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Article

Synthesis, Assembly, and Sizing of Neutral, Lanthanide Substituted Molybdenum Blue Wheels $\{Mo_{90}Ln_{10}\}$

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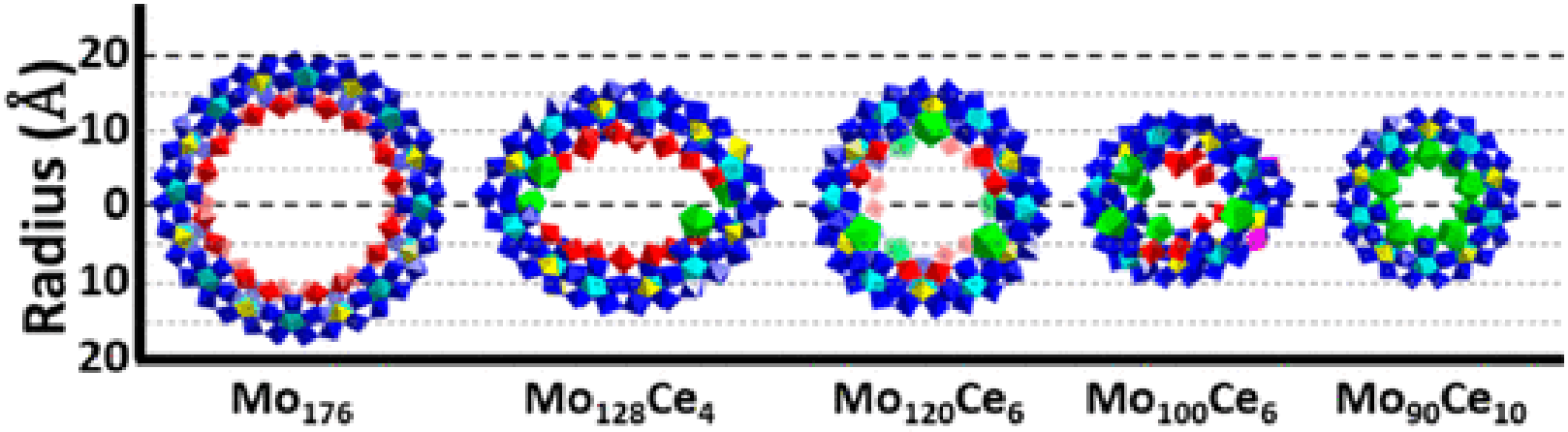

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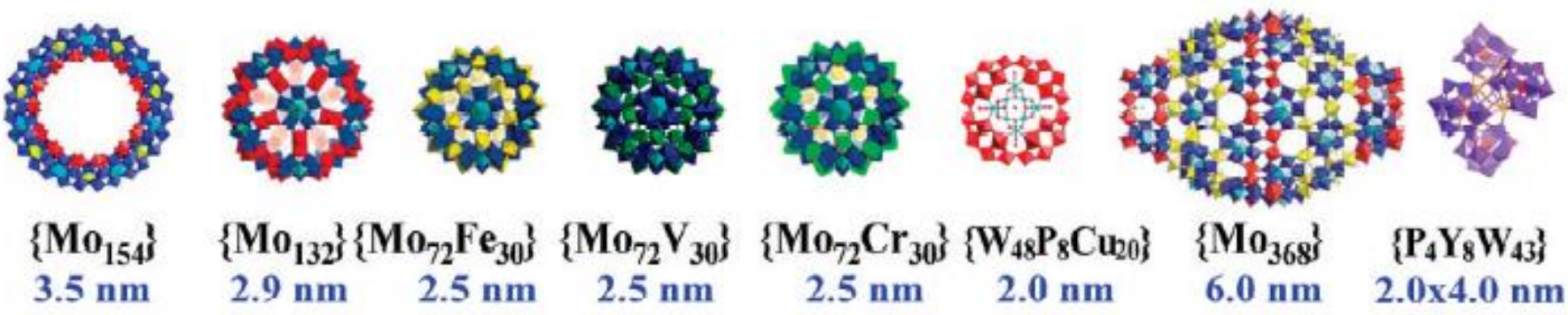
Polyoxometalate

- The POMs are formed by covalently connecting multiple transition metal (Mo, W, V, Cr, Ti, Fe, etc oxide polyhedrals (used as building blocks) and arranging them into geometrically beautiful molecula clusters. Most of large POM clusters are polyoxomolybdates, polyoxotungstates, and their heteropolyoxometalate derivatives.

- They are structurally well-defined and show a wide variety of structural, magnetic, and electronic properties. POMs offer unique opportunities in both fundamental studies and practical applications.

- Mostly, these large POMs are hydrophilic in nature and are very soluble in polar solvents, mainly Due to their surface water ligands coordinated to the metal centers and their inherent charges.

- Moreover, POMs serve as building blocks for the bottom-up assembly of organic–inorganic hybrid materials.



Liu.T, *et al*.,Langmuir 2010, 26(12), 9202–9213

Relevance to our group

- Synthesis and characterization of polyoxo metal nanocluster
- Studies of gas-phase properties of polyoxo metal cluster
- Studies on supramolecular interactions and self-assemblies of various metal clusters.

Spontaneous formation of autocatalytic sets with self-replicating inorganic metal oxide clusters

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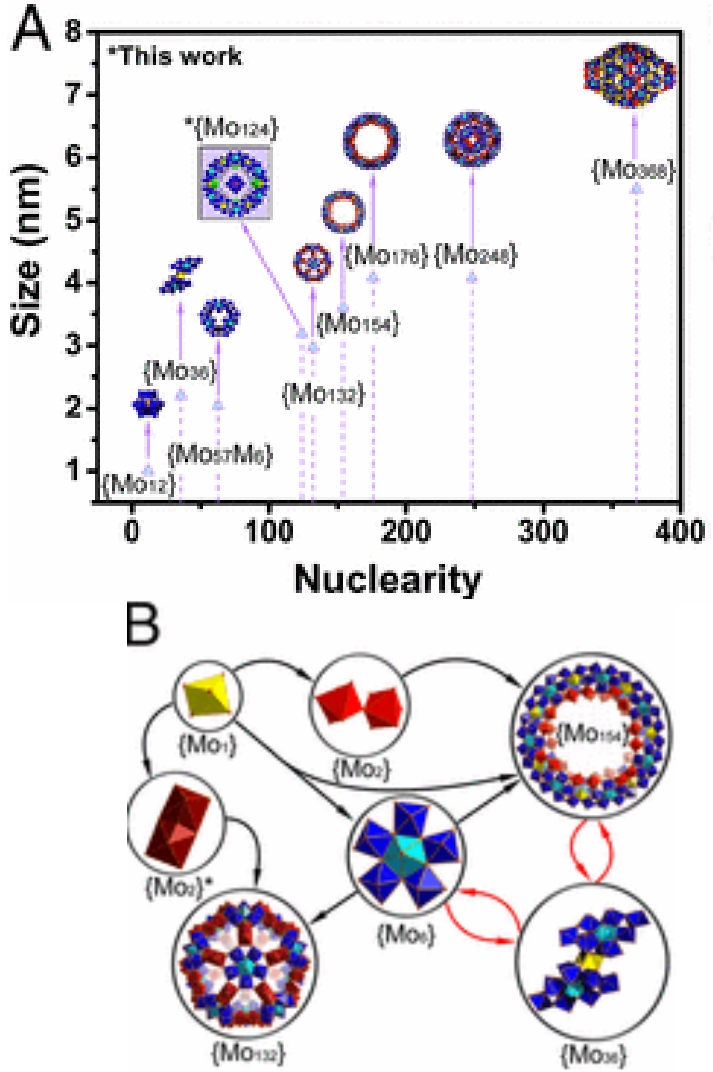

