Supplementary Information

$[CdCl_4]^{2-}$ Anion-induced Coordination of Ln^{3+} to Cucurbit[8]uril and The Formation of Supramolecular Self-Assemblies: Potential Application in Isolation of Light Lanthanides

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Contents:

Synthesis: Chemicals, such as lanthanide nitrates and hydrochloric acid, were of reagent grade and were used without further purification. Q[8] was prepared as reported elsewhere.[1a] Elemental analyses were carried out on a EURO EA-3000 elemental analyzer. Aqueous HCl (6.0 $mol \cdot L^{-1}$) was used to prepare crystals of Q[8]-Ln(III) in the presence of $CdCl_2$. A similar process was used to prepare crystals of related compounds: $Ln(NO_3)_3 \cdot xH_2O$ (0.106 mmol) and $CdCl_2$ (6.08 mg, 0.033 mmol) were dissolved in 2.0 mL 6.0 $mol \cdot L^{-1}$ HCl (solution A), Q[8] (10 mg, 0.007 mmol) was dissolved in 2.0 mL 6.0 $mol \cdot L^{-1}$ HCl (solution B), and was then added in the solution A with stirring for the Ln-Q[8]-Cd^{2+} sysems. X-ray quality crystals were obtained from the solution over a period of 1-3 days. The color of crystals was dependent on the lanthanide ions. Summarizing the preparations, $\{Ce_4(NO_3)_2(H_2O)_{24}Q[8]\} \cdot Q[8] \cdot 2[CdCl_4] \cdot 6Cl \cdot 45(H_2O)$ (**2**) was obtained from $Ce(NO_3)_3 \cdot 6H_2O$ (0.046g); $\{Nd_4(NO_3)_2 (H_2O)_{24}Q[8]\} \cdot Q[8] \cdot 2[CdCl_4] \cdot 6Cl \cdot 48(H_2O)$ (**4**) was obtained from $Nd(NO_3)_3 \cdot$(0.035 g); $\{Sm_4(NO_3)_2 (H_2O)_{24}Q[8]\} \cdot Q[8] \cdot 2[CdCl_4] \cdot 6Cl \cdot 53(H_2O)$ (**6**) was obtained from

$Sm(NO_3)_3·6H_2O$ (0.047 g); $\{Eu_4(NO_3)_2\ (H_2O)_{24}Q[8]\}·Q[8]·2[CdCl_4]·6Cl·70(H_2O)$ (**7**) was obtained from $Eu(NO_3)_3·6H_2O$ (0.047 g); $\{Gd(H_2O)_4(Q[8])_2\}·4Cl·(H_3O)·61(H_2O)$ (**8**) was obtained from $Gd(NO_3)_3·6H_2O$ (0.048 g); $\{Tb(H_2O)_4(Q[8])_2\}·4Cl·(H_3O)·64(H_2O)$ (**9**) was obtained from $Tb(NO_3)_3$ (0.037 g); $\{Ho(H_2O)_4(Q[8])_2\}·4Cl·(H_3O)·66(H_2O)$ (**11**) was obtained from $Ho(NO_3)_3·$(0.037 g); $\{Er(H_2O)_4(Q[8])_2\}·4Cl·(H_3O)·67(H_2O)$ (**12**) was obtained from $Er(NO_3)_3·5H_2O$ (0.047 g); $\{Tm(H_2O)_4(Q[8])_2\}·4Cl·(H_3O)·70(H_2O)$ (**13**) was obtained from $Tm(NO_3)_3$ (0.038 g); $\{Yb(H_2O)_4(Q[8])_2\}·4Cl·(H_3O)·65(H_2O)$ (**14**) was obtained from $Yb(NO_3)_3·5H_2O$ (0.048 g); $\{Lu(H_2O)_4(Q[8])_2\}·4Cl·(H_3O)·67(H_2O)$ (**15**) was obtained from $Lu(NO_3)_3·$(0.038 g); Elemental analysis results for the eleven compounds are given in Table 1.

