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SUPPORTING INFORMATION

Remarkable structural diversity and single-crystal-to-single-crystal transformations in sulfone functionalized lanthanide MOFs

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Methods and Instrumentation

Intensity data for of **La-2**, **Pr-2** and **Ce-3** were collected in ChemMatCARS Sector 15 at APS, Argonne National Labotory, with an APEX2 detector (diamond monochromatized radiation) using a phi-scan technique. Data reduction was performed with the APEX2 software, SAINT and SADABS.

Intensity data for **Ce-2**, **Dy** and **Pr-3** were performed on a STOE IPDS II diffractometer operated at 2000 W power (50 kV, 40 mA) with graphite monochromatized MoKα (λ= 0.71073 Å) radiation. An analytical absorption correction was applied using the program X-RED (routine within the X-AREA software package).

The structures of **La-2**, **Pr-2**, **Ce-2**, **Ce-3** and **Dy** were solved with SHELXL software (Sheldrick, G. M. SHELXL; University of Göttingen, 2002). In the case of **Pr-3** only unit cell determination was performed. All non-hydrogen atoms, except in the case of disordered DMF molecules, were refined anisotropically. The hydrogen atoms were generated with idealized geometries.

The large degree of diffuse scattering from disordered solvent molecules in **La-2**, **Ce-2**, **Ce-3** and **Dy** produces a large background and masked the high-angle data, as commonly have been observed in MOF crystallography.[1, 2, 3, 4] For this reason, 2θ data collection was performed in a limited range (see the corresponding crystallographic tables below). The reduced residuals obtained after operating the SQUEEZE subroutine of PLATON confirms that the uncertainty before SQUEEZE in the crystallographic models stems from the disordered guest molecules reside in the large void spaces and not the framework structure.

Powder X-ray diffraction patterns were collected on a Rigaku D/MAX-2000H rotating anode diffractometer (CuKα radiation) equipped with a secondary pyrolytic graphite monochromator operated at 40 kV and 178 mA. The scan rate was 0.15 deg/min with a step size of 0.01 deg. All samples in their mother liquor were placed inside a 1.5 mm O.D. glass capillary and mounted on the diffractometer. Simulated PXRD patterns were calculated from the corresponding single crystal data using the program Powder Cell 2.3. Thermogravimetric analyses (TGA) were performed using a TA SDT Q 600 analysis system. An amount of 20 mg of sample was placed inside an alumina cup and heated up to 600 ^{o}C under nitrogen flow with a heating rate of 5 ^{o}C/min.

Synthesis of **Ce-1**, **Pr-1** and **Dy**

The solids **Ce-1** and **Pr-1** were synthesized using the corresponding metal chloride salts, following a similar experimental procedure to **La-1**. Accordingly, a mixture of $MCl_3 \cdot 7H_2O$, M = Ce, Pr (0.33mmol) and $\mathbf{H_2L}$ (0.164mmol, 50mg) was dissolved in 10ml of DMF and heated at 95^{o}C for 12h. A crystalline phase was formed in high yield (>80% based on the corresponding metal salts).

In the case of **Dy,** a mixture of $Dy(NO_3)_3 \cdot 5H_2O$ (0.041mmol) and $\mathbf{H_2L}$ (0.082mmol) was dissolved in 10ml of DMF and heated at 95 ^{o}C for 12h. The crystalline solid was formed in high yield (>80% based on $Dy(NO_3)_3 \cdot 5H_2O$).

Optical image of **La-2** and single-crystal data

Figure S1. Optical image of **La-2** single crystals. The crystals were precipitated at room temperature from the supernatant solution of the corresponding solvothermal reaction at 95 ^{o}C.

Table 1. Crystal data and structure refinement for **La-2** at 100(2) K.

Empirical formula	C63 H67 La2 N7 O25 S3
Formula weight	1696.24
Temperature	100(2) K
Wavelength	0.40759 Å
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	a = 19.5011(13) Å, α = 90.00º b = 16.7853(12) Å, β = 112.891(2)º c = 24.2950(17) Å, γ = 90.00º
Volume	7326.2(9) $Å^3$
Z	4
Density (calculated)	1.538 g/cm^3
Absorption coefficient	0.703 mm^{-1}
F(000)	3424
Crystal size	0.15 x 0.1 x 0.1 mm^3
Theta range for data collection	5.85 to 16.93º
Index ranges	-23<=h<=27, -23<=k<=23, -34<=l<=34
Reflections collected	161465
Independent reflections	21354 [R_{int} = 0.0946]
Completeness to θ = 16.93º	96%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	21354 / 66 / 946
Goodness-of-fit on F^2	1.388
Final R indices [>2sigma(I)]	R_{obs} = 0.0717, wR_{obs} = 0.1693
R indices (all data)	R_{all} = 0.1485, wR_{all} = 0.2192
Largest diff. peak and hole	4.110 and -2.563 e.$Å^{-3}$

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and calc $w=1/[\sigma^2(Fo^2)+(0.0512P)^2+59.5859P]$ where $P=(Fo^2+2Fc^2)/3$

Table 2. Bond lengths [Å] for **La-2** at 100(2) K with estimated standard deviations in parentheses.

Label	Distances
La(1)-O(4)	2.441(5)
La(1)-O(1)	2.444(4)
La(1)-O(21)	2.474(7)
La(1)-O(11)	2.550(7)
La(1)-O(20)	2.572(5)
La(1)-O(16)	2.585(6)
La(1)-O(3)	2.629(5)
La(1)-O(19)	2.657(5)
La(1)-O(19)#1	2.682(5)
La(1)-La(1)#1	4.1061(7)
La(2)-O(6)	2.457(6)
La(2)-O(2)	2.473(4)
La(2)-O(13)	2.512(7)
La(2)-O(5)	2.524(5)
La(2)-O(10)	2.540(5)
La(2)-O(7)	2.546(5)
La(2)-O(22)	2.569(8)
La(2)-O(15)	2.652(9)
La(2)-O(10)#2	2.982(6)
S(1)-O(18)	1.436(6)
S(1)-O(14)	1.438(6)
S(1)-C(24)	1.779(6)
S(1)-C(50)	1.779(7)
S(2)-O(17)	1.439(6)
S(2)-O(9)	1.444(6)
S(2)-C(45)	1.755(7)
S(2)-C(54)	1.764(6)
S(3)-O(12)	1.434(7)
S(3)-O(8)	1.447(7)
S(3)-C(53)	1.765(7)
S(3)-C(52)	1.771(6)
O(1)-C(66)	1.257(9)
O(2)-C(7)	1.253(7)
O(3)-C(64)	1.245(8)
O(4)-C(7)	1.261(7)
O(5)-C(49)	1.256(9)
O(6)-C(66)	1.284(9)

