Supporting Information

A Record-Breaking Loading Capacity for Single-Molecule Magnet Mn_{12} Clusters Achieved in a Mesoporous Ln-MOF

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General Procedures

All materials, reagents were of commercial origin and used without further purification. Microanalyses of C, H, and N were determined by a CE instruments EA 1110 elemental analyzer. The infrared spectrum was recorded on a Nicolet AVATAR FT-IR 330 Spectrophotomete with pressed KBr pellets. Magnetic measurement was tested by using a Quantum Design MPMS superconducting quantum interference device (SQUID). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves were measured by a SDT-Q600 thermal analyzer in N_2 atmosphere. Thermogravimetric analysis (TGA) curves were recorded on a Netzsch TG209F1 thermal analyzer in air atmosphere. Powder X-ray diffraction patterns were collected by a Rigaku Ultima IV diffractionmeter with Cu Kα radiation (λ = 1.5418 Å) and a graphite monochromator from 3 to 50° at room temperature. The La-Mn ratio data was evaluated by an Agilent 7700x ICP-MS and analyzed using ICP-MS MassHunter version B01.03. Energy dispersive X-ray (EDX) spectrum was marked on scanning electron microscopy (SEM) (Hitachi S-4800, 15kV). ^{1}H NMR spectrum was recorded on a Bruck Avance III 500MHz spectrometer. The adsorption samples were activated in dired EtOH at first and then were evacuated in a Tousimis Samdri-PVT-3D by supercritical carbon dioxide so that the EtOH guests were completely replaced by liquid CO_2. N_2 adsorption isotherms were performed on Micromeritics ASAP 2020 PLUS. The pore size distribution (PSD) curves were calculated using Harkins and Jura Thickness model for N_2 adsorption.

X-ray crystallography.

Structure Data of **1** were determined by an Agilent technologies Super Nova Micro Focus single Crystal Diffractometer using Cu-Kα radiation (λ = 1.54184 Å). Absorption corrections were carried out by using the multi-scan program. The structure was solved by direct methods (ShelXT),[1] and the non-hydrogen atoms were refined aniostropically by full-matrix least-squares method on F^2 using ShelXL on the OLEX 2.[2,3] Guest molecules were removed through SQUEEZE in structure refinement due to disorder.[4] For **1R**(298K), there are 1887 electrons within 9623 Å^3 void volume per unit cell, corresponding to 7 DMF and 3.5 water molecules per formula unit. For **1S**(298K), the SQUEEZE analyses reveal that there are 2229 electrons within 9788 Å^3 void volume per unit cell. There are extra 7 DMF and 9 water molecules per formula unit based on calculation. However, the amount of water molecules was inconstant at ambient due to the existence of mesopores. TGA results shows 3.37% weight loss from room temperature to 100 ^{o}C in N_2 atmosphere, corresponding to the loss of five water molecules (calcd. 3.60%) (**Figure S8a, S12**). CCDC 1886724-1886727 contain the supplementary crystallographic data for **1R**(100K), **1R**(298K), **1S**(100K) and **1S**(298K), respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Syntheses of samples.

Syntheses of $Mn_{12}O_{12}(Ac)_{16}(H_2O)_4$•HAc•$4H_2O$ ($Mn_{12}Ac$).

$Mn_{12}Ac$ was obtained by the method introduced in previous literature.[5] The filtrated solid materials washed by dried CH_3CN in order to remove partial guest CH_3COOH molecules. X-ray powder diffraction (PXRD) was used to confirm the purity of the crystalline solid (**Figure S13**). Anal. Calcd. for $Mn_{12}H_{68}C_{34}O_{54}$ (FW = 2000.13, based on one CH_3COOH and four water guest molecules): C, 20.42%; H, 3.43%. Found: C, 20.56%; H, 3.65%. IR for **$Mn_{12}Ac$** (KBr pallet, cm^{-1}) (**Figure S14**): 3598(s), 3347(w), 2935(w), 1756(w), 1709(s), 1589(s), 1562(s), 1515(s), 1445(s), 1388(w), 1331(s), 1256(w), 1050(s), 1023(s), 958(s), 931(w), 713(s), 674(s), 641(s), 610(s), 561(s),

514(s), 408(s).

Syntheses of $La_4(HL)_5(HLac)_2(i\text{-}PrOH)_2(DMF)_2 \cdot 7DMF \cdot 5H_2O$ (1).

A mixture of $La(NO_3)_3 \cdot 6H_2O$ (0.217 g, 0.5 mmol), 5-Hydroxyisophthalic acid (H_3L, 0.091 g, 0.5 mmol) and racemic lactic acid (*rac*-H_2Lac, 4 drops) were added to the mixed solution of N,N-dimethylformamide (DMF, 9 mL) and isopropanol (*i*-PrOH,1 mL). The resulting mixture was then sealed in a 23 mL Teflon-lined stainless steel container after stirring for a period of time. The container and its content were heated to 120°C and maintained at this temperature for 2 days, then cooled to 30 °C at a rate of 2 °C/h. Colorless rod-like crystals of **1R** and **1S** (yield 45% based on H_3L) were collected after washing with dried DMF. TGA results shows 3.37% weight loss from room temperature to 100 °C in N_2 atmosphere, corresponding to the loss of five water molecules (calcd. 3.60%) (**Figure S8a, S12**). Anal. Calcd. for $La_4H_{119}C_{79}N_9O_{47}$ (FW = 2502.44, based on seven DMF and five water guest molecules): C, 37.92%; H, 4.79%; N, 5.04%. Found: C, 38.09%; H, 4.76%; N, 4.95%. IR for **1** (KBr pallet, cm^{-1}) (**Figure S14**): 3386(s), 2970(w), 2692(w), 2510(w), 1658(s), 1552(s), 1376(s), 1380(s), 1301(w), 1273(m), 1221(m), 1105(s), 1056(m), 1002(s), 973(s), 936(s), 894(s), 861(s), 777(s), 725(s), 670(s), 613(s), 552(s), 492(m), 440(s).

