# Copper(I)/(II)-Redox Triggered Efficient and Green Rare-Earth Separation using a Heterometallic Metal-Organic Framework

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EXPERIMENTS SECTION

General Remarks

The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a Vario Micro Cube elemental analyzer. X-ray powder diffraction (XRPD) intensities were measured at 293 K on a Rigaku D/max-IIIA diffractometer (Cu-K$\alpha$, $\lambda$ =1.54056 Å). The crystalline powder samples were prepared by crushing the single-crystals and scanned from 3 to 60° at a rate of 5 °/min. To test the separation efficiency of Nd from other lanthanide elements, 10 mg of samples of **1** which were made from different RE1-Nd combinations were decomposed by 10 mL $HNO_3$ solution (1 mol/L), diluted to 100 mL with water and tested by (ICP-OES).

Syntheses

**[RE(ina)$_2$(CuI)(NO$_3$)(DMF)$_2$]·2DMF·0.5H$_2$O** (**1**, RE = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Y). RE(NO$_3$)$_3$·xH$_2$O (383 - 449 mg, 1.0 mmol), isonicotinic acid (246 mg, 2.0 mmol), CuI (191 mg, 1.0 mmol) and NaCl (117 mg, 2.0 mmol) were dissolved in 5 mL of mixed solvents of DMF, MeCN and *i*-PrOH (volume ratio 3 : 1 : 1) and heated at 100 °C for 4 hours. The solution was then cooled to room temperature and orange block crystals formed after 2 hours. These crystals were collected by decantation, washed with MeCN, and stored in dry air (Yield: ca. 98~99 % based on RE). Elem. anal. calcd (found) for **1**-Eu: C 30.34 (30.45), H 3.93 (4.01), N 10.32 (10.36); for **1**-Gd: C 30.17 (30.28), H 3.90 (3.99), N 10.26 (10.35); for **1**-Tb: C 30.12 (30.26), H 3.90 (4.02), N 10.25 (10.29); for **1**-Dy: C 30.01 (29.95), H 3.88 (3.95), N 10.21 (10.24); for **1**-Ho: C 29.93 (30.01), H 3.87 (3.93), N 10.18 (10.22); for **1**-Yb: C 29.68 (29.86), H 3.84 (3.89), N 10.10 (10.15). ICP-OES anal. calcd (found) of RE/Cu mass ratio for **1**-Sm: 0.70 : 0.30 (0.70 : 0.30); **1**-Eu: 0.71 : 0.29 (0.70 : 0.30); for **1**-Gd: 0.71 : 0.29 (0.71 : 0.29); for **1**-Tb: 0.71 : 0.29 (0.72 : 0.28); for **1**-Dy: 0.72 : 0.28 (0.72 : 0.28); for **1**-Ho: 0.72 : 0.28 (0.72 : 0.28); for **1**-Er: 0.72 : 0.28 (0.72 : 0.28); for **1**-Yb: 0.73 : 0.27 (0.72 : 0.28); for **1**-Y: 0.58 : 0.42 (0.59 : 0.41). IR data (KBr, cm$^{-1}$) for **1**-Sm: 3519*s*, 3047*w*, 2967*w*, 1645*m*, 1401*m*, 1178*s*, 1109*s*, 1012*s*, 858*w*, 773*w*, 539*w*; for **1**-Eu: 3527*s*, 3049*w*, 2971*w*, 1647*m*, 1397*m*, 1177*s*, 1107*s*, 1010*s*, 855*w*, 772*w*, 538*w*; for **1**-Gd: 3522*s*, 3045*w*, 2969*w*, 1646*m*, 1398*m*, 1177*s*, 1107*s*, 1010*s*, 856*w*, 773*w*, 540*w*; for **1**-Tb: 3518*s*, 3046*w*, 2969*w*, 1646*m*, 1400*m*, 1178*s*, 1109*s*, 1011*s*, 857*w*, 772*w*, 538*w*; for **1**-Dy: 3521*s*, 3046*w*, 2970*w*, 1645*m*, 1397*m*, 1178*s*, 1107*s*, 1011*s*, 859*w*, 773*w*, 538*w*; for **1**-Ho: 3522*s*, 3047*w*, 2973*w*, 1646*m*, 1397*m*, 1178*s*, 1107*s*, 1011*s*, 858*w*, 772*w*, 537*w*; for **1**-Er: 3520*s*, 3048*w*, 2971*w*, 1645*m*, 1401*m*, 1180*s*, 1110*s*, 1011*s*, 858*w*, 771*w*, 537*w*; for **1**-Yb: 3519*s*, 3048*w*, 2969*w*, 1645*m*, 1400*m*, 1178*s*, 1109*s*, 1010*s*, 860*w*, 773*w*, 539*w*; for **1**-Y: 3522*s*, 3046*w*, 2970*w*, 1646*m*, 1397*m*, 1178*s*, 1107*s*, 1010*s*, 857*w*, 770*w*, 539*w*.

