Supporting Information

Polyoxometalate-based Crystalline Material as Highly Sensitive Electrochemical Sensor for Detecting Trace Cr(VI)

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1. X-ray Crystallography.

Select the block crystal with regular size in the products, adhered it on the top of glass fiber, measured on sample table, and the crystal diffraction point data was collected at the temperature of 296(2) K by using a ray of Mo-K ray (λ = 0.71073 Å). The crystal structure data are analyzed by SHELEXL program, modified by the full matrix least square method, and all non-hydrogen atoms are corrected by anisotropy. The crystal data of compounds **1-2** are shown in Table S1.

Table S1 Crystal analytical data of compounds **1-2**.

Compounds	**1**	**2**
Empirical formula	$C_{26}H_{72}N_4O_{71}P_8Mo_{12}Fe_2Na_4$	$C_{104}H_{182}N_{16}O_{137}P_{16}Mo_{24}Fe_2$
Formula weight	3179.56	6758.48
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	*P*-1
a (Å)	20.839(11)	14.478(8)
b (Å)	18.237(9)	15.038(9)
c (Å)	21.622(11)	26.595(15)
α, β, γ (°)	90, 99.994(7), 90	79.208(8), 81.821(8), 70.161(7)
Volume (Å^3), *Z*	8093(7), 4	5331(5), 1
Density (calculated)	2.601 Mg/m^3	2.106 Mg/m^3
Absorption coefficient	2.444 mm^{-1}	1.719 mm^{-1}
$F_{(000)}$	6136	3318
Goodness-of-fit on F^2	1.064	1.059
Final *R* indices [*I*>2sigma(*I*)]	R_1 = 0.0413, wR_2 = 0.1220	R_1 = 0.0429, wR_2 = 0.1144
R indices (all data)	R_1 = 0.0427, wR_2 = 0.1232	R_1 = 0.0467, wR_2 = 0.1177

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

Table S2 The bond valence sum (BVS) calculated results of heteroatoms in compounds **1-2**.

Compound **1**		Compound **2**			
Mo1	5.314	Mo1	4.564	Fe1	1.511
Mo2	5.403	Mo2	4.544	Fe2	1.592
Mo3	5.313	Mo3	4.562	P1	4.397
Mo4	5.272	Mo4	4.505	P2	4.366
Mo5	5.330	Mo5	4.538	P3	4.375
Mo6	5.399	Mo6	4.632	P4	4.379
P1	4.879	Mo7	4.572	P5	4.366
P2	4.944	Mo8	4.536	P6	4.315
P3	4.991	Mo9	4.521	P7	4.294
P4	4.870	Mo10	4.552	P8	4.393
Fe1	1.917	Mo11	4.593		
Fe2	1.589	Mo12	4.519		
Na1	0.793				
Na2	0.386				

Table S3 Peak potential data (mV) for **1-2** at a sweep rate of 110 mV·s^{-1}.

Scan rate 110 mV s^{-1}	$E_{1/2}$ (I) / mV	$E_{1/2}$ (II) / mV	$E_{1/2}$ (III) / mV
compound **1**	-23.1	229.3	367.5
compound **2**	-27.2	224.8	363.6

Concretely, the possible reaction for each reversible redox peak are as follows:

$$P_4Mo_6O_{31}^{12-} + 2e^- + 2H^+ = H_2P_4Mo_6O_{31}^{12-}$$

$$H_2P_4Mo_6O_{31}^{12-} + 2e^- + 2H^+ = H_4P_4Mo_6O_{31}^{12-}$$

$$H_4P_4Mo_6O_{31}^{12-} + 2e^- + 2H^+ = H_6P_4Mo_6O_{31}^{12-}$$

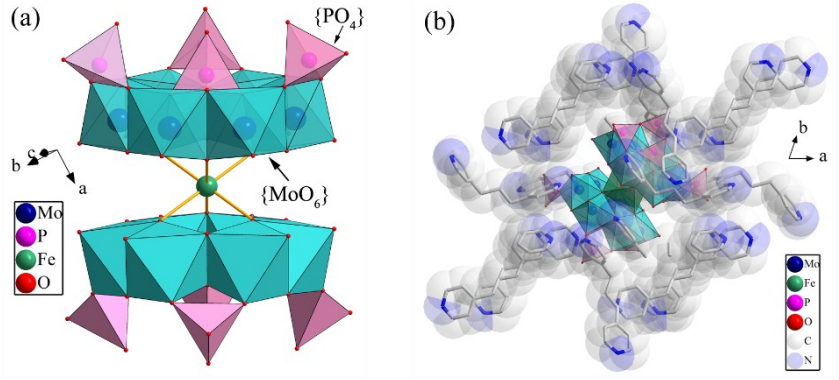

Figure S1 The mixed ball-stick and polyhedral view of (a) $\{Fe(P_4Mo_6)_2\}^{n-}$ unit; (b) The mixed polyhedral and space-filling view showing the $\{Fe(P_4Mo_6)_2\}^{n-}$ unit surrounded by H_2bpp cations in **2** along *c* axis, to formed the 'core-shell' structure.

