Electronic Supporting Information

Multi-Functional Rare-Earth Hybrid Layered Networks: Photoluminescence and Catalysis Studies

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A contribution from

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Contents

1. Powder X-ray Diffraction Studies

1.1 - [Y(H$_2$cmp)(H$_2$O] (1)

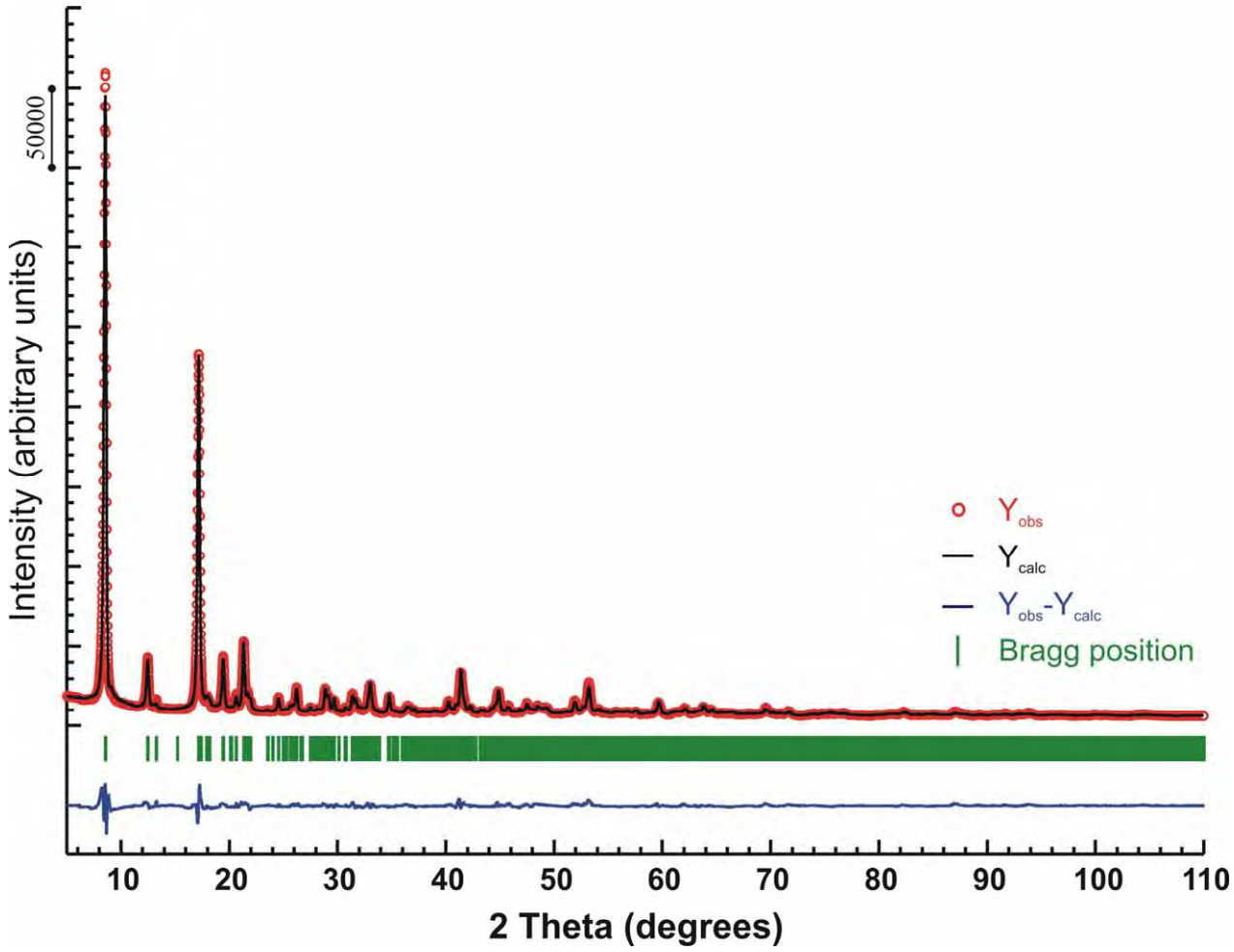

Figure S1 - Final Rietveld plot (powder synchrotron X-ray diffraction data) of [Y(H$_2$cmp)(H$_2$O)] (**1**). Observed data points are indicated as red circles, the best-fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid black and blue lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections.

Data collection details: T = 298 K; 2θ range = 5.00-115.00º; step size = 0.01º; instrument = X'Pert MPD Philips, Cu $K_{\alpha1,2}$ (λ_1 = 1.540598 Å and λ_2 = 1.544426 Å), Bragg-Brentano geometry.

Unit Cell: formula = $C_4H_{10}NO_9P_2Y$;† formula weight = 366.98; crystal system = orthorhombic; space group = *P*bca; *a* = 9.7510(8) Å; *b* = 10.1889(8) Å; *c* = 20.6391(8) Å; volume = 2050.5(3) Å^3; *Z* = 8; D_c = 2.377 g cm^{-3}. M(20)[1] = 16.1 and F(20)[2] = 17.7.

Profile Parameters. Profile function = Pseudo-Voigt with η = 0.642(4). Caglioti law parameters: U = 0.24(2), V = -0.174(8), W = 0.075(1). Asymmetry parameters (up to 30º 2θ) = 0.0555(8) and 0.0130(2). Modified March's function, *G1* (along the [002] vector) = 0.468(1). Zero point = 0.070(1).
Refinement Details. No. of independent reflections = 1508. No. of global refined parameters = 1. No. of profile refined parameters = 11. No. of intensity-dependent refined parameters = 52.

Reliability Factors for all non-excluded points with Bragg contribution (conventional – not corrected for background). R_p = 4.71. R_{wp} = 6.00. R_{exp} = 0.93. χ^2 = 41.3.

Structure Reliability Factors. R_{Bragg} = 9.22. R_F = 26.0.

† Hydrogen atoms associated with the coordinated water molecule have been added to the empirical formula.

1.2 - [Pr(H$_2$cmp)(H$_2$O)] (3)

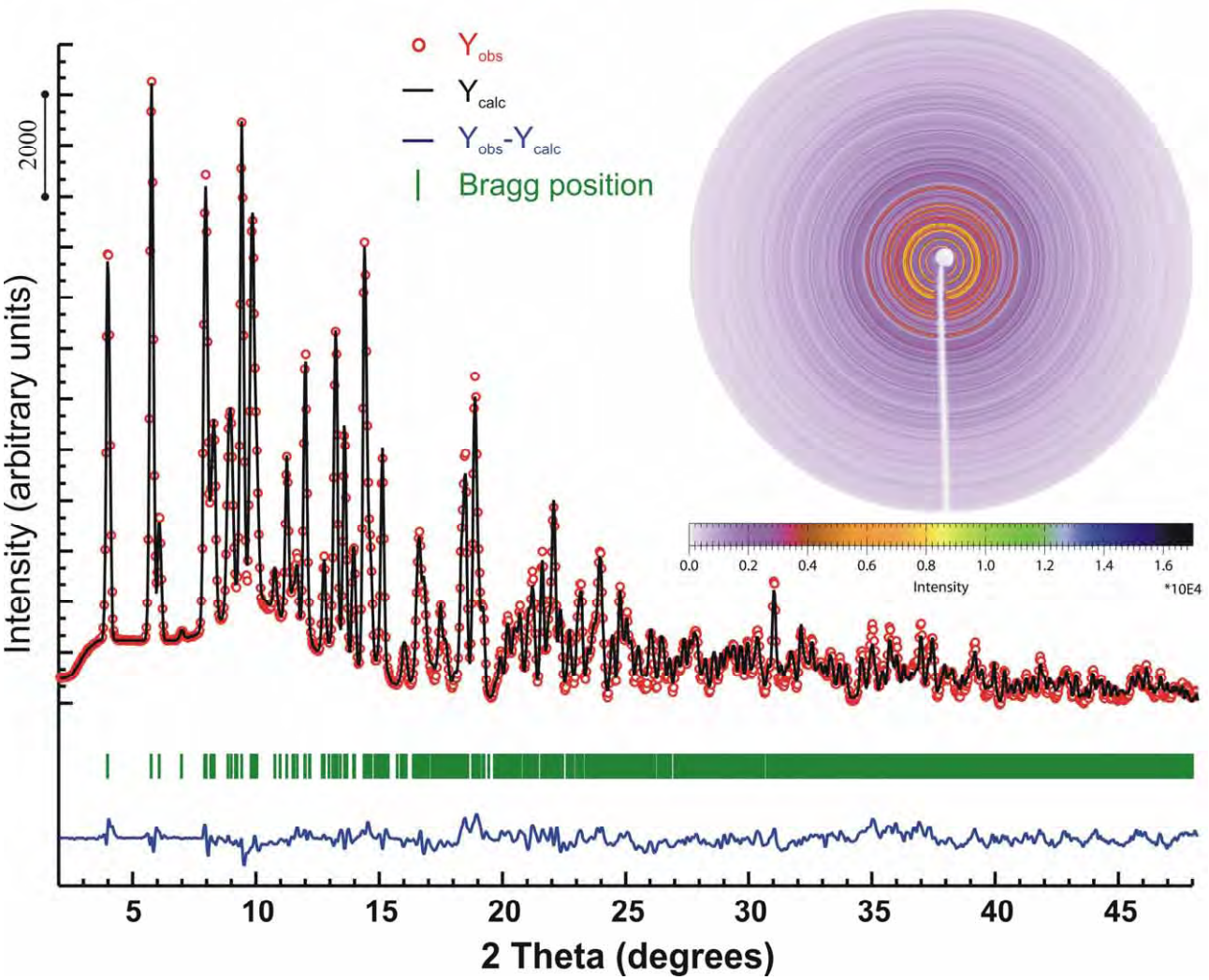

Figure S2 - Final Rietveld plot (powder synchrotron X-ray diffraction data) of [Pr(H$_2$cmp)(H$_2$O)] (**3**). Observed data points are indicated as red circles, the best-fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid black and blue lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections. The inset depicts the 2D powder pattern collected with the MAR345 imaging plate at the BM01a beam line (ESRF).

Data collection details: T = 298 K; 2θ range = 2.02-49.01º; step size = 0.035838º; instrument = MAR345 imaging plate (BM01a, ESRF), λ = 0.71013(1) Å.

