Supporting Information

Synthesis and characterization of the $[(HPO_3)_6Mo_{21}O_{60}(H_2O)_4]^{8-}$: A new redox active heteropoly blue cluster with layered shape containing phosphite template that self-assembly under controlled microwave irradiation

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1. Chemicals and instruments

All chemicals were purchased from commercial sources and used without further purification. The reaction was carried out in a NOVA-2S microwave reactor. The IR spectra were obtained on an Alpha Centauri FTIR spectrometer in the 400-4000 cm^{-1} region with a KBr pellet. The TG-DSC were performed on a PerkinElmer TGA7 instrument under flowing argon with a heating rate of 10K·min^{-1} at 35–800 °C. The UV spectra were obtained on a SHIMADZU UV-VIS spectrophotometer. The CV spectra were performed on a CHI600E electrochemical workstation. The ^{31}P NMR spectra were performed on Bruker DRX500MHz Nuclear Magnetic Resonance. ESI-MS (electrospray ionization mass spectrometry): Measurements were performed using a Waters Synapt-G2 spectrometer. The instrument was operated in negative mode and with an electrospray source from Waters Q-ToF Qualification Standard Kit. Data analysis was performed on the Waters MassLynx v4.1 software. CHN analyses were determined using an 5E-CHN2000 Elemental Analyser.

2. Synthesis

Synthesis of $(C_2H_8N)_8[(HPO_3)_6Mo_{21}O_{64}H_8]\cdot16H_2O$ (**1**). $Na_2MoO_4\cdot2H_2O$ (0.5 g, 2.07 mmol) and $(CH_3)_2NH\cdot HCl$ (1.0g,12.26mmol) were dissolved in 15 mL of distilled water with moderate stirring. $N_2H_4\cdot H_2SO_4$ (0.049 g, 0.414 mmol) was added to the mixture sequentially till resulting in a pale-blue solution, followed by adjustment of the pH to 4.4 with 1 M HCl. Then H_3PO_3(0.0845g,1.035mmol) was added in. The mixture was placed in a microwave reactor (NOVA-2S, PreeKem) and irradiated inside the cavity of labstation. The temperature was up to 35 ℃ after 10 min as set and 10 mL methyl alcohol were added in after 8 min. (The reaction parameters are: atmospheric model; heat-up time:10min; holding time:10min;) After 2min, the mixture was filtered and dark blue claviform crystals formed over a 2-day period. Yield: 0.775g ,15.5%(based on Mo)

Synthesis of $(C_2H_8N)_4[PMo_{12}O_{40}]\cdot2C_2H_7N$ **(2).** $Na_2MoO_4\cdot2H_2O$ (0.5 g, 2.07 mmol) and $(CH_3)_2NH\cdot HCl$ (1.0g, 12.26mmol) were dissolved in 15 mL of distilled water with moderate stirring. $N_2H_4\cdot H_2SO_4$ (0.0245 g, 0.207 mmol) was added to the mixture sequentially till resulting in a pale-blue solution, followed by adjustment of the pH to 4.64 with 10% (wt%) H_3PO_3. The mixture was stirred at room temperature for 1h and 10 mL methyl alcohol was added. After 20min, the mixture was filtered and dark blue cubic crystals formed over a 20-day period. Yield: 0.105g, 28.3% (based on Mo)

3. Crystallographic data

Table S1: Crystallographic Details for Compound **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{16}H_{110}Mo_{21}N_8O_{98}P_6$	$C_{12}H_{46}Mo_{12}N_6O_{40}P$
CCDC number	1436128	1436253
Formula weight	4183.68	2096.80
Temperature (K)	296(2)	296(2)
Crystal system	Triclinic	Orthorhombic
Space group	P-1	Pnma
a (Å)	13.5799(6)	22.5266(5)
b (Å)	20.0897(9)	19.5714(4)
c (Å)	23.0045(10)	11.2097(2)
α (°)	99.020(3)	90.00
β (°)	90.469(3)	90.00
γ (°)	107.358(2)	90.00
V (Å^3)	5906.0(5)	4942.10(17)
Z	2	4
Calculated density	2.353	2.818

