

Supplementary Information

Deeply Reduced Empty Keggin Clusters $[\text{Mo}^{\text{IV}}_x\text{M}^{\text{VI}}_{12-x}\text{O}_{40-x}\text{py}_x]$ ($x = 3, 6$; $\text{M} = \text{Mo}, \text{W}$; $\text{py} = \text{pyridine}$): Synthesis, Structures and Lewis Field Catalysis

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1. Experimental Section

1.1 Methods and Materials

All chemicals were obtained from commercial sources and used without further purification. The elemental analysis (C, H and N) were performed using a vario MICRO elemental analyzer. ICP-OES (inductively coupled plasma-optical emission spectroscopy) analysis (W, Mo) were carried on Ultima 2. IR spectra were recorded with a Magna 750 FTIR spectrometer photometer as KBr pellets in the 4000~400 cm^{-1} region. UV-vis spectra were measured on a Horiba Labram HR800 Evolution spectrometer. Powder X-ray diffraction was recorded on a Rigaku Ultima-IV diffractometer. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a ESCALAB 250Xi spectrometer equipped with an Al $K\alpha$ X-ray source. The intensity data were collected on a Bruker D8-venture (2, 3), Mercury 70 CCD (1) or Saturn 724+ (4) diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All absorption corrections were performed using multiscan. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with the SHELXTL-2016 program package.

1.2 DFT calculations

DFT calculations were performed using the GAUSSIAN 16 program package⁴² and crystal structure parameters. DFT calculations were carried out using the (U)B3LYP functional, that is, Beck's hybrid three-parameter exchange functional⁴³ with the Lee-Yang-Parr correlation function.⁴⁴ In these calculations, the solvent effects were taken into account by the Polarizable Continuum Model (PCM).^{45,46} The natural atomic orbital (NAO) analysis were calculated by the NBO 3.1 module embedded in Gaussian 16 program. The analysis of frontier molecular orbitals and spin densities were performed by Multiwfn,⁴⁷ which is a multifunctional wavefunction analysis program.

1.3 Catalytic hydrogenation tests

The hydrogenation reduction of nitroarenes to anilines with hydrazine hydrate in the presence of $\{\text{Mo}^{\text{IV}}_6\text{W}_6\}$ -**2**, $\{\text{Mo}^{\text{IV}}_6\text{W}_6\text{Na}\}$ -**3** and $\{\text{Mo}^{\text{IV}}_6\text{Mo}^{\text{VI}}\text{W}_5\}$ -**4** were investigated. General procedure for the reduction of nitroarenes: **2** (8.4 mg, 3 mol %, 0.0029 mmol), **3** (8.5 mg, 3 mol %, 0.0029 mmol) and **4** (17.1 mg, 3 mol %, 0.0029 mmol) were respectively added into a 25 mL round bottomed flask containing a mixture of nitroarenes (10 μL , 0.097 mmol), ethanol (2 mL) with magnetic stirring. Then, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (85%) (20 μL , 0.3 mmol) were added into the reactors and heated to reflux with stirring at 80 °C for 2 hours. The reactions were complete (incomplete or messy) detected by TLC (*n*-hexane/ethyl acetate = 5:1). The samples were obtained by centrifugation and filtration and analyzed by Shimadzu GC-2014C. The reduction of nitroarenes to anilines in this catalytic system based on $[\text{Mo}^{\text{IV}}_6\text{Mo}^{\text{VI}}_7\text{O}_{32}(\text{OH})_4\text{py}_6]^{2-}$ has been conducted for performance comparisons and mechanism study.

2. Tables

Table S1 BVS results for **1**

Mo14.551	Mo2 4.471	Mo3 4.487	Mo4 6.214	W4 6.385	Mo5 6.078	W5 6.245
Mo6 6.031	W6 6.196	Mo7 6.037	W7 6.203	Mo8 6.284	W8 6.456	Mo9 5.863
W9 6.023	W10 6.523	W11 6.184	W12 6.213	O1 2.105	O2 2.167	O3 1.428
O4 1.893	O5 2.04	O6 2.404	O7 2.044	O8 1.266	O9 1.852	O10 2.081
O11 1.689	O12 2.089	O13 1.492	O14 1.975	O15 1.894	O16 2.052	O17 2.175
O18 2.134	O19 1.895	O20 1.677	O21 1.832	O22 2.088	O23 1.699	O24 1.927
O25 2.218	O26 1.956	O27 2.269	O28 2.185	O29 2.071	O30 1.969	O31 1.867
O32 1.672	O33 1.672	O34 1.805	O35 1.807	O36 1.787	O37 1.631	

