Lanthanide separation using size-selective crystallization of Ln-MOFs

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Experimental details:

Materials and general methods. Reagents and solvents were commercially available (Alfa) and used without further purification. X-ray powder diffraction was collected by a Bruker AXS D8 Discover powder diffractometer at 40 kV, 40 mA for Cu Kα, (λ = 1.5406Å). The simulated powder patterns were calculated by Mercury 1.4. The purity of the bulk products were determined by comparison of the simulated and experimental XRD patterns. Thermogravimetric analysis (TGA) was performed by a TGA Q500 thermal analysis system. All TGA experiments were performed under a N_2 atmosphere from 40-800°C at a rate of 5°C /min. EDS measurements were prepared by using an Oxford x-max microscope.

X-ray Crystallography. Unit cell measurements and intensity data were collected at room temperature on a Bruker-AXS SMART Breeze CCD diffractometer using graphite monochromated MoKα radiation (λ=0.71073 Å). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). The crystal structure was solved and refined using the SHELXTL program suite. Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms.

Synthesis.

Synthesis of compound $La_2(OLZ)(H_2OLZ)(DMF)(H_2O)_2{\cdot}2H_2O$: A mixture of $La(NO_3)_3$ (0.1 mmol), Na_2H_2OLZ (0.15 mmol), DMF (5mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature. Light yellow needle crystals were obtained with 53.8% yield based on La.

Synthesis of compound $Ce_2(OLZ)(H_2OLZ)(DMF)(H_2O)_2{\cdot}2H_2O$: A mixture of $Ce(NO_3)_3$ (0.1 mmol), Na_2H_2OLZ (0.15 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature. Yellow needle crystals were obtained with 61.2% yield based on Ce.

Synthesis of compound $Pr_2(OLZ)(H_2OLZ)(DMF)(H_2O)_2{\cdot}2H_2O$: A mixture of $Pr(NO_3)_3$ (0.1 mmol), Na_2H_2OLZ (0.15 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml

Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature. Yellow strip crystals were obtained with 59.0% yield based on Pr.

Synthesis of compound $Nd(OLZ)_{0.5}(H_2OLZ)_{0.5}(DMF)(\mu_2\text{-}DMF)_{0.5}$: A mixture of $Nd(NO_3)_3$ (0.1 mmol), Na_2H_2OLZ (0.15 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature. Long strip crystals were obtained with 53.0% yield based on Nd.

Synthesis of compound $Sm(OLZ)_{0.5}(H_2OLZ)_{0.5}(DMF)(\mu_2\text{-}DMF)_{0.5}$: A mixture of $Sm(NO_3)_3$ (0.1 mmol), Na_2H_2OLZ (0.15 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature. The yellow stripe crystals were obtained with 57.4% yield based on Sm.

Synthesis of compound $Eu(OLZ)_{0.5}(H_2OLZ)_{0.5}(DMF)(\mu_2\text{-}DMF)_{0.5}$: A mixture of $Eu(NO_3)_3$ (0.1 mmol), Na_2H_2OLZ (0.15 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature. Acicular crystals were obtained with 54.1% yield based on Eu.

Synthesis of compound $Gd(OLZ)_{0.5}(H_2OLZ)_{0.5}(DMF)(H_2O)\cdot H_2O$: A mixture of $Gd(NO_3)_3$ (0.1 mmol), Na_2H_2OLZ (0.15 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature. The yellow block crystals were obtained with 61.0% yield based on Gd.

Synthesis of compound $Tb(OLZ)_{0.5}(H_2OLZ)_{0.5}(DMF)(H_2O)\cdot H_2O$: A mixture of $Tb(NO_3)_3$ (0.1 mmol), Na_2H_2OLZ (0.15 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature. The yellow strip crystals were obtained with 63.3% yield based on Tb.

Synthesis of compound $Dy(OLZ)_{0.5}(H_2OLZ)_{0.5}(DMF)(H_2O)\cdot H_2O$: A mixture of $Dy(NO_3)_3$ (0.1 mmol), Na_2H_2OLZ (0.15 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature. The yellow strip crystals were obtained with 66.7% yield based on Dy.

Synthesis of compound $Ho(OLZ)_{0.5}(H_2OLZ)_{0.5}(DMF)(H_2O)\cdot H_2O$:A mixture of $Ho(NO_3)_3$ (0.1 mmol), Na_2H_2OLZ (0.15 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml

Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature. The yellow crystals were obtained with 65.8% yield based on Ho.

