

## SUPPLEMENTARY MATERIAL

### **Structural Systematics of Lanthanide(III) Picrate Solvates: Neutral, Mononuclear Ln(pic)<sub>3</sub>(dimethylsulfoxide)<sub>3</sub> Arrays**

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#### A. X-ray structures of the complex molecules

Figure S1 - Molecules present in the monoclinic,  $C2/c$ , form of  $mer-[Ln(pic)_3(dmsO)_3]$ .

Figure S2 - Molecules present in the triclinic,  $P\bar{1}$ , form of  $mer-[Ln(pic)_3(dmsO)_3]$ .

Figure S3 - Molecules present in the triclinic,  $P\bar{1}$ , form of  $fac-[Ln(pic)_3(OH_2)(dmsO)_2]$ .

Figure S4 - Projections of the monoclinic and triclinic forms of  $mer-[La(pic)_3(dmsO)_3]$ .

#### B. Hirshfeld surface diagrams

Figure S5 - The Hirshfeld surface, viewed down  $a$ ,  $b$  and  $c$ , for monoclinic,  $C2/c$  form  $mer-[Y(pic)_3(dmsO)_3]$ .

Figure S6 - The Hirshfeld surfaces (down  $a$ ,  $b$  and  $c$ ) for the inequivalent molecules in triclinic,  $P\bar{1}$   $mer-[La(pic)_3(dmsO)_3]$ .

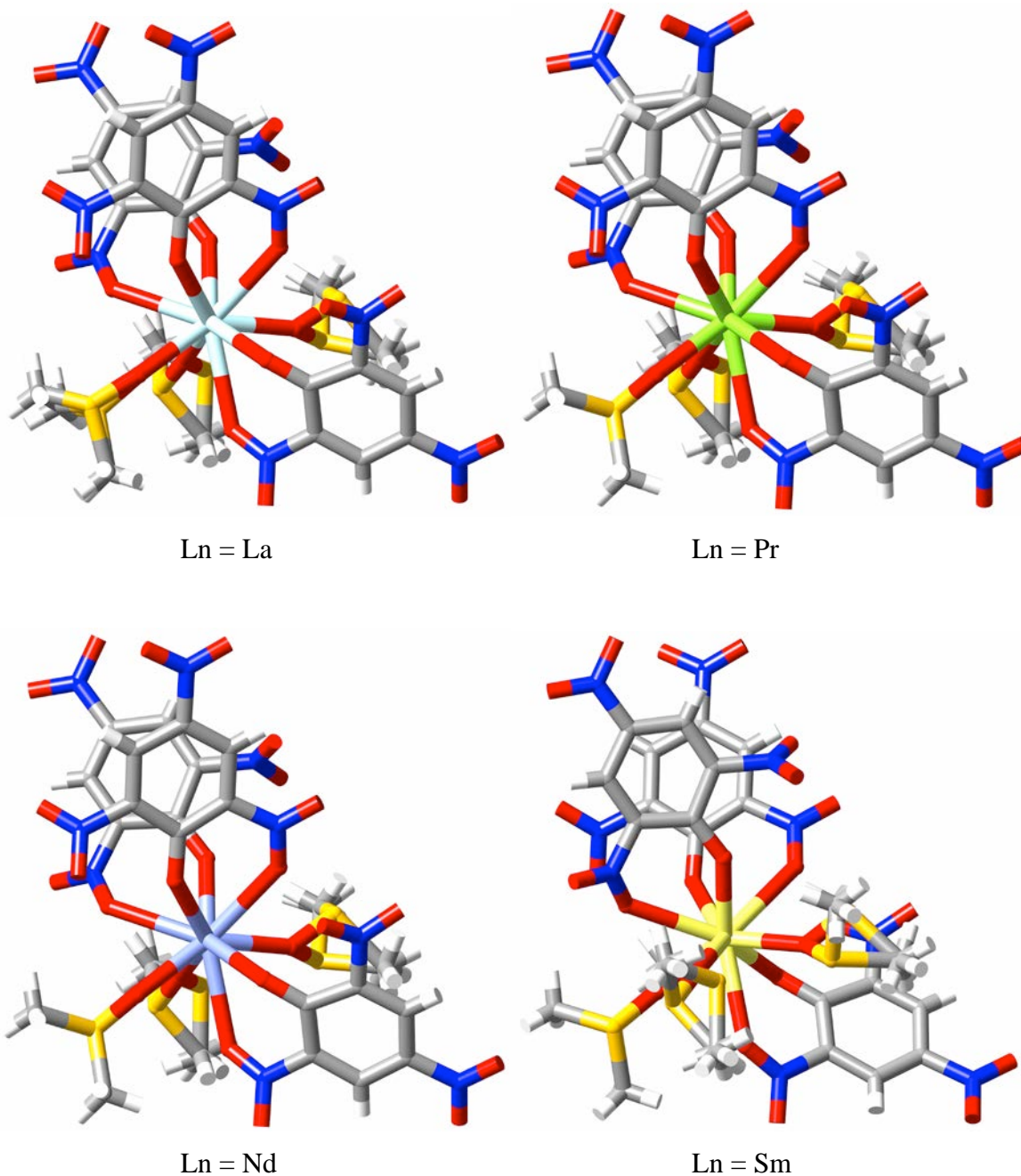
#### C. Tables of selected geometrical parameters