Preparation of Mn_{12}Ac@1 sample.

In the consideration of gradual degradation of **Mn_{12}Ac** in DMF, racemic crystals of **1** were washed by dried CH_3CN for several times and immersed in dried CH_3CN for 3 days to remove the guest DMF molecules. X-ray powder diffraction confirms the integrity of the structure (**Figure S5**). Anal. Calcd. for activated sample ($La_4H_{93}C_{60}N_3O_{50}$, FW = 2211.99, based on one CH_3CN and 15 water guest molecules) : C, 32.58%; H, 4.24%; N, 1.90%. Found: C, 32.23%; H, 4.01%; N, 2.32%. IR for activated sample (KBr pallet, cm^{-1}) (**Figure S14**): 3358(s), 2933(w), 2695(w), 2529(w), 1658(s), 1552(s), 1388(s), 1304(w), 1275(m), 1224(m), 1109(s), 1049(m), 1001(s), 976(s), 937(s), 893(s), 864(s), 781(s), 720(s), 673(s), 616(s), 552(s), 491(m), 440(s).

Mn_{12}Ac@1 sample was obtained by soaking 100 mg activated sample of **1** in 30 mL CH_3CN solution under N_2 atmosphere. In order to keep the integrity of the crystal, the shaking table with rotational speed of 150 r/min, rather than continual stirring, was used to encapsulate the **Mn_{12}Ac**. The deep brown solid was repeatedly washed by dried CH_3CN until supernatant liquid became colorless. IR for activated sample (KBr pallet, cm^{-1}) (**Figure S14**): 3377(s), 2927(w), 2708(w), 2529(w), 1658(s), 1543(s), 1384(s), 1305(w), 1276(m), 1223(m), 1115(s), 1050(m), 1022(m), 1002(s), 976(s), 934(m), 892(m), 867(w), 781(s), 723(s), 669(s), 611(s), 561(w), 495(w), 441(s).

Table S1. Crystal parameters for **1**.

Complex	**1R**	**1R**	**1S**	**1S**
Formula	$La_4C_{58}H_{58}N_2O_{35}$	$La_4C_{58}H_{58}N_2O_{35}$	$La_4C_{58}H_{58}N_2O_{35}$	$La_4C_{58}H_{58}N_2O_{35}$
Formula weight	1898.70	1898.70	1898.70	1898.70
Temperature / K	100	298	100	298
Crystal system	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Space group	$P6_322$	$P6_322$	$P6_322$	$P6_322$
a / Å	33.6836 (8)	34.4634 (4)	33.7571 (7)	34.4770 (4)
b / Å	33.6836 (8)	34.4634 (4)	33.7571 (7)	34.4770 (4)
c / Å	18.6292 (5)	18.7047 (2)	18.6144 (3)	18.7059 (2)
α / °	90.00	90.00	90.00	90.00
β / °	90.00	90.00	90.00	90.00
γ / °	120.00	120.00	120.00	120.00
V / $Å^3$	18304.7 (8)	19239.7 (5)	18370.0 (8)	19256.1 (5)
Formula units Z	6	6	6	6
Dc / g cm^{-3}	1.033	0.983	1.030	0.982
μ / mm^{-1}	11.06	10.52	11.02	10.51
Data/parameters	10460/444	10870/456	11819/444	13005/466
2θ / °	7.0-131.8	7.0-130.0	7.0-143.4	7.0 - 149.8
Observed reflections	39317	92950	44180	49813
F (000)	5568	5568	5568	5568
GOOF	1.05	1.07	1.03	1.06
$R_1[I > 2\sigma(I)]$[a]	0.079	0.059	0.053	0.068
wR_2(All data)[b]	0.204	0.165	0.138	0.195
R(int)	0.068	0.096	0.059	0.062
Absolute structure parameter	0.154 (11)	0.124 (10)	0.110 (8)	0.152 (10)
CCDC number	1886724	1886725	1886726	1886727

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

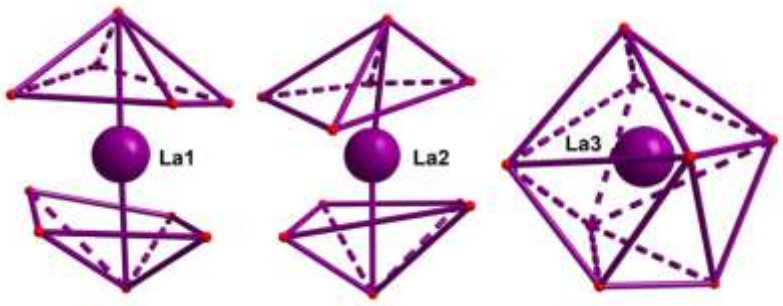

Figure S1. Ball-and-stick representation of coordination environments of La(III) in **1S**.