(A) Size-nuclearity correlation and hypothesized embedded autocatalytic network.
Comparative representation of molybdenum-based family:
$[PMo_{12}O_{40}]^{3-}$, {PMo_{12}}; $[Mo^{VI}_{36}O_{112}(H_2O)_{16}]^{8-}$, {Mo_{36}};
$[H_3Mo_{57}M_6(NO)_6O_{183}(H_2O)_{18}]^{22-}$, {$Mo_{57}M$};
$[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$, {Mo_{132}};
$[Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-}$, {Mo_{154}};
$[H_{16}Mo_{248}O_{720}(H_2O)_{128}]^{16-}$, {Mo_{248}};
$[H_{16}Mo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]^{48-}$, {Mo_{368}}.

(B) Hypothesized embedded autocatalytic set which funnels mass from small {Mo1} (yellow polyhedra) monomers into corner-shared (light red), edge-shared (dark red) dimers {Mo2}, {Mo6} (blue/cyan polyhedra) building blocks, {Mo36} templates and {Mo132} Keplerate ball and {Mo154} molybdenum-blue wheel.

Miras, et al., PNAS, 117, 20, 10699–10705

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Rare earth separations by selective borate crystallization

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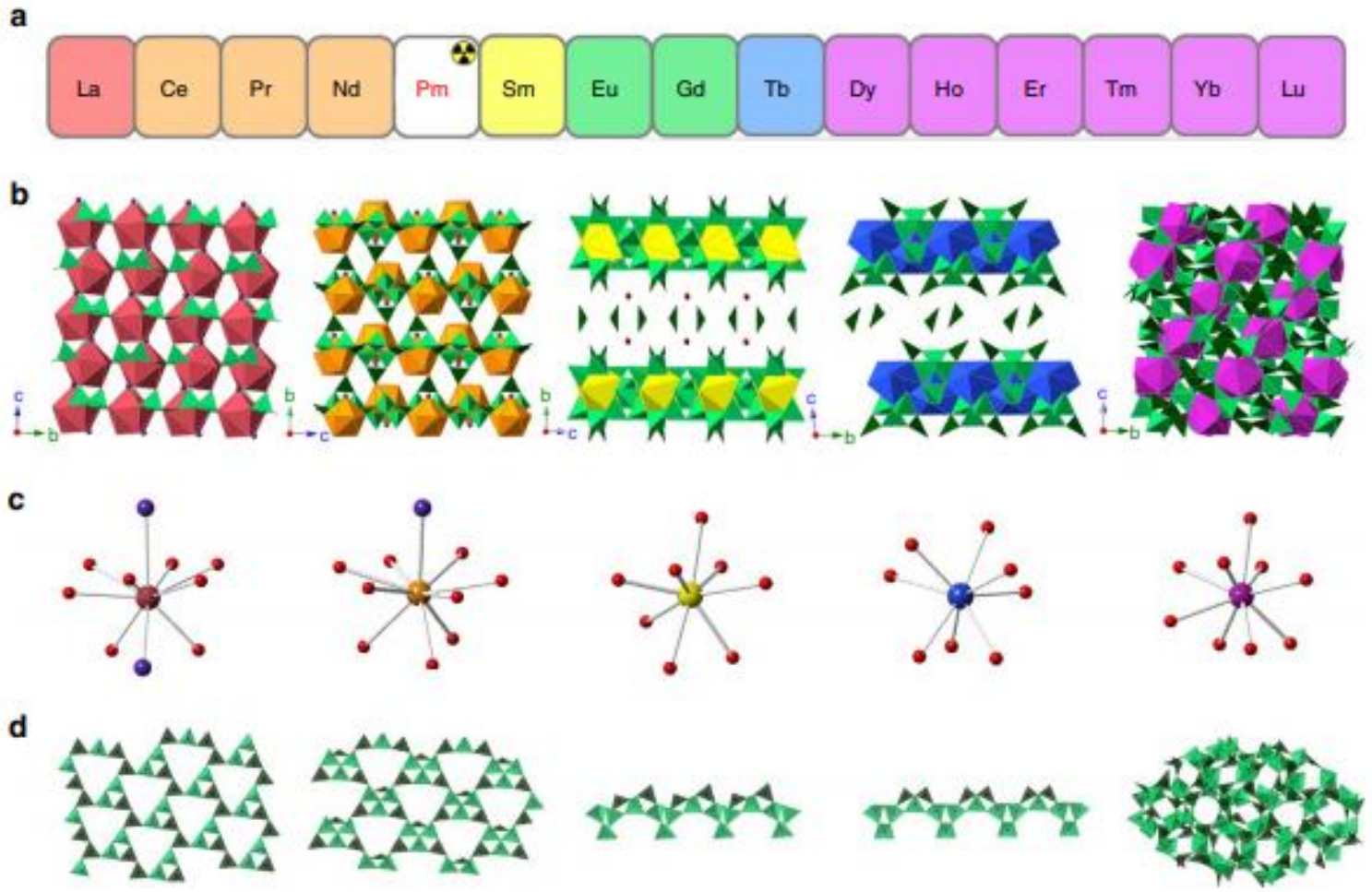
Table 1 | Result summary of Nd/Sm separation experiment.

Reaction times	Element	The molar mass in reactants per mmol	The molar mass in products per mmol	The molar mass in wash solutions per mmol	Crystallization yield	Separation factor*
3d	Nd	0.3 ± 0.015	0.0496 ± 0.0026	0.2204 ± 0.0197	0.2653 ± 0.0104	4.03 ± 0.22
	Sm	0.3 ± 0.015	0.0162 ± 0.0011	0.2861 ± 0.0082	0.0493 ± 0.0011	
5d	Nd	0.3 ± 0.015	0.2053 ± 0.0024	0.0700 ± 0.0020	0.7667 ± 0.0361	5.32 ± 0.18
	Sm	0.3 ± 0.015	0.1090 ± 0.0020	0.1963 ± 0.0009	0.3457 ± 0.0157	

Table 2 | Result summary of Nd/Dy separation experiment.