It should be noted that 1) the compounds (**1~5, 10**) is corresponding to La, Ce, Pr, Nd, Pm and Dy, but we did not obtained crystals of **1**, **3** and **10** which were suitable for determination (except Pm), 2) in order to show the whole systems, the crystal data and structure refinement details of these two compounds are also listed in the corresponding tables.

Table 1. Elemental Analysis Results (%)

Results	2	4	6	7	8	9	11	12	13	14	15
C calcd.	21.73	21.44	21.00	19.86	27.80	27.43	27.16	27.04	26.68	27.22	26.98
found	21.87	21.65	20.88	19.44	28.03	27.56	27.21	27.21	26.77	27.31	27.08
H calcd.	4.44	4.50	4.59	4.93	5.57	5.64	5.68	5.70	5.77	5.64	5.69
found	4.34	4.36	4.44	4.98	5.39	5.46	5.55	5.58	5.65	5.60	5.56
N calcd.	17.42	17.19	16.83	15.93	21.62	21.34	21.13	21.04	20.76	21.17	20.99
found	17.51	17.32	16.84	15.66	21.75	21.47	21.30	21.27	20.85	21.21	21.06

X-ray crystallography: A suitable single crystal (~0.2 × 0.2 × 0.1 mm^3) was taken up in paraffin oil and mounted on a Bruker SMART Apex II CCD diffractometer equipped with a graphite-monochromated Mo-K_α (λ = 0.71073 Å, μ = 0.828 mm^{-1}) radiation source operating in the ω-scan mode and a nitrogen cold stream (–50 C). Data were corrected for Lorentz and polarization effects (SAINT), and semi-empirical absorption corrections based on equivalent reflections were also applied (SADABS). The structure was elucidated by direct methods and refined by the full-matrix least-squares method on F^2 with the SHELXS-97 and SHELXL-97 program packages, respectively.[14] All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were introduced at calculated positions, and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. Most of the water molecules in the compounds were omitted using the SQUEEZE option of the PLATON program. The squeezed water molecules

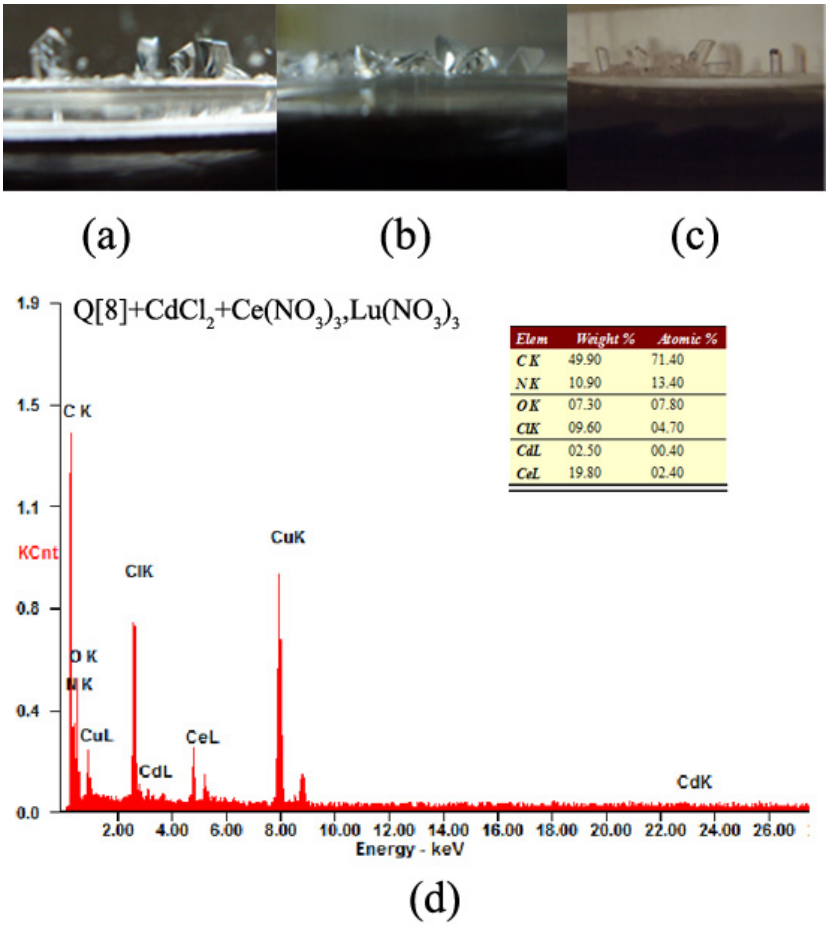
are listed in the Table 2. Analytical expressions for neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Details of the crystal parameters, data collection conditions, and refinement parameters for the twenty five compounds are summarized in Table 2. In addition, the crystallographic data for the reported structures have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-952098 (**2**), 952099 (**4**), 952100 (**6**), 952101 (**7**), 952102 (**8**), 952103 (**9**), 952104 (**11**), 952105 (**12**), 952106 (**13**), 952107 (**14**), 952108 (**15**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table 2. Crystal Data and Structure Refinement Details for Compounds