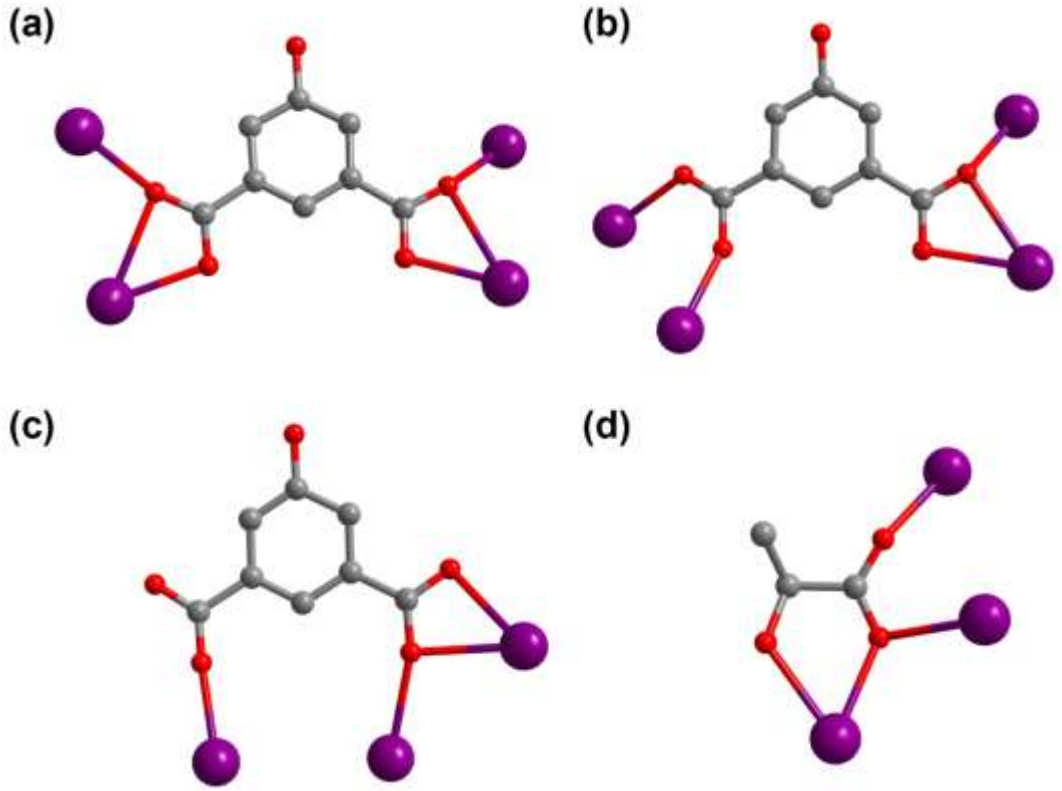

Figure S2. Coordination modes of HL^{2-} in μ_4:η^2:η^1:η^1:η^2:η^0 (a), μ_4:η^2:η^1:η^1:η^1:η^0 (b) and μ_3:η^1:η^2:η^1:η^0:η^0 fashion (c) respectively; coordination mode of deprotonated lactic acid in μ_3:η^1:η^2:η^1 fashion (d) in **1S**.

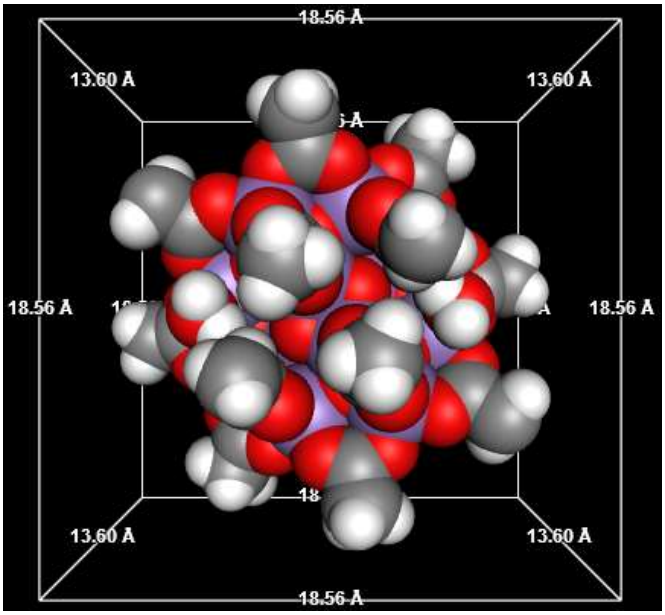

Figure S3. Dimension of single **Mn_{12}Ac** cluster.

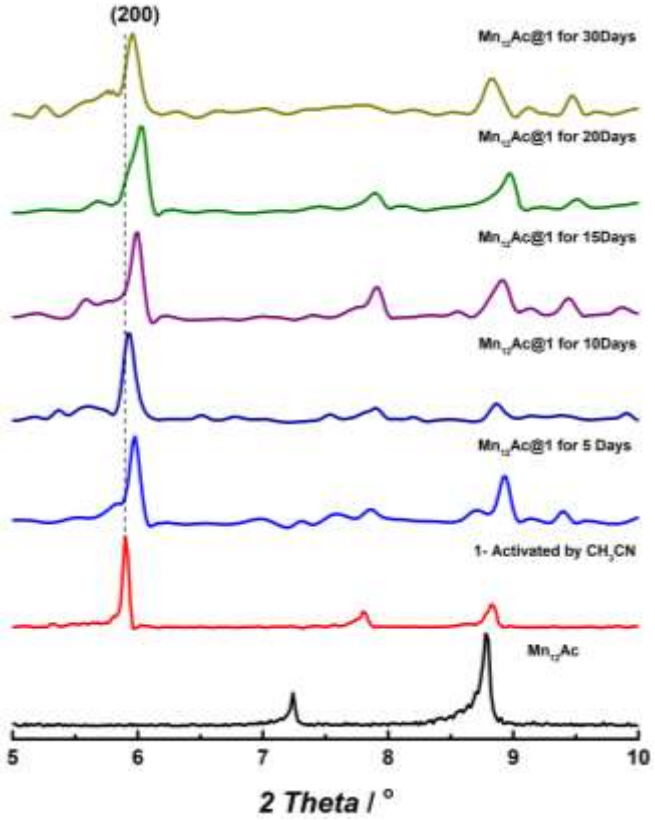

Figure S4. X-ray powder diffraction (PXRD) patterns of **Mn_{12}Ac**, **1** activated by CH_3CN, **Mn_{12}Ac@1** for different immersing times.