Table S2 BVS results for **2**

Mo1 4.246	W2 5.837	W3 5.866	W4 6.082	W5 5.893	W6 6.184
W1 6.219	Mo2 4.274	Mo3 4.197	Mo4 4.188	Mo5 4.347	Mo6 4.271
O1 1.963	O2 1.186	O3 2.207	O4 1.999	O5 2.133	O6 2.043
O7 1.966	O8 1.586	O9 2.022	O10 1.38	O11 1.949	O12 2.136
O13 1.781	O14 1.223	O15 1.923	O16 1.848	O17 1.18	O18 2.091
O19 2.07	O20 1.655	O21 1.887	O22 1.929	O23 2.084	O24 2.026
O25 1.272	O26 1.998	O27 1.752	O28 1.62	O29 1.901	O30 1.328
O31 2.148	O32 2.056	O33 2.104	O34 2.073		

Table S3 BVS results for **3**

W2 6.03	Mo2 4.356	Mo3 4.275	W1 6.023	Mo1 4.231	W3 6.037
W4 5.995	Na 1.93	O22 0.457	O23 0.31	O24 0.432	O1 1.023
O2 1.104	O3 2.124	O4 2.129	O5 2.032	O6 2.073	O7 1.269
O8 1.904	O9 1.209	O10 1.818	O11 1.883	O12 1.272	O13 1.887
O14 1.83	O15 1.891	O16 1.963	O17 2.168	O18 1.617	O19 1.69
O20 2.048	O21 1.858				

Table S4 BVS results for **4**

Zn 1.737	Mo1 4.227	Mo2 4.359	Mo3 4.357	Mo4 4.214	Mo5 4.349	Mo6 4.439
Mo7 5.939	W7 6.102	Mo8 5.851	W8 6.011	Mo9 5.985	W9 6.149	Mo10 5.869
W10 6.03	Mo11 5.921	W11 6.083	Mo12 5.912	W12 6.074	O1 2.469	O2 1.139
O3 1.168	O4 2.097	O5 2.204	O6 1.933	O7 2.106	O8 2.092	O9 2.178
O10 2.081	O11 2.277	O12 2.14	O13 2.233	O14 2.156	O15 1.183	O16 1.947
O17 1.295	O18 2.285	O19 1.972	O20 1.481	O21 2.041	O22 2.088	O23 1.671

O24 1.999	O251.975	O26 2.04	O27 1.793	O28 2.13	O29 2.108	O30 1.782
O31 1.295	O32 1.643	O33 1.681	O34 2.1			

Table S5 Bonding energies of Mo 3d from the literatures ⁴⁸⁻⁵³ and the binding energies of peaks used to assign species from the present measurements of **2**, **4** (C1s calibrated to 284.5 eV for contrast).

Oxidation state	Mo 3d5/2	Mo 3d3/2
Mo(IV)O(OH) ₂	230.2 eV	233.4 eV
Mo(VI)-Na ₂ MoO ₄ ·2H ₂ O	231.9-232.3 eV	235-235.4
Mo(IV)-2	229.90 eV	233.13 eV
Mo(IV)-4	229.98 eV	233.14 eV
Mo(VI)-4	231.89 eV	234.98 eV
Oxidation state	W 4f7/2	W 4f5/2
W(VI)-Na ₂ WO ₄	35.3 eV	37.4 eV
W(VI)-2	34.67 eV	36.79 eV
W(VI)-4	34.61 eV	36.75 eV

Table S6 Structural refinement and crystallographic parameters of **1**, **2**, **3** and **4**

