# *Supporting information for*

## Two series of pH-dependent lanthanide coordination polymers demonstrating solvent-induced single crystal to single crystal transformation, sorption and luminescent properties

**Lina Zhang,[a,b] Chao Zhang,[a] Bin Zhang,[a] Chenxia Du,*[a] and Hongwei Hou*[a]**

[a] *College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, 450052, P.R. China.*

[b] *College of Physics and Chemistry, Henan Polytechnic University, Jiaozuo 454000, P. R. China.*

*E-mail: dcx@zzu.edu.cn, houhongw@zzu.edu.cn*

This file includes **Figures S1−S13** and **Tables S1−S6**.

**Figure S12.** $^{1}H$ NMR spectra in $CDCl_3$ of the supernatant liquids resulted from the reactions of **8a/dry** with acetone in various molar ratios.

**Figure S13.** PXRD patterns for compound **8a/acetone** prepared from: original compound **8a**, original **8a**/**dry** (**8a**/acetone 1st cycle) and regenerated **8a/dry** (**8a**/acetone 2nd cycle).

**Table S1.** Crystallographic data for compounds **1-6**.

**Table S2.** Crystallographic data for compounds **7-10**.

**Table S3.** Crystallographic data for compounds **7a-10a.**

**Table S4**. Crystallographic data for the Solvent Exchanged Compounds of **8a**.

**Table S5.** Selected Bond Distances and Angles for Compounds **1**–**10** and **8a-10a.**

**Table S6**. Selected Bond Distances for the Solvent Exchanged Compounds of **8a**.

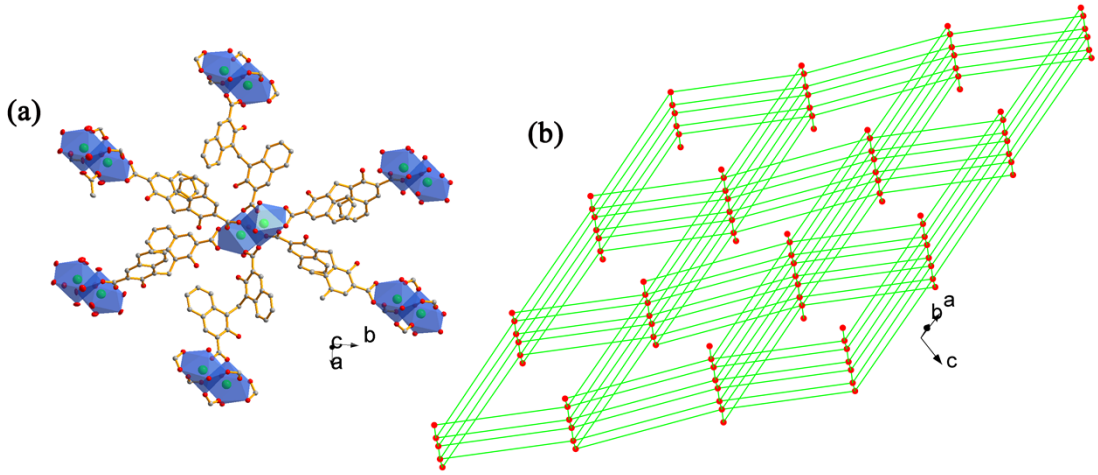


**Figure S1**. (a) Illustration of each SBU connected to six adjacent SBUs through $PA^{2-}$ anions in **8.** (b**)** 3D **pcu** network of **8**. (Color code: $[Ho_2(COO)_6(H_2O)_3(DMF)]$, red ball; $PA^{2-}$ anion, green line.)

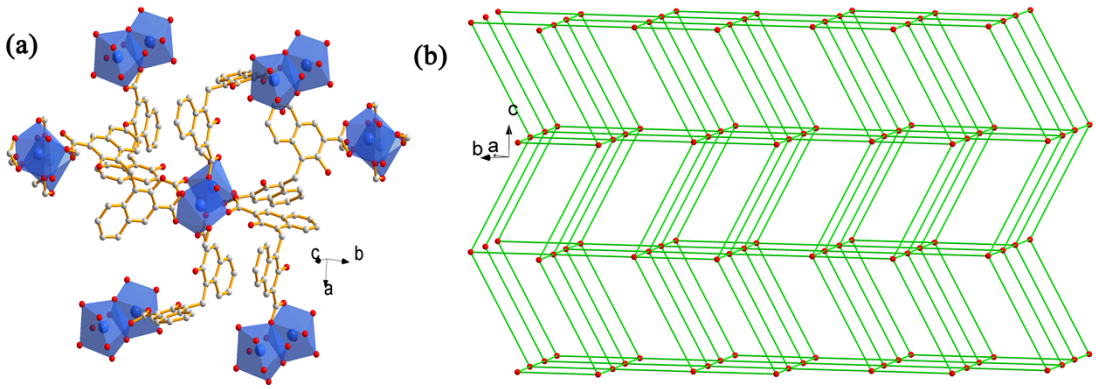


**Figure S2**. (a) Illustration of each SBU connected to six adjacent SBUs through $PA^{2-}$ anions in **8a.** (b) 3D **pcu** network of **8a**. (Color code: $[Ho_2(COO)_6(H_2O)_2(DMF)_2]$, red ball; $PA^{2-}$ anion, green line.)

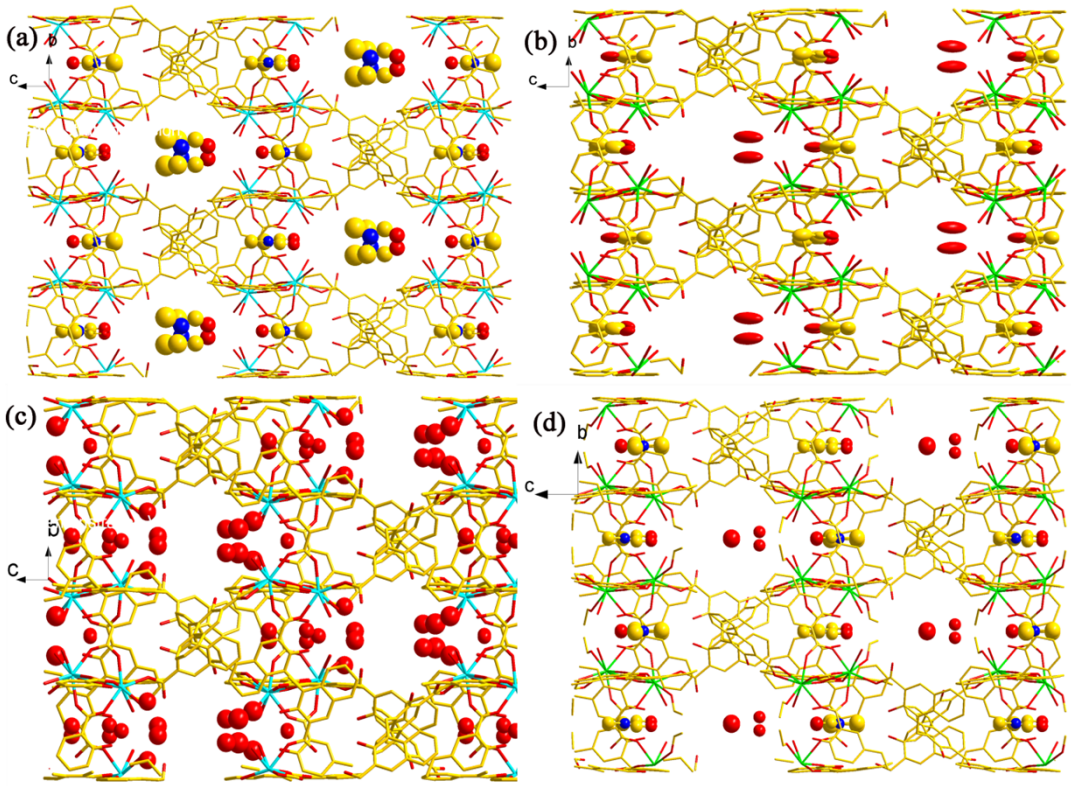


**Figure S3**. Representations of lattice solvent molecules filled in the 1D channel of (a) **8a,** (b) **8a/acetone**, (c) **8a/$H_2O$** and (d) **8a/EtOH**. (Hydrogen atoms were omitted for clarity.)

