tb'}}$ (b).

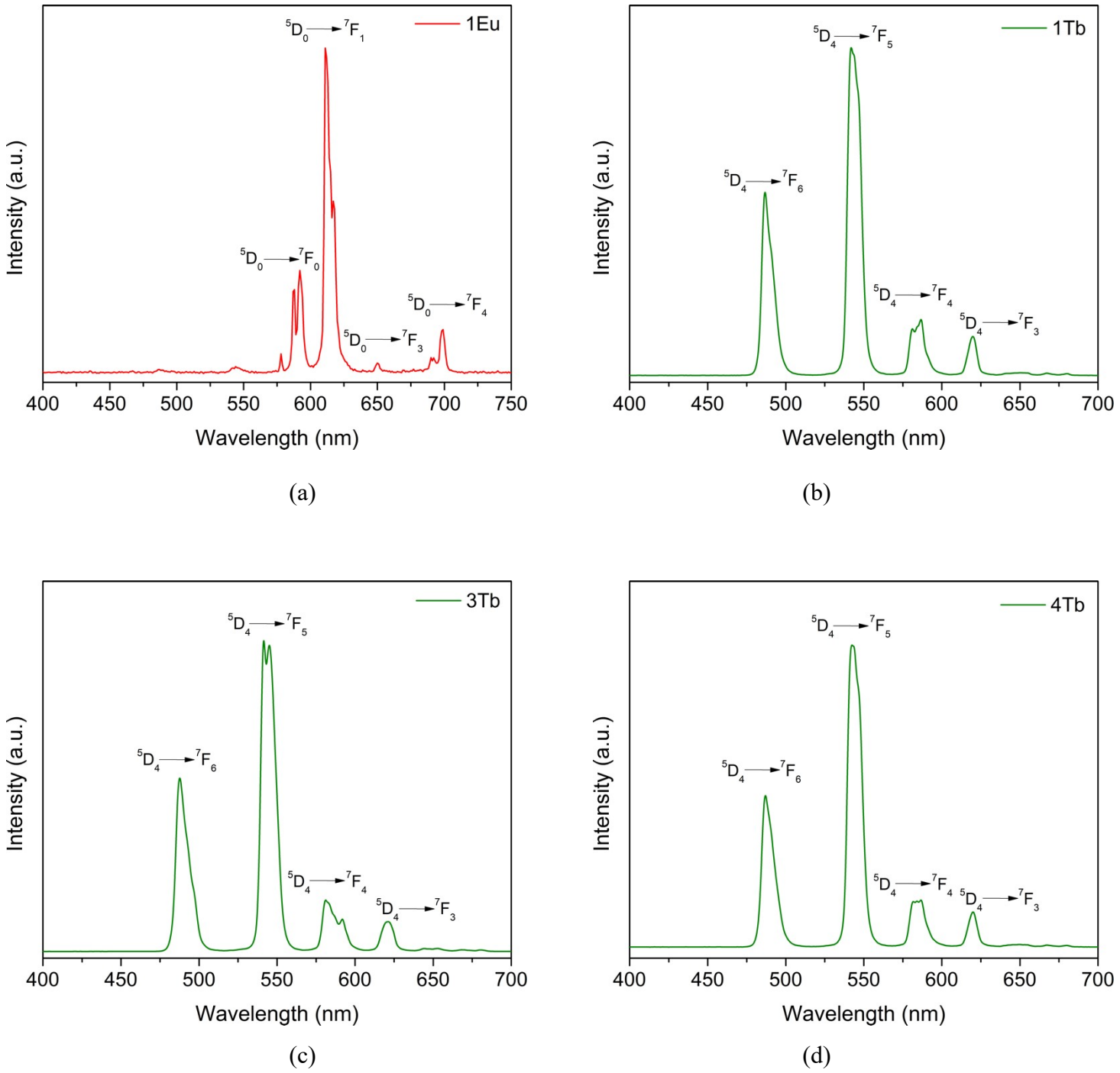


Figure S12. The solid-state photoluminescence spectra of $\mathbf{1}_{\mathbf{Eu}}$ (a), $\mathbf{1}_{\mathbf{Tb}}$ (b), $\mathbf{3}_{\mathbf{Tb}}$ (c), and $\mathbf{4}_{\mathbf{Tb}}$ (d) at room temperature.

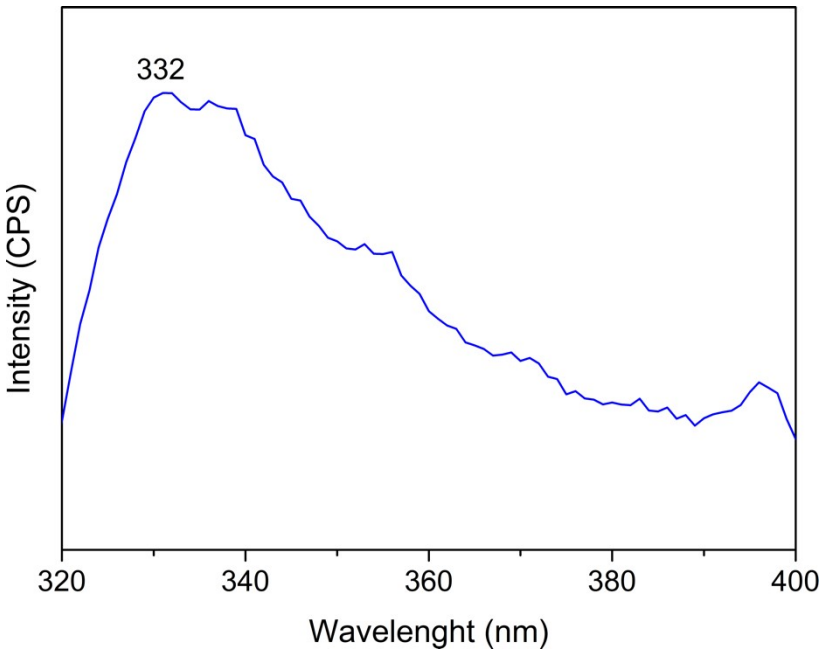


Figure S13. The solid-state photoluminescence spectrum of free ligand H_2Br_4bdc (λ_{ex} = 300 nm).

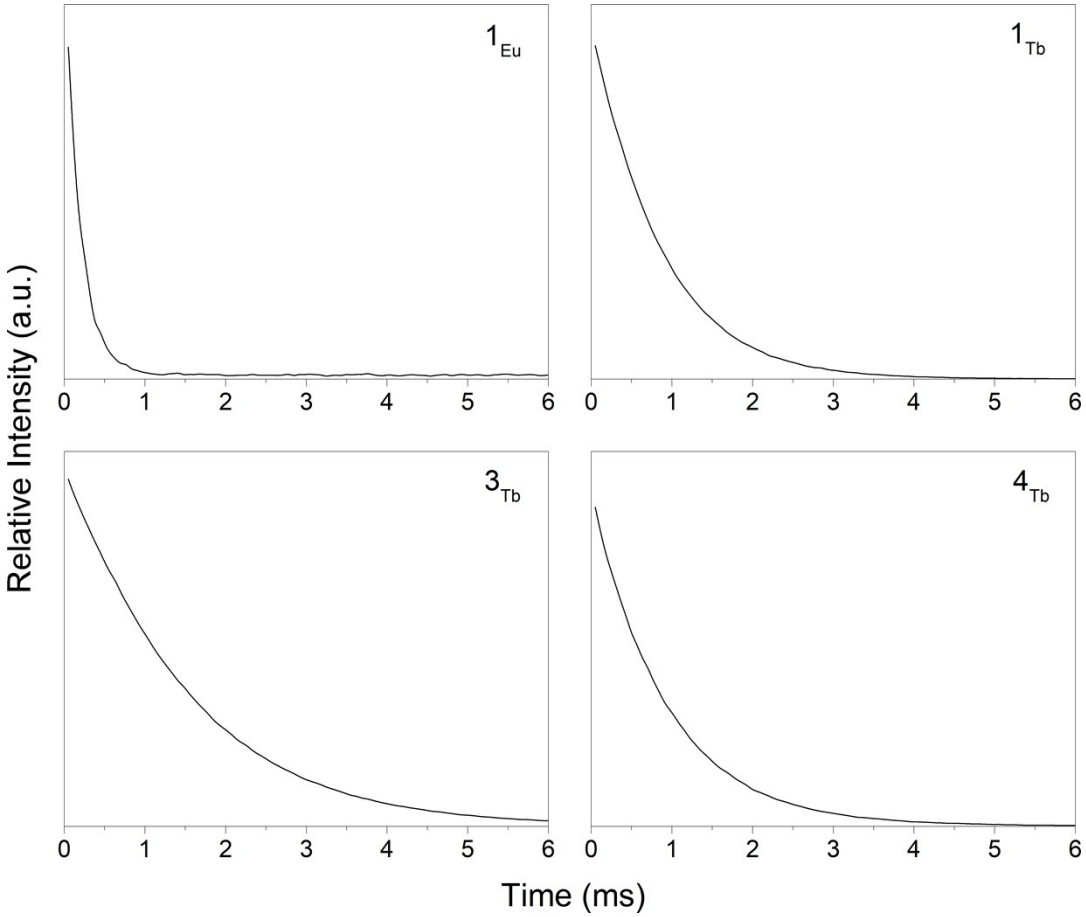


Figure S14. Luminescence decay (τ) curves for $\mathbf{1_{Eu}}$, $\mathbf{1_{Tb}}$, $\mathbf{3_{Tb}}$, and $\mathbf{4_{Tb}}$..