	C ₂₅ H ₄₁ N ₅ Mo ₄ W ₈ O ₄₁	C ₃₄ H ₆₅ N ₈ Mo ₆ W ₆ O _{40.5}	C ₃₄ H ₆₅ N ₈ Mo ₆ W ₆ O ₄₁ Na	C ₉₀ H ₁₁₄ N ₁₈ Mo ₁₄ W ₁₀ O ₇₆ Zn
Empirical formula	C ₂₅ H ₄₁ N ₅ Mo ₄ W ₈ O ₄₁	C ₃₄ H ₆₅ N ₈ Mo ₆ W ₆ O _{40.5}	C ₃₄ H ₆₅ N ₈ Mo ₆ W ₆ O ₄₁ Na	C ₉₀ H ₁₁₄ N ₁₈ Mo ₁₄ W ₁₀ O ₇₆ Zn
Formula weight	2922.12	2912.68	2943.67	5911.02
Temperature	293(2) K	200(2) K	100(2) K	153(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	P2 ₁ /n	P2 ₁ /n	Cmca	Pī
Unit cell dimensions	<i>a</i> = 13.583(8) Å	<i>a</i> = 15.7129(63) Å	<i>a</i> = 23.1566(13) Å	<i>a</i> = 13.645(3) Å
	<i>b</i> = 25.864(14) Å	<i>b</i> = 25.086(2) Å	<i>b</i> = 21.3965(13) Å	<i>b</i> = 15.216(4) Å
	<i>c</i> = 20.044(11) Å	<i>c</i> = 16.0211(65) Å	<i>c</i> = 25.0173(13) Å	<i>c</i> = 21.782(5) Å
	<i>α</i> = 90°	<i>α</i> = 90°	<i>α</i> = 90°	<i>α</i> = 98.179(2)°
	<i>β</i> = 96.074(12)°	<i>β</i> = 94.822(4)°	<i>β</i> = 90°	<i>β</i> = 103.9550(10)°
	<i>γ</i> = 90°	<i>γ</i> = 90°	<i>γ</i> = 90°	<i>γ</i> = 110.613(2)°
Volume	7002(7) Å ³	6292.8(9) Å ³	12395.3(12) Å ³	3977.4(16) Å ³
Z	4	4	8	1
Density (calculated)	2.764 mg/m ³	3.074 mg/m ³	3.097 mg/m ³	2.468 mg/m ³
F(000)	5256	5380	10624	2746
Crystal size (mm)	0.08×0.03×0.02	0.10×0.10×0.10	0.08×0.03×0.03	0.08×0.03×0.02
θ range	2.038 to 27.587°	2.38 to 27.56°	2.397 to 27.496°	2.077 to 27.473°
Index ranges	-17 17, -33 33, -22 24	-20 18, -32 32, -20 20	-30 30, -27 25, -32 31	-17 17, -19 19, -28 28
Independent reflections	14951 [R(int) = 0.0849]	13808 [R(int) = 0.0730]	7287 [R(int) = 0.0587]	18101 [R(int) = 0.0648]
Reflections [I ≥ 2σ(I)]	10577	10849	6192	14382
Completeness	94.0 %	99.9 %	99.6 %	99.7 %
Restraints/parameters	0 / 624	0 / 790	2 / 433	0 / 815
S on F ²	1.122	1.450	1.50	1.074
Final R indices [I > 2σ(I)]	R ₁ =0.068, wR ₂ =0.176	R ₁ =0.063, wR ₂ =0.184	R ₁ =0.039, wR ₂ =0.075	R ₁ =0.056, wR ₂ =0.137
Final R indices [all data]	R ₁ =0.090, wR ₂ =0.190	R ₁ =0.078, wR ₂ =0.201	R ₁ =0.050, wR ₂ =0.078	R ₁ =0.073, wR ₂ =0.147

3. Figures

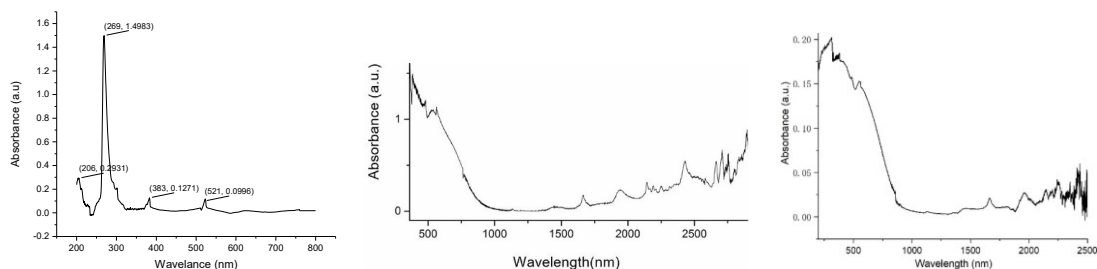


Fig. S1 (a) UV-vis spectrum of **4** in DMF; (b) Solid-state UV-vis spectrum of **4**; (c) Solid-state UV-vis spectrum of **2**.

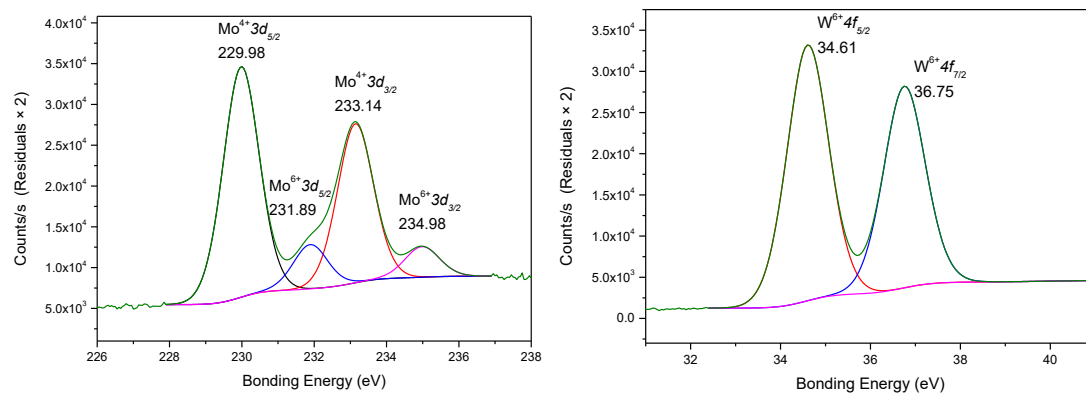


Fig. S2 XPS spectra of **4**.