(Mg m^{-3})		
μ (mm^{-1})	2.338	3.075
θ (°)	25.64	25.99
F (000)	4036	3996
Reflections collected	84891	68965
Independent reflections	11206	4093
R_{int}	0.0825	0.0352
Data / restraints / parameters	22830/35/1080	4998/17/296
Goodness-of-fit on F^2	0.966	1.205
Final R indices	0.0733	0.0554
[I>2σ(I)]	0.1784	0.1300
R indices (all data)	0.1592	0.0725
	0.2034	0.1485

Table S2 the BVS calculation result of the cluster 1a.

Code	Bond Valence	Code	Bond Valence	Protonation Degree
Mo1	5.867	P1	3.862	1
Mo2	5.888	P2	3.903	1
Mo3	5.849	P3	4.006	1
Mo4	5.751	P4	3.919	1
Mo5	5.766	P5	3.876	1
Mo6	5.898	P6	3.996	1
Mo7	5.589	O65	0.164	2
Mo8	5.667	O64	0.227	2
Mo9	5.814	O49	0.266	2
Mo10	5.782	O46	0.218	2
Mo11	5.787	Mo16	6.119	
Mo12	5.801	Mo17	6.084	
Mo13	6.069	Mo18	6.120	
Mo14	5.691	Mo19	6.104	
Mo15	6.156	Mo20	5.932	
		Mo21	6.034	