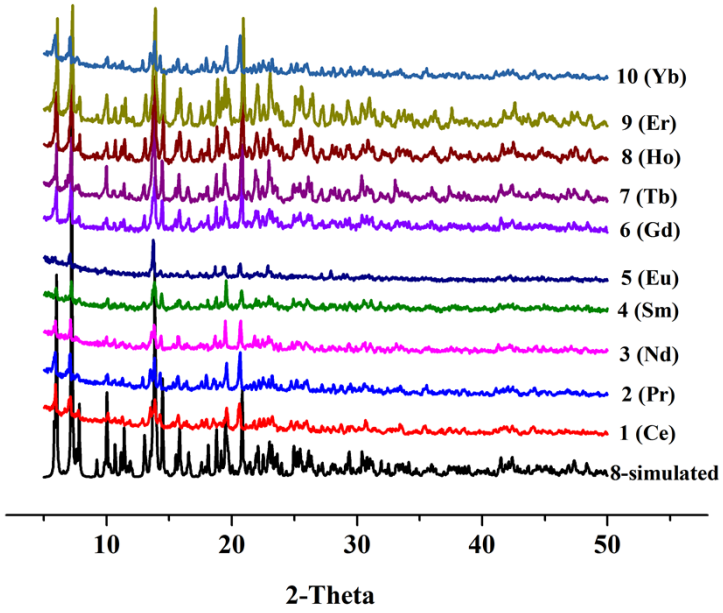


**Figure S4.** The simulated and experimental PXRD patterns for compounds **1**–**10**.

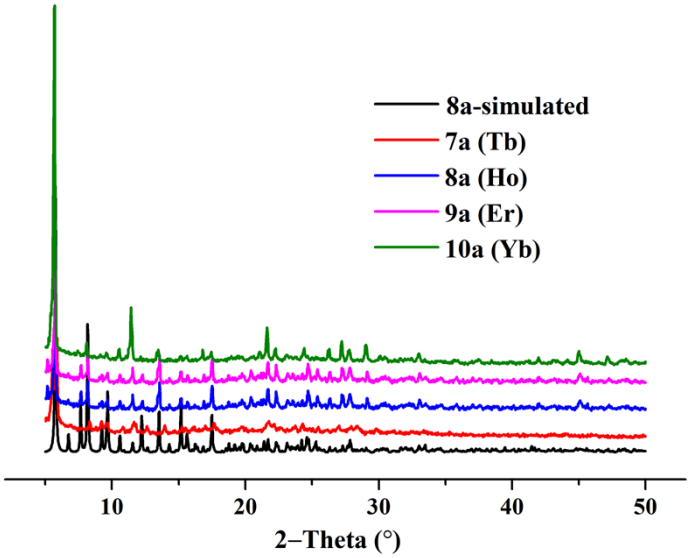


**Figure S5.** The simulated and experimental PXRD patterns for **7a**–**10a**.

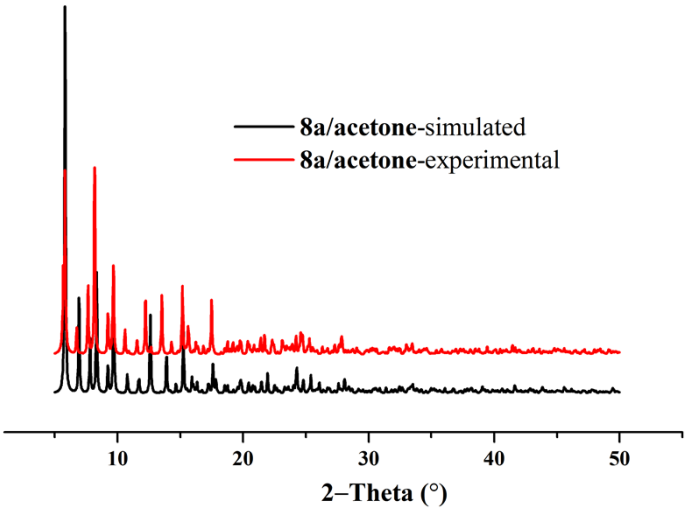


**Figure S6.** The simulated and experimental PXRD patterns for **8a/acetone**.

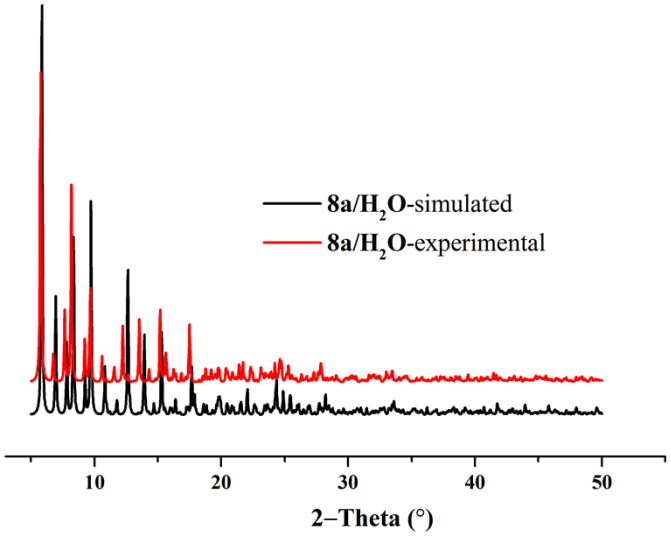


**Figure S7.** The simulated and experimental PXRD patterns for **8a/$H_2O$**.

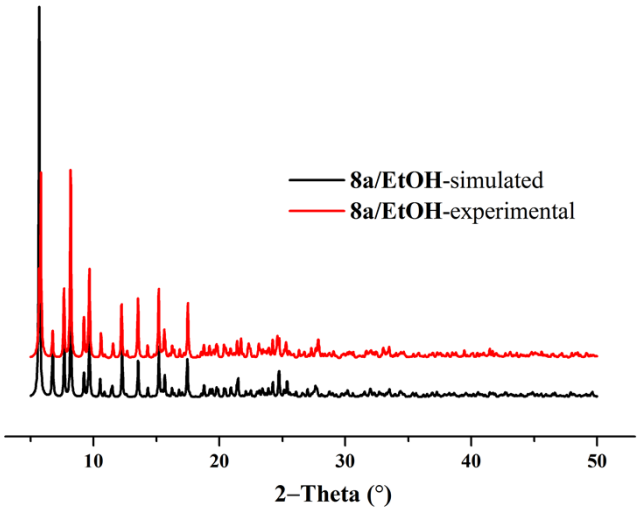


**Figure S8.** The simulated and experimental PXRD patterns for **8a/EtOH**.

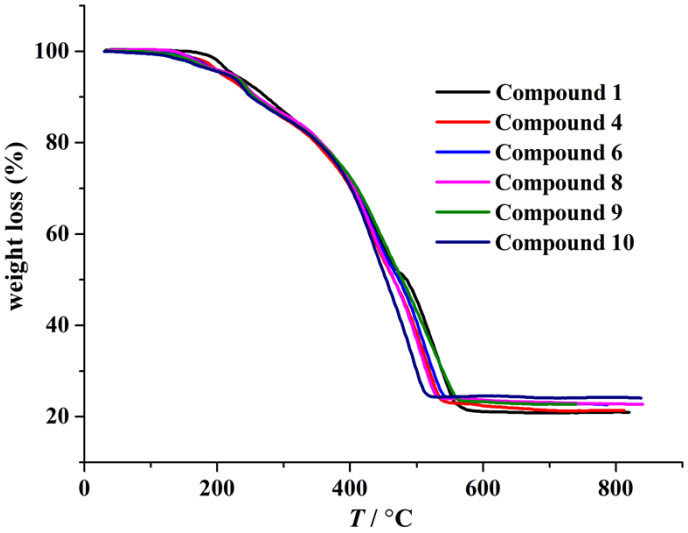


**Figure S9**. TGA plots for selected compounds of **series A**.

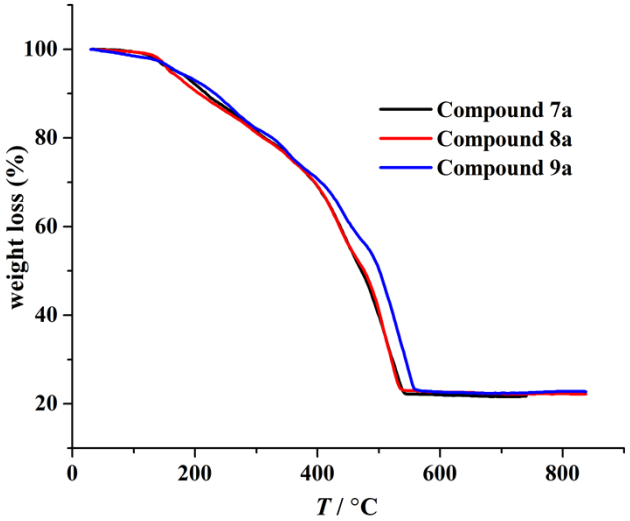


**Figure S10**. TGA plots for selected compounds of **series B**.

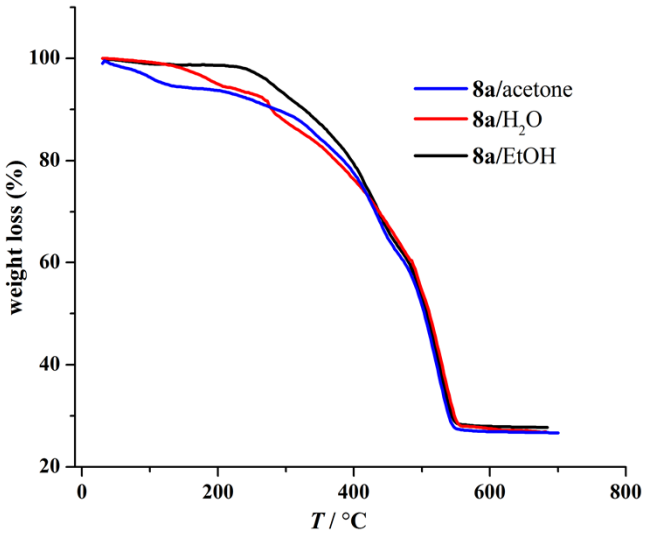


**Figure S11**. TGA plots for complexes **8a/acetone, 8a/$H_2O$** and **8a/EtOH**.

## Acetone adsorption data

The exact quantities of the reactants in the various reactions performed are.: *x0.5* [acetone (2.4 µL, 1.89 mg, 0.0324 mmol, 0.5 eq.), dichloromethane (6.3 µL, 8.30 mg, 0.0972 mmol), **8a**/**dry** (0.1011 