Unit Cell: formula = $C_4H_{10}NO_9P_2Pr$;† formula weight = 418.98; crystal system = orthorhombic; space group = *P*bca; *a* = 9.7951(9) Å; *b* = 10.2777(9) Å; *c* = 20.4047(18) Å; volume = 2054.2(3) Å^3; *Z* = 8; D_c = 2.719 g cm^{-3}. M(15)[1] = 10.8 and F(15)[2] = 31.3.

Profile Parameters. Profile function = Gaussian. Caglioti law parameters: U = -0.01(2), V = -0.05(1), W = 0.0330(9). Asymmetry parameters = -0.020(3) and -0.005(1). Zero point = -0.027(2).

Refinement Details. No. of independent reflections = 2083. No. of global refined parameters = 1. No. of profile refined parameters = 10. No. of intensity-dependent refined parameters = 51.

Reliability Factors for all non-excluded points with Bragg contribution (conventional – not corrected for background). R_p = 3.86. R_{wp} = 5.52. R_{exp} = 2.02. χ^2 = 7.48.

Structure Reliability Factors. R_{Bragg} = 8.89. R_F = 11.5.

† Hydrogen atoms associated with the coordinated water molecule have been added to the empirical formula.

1.3 - [Nd(H$_2$cmp)(H$_2$O)] (4)

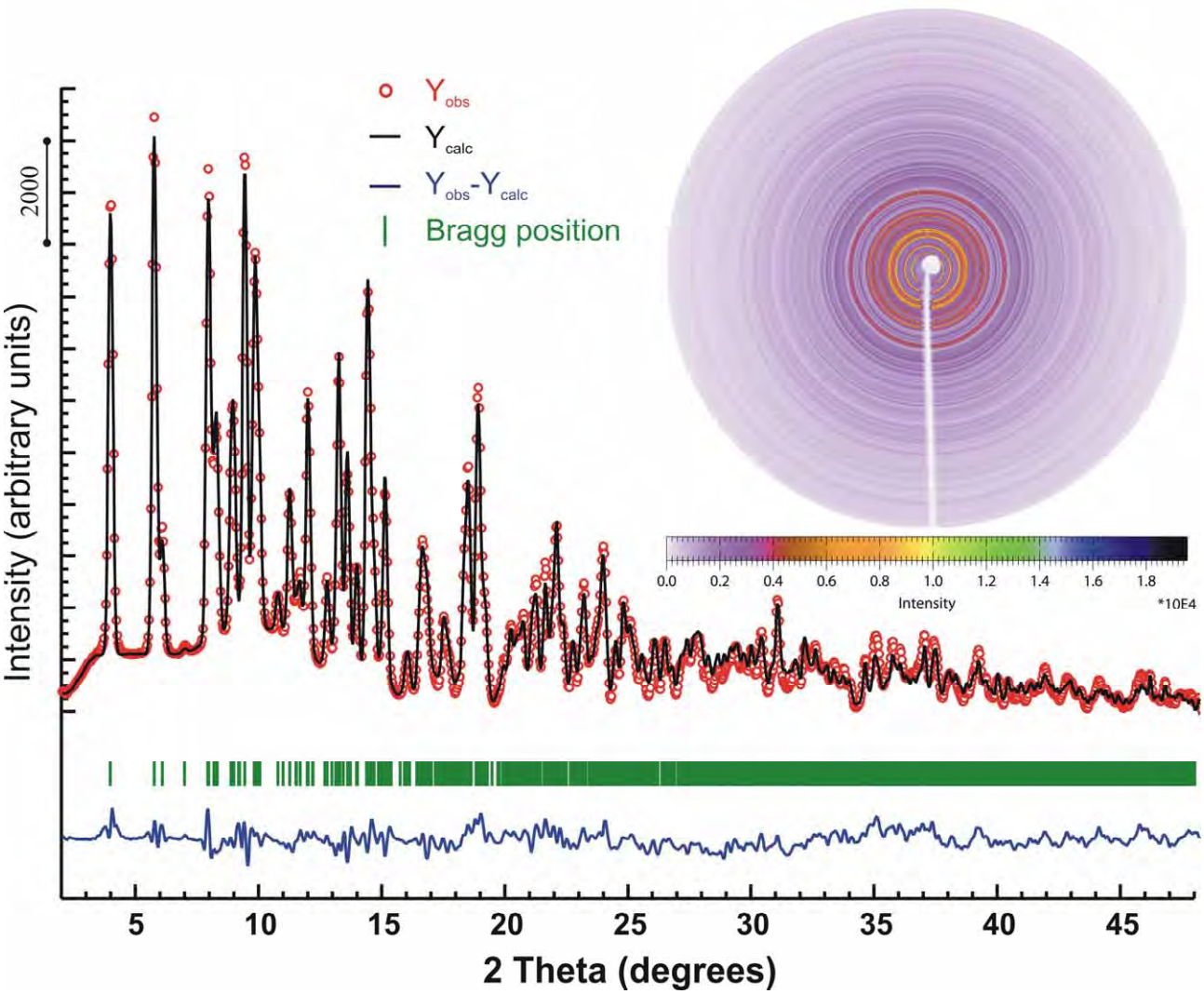

Figure S3 - Final Rietveld plot (powder synchrotron X-ray diffraction data) of [Nd(H$_2$cmp)(H$_2$O)] (**4**). Observed data points are indicated as red circles, the best-fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid black and blue lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections. The inset depicts the 2D powder pattern collected with the MAR345 imaging plate at the BM01a beam line (ESRF).

Data collection details: T = 298 K; 2θ range = 2.00-48.98º; step size = 0.035838º; instrument = MAR345 imaging plate (BM01a, ESRF), λ = 0.71013(1) Å.

Unit Cell: formula = $C_4H_{10}NNdO_9P_2$;† formula weight = 422.31; crystal system = orthorhombic; space group = *P*bca; *a* = 9.7736(14) Å; *b* = 10.2529(15) Å; *c* = 20.400(3) Å; volume = 2044.2(5) Å^3; *Z* = 8; D_c = 2.744 g cm^{-3}. M(10)[1] = 14.0 and F(10)[2] = 34.3.

Profile Parameters. Profile function = Gaussian. Caglioti law parameters: U = -0.07(4), V = -0.05(2), W = 0.050(1). Asymmetry parameters = -0.015(4) and -0.005(1). Zero point = -0.048(3).

Refinement Details. No. of independent reflections = 2170. No. of global refined parameters = 1. No. of profile refined parameters = 10. No. of intensity-dependent refined parameters = 51.

Reliability Factors for all non-excluded points with Bragg contribution (conventional – not corrected for background). R_p = 4.70. R_{wp} = 6.33. R_{exp} = 1.98. χ^2 = 10.2.

Structure Reliability Factors. R_{Bragg} = 9.88. R_F = 12.9.

† Hydrogen atoms associated with the coordinated water molecule have been added to the empirical formula.

1.4 - [Sm(H_2cmp)(H_2O] (5)

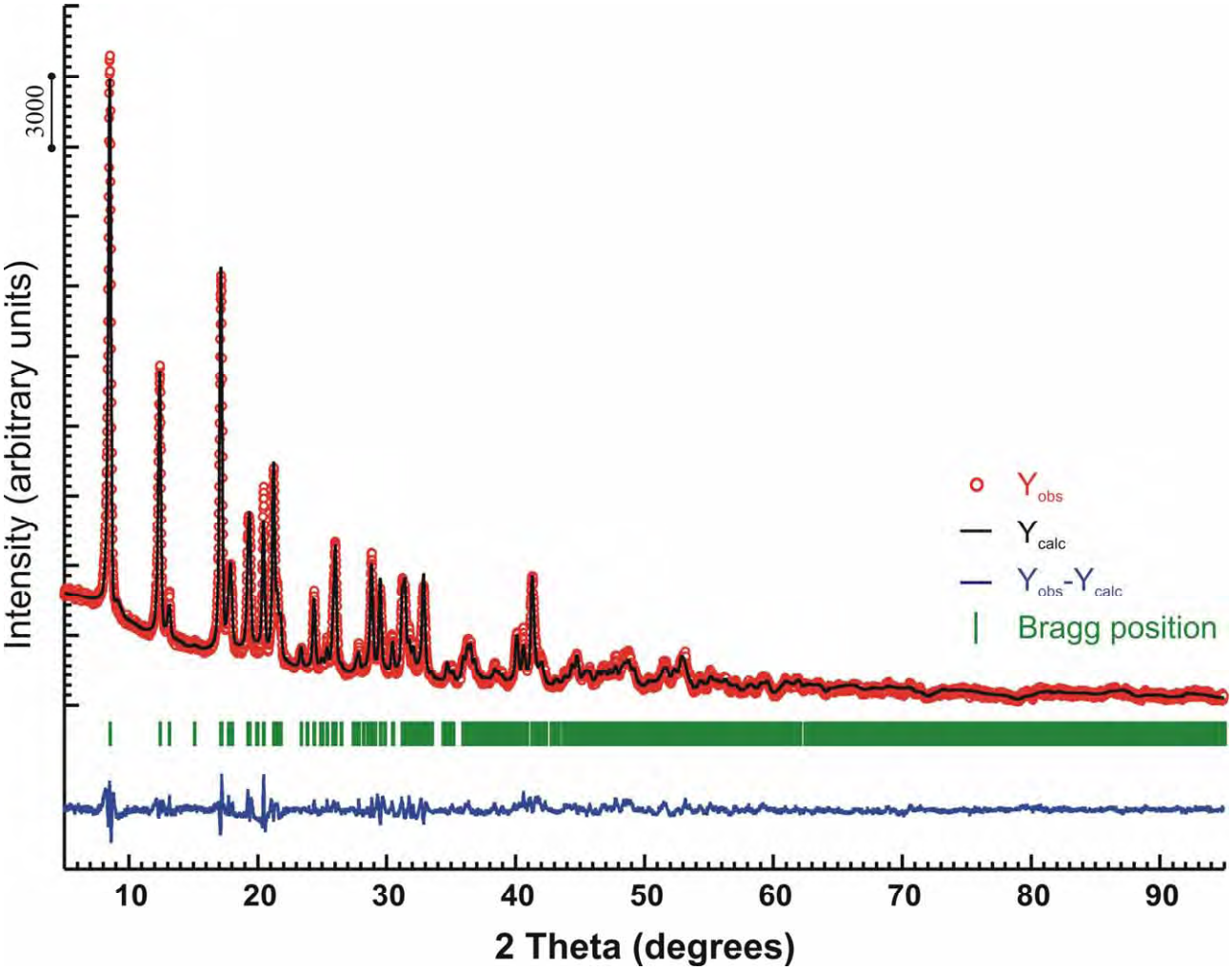

Figure S4 - Final Rietveld plot (powder synchrotron X-ray diffraction data) of [Sm(H_2cmp)(H_2O)] (**5**). Observed data points are indicated as red circles, the best-fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid black and blue lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections.