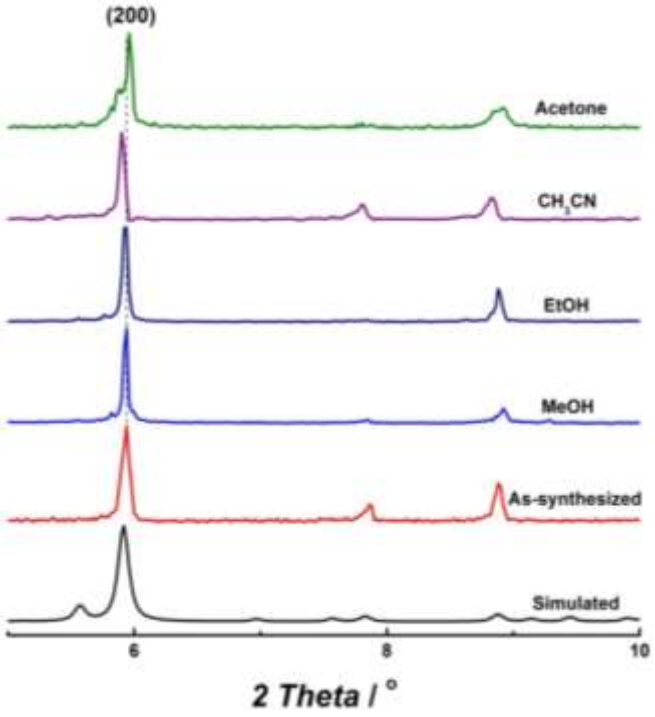

Figure S5. X-ray powder diffraction patterns (PXRD) of MOF **1** and the sample activated by different solvents.

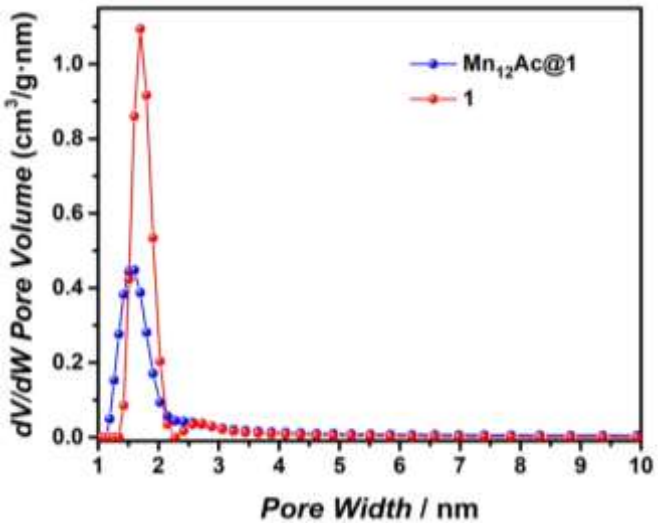

Figure S6. The pore size distribution (PSD) curves of **1** (red) and **Mn_{12}Ac@1** (blue).