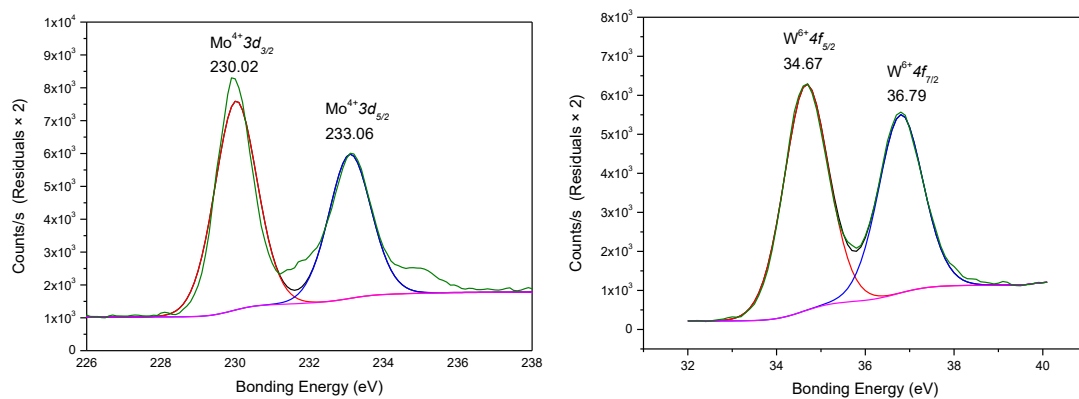


Fig. S3 XPS spectra of **2**.

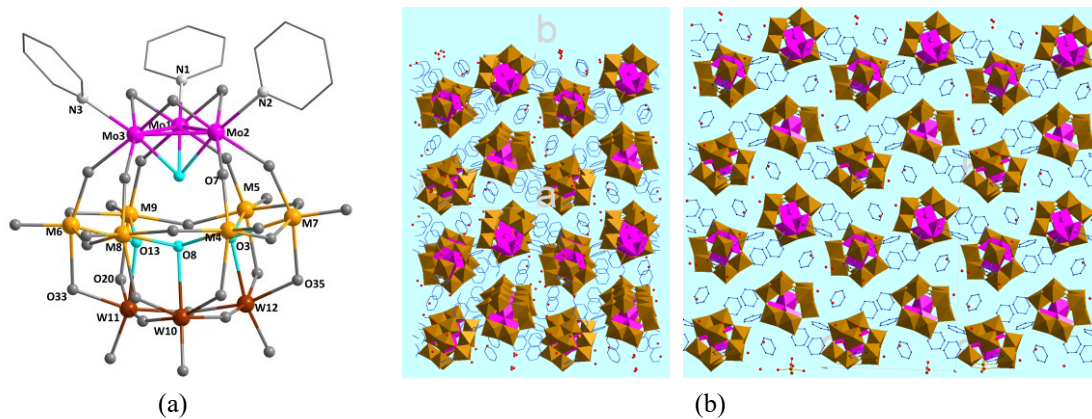


Fig. S4 (a) Structure of **1**; (b) Crystal packing structure of **1**.