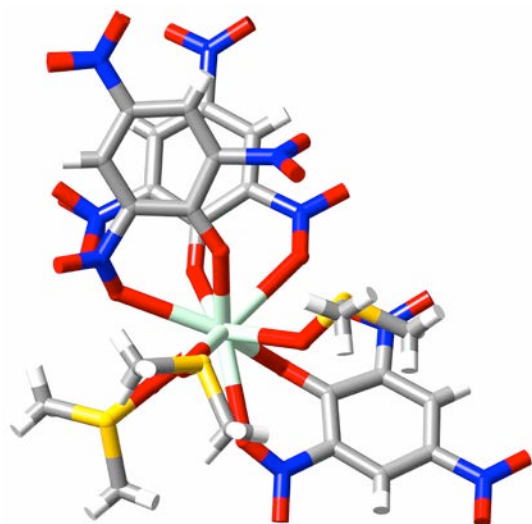
Table S1 - Bond lengths in some  $mer-[Ln(pic)_3(dmsO)_3]$  polymorphs.

Table S2 - Bond lengths in  $fac-[Ln(pic)_3(OH_2)(dmsO)_2]$  species;

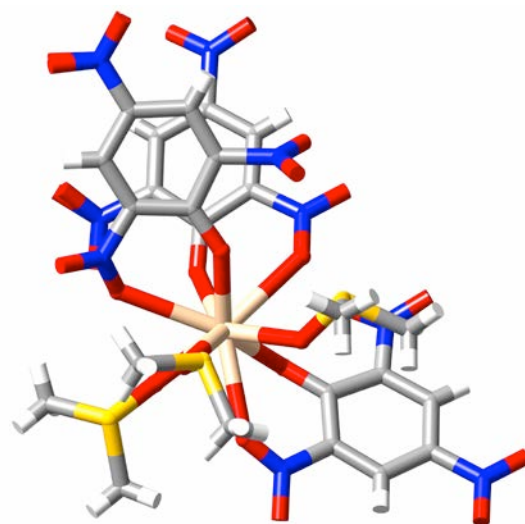
Table S3 - Selected picrate and dmsO parameters.

Figure S1 Structure of the molecules present in the monoclinic,  $C2/c$ , form of  $mer\text{-}[\text{Ln}(\text{pic})_3(\text{dmsO})_3]$ . Stick representations, viewed down  $c$ . Disordered components are shown as if each site is fully occupied. The molecules are chiral but both enantiomers are present in the lattice.