4. ^{31}P-NMR

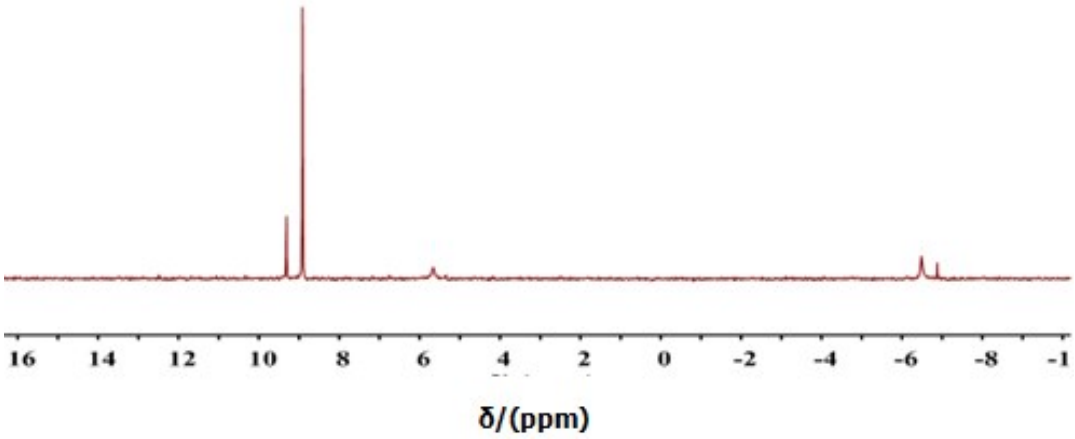

Fig. S1: proton decoupled ^{31}P-NMR of compound 1 in CD_3CN

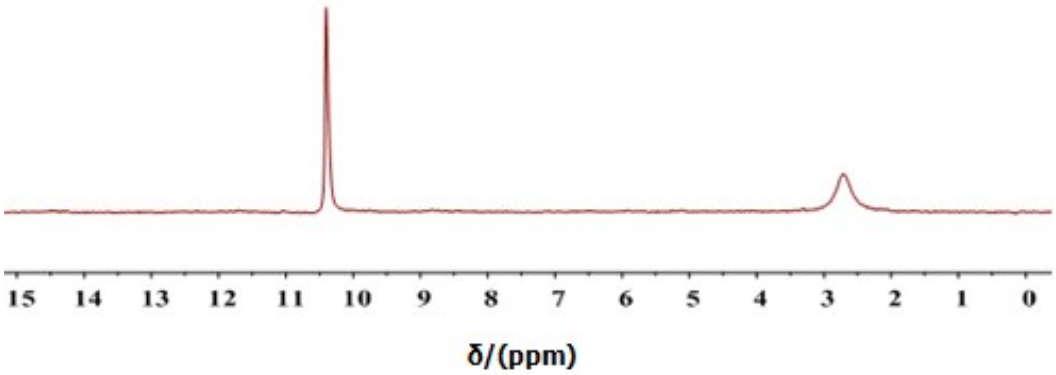

Fig. S2: proton decoupled ^{31}P-NMR of compound 1 in D_2O

5. ESI- MS Mass Spectrometry data

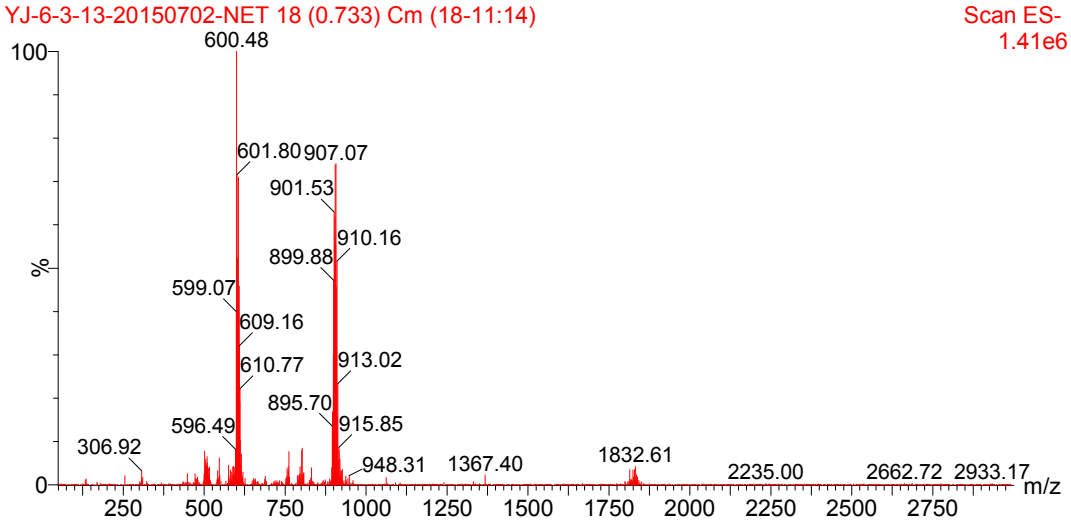

Fig. S3 the negative ESI-MS spectrum of Compound 1 dissolved in CH_3CN

Table S3. Assignments of the major peaks for the ESI-MS analysis of Compound 1.

m/z (Obs)	z Assignment	m/z (Calc)
600.48	$(C_2H_8N)_2[(HPO_3)_6Mo_{21}O_{60}(H_2O)_3]^{6-}$	600.11
907.07	$(C_2H_8N)_2H_2[(HPO_3)_6Mo_{21}O_{60}(H_2O)_4]^{4-}$	905.17
1832.61	$(C_2H_8N)_3H[(HPO_3)_6Mo_{21}O_{60}(H_2O)_4]^{3-}$	1832.81