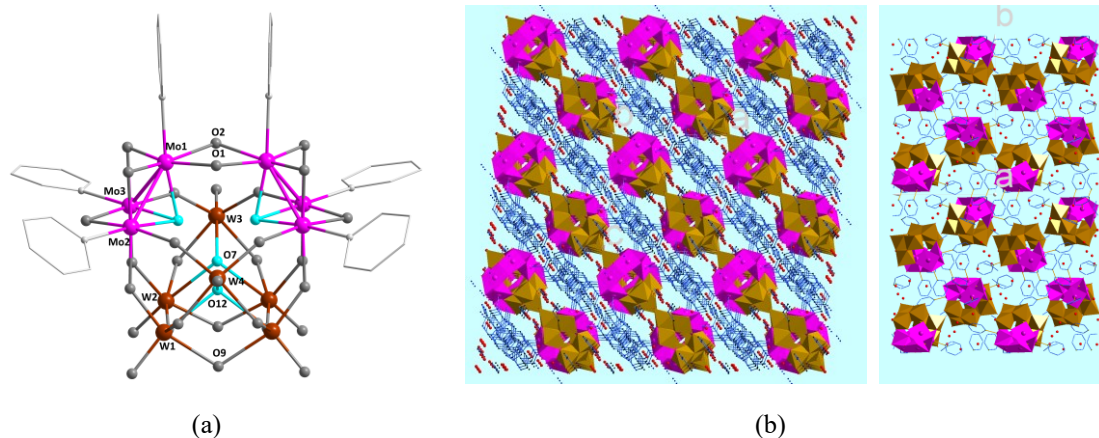


Fig. S5 (a) Structure of **2**; (b) Crystal packing structure of **2**.

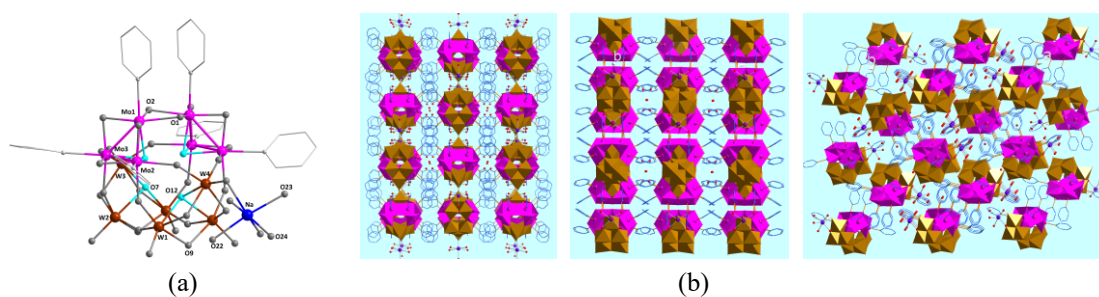


Fig. S6 (a) Structure of **3**; (b) Crystal packing structure of **3**.

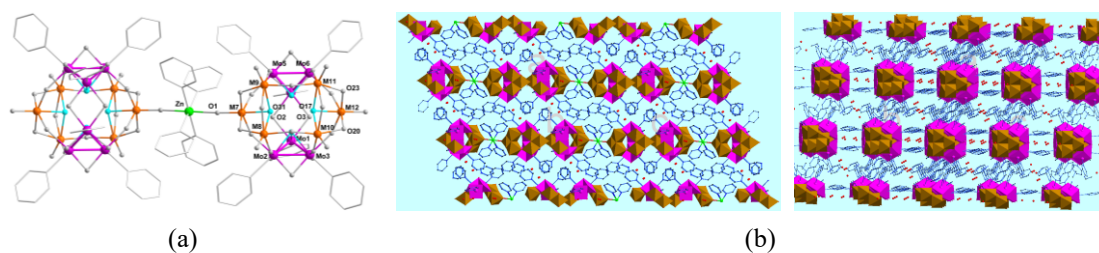


Fig. S7 (a) Structure of **4**; (b) Crystal packing structure of **4**.

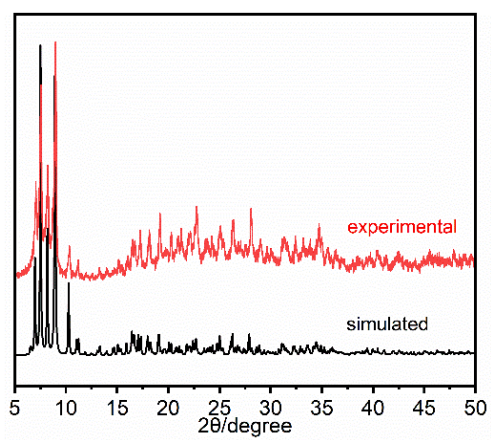


Fig. S8 Powder X-ray diffraction spectrum of **2**.