Compound	**2**	**4**	**6**	**7**	**8**	**9**	**11**	**12**	**13**	**14**	**15**
Empirical formula	$C_{96}H_{234}N_{66}O_{107}Cd_2Ce_4Cl_{14}$	$C_{96}H_{240}N_{66}O_{110}Cd_2Nd_4Cl_{14}$	$C_{96}H_{250}N_{66}O_{115}Cd_2Sm_4Cl_{14}$	$C_{96}H_{284}N_{66}O_{132}Cd_2Eu_4Cl_{14}$	$C_{96}H_{229}N_{64}O_{98}GdCl_4$	$C_{96}H_{235}N_{64}O_{101}TbCl_4$	$C_{96}H_{239}N_{64}O_{103}HoCl_4$	$C_{96}H_{241}N_{64}O_{104}ErCl_4$	$C_{96}H_{247}N_{64}O_{107}TmCl_4$	$C_{96}H_{237}N_{64}O_{102}YbCl_4$	$C_{96}H_{241}N_{64}O_{104}LuCl_4$
Formula weight	5307.07	5377.60	5492.12	5804.83	4147.48	4203.20	4245.24	4265.59	4321.31	4235.34	4255.57
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	P-1	P-1	P-1	P-1	I 41/a	I 41/a	I 41/a	I 41/a	I 41/a	I 41/a	I 41/a
a, Å	17.278(2)	17.1436(6)	17.063(1)	17.0389(17)	28.3249(19)	28.3123(19)	28.464(4)	28.440(3)	28.4011(18)	28.388(3)	28.3363(19)
b, Å	17.861(2)	18.0998(6)	18.020(1)	17.9558(17)	28.3249(19)	28.3123(19)	28.464(4)	28.440(3)	28.4011(18)	28.388(3)	28.3363(19)
c, Å	18.092(2)	18.3169(6)	18.284(1)	18.3397(19)	21.949(3)	21.934(3)	21.992(3)	22.010(5)	21.939(3)	22.036 (5)	21.928(3)
α, deg	82.207(5)	84.896(1)	84.728(2)	84.823(4)	90.00	90.000	90.00	90.00	90.00	90.000	90.00
β, deg	71.356(5)	65.733(1)	65.772(2)	65.727(4)	90.00	90.000	90.00	90.00	90.00	90.000	90.00
γ, deg	66.625 (4)	71.546(1)	71.667(2)	71.616(4)	90.00	90.000	90.00	90.00	90.00	90.000	90.00
V, $Å^3$	4855.7(10)	4909.4(3)	4862.1(5)	4848.9(8)	17609(3)	17582(3)	17817(4)	17803(5)	17696(3)	17758(5)	17607(3)
Z	1	1	1	1	4	4	4	4	4	4	4
Dcalcd, g cm^{-3}	1.815	1.819	1.876	1.988	1.564	1.588	1.583	1.591	1.622	1.584	1.605
T, K	223	223	223	223	223	223	223	223	223	223	223
μ, mm^{-1}	1.447	1.564	1.722	1.821	0.561	0.589	0.630	0.658	0.692	0.713	0.742
Unique reflns	17141	17027	17129	16888	8607	7734	8723	8683	8627	8683	8619
Obsd reflns	10873	12318	12192	11768	5493	4921	5167	4206	4408	4065	4903
Params	1103	1109	1082	1069	480	480	480	480	480	480	480
Rint	0.0863	0.0547	0.0588	0.0792	0.0749	0.0859	0.0845	0.0874	0.1117	0.1019	0.0829