g, 0.0648 mmol) in 2mL $CDCl_3$], *x1* [acetone (4.8 µL, 3.78 mg, 0.0648 mmol, 1 eq.), dichloromethane (12.6 µL, 16.60 mg, 0.1944 mmol), **8a**/**dry** (0.1011 g, 0.0648 mmol) in 2mL $CDCl_3$], *x1.5* [acetone (7.2 µL, 5.67 mg, 0.0972 mmol, 1.5 eq.), dichloromethane (18.9 µL, 24.90 mg, 0.2916 mmol), **8a**/**dry** (0.1011 g, 0.0648 mmol) in 2mL $CDCl_3$], *x2* [acetone (9.6 µL, 7.56 mg, 0.1296 mmol, 2 eq.), dichloromethane (25.2 µL, 33.20 mg, 0.3888 mmol), **8a**/**dry** (0.1011 g, 0.0648 mmol) in 2mL $CDCl_3$], *x2.5* [acetone (12.0 µL, 9.45 mg, 0.1620 mmol, 2.5 eq.), dichloromethane (31.5 µL, 41.5 mg, 0.4860 mmol), **8a**/**dry** (0.1011 g, 0.0648 mmol) in 2mL $CDCl_3$], *x3* [acetone (14.4 µL, 11.34 mg, 0.1944 mmol, 3 eq.), dichloromethane (37.8 µL, 49.80 mg, 0.5832 mmol), **8a**/**dry** (0.1011 g, 0.0648 mmol) in 2mL $CDCl_3$], *x3.5* [acetone (16.8 µL, 13.23 mg, 0.2268 mmol, 3.5 eq.), dichloromethane (44.1 µL, 58.10 mg, 0.6804 mmol), **8a**/**dry** (0.1011 g, 0.0648 mmol) in 2mL $CDCl_3$].

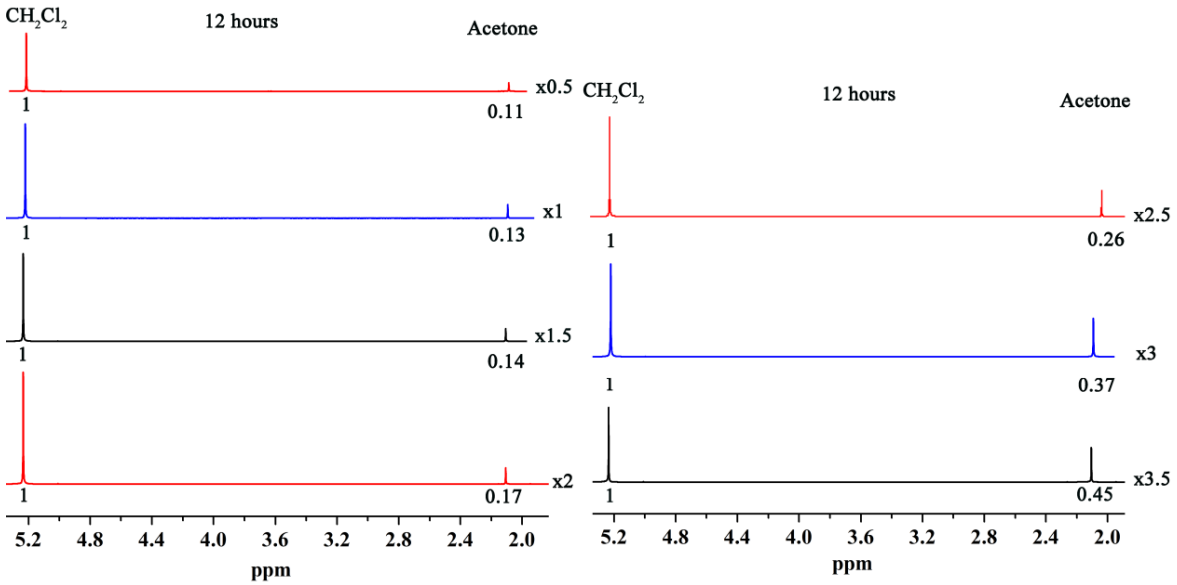


**Figure S12.** $^1H$ NMR spectra in $CDCl_3$ of the supernatant liquids resulted from the reactions of **8a**/dry with acetone in various molar ratios.