Reaction times	Element	The molar mass in reactants per mmol	The molar mass in NdBOCl-2 phase per mmol	The molar mass in LnBOCl-5 /LnBOCl-6 phase per mmol	The molar mass in wash solutions per mmol	Crystallization yield	Separation factor*
3d	Nd	0.3 ± 0.015	0.0412 ± 0.0036	—	0.1954 ± 0.0047	0.3487 ± 0.0090	67.76 ± 0.60
	Dy	0.3 ± 0.015	0.0007 ± 4E-5	—	0.2248 ± 0.0151	0.2607 ± 0.0045	
5d	Nd	0.3 ± 0.015	0.2960 ± 0.0034	0.0058 ± 0.0003	5.6E-5 ± 1.0E-5	0.9999 ± 0.0500	986.33 ± 57.15
	Dy	0.3 ± 0.015	0.0147 ± 0.0012	0.2871 ± 0.0033	3.4E-5 ± 0.6E-5	0.9999 ± 0.0500	



Periodic trend for the formation of lanthanide borates and crystal structures of five different structure types.
(a) Periodic trend of lanthanides for the crystallization products;
(b) depiction of the crystal structures; (c) Ln3 þ coordination geometries; (d) borate networks;

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Introduction

- They synthesize the first example of a neutral molybdenum blue ring by developing a new synthetic strategy using lanthanide ions (La, Ce, Pr) that replace all the $\{Mo_2\}$ building blocks. High temperatures, pH control, and carefully choosing the starting reagents are essential for a successful synthesis.

- Molecular compounds **1**, $\{Mo_{90}Ce_{10}O_{280}(H_2O)_{80}H_{10}\}$; **2,**$\{Mo_{90}La_{10}O_{280}(H_2O)_{80}H_{10}\}$ **3**, $\{Mo_{90}Pr_{10}O_{280}(H_2O)_{80}H_{10}\}\cdot 188H_2O$; **4**, $H\{Mo_{92}Nd_9O_{285}(H_2O)_{77}H_{10}\}$; **5**, $H\{Mo_{92}Sm_9O_{285}(H_2O)_{77}H_{10}\}$ are synthesized here.

- The $\{Mo_{90}Ln_{10}\}$ framework present herein is not only the first formally charge neutral polyoxometalate but also the smallest accessible molybdenum blue wheel of this type.

- All three structures share the same framework of $\{Mo_{90}Ln_{10}\}$ with the lanthanides occupying the inner circle of the ring. These structures are the first example of a neutral and smallest MB wheel till date.

- A similar structure has been obtained for Nd and Sm where one of the {Mo2} units remains in the cluster due to the inherent constriction caused by the smaller ionic radius of these lanthanides These structures are thought to be a reaction intermediate since it was also observed with larger lanthanide ions in some reactions.

Schematic representation of synthesis

Figure 1

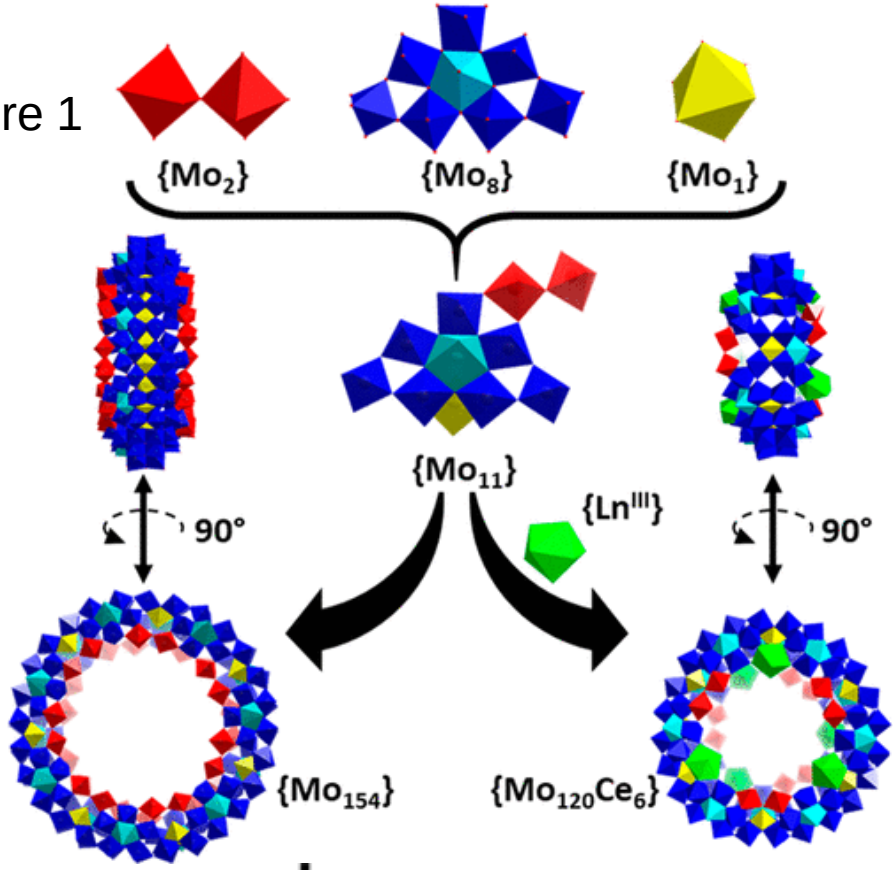
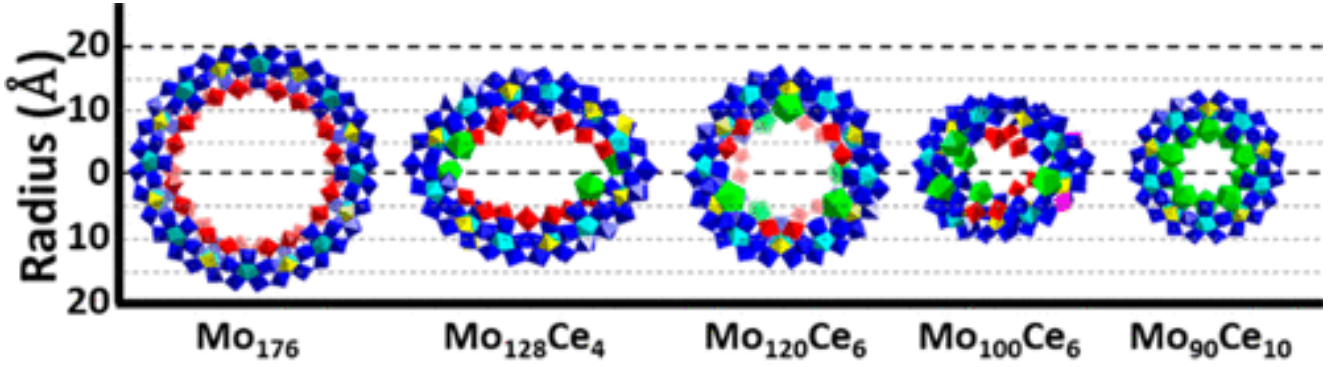


Figure 1. Schematic representation of the different MB rings obtained by adding or Omitting lanthanides from the reaction mixture: $\{Mo_{154}\}$,$\{Mo_{120}Ce_6\}$.

Figure 2. Schematic showing the relative change in radius (Å) of MB POMs upon increasing Ln incorporation: {Mo176}, {Mo128Ce4), {Mo120Ce6}, {Mo100Ce6), {Mo90Ce10}.