Synthesis of compound $Er_2(OLZ)(H_2OLZ)(H_2O)_4$: A mixture of $Er(NO_3)_3$ (0.1 mmol), Na_2H_2OLZ (0.15 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature. The yellow crystals were obtained with 55.9% yield based on Er.

Synthesis of compound $Tm_2(OLZ)(H_2OLZ)(H_2O)_4$: A mixture of $Tm(NO_3)_3$ (0.1 mmol), Na_2H_2OLZ (0.15 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature. The yellow crystals were obtained with 58.8% yield based on Tm.

Synthesis of compound $Lu_2(OLZ)(H_2OLZ)(H_2O)_4$: A mixture of $Lu(NO_3)_3$ (0.1 mmol), Na_2H_2OLZ (0.15 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature. The yellow crystals were obtained with 56.2% yield based on Lu.

Mixed modes:

For example, type I plus type II: A mixture of $La(NO_3)_3$ (0.05 mmol), $Nd(NO_3)_3$ (0.05 mmol), Na_2H_2OLZ (0.09 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature.

For example, type II plus type III: A mixture of $Nd(NO_3)_3$ (0.05 mmol), $Dy(NO_3)_3$ (0.05 mmol), Na_2H_2OLZ (0.09 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature.

For example, type III plus type IV: A mixture of $Dy(NO_3)_3$ (0.05 mmol), $Tm(NO_3)_3$ (0.05 mmol), Na_2H_2OLZ (0.09 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature.

For example, type **I**+type **II**+type **III:** A mixture of $La(NO_3)_3$ (0.03 mmol), $Nd(NO_3)_3$ (0.03 mmol), $Dy(NO_3)_3$ (0.03 mmol), Na_2H_2OLZ (0.05 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature.

For example, type **II**+type **III**+type **IV:** A mixture of $Nd(NO_3)_3$ (0.03 mmol), $Dy(NO_3)_3$ (0.03 mmol), $Tm(NO_3)_3$ (0.03 mmol), Na_2H_2OLZ (0.05 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature.

For example, type **I**+type **II**+type **III**+type **IV:** A mixture of $La(NO_3)_3$ (0.025 mmol), $Nd(NO_3)_3$ (0.025 mmol), $Dy(NO_3)_3$ (0.025 mmol), $Tm(NO_3)_3$ (0.025 mmol), Na_2H_2OLZ (0.04 mmol), DMF (5 mL) and H_2O (10 mL) was placed in a closed 25 ml Teflon reactor and heated at 115℃ for 4320 min, and cooled to room temperature.

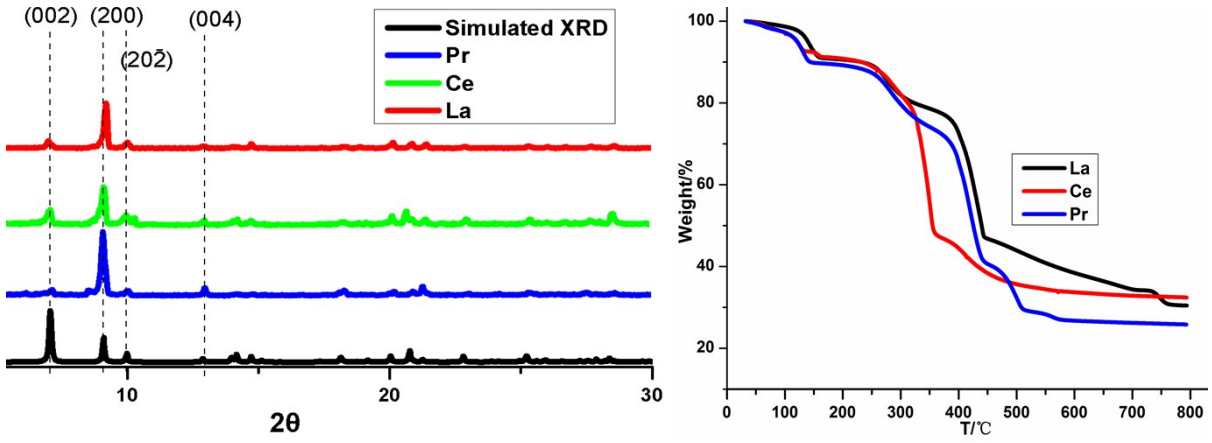

Fig. S1 *Left:*The experimental XRD patterns of type I and the corresponding data simulated from single crystal data. *Right:* TG plots of type I, where before 150° C the weight loss is ascribed to free guest molecules.