R[I> 2σ(I)][a]	0.0679	0.0594	0.0687	0.1102	0.0894	0.0791	0.0832	0.0752	0.0880	0.0893	0.0775
wR[I> 2σ(I)][b]	0.1885	0.1760	0.2066	0.3205	0.2683	0.2312	0.2333	0.2098	0.2448	0.2612	0.2289
R(all data)	0.0979	0.0777	0.0878	0.1313	0.1250	0.1109	0.1202	0.1363	0.1480	0.1579	0.1176
wR(all data)	0.2087	0.1934	0.2254	0.3432	0.2925	0.2506	0.2563	0.2323	0.2711	0.2945	0.2475
GOF on F^2	1.069	0.969	1.126	1.251	1.085	1.055	1.038	0.992	0.944	0.967	0.948
The squeezed water molecules	45	48	53	70	62	65	67	68	71	66	68

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = (F_o^2 + 2F_c^2)/3$.



Figgure S1 Crystals grown from (a) Ce^{3+}-Q[6]-$[CdCl_4]^{2-}$ system; (b) Lu^{3+}-Q[6]-$[CdCl_4]^{2-}$ system; (c) Ce^{3+}-Lu^{3+}-Q[6]-$[CdCl_4]^{2-}$ system; and (d) electron spectroscopy data of the stick-like crystals from the Ce-Lu-Q[8]-$[CdCl_4]^{2-}$ system.