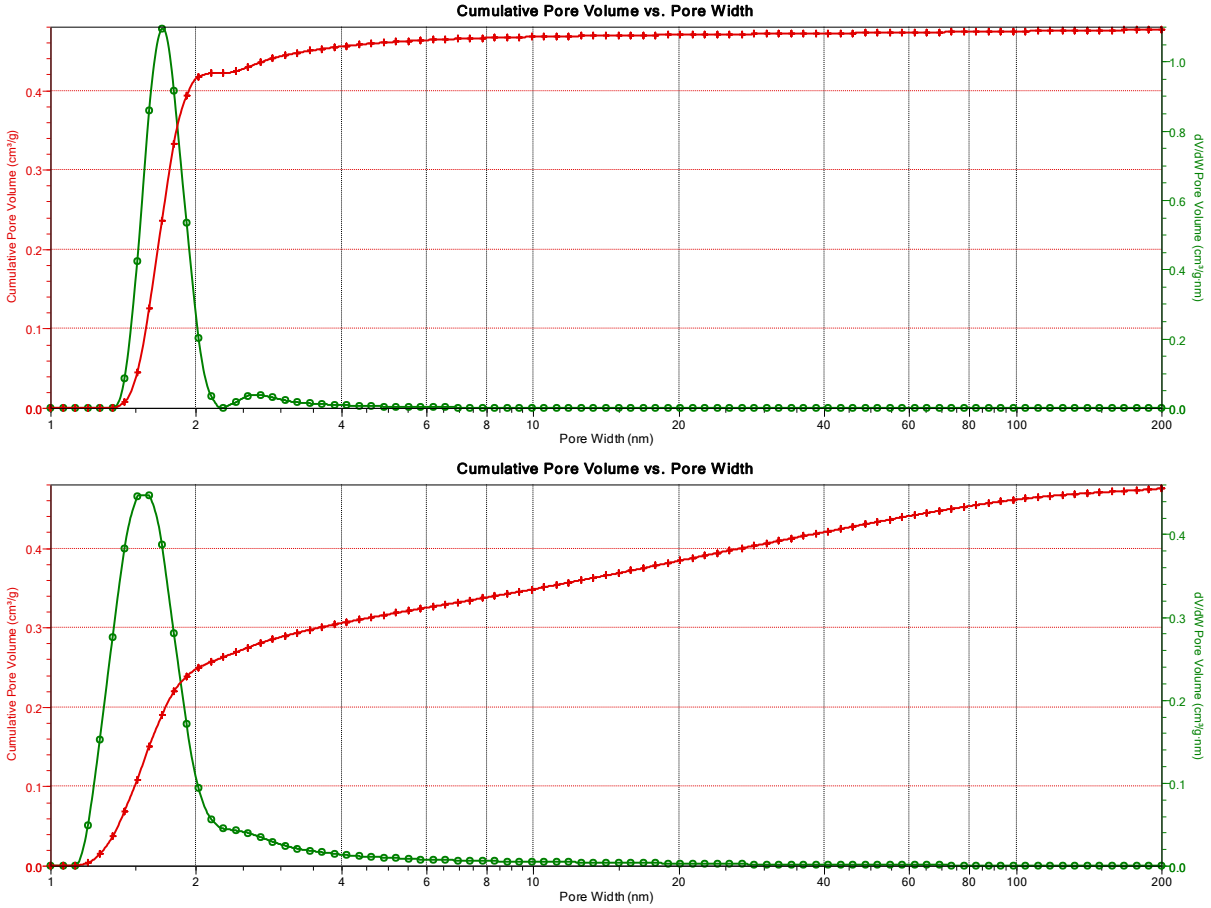

Figure S7. Calculation of pore size distribution (PSD) curves based on Harkins and Jura Thickness model for N_2 adsorption, **1** (top) and **Mn_{12}Ac@1** (bottom).

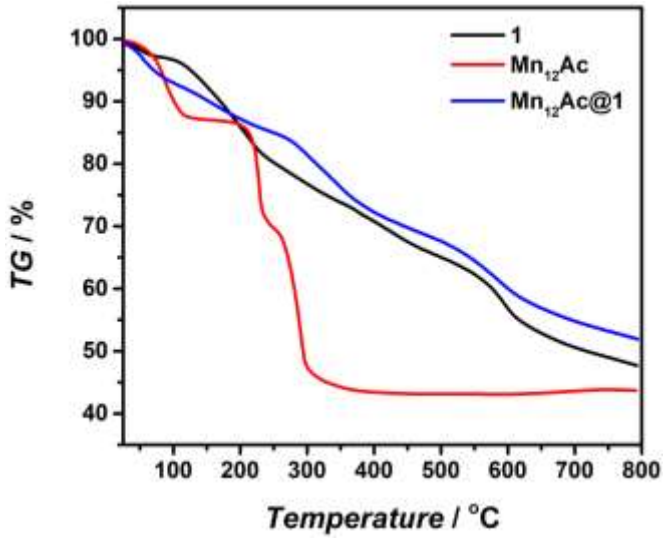

Figure S8a. Thermogravimetric analysis (TGA) curves of MOF **1** (black), **Mn_{12}Ac** (red) and **Mn_{12}Ac@1** (blue) in N_2 atmosphere.

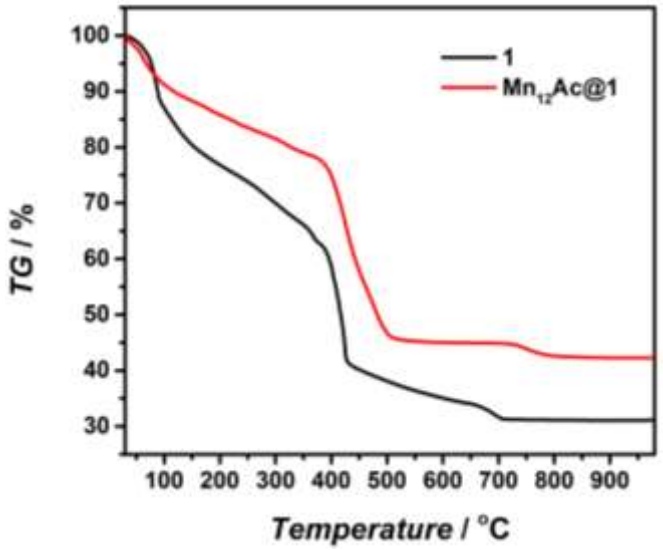

Figure S8b. Thermogravimetric analysis (TGA) curves of MOF **1** (black), **Mn_{12}Ac@1** (red) in air atmosphere.

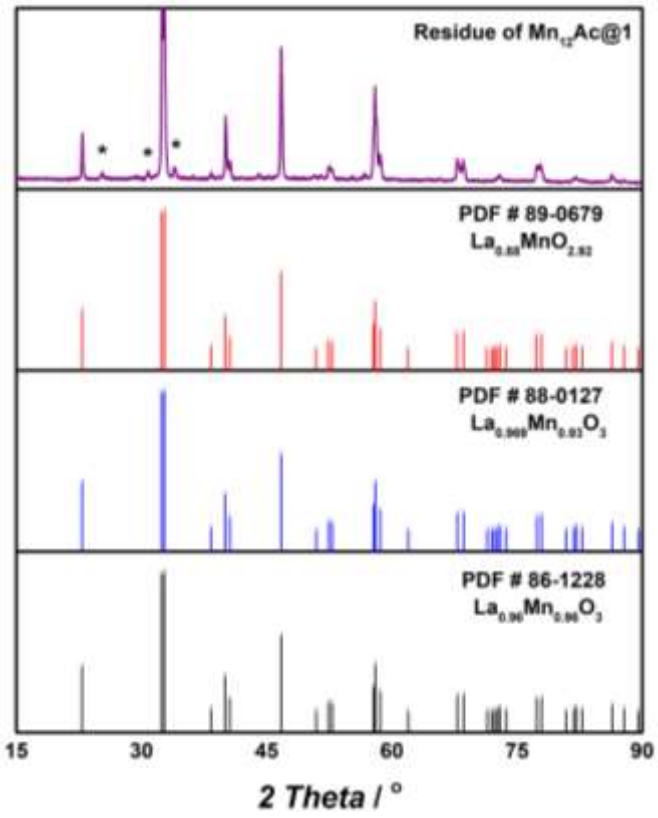

Figure S8c. X-ray powder diffraction (PXRD) patterns of TGA residual of **Mn_{12}Ac@1** in air atmosphere, $La_{0.96}Mn_{0.96}O_3$ (PDF # 86-1228), $La_{0.969}Mn_{0.93}O_3$ (PDF # 88-0127) and $La_{0.88}MnO_{2.92}$ (PDF # 89-0679).