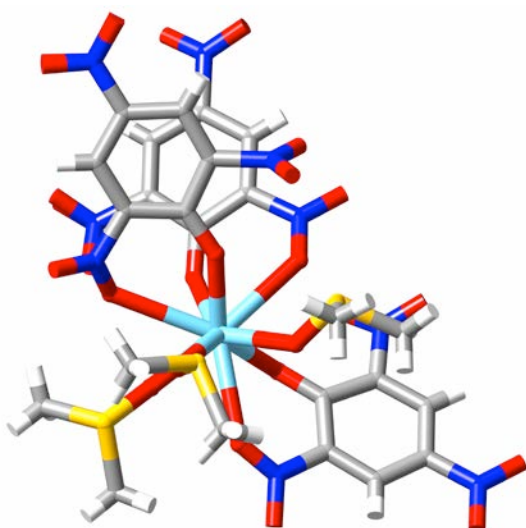




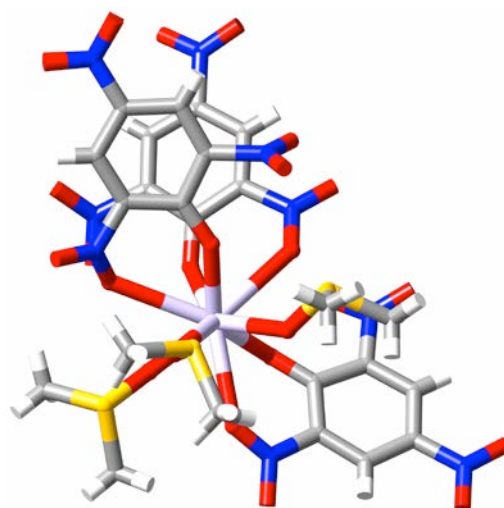
Ln = Gd



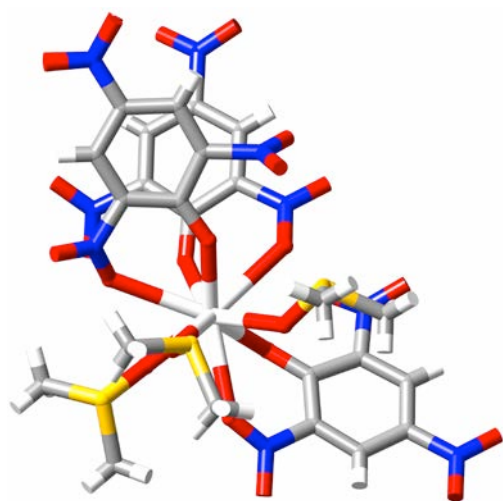
Ln = Dy



Ln = Yb



Ln = Lu



Ln = Y

Figure S2 Molecules present in the triclinic,  $P\bar{1}$ , form of  $mer$ -[Ln(pic)<sub>3</sub>(dmsu)<sub>3</sub>]. Stick representations, viewed down  $c$ . Disordered components are shown as if each site is fully occupied. The two inequivalent molecules are chiral but both enantiomers of each are present in the lattice.