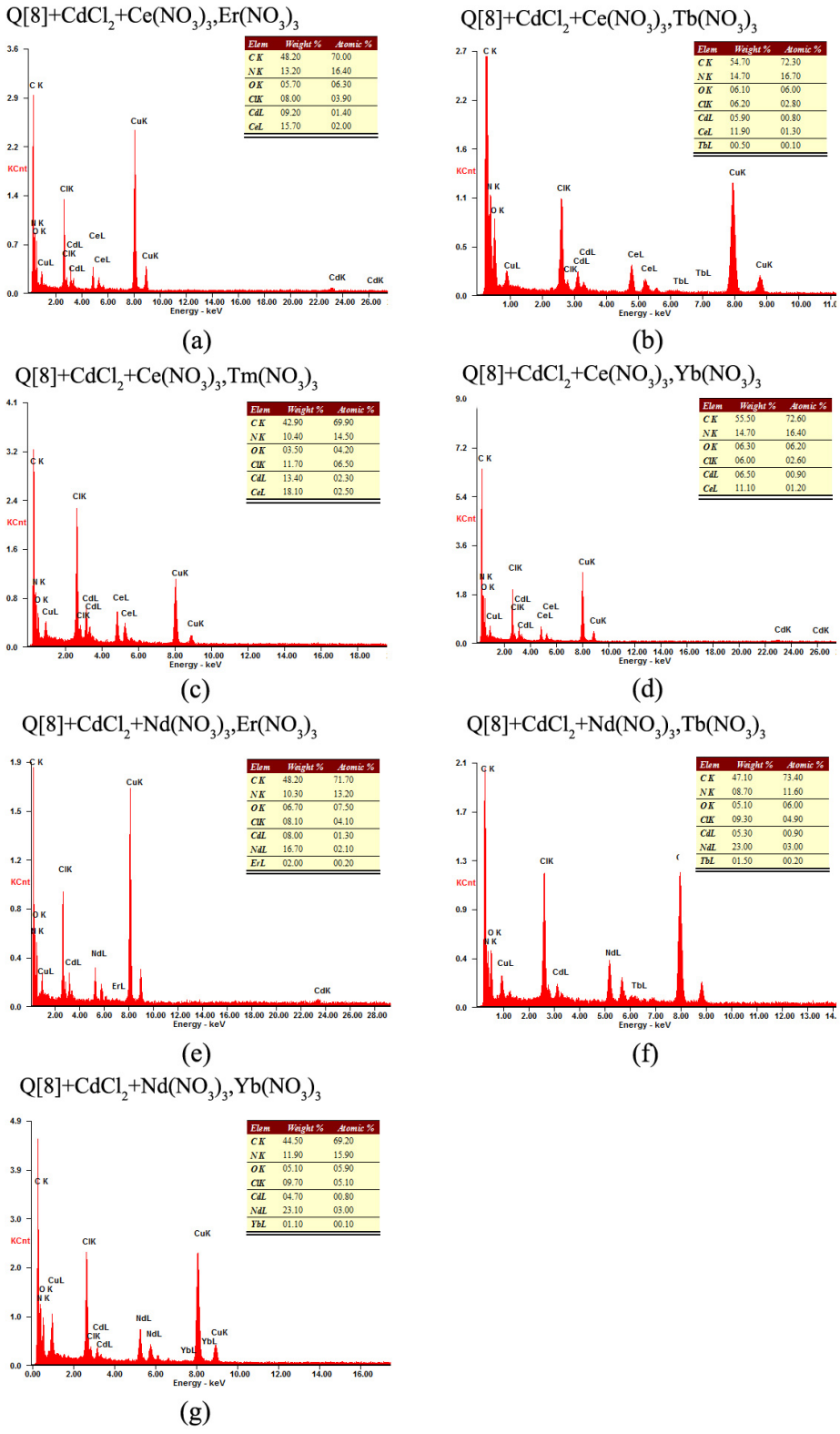


Figure S2 Electron spectroscopies of the stick-like crystals from the (a) Ce-Er-; (b) Ce-Tb-; (c) Ce-Tm-; (d) Ce-Yb-; (e) Nd-Er-; (f) Nd-Tb-; (g) Nd-Yb-Q[8]-$[CdCl_4]^{2-}$ systems.