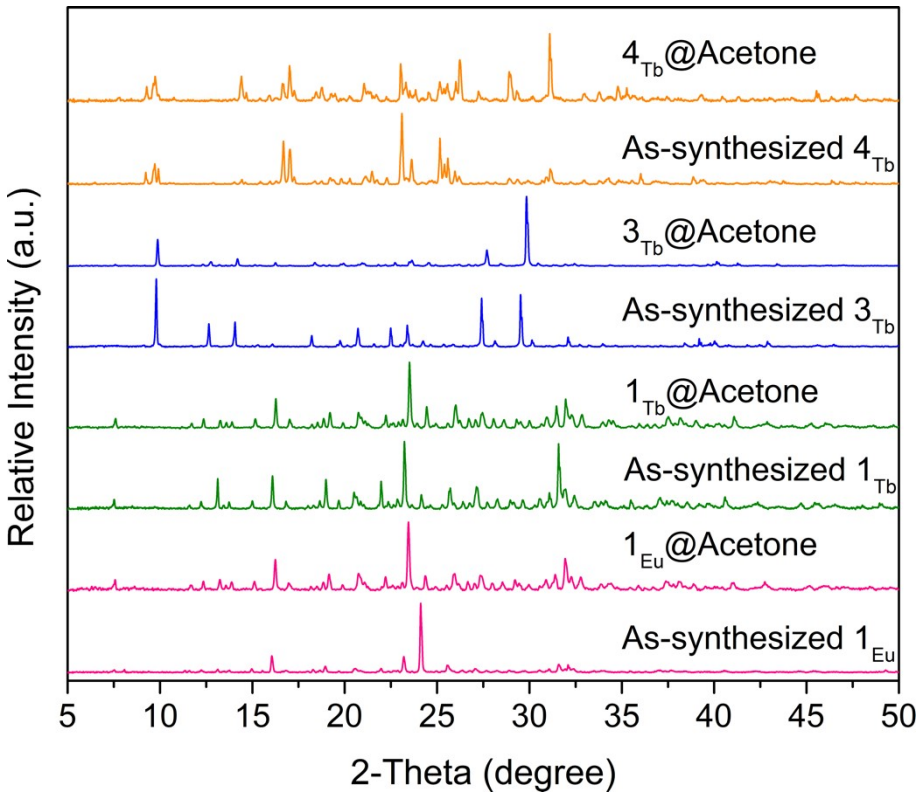


Figure S15. Experimental PXRD patterns of $\mathbf{1_{Eu}}$, $\mathbf{1_{Tb}}$, $\mathbf{3_{Tb}}$, and $\mathbf{4_{Tb}}$ before and after the fluorescence quenching experiments.

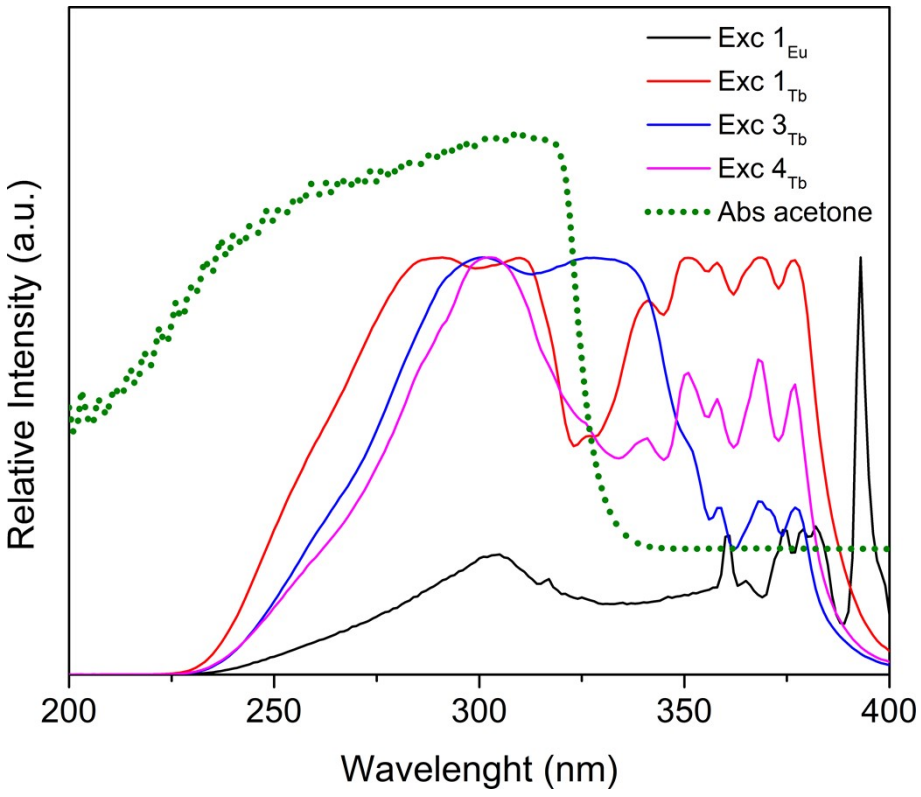


Figure S16. UV-Vis spectra of acetone and excitation spectra of $\mathbf{1_{Eu}}$, $\mathbf{1_{Tb}}$, $\mathbf{3_{Tb}}$ and $\mathbf{4_{Tb}}$.