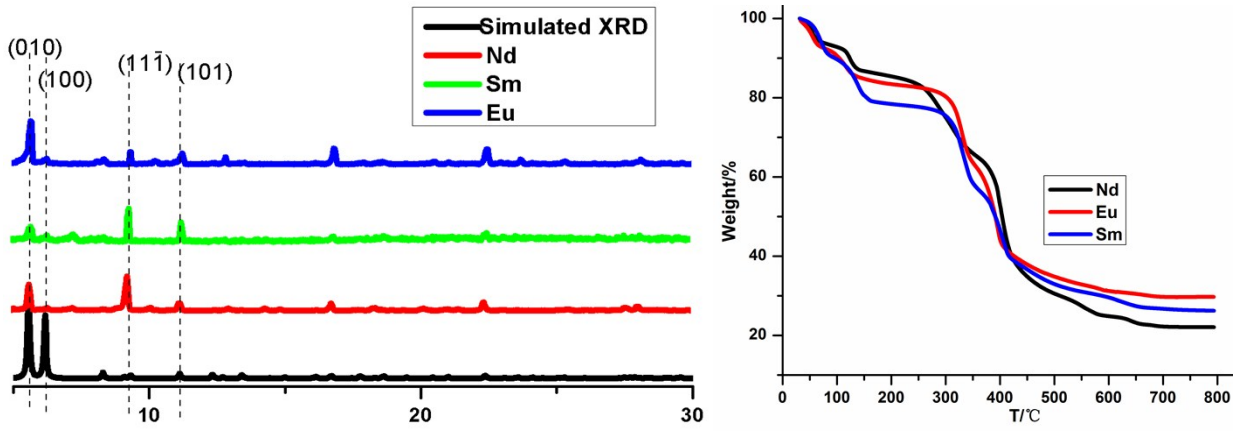

Fig. S2 *Left:*The experimental XRD patterns of type II and the corresponding data simulated from single crystal data. *Right:* TG plots of type II, where before 160° C the weight loss is ascribed to free guest molecules.

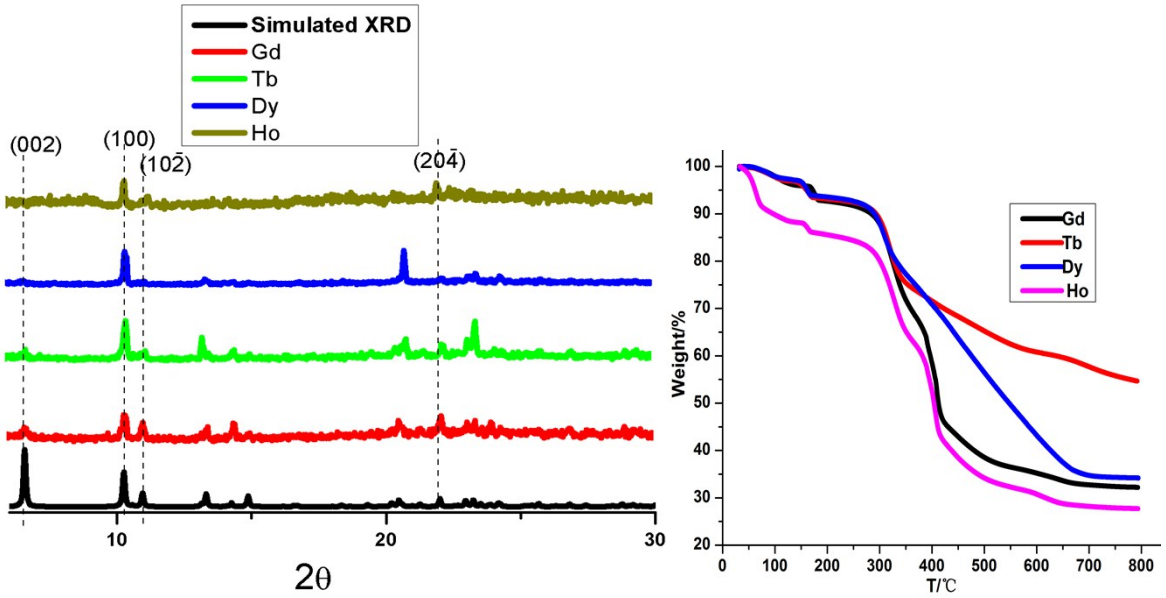

Fig. S3 *Left:* The experimental XRD patterns of type III and the corresponding data simulated from single crystal data. *Right:* TG plots of type III, where before 170° C the weight loss is ascribed to free guest molecules. For Ho sample, its crystal is slight polluted by some unknown phase on its crystal surface, thus leading to some abnormality in both XRD and TG, relative to other Ln ions. We try to get clean Ho crystal by washing it with various solvents, however without obvious improvement.