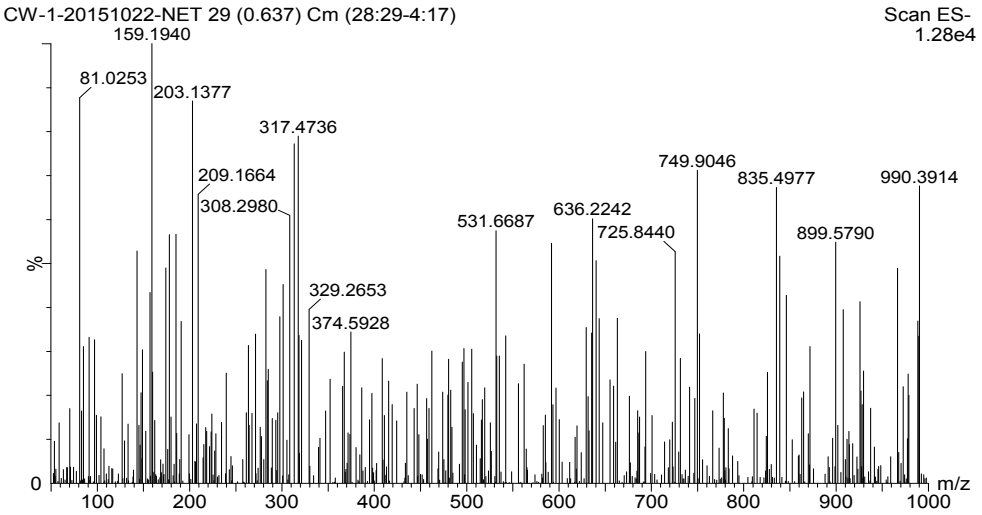

Fig. S4 the negative ESI-MS spectrum of Compound 1 dissolved in H_2O

6. Cyclic voltammograms and Differential pulse voltammetry data

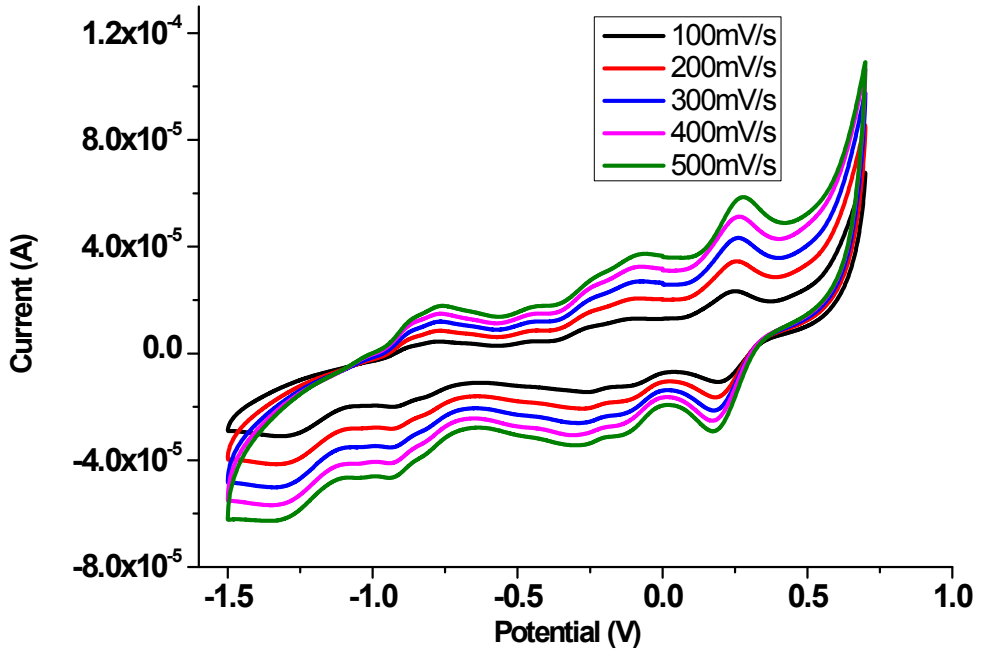

Fig S5 Cyclic voltammograms of 2.5×10^{-5} M solution of **1** in CH_3CN with different scan rates. The working electrode was glassy carbon, the counter electrode was Pt wire, and the reference electrode was Ag/AgCl