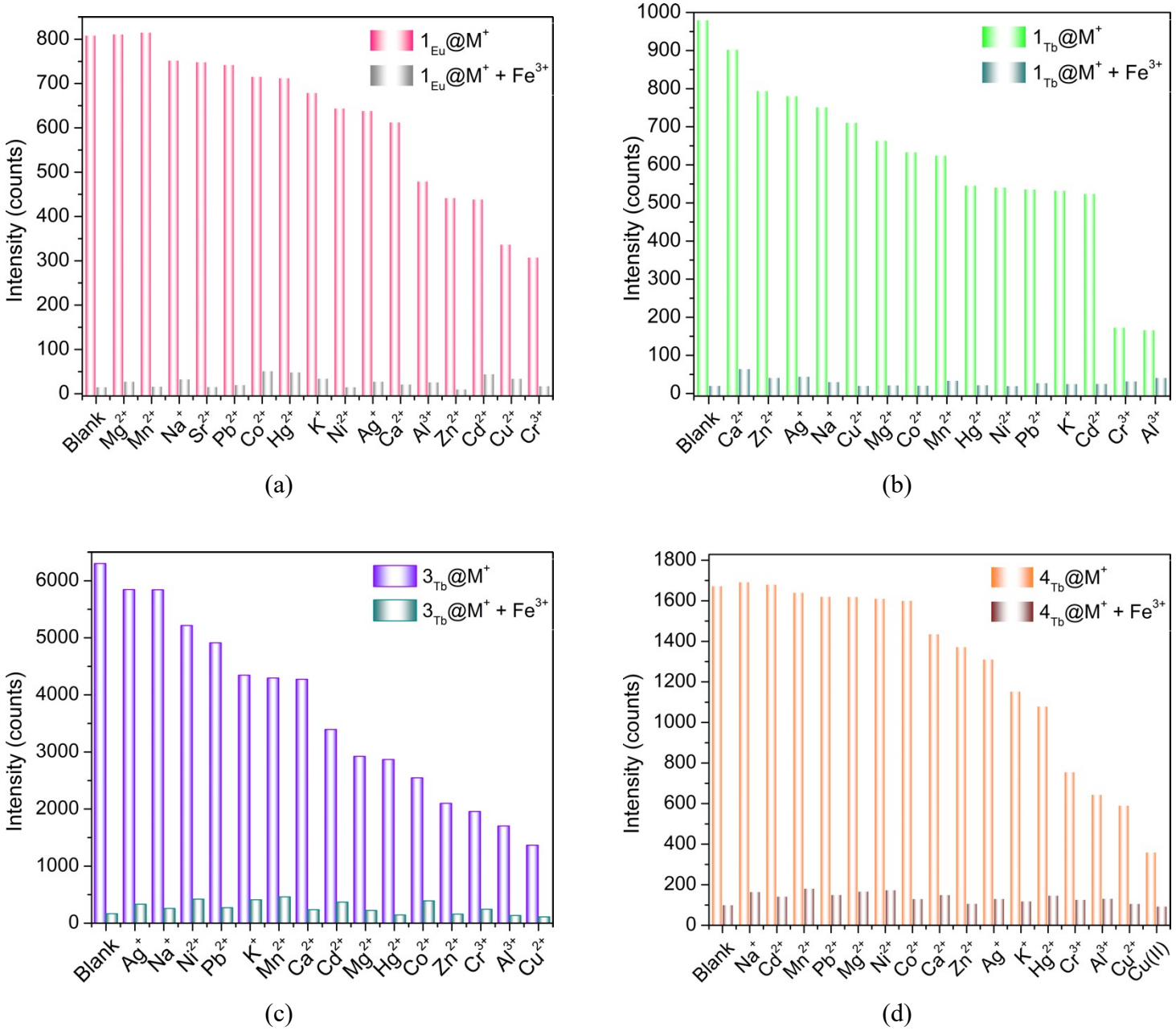


Figure S17. Relative luminescence intensities of $\mathbf{1}_{\mathbf{Eu}}$ (a), $\mathbf{1}_{\mathbf{Tb}}$ (b), $\mathbf{3}_{\mathbf{Tb}}$ (c), and $\mathbf{4}_{\mathbf{Tb}}$ (d) dispersed in the solutions of individual metal ions and the quenched luminescence intensities after the addition of solutions of Fe^{3+} in MeOH solution.

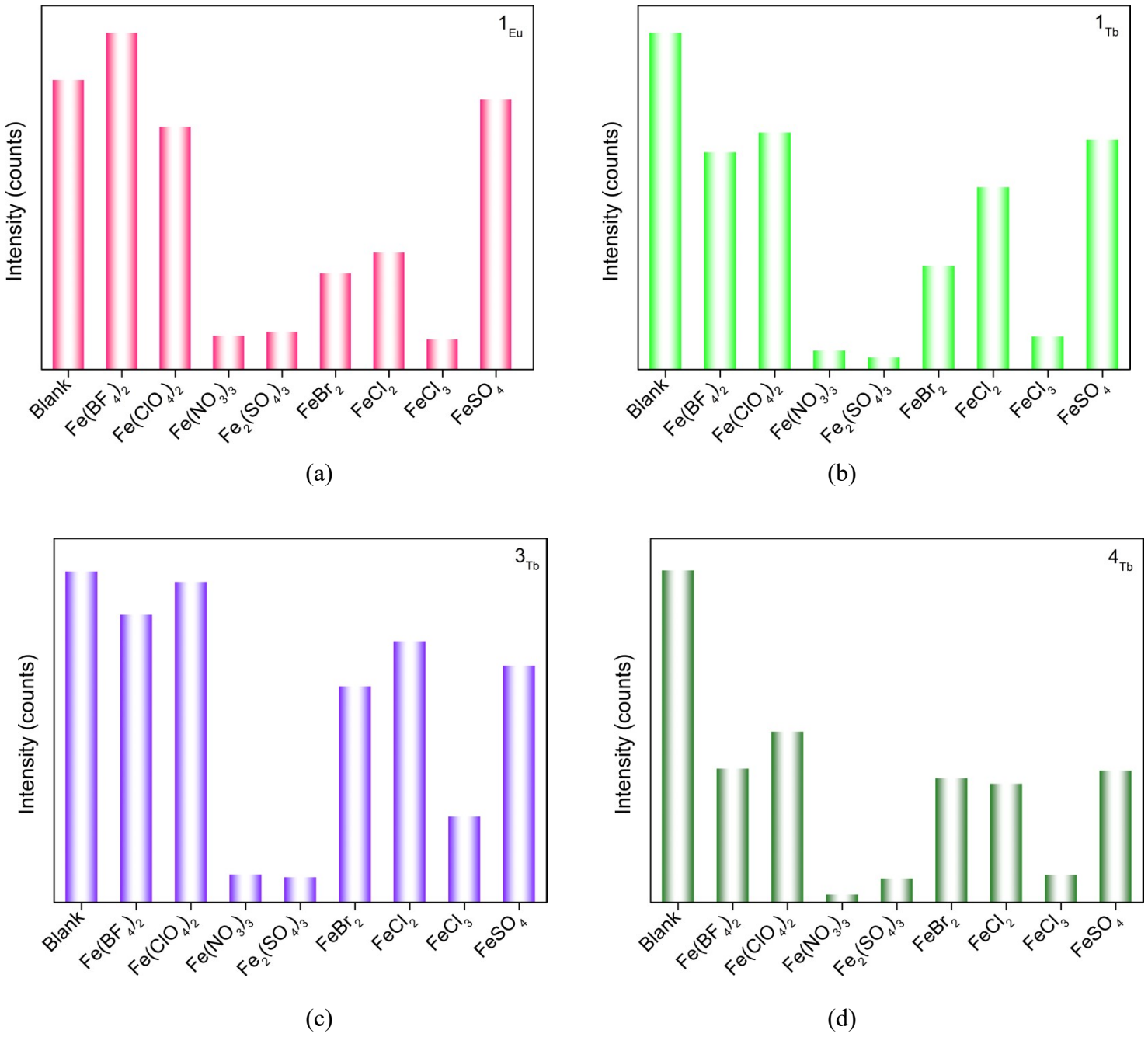


Figure S18. Emission intensities of $\mathbf{1_{Eu}}$ (a), $\mathbf{1_{Tb}}$ (b), $\mathbf{3_{Tb}}$ (c), and $\mathbf{4_{Tb}}$ (d) in MeOH solutions after the addition of various iron salts.

