Electronic Supplementary Material (ESI) for ChemComm.
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Supporting Information

Octahedral Polyoxomolybdate-Organic Molecular Cage

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1. Materials and instruments

All commercially obtained reagent, including ammonium heptamolybdate, benzene-1,3,5-tricaboxyllic acid, tetrabutylammonium bromide, N,N-dimethylacetamide, methanol, CsCl, tri(4-bromophenyl)amine, and deuterated methanol (CD_3OD) were purchased from Aldrich and used without further purification. The reaction mixtures were agitated in the round bottomed flasks on a CL-1A-type agitator purchased from GongYi Company in China. Powder X-ray diffraction (PXRD) measurement was recorded ranging from 5 to 50° at room temperature on a Siemens D5005 diffractometer with Cu-K_α (λ = 1.5418 Å). The C, H, and N elemental analyses were conducted on a Perkin-Elmer 2400CHN elemental analyzer. Thermogravimetric analysis (TGA) of the samples was performed using a Perkin-Elmer TG-7 analyzer heated from room temperature to 800 °C under nitrogen at the heating rate of 10 °C·min^{-1}. IR spectrum was performed in the range 4000–400 cm^{-1} using KBr pellets on an Alpha Centaurt FT/IR spectrophotometer. The morphology and microstructure of the samples were investigated using a field emission scanning electron microscopy (FESEM, Hitachi SU8010) equipped with an energy-dispersive X-ray (EDX) detector for elemental analysis and mapping. X-ray photoelectron spectroscopy analyses were performed on a VG ESCALABMKII spectrometer with an Al-K_α (1486.6 eV) achromatic X-ray source. ^{1}H NMR spectra were recorded on Bruker 500 MHz instrument. In general, the chemical shift of active hydrogen is not fixed and the peak shape is variable under different conditions. The N-H signal of $H_2NMe_2^+$ in our proton NMR is disappeared due to the fast deuterium exchange. This phenomenon is known in many reported documents.

2. Synthesis and Characterization

Synthesis of Mo_{12} cage: Ammonium heptamolybdate (20 mg, 0.016 mmol), benzene-1,3,5-tricaboxyllic acid (H_3BTC) (20 mg, 0.095 mmol) and tetrabutylammonium bromide (10 mg, 0.031 mmol) in 2 ml N,N-Dimethylacetamide (DMA) and 0.2 ml methanol solvent were transferred to a Parr Teflon-lined stainless steel vessel heated to 150°C and held at this temperature for 3 days. After slow cooling to room temperature, yellow crystals were obtained with a yield of 16.7 % (8.02 mg) based on H_3BTC. Elemental analysis (%) Cacld: C, 45.33; H, 6.38; N, 4.03; Mo, 20.69. Found: C, 46.24; H, 6.44; N, 3.92; Mo, 19.85. IR (KBr, cm^{-1}): 3364(w), 3132(w), 2961(w), 1643(w), 1618(w), 1579(m), 1439(s), 1375(s), 1196(m), 938(s), 901(s), 763(s), 710(m), 588 (m), 482(m), 423(w).

3. Single-crystal X-ray Crystallography

The crystallographic data for Mo_{12} cage and Cs-Mo_{12} cage are given in Table S1. The crystallographic diffraction data were collected at 293 K on Bruker D8 VENTURE with Mo *Kα* radiation (λ = 0.71073 Å). Absorption corrections were applied using a multi–scan technique. (CCDC number: 2027865 for Mo_{12} cage; 2027866 for Cs-Mo_{12} cage)

Latest PLATON software (Version: 230920) was used for SQUEEZE subroutine. About 2 $H_2NMe_2^+$ cations were found from the Fourier maps, however, there are still a very large accessible solvent voids (see below) in the crystal structure caculated by SQUEEZE subroutine of PLATON software, indicating that some more solvent molecules and cations should exist in the structure, but cannot be found from the weak residual electron peaks. Based on the TGA curve and elemental analyses, another 4 DMA molecules, 3 $H_2NMe_2^+$ and 7 TBA^+ cations were included into the molecular formula directly. The count electrons for DMA, $H_2NMe_2^+$ and TBA^+ cations are 48, 26, and 139, respectively. The aforementioned total count electrons are about 1243. The void is large enough and contains enough electronic density to accommodate all organic ammonium cations/DMA molecules that cannot be determined crystallographically. The 4 DMA molecules in this formula were further confirmed by TGA curve, the first weight decrease is the loss of DMA molecules (cacld: 6.25%; Found: 6.07%) and then the loss of all organic cations as well as the structure begins to decompose. Elemental analysis (%) supports this molecular formula once again (Cacld: C, 45.33; H, 6.38; N, 4.03; Mo, 20.69. Found: C, 46.24; H, 6.44; N, 3.92; Mo, 19.85).