Based on the XPRD patterns in **Figure S8c**, it is difficult for us to determine the composition of the residual of **Mn_{12}Ac@1**, the accurate estimation of the loading amount of **Mn_{12}Ac** in **1** based on the TGA data was unsuccessful, despite that the residual weight in **Mn_{12}Ac@1** is significantly higher than that of **1**.

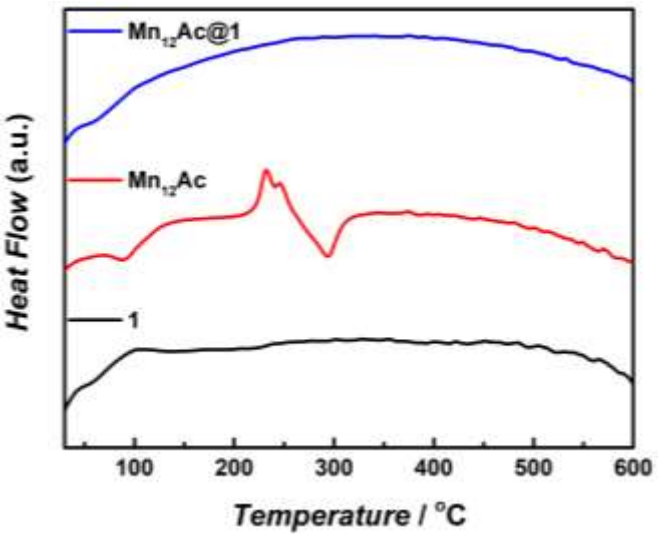

Figure S9. Differential scanning calorimetry (DSC) curves of MOF **1** (black), **Mn_{12}Ac** (red) and **Mn_{12}Ac@1** (blue).

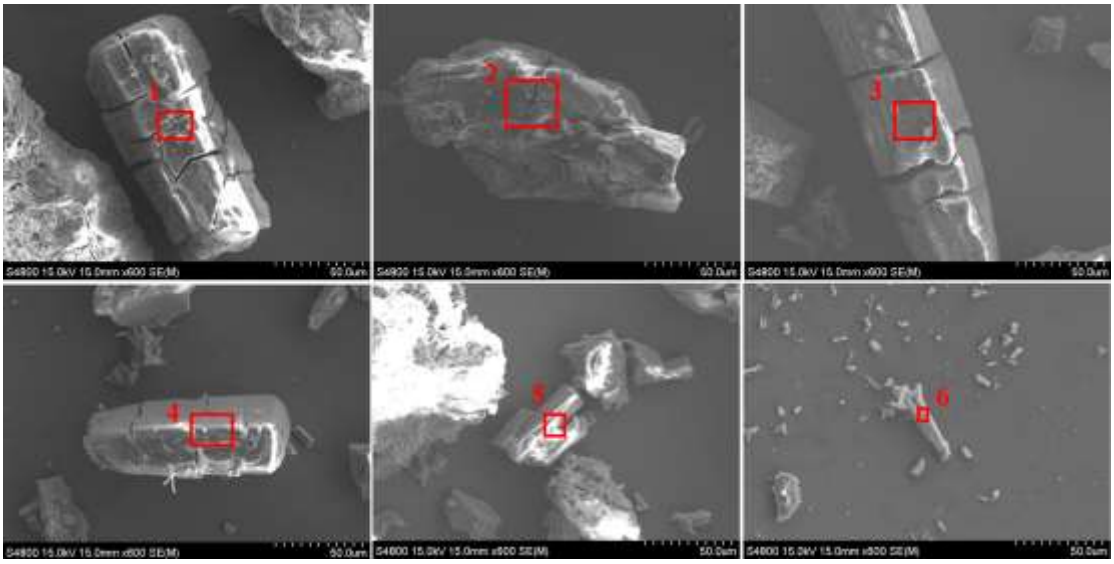

Figure S10. Scanning electron microscopy (SEM) images of **Mn_{12}Ac@1** at the same amplification used for EDX analysis.

Table S2. La-Mn atom ratios at different selected areas according to EDX results.

Selected Areas	La (atom %)	Mn (atom %)	**Mn_{12}Ac:1** (mol %)	**Average Mn_{12}Ac:1** (mol %)
1	52.18	47.82	30.55	42.31
2	53.37	46.63	29.12	
3	57.59	42.41	24.55	
4	45.76	54.24	39.51	
5	30.72	69.28	75.17	
6	37.75	62.25	54.97	

Mn_{12}Ac:1 (mol %) = (Mn : La) * (4/12)*100

(4/12) represents the metal atom ratio of **1** and **Mn_{12}Ac** based on their molecular formulas.

Table S3. La-Mn atom ratios according to ICP-MS results.