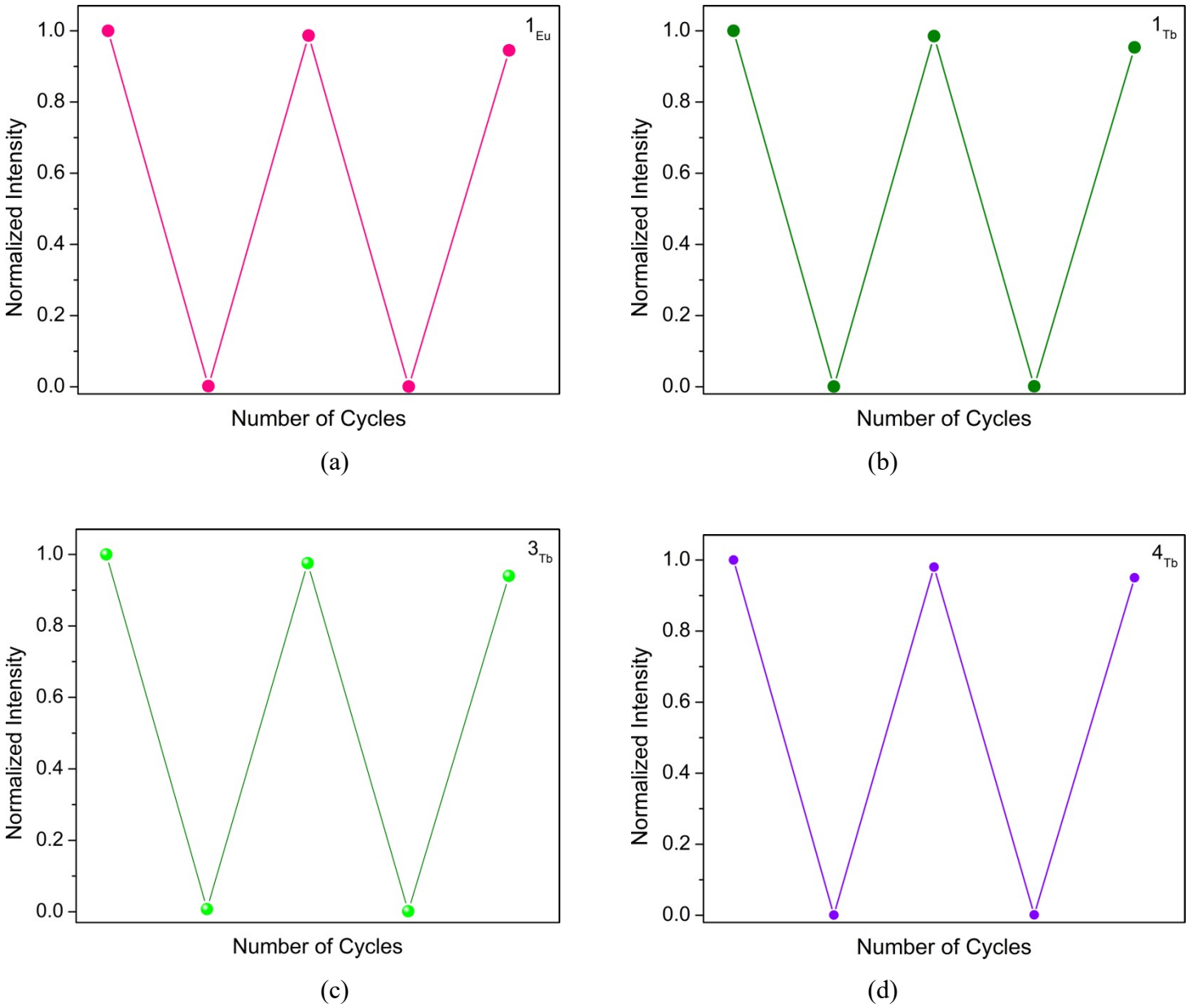


Figure S19. Recyclability test of $\mathbf{1_{Eu}}$ (a), $\mathbf{1_{Tb}}$ (b), $\mathbf{3_{Tb}}$ (c), and $\mathbf{4_{Tb}}$ (d) up to three cycles, the upper dots present initial intensity emission and lower dots present quenching intensity after added 5×10^{-4} M of Fe^{3+} solution.

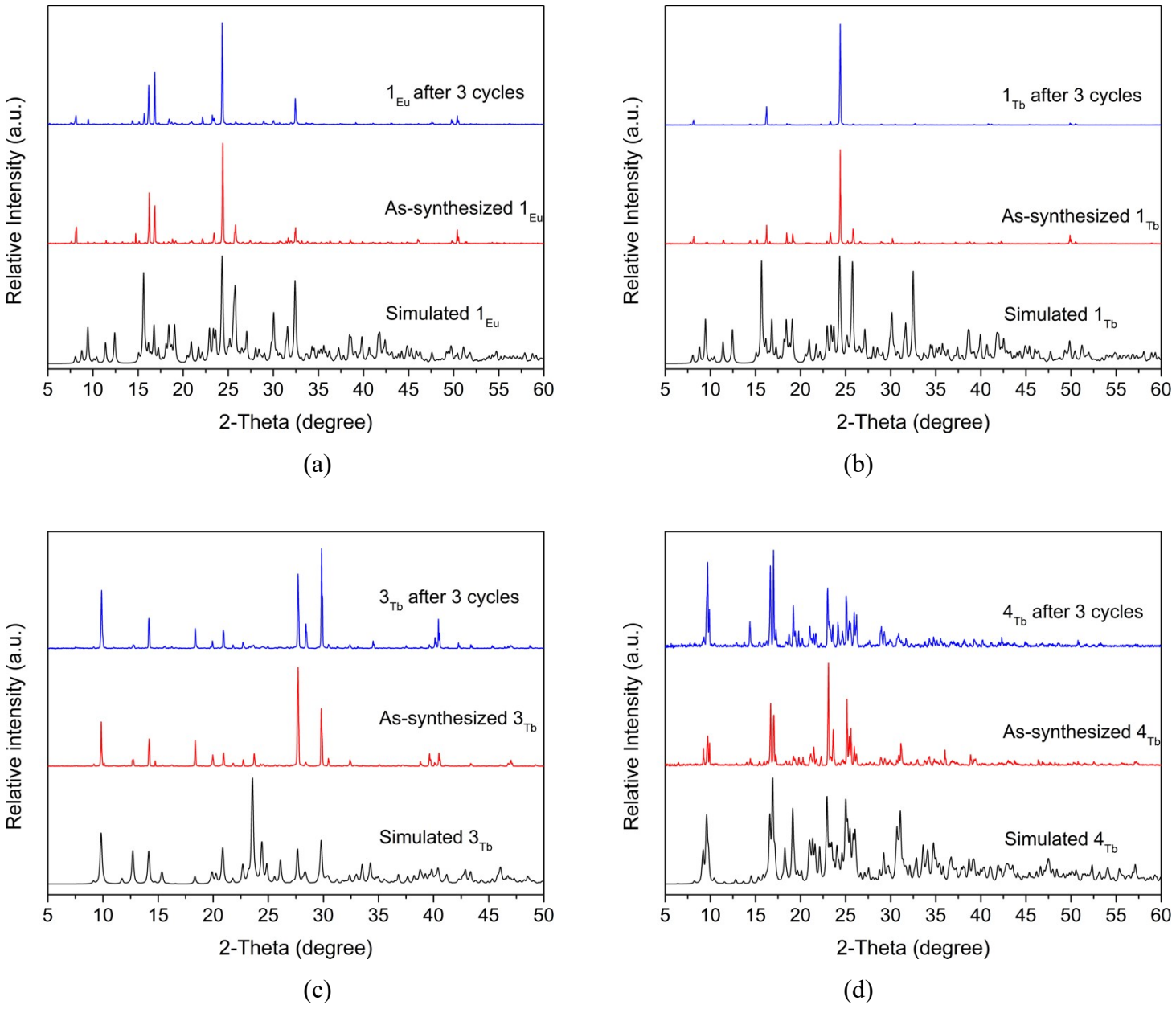
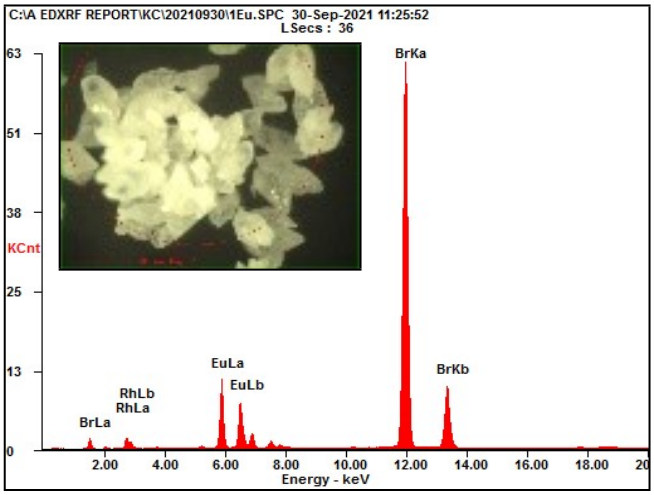
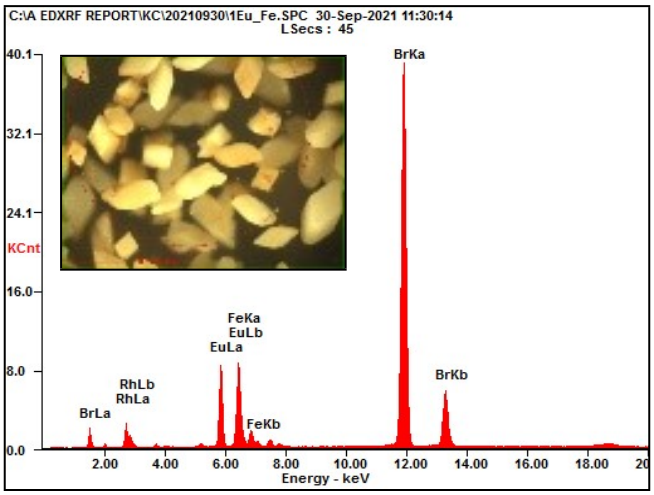