Figure 2



Crystal structure

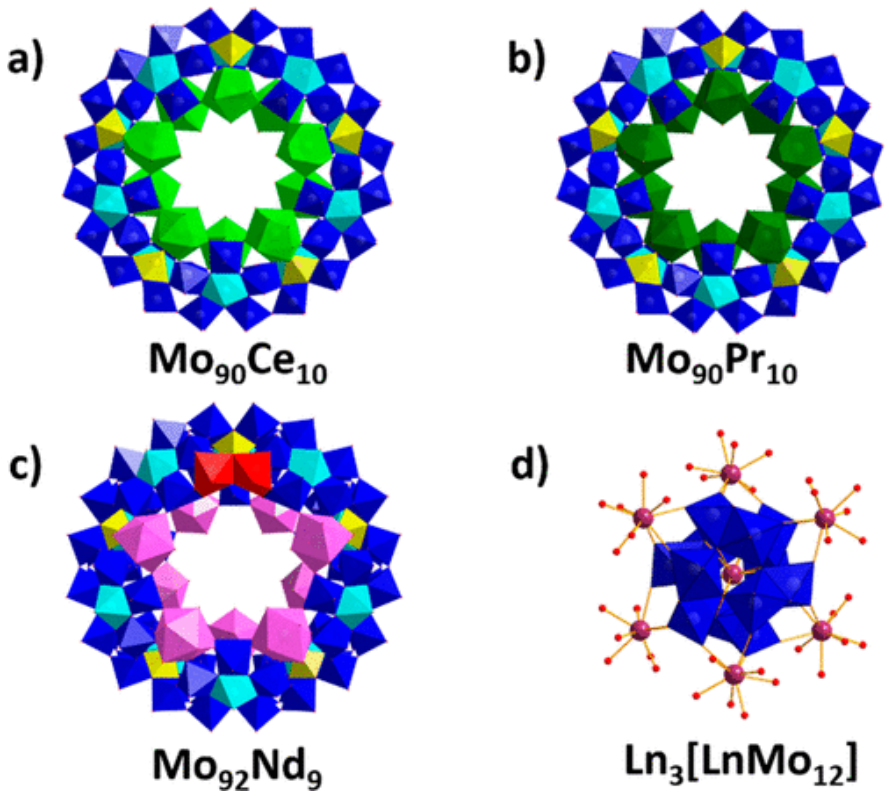


Figure 3. Polyhedral view of the solid state structure of 1 (a), 3 (b), and 4 (c). The general structure obtained as an oxidation product Ln3[LnMo12], where Ln = La, Ce, Pr, Nd is shown in (d). {Mo1}: yellow polyhedra. {Mo8}: blue polyhedra with central pentagonal units in cyan polyhedra. Nd: pink polyhedra. Ce: green polyhedra. Pr: dark green polyhedra. Ln ion: purple ball. O: red ball.

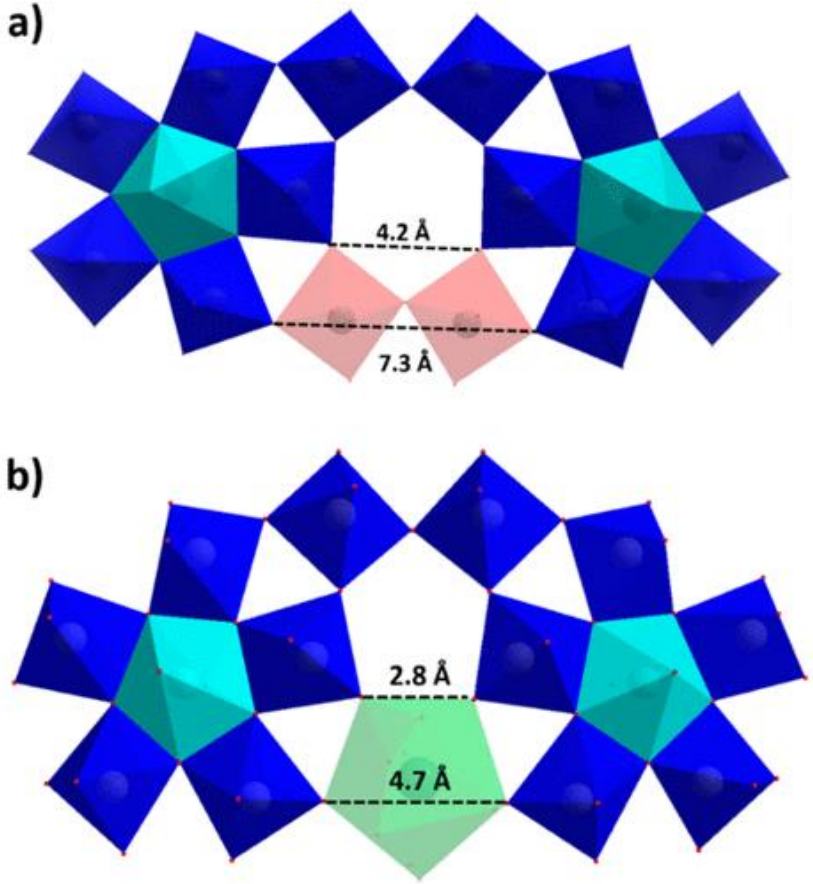


Figure 4. Comparison of the distances between equivalent oxygen atoms for two adjacent {Mo8} units for Mo154 (a) and Mo90Ln10 (b)