Data collection details: T = 298 K; 2θ range = 5.00-95.00º; step size = 0.01º; instrument = X'Pert MPD Philips, Cu $K_{\alpha 1,2}$ (λ_1 = 1.540598 Å and λ_2 = 1.544426 Å), Bragg-Brentano geometry.

Unit Cell: formula = $C_4H_{10}NO_9P_2Sm$;† formula weight = 428.42; crystal system = orthorhombic; space group = *P*bca; *a* = 9.8402(7) Å; *b* = 10.3073(8) Å; *c* = 20.6805(13) Å; volume = 2097.5(3) $Å^3$; *Z* = 8; D_c = 2.713 g cm^{-3}. $M(19)^1$ = 11.5 and $F(19)^2$ = 18.8.

Profile Parameters. Profile function = Pseudo-Voigt with η = 0.654(8). Caglioti law parameters: U = 0.82(4), V = -0.44(2), W = 0.099(2). Asymmetry parameters (up to 30º 2θ) = 0.068(1) and 0.0131(4). Modified March's function, *G1* (along the [002] vector) = 0.713(2). Zero point = 0.059(2).
Refinement Details. No. of independent reflections = 1080. No. of global refined parameters = 1. No. of profile refined parameters = 11. No. of intensity-dependent refined parameters = 52.

Reliability Factors for all non-excluded points with Bragg contribution (conventional – not corrected for background). R_p = 2.47. R_{wp} = 3.19. R_{exp} = 1.44. χ^2 = 4.93.

Structure Reliability Factors. R_{Bragg} = 8.91. R_F = 14.3.

† Hydrogen atoms associated with the coordinated water molecule have been added to the empirical formula.

1.5 - [Eu(H_2cmp)(H_2O)] (6)

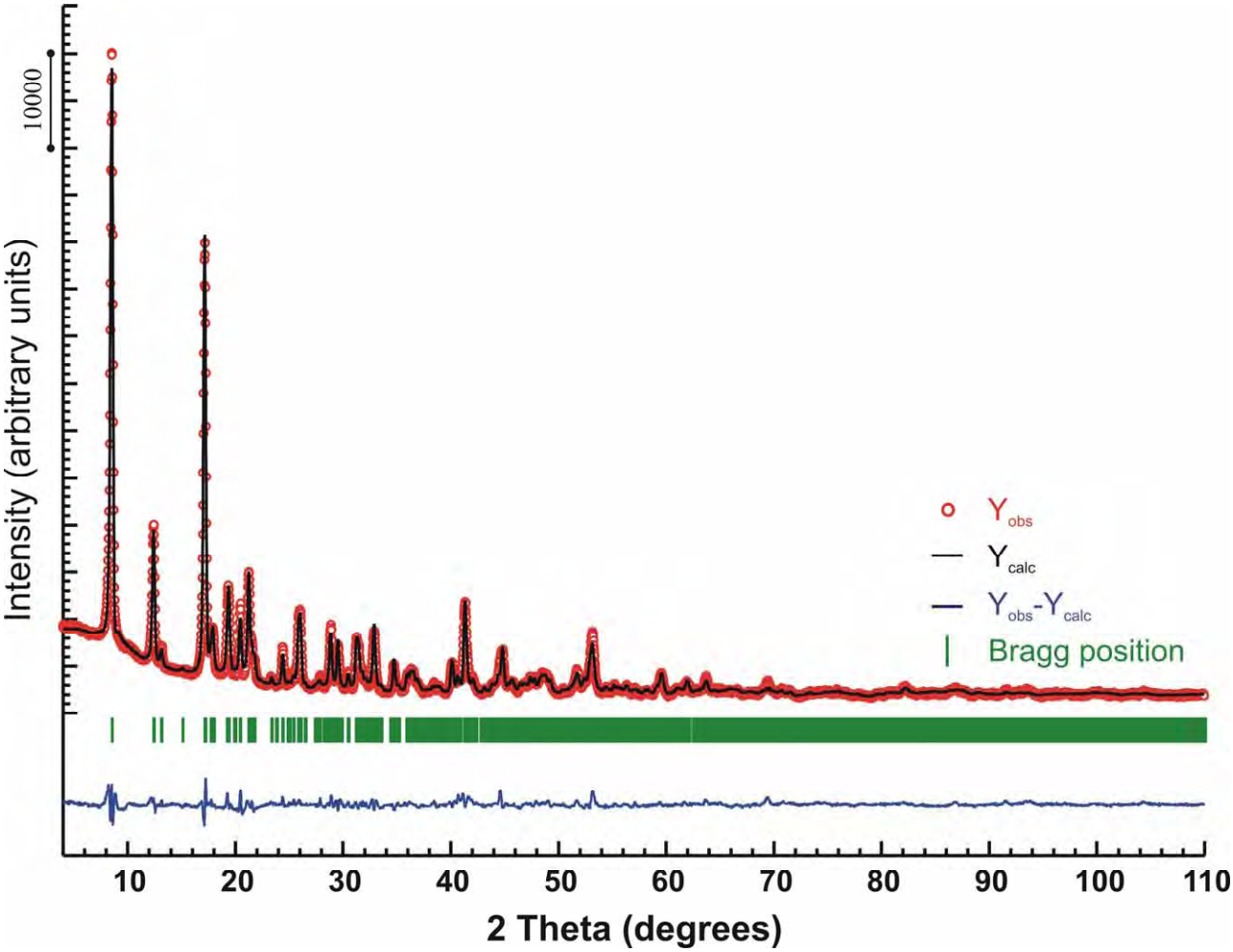

Figure S5 - Final Rietveld plot (powder synchrotron X-ray diffraction data) of [Eu(H_2cmp)(H_2O)] (**6**). Observed data points are indicated as red circles, the best-fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid black and blue lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections.

Data collection details: T = 298 K; 2θ range = 4.00-110.00º; step size = 0.02º; instrument = X'Pert MPD Philips, Cu $K_{\alpha1,2}$ (λ_1 = 1.540598 Å and λ_2 = 1.544426 Å), Bragg-Brentano geometry.

Unit Cell: formula = $C_4H_{10}EuNO_9P_2$;† formula weight = 430.03; crystal system = orthorhombic; space group = *P*bca; a = 9.8328(10) Å; b = 10.2989(11) Å; c = 20.6667(12) Å; volume = 2092.8(3) $Å^3$; Z = 8; D_c = 2.730 g cm^{-3}. $M(15)^1$ = 10.4 and $F(15)^2$ = 16.2.

Profile Parameters. Profile function = Pseudo-Voigt with η = 0.562(8). Caglioti law parameters: U = 0.63(3), V = -0.35(2), W = 0.103(2). Asymmetry parameters (up to 30º 2θ) = 0.069(1) and 0.0122(4. Modified March's function, *G1* (along the [002] vector) = 0.539(1). Zero point = 0.068(2).
Refinement Details. No. of independent reflections = 1464. No. of global refined parameters = 1. No. of profile refined parameters = 11. No. of intensity-dependent refined parameters = 52.

Reliability Factors for all non-excluded points with Bragg contribution (conventional – not corrected for background). R_p = 2.09. R_{wp} = 2.78. R_{exp} = 1.06. χ^2 = 6.88.

Structure Reliability Factors. R_{Bragg} = 9.11. R_F = 13.1.

† Hydrogen atoms associated with the coordinated water molecule have been added to the empirical formula.

1.6 - [Gd(H_2cmp)(H_2O)] (7)