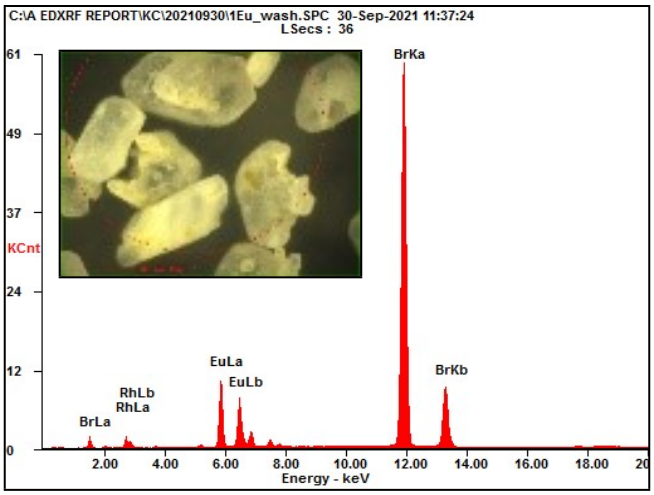
Figure S20. PXRD patterns of $\mathbf{1_{Eu}}$ (a), $\mathbf{1_{Tb}}$ (b), $\mathbf{3_{Tb}}$ (c), and $\mathbf{4_{Tb}}$ (d) before and after three cycles of sensing test.



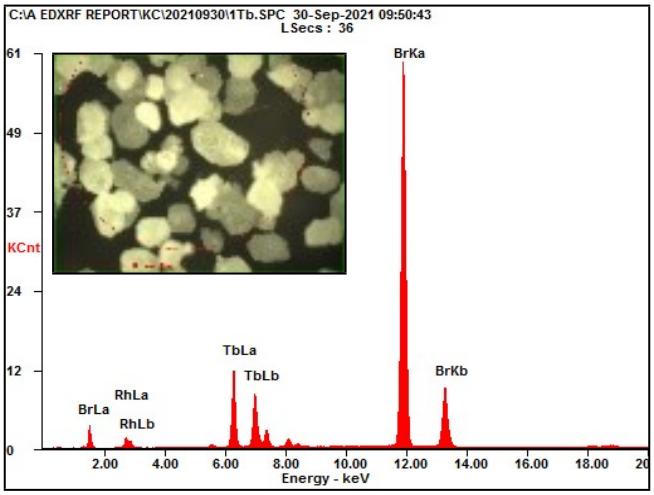
(a)



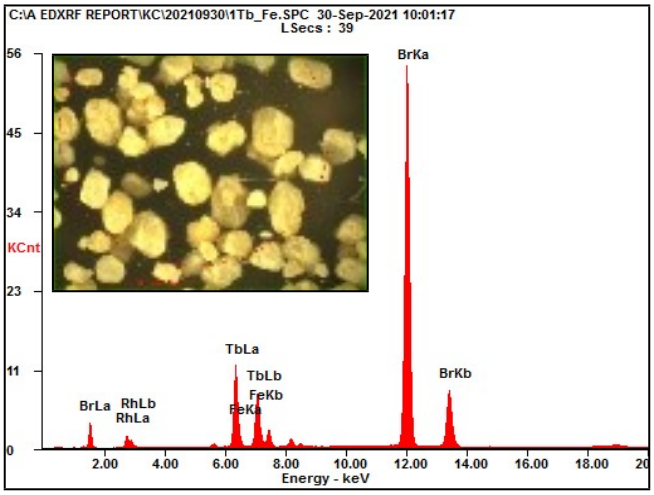
(b)



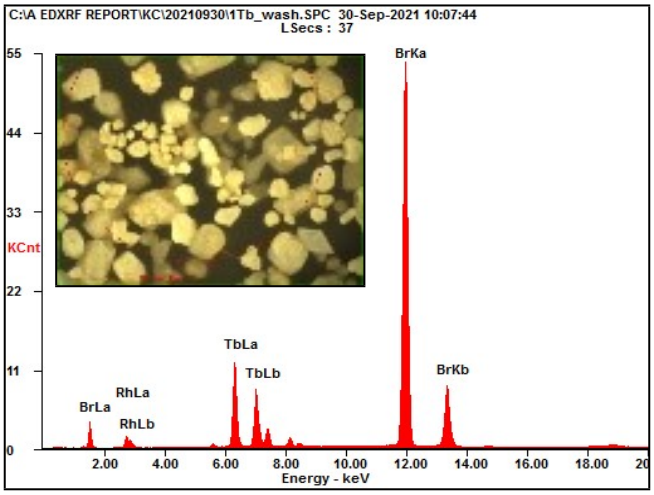
(c)



(d)

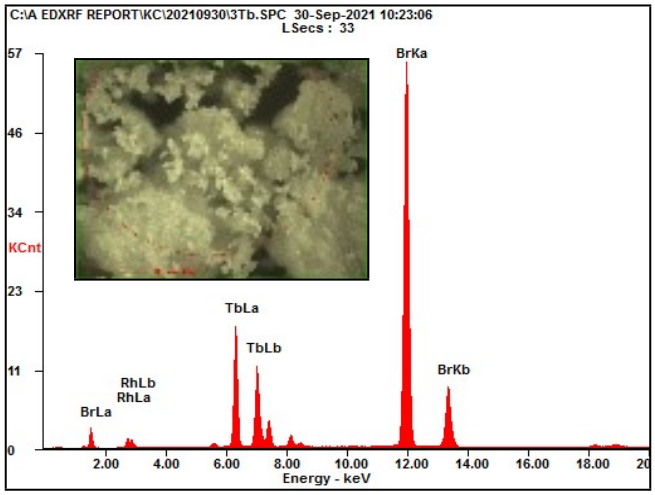


(e)

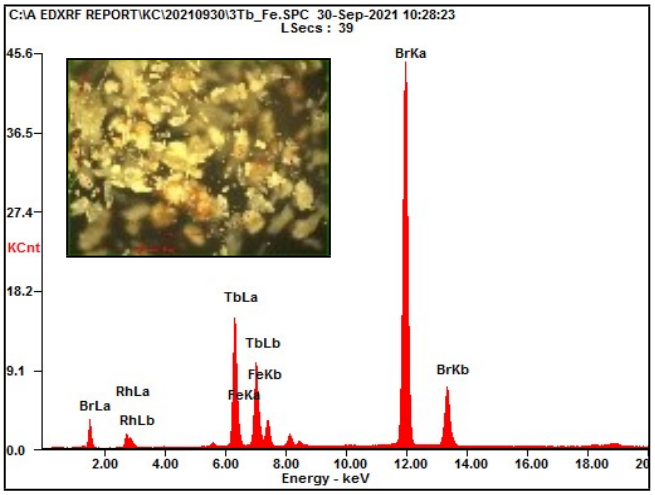


(f)

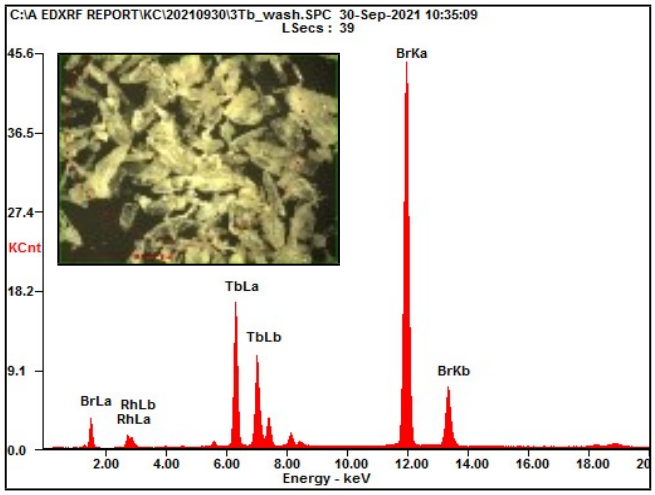
Figure S21. XRF spectra of $\mathbf{1}_{\mathbf{Eu}}$ (a), $\mathbf{1}_{\mathbf{Eu}}$@Fe^{3+} (b), $\mathbf{1}_{\mathbf{Eu}}$@washed by MeOH (c), $\mathbf{1}_{\mathbf{Tb}}$ (d), $\mathbf{1}_{\mathbf{Tb}}$@Fe^{3+} (e), $\mathbf{1}_{\mathbf{Tb}}$@washed by MeOH (f), $\mathbf{3}_{\mathbf{Tb}}$ (g), $\mathbf{3}_{\mathbf{Tb}}$@Fe^{3+} (h), $\mathbf{3}_{\mathbf{Tb}}$@washed by MeOH (i), $\mathbf{4}_{\mathbf{Tb}}$ (j), $\mathbf{4}_{\mathbf{Tb}}$@Fe^{3+} (k), $\mathbf{4}_{\mathbf{Tb}}$@washed by MeOH (l).