Synthesis of different Ln compounds

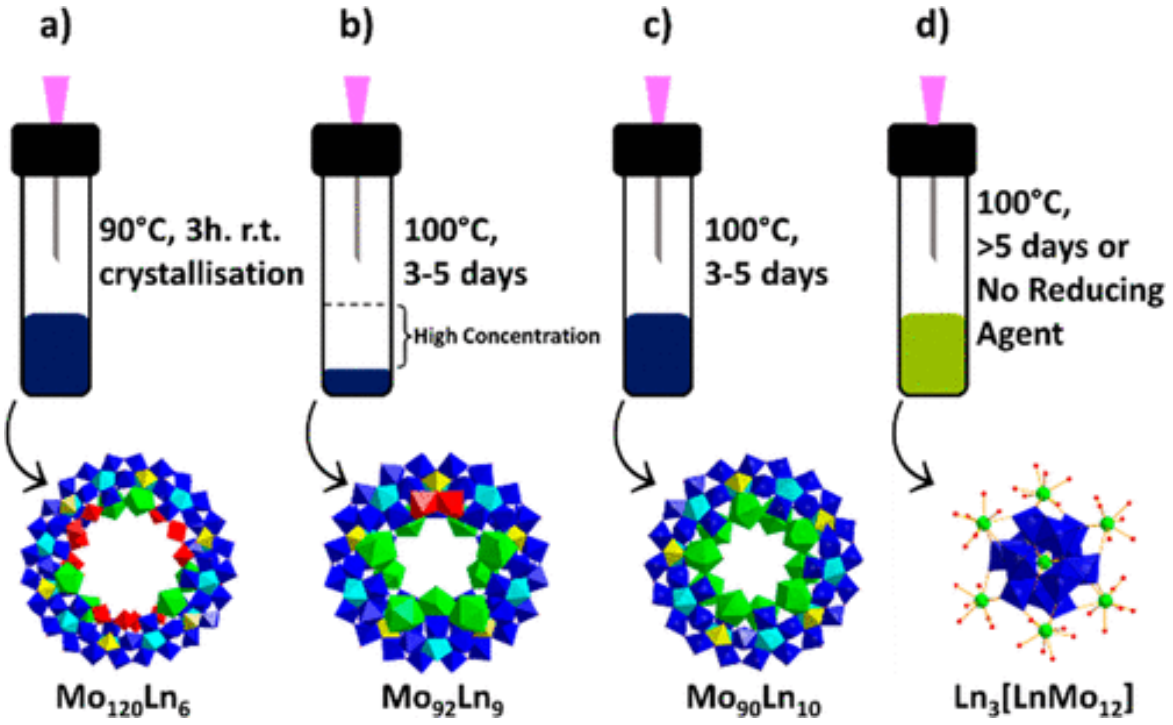


Figure 5. Schematic representation of the different compounds obtained under different conditions. The same acidified molybdate solution can yield these different clusters if they
(a) crystallize at room temperature,
(b) are under reducing conditions with high evaporation rate, (c) are under reducing conditions, or (d) are under nonreducing hydrothermal conditions.

Solution studies

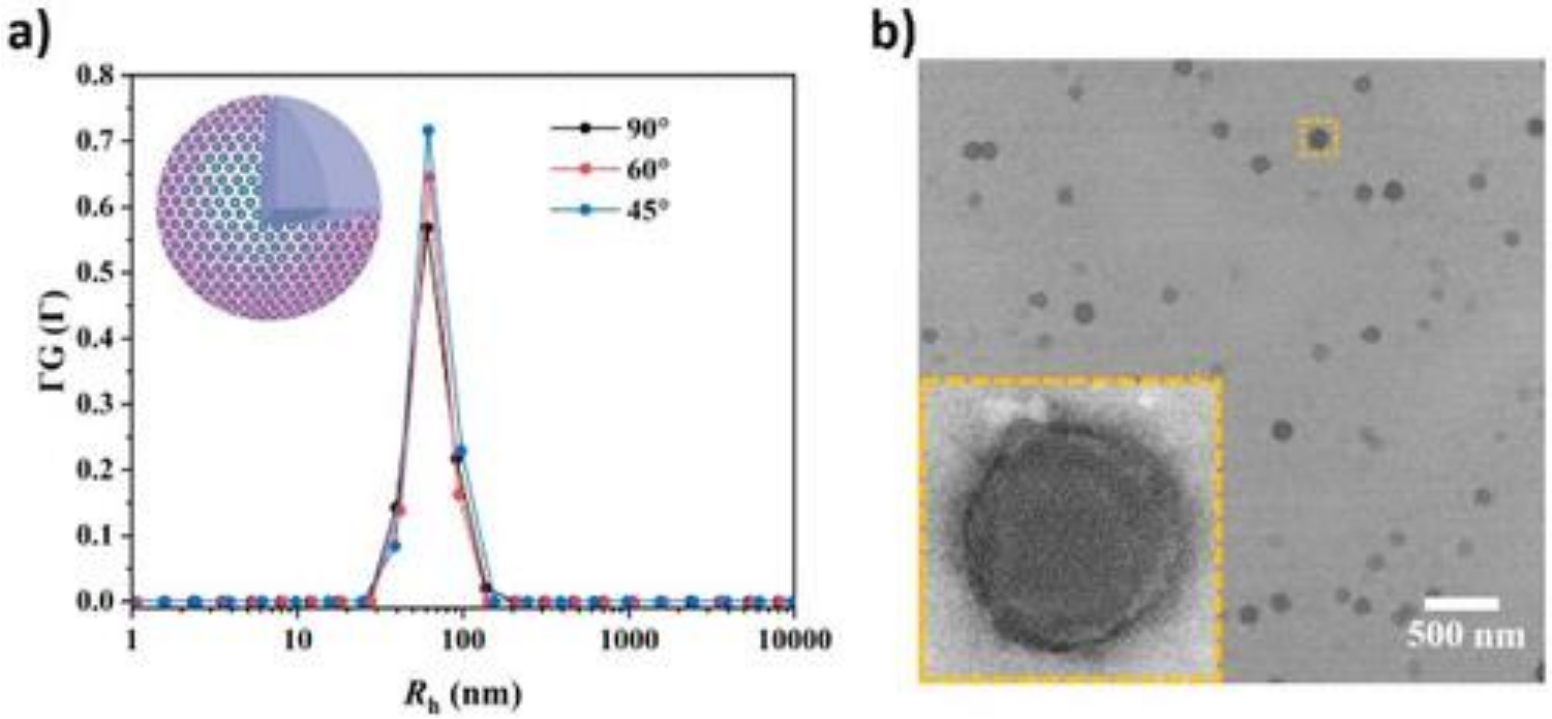


Figure 6. (a) DLS results of a solution of 1, $\{Mo_{90}Ce_{10}\}$ (40 equiv of $BaCl_2$) at different scattering angles. The R_h value is 62(±5) nm. (b) TEM images obtained from $\{Mo_{90}Ce_{10}\}$ solution with 40 equiv of $BaCl_2$.