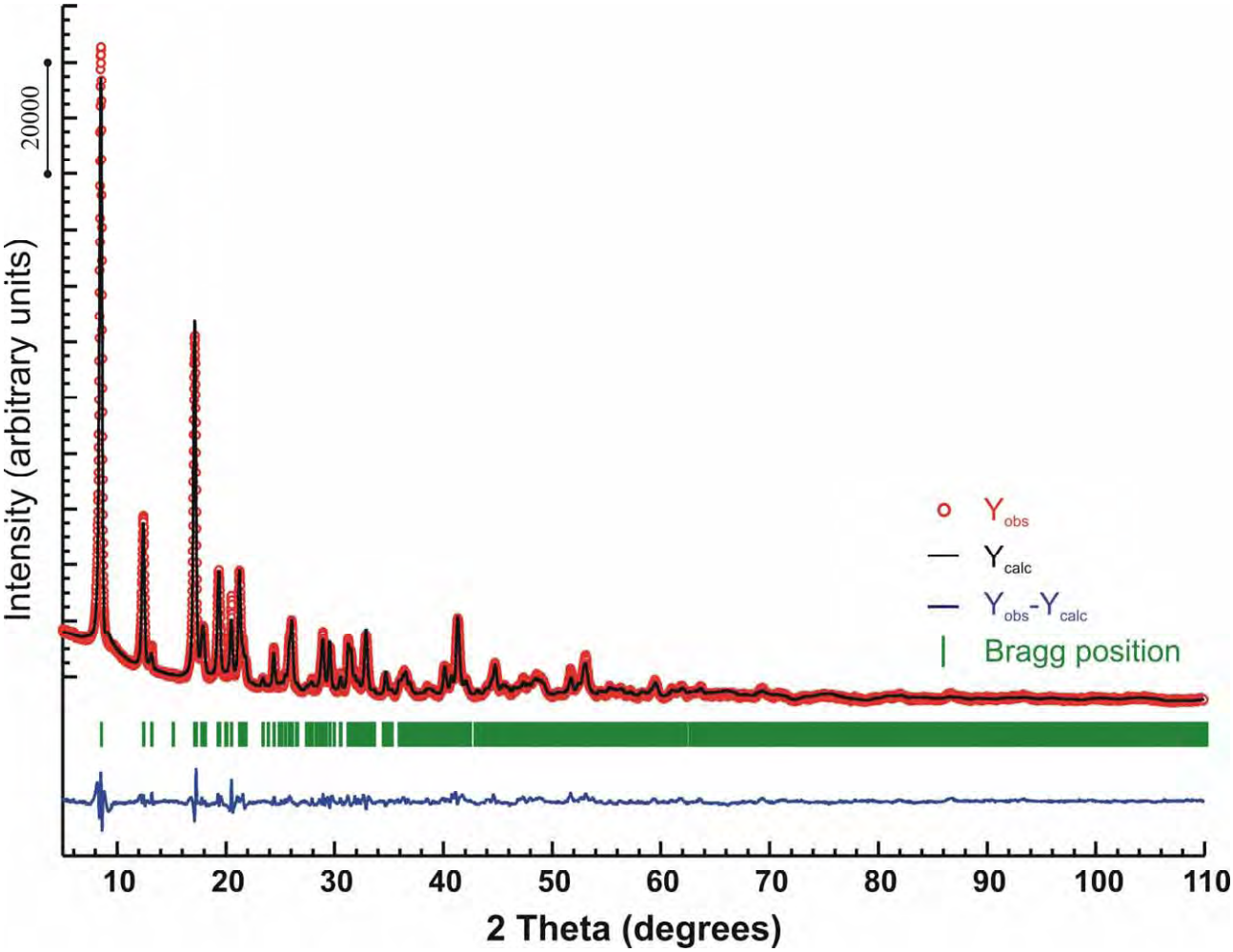

Figure S6 - Final Rietveld plot (powder synchrotron X-ray diffraction data) of [Gd(H_2cmp)(H_2O)] (**7**). Observed data points are indicated as red circles, the best-fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid black and blue lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections.

Data collection details: T = 298 K; 2θ range = 5.00-110.00º; step size = 0.01º; instrument = X'Pert MPD Philips, Cu $K_{\alpha1,2}$ (λ_1 = 1.540598 Å and λ_2 = 1.544426 Å), Bragg-Brentano geometry.

Unit Cell: formula = $C_4H_{10}GdNO_9P_2$;† formula weight = 435.32; crystal system = orthorhombic; space group = *P*bca; *a* = 9.8093(7) Å; *b* = 10.2734(8) Å; *c* = 20.6812(11) Å; volume = 2084.1(2) $Å^3$; *Z* = 8; D_c = 2.775 g cm^{-3}. $M(19)^1$ = 12.8 and $F(19)^2$ = 21.4.

Profile Parameters. Profile function = Pseudo-Voigt with η = 0.594(6). Caglioti law parameters: U = 0.99(3), V = -0.53(1), W = 124(2). Asymmetry parameters (up to 30º 2θ) = 0.0721(7) and 0.0101(3). Modified March's function, *G1* (along the [002] vector) = 0.591(1). Zero point = 0.074(2).
Refinement Details. No. of independent reflections = 1475. No. of global refined parameters = 1. No. of profile refined parameters = 11. No. of intensity-dependent refined parameters = 52.

Reliability Factors for all non-excluded points with Bragg contribution (conventional – not corrected for background). R_p = 1.61. R_{wp} = 2.15. R_{exp} = 0.72. χ^2 = 8.88.

Structure Reliability Factors. R_{Bragg} = 9.94. R_F = 18.3.

† Hydrogen atoms associated with the coordinated water molecule have been added to the empirical formula.

1.7 - [Tb(H_2cmp)(H_2O)] (8)

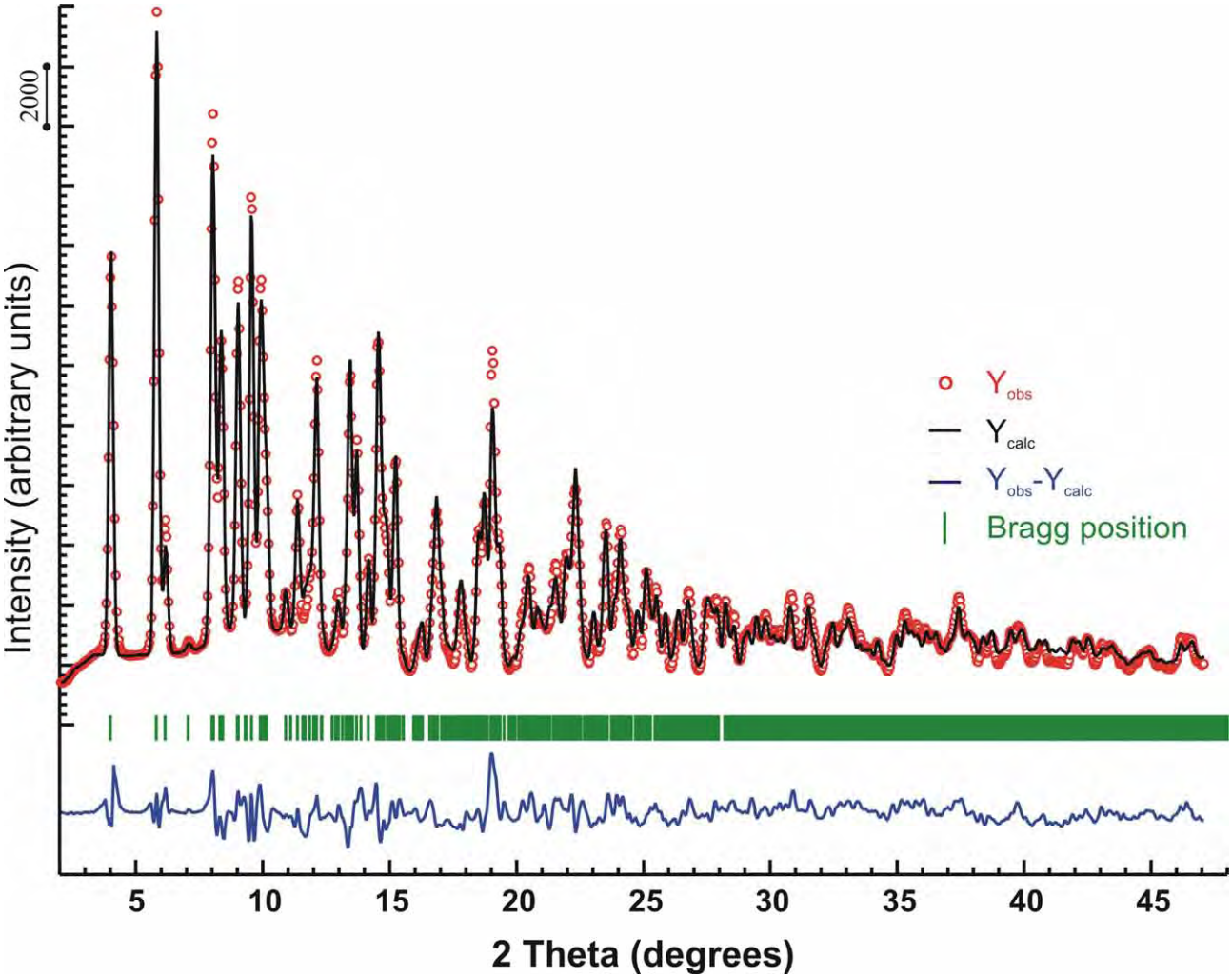

Figure S7 - Final Rietveld plot (powder synchrotron X-ray diffraction data) of [Tb(H_2cmp)(H_2O)] (**8**). Observed data points are indicated as red circles, the best-fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid black and blue lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections.

Data collection details: T = 298 K; 2θ range = 2.00-47.01º; step size = 0.035838º; instrument = MAR345 imaging plate (BM01a, ESRF), λ = 0.71013(1) Å.

Unit Cell: formula = $C_4H_{10}NO_9P_2Tb$;† formula weight = 436.99; crystal system = orthorhombic; space group = *P*bca; *a* = 9.6686(17) Å; *b* = 10.1018(18) Å; *c* = 20.359(4) Å; volume = 1988.5(6) Å^3; *Z* = 8; D_c = 2.919 g cm^{-3}. M(15)[1] = 11.2 and F(15)[2] = 32.8.

Profile Parameters. Profile function = Gaussian. Caglioti law parameters: U = 0.20(9), V = -0.11(3), W = 0.051(2). Asymmetry parameters = -0.030(3) and -0.006(1). Zero point = -0.061(3).

Refinement Details. No. of independent reflections = 1917. No. of global refined parameters = 1. No. of profile refined parameters = 10. No. of intensity-dependent refined parameters = 49.

Reliability Factors for all non-excluded points with Bragg contribution (conventional – not corrected for background). R_p = 6.14. R_{wp} = 7.73. R_{exp} = 1.57. χ^2 = 24.2.

Structure Reliability Factors. R_{Bragg} = 11.0. R_F = 12.4.

† Hydrogen atoms associated with the coordinated water molecule have been added to the empirical formula.