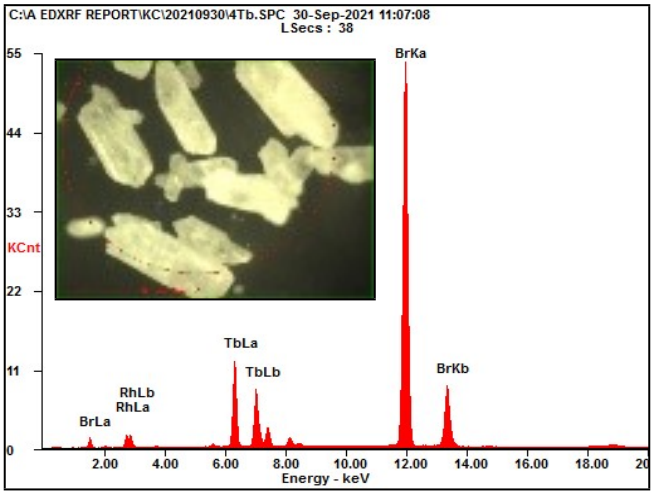
(g)



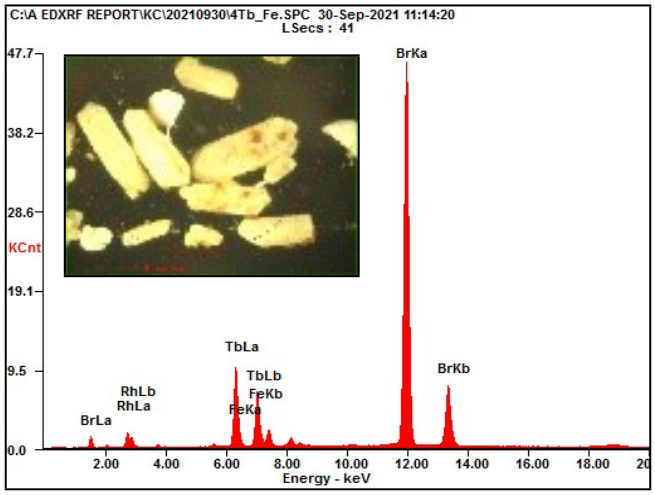
(h)



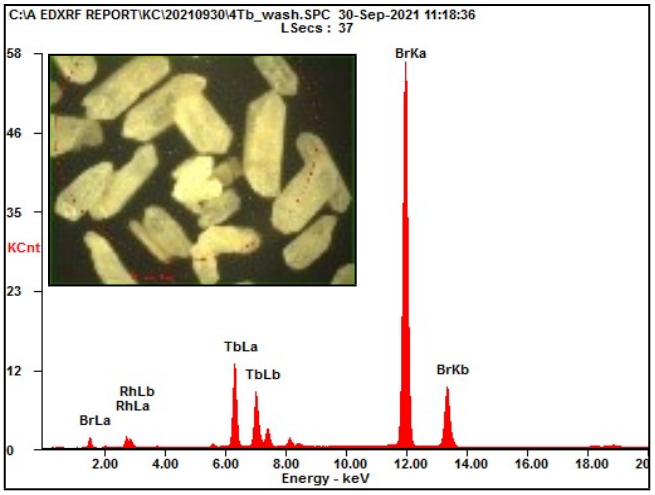
(i)



(j)



(k)



(l)

Figure S20. (Continued).

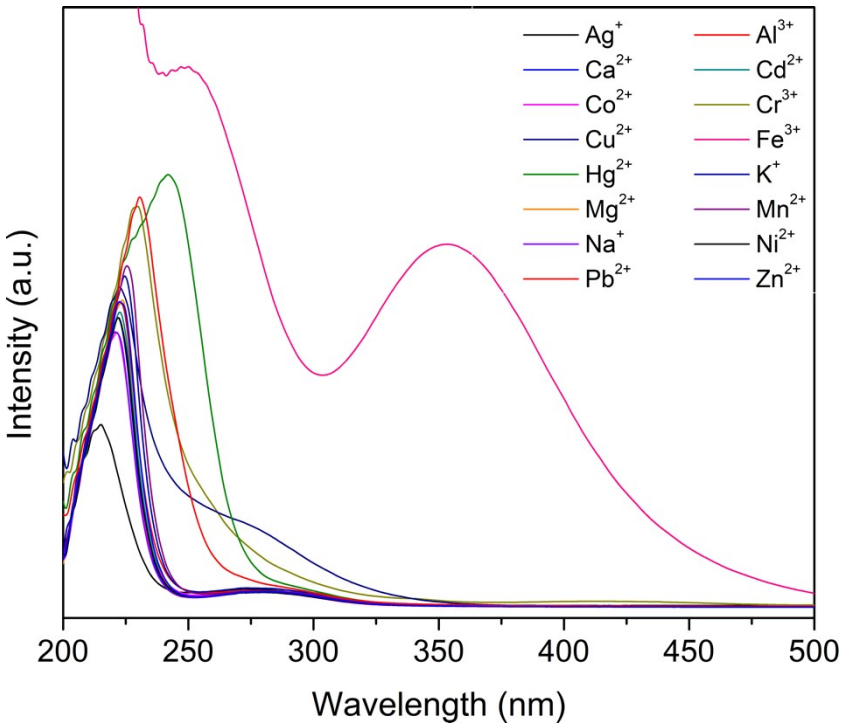


Figure S22. UV-Vis absorption spectra for metal ions in methanol solutions.

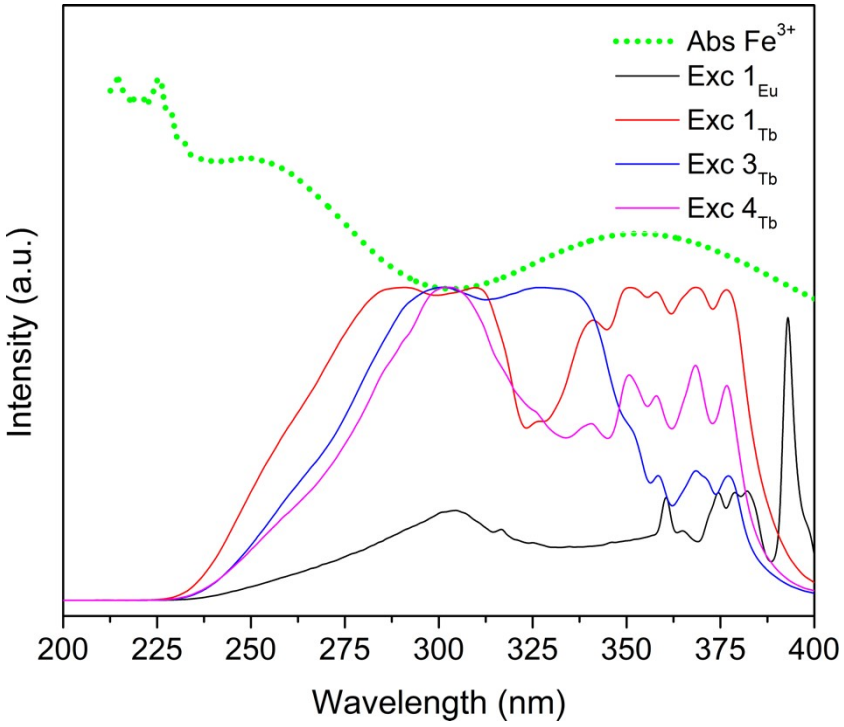


Figure S23. UV-Vis absorption spectra of Fe^{3+} ions and excitation of $\mathbf{1}_{Eu}$, $\mathbf{1}_{Tb}$, $\mathbf{3}_{Tb}$, and $\mathbf{4}_{Tb}$.