As shown in **Figure S12**, the peaks at 2.17 ppm and 5.30 ppm correspond to the methyl groups of acetone and methylene group of dichloromethane respectively. The concentrations of acetone

after the sorption processes were determined using as reference the dichloromethane that is not absorbed by **8a/dry** at these reaction conditions (i.e magnetic stirring at room temperature and atmospheric pressure) and thus its concentration remains unchanged after the treatment of the solution with **8a/dry**. For each experiment, the initial concentrations of acetone and dichloromethane were 1:3 (i.e. the ratio of the peak integrals for the H atom of acetone and dichloromethane were equal to 1 in the $^1$H NMR spectra of the initial solutions).

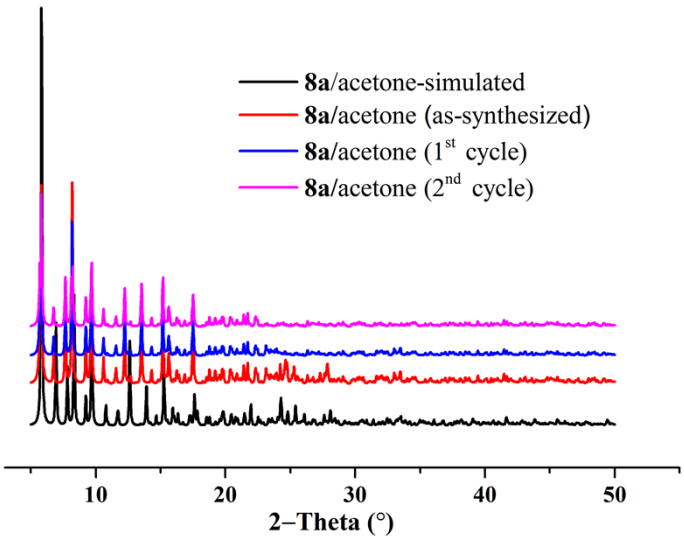


**Figure S13.** PXRD patterns for compound **8a/acetone** prepared from: original compound **8a**; original **8a/dry** (**8a/acetone** 1$^{st}$ cycle) and regenerated **8a/dry** (**8a/acetone** 2$^{nd}$ cycle).

**Table S1**. Crystallographic data for compounds **1-6**

| | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{81}H_{74}N_4O_{24}Ce_2$ | $C_{79.5}H_{71.5}N_{3.5}O_{24}Pr_2$ | $C_{79.5}H_{71.5}N_{3.5}Nd_2O_{24}$ | $C_{79.5}H_{71.5}N_{3.5}O_{24}Sm_2$ | $C_{79.5}H_{71.5}Eu_2N_{3.5}O_{24}$ | $C_{79.5}H_{71.5}Gd_2N_{3.5}O_{24}$ |
| Formula weight | 1767.63 | 1741.66 | 1748.31 | 1760.55 | 1763.79 | 1774.35 |
| $T$ (K) | 291.15 | 291.15 | 291.15 | 291.15 | 291.15 | 291.15 |
| crystal system | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| $a$(Å) | 14.2831(2) | 14.26463(15) | 14.21191(16) | 14.1785(2) | 14.13790(15) | 14.11880(17) |
| $b$(Å) | 29.8625(4) | 29.8504(3) | 29.7396(3) | 29.6106(4) | 29.5535(3) | 29.5116(3) |
| $c$(Å) | 18.2631(3) | 18.2812(2) | 18.3087(3) | 18.3573(3) | 18.3735(3) | 18.3851(3) |
| $\alpha$(°) | 90.00 | 90.00 | 90 | 90 | 90.00 | 90.00 |
| $\beta$(°) | 106.9678(17) | 107.0122(12) | 107.0015(14) | 107.0285(17) | 107.0296(13) | 107.0169(14) |
| $\gamma$(°) | 90.00 | 90.00 | 90 | 90 | 90.00 | 90.00 |
| $V$(Å$^3$) | 7450.7(2) | 7443.61(15) | 7400.10(16) | 7369.1(2) | 7340.32(15) | 7325.10(16) |
| Z | 4 | 4 | 4 | 4 | 4 | 4 |
| $D_c$ [g /cm$^3$] | 1.570 | 1.547 | 1.562 | 1.581 | 1.592 | 1.603 |
| $\mu$(mm$^{-1}$) | 10.024 | 1.376 | 11.28 | 1.661 | 1.777 | 1.879 |
| $F$(000) | 3556.0 | 3500.0 | 3506 | 3530 | 3546.0 | 3546.0 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Reflections | 27291 | 32578 | 26071 | 32358 | 41239 | 31199 |
| Unique reflections | 12916 | 15633 | 13073 | 15041 | 14949 | 14947 |
| Goodness-of-fit | 1.025 | 1.017 | 1.017 | 1.020 | 1.037 | 1.042 |
| $R_1$ [a] ($I>2\sigma(I)$) | 0.0376 | 0.0369 | 0.0409 | 0.0393 | 0.0355 | 0.0332 |
| $wR_2$ [b] (all data) | 0.1047 | 0.0873 | 0.1067 | 0.0917 | 0.0808 | 0.0771 |
| $R$(int) | 0.0258 | 0.0234 | 0.0282 | 0.0340 | 0.0324 | 0.0238 |

[a] $R_1=\Sigma||Fo|-|Fc||/\Sigma|Fo|$. [b] $wR_2=[\Sigma[w(Fo^2-Fc^2)^2]/\Sigma w(Fo^2)^2]^{1/2}$