1.8 - [Dy(H$_2$cmp)(H$_2$O)] (9)

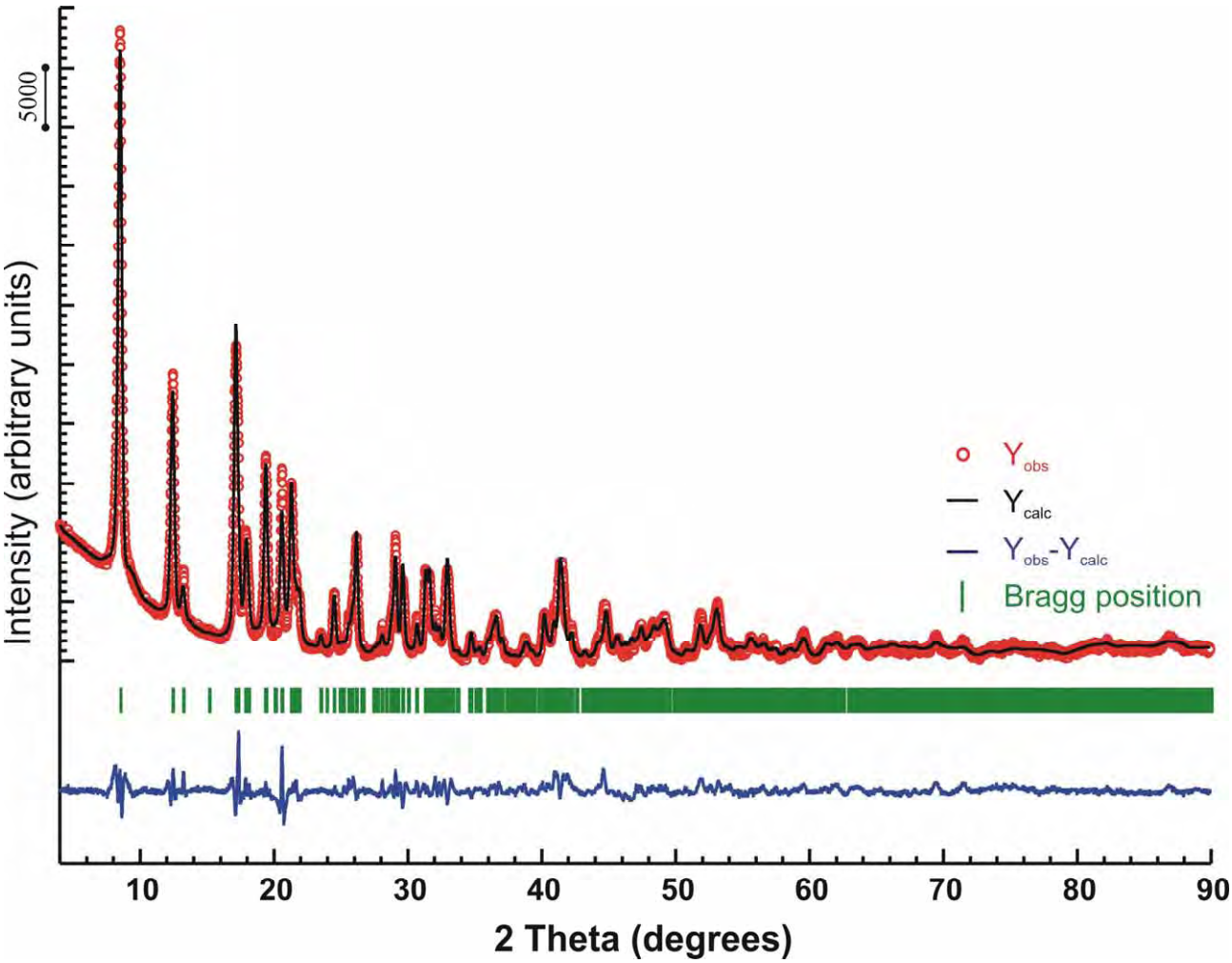

Figure S8 - Final Rietveld plot (powder synchrotron X-ray diffraction data) of [Dy(H$_2$cmp)(H$_2$O)] (**9**). Observed data points are indicated as red circles, the best-fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid black and blue lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections.

Data collection details: T = 298 K; 2θ range = 4.00-90.00º; step size = 0.01º; instrument = X'Pert MPD Philips, Cu $K_{\alpha 1,2}$ (λ_1 = 1.540598 Å and λ_2 = 1.544426 Å), Bragg-Brentano geometry.

Unit Cell: formula = $C_4H_{10}DyNO_9P_2$;† formula weight = 440.57; crystal system = orthorhombic; space group = *P*bca; a = 9.7725(10) Å; b = 10.2143(11) Å; c = 20.6600(18) Å; volume = 2062.3(4) Å^3; Z = 8; D_c = 2.838 g cm^{-3}. M(14)[1] = 11.4 and F(14)[2] = 14.5.

Profile Parameters. Profile function = Pseudo-Voigt with η = 0.460(9). Caglioti law parameters: U = 1.79(6), V = -0.99(3), W = 0.202(3). Asymmetry parameters (up to 30º 2θ) = 0.064(1) and 0.0066(5). Modified March's function, *G1* (along the [002] vector) = 0.694(2). Zero point = 0.062(3).
Refinement Details. No. of independent reflections = 971. No. of global refined parameters = 1. No. of profile refined parameters = 11. No. of intensity-dependent refined parameters = 52.

Reliability Factors for all non-excluded points with Bragg contribution (conventional – not corrected for background). R_p = 1.64. R_{wp} = 2.28. R_{exp} = 0.75. χ^2 = 9.34.

Structure Reliability Factors. R_{Bragg} = 10.2. R_F = 15.3.

† Hydrogen atoms associated with the coordinated water molecule have been added to the empirical formula.

1.9 - [Ho(H$_2$cmp)(H$_2$O)] (10)

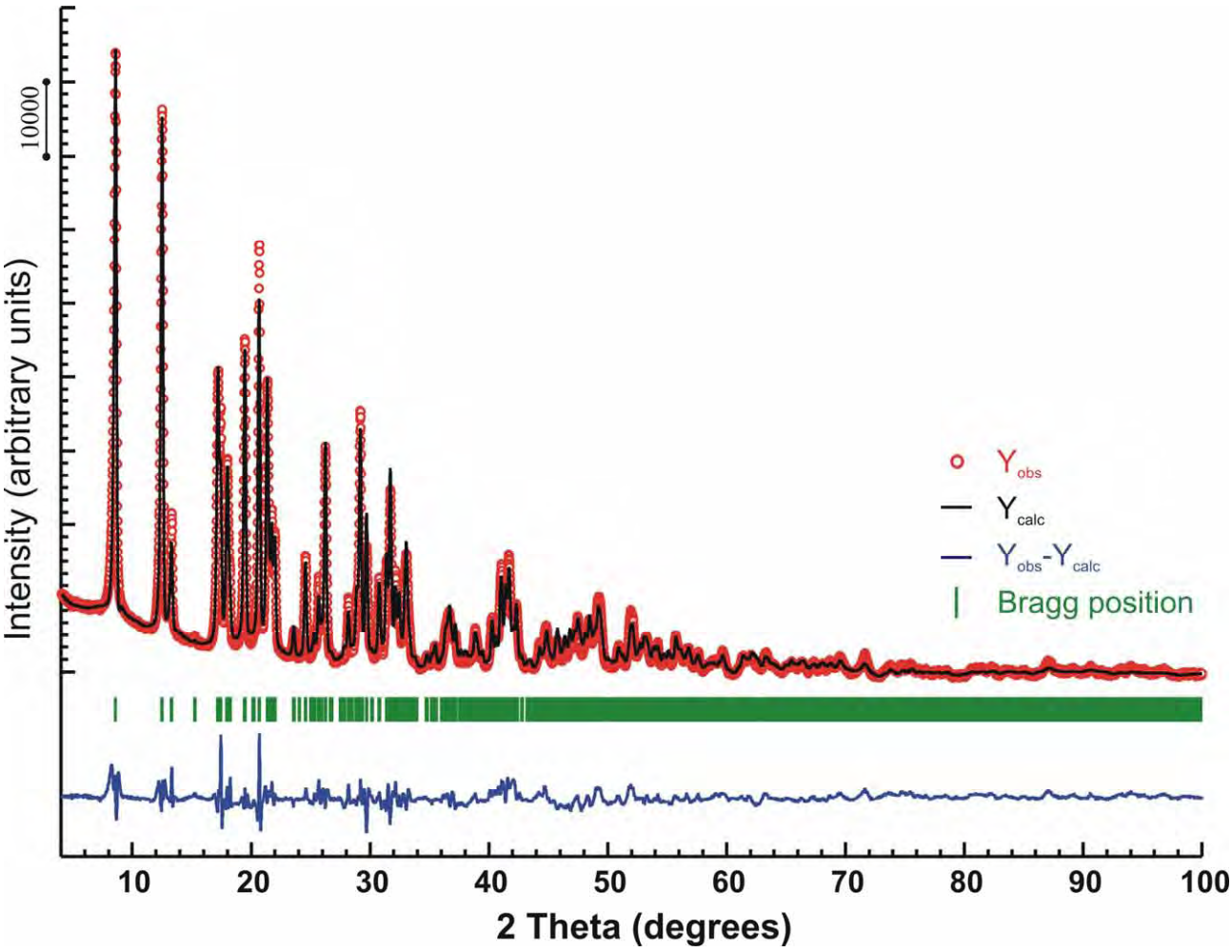

Figure S9 - Final Rietveld plot (powder synchrotron X-ray diffraction data) of [Ho(H$_2$cmp)(H$_2$O)] (**10**). Observed data points are indicated as red circles, the best-fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid black and blue lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections.

Data collection details: T = 298 K; 2θ range = 4.00-100.00º; step size = 0.01º; instrument = X'Pert MPD Philips, Cu $K_{\alpha1,2}$ (λ_1 = 1.540598 Å and λ_2 = 1.544426 Å), Bragg-Brentano geometry.

Unit Cell: formula = $C_4H_{10}HoNO_9P_2$;† formula weight = 443.00; crystal system = orthorhombic; space group = *P*bca; *a* = 9.7409(6) Å; *b* = 10.1812(6) Å; *c* = 20.6262(13) Å; volume = 2045.6(2) Å^3; *Z* = 8; D_c = 2.877 g cm^{-3}. $M(20)^1$ = 32.0 and $F(20)^2$ = 56.0.

Profile Parameters. Profile function = Pseudo-Voigt with η = 0.531(8). Caglioti law parameters: U = 0.33(2), V = -0.22(1), W = 0.071(1). Asymmetry parameters (up to 30º 2θ) = 0.047(2) and 0.0230(5). Modified March's function, *G1* (along the [002] vector) = 0.962(2). Zero point = -0.058(2).
Refinement Details. No. of independent reflections = 1150. No. of global refined parameters = 1. No. of profile refined parameters = 11. No. of intensity-dependent refined parameters = 52.

Reliability Factors for all non-excluded points with Bragg contribution (conventional – not corrected for background). R_p = 3.38. R_{wp} = 4.57. R_{exp} = 0.84. χ^2 = 29.6.

Structure Reliability Factors. R_{Bragg} = 11.9. R_F = 16.3.

† Hydrogen atoms associated with the coordinated water molecule have been added to the empirical formula.