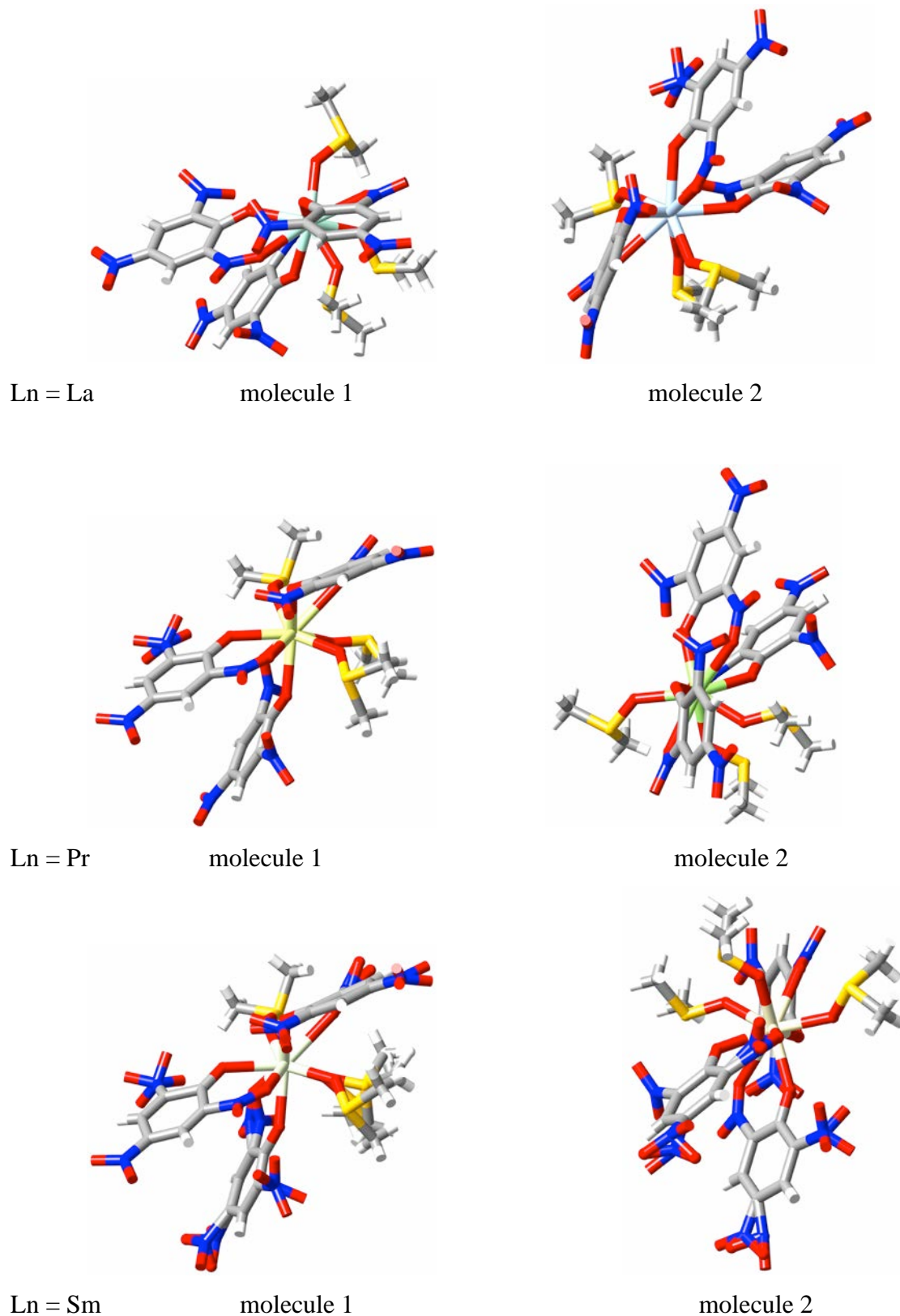


Figure S3 Molecules present in the triclinic,  $P\bar{1}$ , form of  $fac$ -[Ln(pic)<sub>3</sub>(OH<sub>2</sub>)(dmsO)<sub>2</sub>]. Stick representations, viewed down  $b$ . Disordered components are shown as if each site is fully occupied. The molecules are chiral but both enantiomers of each are present in the lattice.