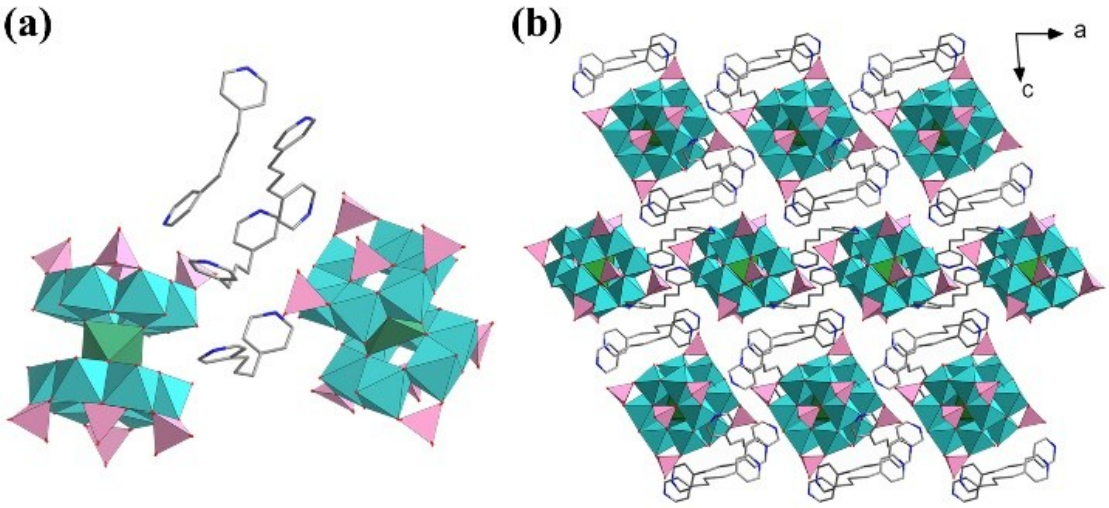

Figure S2 (a) The polyhedral and ball-and-stick views of the basic unsymmetrical units in 2; (b) the stacking view of $\{Fe(P_4Mo_6)_2\}$ polyanions and bpp cations in **2** along *b* axis.

2. Structural characterization

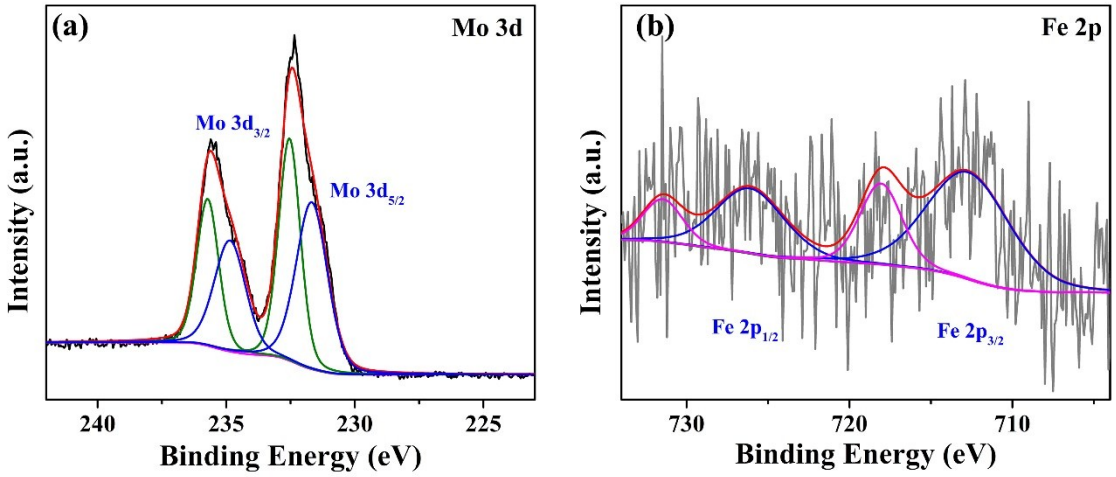

Figure S3 (a)-(b) The XPS spectra of Mo and Fe elements in compound **2**.

The IR spectrum of **1-2** exhibits various characteristic peaks at 1012, 960, 744 and 686 cm^{-1} are attributed to ν(P-O), ν(Mo=O_t) and ν(Mo-O-Mo) vibrations, which proves the existence of phosphomolybdates basic framework; the peaks at 1506 and 1635 cm^{-1} are corresponding to the ν(C-C) and ν(C-N) in the organic molecules H_2bpp.