O(7)-C(51)	1.240(8)
O(10)-C(51)#2	1.259(9)
O(10)-La(2)#2	2.982(6)
O(11)-C(48)	1.173(10)
O(13)-C(49)#2	1.257(10)
O(15)-C(17)	1.218(17)
O(16)-C(56)	1.255(14)
O(19)-C(64)	1.298(9)
O(19)-La(1)#1	2.682(5)
O(20)-C(62)	1.251(8)
O(21)-C(56)#1	1.339(15)
O(22)-C(58)	1.123(15)
O(23)-C(36)	1.235(13)
O(24)-C(38)	1.213(13)
O(25)-C(40)	1.226(16)
N(1)-C(62)	1.322(10)
N(1)-C(59)	1.437(11)
N(1)-C(57)	1.446(9)
N(2)-C(48)	1.308(10)
N(2)-C(55)	1.415(17)
N(2)-C(6)	1.48(2)
N(3)-C(58)	1.37(2)
N(3)-C(2)	1.414(17)
N(3)-C(18)	1.455(19)
N(4)-C(17)	1.351(19)
N(4)-C(8)	1.377(15)
N(4)-C(5)	1.590(14)
N(5)-C(36)	1.312(12)
N(5)-C(37)	1.446(13)
N(5)-C(39)	1.468(13)
N(6)-C(38)	1.342(14)
N(6)-C(16)	1.432(13)
N(6)-C(29)	1.446(14)
N(7)-C(40)	1.301(16)
N(7)-C(1)	1.45(2)
N(7)-C(4)	1.50(2)
C(7)-C(9)	1.500(9)
C(9)-C(34)	1.397(8)
C(9)-C(10)	1.400(8)
C(10)-C(20)	1.396(9)

C(11)-C(14)	1.380(9)
C(11)-C(45)	1.423(8)
C(11)-C(26)	1.480(9)
C(12)-C(26)	1.384(8)
C(12)-C(30)	1.407(9)
C(13)-C(42)	1.392(9)
C(13)-C(25)	1.406(8)
C(13)-C(66)	1.497(9)
C(14)-C(25)	1.398(9)
C(15)-C(27)	1.383(8)
C(15)-C(47)	1.388(9)
C(20)-C(28)	1.391(8)
C(21)-C(33)	1.392(9)
C(21)-C(50)	1.394(8)
C(21)-C(27)	1.472(9)
C(22)-C(60)	1.388(9)
C(22)-C(43)	1.389(9)
C(23)-C(47)	1.401(9)
C(23)-C(41)	1.401(8)
C(23)-C(51)	1.502(9)
C(24)-C(41)	1.372(9)
C(24)-C(27)	1.400(8)
C(26)-C(54)	1.400(9)
C(28)-C(52)	1.408(8)
C(28)-C(43)	1.484(9)
C(30)-C(44)	1.397(10)
C(31)-C(50)	1.388(9)
C(31)-C(46)	1.390(10)
C(32)-C(65)	1.395(12)
C(32)-C(60)	1.416(11)
C(32)-C(56)#3	1.495(11)
C(33)-C(63)	1.390(9)
C(34)-C(52)	1.374(9)
C(42)-C(45)	1.381(9)
C(43)-C(53)	1.406(9)
C(44)-C(61)	1.394(9)
C(44)-C(49)#4	1.515(11)
C(46)-C(63)	1.415(9)
C(46)-C(64)#5	1.506(10)
C(49)-O(13)#2	1.257(10)

C(49)-C(44)#3	1.515(11)
C(51)-O(10)#2	1.259(9)
C(53)-C(65)	1.369(10)
C(54)-C(61)	1.378(10)
C(56)-O(21)#1	1.339(15)
C(56)-C(32)#4	1.495(11)
C(64)-C(46)#6	1.506(10)

Symmetry transformations used to generate equivalent atoms:
1# -x,-y+1,-z 2# -x+1,-y+1,-z 3# x+1/2,-y+3/2,z+1/2 4# x-1/2,-y+3/2,z-1/2 5# x+1/2,-y+3/2,z-1/2 6# x-1/2,-y+3/2,z+1/2

Optical image of **Ce-2** and single-crystal data

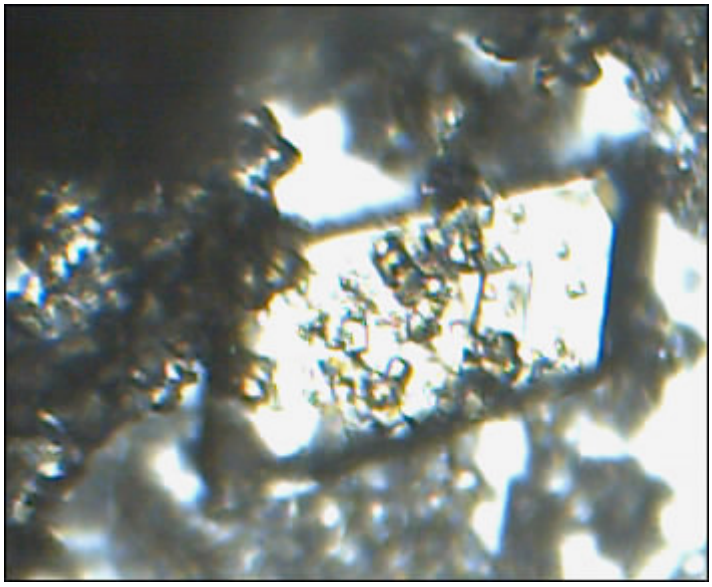

Figure S2. Optical image of **Ce-2** single crystal. The crystals were precipitated at room temperature from the supernatant solution of the corresponding solvothermal reaction at 95 ^{o}C. **Ce-2** is isostructural to **La-2**.

Table 3. Crystal data and structure refinement for **Ce-2** at 130(1) K.

Empirical formula	C60 H60 Ce2 N6 O24 S3
Formula weight	1625.56
Temperature	130(1) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 19.711(4) Å, α = 90.00º b = 18.928(4) Å, β = 116.74(3)º c = 23.826(5) Å, γ = 90.00º
Volume	7938(3) $Å^3$
Z	4
Density (calculated)	1.360 g/cm^3
Absorption coefficient	1.281 mm^{-1}
F(000)	3272
Crystal size	0.15 x 0.1 x 0.1 mm^3
Theta range for data collection	1.44 to 23.48º
Index ranges	-21<=h<=21, -20<=k<=21, -26<=l<=26
Reflections collected	55316
Independent reflections	11543 [R_{int} = 0.0565]
Completeness to θ = 23.48º	99%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11543 / 66 / 856
Goodness-of-fit on F^2	0.852
Final R indices [>2sigma(I)]	R_{obs} = 0.0420, wR_{obs} = 0.0915
R indices (all data)	R_{all} = 0.0693, wR_{all} = 0.0969
Extinction coefficient	
Largest diff. peak and hole	1.599 and -1.054 e.$Å^{-3}$

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and calc $w=1/[\sigma^2(Fo^2)+(0.0549P)^2+0.0000P]$ where $P=(Fo^2+2Fc^2)/3$

Table 4. Bond lengths [Å] for **Ce-2** at 130(1) K with estimated standard deviations in parentheses.