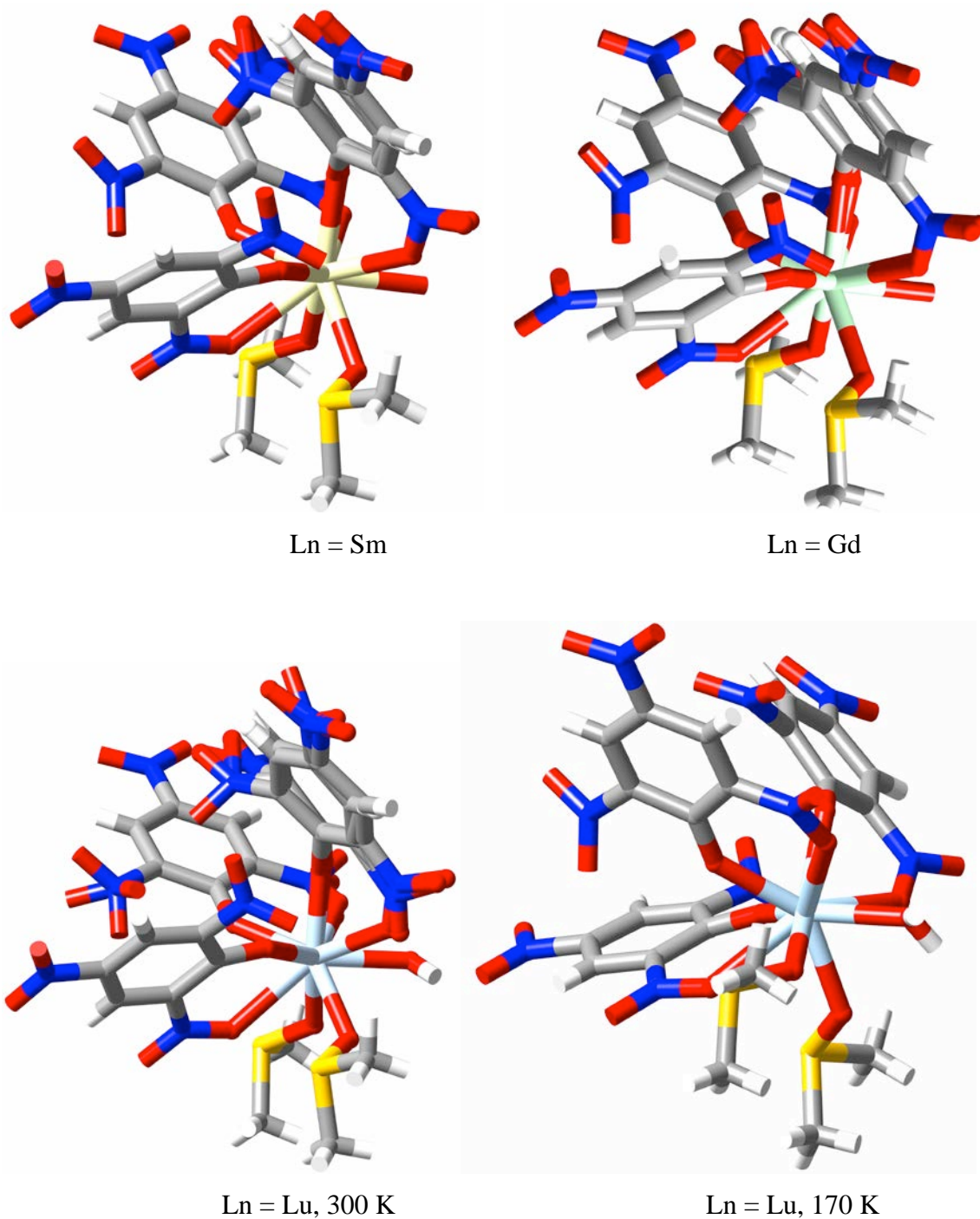


Figure S5 Projections down  $b$ , with the  $c$  axis vertical of portions of the lattices of the triclinic (upper) and monoclinic (lower) forms of  $mer$ -[La(pic)<sub>3</sub>(dms)<sub>3</sub>]. For clarity, hydrogen atoms and lesser components of disorder are not shown. Inequivalent La atoms of the triclinic form are shown in two shades of blue.

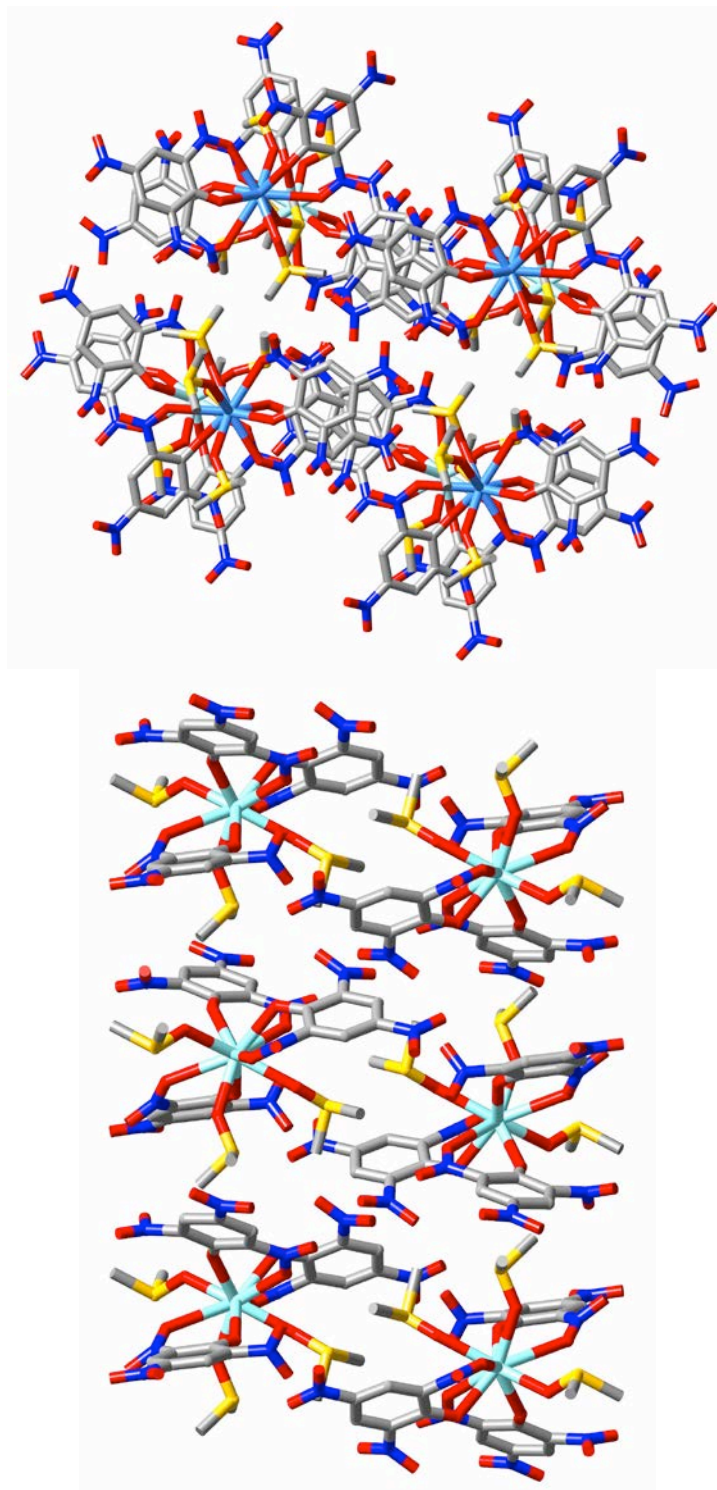


Figure S5 The Hirshfeld surface, "transparent"  $d_{nom}$  representation from CrystalExplorer, viewed down  $a$ ,  $b$  and  $c$ , for monoclinic,  $C2/c$  form,  $mer$ -[Y(pic)<sub>3</sub>(dms)<sub>3</sub>]. Red regions indicate points where interaction with external atoms exceed dispersion.