**{[NaRE(ina)$_4$(Cu$_4$I$_4$)]·3H$_2$O}$_n$** (**2**, RE = La, Ce, Pr and Nd). RE(NO$_3$)$_3$·xH$_2$O (433 - 439 mg, 1.0 mmol), isonicotinic acid (246 mg, 2.0 mmol), CuI (191 mg, 1.0 mmol) and NaCl (117 mg, 2.0 mmol) were dissolved in 5 mL of mixed solvents of DMF, MeCN and *i*-PrOH (volume ratio 3 : 1 : 1) and heated at 100 °C for 4 hours. The

yellow solution was cooled to room temperature, and light yellow sheet crystals formed after 12 hours. These crystals were collected by decantation, washed with MeCN, and stored in cyclohexane (Yield: *ca.* 40 % based on ina). Elem. anal. calcd (found) for **2**-Pr: C, 19.16 (19.24); H, 1.74 (1.82); N, 3.72 (3.76).; for **2**-Nd: C, 19.14 (19.20); H, 1.72 (1.78); N, 3.70 (3.79). ICP-OES anal. calcd (found) of RE/Cu/Na mass ratio for **2**-Pr: 0.34 : 0.61 : 0.05 (0.34 : 0.60 : 0.06); for **2**-Nd: 0.34 : 0.60 : 0.06 (0.35 : 0.59 : 0.06). IR data (KBr, $cm^{-1}$) for **2**-Pr: 3428*s*, 3040*w*, 2957*w*, 1598*m*, 1403*m*, 1209*s*, 1051*s*, 865*w*, 771*w*, 539*w*; for **2**-Nd: 3422*s*, 3039*w*, 2957*w*, 1601*m*, 1396*m*, 1205*s*, 1049*s*, 855*w*, 770*w*, 540*w*.

The mixed-metal complexes of **1** (Nd : RE1 = 1 : 1) was synthesized as following: 1.0 mmol $Nd(NO_3)_3 \cdot 6H_2O$, 1.0 mmol $RE1(NO_3) \cdot 6H_2O$ (RE1 = Eu, Gd, Tb, Dy, Ho, Er, Yb, Y), 2.0 mmol isonicotinic acid, 1.0 mmol CuI and 2.0 mmol NaCl were added in a DMF/MeCN/*i*-PrOH (3:1:1) mixture. The solution was heated at 100 °C for 4 hours to form a yellow solution. Then the solution was cooled to room temperature, and orange block crystals formed after 2 hours (Yield of all products are all about 96 % based on RE1/Nd or 48 % based on RE1+Nd).

**X-ray Crystallography**

Single-crystal X-ray diffraction data collection for **1**, **2** and **3** was conducted on a Bruker SMART APEX II CCD diffractometer (Mo, $\lambda$ = 0.71073 Å) by using the $\theta$-$\omega$ scan technique at 150 K. The structures were solved by direct methods and refined with a full-matrix least-squares technique within the SHELXTL program package.[1] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined using the riding model. The Alert A's in compounds **2** are due to the high volume of voids in the frameworks. The crystallographic details are provided in Table S1 and S3. Selected bond distances and bond angles are listed in Table S2 and S4. Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Center. The CCDC reference numbers for **1** are: 1430390 (Sm), 1430391 (Eu), 1430392 (Gd), 1430393 (Tb), 1430394 (Dy), 1430395 (Ho), 1430396 (Er), 1430397 (Yb), 1430398 (Y); for **2** are: 1419821 (Pr), 1502069 (Nd). The supplementary crystallographic data for two compounds can be found in the Supporting Information or can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://**www.ccdc**.cam.ac.uk/data_request/cif.

**Table S1** Crystal data and structure refinements for **1** (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Y).

| | **1**-Sm | **1**-Eu | **1**-Gd | **1**-Tb | **1**-Dy |
|---|---|---|---|---|---|
| Formula | $SmCuIC_{24}H_{36}N_7O_{11.5}$ | $EuCuIC_{24}H_{36}N_7O_{11.5}$ | $GdCuIC_{24}H_{36}N_7O_{11.5}$ | $TbCuIC_{24}H_{36}N_7O_{11.5}$ | $DyCuIC_{24}H_{36}N_7O_{11.5}$ |
| formula weight | 947.39 | 949.00 | 954.28 | 955.96 | 959.53 |
| crystal system | Triclinic | Triclinic | Triclinic | Triclinic | Triclinic |
| space group | *P*-1 | *P*-1 | *P*-1 | *P*-1 | *P*-1 |
| $T$ (K) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) |
| $a$ (Å) | 11.0928(2) | 11.1874(8) | 11.199(1) | 11.201(1) | 11.1272(5) |
| $b$ (Å) | 12.4805(2) | 12.6000(9) | 12.588(1) | 12.580(1) | 12.4509(6) |
| $c$ (Å) | 15.1388(2) | 15.180(1) | 15.174(2) | 15.158(1) | 15.1320(7) |
| $\alpha$ (deg) | 81.463(1) | 92.528(1) | 92.438(2) | 92.291(1) | 81.365(1) |
| $\beta$ (deg) | 83.416(1) | 96.837(1) | 96.979(2) | 97.131(1) | 82.847(1) |
| $\gamma$ (deg) | 64.133(1) | 116.289(1) | 116.308(1) | 116.347(1) | 63.926(1) |
| $V$ (Å$^3$) | 1862.06(5) | 1893.5(2) | 1892.3(4) | 1888.2(3) | 1857.7(2) |
| $D_c$ (g cm$^{-3}$) | 1.690 | 1.664 | 1.675 | 1.681 | 1.715 |
| $F$ (000) | 930 | 932 | 934 | 936 | 938 |
| **Z** | 1 | 1 | 1 | 1 | 1 |
| $\mu$ (mm$^{-1}$) | 3.020 | 3.076 | 3.173 | 3.296 | 3.458 |
| reflns collected | 15226 | 15346 | 15372 | 15120 | 13830 |
| unique reflns | 6260 | 6315 | 6323 | 6304 | 6221 |
| $R_{int}$ | 0.0148 | 0.0156 | 0.0179 | 0.0160 | 0.0142 |
| data/parameters | 6260 / 412 | 6315 / 412 | 6323 / 407 | 6304 / 412 | 6221 / 412 |
| GOF | 1.024 | 1.020 | 1.024 | 1.024 | 1.025 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0245, 0.0764 | 0.0274, 0.0894 | 0.0261, 0.0796 | 0.0249, 0.0779 | 0.0222, 0.0698 |
| $R_1$, $wR_2$ (all data) | 0.0279, 0.0791 | 0.0326, 0.0975 | 0.0291, 0.0821 | 0.0269, 0.0799 | 0.0240, 0.0713 |