Label	Distances
Ce(1)-O(8)	2.372(6)
Ce(1)-O(2)	2.428(5)
Ce(1)-O(3)	2.480(6)
Ce(1)-O(4)	2.483(4)
Ce(1)-O(15)	2.486(5)
Ce(1)-O(19)	2.491(6)
Ce(1)-O(7)	2.499(4)
Ce(1)-O(22)	2.625(5)
Ce(2)-O(16)	2.422(4)
Ce(2)-O(17)	2.469(4)
Ce(2)-O(1)	2.478(4)
Ce(2)-O(12)	2.497(4)
Ce(2)-O(13)	2.522(4)
Ce(2)-O(18)	2.546(5)
Ce(2)-O(20)	2.553(4)
Ce(2)-O(9)	2.568(4)
Ce(2)-O(17)#1	2.812(4)
Ce(2)-C(26)	3.052(6)
O(1)-C(1)	1.261(7)
O(2)-C(1)	1.265(7)
C(1)-C(2)	1.513(8)
C(2)-C(4)	1.392(9)
C(2)-C(3)	1.395(9)
C(3)-C(59)	1.386(8)
C(4)-C(5)	1.389(9)
C(59)-C(6)	1.380(9)
C(5)-C(6)	1.394(9)
C(5)-S(1)	1.770(7)
C(6)-C(7)	1.488(9)
C(7)-C(9)	1.388(9)
C(7)-C(8)	1.410(9)
C(8)-C(10)	1.366(9)
C(8)-S(1)	1.773(7)
C(9)-C(11)	1.398(8)
C(10)-C(12)	1.409(9)
C(11)-C(12)	1.376(9)
C(12)-C(13)	1.505(10)

C(13)-O(4)#2	1.227(10)
C(13)-O(3)#3	1.265(10)
O(3)-C(13)#4	1.265(10)
O(4)-C(13)#5	1.227(10)
S(1)-O(6)	1.433(5)
S(1)-O(5)	1.448(6)
O(7)-C(14)	1.246(8)
O(8)-C(14)#6	1.239(8)
C(14)-O(8)#6	1.239(8)
C(14)-C(15)#7	1.504(9)
C(15)-C(16)	1.392(9)
C(15)-C(17)	1.400(9)
C(15)-C(14)#8	1.504(9)
C(16)-C(60)	1.398(9)
C(17)-C(18)	1.373(9)
C(18)-C(19)	1.394(8)
C(18)-S(2)	1.780(6)
C(19)-C(60)	1.402(9)
C(19)-C(20)	1.466(9)
C(20)-C(22)	1.389(9)
C(20)-C(21)	1.408(8)
C(21)-C(23)	1.364(8)
C(21)-S(2)	1.788(6)
C(22)-C(24)	1.378(9)
C(23)-C(25)	1.405(8)
C(24)-C(25)	1.400(9)
C(25)-C(26)	1.507(8)
C(26)-O(9)	1.255(7)
C(26)-O(17)#1	1.280(7)
S(2)-O(11)	1.430(5)
S(2)-O(10)	1.453(5)
O(12)-C(27)	1.247(7)
O(13)-C(27)#1	1.266(7)
C(27)-O(13)#1	1.266(7)
C(27)-C(28)	1.520(9)
C(28)-C(30)	1.386(8)
C(28)-C(29)	1.403(8)
C(29)-C(32)	1.384(8)
C(30)-C(31)	1.385(9)
C(31)-C(33)	1.422(8)

C(31)-S(3)	1.771(6)
C(32)-C(33)	1.386(8)
C(33)-C(34)	1.479(8)
C(34)-C(35)	1.392(9)
C(34)-C(36)	1.411(8)
C(35)-C(38)	1.411(8)
C(36)-C(37)	1.376(8)
C(36)-S(3)	1.769(6)
C(37)-C(39)	1.398(9)
C(38)-C(39)	1.405(9)
C(39)-C(40)#2	1.514(8)
C(40)-O(16)	1.254(7)
C(40)-O(15)	1.257(8)
C(40)-C(39)#5	1.514(8)
O(14)-S(3)	1.434(5)
S(3)-O(24)	1.451(5)
O(17)-C(26)#1	1.280(7)
O(17)-Ce(2)#1	2.812(4)
O(18)-C(41)	1.182(8)
C(41)-N(1)	1.272(10)
N(1)-C(43)	1.416(12)
N(1)-C(42)	1.449(14)
O(19)-C(44)	1.200(12)
C(44)-N(2)	1.343(13)
N(2)-C(45)	1.367(13)
N(2)-C(46)	1.453(15)
O(20)-C(47)	1.216(9)
C(47)-N(3)	1.325(10)
N(3)-C(48)	1.432(10)
N(3)-C(49)	1.451(9)
O(21)-C(50)	1.229(8)
C(50)-N(4)	1.329(8)
N(4)-C(52)	1.440(8)
N(4)-C(51)	1.444(9)
O(22)-C(53)	1.253(9)
C(53)-N(5)	1.319(9)
N(5)-C(54)	1.444(10)
N(5)-C(55)	1.454(9)
O(23)-C(56)	1.28(3)
C(56)-N(6)	1.40(3)

N(6)-C(58)	1.413(19)
N(6)-C(57)	1.52(2)

Symmetry transformations used to generate equivalent atoms:
1# -x,-y+2,-z 2# x,-y-1/2,z+1/2 3# -x+1,y+1/2,-z+1/2 4# -x+1,y-1/2,-z+1/2 5# x,-y-1/2,z-1/2 6# -x+1,-y+2,-z 7# x+1,-y-1/2,z+1/2 8# x-1,-y-1/2,z-1/2

Single-crystal data for **Ce-3**

Table 5. Crystal data and structure refinement for **Ce-3** at 100(2) K.

Empirical formula	C28 H12 Ce O12 S2
Formula weight	744.62
Temperature	100(2) K
Wavelength	0.41382 Å
Crystal system	Trigonal
Space group	R-3
Unit cell dimensions	a = 25.0566(12) Å, α = 90.00º b = 25.0566(12) Å, β = 90.00º c = 29.944(3) Å, γ = 120.00º
Volume	16281.3(19) $Å^3$
Z	9
Density (calculated)	0.683 g/cm^3
Absorption coefficient	0.379 mm^{-1}
F(000)	3294
Crystal size	0.1 x 0.1 x 0.1 mm^3
Theta range for data collection	4.75 to 12.81º
Index ranges	-24<=h<=23, -24<=k<=24, -29<=l<=30
Reflections collected	52820
Independent reflections	4088 [R_{int} = 0.0815]
Completeness to θ = 21.20º	97%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4088 / 0 / 195
Goodness-of-fit on F^2	1.339
Final R indices [>2sigma(I)]	R_{obs} = 0.0790, wR_{obs} = 0.2104
R indices (all data)	R_{all} = 0.0924, wR_{all} = 0.2168
Extinction coefficient	
Largest diff. peak and hole	1.127 and -1.417 e.$Å^{-3}$

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and calc $w=1/[\sigma^2(Fo^2)+(0.1201P)^2+0.0000P]$ where $P=(Fo^2+2Fc^2)/3$

Table 6. Bond lengths [Å] for **Ce-3** at 100(2) K with estimated standard deviations in parentheses.

Label	Distances
Ce(1)-O(2)	2.470(5)
Ce(1)-O(2)#1	2.471(5)
Ce(1)-O(2)#2	2.471(5)
Ce(1)-O(3)#3	2.527(5)
Ce(1)-O(3)#4	2.527(6)
Ce(1)-O(3)#5	2.527(5)
Ce(1)-O(4)#3	2.555(5)
Ce(1)-O(4)#5	2.555(5)
Ce(1)-O(4)#4	2.555(5)
Ce(1)-C(14)#3	2.888(8)
Ce(1)-C(14)#5	2.888(8)
Ce(1)-C(14)#4	2.888(8)
Ce(2)-O(1)#6	2.626(5)
Ce(2)-O(1)#1	2.626(5)
Ce(2)-O(1)#2	2.626(5)
Ce(2)-O(1)#7	2.626(5)
Ce(2)-O(1)	2.626(5)
Ce(2)-O(1)#8	2.626(5)
Ce(2)-O(2)#6	2.702(5)
Ce(2)-O(2)#8	2.702(5)
Ce(2)-O(2)#1	2.702(5)
Ce(2)-O(2)#2	2.702(5)
Ce(2)-O(2)#7	2.702(5)
Ce(2)-O(2)	2.702(5)
S(1)-O(6)	1.452(8)
S(1)-O(5)	1.460(8)
S(1)-C(9)	1.757(8)
S(1)-C(6)	1.761(8)
O(1)-C(1)	1.241(9)
O(2)-C(1)	1.296(9)
O(3)-C(14)	1.264(10)
O(3)-Ce(1)#5	2.527(5)