In all, the molecular formula was defined as $TBA_7(H_2NMe_2)_5[(Mo_2O_5)_6(BTC)_8]\cdot 4DMA$ according to single crystal analysis, charge balance, SQUEEZE subroutine, TGA curve as well as elemental analyses.

```
# SQUEEZE RESULTS (Version = 230920)
# Note: Data are Listed for all Voids in the P1 Unit Cell
# i.e. Centre of Gravity, Solvent Accessible Volume,
# Recovered number of Electrons in the Void and
# Details about the Squeezed Material
loop_
 _platon_squeeze_void_nr
 _platon_squeeze_void_average_x
 _platon_squeeze_void_average_y
 _platon_squeeze_void_average_z
 _platon_squeeze_void_volume
 _platon_squeeze_void_count_electrons
 _platon_squeeze_void_content
  1 -0.212  0.200 -0.043     7960     2971 ' '
  2 0.000  0.500  0.250      312      241 ' '
  3 0.000  0.500  0.750      312      241 ' '
  4 0.500  0.000  0.250      312      242 ' '
  5 0.500  0.000  0.750      312      242 ' '
_platon_squeeze_void_probe_radius            1.20
_platon_squeeze_details                      ?
```

Table S1. Crystallographic data for Mo_{12} cage and Cs-Mo_{12} cage.

	Mo_{12} cage	Cs-Mo_{12} cage
Empirical formula	$C_{210}H_{352}Mo_{12}N_{16}O_{82}$	$C_{72}H_{56}Cl_{10}Cs_{22}Mo_{12}O_{94}$
Formula weight	5564.33	6854.96
Crystal system	Tetragonal	Tetragonal
Space group	$P4_2/mcm$	$P4_2/mcm$
Temperature(K)	293(2)	173(2)
Wavelength (Å)	0.71073	0.71073
a (Å)	24.4515(10)	24.2478(9)
b (Å)	24.4515(10)	24.2478(9)
c (Å)	37.034(3)	36.721(2)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume (Å^3)	22142(3)	21341.2(15)
Z	4	4
ρ_{calc}(mg/m^3)	1.669	2.134
μ/mm^{-1}	0.752	4.578
F(000)	11536	12496
θ (°)	2.352 to 25.053	2.231 to 20.839
Reflections collected	94757	83092
Independent reflections	10307 [*R*(int) = 0.0416]	5944 [*R*(int) = 0.0407]
GOOF	1.015	1.036
Final *R* indices [I>2sigma(I)]	R_1 = 0.0595, wR_2 = 0.1761	R_1 = 0.0777, wR_2 = 0.2308
R indices (all data)	R_1 = 0.0781, wR_2 = 0.2052	R_1 = 0.0910, wR_2 = 0.2541
Largest diff. peak and hole	1.190 Å and -0.617 Å^3	2.529 Å and -0.968 Å^3

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b] $wR_2=\{\Sigma [w(F_o^2-F_c^2)^2]/\Sigma [w(F_o^2)^2]\}^{1/2}$

Table S2. The Mo-O bond distances for Mo_{12} cage.

Mo-O bond	Length/Å	Mo-O bond	Length/Å
Mo(1)-O(19)	1.691(4)	Mo(3)-O(5)	1.689(5)
Mo(1)-O(2)	1.697(4)	Mo(3)-O(8)	1.695(5)
Mo(1)-O(1)	1.8983(15)	Mo(3)-O(10) $^{\#1}$	1.897(4)
Mo(1)-O(7)	2.018(4)	Mo(3)-O(9)$^{\#2}$	2.044(4)
Mo(1)-O(4)	2.194(4)	Mo(3)-O(14)$^{\#1}$	2.216(4)
Mo(1)-O(11)	2.253(4)	Mo(3)-O(20)	2.248(4)
Mo(2)-O(6)	1.686(5)	O(1)-Mo(1) $^{\#2}$	1.8983(15)
Mo(2)-O(13)	1.691(5)	O(9)-Mo(3) $^{\#2}$	2.044(4)
Mo(2)-O(10)	1.893(4)	O(10)-Mo(3) $^{\#1}$	1.897(4)
Mo(2)-O(3)	2.041(4)	O(14)-Mo(3) $^{\#1}$	2.216(4)
Mo(2)-O(15) $^{\#1}$	2.208(4)	O(15)-Mo(2) $^{\#1}$	2.208(4)
Mo(2)-O(17)	2.229(4)		

Symmetry transformations used to generate equivalent atoms: $^{\#1}$-x+1,y,-z+1/2, $^{\#2}$x,-y,-z+1/2

Table S3. BVS results for the molybdenum atoms in Mo_{12} cage.