**Table S2**. Crystallographic data for compounds **7-10**

| | **7** | **8** | **9** | **10** |
|---|---|---|---|---|
| Empirical formula | $C_{79.5}H_{71.5}N_{3.5}O_{24}Tb_2$ | $C_{78}H_{71}Ho_2N_3O_{25}$ | $C_{78}H_{71}Er_2N_3O_{25}$ | $C_{78}H_{71}N_3O_{25}Yb_2$ |
| Formula weight | 1777.19 | 1780.22 | 1784.88 | 1796.43 |
| $T$ (K) | 291.15 | 291.15 | 291.15 | 291.15 |
| crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| $a$(Å) | 14.0878(3) | 14.042(3) | 14.0233(4) | 14.0088(4) |
| $b$(Å) | 29.4702(7) | 29.367(6) | 29.3110(8) | 29.2317(6) |
| $c$(Å) | 18.4237(4) | 18.456(4) | 18.4183(9) | 18.4902(5) |
| $\alpha$(°) | 90 | 90.00 | 90.00 | 90.00 |
| $\beta$(°) | 107.034(2) | 107.15(3) | 107.095(4) | 107.187(3) |
| $\gamma$(°) | 90 | 90.00 | 90.00 | 90.00 |
| $V$(Å$^3$) | 7313.4(3) | 7273(3) | 7236.1(4) | 7233.7(3) |
| Z | 4 | 4 | 4 | 4 |
| $D_c$ [g /cm$^3$] | 1.61 | 1.624 | 1.637 | 1.646 |
| $\mu$(mm$^{-1}$) | 2.002 | 2.245 | 4.896 | 2.655 |
| $F$(000) | 3558 | 3568 | 3576.0 | 3584.0 |
| Reflections collected | 31944 | 73874 | 26228 | 32154 |
| Unique reflections | 15387 | 14866 | 12649 | 14771 |
| Goodness-of-fit | 0.996 | 1.168 | 1.021 | 1.008 |
| $R^a_1$($I>2\sigma(I)$) | 0.0387 | 0.0686 | 0.0358 | 0.0654 |
| $wR^b_2$ (all data) | 0.0872 | 0.1402 | 0.0954 | 0.1177 |
| $R$(int) | 0.0369 | 0.0793 | 0.0276 | 0.0808 |

[a] $R_1=\Sigma||Fo|-|Fc||/\Sigma|Fo|$. [b] $wR_2=[\Sigma[w(Fo^2-Fc^2)^2]/\Sigma w(Fo^2)^2]^{1/2}$

**Table S3**. Crystallographic data for compounds **7a-10a**

| | **7a** | **8a** | **9a** | **10a** |
|---|---|---|---|---|
| Empirical formula | $C_{84}H_{83}Tb_2N_5O_{26}$ | $C_{84}H_{83}Ho_2N_5O_{26}$ | $C_{84}H_{83}Er_2N_5O_{26}$ | $C_{84}H_{83}Yb_2N_5O_{26}$ |
| Formula weight | 1896.38 | 1908.35 | 1913.06 | 1924.62 |
| $T$ (K) | 291.15 | 291.15 | 291.15 | 291.15 |
| crystal system | orthorhombic | orthorhombic | orthorhombic | orthorhombic |
| space group | $Pna2_1$ | $Pna2_1$ | $Pna2_1$ | $Pna2_1$ |
| $a$(Å) | 19.1407(3) | 19.0994(2) | 19.0983(3) | 19.08923(19) |
| $b$(Å) | 14.4612(2) | 14.41797(17) | 14.4221(3) | 14.38724(17) |
| $c$(Å) | 30.6467(6) | 30.5930(5) | 30.5560(10) | 30.5462(4) |
| $\alpha$(°) | 90.00 | 90.00 | 90.00 | 90.00 |
| $\beta$(°) | 90.00 | 90.00 | 90.00 | 90.00 |
| $\gamma$(°) | 90.00 | 90.00 | 90.00 | 90.00 |

| | | | | |
|---|---|---|---|---|
| ***V*(Å$^3$)** | 8482.9(2) | 8424.51(19) | 8416.3(4) | 8389.26(17) |
| Z | | 4 | 4 | 4 |
| $D_c$ [g /cm$^3$] | | 1.498 | 1.508 | 1.522 |
| $\mu$(mm$^{-1}$) | | 1.945 | 2.061 | 2.296 |
| *F*(000) | | 3824 | 3856 | 3872 |
| Reflections collected | | 22596 | 27069 | 44578 |
| Unique reflections | | 12351 | 11460 | 16301 |
| Goodness-of-fit | | 1.057 | 1.039 | 1.051 |
| $R^a_1$ ($I$ >2σ( $I$ )) | | 0.0347 | 0.0423 | 0.0409 |
| $wR^b_2$ (all data) | | 0.0889 | 0.1025 | 0.0986 |
| *R*(int) | | 0.0228 | 0.0462 | 0.0396 |

$^aR_1$=Σ||*Fo*| - |*Fc*||/Σ|*Fo*|. $^b wR_2$=[Σ[$w$(*Fo*$^2$ - *Fc*$^2$)$^2$]/Σ$w$(*Fo*$^2$)$^2$]$^{1/2}$

**Table S4.** Crystallographic data for the Solvent Exchanged Compounds of **8a**

| | **8a/acetone** | **8a/dry** | **8a/$H_2O$** | **8a/ EtOH** | **8a/acetone'** |
|---|---|---|---|---|---|
| Empirical formula | $C_{75}H_{68}Ho_2O_{27}$ | $C_{69}H_{50}Ho_2O_{22}$ | $C_{69}H_{68}Ho_2O_{31}$ | $C_{79}H_{78}Ho_2N_2O_{28}$ | $C_{75}H_{68}Ho_2O_{27}$ |
| Formula weight | 1731.09 | 1560.95 | 1722.95 | 1833.23 | 1731.11 |
| $T$ (K) | 291.15 | 291.15 | 291.15 | 291.15 | 291.15 |
| crystal system | orthorhombic | orthorhombic | orthorhombic | orthorhombic | orthorhombic |
| space group | $Pna2_1$ | $Pna2_1$ | $Pna2_1$ | $Pna2_1$ | $Pna2_1$ |
| $a$(Å) | 19.1046(4) | 19.1289(5) | 19.0413(9) | 19.0988(3) | 19.1050(5) |
| $b$(Å) | 13.9553(3) | 13.8909(5) | 13.9578(5) | 14.3508(3) | 13.9575(6) |
| $c$(Å) | 30.1931(8) | 30.0581(11) | 30.1263(15) | 30.9762(5) | 30.2155(9) |
| $\alpha$(°) | 90 | 90.00 | 90 | 90 | 90 |
| $\beta$(°) | 90 | 90.00 | 90 | 90 | 90 |
| $\gamma$(°) | 90 | 90.00 | 90 | 90 | 90 |
| *V*(Å$^3$) | 8049.83(3) | 7987.0(5) | 8006.8(6) | 8490.1(3) | 8057.2(5) |
| Z | 4 | 4 | 4 | 4 | 4 |
| $D_c$ [g /cm$^3$] | 1.395 | 1.298 | 1.414 | 1.403 | 1.396 |
| $\mu$(mm$^{-1}$) | 4.163 | 4.123 | 2.040 | 3.995 | 2.021 |
| *F*(000) | 3376.0 | 3096.0 | 3384.0 | 3600.0 | 3384.0 |
| $R^a_1$ ($I$ >2σ( $I$ )) | 0.0490 | 0.0699 | 0.0649 | 0.0771 | 0.0537 |
| $wR^b_2$ (all data) | 0.1394 | 0.1913 | 0.1642 | 0.2072 | 0.1148 |
| *R*(int) | 0.0275 | 0.0828 | 0.0584 | 0.0469 | 0.0523 |

$^aR_1$=Σ||*Fo*| - |*Fc*||/Σ|*Fo*|. $^b wR_2$=[Σ[$w$(*Fo*$^2$ - *Fc*$^2$)$^2$]/Σ$w$(*Fo*$^2$)$^2$]$^{1/2}$