O(4)-C(14)	1.247(10)
O(4)-Ce(1)#5	2.555(5)
C(1)-C(2)	1.476(10)
C(2)-C(3)	1.380(11)
C(2)-C(5)	1.408(11)
C(3)-C(4)	1.392(11)
C(4)-C(7)	1.396(11)
C(5)-C(6)	1.378(11)
C(6)-C(7)	1.389(12)
C(7)-C(8)	1.494(11)
C(8)-C(9)	1.381(11)
C(8)-C(10)	1.427(12)
C(9)-C(11)	1.404(12)
C(10)-C(12)	1.364(11)
C(11)-C(13)	1.376(12)
C(12)-C(13)	1.403(12)
C(13)-C(14)	1.499(11)
C(14)-Ce(1)#5	2.888(8)

Symmetry transformations used to generate equivalent atoms:

1# -x+y,-x+1,z 2# -y+1,x-y+1,z 3# x-y+1/3, x+2/3, -z+2/3 4# y+1/3, -x+y+2/3, -z+2/3 5# -x+1/3, -y+2/3, -z+2/3 6# x-y+2/3, x+1/3, -z+1/3 7# -x+2/3,-y+1/3+1,-z+1/3 8# y+2/3-1,-x+y+1/3,-z+1/3

Thermogravimetric analysis (TGA) of **Ce-3**

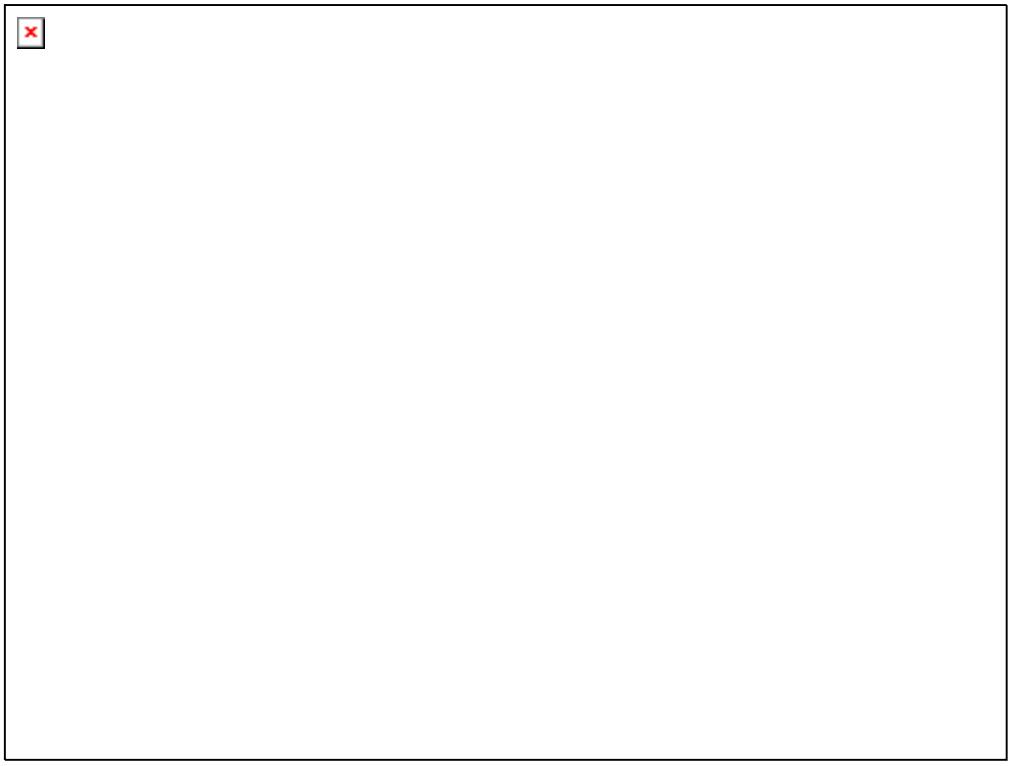

Figure S3. TGA curve of as-made **Ce-3** recorded under N_2 flow (heating rate 5 deg/min).

The initial 10% weight loss up to 100 ^{o}C is attributed to adsorbed moisture (the sample was exposed to air for few minutes during setup of the TGA experiment). Between 100-300 ^{o}C the observed weight loss (20 %) is attributed to the removal of the organic molecules (DMF, dimethylamine). Based on these results, the estimated chemical formula of **Ce-3**, is $[(CH_3)_2NH_2]_3[Ce_3\mathbf{L}_6](DMF)_6$.

Optical images of **Pr-1**, **Pr-2** and **Pr3** and single crystal data for **Pr-2**

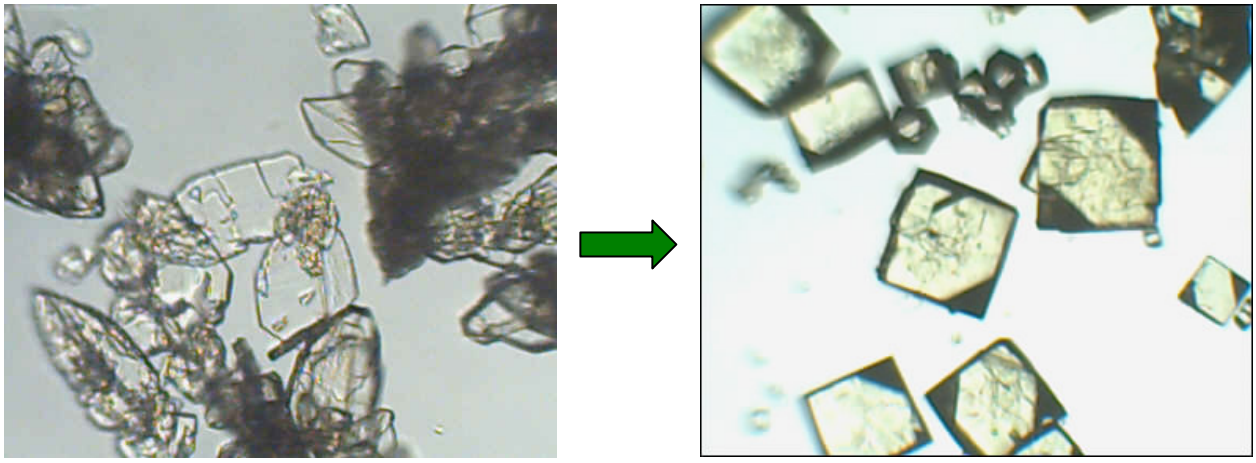

Figure S4. Optical image of **Pr-1** (left) and **Pr-3** (right). **Pr-3** is isostructural to **Ce-3** and formed quantitatively from **Pr-1** through a single-crystal-to-single-crystal transformation at room temperature.

Single-crystal X-ray diffraction data for **Pr-3** at 130 K: Trigonal system, space group *R* -3, a = b = 25.022(4) Å, c = 29.791(6) Å, α = β = 90°, γ = 120° and V = 16154(5) Å^3. At least 10 different single-crystals from the same batch were examined by single-crystal X-ray diffraction, leading to the same unit cell size in all cases.