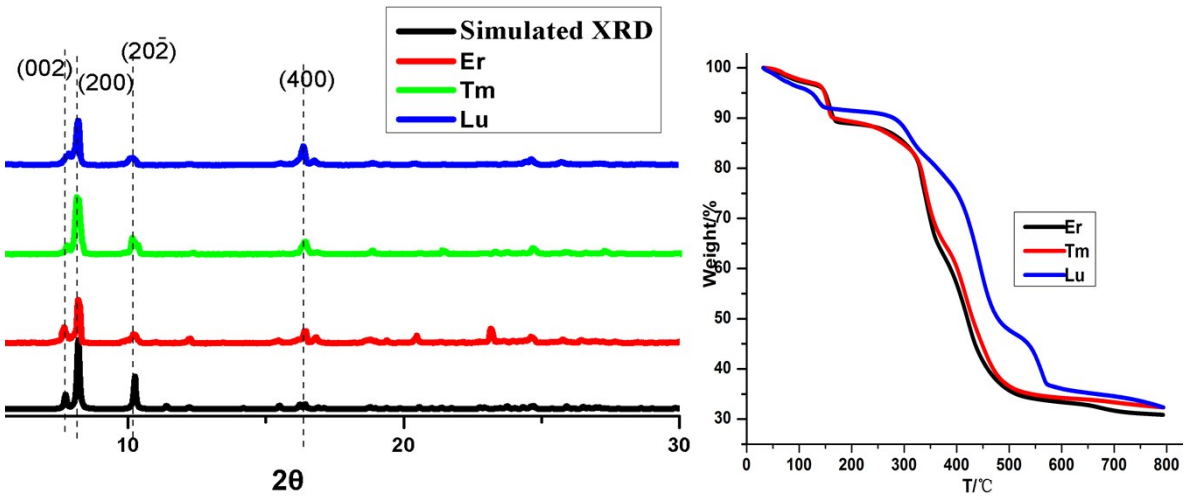

Fig. S4 *Left:* The experimental XRD patterns of type IV and the corresponding data simulated from single crystal data. *Right:* TG plots of type IV, where before 170° C the weight loss is ascribed to free guest molecules.