Batch	La (ppb)	Mn (ppb)	La (μmol / mL)	Mn (μmol / mL)	**1** (μmol / mL)	**Mn_{12}Ac** (μmol / mL)	**Mn_{12}Ac:1** (mol %)
1	1139	552	8.200144×10^{-3}	1.0047324×10^{-2}	2.050036×10^{-3}	8.37277×10^{-4}	40.84
2	1168	550	8.408927×10^{-3}	1.0010921×10^{-2}	2.102232×10^{-3}	8.34243×10^{-4}	39.68
3	1047	496	7.537797×10^{-3}	9.028031×10^{-3}	1.884449×10^{-3}	7.52336×10^{-4}	39.92

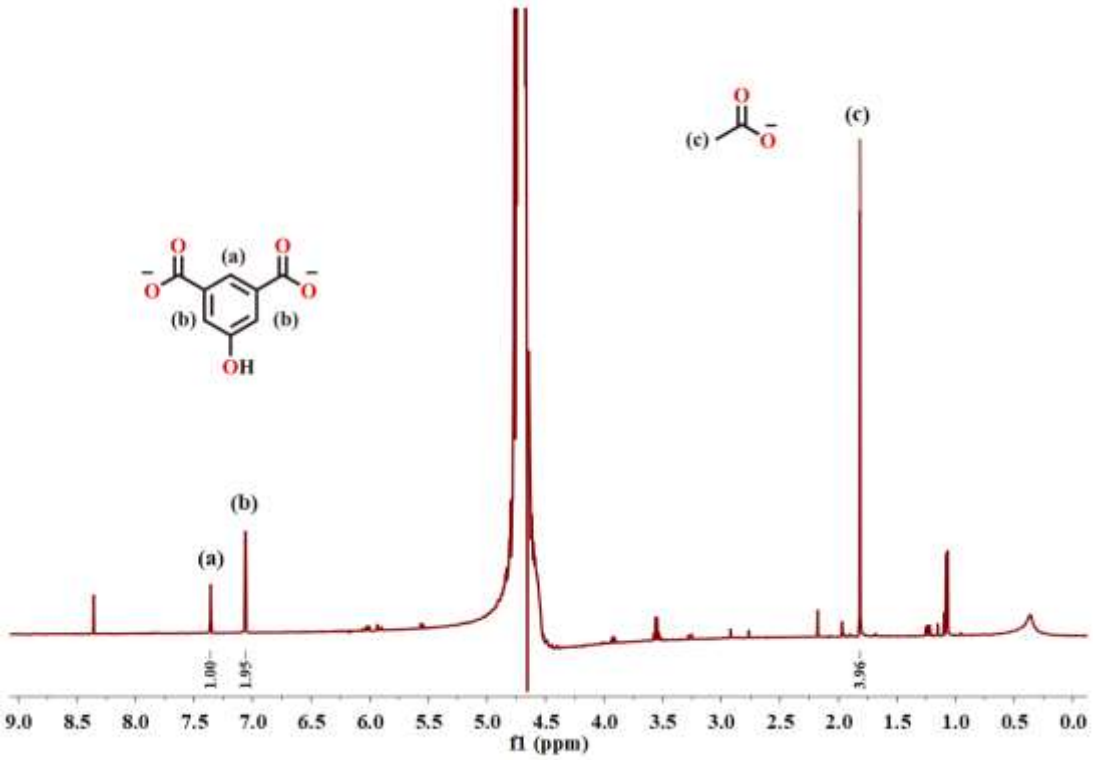

Figure S11. ^{1}H NMR spectrum of **Mn_{12}Ac@1** in NaOD/D_2O.

Sample pretreatment: 8 μL 40 wt% NaOD was added into 1.0 mg **Mn_{12}Ac@1** sample, and the mixture was diluted by 1mL D_2O. After sonication and filtration, colorless solution was obtained at last.

1-[$La_4(HL)_5(HLac)_2$(*i*-$PrOH)_2(DMF)_2$]: Signals at 7.3 ppm and 7.0 ppm with integral of 1.00 and 1.95 respectively, which were attributed to the hydrogen atoms in HL^- ligands. There are 5 H_a atoms per formula unit based on Single-crystal X-ray diffraction measurement.

Mn_{12}Ac-[$Mn_{12}O_{12}(Ac)_{16}(H_2O)_4$]: There are 16 acetates per formula unit, which represent 48 H_c atoms equivalently.

Mn_{12}Ac@1: **1**: **Mn_{12}Ac** = 0.4015 according to ICP-MS measurement, that is to say, there should be 19.27 (0.4015*48) H_c atoms.

According to ^{1}H NMR spectra, the signal at 7.3 ppm with integral of 1.00 represents 5 H_a, indicating that the signals around 1.8 ppm should be attributed to 19.8 Hc atoms (3.96*5). Thus, the loading capacity is 41.25 mol% (19.8/48), well consistent with that of 40.15 mol% obtained from ICP-MS.

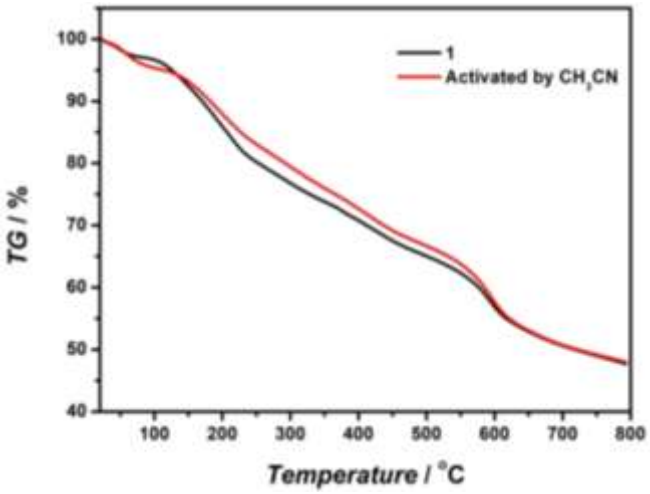

Figure S12. Thermogravimetric analysis (TGA) curves of MOF **1** (black) and the sample activated by CH_3CN (red) in N_2 atmosphere.