**Table S5.** Selected Bond Distances (Å) and Angles (°) for Compounds **1**–**10** and **8a-10a.**

| Compound **1** | | | |
|---|---|---|---|
| Ce(1)–O(1) | 2.402(3) | Ce(2)–O(2) | 2.478(3) |
| Ce(1))–O(4) | 2.490(3) | Ce(2)–O(7) | 2.439(3) |
| Ce(1)–O(5) | 2.586(3) | Ce(2)–O(10) | 2.539(3) |
| Ce(1)–O(8) | 2.451(3) | Ce(2)–O(11) | 2.586(3) |
| Ce(1)–O(13) | 2.471(4) | Ce(2)–O(14) | 2.484(3) |
| Ce(1)–O(16) | 2.452(3) | Ce(2)–O(17) | 2.429(3) |
| Ce(1)–O(21) | 2.556(3) | Ce(2)–O(19) | 2.467(3) |
| Ce(1)–O(22) | 2.553(4) | Ce(2)–O(20) | 2.529(4) |

| | | | |
|---|---|---|---|
| O(1) –Ce(1)– O(4) | 143.51(12 | O(1) –Ce(1)– O(4) | 142.16(12) |
| O(1) –Ce(1)– O(8) | 129.22(12) | O(2) –Ce(2)– O(10) | 81.97(11) |
| O(2) –Ce(2)– O(11) | 69.21(11) | O(2) –Ce(2)– O(14) | 74.52(13) |
| Compound **2** | | | |
| Pr(1)–O(2) | 2.4062(19) | Pr(2)–O(1) | 2.4325(17) |
| Pr(1)–O(5)[1] | 2.4628(18) | Pr(2)–O(4)[1] | 2.438(2) |
| Pr(1)–O(8) | 2.461(2) | Pr(2)–O(7) | 2.3950(19) |
| Pr(1)–O(16) | 2.5236(19) | Pr(2)–O(10) | 2.4863(19) |
| Pr(1)–O(17) | 2.5725(18) | Pr(2)–O(11) | 2.5714(18) |
| Pr(1)–O(19) | 2.449(2) | Pr(2)–O(14) | 2.438(2) |
| Pr(1)–O(20) | 2.543(2) | Pr(2)–O(21) | 2.536(2) |
| Pr(1)–O(13) | 2.4243(19) | Pr(2)–O(22) | 2.5447(19) |
| O(2)–Pr(1)–O(5)[1] | 134.88(8) | O(2)–Pr(1)–O(8) | 75.28(7) |
| O(2)–Pr(1)–O(13) | 74.21(7) | O(1)–Pr(2)–O(4)[1] | 108.13(8) |
| O(1)–Pr(2)–O(10) | 96.80(7) | O(1)–Pr(2)–O(11) | 134.97(7 |
| [1]−1+X, 1/2−Y, −1/2+Z; | | | |
| Compound **3** | | | |
| Nd(1)–O(7) | 2.511(2) | Nd(2)–O(11) | 2.427(3) |
| Nd(1)–O(8) | 2.553(2) | Nd(2)–O(13) | 2.415(2) |
| Nd(1)–O(10) | 2.406(2) | Nd(2)–O(21) | 2.526(3) |
| Nd(1)–O(17)[2] | 2.440(3) | Nd(2)–O(22) | 2.521(3) |
| Nd(1)–O(2) | 2.433(3) | Nd(2)–O(1) | 2.367(2) |
| Nd(1)–O(14) | 2.389(3) | Nd(2)–O(16)[2] | 2.404(3) |
| Nd(1)–O(20) | 2.516(3) | Nd(2)–O(5) | 2.553(2) |
| Nd(1)–O(19) | 2.428(3) | Nd(2)–O(4) | 2.462(3) |
| O(7)– Nd(1)–O(8) | 51.33(8) | O(11)– Nd(2)–O(21) | 139.97(8) |
| O(7)– Nd(1)–O(20) | 75.31(9) | O(11)– Nd(2)–O(22) | 141.99(9) |
| O(10)– Nd(1)–O(7) | 150.80(9) | O(13)– Nd(2)–O(5) | 135.18(9) |
| [2]−1+X, 1/2−Y, −1/2+Z | | | |
| Compound **4** | | | |
| Sm(1)–O(2) | 2.408(2) | Sm(2)–O(1) | 2.349(2) |
| Sm(1)–O(7) | 2.480(2) | Sm(2)–O(4) | 2.444(2) |
| Sm(1)–O(8) | 2.524(2) | Sm(2)–O(5) | 2.529(2) |
| Sm(1)–O(11) | 2.4057(19) | Sm(2)–O(10) | 2.356(2) |
| Sm(1)–O(14) | 2.363(2) | Sm(2)–O(13) | 2.3887(19) |
| Sm(1)–O(16) | 2.374(2) | Sm(2)–O(17) | 2.397(2) |
| Sm(1)–O(19) | 2.510(2) | Sm(2)–O(20) | 2.505(2) |
| Sm(1)–O(22) | 2.402(2) | Sm(2)–O(21) | 2.487(2) |
| O(2)– Sm(1)–O(7) | 82.21(7) | O(1)– Sm(2)–O(4) | 144.38(8) |
| O(2)– Sm(1)–O(8) | 70.34(7) | O(1)– Sm(2)–O(5) | 141.96(7) |
| O(11)– Sm(1)–O(7) | 80.09(8) | O(10)– Sm(2)–O(4) | 136.49(8) |
| Compound **5** | | | |
| Eu(1)–O(1) | 2.351(3) | Eu(2)–O(2) | 2.375(3) |
| Eu(1)–O(6)[1] | 2.397(3) | Eu(2)–O(5)[1] | 2.338(3) |

| | | | |
|---|---|---|---|
| Eu(1)–O(7) | 2.509(2) | Eu(2)–O(11)[2] | 2.379(3) |
| Eu(1)–O(8) | 2.472(3) | Eu(2)–O(14) | 2.334(3) |
| Eu(1)–O(12) [2] | 2.355(3) | Eu(2)–O(17) [3] | 2.518(3) |
| Eu(1)–O(13) | 2.386(3) | Eu(2)–O(18) [3] | 2.431(3) |
| Eu(1)–O(21) | 2.384(3) | Eu(2)–O(19) | 2.485(3) |
| Eu(1)–O(22) | 2.500(3) | Eu(2)–O(20) | 2.468(3) |
| O(1)–Eu(1)–O(7) | 78.58(9) | O(2)–Eu(2)–O(19) | 75.28(10) |
| O(1)–Eu(1)–O(8) | 130.50(9) | O(2)–Eu(2)–O(20) | 144.72(11) |
| O(1)–Eu(1)–O(22) | 142.12(10) | O(2)–Eu(2)–O(14) | 81.52(10) |

[1]−1+X, 1/2−Y, −1/2+Z; [2]2−X, −1/2+Y, 3/2−Z; [3]1−X, −1/2+Y, 3/2−Z

| Compound **6** | | | |
|---|---|---|---|
| Gd(1)–O(2) | 2.341(3) | Gd(2)–O(1) | 2.364(2) |
| Gd(1)–O(6)[1] | 2.384(3) | Gd(2)–O(11)#2 | 2.371(3) |
| Gd(1)–O(7) | 2.497(2) | Gd(2)–O(14) | 2.325(2) |
| Gd(1)–O(8) | 2.459(2) | Gd(2)–O(17)#3 | 2.511(2) |
| Gd(1)–O(12)[2] | 2.348(2) | Gd(2)–O(18)#3 | 2.424(3) |
| Gd(1)–O(13) | 2.376(3) | Gd(2)–O(19) | 2.469(3) |
| Gd(1)–O(21) | 2.374(3) | Gd(2)–O(20) | 2.463(3) |
| Gd(1)–O(22) | 2.484(3) | Gd(2)–O(1A)#1 | 2.844(4) |
| O(2)–Gd(1)–O(7) | 78.55(9) | O(1)–Gd(2)–O(19) | 75.07(10) |
| O(2)–Gd(1)–O(8) | 130.66(9) | O(1)–Gd(2)–O(20) | 144.39(11) |
| O(2)–Gd(1)–O(13) | 76.19(10) | O(1)–Gd(2)–O(14) | 81.17(10) |