1.10 - [Er(H$_2$cmp)(H$_2$O] (11)

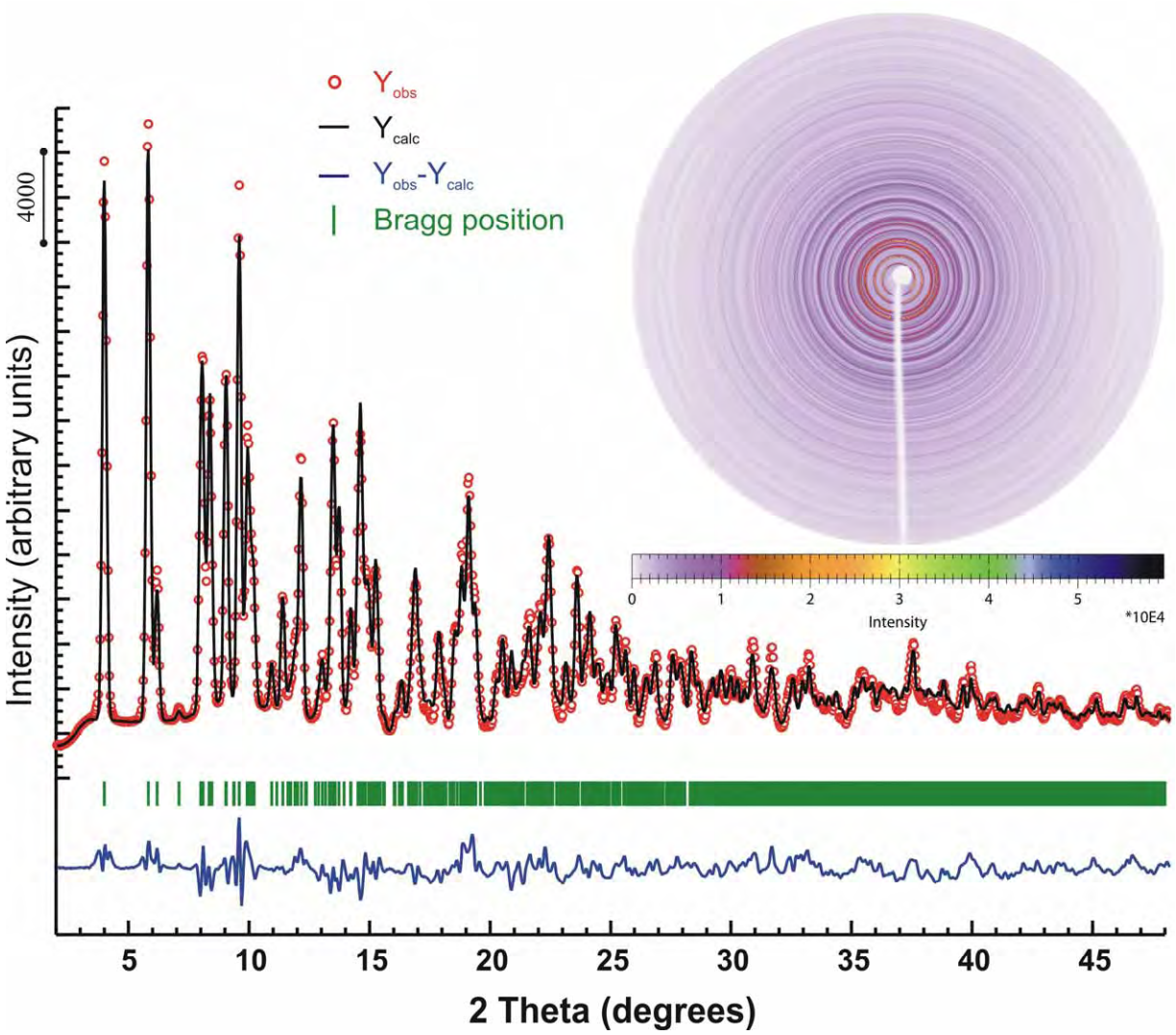

Figure S10 - Final Rietveld plot (powder synchrotron X-ray diffraction data) of [Er(H$_2$cmp)(H$_2$O)] (**11**). Observed data points are indicated as red circles, the best-fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid black and blue lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections. The inset depicts the 2D powder pattern collected with the MAR345 imaging plate at the BM01a beam line (ESRF).

Data collection details: T = 298 K; 2θ range = 2.02-49.01º; step size = 0.035838º; instrument = MAR345 imaging plate (BM01a, ESRF), λ = 0.71013(1) Å.

Unit Cell: formula = $C_4H_{10}ErNO_9P_2$;[†] formula weight = 445.33; crystal system = orthorhombic; space group = *P*bca; a = 9.6224(14) Å; b = 10.0504(15) Å; c = 20.334(3) Å; volume = 1966.4(5) Å^3; Z = 8; D_c = 3.008 g cm^{-3}. M(20)[1] = 13.3 and F(20)[2] = 47.5.

Profile Parameters. Profile function = Gaussian. Caglioti law parameters: U = 0.03(5), V = -0.08(2), W = 0.045(1). Asymmetry parameters = -0.004(4) and -0.002(1). Zero point = -0.010(3).

Refinement Details. No. of independent reflections = 2062. No. of global refined parameters = 1. No. of profile refined parameters = 10. No. of intensity-dependent refined parameters = 51.

Reliability Factors for all non-excluded points with Bragg contribution (conventional – not corrected for background). R_p = 5.54. R_{wp} = 7.12. R_{exp} = 1.42. χ^2 = 25.0.

Structure Reliability Factors. R_{Bragg} = 10.4. R_F = 13.9.

[†] Hydrogen atoms associated with the coordinated water molecule have been added to the empirical formula.

2. Crystallographic Details

2.1 - Additional Structural Drawings

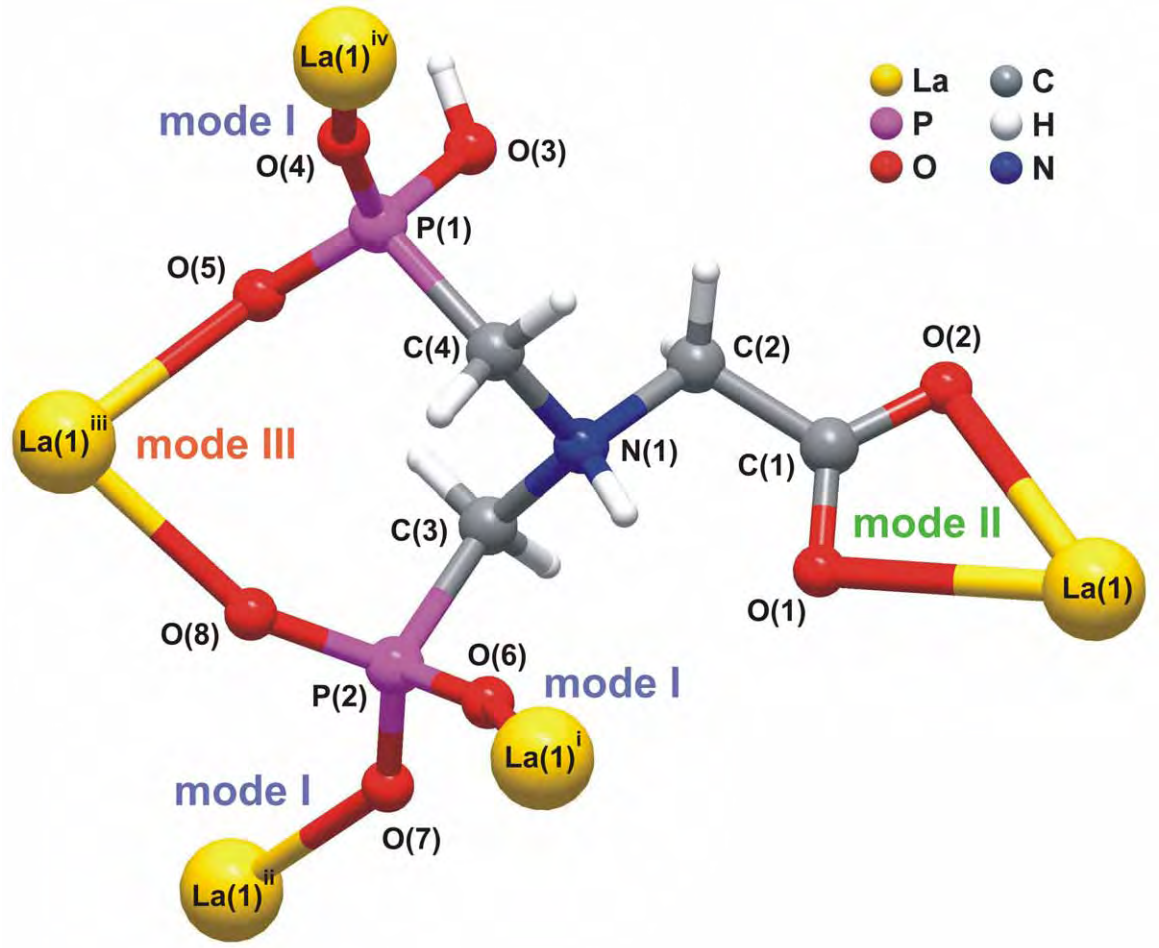

Figure S11 - Ball-and-Stick representation of the coordination modes of the H_2cmp^{3-} anionic ligand in $[La(H_2cmp)(H_2O)]$ (**2s**), showing the labeling scheme for all non-hydrogen atoms. Symmetry transformations used to generate equivalent La^{3+} centres: (i) *x*+½, y, ½−*z*; (ii) −*x*+3/2, *y*−½, *z*; (iii) *1*+*x*, *y*, *z*; (iv) −*x*+3/2, *y*+½, *z*.