| | **1**-Ho | **1**-Er | **1**-Yb | **1**-Y |
|---|---|---|---|---|
| Formula | $HoCuIC_{24}H_{36}N_7O_{11.5}$ | $ErCuIC_{24}H_{36}N_7O_{11.5}$ | $YbCuIC_{24}H_{36}N_7O_{11.5}$ | $YCuIC_{24}H_{36}N_7O_{11.5}$ |
| formula weight | 961.96 | 964.29 | 970.07 | 885.94 |
| crystal system | Triclinic | Triclinic | Triclinic | Triclinic |
| space group | *P*-1 | *P*-1 | *P*-1 | *P*-1 |
| *T* (K) | 150(2) | 150(2) | 150(2) | 150(2) |
| *a* (Å) | 11.1399(9) | 11.2006(9) | 11.1943(4) | 11.2135(7) |
| *b* (Å) | 12.456(1) | 12.523(1) | 12.4986(4) | 12.5387(7) |
| *c* (Å) | 15.124(1) | 15.113(1) | 15.0770(5) | 15.1202(9) |
| $\alpha$ (deg) | 81.320(1) | 92.084(1) | 91.996(2) | 92.092(1) |
| $\beta$ (deg) | 82.723(1) | 97.414(1) | 97.522(2) | 97.415(1) |
| $\gamma$ (deg) | 63.883(1) | 116.450(1) | 116.512(2) | 116.389(1) |
| *V* (Å$^3$) | 1858.5(3) | 1871.5(3) | 1861.0(1) | 1877.9(2) |
| $D_c$ (g cm$^{-3}$) | 1.719 | 1.711 | 1.731 | 1.567 |
| *F* (000) | 940 | 942 | 946 | 884 |
| **Z** | 1 | 1 | 1 | 1 |
| $\mu$ (mm$^{-1}$) | 3.575 | 3.678 | 3.957 | 2.984 |
| reflns collected | 13536 | 13597 | 13229 | 15343 |
| unique reflns | 6191 | 6257 | 6201 | 6287 |
| $R_{int}$ | 0.0135 | 0.0101 | 0.0123 | 0.0131 |
| data/parameters | 6191 / 412 | 6257 / 412 | 6201 / 412 | 6287 / 407 |
| GOF | 1.029 | 1.047 | 1.043 | 1.027 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0218, 0.0705 | 0.0228, 0.0722 | 0.0248, 0.0780 | 0.0322, 0.1095 |
| $R_1$, $wR_2$ (all data) | 0.0232, 0.0719 | 0.0250, 0.0740 | 0.0281, 0.0810 | 0.0379, 0.1141 |

**Table S2** Selected bond lengths (Å) for compounds **1** (Ln= Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Y).

| **1**-Sm | | **1**-Eu | | **1**-Gd | | **1**-Tb | |
|---|---|---|---|---|---|---|---|
| Sm(1)-O(2) | 2.344(3) | Eu(1)-O(2) | 2.332(3) | Gd(1)-O(2) | 2.319(3) | Tb(1)-O(2) | 2.301(3) |
| Sm(1)-O(3)[a] | 2.371(3) | Eu(1)-O(3)[a] | 2.366(3) | Gd(1)-O(3)[a] | 2.351(3) | Tb(1)-O(3)[a] | 2.337(3) |
| Sm(1)-O(4) | 2.391(3) | Eu(1)-O(4) | 2.390(3) | Gd(1)-O(6) | 2.381(3) | Tb(1)-O(6) | 2.361(3) |
| Sm(1)-O(6) | 2.393(3) | Eu(1)-O(6) | 2.390(4) | Gd(1)-O(4) | 2.381(3) | Tb(1)-O(4) | 2.365(3) |
| Sm(1)-O(5) | 2.426(3) | Eu(1)-O(5) | 2.420(4) | Gd(1)-O(5) | 2.407(3) | Tb(1)-O(1)[a] | 2.398(3) |
| Sm(1)-O(1)[a] | 2.437(3) | Eu(1)-O(1)[a] | 2.423(3) | Gd(1)-O(1)[a] | 2.411(3) | Tb(1)-O(5) | 2.398(3) |
| Sm(1)-O(8) | 2.520(3) | Eu(1)-O(8) | 2.512(4) | Gd(1)-O(8) | 2.503(4) | Tb(1)-O(7) | 2.491(4) |
| Sm(1)-O(7) | 2.527(3) | Eu(1)-O(7) | 2.513(4) | Gd(1)-O(7) | 2.506(4) | Tb(1)-O(8) | 2.491(4) |
| a = -x+2,-y+1,-z | | a = -x+1,-y+2,-z+2 | | a = -x+2,-y+1,-z+2 | | a = -x+1,-y,-z | |