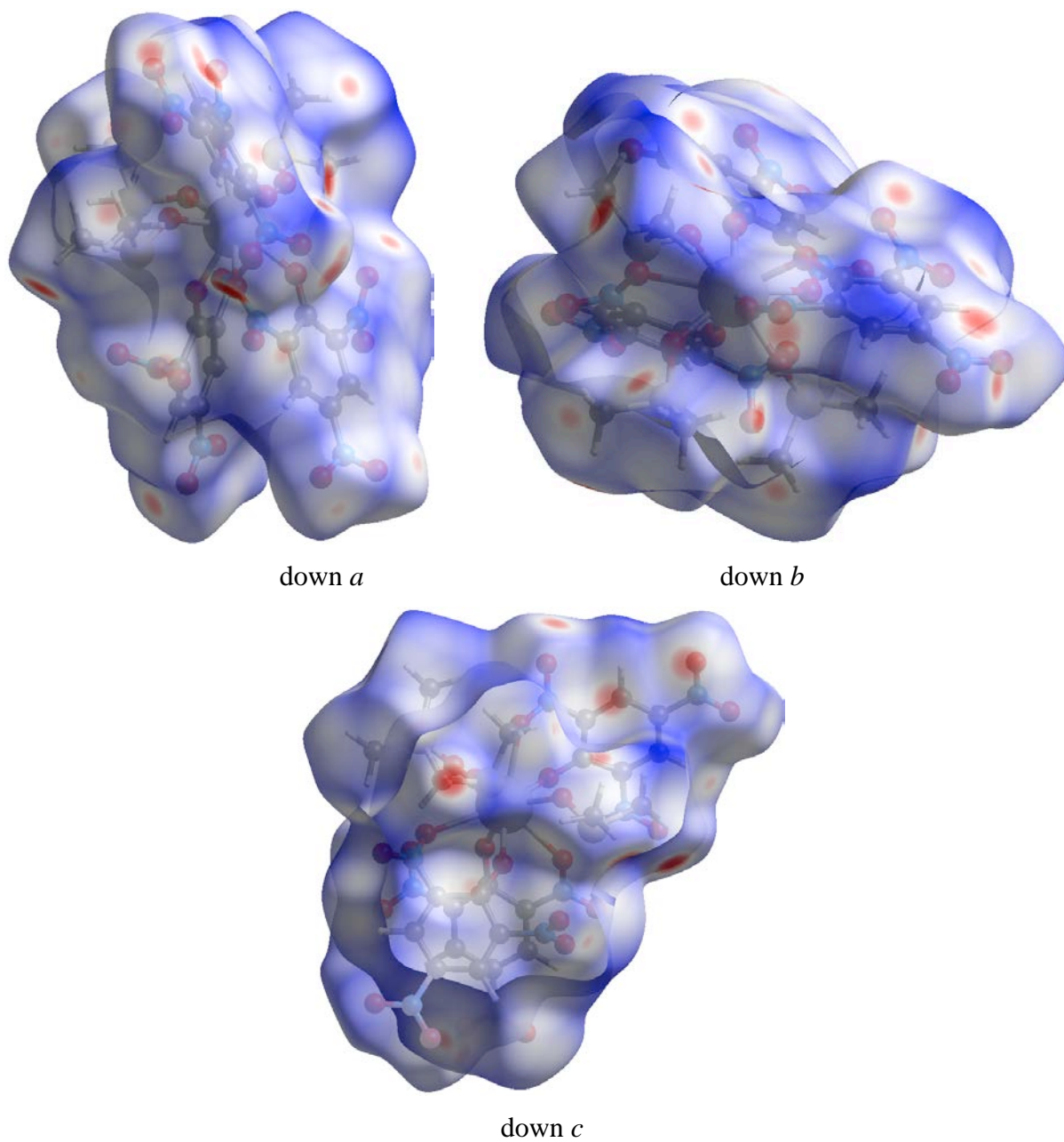
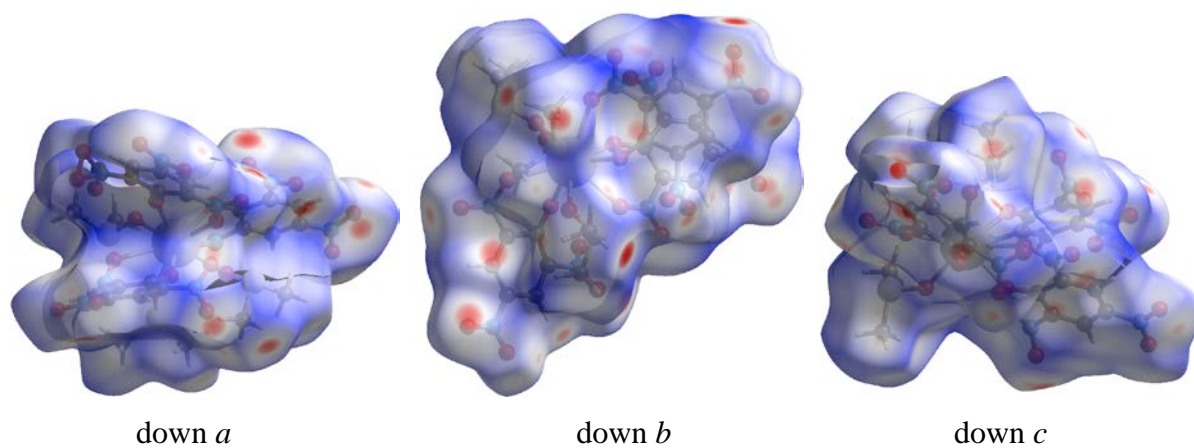