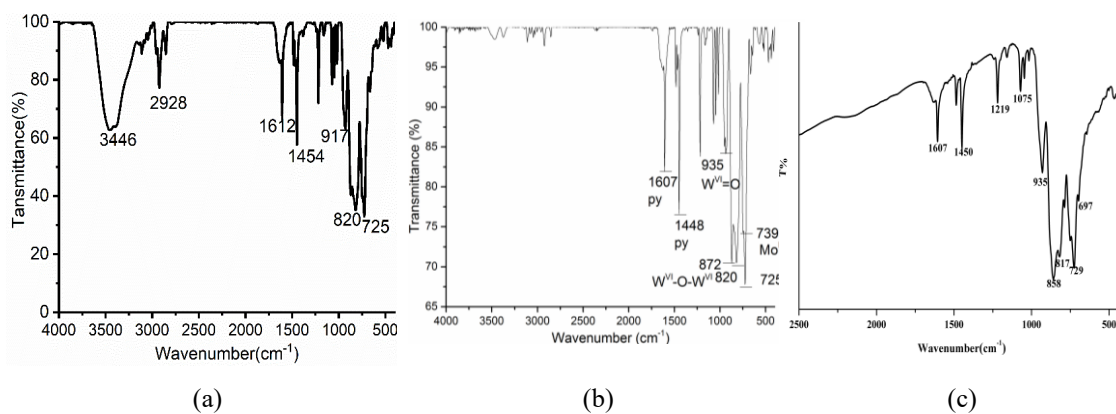


Fig. S9 IR spectra of **2** (a), **3** (b) and **4** (c).

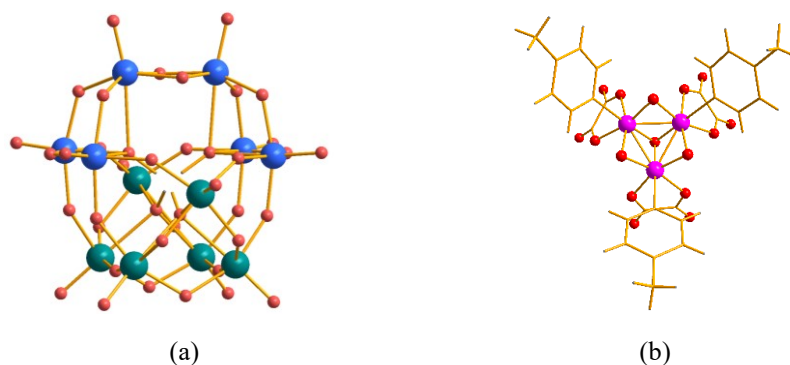


Fig. S10 Structures of the simulated γ -Keggin cluster $[\text{H}_4\text{Mo}_6\text{W}_6\text{O}_{40}]^{4+}$ (a), and the discrete $[\text{Mo}^{\text{IV}}_3\text{O}_4(\text{C}_2\text{O}_4)_3(\text{Mepy})_3]^{2-}$ (b) for DFT calculations (Mo^{IV}, pink; Mo^{VI}, blue; W, dark green; O, red).