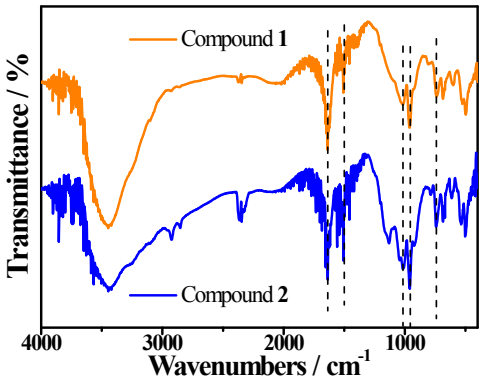

Figure S4 The IR spectrum of compounds **1-2**.

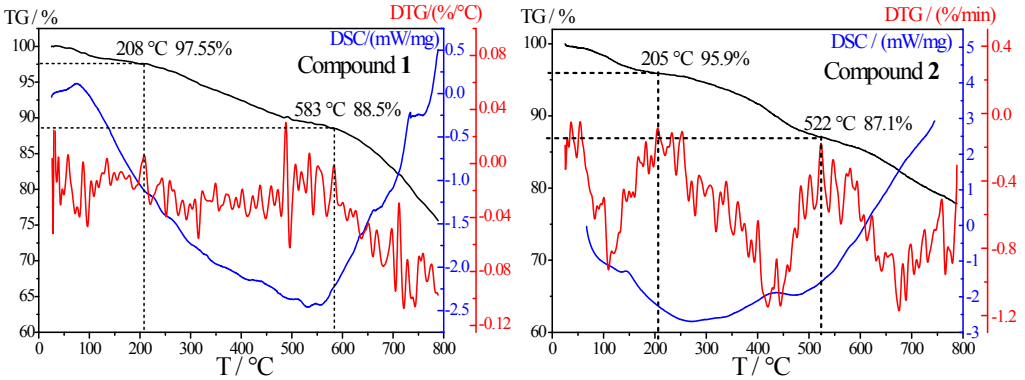

Figure S5 The TG, DSC and DTG curves of compounds **1-2**.

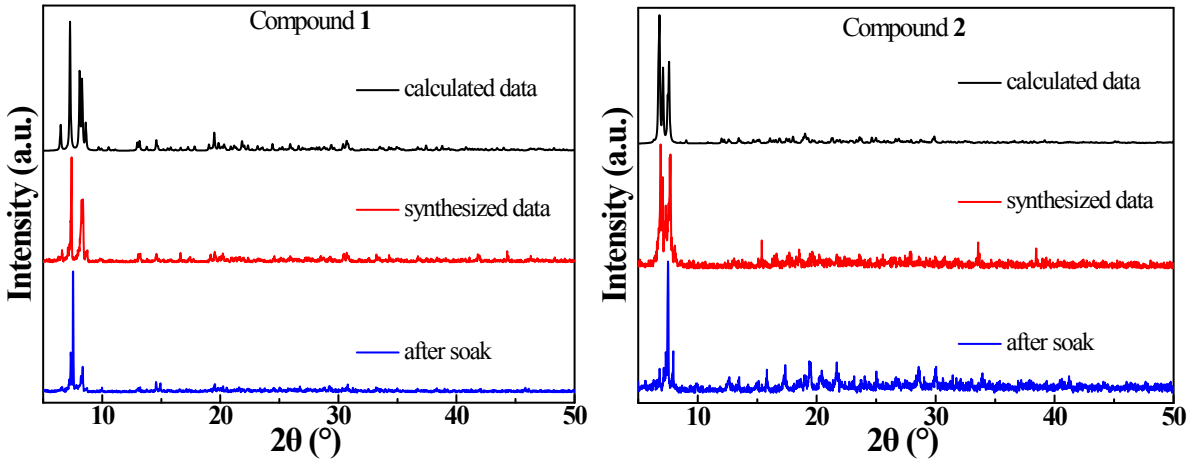

Figure S6 The XRD patterns of compounds **1**-**2**.

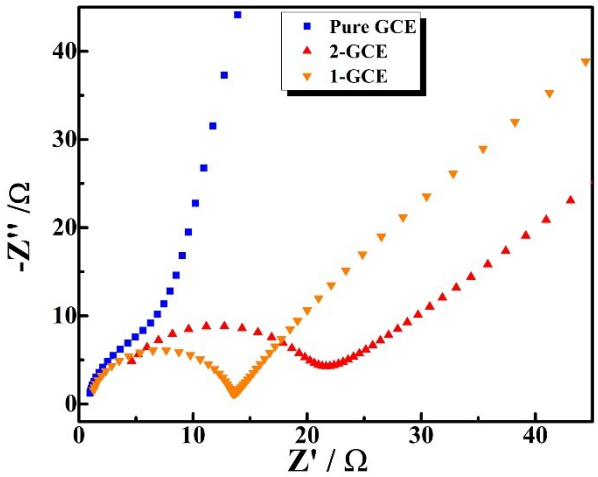

Figure S7 Nyquist plots of electrochemical impedance spectra (EIS) of **1**/**2**-GCE, pure GCE and carbon powder modified GCE recorded in 0.5 M H_2SO_4 under -0.052 V.