Figure S6 The Hirshfeld surface, "transparent"  $d_{nom}$  representation from CrystalExplorer, viewed down  $a$ ,  $b$  and  $c$ , for the two inequivalent molecules present in the lattice of the triclinic  $P\bar{1}$  form of  $mer$ -[La(pic)<sub>3</sub>(dmsu)<sub>3</sub>]. Red regions indicate points where interaction with external atoms exceed dispersion.

For La1:



For La2:

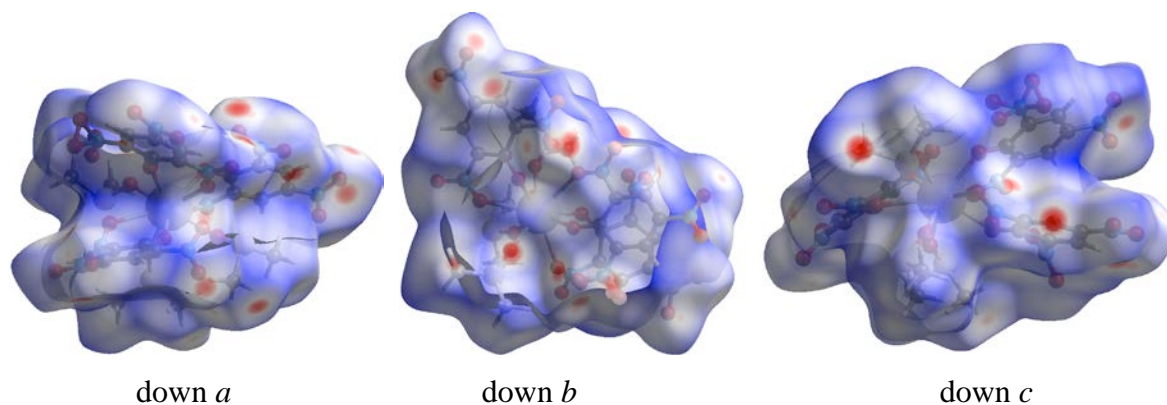


Table S1  
Some selected Ln-O bond lengths, *mer*-[Ln(dmsO-O)<sub>3</sub>(pic-O,O')<sub>3</sub>], 300 K

Phase Ln	Monoclinic			Triclinic			
	La	Lu	Y	(mol. 1)	La (mol. 2)	(mol. 1)	Pr (mol. 2)
<i>Distances (Å)</i>							
Ln-O(11)	2.442(3)	2.248(2)	2.292(4)	2.450(4)	2.458(4)	2.407(3)	2.431(3)
Ln-O(121)	2.755(4)	2.792(2)	2.771(4)	2.740(5)	2.798(4)	2.729(3)	2.798(3)
Ln-O(21)	2.417(3)	2.211(2)	2.263(4)	2.453(4)	2.440(5)	2.435(3)	2.399(3)
Ln-O(221)	2.758(4)	2.712(2)	2.699(4)	2.774(4)	2.676(5)	2.765(3)	2.660(3)
Ln-O(31)	2.450(3)	2.250(2)	2.290(4)	2.450(4)	2.436(4)	2.415(3)	2.407(3)
Ln-O(321)	2.786(4)	2.663(2)	2.651(4)	2.702(4)	2.762(3)	2.687(3)	2.757(3)
Ln-O(01)	2.419(3)	2.243(2)	2.272(4)	2.452(4)	2.448(4)	2.431(3)	2.416(3)
Ln-O(02)	2.414(4)	2.247(2)	2.291(4)	2.456(4)	2.426(4)	2.433(3)	2.399(4)
Ln-O(03)	2.413(3)	2.246(2)	2.291(4)	2.453(4)	2.462(4)	2.425(3)	2.434(3)