Atom	BVS calc. for Mo
Mo1	6.281
Mo2	5.980
Mo3	6.377
Mo4	6.371
Mo5	6.006
Mo6	6.061

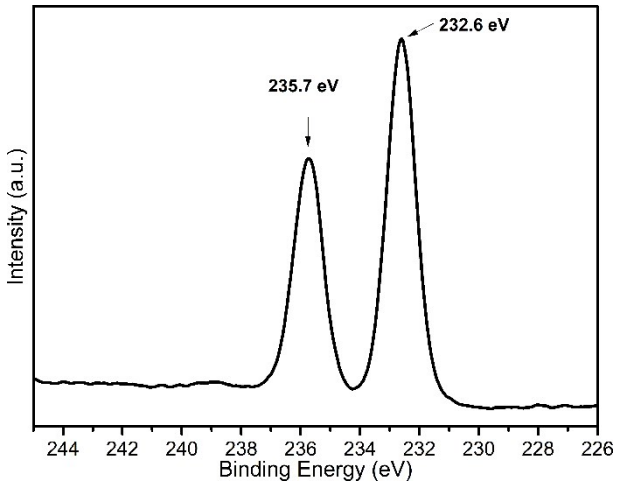

Fig. S1 The Mo XPS spectrum of Mo_{12} cage.

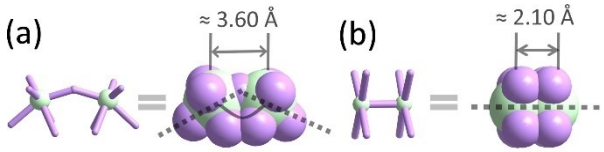

Fig. S2 (a) $\{Mo_2O_5\}$ SBUs in Mo_{12} cage; (b) quadruply-bonded Mo_2^{4+} SBUs reported by *Cotton et al.* (*Chem. Commun.*, 1999, 841–842) and Zhou *et al.* (*J. Am. Chem. Soc.*, 2010, **132**, 17599–17610).

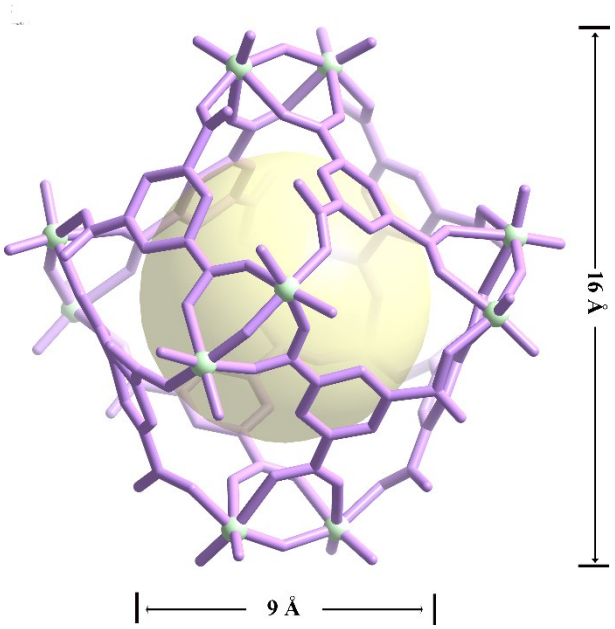

Fig. S3 Outer diameter and inner cavity diameter of Mo_{12} cage.