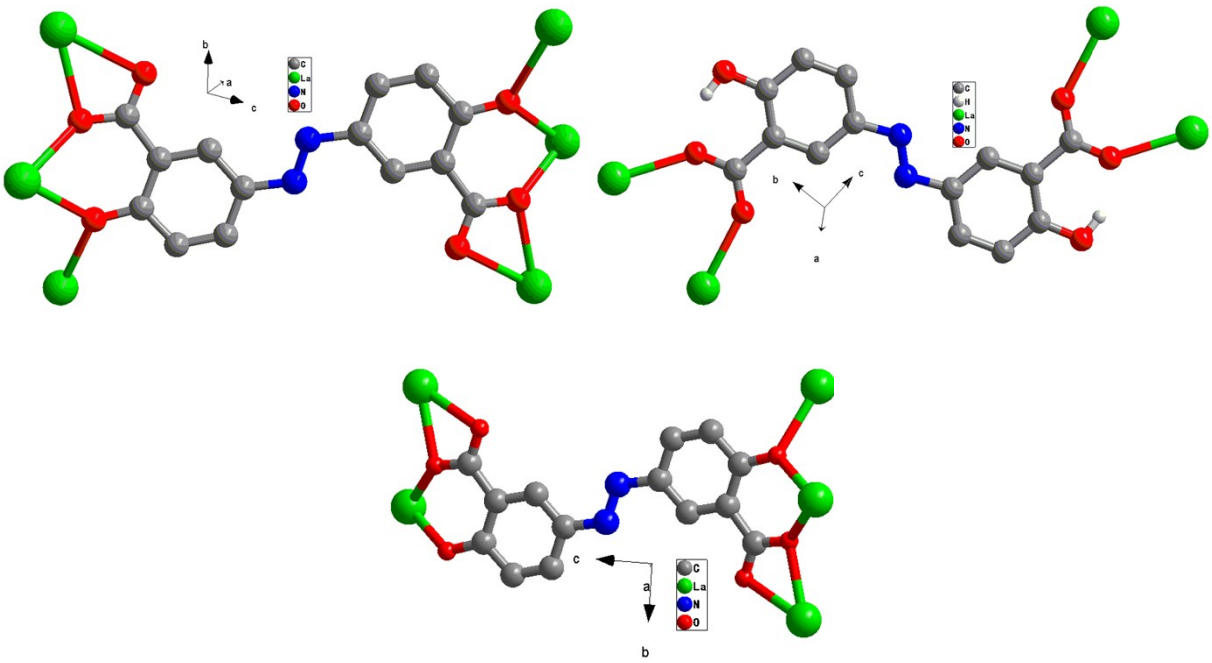

Fig. S5 The coordination models of organic ligands in this work.

Table S1. Summary of crystal data of type **I**.

type **I**	La	Ce	Pr
formula	$La_2(OLZ)(H_2OLZ)(DMF)(H_2O)_2{\cdot}2\,H_2O$	$Ce_2(OLZ)(H_2OLZ)(DMF)(H_2O)_2{\cdot}\,2\,H_2O$	$Pr_2(OLZ)(H_2OLZ)(DMF)(H_2O)_2{\cdot}2\,H_2O$
FW	1075.40	1077.84	1079.42
Crystal system	Monoclinic	Monoclinic	Monoclinic
space group	C2/c	C2/c	C2/c
a, Å	20.108(2)	20.0164(6)	20.0308(9)
b, Å	7.4444(9)	7.3972(2)	7.3601(3)
c, Å	25.868(3)	25.7120(7)	25.6802(12)
α, °	90	90	90
β, °	104.940(4)	105.0930(10)	105.047(2)
γ, °	90	90	90

V, Å3	3741.5(8)	3675.73(18)	3656.2(3)
Z	4	4	4
dcalcd,, g cm-3	1.900	1.939	1.945
Final R indices [I>2sigma(I)]	R1 = 0.0299, wR2 = 0.0761	R1 = 0.0300, wR2 = 0.0765	R1 = 0.0271, wR2 = 0.0701
R indices	R1 = 0.0312, wR2 = 0.0775	R1 = 0.0325, wR2 = 0.0785	R1 = 0.0300, wR2 = 0.0723
GOF	1.083	0.979	1.056
CCDC number	1537206	1537207	1537208

Table S2. Summary of crystal data of type **II**.

type **II**	Nd	Sm	Eu
formula	$Nd(OLZ)_{0.5}(H_2OLZ)_{0.5}(DMF)(\mu_2\text{-}DMF)_{0.5}$	$Sm(OLZ)_{0.5}(H_2OLZ)_{0.5}(DMF)(\mu_2\text{-}DMF)_{0.5}$	$Eu(OLZ)_{0.5}(H_2OLZ)_{0.5}(DMF)(\mu_2\text{-}DMF)_{0.5}$
FW	553.0	559.2	560.8
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	P2/c	P2/c	P2/c
a, Å	15.528(4)	15.5354(8)	15.516(4)
b, Å	15.528(4)	15.8981(10)	15.899(5)
c, º	13.519(3)	13.3111(8)	13.270(4)
α, º	90	90	90
β, deg	112.643(16)	112.592(3)	112.469(11)
γ, º	90	90	90
V, Å3	3099.7(13)	3035.3(3)	3025.1(15)
Z	4	4	4

dcalcd,, g cm-3	1.000	1.146	1.230
Final R indices [I>2sigma(I)]	R1 = 0.1276, wR2 = 0.3124	R1 = 0.0818, wR2 = 0.2122	R1 = 0.0433, wR2 = 0.1291
R indices	R1 = 0.1390, wR2 = 0.3178	R1 = 0.1125, wR2 = 0.2345	R1 = 0.0573, wR2 = 0.1417
GOF	1.158	1.164	1.063
CCDC number	1537213	1537215	1537214

Table S3. Summary of crystal data of type **III**.