Table S2  
Some selected Ln-O bond lengths/Å, *fac*-[Ln(dmsO-O)<sub>3</sub>(OH<sub>2</sub>)(pic-O,O')<sub>2</sub>]

Bond	Sm (153 K)	Lu (170 K)
	Ln-O(11)	2.304(1)
Ln-O(121)	2.568(2)	2.501(3)
Ln-O(21)	2.342(1)	2.234(3)
Ln-O(221)	2.580(2)	2.591(3)
Ln-O(31)	2.34(2)	2.217(3)
Ln-O(321)	2.634(1)	2.658(3)
Ln-O(1)	2.412(1)	2.300(3)
Ln-O(01)	2.437(1)	2.325(3)
Ln-O(02)	2.438(1)	2.333(3)

For Sm only the bond lengths involving the major component of the disordered array are given. O(1) is the water molecule oxygen.

Table S3  
Selected picrate and dmsO parameters, [Ln(pic-O,O')<sub>3</sub>(dmsO)<sub>3</sub>]

Phase Ln	Monoclinic			Triclinic				Hydrated	
	La*	Lu	Y	(mol. 1)	La (mol. 2)	(mol. 1)	Pr (mol. 2)	Sm <sup>†</sup>	Lu (170 K)
<i>Phenoxide distances (Å)</i>									
O(11)-C(11)	1.257(6)	1.274(3)	1.269(7)	1.259(7)	1.265(7)	1.269(4)	1.260(5)	1.261(2)	1.268(5)
O(21)-C(21)	1.265(6)	1.274(3)	1.276(7)	1.284(7)	1.270(8)	1.274(5)	1.279(5)	1.265(2)	1.271(5)
O(31)-C(31)	1.265(5)	1.269(3)	1.281(7)	1.270(7)	1.278(7)	1.280(4)	1.278(4)	1.26(2)	1.266(5)
<i>C<sub>6</sub> (phenyl) Interplanar dihedral angles (°)</i>									
1/2	33.74(2)	34.76(13)	34.2(3)	29.4(2)	38.7(2)	30.57(15)	38.7(2)	72.62(7)	74.2(2)
1/3	40.3(2)	44.35(12)	43.4(2)	43.4(2)	43.0(2)	44.49(15)	42.6(2)	57.9(2)	60.7(2)
2/3	20.4(2)	24.41(13)	23.6(3)	19.3(2)	24.5(2)	20.62(15)	24.2(2)	62.8(2)	62.4(2)
<i>Inter-centroid distances (Å)</i>									
1/2	4.53 <sub>5</sub>	4.40 <sub>4</sub>	4.41 <sub>7</sub>	4.2 <sub>1</sub>	4.79 <sub>1</sub>	4.25 <sub>1</sub>	4.77 <sub>8</sub>	6.83 <sub>3</sub>	6.61 <sub>7</sub>
1/3	9.00 <sub>8</sub>	8.80 <sub>6</sub>	8.82 <sub>3</sub>	8.87 <sub>2</sub>	9.07 <sub>9</sub>	8.87 <sub>3</sub>	9.07 <sub>5</sub>	6.41 <sub>1</sub>	6.24 <sub>0</sub>
2/3	7.87 <sub>9</sub>	7.61 <sub>3</sub>	7.65 <sub>3</sub>	8.00 <sub>4</sub>	7.87 <sub>1</sub>	7.96 <sub>8</sub>	7.86 <sub>8</sub>	5.33 <sub>7</sub>	5.23 <sub>0</sub>
<i>Sulfoxide distances (Å)</i>									
O(01)-S(01)	1.531(4)	1.528(2)	1.527(4)	1.534(4)	1.517(5)	1.533(3)	1.530(3)	1.527(2)	1.525(3)
O(02)-S(02)	1.465(6)	1.527(2)	1.524(4)	1.525(4)	1.517(6)	1.533(3)	1.530(3)	1.539(14)	1.539(3)
O(03)-S(03)	1.474(4)	1.528(2)	1.530(4)	1.526(4)	1.523(4)	1.531(3)	1.523(3)		

\* Values for disordered components (Ln = La): sulfoxide distances O(01')-S(01') = 1.48(2), O(02')-S(02') = 1.426(5), O(03')-S(03') = 1.456(9) Å.

† Values for disordered components (Ln = Sm): phenoxide distance O(31')-C(31') = 1.26(2) Å; The inter-planar dihedral angle between C<sub>6</sub> 'phenyl' rings 3' and 1, 2 is 63.2(2), 55.9(2)°. The distances between C<sub>6</sub> 'phenyl' centroids 3'-1, 2 is 6.695, 5.329 Å.