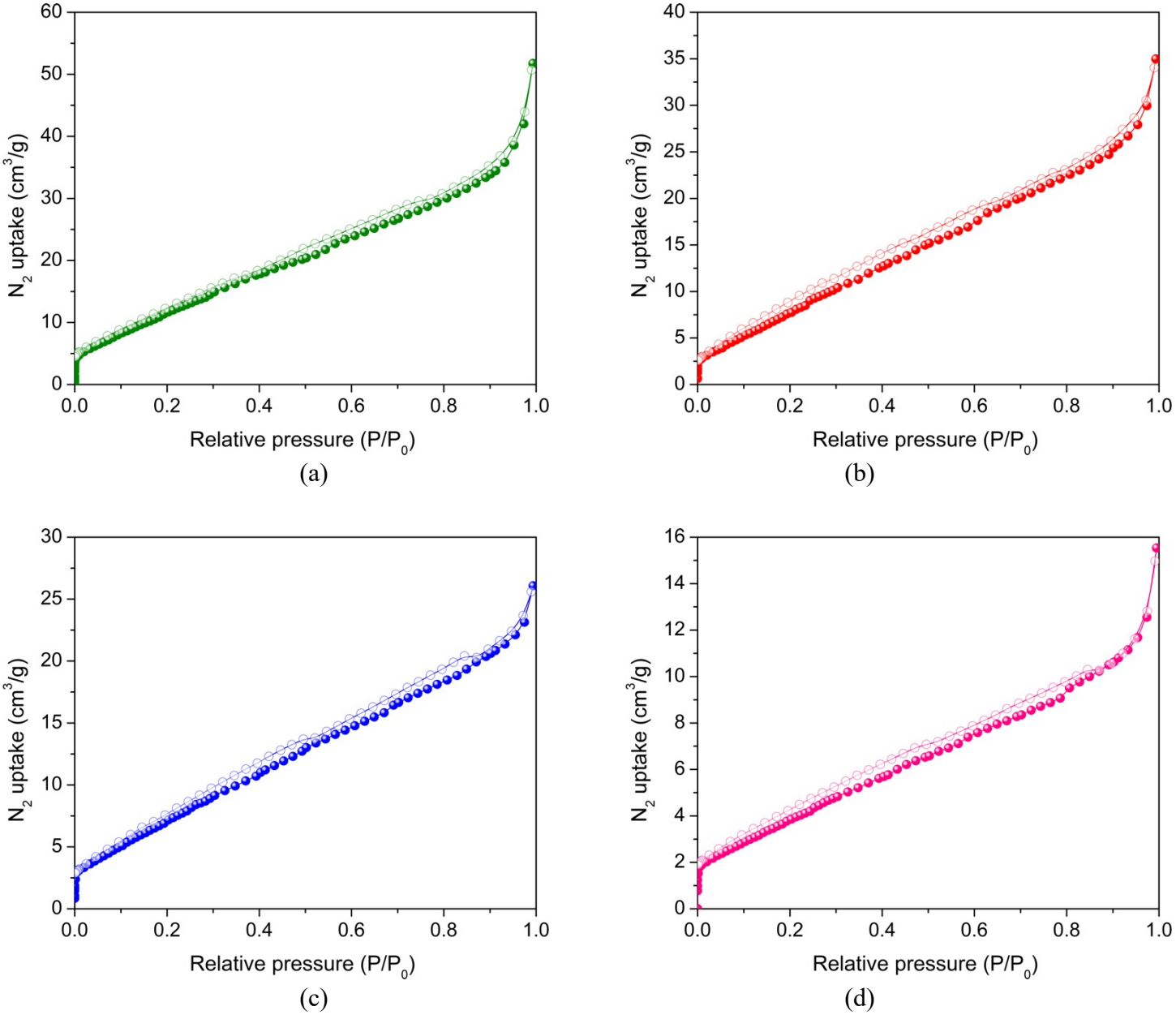


Figure S24. N_2 sorption isotherms for $\mathbf{1}_{\mathbf{Tb}}$ (a), $\mathbf{2}_{\mathbf{Pr}}$ (b), $\mathbf{3}_{\mathbf{Tb}}$ (c), and $\mathbf{4}_{\mathbf{Tb}}$ (d) at 77 K and 1 bar.

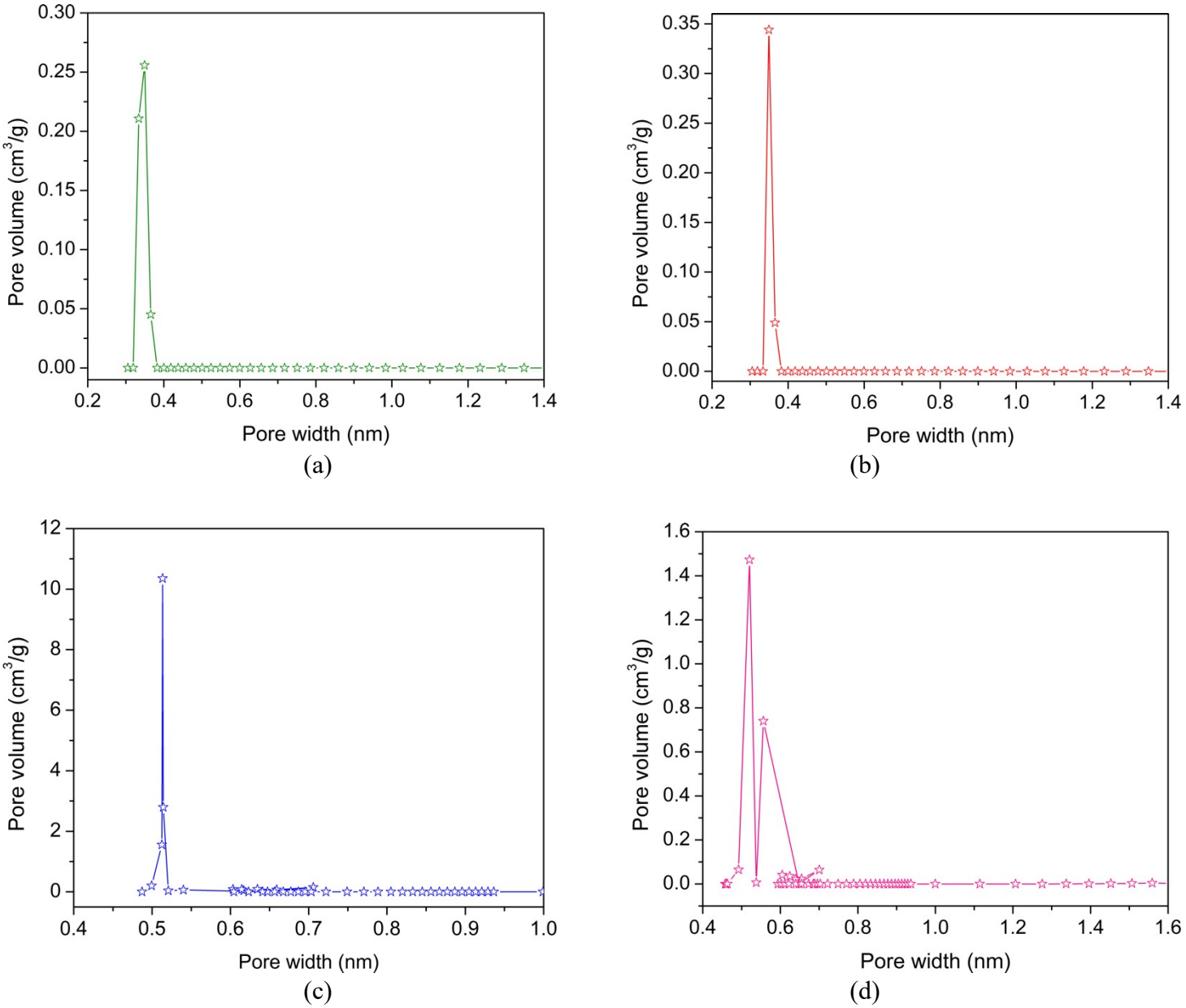


Figure S25. DFT pore size distribution plots for $\mathbf{1}_{\mathbf{Tb}}$ (a), $\mathbf{2}_{\mathbf{Pr}}$ (b), $\mathbf{3}_{\mathbf{Tb}}$ (c), and $\mathbf{4}_{\mathbf{Tb}}$ (d).