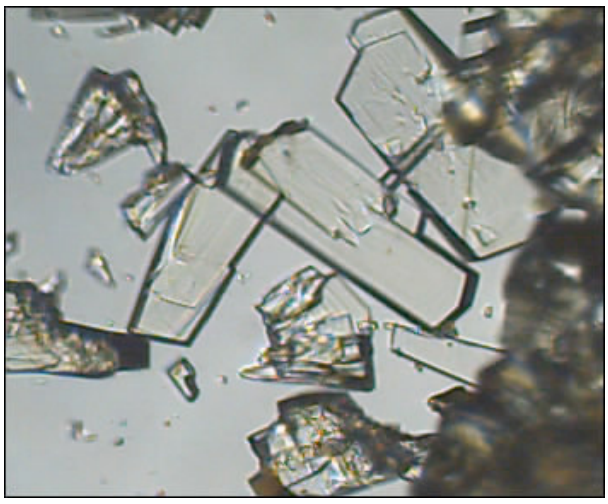

Figure S5. Optical image of **Pr-2**. The crystals were precipitated at room temperature from the supernatant solution of the corresponding solvothermal reaction at 95 °C.

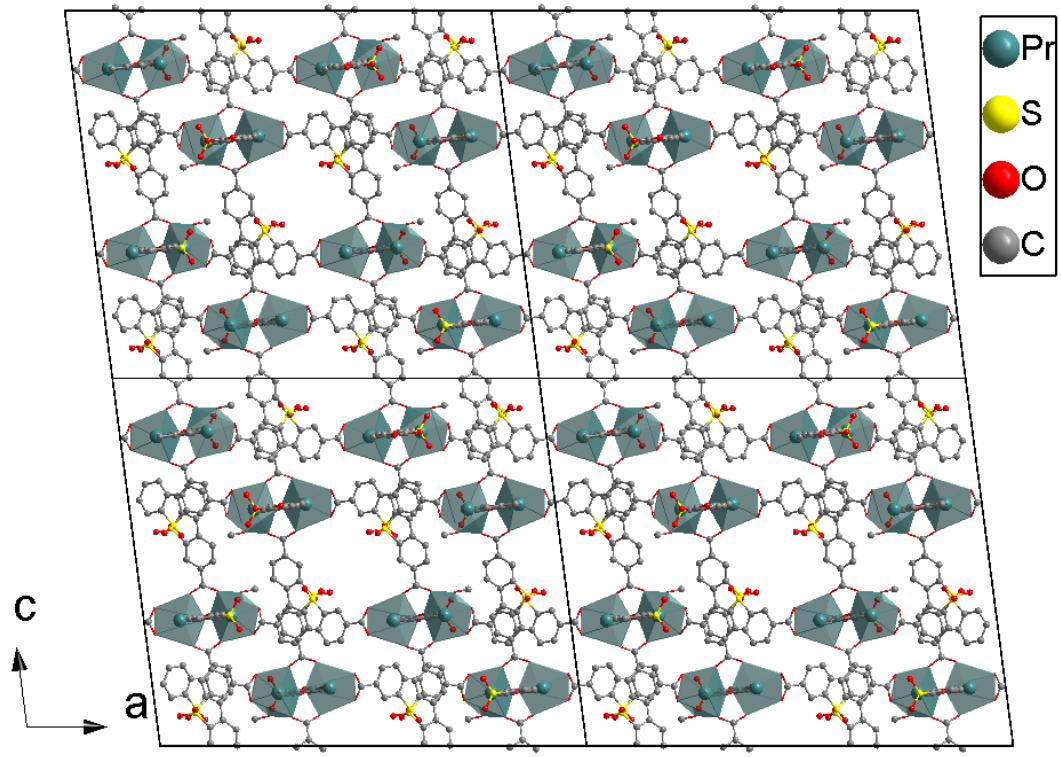

Figure S6. A 2x2x2 representation of **Pr-2** looking down the *b*-axis. **Pr-2** is a 3D, two-fold interpenetrating MOF.

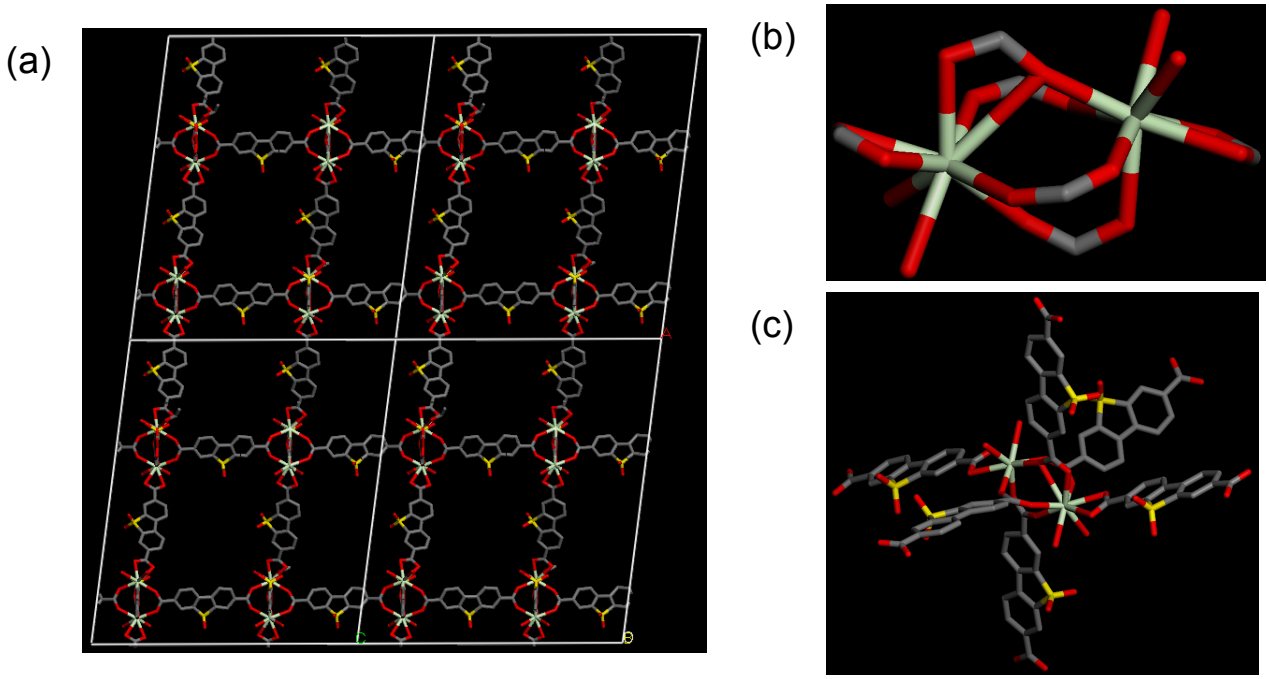

Figure S7. (a) A single 3D net in **Pr-2**, (b) the dimmeric SBU and (c) its pseudo-octahedral connectivity.

Table 7. Crystal data and structure refinement for **Pr-2** at 100(2) K.