type **III**	Gd	Tb	Dy	Ho
formula	$Gd(OLZ)_{0.5}(H_2OLZ)_{0.5}(DMF)(H_2O)\cdot H_2O$	$Tb(OLZ)_{0.5}(H_2OLZ)_{0.5}(DMF)(H_2O)\cdot H_2O$	$Dy(OLZ)_{0.5}(H_2OLZ)_{0.5}(DMF)(H_2O)\cdot H_2O$	$Ho(OLZ)_{0.5}(H_2OLZ)_{0.5}(DMF)(H_2O)\cdot H_2O$
FW	564.5	566.2	569.8	572.2
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	P2(1)/c	P2(1)/c	P2(1)/c	P2(1)/c
a, Å	8.8181(2)	8.742(2)	8.7525(13)	8.8304(17)
b, Å	8.78790(10)	8.729(2)	8.7492(12)	8.8257(17)
c, Å	27.5387(4)	27.415(7)	27.498(4)	27.644(5)
α, º	90	90	90	90
β, º	102.1830(10)	102.193(10)	102.074(9)	102.142(9)
γ, º	90	90	90	90
V, Å3	2085.98(6)	2044.8(8)	2059.1(5)	2106.2(7)
Z	4	4	4	4

dcalcd,, g cm^{-3}	1.795	1.843	1.841	1.808
Final R indices [I>2sigma(I)]	R1 = 0.0178, wR2 = 0.0504	R1 = 0.0228, wR2 = 0.0509	R1 = 0.0187, wR2 = 0.0461	R1 = 0.0414, wR2 = 0.1083
R indices	R1 = 0.0215, wR2 = 0.0626	R1 = 0.0276, wR2 = 0.0554	R1 = 0.0223, wR2 = 0.0472	R1 = 0.0425, wR2 = 0.1090
GOF	1.253	1.162	1.056	1.177
CCDC number	1537218	1537219	1537220	1537221

Table S4. Summary of crystal data of type **IV**.

type **IV**	Er	Tm	Lu
formula	$Er_2(OLZ)(H_2OLZ)(H_2O)_4$	$Tm_2(OLZ)(H_2OLZ)(H_2O)_4$	$Lu_2(OLZ)(H_2OLZ)(H_2O)_4$
FW	1005.0	1008.3	1020.4
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	C2/c	C2/c	C2/c
a, Å	21.8947(18)	21.8947(18)	21.617(3)
b, Å	8.3062(7)	8.3062(7)	8.2378(10)
c, Å	23.2034(18)	23.2034(18)	23.158(3)
α,º	90	90	90
β, º	100.053(4)	100.053(4)	99.426(5)
γ, º	90	90	90
V, Å3	4155.0(6)	4155.0(6)	4068.2(8)
Z	4	4	4

dcalcd,, g cm-3	1.607	1.612	1.650
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0696	R1 = 0.0339, wR2 = 0.0717	R1 = 0.0825, wR2 = 0.2319
R indices	R1 = 0.0407, wR2 = 0.0737	R1 = 0.0411, wR2 = 0.0756	R1 = 0.0904, wR2 = 0.2492
GOF	1.134	1.155	1.179
CCDC number	1537250	1537558	1545014

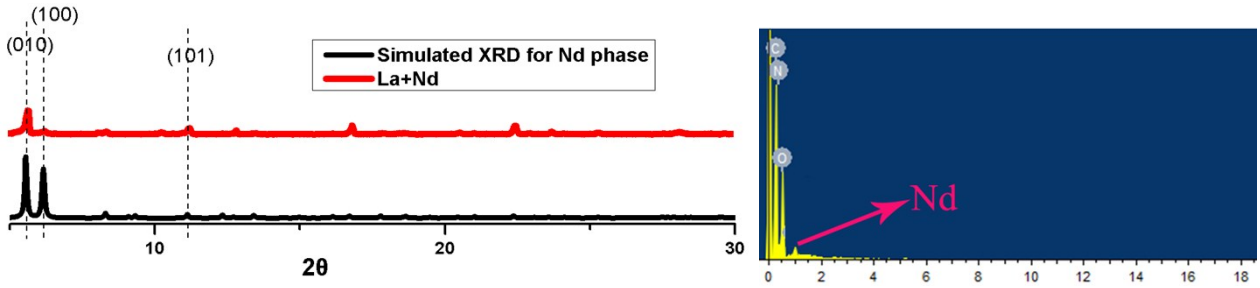

Fig. S6 *Left:*The experimental XRD patterns for the resulted samples from a mixed La+Nd ions and the data simulated from single crystal data of Nd phase. *Right:* EDS results for the resulted samples from a mixed La+Nd ions.