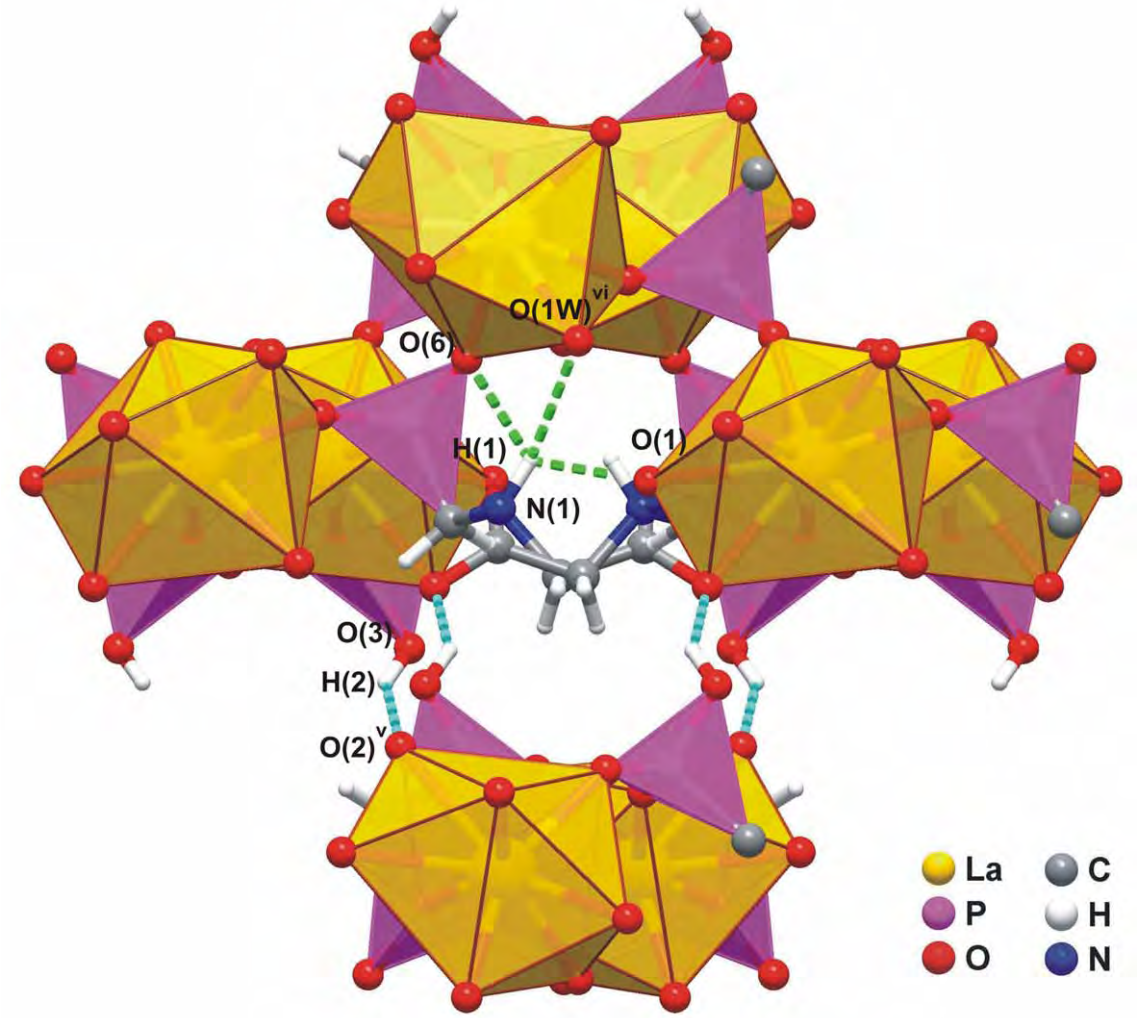

Figure S12 - Mixed ball-and-stick and polyhedral representation of a portion of the structure of [La(H_2cmp)(H_2O)] (**2s**) emphasizing the intra-layer N–H···O hydrogen bonding interactions involving the protonated nitrogen and the neighbouring oxygen atoms (dashed green lines), and the inter-layer O–H···O hydrogen bonds (dashed blue lines). For hydrogen bonding geometry see Table 4 (in the main paper). Symmetry transformations used to generate equivalent atoms: (v) *x*+½, *-y+3/2*, *-z+1*; (vi) *x*+½, *y*, *-z*+½.

2.2 - Topology

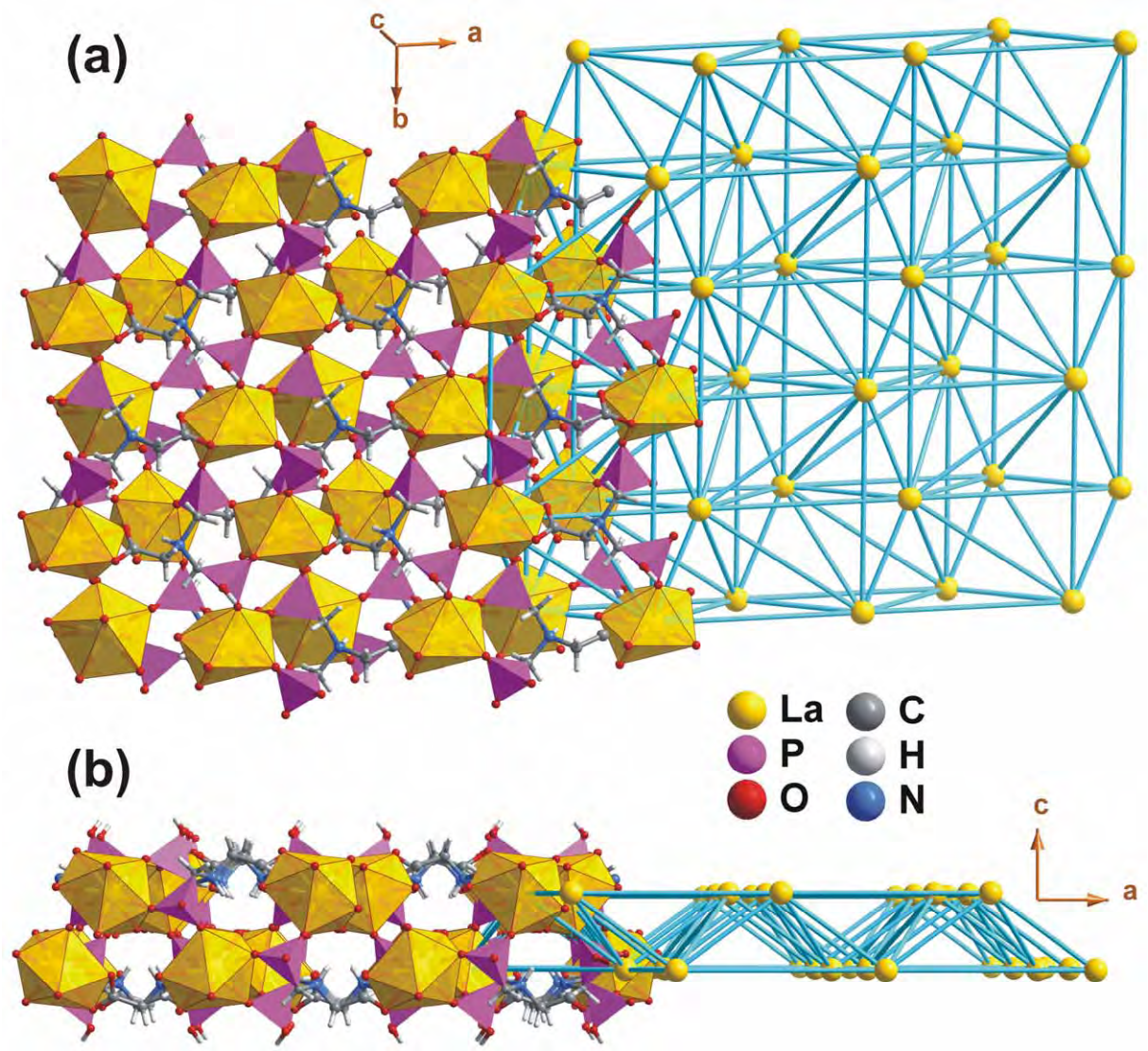

Figure S13 - Perspective views of the overlay of the $_{\infty}^{2}$[La(H_2cmp)(H_2O] layer with its topological representation (12-connected uninodal plane nets with total Schäfli symbol of $3^{30}.4^{34}.5^{2}$).

2.3 - Bond Lengths for the {REO_8} Coordination Environments

Table S1 - Selected bond lengths (in Å) for the {REO_8} coordination environments found in the [RE(H_2cmp)(H_2O)] materials [RE = Y^{3+} (**1**), La^{3+} (**2**), Pr^{3+} (**3**), Nd^{3+} (**4**), Sm^{3+} (**5**), Gd^{3+} (**6**), Eu^{3+} (**7**), Tb^{3+} (**8**), Dy^{3+} (**9**), Ho^{3+} (**10**) and Er^{3+} (**11**)].[a]

	1 (Y^{3+})	**3** (Pr^{3+})	**4** (Nd^{3+})	**5** (Sm^{3+})	**6** (Eu^{3+})
RE(1)–O(1)	2.502(6)	2.6039(7)	2.593(4)	2.639(5)	2.589(11)
RE(1)–O(2)	2.588(5)	2.5667(8)	2.610(4)	2.630(5)	2.677(11)
RE(1)–O(4)^{iii}	2.376(6)	2.3861(6)	2.372(5)	2.465(5)	2.397(10)
RE(1)–O(5)^{ii}	2.390(5)	2.3924(6)	2.372(4)	2.319(5)	2.329(10)
RE(1)–O(6)^{i}	2.213(5)	2.3310(6)	2.316(4)	2.242(4)	2.220(10)
RE(1)–O(7)^{iv}	2.426(6)	2.4708(7)	2.486(4)	2.645(5)	2.548(10)
RE(1)–O(8)^{ii}	2.228(5)	2.4109(6)	2.393(4)	2.359(4)	2.382(11)
RE(1)–O(1W)	2.486(5)	2.5767(6)	2.554(5)	2.623(5)	2.534(10)

	7 (Gd^{3+})	**8** (Tb^{3+})	**9** (Dy^{3+})	**10** (Ho^{3+})	**11** (Er^{3+})
RE(1)–O(1)	2.5816(14)	2.589(3)	2.613(12)	2.556(14)	2.602(3)
RE(1)–O(2)	2.5912(15)	2.535(2)	2.627(8)	2.726(15)	2.590(3)
RE(1)–O(4)^{iii}	2.4586(13)	2.351(2)	2.412(7)	2.242(15)	2.234(2)
RE(1)–O(5)^{ii}	2.3827(14)	2.310(2)	2.358(10)	2.220(18	2.219(3)
RE(1)–O(6)^{i}	2.1920(12)	2.249(2)	2.189(8)	2.236(16)	2.173(2)
RE(1)–O(7)^{iv}	2.7008(15)	2.358(2)	2.670(8)	2.486(17)	2.309(3)
RE(1)–O(8)^{ii}	2.2824(14)	2.193(2)	2.255(9)	2.283(14)	2.240(2)
RE(1)–O(1W)	2.4865(13)	2.499(2)	2.482(9)	2.548(18)	2.502(3)

[a] Symmetry transformations used to generate equivalent atoms: (i) *x−½*, y, *−z+½*; (ii) *x−1, y, z*; (iii) *−x+3/2, y−1/2, z*; (iv) *−x+3/2, y+½, z*.