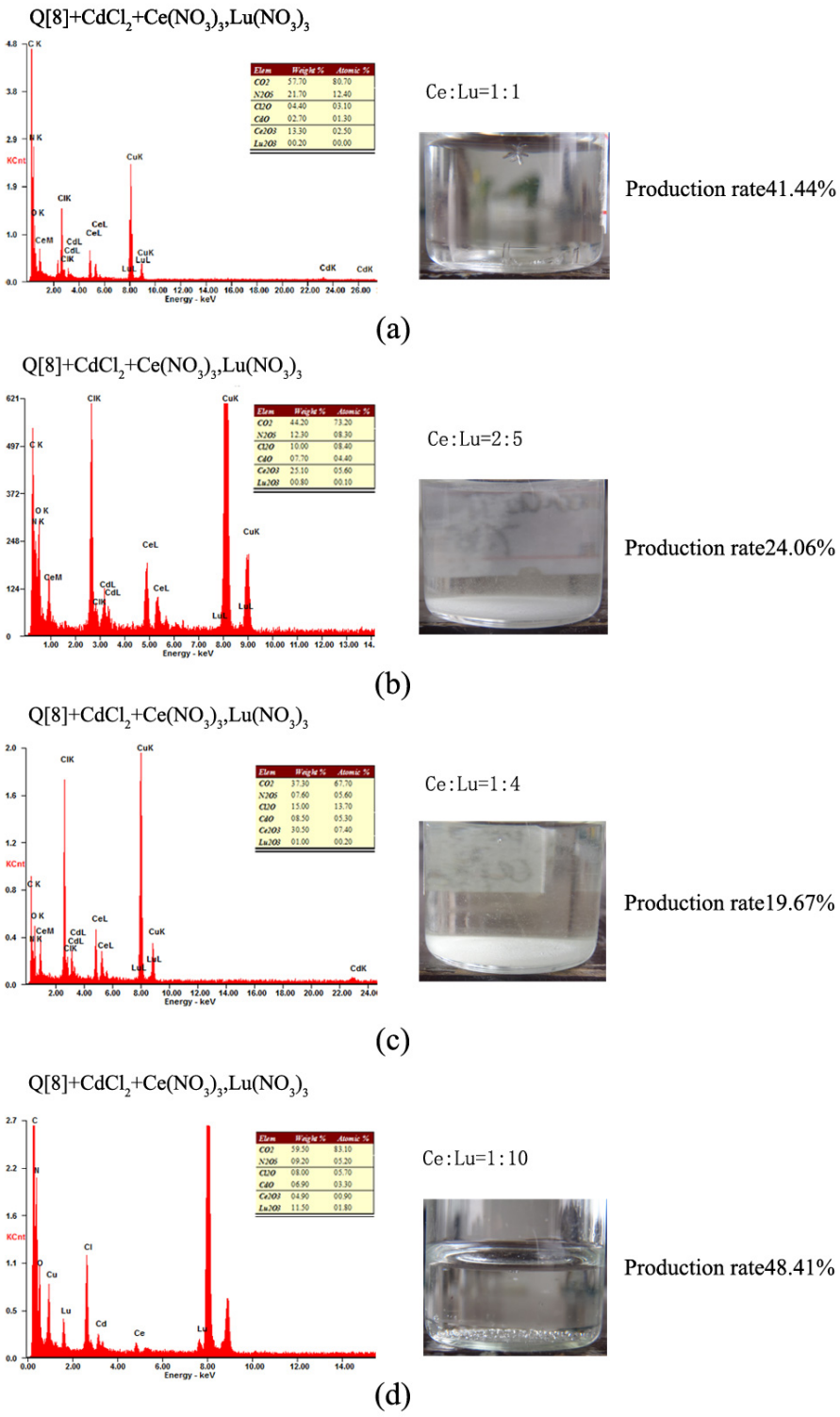


Figure S3 Crystals grown from (a) a Ce^{3+}-Lu^{3+}-Q[8]-$[CdCl_4]^{2-}$ system for the first time, (b) the same system with a supplementary Q[8]; (c) the same system with a supplementary Q[8] again and the corresponding electron spectroscopy of the crystals from this Ce-Lu-Q[8]-$[CdCl_4]^{2-}$ system.