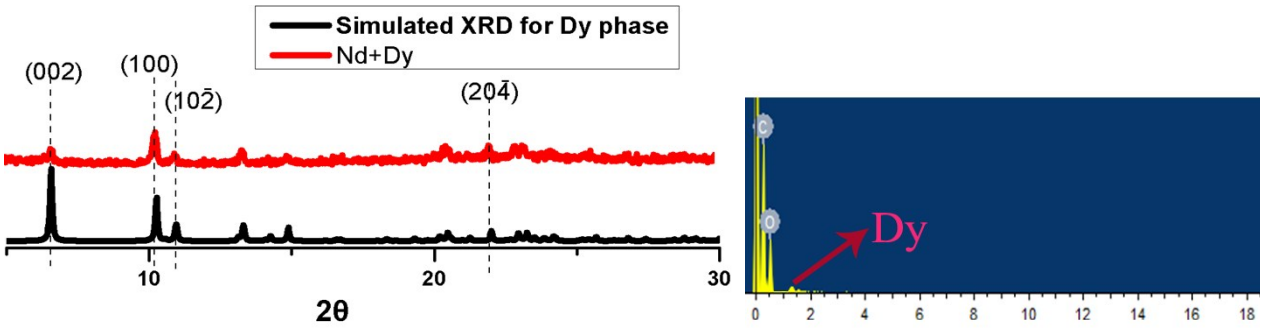

Fig. S7 *Left:*The experimental XRD patterns for the resulted samples from a mixed Nd+Dy ions and the data simulated from single crystal data of Nd phase. *Right:* EDS results for the resulted samples from a mixed Nd+Dy ions.

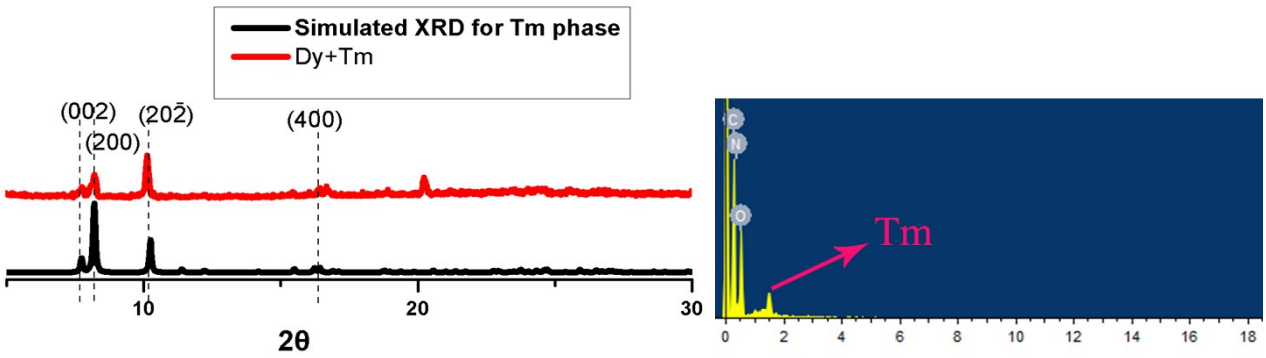

Fig. S8 *Left:*The experimental XRD patterns for the resulted samples from a mixed Dy+Tm ions and the data simulated from single crystal data of Nd phase. *Right:* EDS results for the resulted samples from a mixed Dy+Tm ions.