Empirical formula	C60 H60 N6 O24 Pr2 S3
Formula weight	1627.14
Temperature	100(2) K
Wavelength	0.41328 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 35.0141(19) Å, α = 90.00º b = 14.9351(8) Å, β = 97.4220(10)º c = 30.3411(17) Å, γ = 90.00º
Volume	15733.6(15) $Å^3$
Z	8
Density (calculated)	1.374 g/cm^3
Absorption coefficient	0.732 mm^{-1}
F(000)	6560
Crystal size	0.15 x 0.1 x 0.1 mm^3
Theta range for data collection	5.93 to 20.13º
Index ranges	-58<=h<=56, -24<=k<=16, -50<=l<=50
Reflections collected	206217
Independent reflections	35429 [R_{int} = 0.0554]
Completeness to θ = 20.13º	93%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	35429 / 26 / 856
Goodness-of-fit on F^2	1.069
Final R indices [>2sigma(I)]	R_{obs} = 0.0591, wR_{obs} = 0.1516
R indices (all data)	R_{all} = 0.0768, wR_{all} = 0.1601
Extinction coefficient	
Largest diff. peak and hole	4.284 and -2.259 e.$Å^{-3}$

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and calc $w=1/[\sigma^2(Fo^2)+(0.0705P)^2+75.7846P]$ where $P=(Fo^2+2Fc^2)/3$

Table 8. Bond lengths [Å] for **Pr-2** at 100(2) K with estimated standard deviations in parentheses.

Label	Distances
Pr(1)-O(9)	2.399(2)
Pr(1)-O(4)	2.424(2)
Pr(1)-O(12)	2.438(3)
Pr(1)-O(2)	2.455(2)
Pr(1)-O(13)	2.466(3)
Pr(1)-O(1)	2.472(2)
Pr(1)-O(3)	2.502(3)
Pr(1)-O(6)	2.583(2)
Pr(1)-C(2)	2.872(3)
Pr(2)-O(8)	2.387(3)
Pr(2)-O(15)	2.392(3)
Pr(2)-O(5)	2.434(2)
Pr(2)-O(22)	2.488(3)
Pr(2)-O(7)	2.499(2)
Pr(2)-O(24)	2.512(3)
Pr(2)-O(14)	2.533(2)
Pr(2)-O(10)	2.560(2)
Pr(2)-C(14)	2.863(3)
Pr(2)-O(9)	2.930(3)
S(1)-O(16)	1.430(4)
S(1)-O(11)	1.436(4)
S(1)-C(35)	1.774(3)
S(1)-C(17)	1.775(3)
S(2)-O(20)	1.432(4)
S(2)-O(17)	1.435(4)
S(2)-C(26)	1.764(3)
S(2)-C(25)	1.771(4)
S(3)-O(18)	1.426(5)
S(3)-O(19)	1.436(4)
S(3)-C(24)	1.769(3)
S(3)-C(28)	1.774(3)
O(1)-C(2)	1.271(4)

O(2)-C(13)	1.255(4)
O(3)-C(31)	1.249(5)
O(4)-C(15)	1.263(4)
O(5)-C(15)	1.256(4)
O(6)-C(2)	1.256(4)
O(7)-C(14)	1.275(5)
O(8)-C(13)	1.260(4)
O(9)-C(27)	1.266(4)
O(10)-C(14)	1.243(5)
O(12)-C(18)	1.247(5)
O(13)-C(43)	1.266(6)
O(14)-C(27)	1.251(4)
O(15)-C(18)	1.263(4)
O(21)-C(52)	1.189(9)
O(22)-C(55)	1.203(6)
O(23)-C(44)	1.266(19)
O(24)-C(48)	1.209(6)
N(1)-C(43)	1.316(6)
N(1)-C(54)	1.453(13)
N(1)-C(58)	1.485(12)
N(2)-C(52)	1.377(11)
N(2)-C(53)	1.407(12)
N(2)-C(57)	1.452(12)
N(3)-C(31)	1.318(5)
N(3)-C(50)	1.445(6)
N(3)-C(59)	1.460(13)
N(4)-C(55)	1.318(7)
N(4)-C(45)	1.393(11)
N(4)-C(32)	1.45(3)
N(5)-C(44)	1.25(3)
N(5)-C(61)	1.38(3)
N(5)-C(60)	1.464(18)
N(6)-C(48)	1.320(7)
N(6)-C(56)	1.434(14)
N(6)-C(62)	1.471(12)

C(1)-C(20)	1.387(4)
C(1)-C(8)	1.405(4)
C(2)-C(8)	1.496(4)
C(3)-C(35)#1	1.382(4)
C(3)-C(23)	1.404(5)
C(4)-C(40)	1.388(5)
C(4)-C(28)	1.391(5)
C(4)-C(5)	1.481(5)
C(5)-C(33)	1.388(5)
C(5)-C(24)	1.395(5)
C(6)-C(20)	1.397(4)
C(6)-C(17)	1.399(5)
C(6)-C(34)	1.480(4)
C(7)-C(19)	1.380(5)
C(7)-C(25)	1.400(5)
C(8)-C(10)	1.406(4)
C(9)-C(36)	1.389(5)
C(9)-C(42)	1.427(6)
C(9)-C(27)	1.494(4)
C(10)-C(17)	1.383(4)
C(11)-C(29)	1.394(5)
C(11)-C(21)	1.406(5)
C(11)-C(15)	1.493(4)
C(12)-C(22)	1.385(5)
C(12)-C(38)	1.402(5)
C(12)-C(13)	1.502(4)
C(14)-C(23)	1.503(4)
C(16)-C(34)#1	1.391(5)
C(16)-C(30)	1.392(5)
C(18)-C(19)	1.501(4)
C(19)-C(49)	1.430(5)
C(21)-C(33)#2	1.388(5)
C(22)-C(28)	1.385(4)
C(23)-C(30)	1.405(5)
C(24)-C(29)#3	1.393(4)

C(25)-C(41)	1.394(5)
C(26)-C(39)	1.391(5)
C(26)-C(36)#4	1.397(5)
C(29)-C(24)#2	1.393(4)
C(33)-C(21)#3	1.388(5)
C(34)-C(16)#5	1.391(5)
C(34)-C(35)	1.402(5)
C(35)-C(3)#5	1.382(4)
C(36)-C(26)#6	1.397(5)
C(38)-C(40)	1.388(5)
C(39)-C(47)#4	1.378(6)
C(39)-C(41)	1.488(6)
C(41)-C(51)	1.377(6)
C(42)-C(47)	1.384(6)
C(47)-C(39)#6	1.378(6)
C(49)-C(51)	1.379(6)

Symmetry transformations used to generate equivalent atoms:

1# x+1/2, y+1/2, z 2# x,-y+1,z+1/2 3# x,-y+1,z-1/2 4# x,y-1,z 5# x-1/2,y-1/2,z 6# x,y+1,z

Single-crystal data for **Dy**

Table 9. Crystal data and structure refinement for **Dy** at 130(2) K.

Empirical formula	C60 H59 Dy2 N6 O25 S3
Formula weight	1685.31
Temperature	130(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 25.022(4) Å, α = 79.657(7)º b = 17.7008(16) Å, β = 80.452(7)º c = 22.3869(18) Å, γ = 81.326(8)º
Volume	4767.6(7) $Å^3$
Z	2
Density (calculated)	1.174 g/cm^3
Absorption coefficient	1.680 mm^{-1}
F(000)	1682
Crystal size	0.15 x 0.1 x 0.1 mm^3
Theta range for data collection	1.79 to 25.09º
Index ranges	-14<=h<=14, -21<=k<=21, -26<=l<=26
Reflections collected	46387
Independent reflections	16433 [R_{int} = 0.1589]
Completeness to θ = 21.20º	97%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16433 / 96 / 865
Goodness-of-fit on F^2	0.866
Final R indices [>2sigma(I)]	R_{obs} = 0.0714, wR_{obs} = 0.1719
R indices (all data)	R_{all} = 0.1711, wR_{all} = 0.2047
Extinction coefficient	
Largest diff. peak and hole	5.456 and -15.137 e.$Å^{-3}$

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and calc $w=1/[\sigma^2(Fo^2)+(0.0869P)^2+0.0000P]$ where $P=(Fo^2+2Fc^2)/3$

Table 10. Bond lengths [Å] for **Dy** at 130(2) K with estimated standard deviations in parentheses.