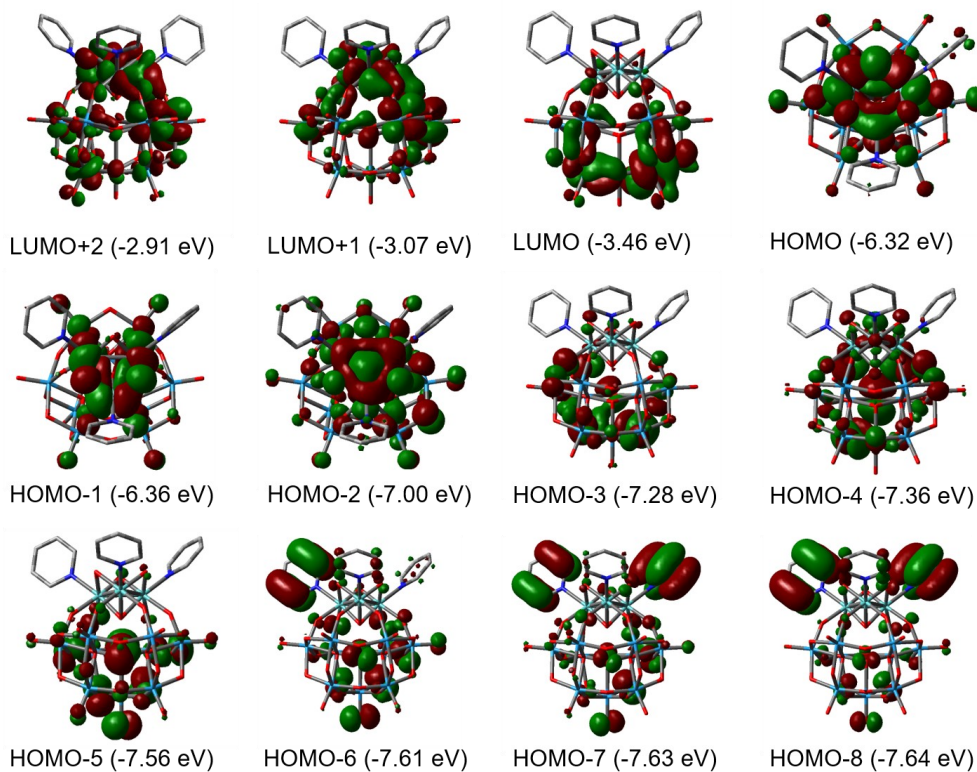


Fig. S11 MOs of **1**

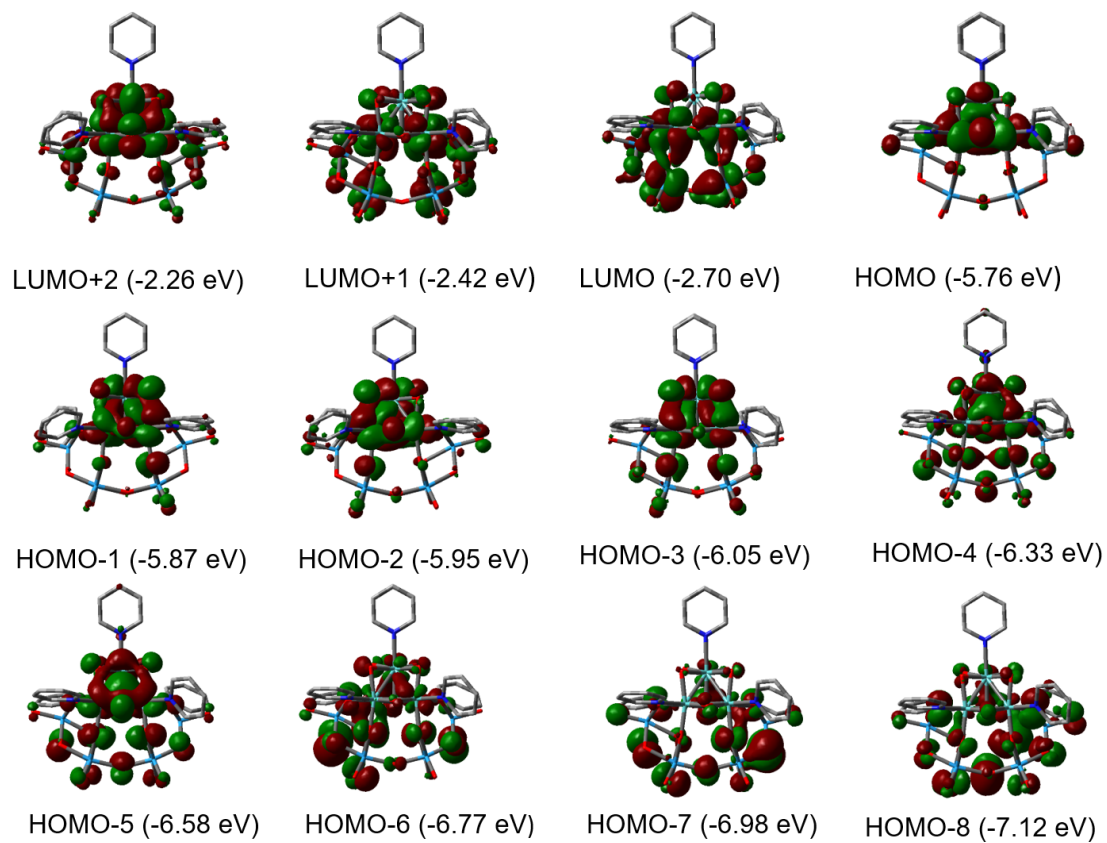


Fig. S12 MOs of 2

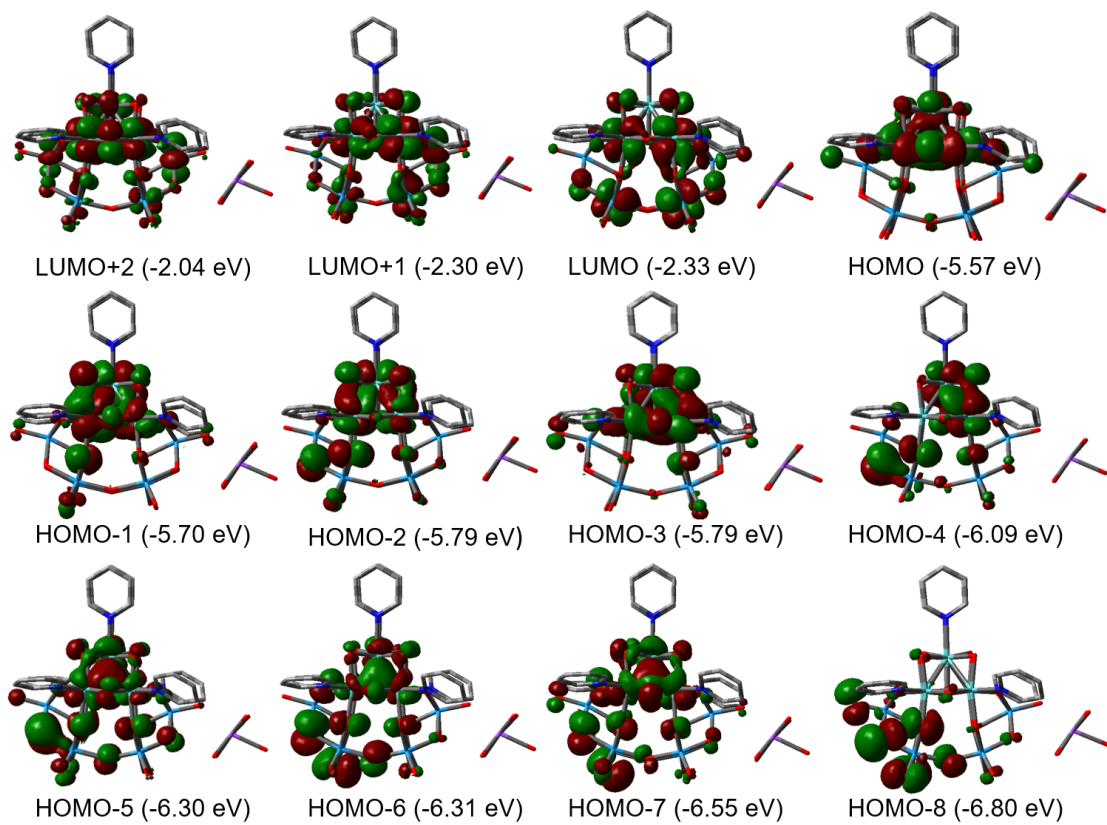