Encapsulation experiments

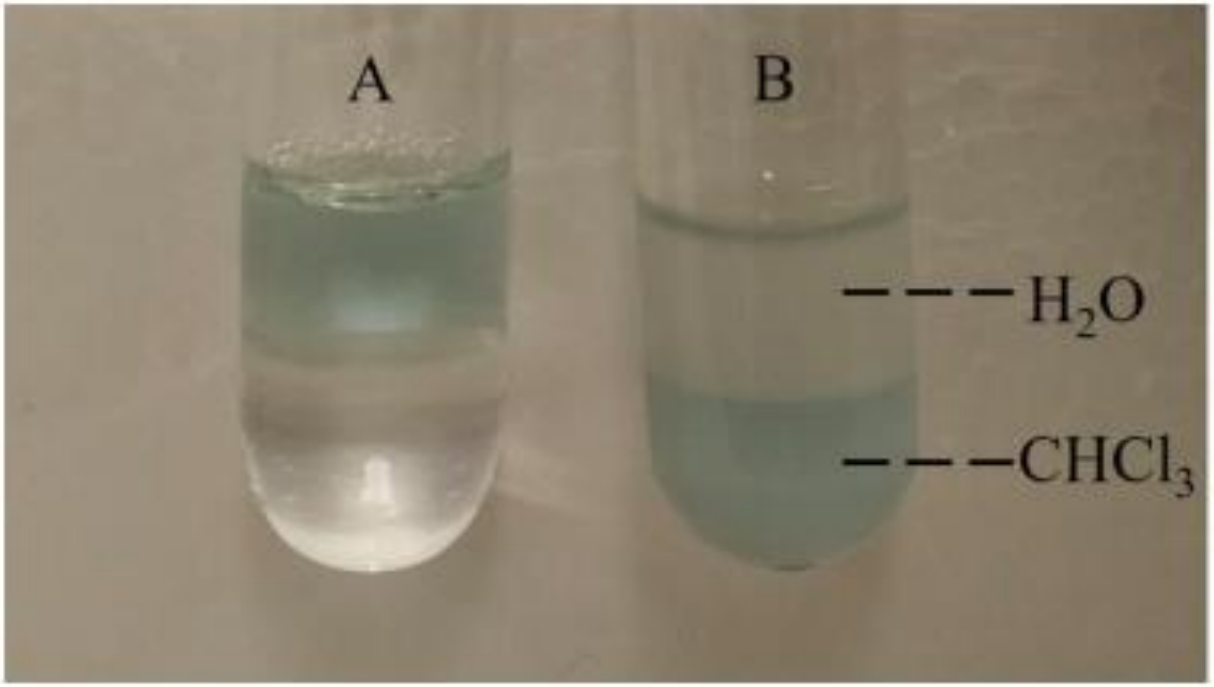


Figure S21. Encapsulation experiments to determine the charge nature of Mo90Ce10 ring.
A: Mo90Ce10 solution by adding negatively charged SDS surfactant.
B: Mo90Ce10 solution by adding positively charged CTAB surfactant.
The Mo90Ce10 ring can bind with positively charged CTAB and therefore,
the overall surfactant-encapsulated complexes are more soluble in organic solvent (CHCl3).

Solution studies- TGA analysis

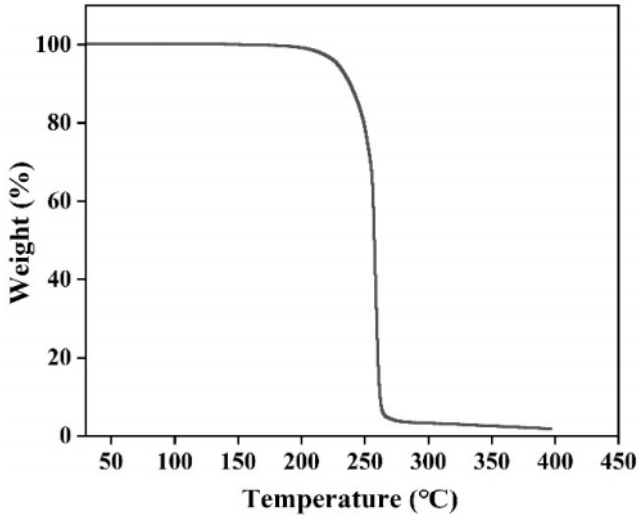


Figure S22. TGA results of CTAB. The weight loss of CTAB occurs at temperature between 200℃ and 300 ℃.

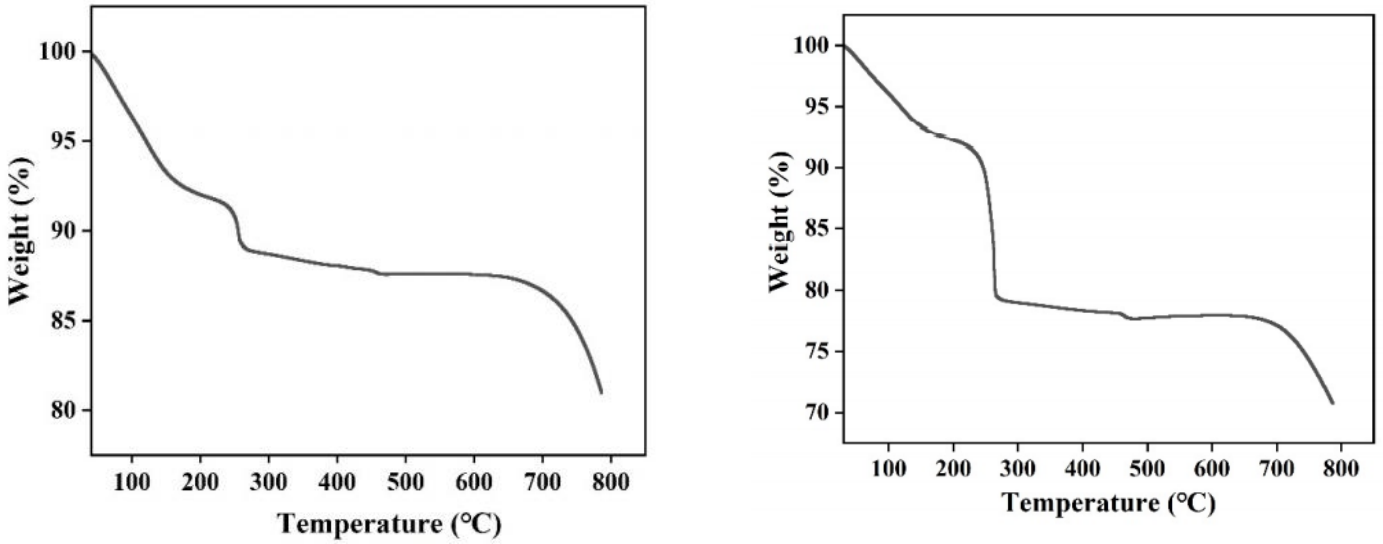


Figure S23. TGA results of dried solids obtained from solution of Mo90Ce10-CTAB complex at pH=0.5, and pH=2.

Solution studies-self assembly study

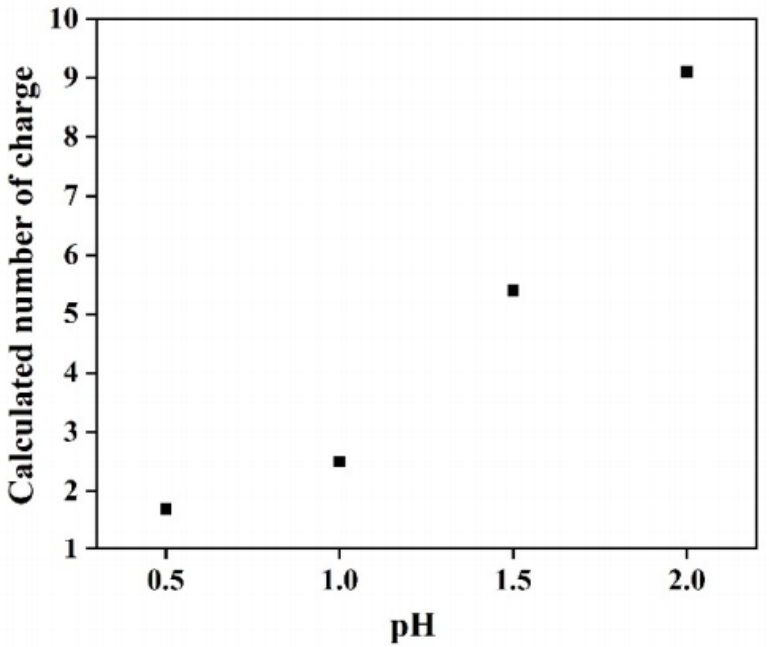


Figure S27. The correlation between surface charge of $Mo_{90}Ce_{10}$ and solution pH.
The charge number is calculated based on the weight loss of CTAB in $Mo_{90}Ce_{10}$-CTAB complex.