[1]−1+X, 1/2−Y, −1/2+Z; [2]2−X, −1/2+Y, 1/2−Z; [3]1−X, −1/2+Y, 1/2−Z;

| Compound **7** | | | |
|---|---|---|---|
| Tb(1)–O(1) | 2.452(2) | Tb(2)–O(5) | 2.355(2) |
| Tb(1)–O(2) | 2.482(2) | Tb(2)–O(7) | 2.3480(2) |
| Tb(1)–O(4) | 2.326(2) | Tb(2)–O(10) | 2.299(2) |
| Tb(1)–O(8) | 2.3309(2) | Tb(2)–O(13) | 2.303(2) |
| Tb(1)–O(11) | 2.3649(2) | Tb(2)–O(16) | 2.410(2) |
| Tb(1)–O(14) | 2.362(2) | Tb(2)–O(17) | 2.494(2) |
| Tb(1)–O(19) | 2.473(2) | Tb(2)–O(20) | 2.433(2) |
| Tb(1)–O(22) | 2.360(2) | Tb(2)–O(21) | 2.4591(2) |
| O(1)–Tb(1)–O(2) | 52.80(6) | O(5)–Tb(2)–O(16) | 83.01(8) |
| O(1)–Tb(1)–O(19) | 74.37(7) | O(5)–Tb(2)–O(17) | 72.03(7) |
| O(4)–Tb(1)–O(1) | 150.79(7) | O(5)–Tb(2)–O(20) | 142.03(8) |

| Compound **8** | | | |
|---|---|---|---|
| Ho (1)–O(1) | 2.421(3) | Ho (2)–O(5)[1] | 2.331(4) |
| Ho (1)–O(2) | 2.456(3) | Ho(2)–O(7) | 2.291(3) |
| Ho (1)–O(4)[1] | 2.303(3) | Ho(2)–O(10) | 2.389(3) |
| Ho (1)–O(8) | 2.331(4) | Ho(2)–O(11) | 2.476(3) |
| Ho (1)–O(14) | 2.341(3) | Ho(2)–O(13) | 2.272(4) |
| Ho (1)–O(17) | 2.309(3) | Ho(2)–O(16) | 2.317(3) |
| Ho (1)–O(19) | 2.330(4) | Ho(2)–O(21) | 2.432(3) |
| Ho (1)–O(20) | 2.465(4) | Ho(2)–O(22) | 2.406(4) |

| | | | |
|---|---|---|---|
| O(1)–Ho (1)–O(2) | 53.31(11) | O(5)[1]–Ho (2)–O(11) | 72.11(13) |
| O(1)–Ho (1)–O(20) | 74.10(12) | O(5)[1]–Ho (2)–O(21) | 138.96(12) |
| O(2)–Ho (1)–O(20) | 115.04(12) | O(5)[1]–Ho (2)–O(22) | 142.28(13) |
| O(4)[1]–Ho (1)–O(1) | 150.27(12) | O(5)[1]–Ho (2)–O(7) | 128.26(13) |
| O(4)[1]–Ho (1)–O(2) | 147.10(11) | O(7)–Ho (2)–O(10) | 144.98(13) |
| O(4)[1]–Ho (1)–O(8) | 120.64(13) | O(7)–Ho (2)–O(11) | 142.03(12) |

[1]1–X, 1/2+Y, 3/2–Z

| Compound **9** | | | |
|---|---|---|---|
| Er(1)–O(1) | 2.374(3) | Er(2)–O(5)[1] | 2.324(3) |
| Er(1)–O(2) | 2.471(3) | Er(2)–O(8) | 2.300(3) |
| Er(1)–O(4)1 | 2.274(3) | Er(2)–O(11) | 2.325(3) |
| Er(1)–O(7) | 2.313(3) | Er(2)–O(13) | 2.293(3) |
| Er(1)–O(10) | 2.251(3) | Er(2)–O(16) | 2.407(3) |
| Er(1)–O(14) | 2.322(3) | Er(2)–O(17) | 2.454(3) |
| Er(1)–O(19) | 2.393(3) | Er(2)–O(21) | 2.452(3) |
| Er(1)–O(20) | 2.427(3) | Er(2)–O(22) | 2.321(3) |
| O(4)[1]– Er(1)–O(1) | 145.05(11) | O(5)[1]–Er(2)–O(11) | 75.13(11) |
| O(4)[1]– Er(1)–O(2) | 142.03(10) | O(5)[1]–Er(2)–O(16) | 82.56(10) |
| O(4)[1]– Er(1)–O(7) | 80.66(11) | O(5)[1]–Er(2)–O(17) | 71.62(10) |

[1]1–X, 1/2+Y, 3/2–Z

| Compound **10** | | | |
|---|---|---|---|
| Yb(1)–O(1) | 2.239(3) | Yb(2)–O(2) | 2.312(3) |
| Yb(1)–O(4) | 2.298(3) | Yb(2)–O(5) | 2.278(3) |
| Yb(1)–O(7) | 2.356(3) | Yb(2)–O(11) | 2.297(3) |
| Yb(1)–O(8) | 2.457(3) | Yb(2)–O(13) | 2.394(3) |
| Yb(1)–O(10) | 2.248(3) | Yb(2)–O(14) | 2.445(3) |
| Yb(1)–O(17) | 2.296(3) | Yb(2)–O(16) | 2.270(3) |
| Yb(1)–O(19) | 2.425(3) | Yb(2)–O(21) | 2.451(3) |
| Yb(1)–O(20) | 2.394(3) | Yb(2)–O(22) | 2.300(3) |
| O(1)– Yb(1)–O(4) | 113.34(12) | O(1)– Yb(2)–O(13) | 82.99(11) |
| O(1)– Yb(1)–O(7) | 134.20(11) | O(1)– Yb(2)–O(14) | 127.62(11) |
| O(1)– Yb(1)–O(8) | 80.95(11) | O(1)– Yb(2)–O(21) | 70.83(11) |

| Compound **8a** | | | |
|---|---|---|---|
| Ho (1)–O(2) | 2.310(3) | Ho (2)–O(1) | 2.350(3) |
| Ho (1)–O(4)[1] | 2.384(3) | Ho(2)–O(5)[1] | 2.328(3) |
| Ho (1)–O(5)[1] | 2.676(3) | Ho(2)–O(10) | 2.438(3) |
| Ho (1)–O(8) | 2.284(3) | Ho(2)–O(11) | 2.420(3) |
| Ho (1)–O(14) | 2.303(3) | Ho(2)–O(13) | 2.340(3) |
| Ho (1)–O(16) | 2.254(3) | Ho(2)–O(22) | 2.359(3) |
| Ho (1)–O(19) | 2.358(3) | Ho(2)–O(17) | 2.388(3) |
| Ho (1)–O(21) | 2.319(4) | Ho(2)–O(20) | 2.384(3) |
| O(2)–Ho (1)–O(4)[1] | 82.99(12) | O(1)–Ho (2)–O(11) | 146.30(11) |
| O(2)–Ho (1)–O(5)[1] | 71.42(9) | O(1)–Ho (2)–O(16) | 66.31(9) |
| O(2)–Ho (1)–O(19) | 131.89(12) | O(1)–Ho (2)–O(17) | 78.54(11) |

| | | | |
|---|---|---|---|
| O(4)[1]–Ho (1)–O(5)[1] | 50.59(10) | O(16)–Ho (2)–O(21) | 152.58(14) |