Label	Distances
Dy(1)-O(7)#1	2.325(10)
Dy(1)-O(18)	2.340(10)
Dy(1)-O(19)	2.350(10)
Dy(1)-O(8)	2.379(9)
Dy(1)-O(1)	2.392(10)
Dy(1)-O(15)	2.395(10)
Dy(1)-O(20)	2.433(11)
Dy(1)-O(2)	2.546(10)
Dy(1)-C(1)	2.798(15)
Dy(1)-O(7)	2.874(9)
Dy(1)-C(15)	2.982(15)
Dy(2)-O(9)#2	2.293(9)
Dy(2)-O(14)#3	2.365(9)
Dy(2)-O(10)	2.375(9)
Dy(2)-O(13)#4	2.387(9)
Dy(2)-O(21)	2.391(11)
Dy(2)-O(22)	2.427(12)
Dy(2)-O(4)#5	2.439(10)
Dy(2)-O(3)#5	2.473(10)
Dy(2)-C(14)#5	2.768(15)
O(1)-C(1)	1.254(17)
O(2)-C(1)	1.305(17)
C(1)-C(2)	1.53(2)
C(2)-C(4)	1.39(2)
C(2)-C(3)	1.41(2)
C(3)-C(6)	1.38(2)
C(3)-H(3)	0.9300
C(4)-C(5)	1.37(2)
C(4)-H(4)	0.9300
C(5)-C(7)	1.39(2)
C(5)-S(1)	1.782(15)
C(6)-C(7)	1.39(2)

C(6)-H(6)	0.9300
C(7)-C(8)	1.49(2)
C(8)-C(10)	1.39(2)
C(8)-C(9)	1.394(19)
C(9)-C(11)	1.39(2)
C(9)-S(1)	1.791(16)
C(10)-C(12)	1.39(2)
C(10)-H(10)	0.9300
C(11)-C(13)	1.37(2)
C(11)-H(11)	0.9300
C(12)-C(13)	1.395(19)
C(12)-H(12)	0.9300
C(13)-C(14)	1.53(2)
C(14)-O(4)	1.240(17)
C(14)-O(3)	1.276(17)
C(14)-Dy(2)#6	2.768(15)
O(3)-Dy(2)#6	2.473(10)
O(4)-Dy(2)#6	2.439(10)
S(1)-O(5)	1.449(12)
S(1)-O(6)	1.459(12)
O(7)-C(15)	1.274(17)
O(7)-Dy(1)#1	2.325(10)
O(8)-C(15)	1.241(17)
C(15)-C(16)	1.506(19)
C(16)-C(17)	1.40(2)
C(16)-C(18)	1.40(2)
C(17)-C(20)	1.401(19)
C(17)-H(17)	0.9300
C(18)-C(19)	1.41(2)
C(18)-H(18)	0.9300
C(19)-C(21)	1.39(2)
C(19)-H(19)	0.9300
C(20)-C(21)	1.37(2)
C(20)-S(2)	1.781(15)
C(21)-C(22)	1.53(2)

C(22)-C(24)	1.39(2)
C(22)-C(23)	1.42(2)
C(23)-C(26)	1.35(2)
C(23)-S(2)	1.766(15)
C(24)-C(25)	1.43(2)
C(24)-H(24)	0.9300
C(25)-C(27)	1.44(2)
C(25)-H(25)	0.9300
C(26)-C(27)	1.39(2)
C(26)-H(26)	0.9300
C(27)-C(28)	1.47(2)
C(28)-O(10)	1.271(17)
C(28)-O(9)	1.274(17)
O(9)-Dy(2)#2	2.293(9)
S(2)-O(11)	1.412(14)
S(2)-O(12)	1.456(14)
O(13)-C(29)	1.232(16)
O(13)-Dy(2)#4	2.387(9)
O(14)-C(29)	1.267(16)
O(14)-Dy(2)#7	2.365(9)
C(29)-C(30)	1.532(19)
C(30)-C(32)	1.38(2)
C(30)-C(31)	1.398(19)
C(31)-C(33)	1.40(2)
C(31)-H(31)	0.9300
C(32)-C(34)	1.42(2)
C(32)-H(32)	0.9300
C(33)-C(35)	1.39(2)
C(33)-S(3)	1.794(14)
C(34)-C(35)	1.40(2)
C(34)-H(34)	0.9300
C(35)-C(36)	1.488(19)
C(36)-C(38)	1.36(2)
C(36)-C(37)	1.39(2)
C(37)-C(39)	1.41(2)

C(37)-S(3)	1.787(15)
C(38)-C(40)	1.39(2)
C(38)-H(38)	0.9300
C(39)-C(41)	1.37(2)
C(39)-H(39)	0.9300
C(40)-C(41)	1.392(19)
C(40)-H(40)	0.9300
C(41)-C(42)	1.530(19)
C(42)-O(15)	1.259(16)
C(42)-O(18)#1	1.268(17)
S(3)-O(16)	1.435(12)
S(3)-O(17)	1.452(13)
O(18)-C(42)#1	1.268(17)
O(19)-C(44)	1.24(2)
O(20)-C(45)	1.22(2)
O(21)-C(43)	1.182(18)
C(43)-N(2)	1.33(2)
C(43)-H(43)	0.9300
C(44)-N(1)	1.33(2)
C(45)-N(3)	1.34(3)
C(45)-H(45)	0.9300
N(1)-C(49)	1.46(2)
N(1)-C(46)	1.53(2)
N(2)-C(48)	1.47(2)
N(2)-C(47)	1.51(2)
N(3)-C(50)	1.44(3)
N(3)-C(51)	1.51(3)
C(46)-H(46A)	0.9600
C(46)-H(46B)	0.9600
C(46)-H(46C)	0.9600
C(47)-H(47A)	0.9600
C(47)-H(47B)	0.9600
C(47)-H(47C)	0.9600
C(48)-H(48A)	0.9600
C(48)-H(48B)	0.9600

C(48)-H(48C)	0.9600
C(49)-H(49A)	0.9600
C(49)-H(49B)	0.9600
C(49)-H(49C)	0.9600
C(50)-H(50A)	0.9600
C(50)-H(50B)	0.9600
C(50)-H(50C)	0.9600
C(51)-H(51A)	0.9600
C(51)-H(51B)	0.9600
C(51)-H(51C)	0.9600
O(23)-C(52)	1.30(3)
C(52)-N(4)	1.32(3)
C(52)-H(52)	0.9300
N(4)-C(54)	1.35(3)
N(4)-C(53)	1.44(3)
C(53)-H(53A)	0.9600
C(53)-H(53B)	0.9600
C(53)-H(53C)	0.9600
C(54)-H(54A)	0.9600
C(54)-H(54B)	0.9600
C(54)-H(54C)	0.9600
O(24)-C(55)	1.32(3)
C(55)-N(5)	1.42(3)
C(55)-H(55)	0.9300
N(5)-C(56)	1.36(3)
N(5)-C(57)	1.39(3)
C(56)-H(56A)	0.9600
C(56)-H(56B)	0.9600
C(56)-H(56C)	0.9600
C(57)-H(57A)	0.9600
C(57)-H(57B)	0.9600
C(57)-H(57C)	0.9600
O(25)-C(58)	1.20(2)
C(58)-N(6)	1.31(2)
C(58)-H(58)	0.9300