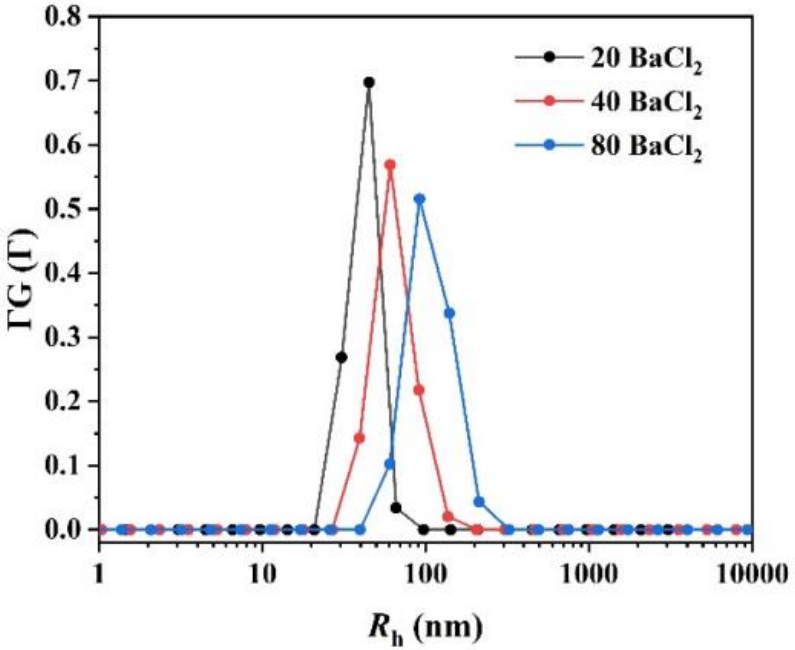
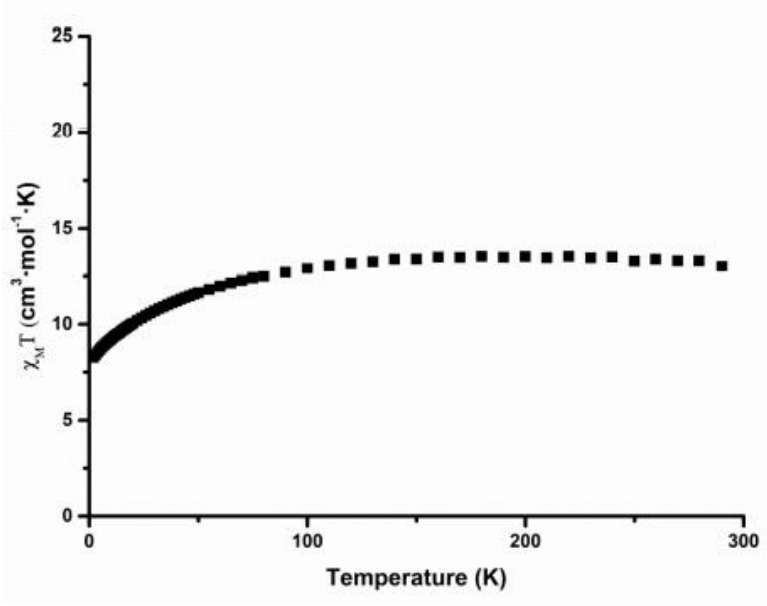
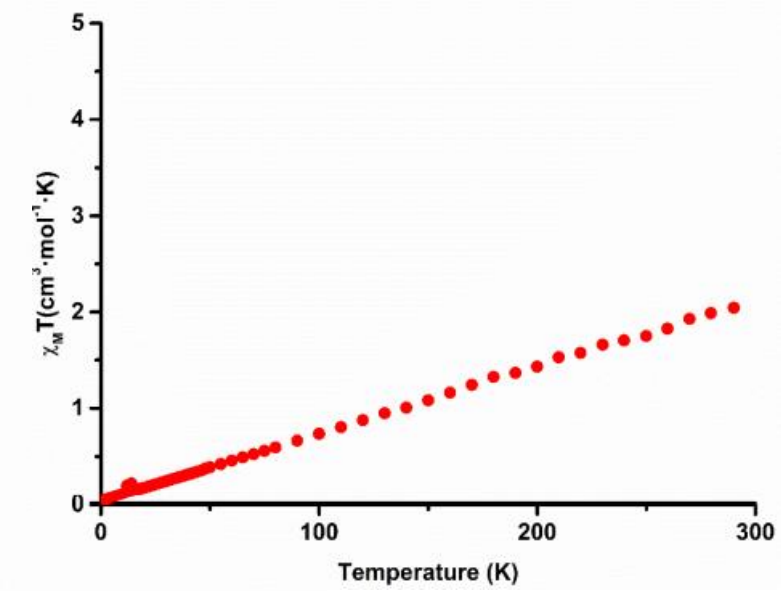


Figure S29. DLS measurements of $Mo_{90}Ce_{10}$ solution when adding different amounts of $BaCl_2$.

Magnetic studies





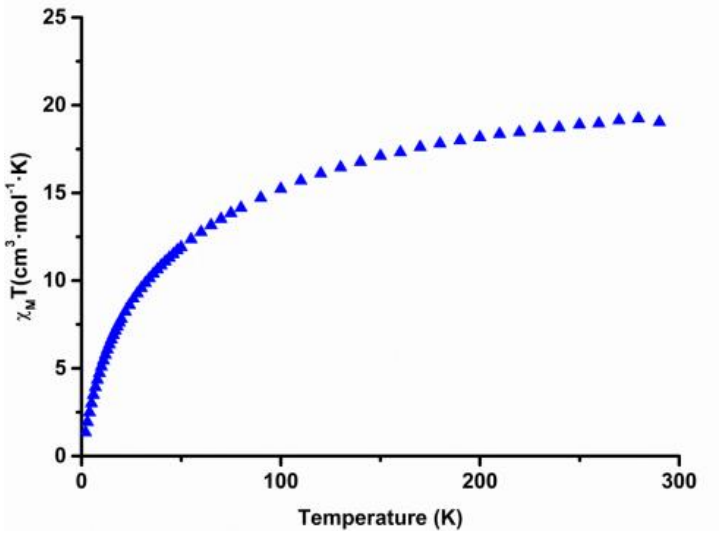


Figure S14-S17. Temperature dependence of χMT from 290 to 2 K measured with a DC field of 0.1 T for compound 1-4.