[1]-1/2+X,3/2-Y,+Z

| Compound **9a** | | | |
|---|---|---|---|
| Er(1)–O(4) | 2.428(6) | Er(2)–O(2) | 2.271(7) |
| Er(1)–O(5) | 2.401(6) | Er(2)–O(7) | 2.297(5) |
| Er(1)–O(8) | 2.331(5) | Er(2)–O(10) | 2.680(6) |
| Er(1)–O(10) | 2.298(6) | Er(2)–O(11) | 2.367(6) |
| Er(1)–O(13) | 2.324(5) | Er(2)–O(14) | 2.299(6) |
| Er(1)–O(17) | 2.374(5) | Er(2)–O(16) | 2.252(6) |
| Er(1)–O(19) | 2.370(6) | Er(2)–O(20) | 2.356(6) |
| Er(1)–O(21) | 2.340(6) | Er(2)–O(22) | 2.306(7) |
| O(8)– Er(1)–O(4) | 140.47(19) | O(2)– Er(2)–O(10) | 141.25(18) |
| O(8)– Er(1)–O(5) | 146.6(2) | O(2)– Er(2)–O(11) | 109.8(2) |
| O(8)– Er(1)–O(17) | 78.1(2) | O(2)– Er(2)–O(14) | 149.0(2) |
| Compound **10a** | | | |
| Yb(1)–O(17)[1] | 2.314(3) | Yb(2)–O(4) | 2.213(3) |
| Yb(1)–O(13) | 2.275(3) | Yb(2)–O(13) | 2.726(3) |
| Yb(1)–O(5) | 2.354(3) | Yb(2)–O(8) | 2.270(3) |
| Yb(1)–O(11) | 2.373(3) | Yb(2)–O(14) | 2.348(3) |
| Yb(1)–O(22) | 2.357(3) | Yb(2)–O(21) | 2.336(3) |
| Yb(1)–O(10) | 2.421(3) | Yb(2)–O(2) | 2.280(3) |
| Yb(1)–O(1) | 2.300(3) | Yb(2)–O(19) | 2.284(4) |
| Yb(1)–O(20) | 2.319(3) | Yb(2)–O(16)[1] | 2.275(3) |
| O(13)– Yb(1)–O(4) | 73.93(10) | O(4)– Yb(2)–O(13) | 80.21(11) |
| O(13)– Yb(1)–O(5) | 120.67(11) | O(4)– Yb(2)–O(8) | 104.67(14) |
| O(31)– Yb(1)–O(11) | 100.97(11) | O(4)– Yb(2)–O(14) | 130.34(12) |

[1]-1/2+X,1/2-Y,+Z.

**Table S6.** Selected Bond Distances (Å) for and the Solvent Exchanged Compounds of **8a**

| Compound **8a/acetone** | | | |
|---|---|---|---|
| Ho(1)–O(20) | 2.429(5) | Ho(2)–O(1) | 2.271(5) |
| Ho(1)–O(2) | 2.376(5) | Ho(2)–O(5) | 2.288(5) |
| Ho(1)–O(4) | 2.336(4) | Ho(2)–O(7) | 2.616(6) |
| Ho(1)–O(7) | 2.317(5) | Ho(2)–O(8) | 2.373(5) |
| Ho(1)–O(11) | 2.352(5) | Ho(2)–O(10) | 2.309(4) |
| Ho(1)–O(16)[1] | 2.388(6) | Ho(2)–O(14) | 2.263(6) |
| Ho(1)–O(17)[1] | 2.402(6) | Ho(2)–O(21 ) | 2.365(5) |
| Ho(1)–O(19) | 2.387(6) | Ho(2)–O(22) | 2.414(7) |

[1]3/2−X, 1/2+Y, 1/2+Z

| Compound **8a/dry** | | | |
|---|---|---|---|
| Ho(1)–O(1) | 2.305(7) | Ho(2)–O(2) | 2.363(6) |
| Ho(1)–O(4)[1] | 2.281(6) | Ho(2)–O(22) | 2.428(8) |
| Ho(1)–O(7) | 2.599(7) | Ho(2)–O(5)[1] | 2.383(6) |

| | | | |
|---|---|---|---|
| Ho(1)–O(8) | 2.410(6) | Ho(2)–O(7) | 2.349(6) |
| Ho(1)–O(10)[2] | 2.326(5) | Ho(2)–O(11)[2] | 2.351(7) |
| Ho(1)–O(14) | 2.242(7) | Ho(2)–O(16) | 2.370(7) |
| Ho(1)–O(19) | 2.397(9) | Ho(2)–O(17) | 2.401(8) |
| Ho(1)–O(20) | 2.354(7) | Ho(2)–O(21) | 2.465(7) |

[1]-1/2+X,3/2-Y,+Z; [2]-1/2+X,1/2-Y,+Z

| Compound **8a/$H_2O$** | | | |
|---|---|---|---|
| Ho(1)–O(4)[4] | 2.464(6) | Ho(2)–O(2) | 2.300(6) |
| Ho(1)–O(5)[4] | 2.394(6) | Ho(2)–O(7) | 2.321(5) |
| Ho(1)–O(8) | 2.368(5) | Ho(2)–O(10)[6] | 2.716(7) |
| Ho(1)–O(10)[6] | 2.337(6) | Ho(2)–O(11)[6] | 2.353(7) |
| Ho(1)–O(13) | 2.312(6) | Ho(2)–O(14) | 2.328(5) |
| Ho(1)–O(17)[5] | 2.398(6) | Ho(2)–O(16)[5] | 2.259(6) |
| Ho(1)–O(19) | 2.403(6) | Ho(2)–O(21) | 2.326(8) |
| Ho(1)–O(20) | 2.421(6) | Ho(2)–O(22) | 2.393(6) |

[4]1/2-X,1/2+Y,1/2+Z; [5]1/2+X,3/2-Y,+Z; [6]-1/2+X,1/2-Y,+Z.

| Compound **8a/EtOH** | | | |
|---|---|---|---|
| Ho(1)–O(2) | 2.320(6) | Ho(2)–O(4) | 2.451(6) |
| Ho(1)–O(8) | 2.323(6) | Ho(2)–O(5) | 2.438(7) |
| Ho(1)–O(10) | 2.295(6) | Ho(2)–O(7) | 2.303(6) |
| Ho(1)–O(13) | 2.312(5) | Ho(2)–O(11) | 2.395(6) |
| Ho(1)–O(16) | 2.647(7) | Ho(2)–O(14) | 2.366(6) |
| H (1)–O(17) | 2.391(6) | Ho(2)–O(16) | 2.338(6) |
| Ho(1)–O(19) | 2.236(7) | Ho(2)–O(21) | 2.321(6) |
| Ho(1)–O(20) | 2.354(7) | Ho(2)–O(22) | 2.378(6) |