Fig. S13 MOs of 3

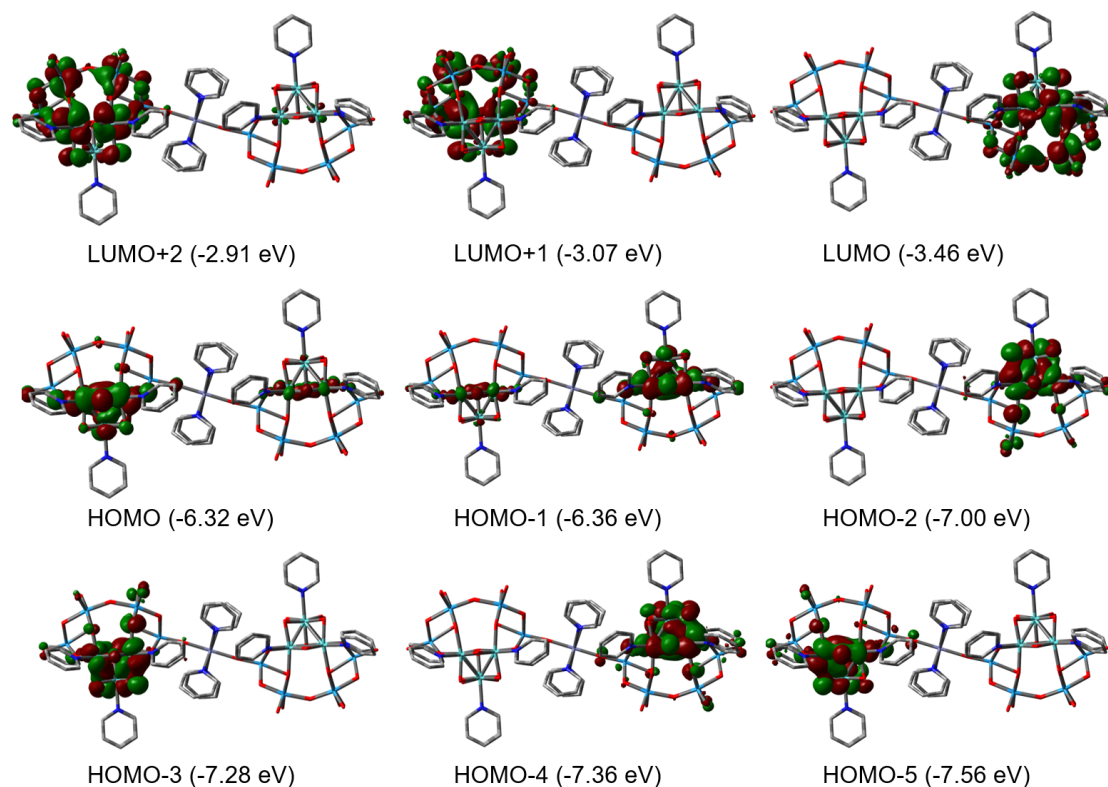


Fig. S14 MOs of 4

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