| **1**-Dy | | **1**-Ho | | **1**-Er | | **1**-Yb | |
|---|---|---|---|---|---|---|---|
| Dy(1)-O(2) | 2.283(3) | Ho(1)-O(2) | 2.272(3) | Er(1)-O(2)[a] | 2.257(3) | Yb(1)-O(2) | 2.232(3) |
| Dy(1)-O(3)[a] | 2.324(3) | Ho(1)-O(3)[a] | 2.311(3) | Er(1)-O(3) | 2.296(3) | Yb(1)-O(3)[a] | 2.271(3) |
| Dy(1)-O(4) | 2.346(3) | Ho(1)-O(4) | 2.338(3) | Er(1)-O(5) | 2.325(3) | Yb(1)-O(4) | 2.300(3) |
| Dy(1)-O(6) | 2.349(3) | Ho(1)-O(6) | 2.341(3) | Er(1)-O(4)[a] | 2.328(3) | Yb(1)-O(6) | 2.303(4) |
| Dy(1)-O(5) | 2.377(3) | Ho(1)-O(1)[a] | 2.367(3) | Er(1)-O(1) | 2.351(3) | Yb(1)-O(1)[a] | 2.323(3) |
| Dy(1)-O(1)[a] | 2.381(3) | Ho(1)-O(5) | 2.367(3) | Er(1)-O(6) | 2.356(3) | Yb(1)-O(5) | 2.333(4) |
| Dy(1)-O(8) | 2.476(3) | Ho(1)-O(8) | 2.463(3) | Er(1)-O(7) | 2.451(4) | Yb(1)-O(7) | 2.428(4) |
| Dy(1)-O(7) | 2.482(3) | Ho(1)-O(7) | 2.470(3) | Er(1)-O(8) | 2.452(4) | Yb(1)-O(8) | 2.431(4) |
| a = -x+2,-y,-z | | a = -x+1,-y+2,-z | | a = -x,-y,-z+1 | | a = -x+1,-y+1,-z+1 | |

| **1**-Y | |
|---|---|
| Y(1)-O(2) | 2.263(3) |
| Y(1)-O(3)[c] | 2.304(3) |
| Y(1)-O(4) | 2.336(3) |
| Y(1)-O(6) | 2.337(3) |
| Y(1)-O(5) | 2.362(3) |
| Y(1)-O(1)[c] | 2.364(3) |
| Y(1)-O(7) | 2.459(3) |
| Y(1)-O(8) | 2.467(4) |
| c = -x+1,-y+1,-z | |

**Table S3** Crystal Data and Structure Refinement for **2** (Ln=La, Ce, Pr, Nd).

| | **2**-La | **2**-Ce | **2**-Pr | **2**-Nd |
|---|---|---|---|---|
| Formula | $Na_2La_2Cu_8I_8C_{48}O_{25}N_8H_{40}$ | $Na_2Ce_2Cu_8I_8C_{48}O_{25}N_8H_{40}$ | $Na_2Pr_2Cu_8I_8C_{48}O_{25}N_8H_{40}$ | $Na_2Nd_2Cu_8I_8C_{48}O_{25}N_8H_{40}$ |
| formula weight | 2980.20 | 2980.20 | 2980.20 | 2980.20 |
| crystal system | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic |
| space group | | | $C222_1$ | $C222_1$ |
| $T$ (K) | 150(2) | 150(2) | 150(2) | 150(2) |
| $a$ (Å) | 17.921(2) | 17.908(2) | 17.896(2) | 17.889(2) |
| $b$ (Å) | 31.942(3) | 31.935(3) | 31.932(3) | 31.835(4) |
| $c$ (Å) | 25.105(3) | 25.096(3) | 25.078(3) | 24.831(3) |
| $\beta$ (deg) | 90 | 90 | 90 | 90 |
| $V$ (Å$^3$) | 14371(3) | 14352(3) | 14331(3) | 14141(3) |
| $D_c$ (g cm$^{-3}$) | | | 1.381 | 1.403 |
| $F$ (000) | | | 5520 | 5528 |
| Z | | | 4 | 4 |
| $\mu$ (mm$^{-1}$) | | | 3.597 | 3.690 |
| reflns collected | | | 41369 | 36780 |
| unique reflns | | | 11762 | 13898 |
| $R_{int}$ | | | 0.0293 | 0.0575 |
| data/parameters | | | 11762/440 | 13898/386 |
| GOF | | | 1.060 | 1.071 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | | | 0.0862, 0.2128 | 0.0853, 0.2168 |
| $R_1$, $wR_2$ (all data) | | | 0.1060, 0.2290 | 0.1594, 0.2635 |