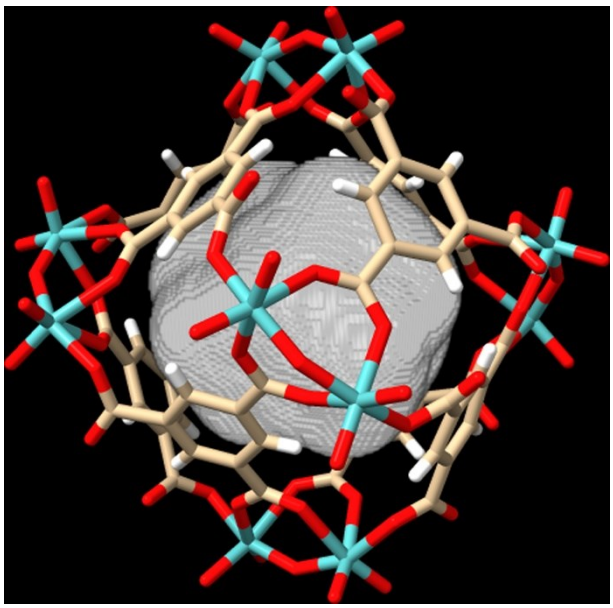

Fig. S4 The void space (gray sphere) of Mo_{12} cage calculated by VOIDOO.

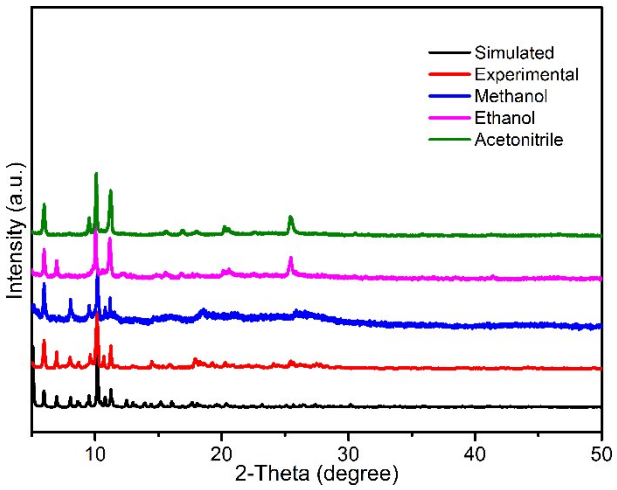

Fig. S5 The simulated and experimental PXRD patterns of Mo_{12} cage in solvents.

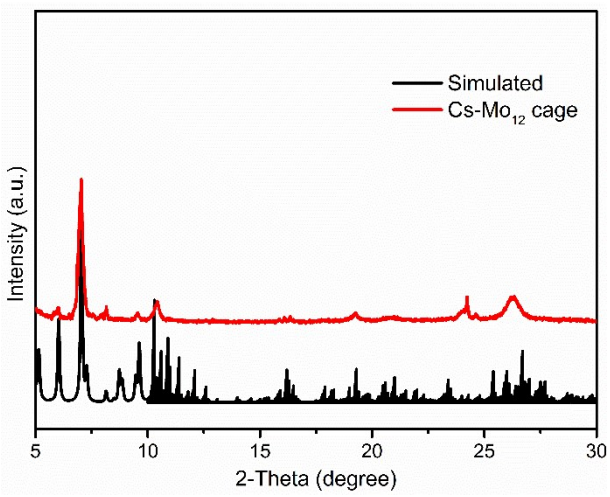

Fig. S6 The simulated and experimental powder X–Ray diffraction patterns of Cs-Mo_{12} cage.

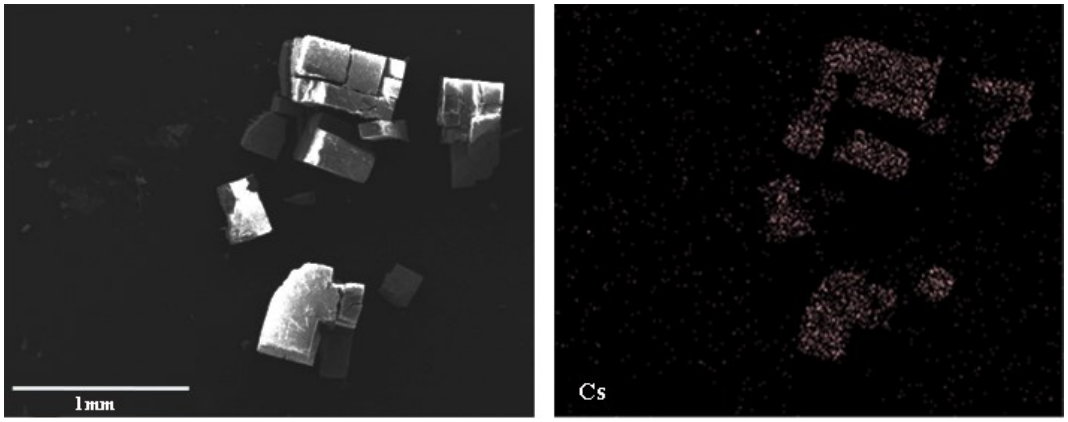

Fig. S7 The morphology and cesium elemental mapping of Cs-Mo_{12} cage by SEM.