2.4 - Bond Angles for the {REO_8} Coordination Environments

Table S2 - Selected bond angles (in degrees) for the {REO_8} coordination environments found in the [$RE(H_2cmp)(H_2O)$] materials [RE = Y^{3+} (**1**), La^{3+} (**2**), Pr^{3+} (**3**), Nd^{3+} (**4**), Sm^{3+} (**5**), Gd^{3+} (**6**), Eu^{3+} (**7**), Tb^{3+} (**8**), Dy^{3+} (**9**), Ho^{3+} (**10**) and Er^{3+} (**11**)].[a]

	1 (Y^{3+})	**3** (Pr^{3+})	**4** (Nd^{3+})	**5** (Sm^{3+})	**6** (Eu^{3+})
O(1)–RE(1)–O(2)	47.73(16)	48.634(19)	47.85(15)	47.54(12)	47.0(3)
O(1)–RE(1)–O(4)^{iii}	81.9(2)	77.77(2)	77.05(13)	84.68(13)	88.3(4)
O(1)–RE(1)–O(5)^{ii}	129.11(16)	127.401(17)	127.96(14)	130.57(13)	121.5(3)
O(1)–RE(1)–O(6)^{i}	77.18(17)	76.143(17)	77.99(16)	79.47(14)	79.9(3)
O(1)–RE(1)–O(7)^{iv}	72.62(15)	71.38(2)	72.69(12)	67.28(12)	64.5(4)
O(1)–RE(1)–O(8)^{ii}	146.2(2)	135.277(19)	135.88(14)	146.70(13)	148.6(3)
O(1)–RE(1)–O(1W)	126.25(17)	132.82(2)	130.27(14)	123.39(14)	121.2(4)
O(2)–RE(1)–O(4)^{iii}	71.9(2)	73.99(2)	74.08(15)	75.76(13)	76.9(4)
O(2)–RE(1)–O(5)^{ii}	81.39(18)	79.46(2)	80.84(11)	83.11(15)	74.5(3)
O(2)–RE(1)–O(6)^{i}	124.88(19)	124.71(2)	125.65(14)	126.75(16)	126.9(4)
O(2)–RE(1)–O(7)^{iv}	76.60(19)	75.42(2)	76.97(16)	70.93(14)	68.6(4)
O(2)–RE(1)–O(8)^{ii}	144.7(2)	143.78(2)	144.79(14)	148.04(14)	146.6(3)
O(2)–RE(1)–O(1W)	132.26(19)	135.42(2)	134.40(17)	126.53(14)	126.8(4)
O(4)^{iii}–RE(1)–O(5)^{ii}	81.14(19)	80.59(2)	81.58(16)	79.64(15)	78.1(4)
O(4)^{iii}–RE(1)–O(6)^{i}	102.9(2)	99.89(2)	101.38(17)	108.68(17)	105.3(4)
O(4)^{iii}–RE(1)–O(7)^{iv}	148.00(19)	146.22(2)	147.52(14)	145.81(11)	145.2(4)
O(4)^{iii}–RE(1)–O(8)^{ii}	78.9(2)	73.25(2)	74.23(15)	78.23(14)	75.5(4)
O(4)^{iii}–RE(1)–O(1W)	150.3(2)	145.72(2)	148.36(13)	151.21(16)	149.8(4)
O(5)^{ii}–RE(1)–O(6)^{i}	153.57(16)	155.25(2)	153.33(16)	149.93(17)	158.6(4)
O(5)^{ii}–RE(1)–O(7)^{iv}	99.93(16)	107.51(2)	108.09(18)	103.45(15)	97.2(4)
O(5)^{ii}–RE(1)–O(8)^{ii}	74.8(2)	80.379(19)	79.73(16)	74.18(16)	81.7(3)
O(5)^{ii}–RE(1)–O(1W)	85.82(18)	87.80(2)	89.32(16)	85.04(16)	90.1(3)
O(6)^{i}–RE(1)–O(7)^{iv}	90.3(2)	85.97(2)	83.76(18)	85.84(18)	91.5(4)
O(6)^{i}–RE(1)–O(8)^{ii}	80.31(19)	76.18(2)	75.73(15)	79.28(15)	78.8(4)
O(6)^{I}–RE(1)–O(1W)	60.6(2)	77.96(2)	74.22(17)	74.22(17)	76.5(3)
O(7)^{iv}–RE(1)–O(8)^{ii}	132.6(2)	139.785(18)	137.25(14)	135.76(16)	138.6(4)
O(7)^{iv}–RE(1)–O(1W)	78.0(2)	68.06(2)	64.04(15)	61.68(15)	63.2(4)
O(8)^{ii}–RE(1)–O(1W)	71.9(2)	73.06(2)	74.35(16)	74.19(16)	75.4(4)

Table S2 (cont.) - Selected bond angles (in degrees) for the {REO_8} coordination environments found in the [RE(H_2cmp)(H_2O)] materials [RE = Y^{3+} (**1**), La^{3+} (**2**), Pr^{3+} (**3**), Nd^{3+} (**4**), Sm^{3+} (**5**), Gd^{3+} (**6**), Eu^{3+} (**7**), Tb^{3+} (**8**), Dy^{3+} (**9**), Ho^{3+} (**10**) and Er^{3+} (**11**)].[a]

	7 (Gd^{3+})	**8** (Tb^{3+})	**9** (Dy^{3+})	**10** (Ho^{3+})	**11** (Er^{3+})
O(1)–RE(1)–O(2)	46.93(4)	48.10(7)	48.0(3)	47.1(5)	48.12(8)
O(1)–RE(1)–O(4)^{iii}	83.89(4)	79.19(8)	81.6(3)	78.1(5)	78.87(9)
O(1)–RE(1)–O(5)^{ii}	127.35(4)	129.10(7)	123.2(3)	127.1(5)	126.41(8)
O(1)–RE(1)–O(6)^{i}	78.27(4)	71.80(7)	78.9(2)	80.4(4)	73.76(7)
O(1)–RE(1)–O(7)^{iv}	67.17(4)	74.43(8)	72.2(3)	68.3(5)	73.22(8)
O(1)–RE(1)–O(8)^{ii}	146.91(4)	135.90(7)	148.1(2)	144.1(6)	138.72(7)
O(1)–RE(1)–O(1W)	124.10(5)	131.93(7)	127.8(3)	125.3(5)	130.87(7)
O(2)–RE(1)–O(4)^{iii}	74.78(5)	79.32(7)	70.1(3)	72.0(5)	73.29(10)
O(2)–RE(1)–O(5)^{ii}	80.48(4)	82.96(7)	75.2(3)	80.0(5)	78.39(9)
O(2)–RE(1)–O(6)^{i}	124.37(5)	118.76(9)	126.0(3)	127.5(5)	121.80(9)
O(2)–RE(1)–O(7)^{iv}	67.88(5)	65.50(8)	74.3(3)	73.2(6)	75.64(9)
O(2)–RE(1)–O(8)^{ii}	149.74(5)	149.80(8)	148.5(3)	144.5(5)	147.40(8)
O(2)–RE(1)–O(1W)	127.90(6)	124.72(8)	137.9(3)	131.4(6)	132.46(8)
O(4)^{iii}–RE(1)–O(5)^{ii}	79.12(4)	78.66(8)	79.3(3)	86.3(6)	83.41(9)
O(4)^{iii}–RE(1)–O(6)^{i}	113.55(4)	102.74(9)	117.3(2)	103.4(6)	101.65(10)
O(4)^{iii}–RE(1)–O(7)^{iv}	142.31(4)	144.58(9)	144.2(3)	142.6(6)	147.42(11)
O(4)^{iii}–RE(1)–O(8)^{ii}	80.53(4)	73.75(7)	84.7(3)	79.0(5)	77.73(10)
O(4)^{iii}–RE(1)–O(1W)	151.19(5)	148.07(8)	147.6(4)	153.8(6)	148.29(10)
O(5)^{ii}–RE(1)–O(6)^{i}	153.63(4)	158.24(8)	155.5(3)	152.4(5)	159.81(9)
O(5)^{ii}–RE(1)–O(7)^{iv}	99.15(5)	100.15(8)	94.8(3)	100.7(5)	99.78(10)
O(5)^{ii}–RE(1)–O(8)^{ii}	77.88(5)	78.63(8)	81.9(3)	78.2(5)	83.82(10)
O(5)^{ii}–RE(1)–O(1W)	87.07(4)	83.65(8)	91.8(3)	87.0(6)	84.84(8)
O(6)^{i}–RE(1)–O(7)^{iv}	84.61(4)	91.10(8)	81.6(2)	87.3(6)	86.50(10)
O(6)^{i}–RE(1)–O(8)^{ii}	81.51(4)	80.95(8)	81.9(2)	78.4(5)	78.29(9)
O(6)^{i}–RE(1)–O(1W)	70.88(5)	84.47(9)	64.4(3)	72.9(6)	80.76(10)
O(7)^{iv}–RE(1)–O(8)^{ii}	136.44(4)	141.28(8)	129.7(3)	138.4(6)	134.79(9)
O(7)^{iv}–RE(1)–O(1W)	64.57(5)	64.65(8)	67.0(3)	63.6(6)	63.81(9)
O(8)^{ii}–RE(1)–O(1W)	71.86(5)	76.85(8)	63.0(3)	74.9(6)	71.78(7)

[a] Symmetry transformations used to generate equivalent atoms: (i) *x*−½, y, −*z*+½; (ii) *x*−*1, y, z*; (iii) −*x*+*3/2, y*−½, *z*; (iv) −*x*+*3/2, y*+½, *z*.