**Table S4** Selected bond lengths (Å) and Ln−O−Ln angles (°) for **2**-Pr and **2**-Nd.

| **2**-Pr | | **2**-Nd | |
|---|---|---|---|
| Pr(1)-O(10) | 2.48(2) | Nd(1)-O(9) | 2.40(2) |
| Pr(1)-O(7) | 2.50(2) | Nd(1)-O(7) | 2.47(2) |
| Pr(1)-O(9) | 2.53(2) | Nd(1)-O(1) | 2.50(2) |
| Pr(1)-O(4) | 2.53(2) | Nd(1)-O(3) | 2.51 (1) |
| Pr(1)-O(8) | 2.53(2) | Nd(1)-O(6) | 2.52(1) |
| Pr(1)-O(6) | 2.54(2) | Nd(1)-O(10) | 2.53(2) |
| Pr(1)-O(2) | 2.56(1) | Nd(1)-O(8) | 2.54(2) |
| Pr(1)-O(5) | 2.57(1) | Nd(1)-O(2) | 2.56(2) |
| Pr(1)-O(3) | 2.59(1) | Nd(1)-O(5) | 2.56(1) |
| Pr(1)-O(1) | 2.62(2) | Nd(1)-O(4) | 2.57(2) |
| Na(1)-O(5)$^{g}$ | 2.29(1) | Na(1)-O(5) | 2.29(2) |
| Na(1)-O(2)$^{g}$ | 2.35(1) | Na(1)-O(3) | 2.33(2) |
| Na(1)-O(3)$^{g}$ | 2.38(1) | Na(1)-O(2) | 2.34(1) |
| Na(1)-O(2)-Pr(1) | 94.3(5) | Na(1)-O(2)-Nd(1) | 94.1(5) |
| Na(1)-O(3)-Pr(1) | 92.7(5) | Na(1)-O(3)-Nd(1) | 95.5(5) |
| Na(1)-O(5)-Pr(1) | 95.5(5) | Na(1)-O(5)-Nd(1) | 95.3(5) |
| g = x,-y+2,-z. | | | |

**Table S5** Crystal Data and Structure Refinement for **3**.

| | **3** |
|---|---|
| Formula | $CuC_{12}H_{16}N_2O_8$ |
| formula weight | 379.81 |
| crystal system | Orthorhombic |
| space group | *P*-1 |
| *T* (K) | 150(2) |
| *a* (Å) | 6.361(4) |
| *b* (Å) | 6.888(4) |
| *c* (Å) | 9.202(6) |
| $\alpha$ (deg) | 99.359(8) |
| $\beta$ (deg) | 105.201(8) |
| $\gamma$ (deg) | 108.448(8) |
| *V* (Å$^3$) | 355.6(4) |
| $D_c$ (g cm$^{-3}$) | 1.774 |
| *F* (000) | 195 |
| Z | 1 |
| $\mu$ (mm$^{-1}$) | 1.583 |
| reflns collected | 2130 |
| unique reflns | 1156 |
| $R_{int}$ | 0.1111 |
| data/parameters | 1156/106 |
| GOF | 1.051 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0532, 0.1462 |
| $R_1$, $wR_2$ (all data) | 0.0542, 0.1471 |

**Refinement details:** The elemental composition of mixed-metal single crystals were achieved by following method: based on linear restraint of two atoms on the same site (c = c1*fv(m1) + c2*fv(m2)), a "SUMP c sigma c1 m1 c2 m2" command has been used to refine the crystal data. The sum of occupancies of two metals should be strictly restricted to 1.000 by setting the effective standard deviation "sigma" as 0.001. Excess refinement cycles (typically > 50) were performed to make sure the convergency is achieved.[3-5] The results of the refinement data are showed in Table S6.

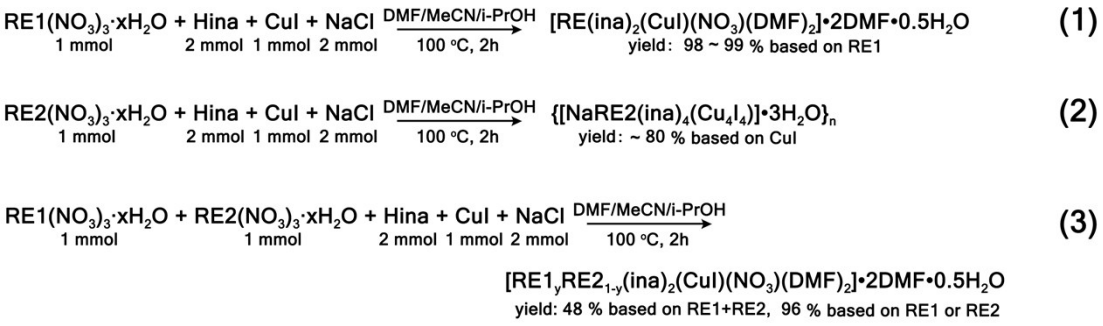
**Table S6** The separation efficiency data from single crystal of **1**-RE1/Nd.

| RE1-Nd | Refinement |
|---|---|
| Eu-Nd | TITL 1 in P-1 |
| | CELL 0.71073 11.0449 12.3773 15.1350 81.536 83.593 64.737 |
| | ZERR 1.00 0.0008 0.0009 0.0011 0.001 0.001 0.001 |
| | LATT 1 |
| | SFAC C H N O Cu I Nd Eu |
| | UNIT 48 72 14 22 2 2 0.37 1.63 |
| | L.S. 10 |
| | BOND |
| | ACTA |
| | FMAP 2 |
| | PLAN 5 |
| | SUMP 1.0 0.0001 1.0 2 1.0 3 |
| | EXYZ Eu1 Nd1 |
| | EADP Eu1 Nd1 |
| | TEMP 23.000 |
| | WGHT 0.060400 7.746500 |
| | FVAR **0.37458 0.80879 0.19121** |
| | EU1 8 0.903164 0.887974 0.037161 21.00000 0.01379 |
| | 0.01118 = 0.01207 -0.00119 -0.00061 -0.00395 |
| | ND1 7 0.903164 0.887974 0.037161 -21.00000 0.01379 |
| | 0.01118 = 0.01207 -0.00119 -0.00061 -0.00395 |
| Gd-Nd | TITL 1 in P-1 |
| | CELL 0.71073 11.0568 12.3715 15.1312 81.495 83.441 64.670 |
| | ZERR 1.00 0.0007 0.0008 0.0010 0.001 0.001 0.001 |
| | LATT 1 |
| | SFAC C H N O Cu I Nd Gd |
| | UNIT 48 72 14 22 2 2 0.39 1.61 |
| | L.S. 10 |
| | BOND |
| | ACTA |
| | FMAP 2 |
| | PLAN 5 |
| | SUMP 1.0 0.0001 1.0 2 1.0 3 |
| | EXYZ Gd1 ND1 |