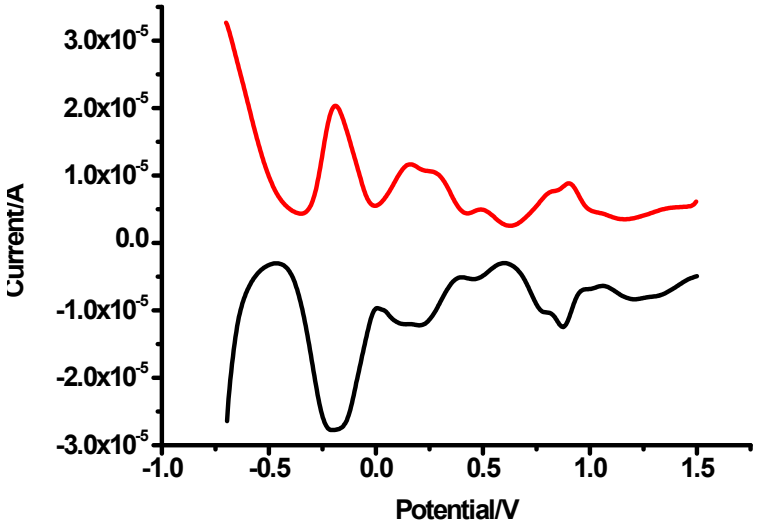

Fig. S6. Differential pulse voltammetry of 2.5×10^{-5} M solution of **1** in CH_3CN.

Table S4: DPV data for Compound **1**

From negative to positive electrode	From positive to negtive electrode
Init E (V) = -0.7	Init E (V) = 1.5
Final E (V) = 1.5	Final E (V) = -0.7
Incr E (V) = 0.004	Incr E (V) = 0.004
Amplitude (V) = 0.05	Amplitude (V) = 0.05
Pulse Width (sec) = 0.05	Pulse Width (sec) = 0.05
Sample Width (sec) = 0.0167	Sample Width (sec) = 0.0167
Pulse Period (sec) = 0.5	Pulse Period (sec) = 0.5
Quiet Time (sec) = 2	Quiet Time (sec) = 2
Sensitivity (A/V) = 1e-4	Sensitivity (A/V) = 1e-4
Ep = -0.200V	Ep = 0.900V
ip = -2.106e-5A	ip = 1.975e-6A
Ap = -4.885e-6VA	Ap = 1.450e-7VA
Ep = 0.456V	Ep = 0.492V
ip = -9.110e-7A	ip = 1.179e-6A
Ap = -9.613e-8VA	Ap = 1.127e-7VA
Ep = 0.876V	Ep = 0.160V
ip = -3.366e-6A	ip = 2.746e-6A
Ap = -2.383e-7VA	Ap = 3.357e-7VA
	Ep = -0.188V
	ip = 1.544e-5A
	Ap = 2.375e-6VA

7. UV- visible spectrum

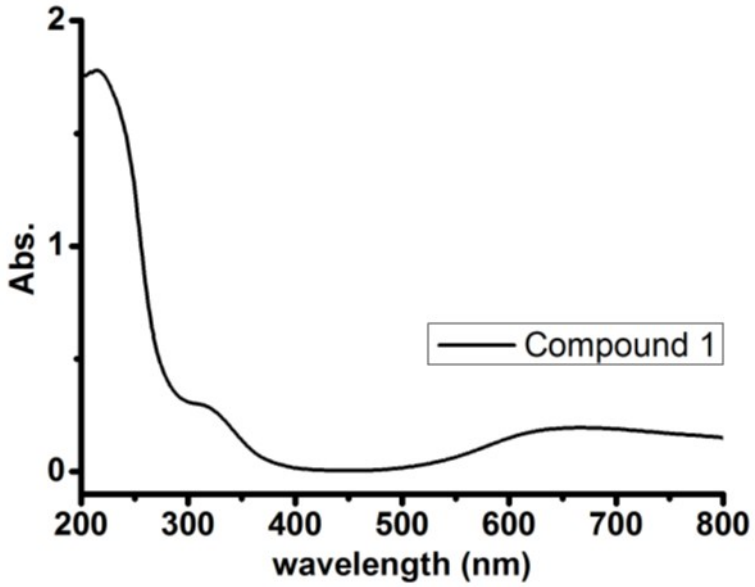

Fig. S7. UV- visible spectrum ranging from 210 nm to 800 nm of 2.18×10^{-6} M solution of 1 in CH_3CN .