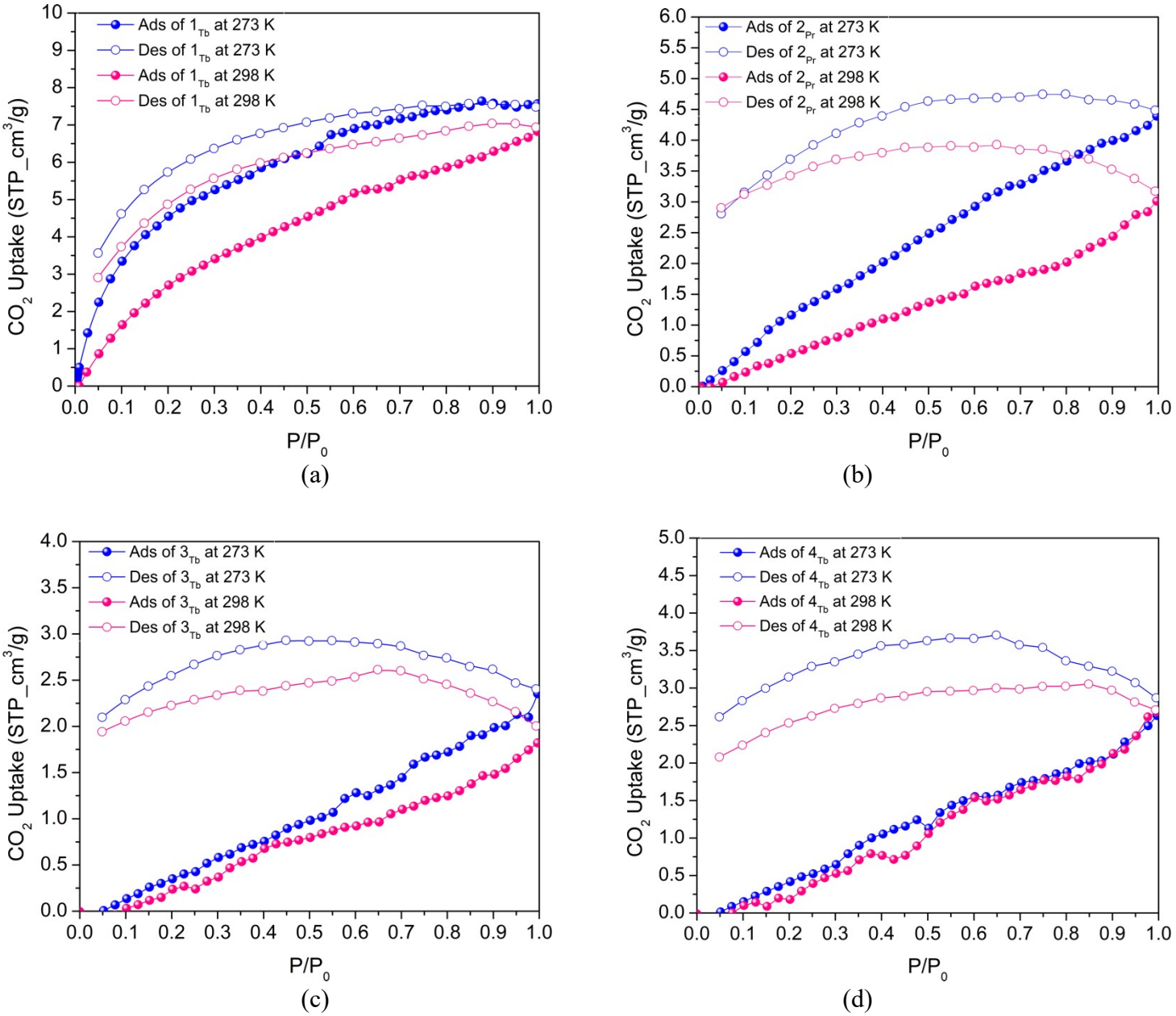


Figure S26. CO_2 adsorptions for $\mathbf{1_{Eu}}$ (a), $\mathbf{1_{Tb}}$ (b), $\mathbf{3_{Tb}}$ (c), and $\mathbf{4_{Tb}}$ (d) at 1 bar and at temperatures of 273 and 298 K.

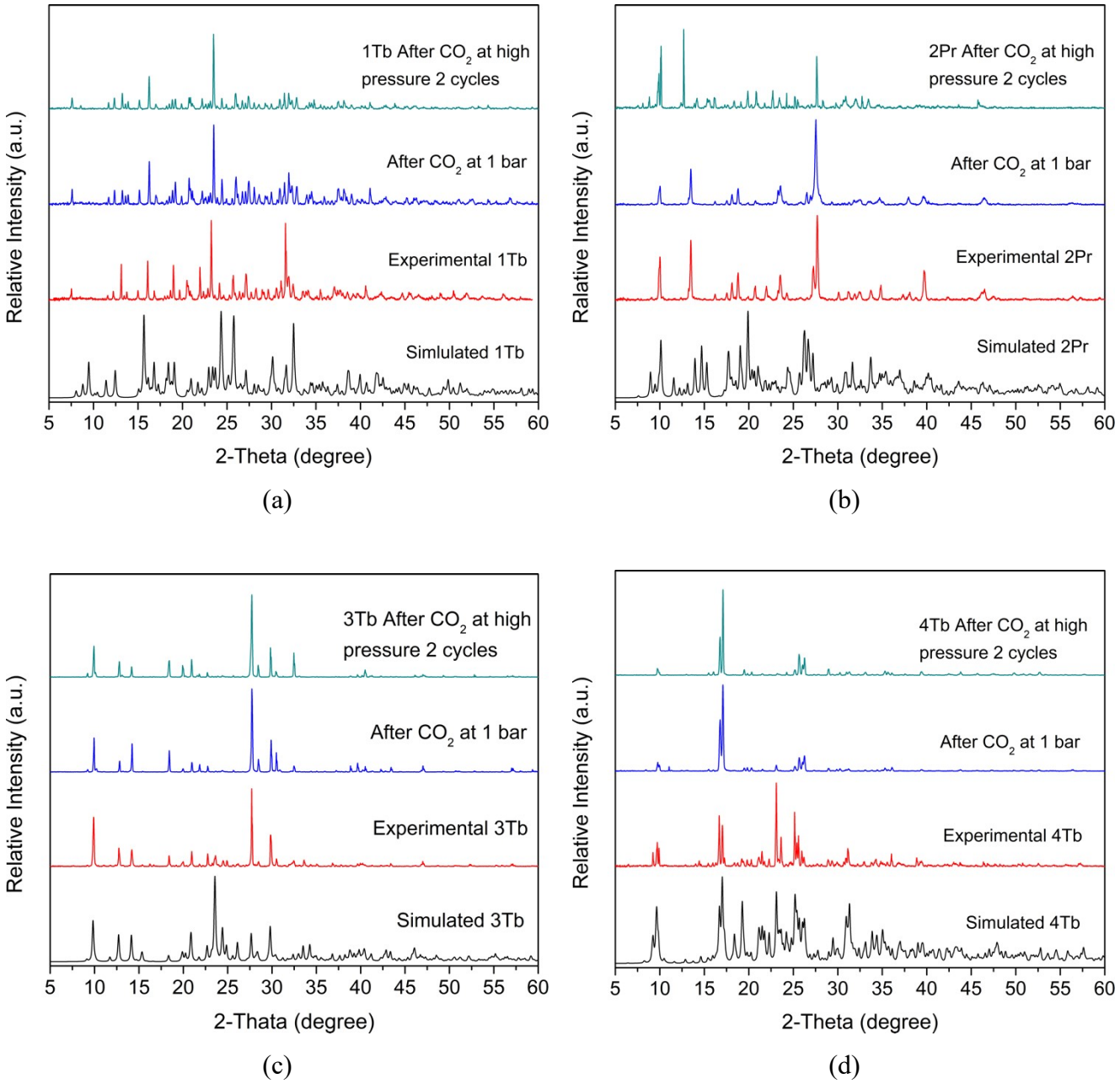


Figure S27. PXRD patterns of $\mathbf{1}_{\mathbf{Eu}}$ (a), $\mathbf{1}_{\mathbf{Tb}}$ (b), $\mathbf{3}_{\mathbf{Tb}}$ (c), and $\mathbf{4}_{\mathbf{Tb}}$ (d) before and after CO_2 adsorption-desorption (1-50 bar at 298 K).