| | |
|---|---|
| | EADP Gd1 ND1 |
| | TEMP 23.000 |
| | WGHT 0.062400 9.824300 |
| | FVAR **0.34839 0.84946 0.15054** |
| | GD1 8 0.096883 1.112525 0.462817 21.00000 0.01371 |
| | 0.01257 = 0.01278 -0.00135 -0.00064 -0.00411 |
| | ND1 7 0.096883 1.112525 0.462817 -21.00000 0.01371 |
| | 0.01257 = 0.01278 -0.00135 -0.00064 -0.00411 |
| Tb-Nd | TITL 1 in P-1 |
| | CELL 0.71073 11.0521 12.3523 15.1200 81.464 83.249 64.623 |
| | ZERR 1.00 0.0007 0.0008 0.0009 0.001 0.001 0.001 |
| | LATT 1 |
| | SFAC C H N O Cu I Nd Tb |
| | UNIT 48 72 14 22 2 2 0.35 1.65 |
| | L.S. 10 |
| | BOND |
| | FMAP 2 |
| | ACTA |
| | PLAN 5 |
| | TEMP 23.000 |
| | SUMP 1.0 0.0001 1.0 2 1.0 3 |
| | EXYZ TB1 ND1 |
| | EADP TB1 ND1 |
| | WGHT 0.053600 9.649600 |
| | FVAR **0.36411 0.83094 0.16906** |
| | TB1 8 0.402941 0.886831 0.537377 21.00000 0.01326 |
| | 0.01252 = 0.01189 -0.00195 -0.00049 -0.00411 |
| | ND1 7 0.402941 0.886831 0.537377 -21.00000 0.01326 |
| | 0.01252 = 0.01189 -0.00195 -0.00049 -0.00411 |
| Dy-Nd | TITL 1 in P-1 |
| | CELL 0.71073 11.0618 12.3348 15.1047 81.459 83.103 64.504 |
| | ZERR 1.00 0.0009 0.0010 0.0013 0.001 0.001 0.001 |
| | LATT 1 |
| | SFAC C H N O Cu I Nd Dy |
| | UNIT 48 72 14 22 2 2 0.3 1.7 |
| | L.S. 10 |
| | BOND |
| | FMAP 2 |
| | PLAN 5 |
| | SUMP 1.0 0.0001 1.0 2 1.0 3 |
| | EXYZ Dy1 ND1 |
| | EADP Dy1 ND1 |
| | TEMP 23.000 |
| | ACTA |

| | |
|---|---|
| | WGHT 0.053000 8.418100 |
| | FVAR **0.35978 0.85123 0.14877** |
| | DY1 8 0.902717 0.386168 0.037648 21.00000 0.01264 |
| | 0.01280 = 0.01147 -0.00185 -0.00018 -0.00374 |
| | ND1 7 0.902717 0.386168 0.037648 -21.00000 0.01264 |
| | 0.01280 = 0.01147 -0.00185 -0.00018 -0.00374 |
| Ho-Nd | TITL 1 in P-1 |
| | CELL 0.71073 11.0595 12.3332 15.1015 81.337 82.948 64.478 |
| | ZERR 1.00 0.0009 0.0010 0.0012 0.001 0.001 0.001 |
| | LATT 1 |
| | SFAC C H N O Cu I Nd Ho |
| | UNIT 48 72 14 22 2 2 0.22 1.78 |
| | L.S. 10 |
| | BOND |
| | FMAP 2 |
| | PLAN 5 |
| | FREE O6 N1 |
| | TEMP 23.000 |
| | SUMP 1.0 0.0001 1.0 2 1.0 3 |
| | EXYZ Ho1 ND1 |
| | EADP Ho1 ND1 |
| | WGHT 0.060500 7.747000 |
| | FVAR **0.34616 0.88843 0.11157** |
| | HO1 8 0.402847 0.885701 1.037631 21.00000 0.01408 |
| | 0.01358 = 0.01270 -0.00156 -0.00002 -0.00482 |
| | ND1 7 0.402847 0.885701 1.037631 -21.00000 0.01408 |
| | 0.01358 = 0.01270 -0.00156 -0.00002 -0.00482 |
| Er-Nd | TITL 1 in P-1 |
| | CELL 0.71073 11.0696 12.3189 15.1050 81.377 82.802 64.383 |
| | ZERR 1.00 0.0007 0.0008 0.0009 0.001 0.001 0.001 |
| | LATT 1 |
| | SFAC C H N O Cu I Nd Er |
| | UNIT 48 72 14 22 2 2 0.21 1.79 |
| | L.S. 10 |
| | BOND |
| | FMAP 2 |
| | PLAN 5 |
| | TEMP 23.000 |
| | SUMP 1.0 0.0001 1.0 2 1.0 3 |
| | EXYZ Er1 ND1 |
| | EADP Er1 ND1 |
| | WGHT 0.058100 9.235000 |
| | FVAR **0.34462 0.89189 0.10811** |
| | ER1 8 0.596434 1.114660 -0.036721 11.00000 0.00980 |