Lanthanide Separation studies

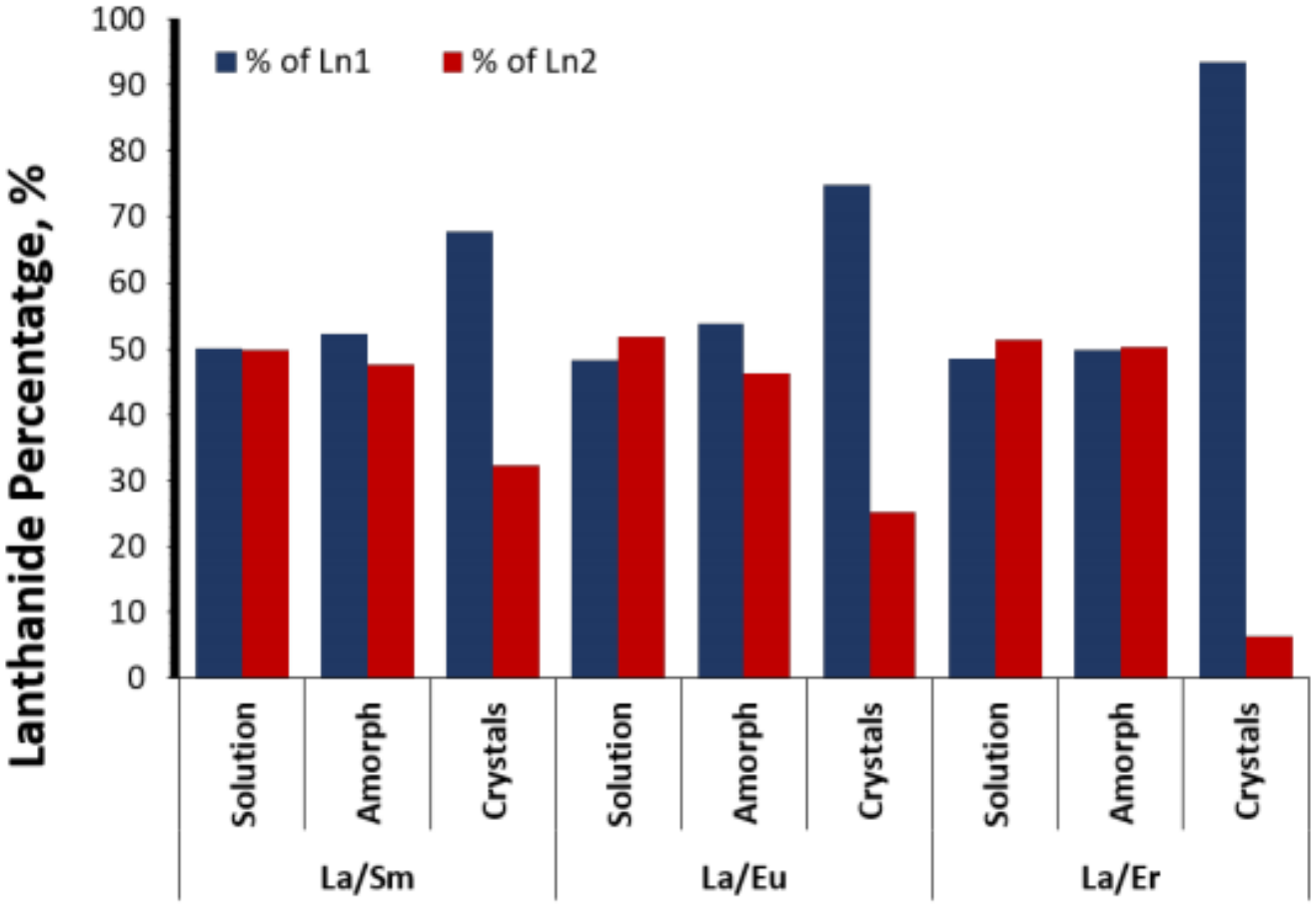


Figure S3. Comparison of the lanthanide composition between the different states (in solution, precipitated amorph and the isolated crystals) of the sample for the mixtures of La with Sm, Eu and Er.

Structural transformation

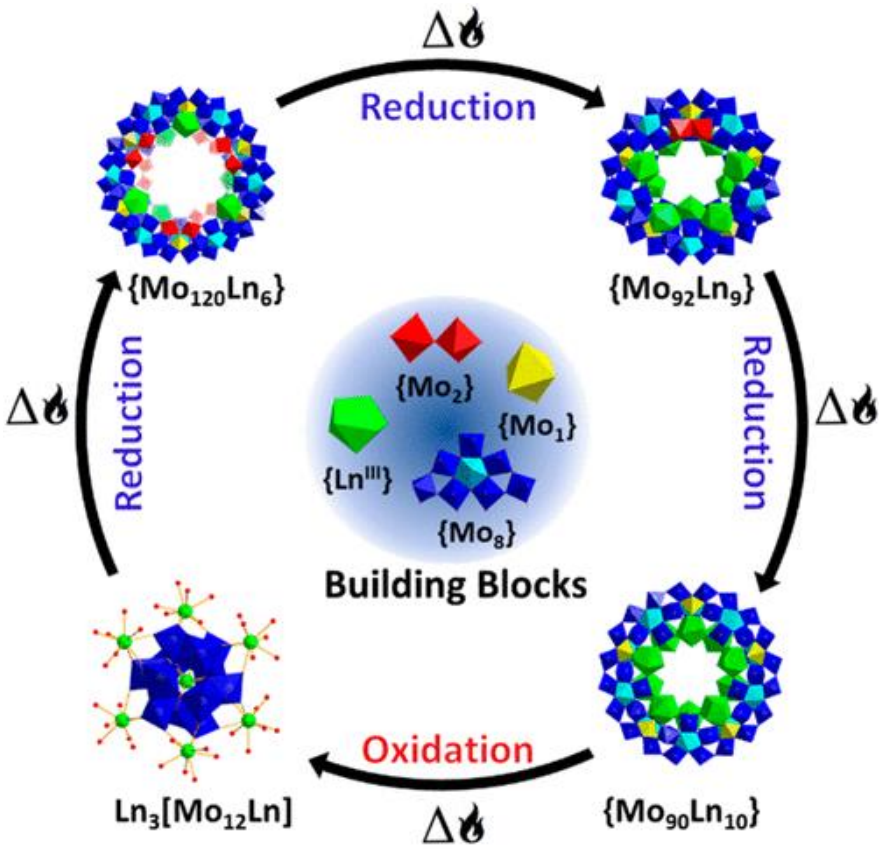


Figure 7. Structure transformation from $\{Mo_{120}Ln_6\}$ to $\{Mo_{92}Ln_9\}$ to $\{Mo_{90}Ln_{10}\}$ and finally to $Ln_3[LnMo_{12}]$ depending on the reaction conditions.

Conclusion

- We have successfully synthesized the first example of a neutral molybdenum blue ring by developing a new synthetic strategy using lanthanide ions (La, Ce, Pr) that replace all the {Mo2} building blocks.

- High temperatures, pH control, and carefully choosing the starting reagents are essential for a successful synthesis. All three structures share the same framework of {Mo90Ln10} with the lanthanides occupying the inner circle of the ring. These structures are the first example of a neutral MB wheel and the smallest ones reported to date.

- As the ionic radius of the lanthanide plays a role in the structure formation, several tests of lathanide separation were conducted showing promising results separating early lanthanides from later ones. Taking advantage of the subtleties of the self-assembly process, we have demonstrated effective enrichment of lanthanide ions from binary mixtures in the synthesis of {Mo90Ln10}.

- Continued exposure to these high temperatures eventually consumes all the reducing agent present in the system, causing a structure transformation from {Mo90Ln10} to Ln3[LnMo12], which in turn can be rereduced to the {Mo120Ln6} and, if heated again, back to the {Mo90Ln10}.

- These results to utilize the self-assembly of molybdenum blue POMs for high-yielding scalable lanthanide separation processes.