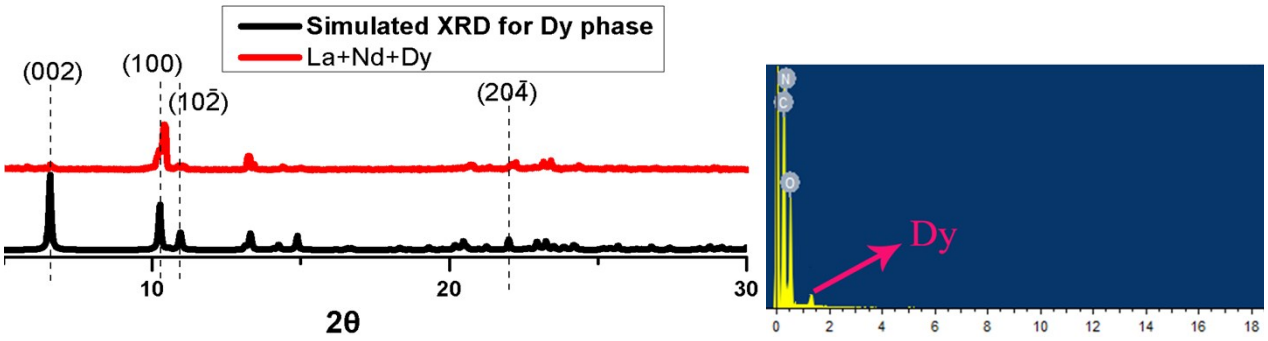

Fig. S9 *Left:*The experimental XRD patterns for the resulted samples from a mixed La+Nd+Dy ions and the data simulated from single crystal data of Nd phase. *Right:* EDS results for the resulted samples from a mixed La+Nd+Dy ions.

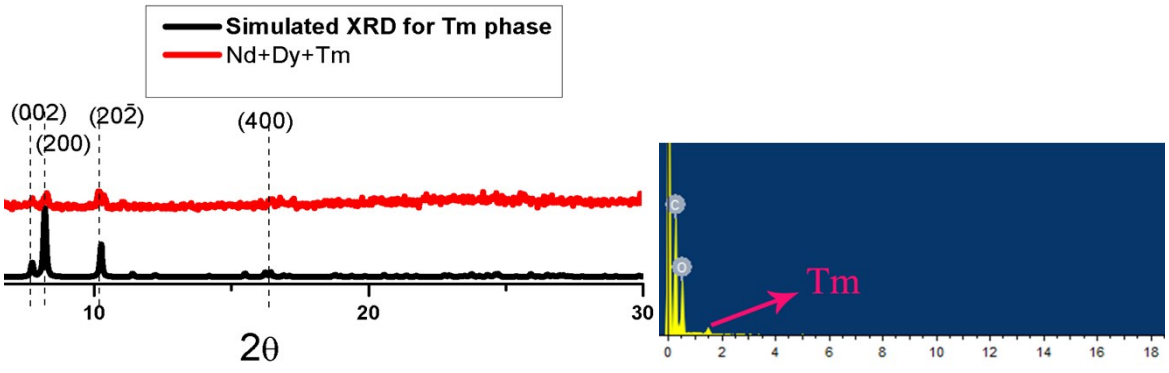

Fig. S10 *Left:*The experimental XRD patterns for the resulted samples from a mixed Nd+Dy+Tm ions and the data simulated from single crystal data of Nd phase. *Right:* EDS results for the resulted samples from a mixed Nd+Dy+Tm ions.

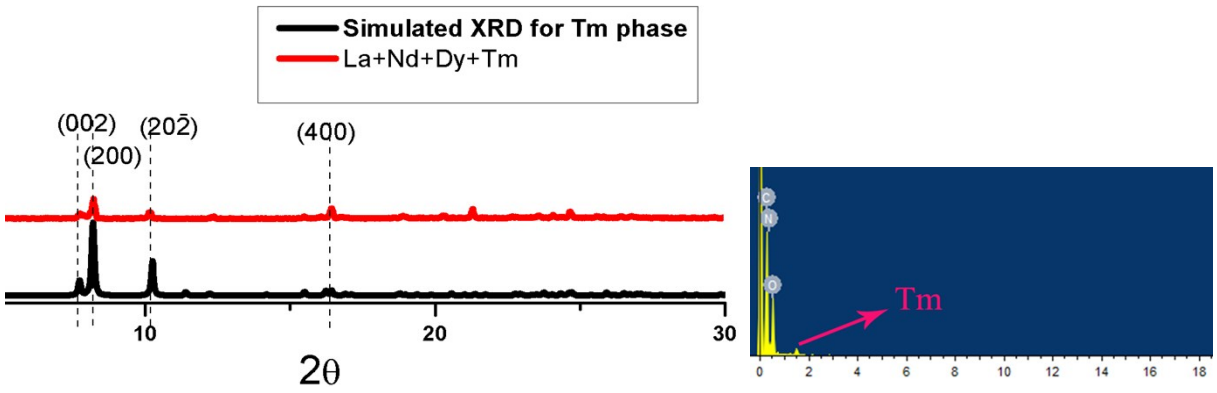

Fig. S11 *Left:* The experimental XRD patterns for the resulted samples from a mixed La+Nd+Dy+Tm ions and the data simulated from single crystal data of Nd phase. *Right:* EDS results for the resulted samples from a mixed La+Nd+Dy+Tm ions.