| | |
|---|---|
| | 0.00386 = 0.01365 -0.00015 -0.00331 0.00146 |
| | ND1 7 0.596434 1.114660 -0.036721 11.00000 0.00980 |
| | 0.00386 = 0.01365 -0.00015 -0.00331 0.00146 |
| Yb-Nd | TITL 1 in P-1 |
| | CELL 0.71073 11.0728 12.2852 15.0593 81.387 82.667 64.308 |
| | ZERR 1.00 0.0029 0.0033 0.0040 0.004 0.004 0.003 |
| | LATT 1 |
| | SFAC C H N O Cu I Nd Yb |
| | UNIT 48 72 14 22 2 2 0.21 1.79 |
| | L.S. 10 |
| | BOND |
| | ACTA |
| | FMAP 2 |
| | PLAN 5 |
| | TEMP 23.000 |
| | SUMP 1.0 0.0001 1.0 2 1.0 3 |
| | EXYZ YB1 ND1 |
| | EADP YB1 ND1 |
| | WGHT 0.056300 10.150500 |
| | FVAR **0.34336 0.90794 0.09206** |
| | YB1 8 -0.097201 0.884707 0.537847 21.00000 0.01412 |
| | 0.01307 = 0.01206 -0.00136 -0.00157 -0.00386 |
| | ND1 7 -0.097201 0.884707 0.537847 -21.00000 0.01412 |
| | 0.01307 = 0.01206 -0.00136 -0.00157 -0.00386 |




**Scheme S1** The synthesis of complex **1**, **2** and **1**-RE1/RE2.

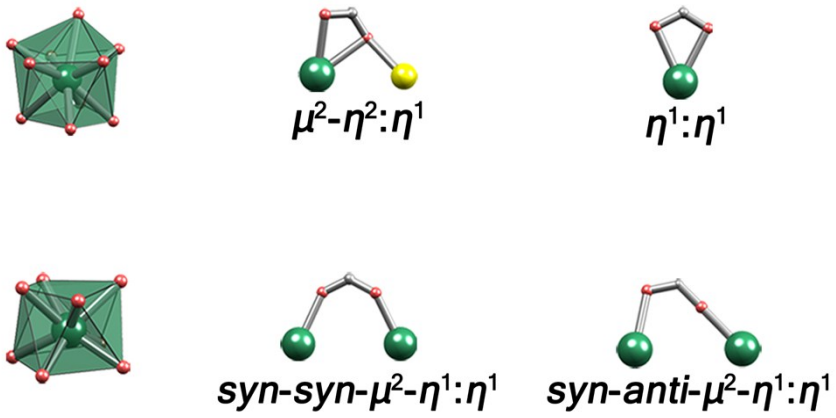



**Fig. S1** Coordination configuration of RE ions and coordination modes of ligand in complex **1** (bottom) and **2** (top).

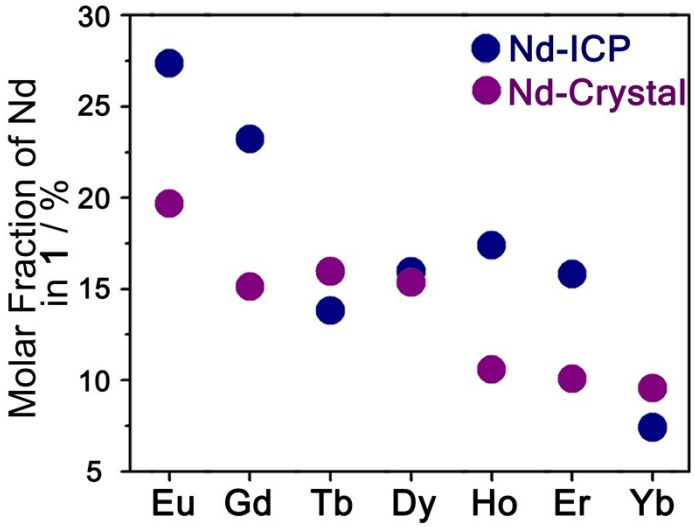



**Fig. S2** Comparison of metal distributions obtained from single crystal X-ray crystallography (●) and ICP measurements (●).