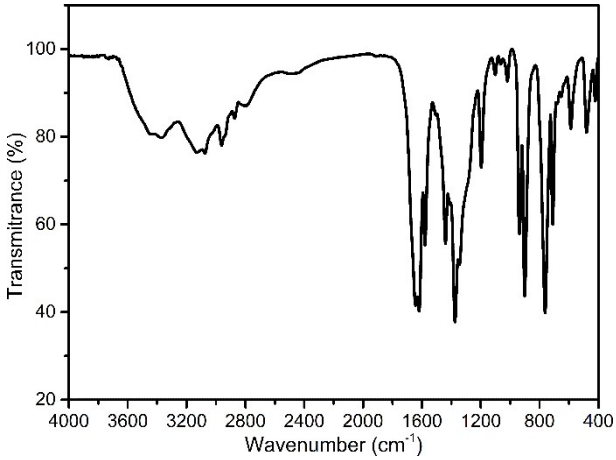

Fig. S8 IR spectrum of Mo_{12} cage.

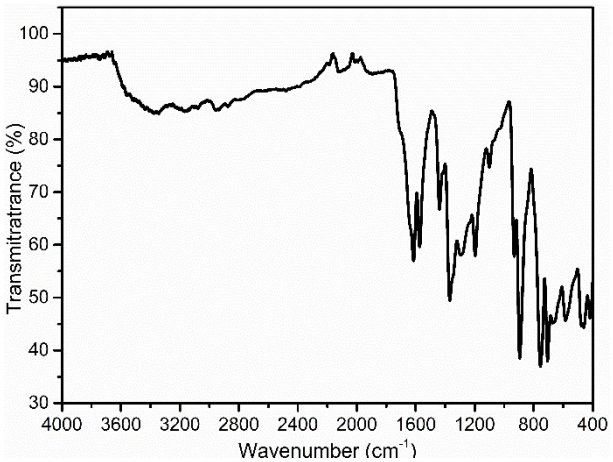

Fig. S9 IR spectrum of Cs-Mo_{12} cage.

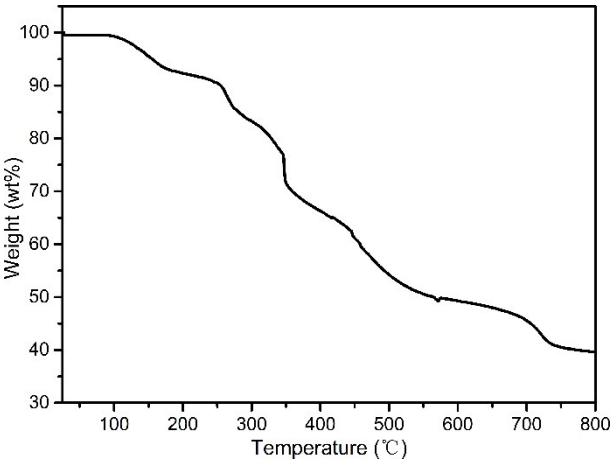

Fig. S10 TG curve of Mo_{12} cage.

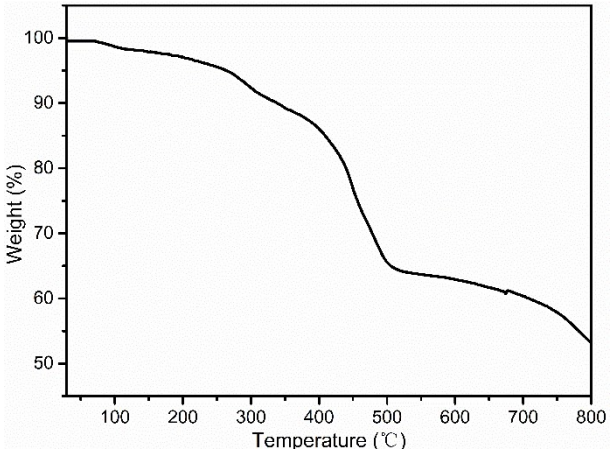

Fig. S11 TG curve of Cs-Mo_{12} cage.