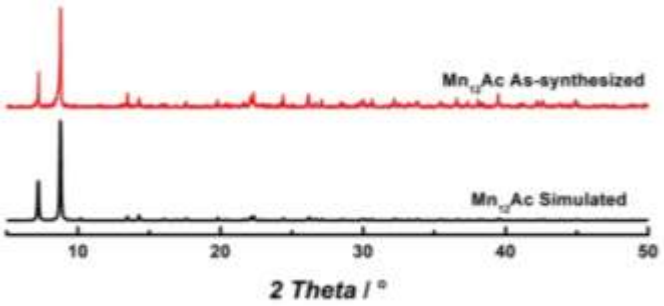

Figure S13. Experimental and simulated X-ray powder diffraction patterns (PXRD) of **Mn_{12}Ac**.

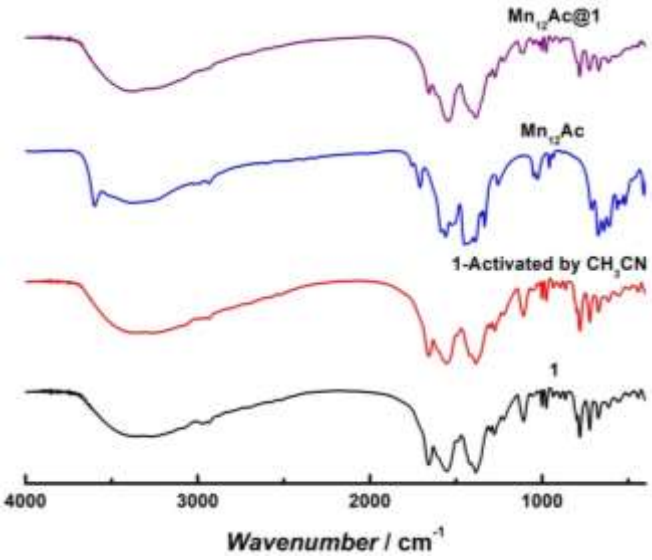

Figure S14. Infrared spectrum of compound **1** (black), the sample activated by CH_3CN (red), **Mn_{12}Ac** (blue) and **Mn_{12}Ac@1** (purple).

Table S4. Selected bond diatances (Å) for compound **1R** at 100K.

Bond	Dist.	Bond	Dist.
La1—O1	2.434 (9)	La1—O3^{i}	2.758 (11)
La1—O4^{i}	2.594 (10)	La1—O15^{i}	2.510 (8)
La1—O16^{i}	2.647 (9)	La2—O6	2.594 (10)
La2—O11	2.500 (10)	La2—O12	2.858 (10)
La2—O14	2.457 (9)	La2—O17	2.530 (11)
La3—O2^{ii}	2.586 (11)	La3—O3	2.492 (10)
La3—O6^{iii}	2.629 (10)	La3—O7^{iii}	2.635 (11)
La3—O8	2.378 (12)	La3—O12	2.428 (10)
La3—O15	2.585 (10)	La3—O18	2.403 (9)

Symmetry codes: (i) −x+y+1, y, −z+1/2; (ii) −x+y+1, −x+1, z; (iii) −x+2, −x+y+1, −z+1.

Table S5. Selected bond diatances (Å) for compound **1R** at 298K.

Bond	Dist.	Bond	Dist.
La1—O1	2.420 (8)	La1—O3^{i}	2.767 (9)
La1—O4^{i}	2.634 (8)	La1—O15^{i}	2.552 (7)
La1—O16^{i}	2.659 (8)	La2—O6	2.587 (8)
La2—O11	2.823 (9)	La2—O12	2.500 (8)
La2—O14	2.528 (8)	La2—O17	2.526 (10)
La3—O2^{ii}	2.538 (10)	La3—O3	2.485 (8)
La3—O6^{iii}	2.659 (8)	La3—O7^{iii}	2.607 (9)
La3—O8	2.383 (9)	La3—O11	2.459 (9)
La3—O15	2.559 (8)	La3—O18	2.444 (7)

Symmetry codes: (i) −x+y, −x+1, z; (ii) −y+1, x−y+1, z; (iii) x−y+1, −y+2, −z+1.

Table S6. Selected bond distances (Å) for compound **1S** at 100K.

Bond	Dist.	Bond	Dist.
La1—O1	2.417 (6)	La1—O3^{i}	2.757 (7)
La1—O4^{i}	2.606 (7)	La1—O12^{i}	2.512 (6)
La1—O13^{i}	2.645 (7)	La2—O6	2.592 (7)
La2—O11	2.455 (6)	La2—O14	2.504 (7)
La2—O15	2.841 (8)	La2—O17	2.508 (8)
La3—O2^{ii}	2.568 (8)	La3—O3	2.488 (7)
La3—O6^{iii}	2.631 (8)	La3—O7^{iii}	2.623 (8)
La3—O8	2.384 (9)	La3—O12	2.573 (7)
La3—O15	2.841 (8)	La3—O17	2.508 (8)

Symmetry codes: (i) −y+1, x−y, z; (ii) −x+y+1, −x+1, z; (iii) −x+2, −x+y+1, −z+1.

Table S7. Selected bond distances (Å) for compound **1S** at 298K.

Bond	Dist.	Bond	Dist.
La1—O1	2.407 (8)	La1—O3^{i}	2.635 (9)
La1—O4^{i}	2.787 (9)	La1—O6^{ii}	2.514 (7)
La1—O8^{ii}	2.661 (9)	La2—O7	2.498 (8)
La2—O9	2.487 (9)	La2—O10	2.835 (9)
La2—O12	2.576 (9)	La2—O17	2.526 (11)
La3—O2	2.528 (11)	La3—O4^{iii}	2.481 (9)
La3—O6^{ii}	2.576 (8)	La3—O10	2.439 (9)
La3—O12^{ii}	2.675 (9)	La3—O13^{ii}	2.612 (11)
La3—O14	2.371 (11)	La3—O18	2.375 (8)

Symmetry codes: (i) −x+y, y, −z+3/2; (ii) y, x, −z+1; (iii) −y+1, x−y+1, z.

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