N(6)-C(60)	1.41(3)
N(6)-C(59)	1.43(3)
C(59)-H(59A)	0.9600
C(59)-H(59B)	0.9600
C(59)-H(59C)	0.9600
C(60)-H(60A)	0.9600
C(60)-H(60B)	0.9600
C(60)-H(60C)	0.9600

Symmetry transformations used to generate equivalent atoms:

1# -x+1,-y+2,-z 2# -x+2,-y+1,-z+1 3# x+1,y-1,z 4# -x+1,-y+2,-z+1 5# x+1,y,z+1 6# x-1,y,z-1 7# x-1,y+1,z

Powder X-ray diffraction measurements (PXRD)

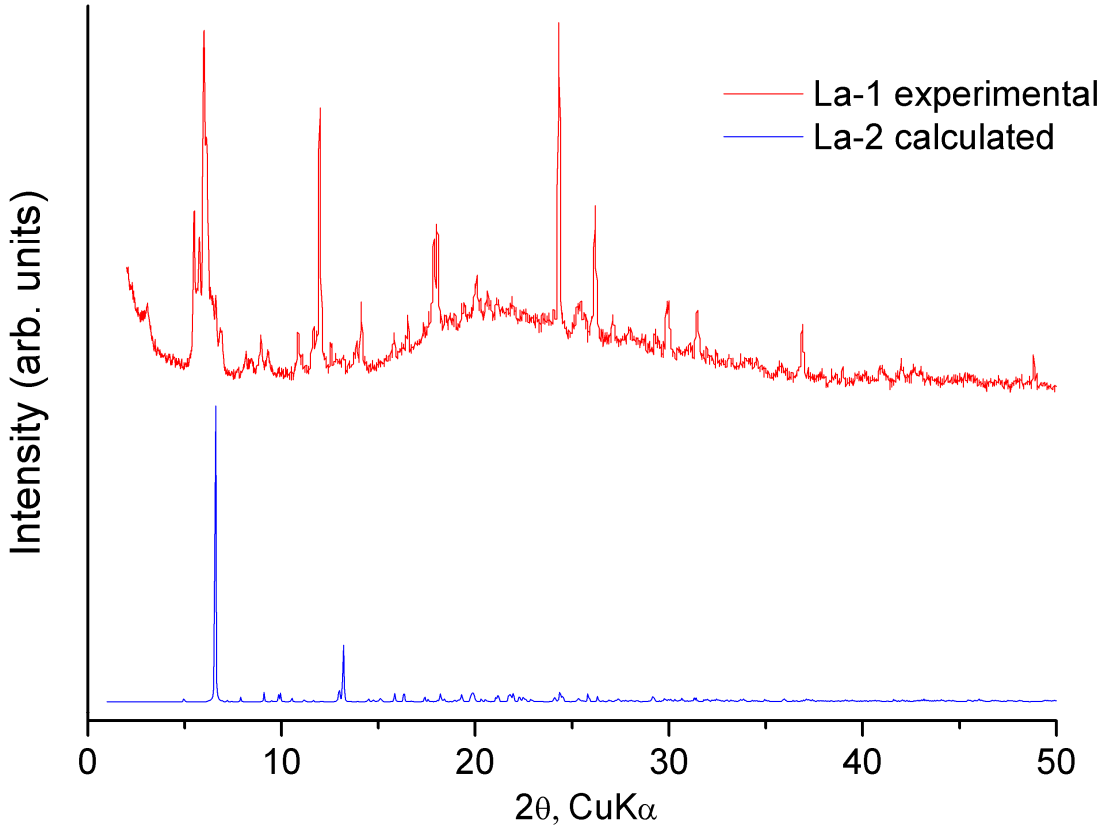

Figure S8. Experimental PXRD pattern of **La-1** (top) and calculated PXRD pattern of **La-2** (bottom). The mismatch between these two patterns indicate that **La-1** and **La-2** are different crystalline phases.

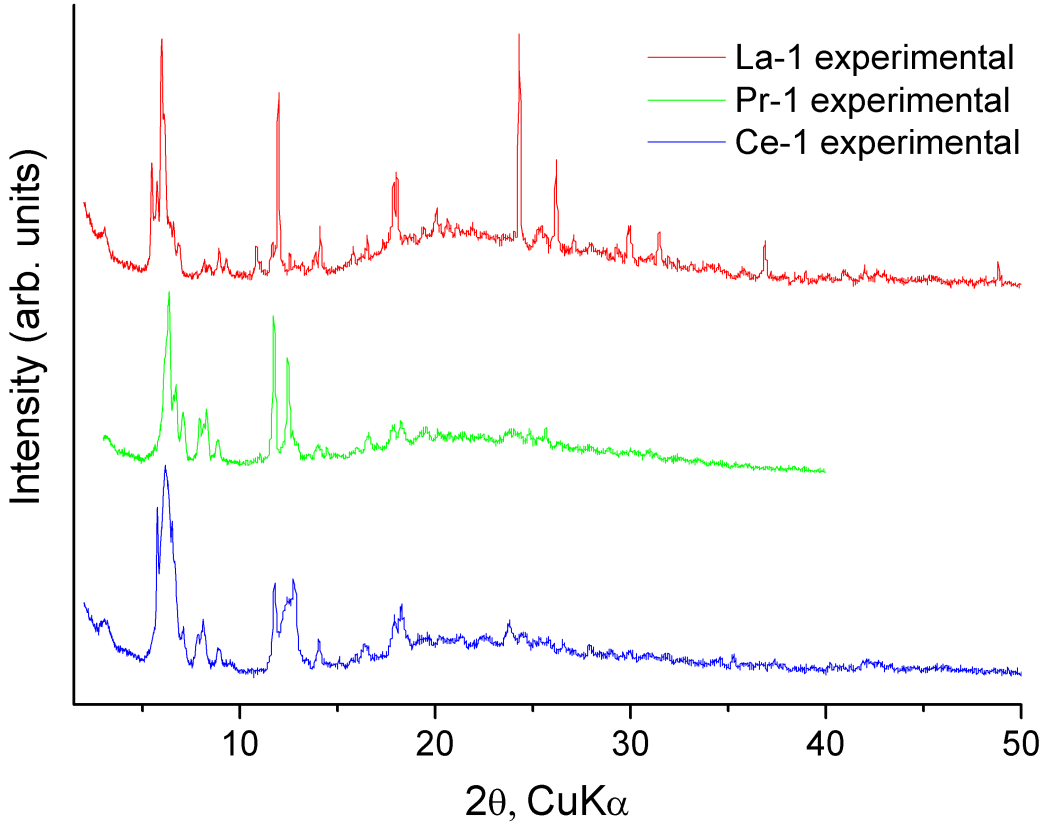

Figure S9. Experimental PXRD pattern for **La-1**, **Pr-1** and **Ce-1**. The patterns of **Pr-1** and **Ce-1** are similar and most likely these two phases are isostructural.

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