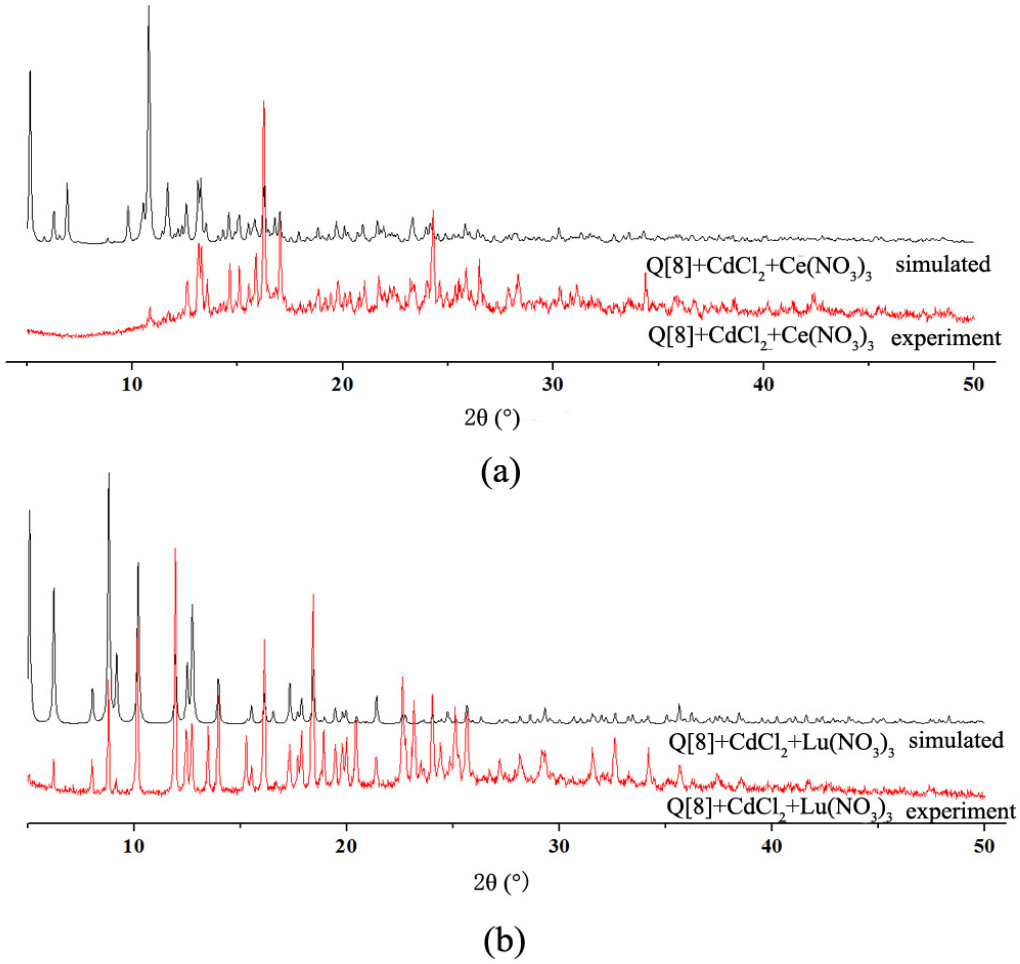


Figure S4 Powder X-ray diffraction (PXRD) of the crystals from (a) Ce^{3+}-Q[8]-$[CdCl_4]^{2-}$ and (b) Lu^{3+}-Q[8]-$[CdCl_4]^{2-}$ systems respectively

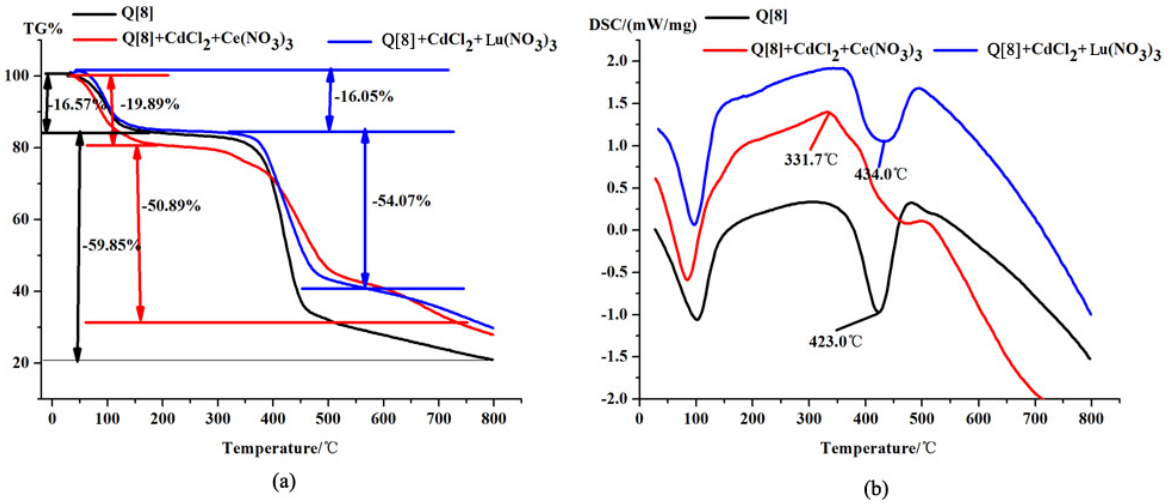


Figure S5 DSC (left) and TG (right) curves of the crystals from Ce^{3+}-Q[8]-$[CdCl_4]^{2-}$ and Lu^{3+}-Q[8]-$[CdCl_4]^{2-}$ systems respectively with a comparison of Q[8] in N_2