8. Infrared spectra

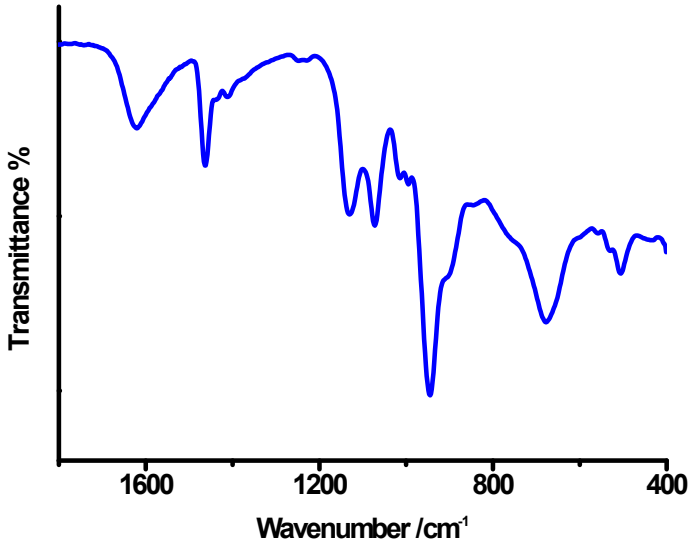

Fig S8. Infrared spectra ranging from 400 cm^{-1} to 1800 cm^{-1} of compound **1**

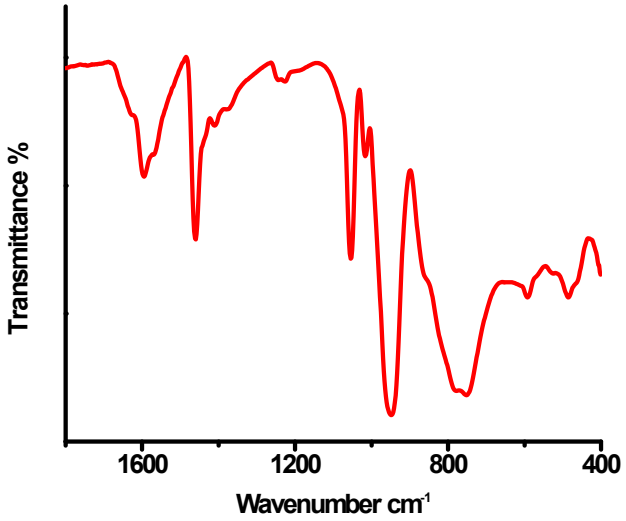

Fig S9. Infrared spectra ranging from 400 cm^{-1} to 1800 cm^{-1} of compound **2**

9. TGA and DSC

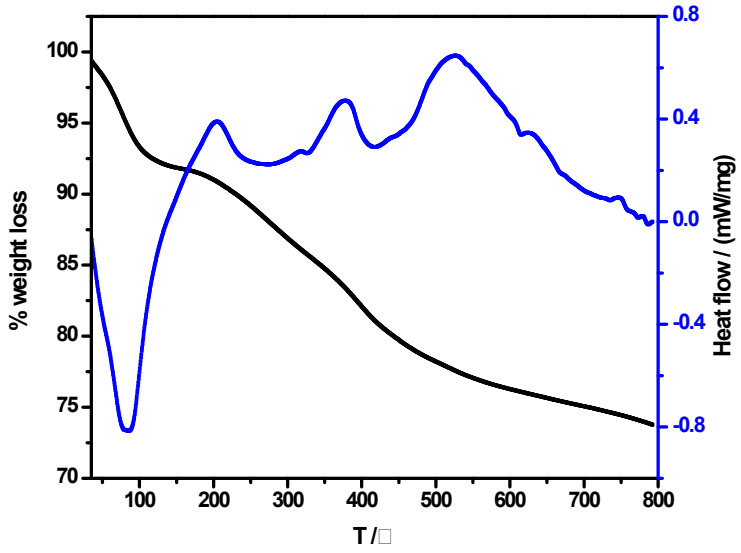

Fig. S10. TGA and DSC analysis of compound **1**.

The TG curve shows three consecutive weight loss stages in the entire temperature range. The simultaneous TG-DSC data for compound 1 evolved that, in the range of 35–100 °C, a mass of weight (7.6%) was desorbed corresponding to the release of the solvent water about 16 H_2O per cluster at around 90°C.