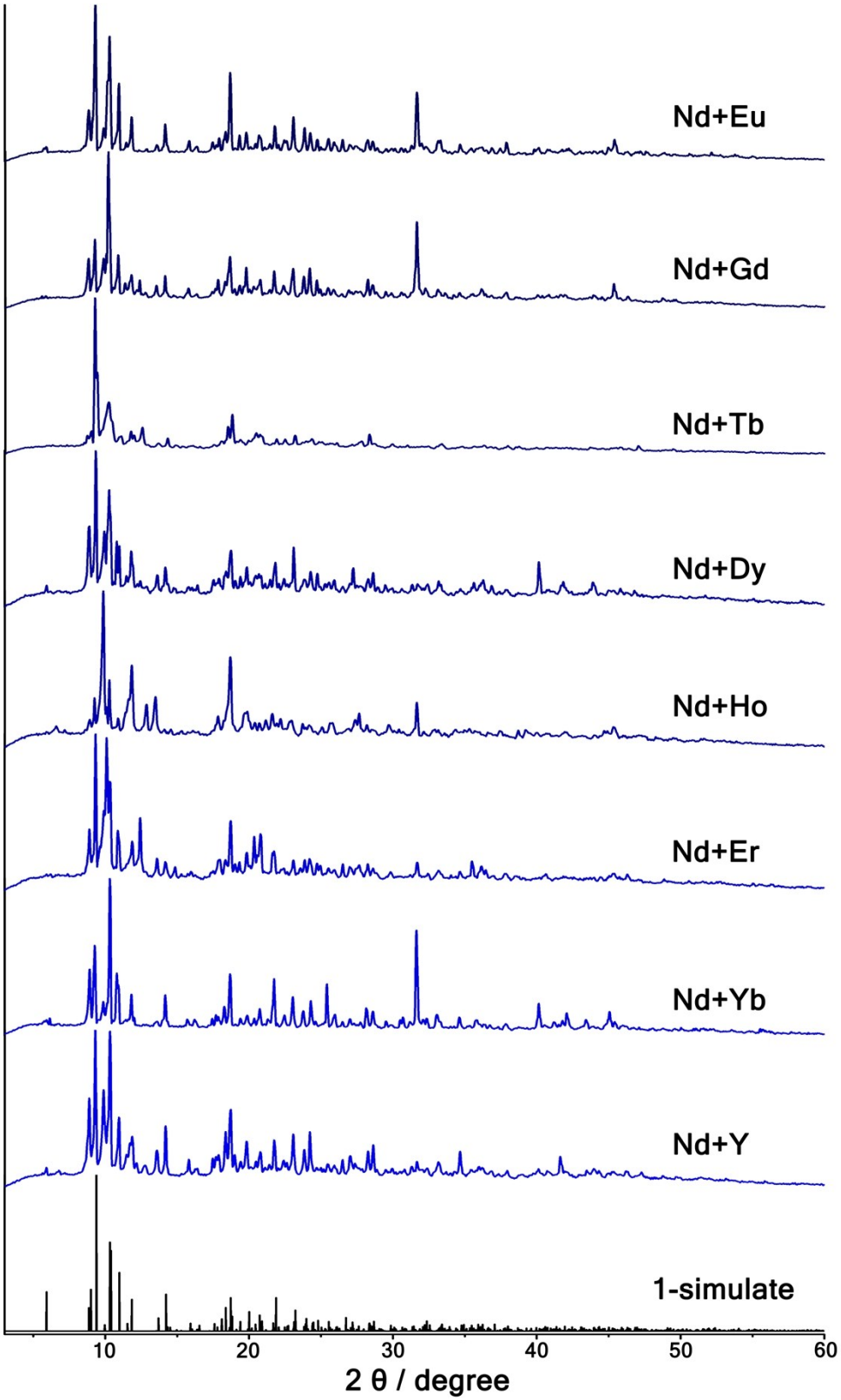



**Fig. S3** PXRD data of **1**-RE1/Nd.

**Table S7** Separation results of **1**-RE1/RE2.

| Stating Ln elements | | Starting materials radio (mmol/mmol) | Mole percentage of Ln in Crystalline samples by ICP | |
|---|---|---|---|---|
| RE2 | RE1 | | RE2 / % | RE1 / % |
| Nd | Eu | 1 : 1 | 27.36 | 72.64 |
| Nd | Gd | 1 :1 | 23.21 | 76.79 |
| Nd | Tb | 1 : 1 | 13.80 | 86.20 |
| Nd | Dy | 1 : 1 | 15.96 | 84.04 |
| Nd | Ho | 1 :1 | 17.40 | 82.60 |
| Nd | Er | 1 : 1 | 15.82 | 84.18 |
| Nd | Yb | 1 : 1 | 7.41 | 92.59 |
| Nd | Y | 1 : 1 | 12.74 | 87.26 |

**Table S8** Maximum allowable emission concentration for basic control projects (average daily value, GB8978--1996). Since the wastewater discharge standards are different in different countries (even different in different states in USA), and now China is the largest producer of rare earth in the world, so we refer to China's wastewater discharge standards.

| No. | Basic control projects | Grade I | | Grade II | Grade II |
|---|---|---|---|---|---|
| | | Standard A | Standard B | | |
| 1 | Chemical oxygen demand (COD) (mg/L) | 50/60 | 60 | 100/120 | 120 |
| 2 | Biochemical oxygen demand (BOD) (mg/L) | 10/20 | 20 | 30 | 60 |
| 3 | Suspended solids (SS) (mg/L) | 10/20 | 20 | 30 | 50 |
| 4 | Animal and vegetable oils (mg/L) | 1/20 | 3/20 | 5/20 | 20 |
| 5 | Petroleum (mg/L) | 1/10 | 3/10 | 5/10 | 15 |
| 6 | Anionic surface-active agent (mg/L) | 0.5/5 | 1/5 | 2/5 | 5 |
| 7 | Nitrogen content (mg/L) | 15 | 20 | - | - |
| 8 | Ammonia nitrogen content (mg/L) | 5(8)/15 | 8(15)/(15) | 25(30)/25 | - |
| 9 | Phosphorus content (mg/L) | 0.5 | 1 | 3 | 5 |
| 10 | Chroma (dilution ratio) | 30/50 | 30/50 | 3 | 5 |
| 11 | PH | 6-9 | | | |
| 12 | Fecal escherichia coli (/L) | 103 | 104 | 104 | - |

**Notes and references**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