Supporting Information

Synthesis, structures and catalytic properties of two organic-inorganic hybrid polyoxometalates built from $\{Ni_6PW_9\}$ units

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Preparation of 1 bulk modified carbon paste electrode

The preparation method of **1** bulk modified carbon paste electrode (**1**-CPE) is to mix 0.1 g graphite powder and 0.01 g compound **1** in agate mortar for about 30 minutes to obtain a uniform solution. Then add 0.10 mL of paraffin oil and stir with a glass rod. The homogenized mixture was put into a glass tube with an inner diameter of 3 mm, and the surface of the tube was wiped with a weighing paper. An electrical contact is established with the copper wire through the back of the electrode.

Performance evaluation of oxidative desulfurization reactions

Oxidative desulfurization experiments were conducted in a three-necked flask containing 20 mL of simulated oil (DBT dissolved in n-nonane, 1000 μg/g sulfur), 20 mL of acetonitrile, 0.0700 g of catalyst, and 30 wt% H_2O_2. The mixture was refluxed at the designated temperature with a consta nt stirring speed of 1000 r/min. Following the reaction, the upper oil phase was sampled, centrifuged, and analyzed for sulfur content using an RPP-2000S Fluorescence Sulfur Determination Instrument.

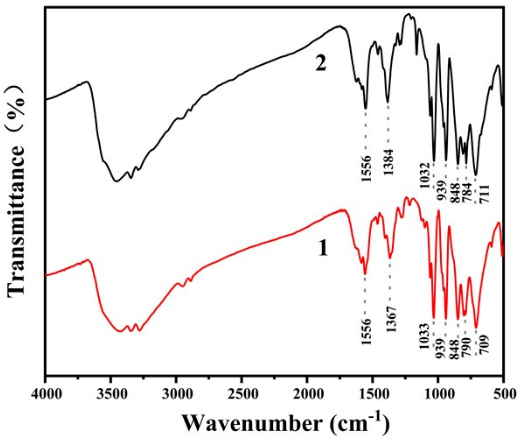

Fig. S1 FT-IR spectra of **1-2**.

Characteristic absorption peaks can be observed at 1033, 939, 848–790, 709cm^{-1} for **1** and 1032, 939, 848–784, 711 cm^{-1} for **2**, which are attributed to *v*(P–O), *v*($W–O_t$), *v*($W–O_b$) and *v*($W–O_c$) respectively, indicating the existence of [B-*α*-PW_9O_{34}]$^{9-}$ fragments. The characteristic peak of benzene also appear at 1560 cm^{-1} for **1** and **2**. In addition, the characteristic peaks observed at 2925 cm^{-1}, 1367 cm^{-1} for **1**, and 2950 cm^{-1}, 1384 cm^{-1} for compound **2** are attributed to $–NH_2$ and $–CH_2$ of organic amine.

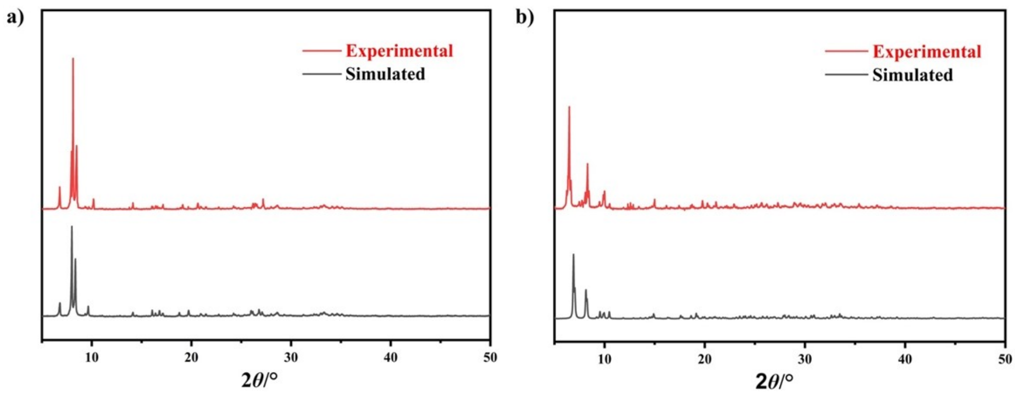

Fig. S2 The PXRD spectra of **1** (a) and **2** (b).

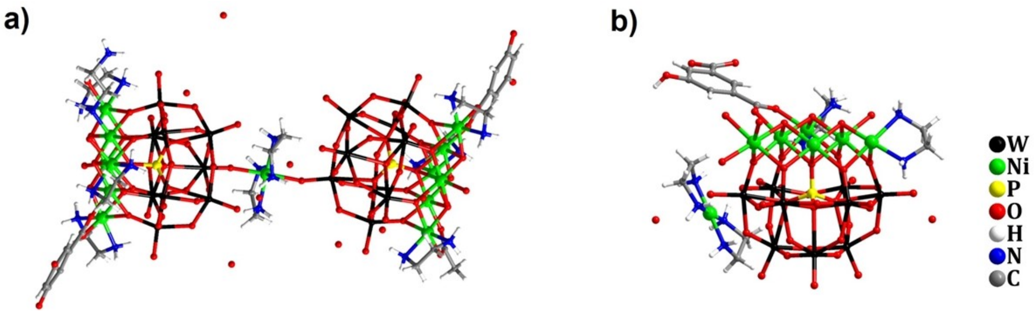

Fig. S3 The asymmetric units of compounds **1** (a) and **2** (b).

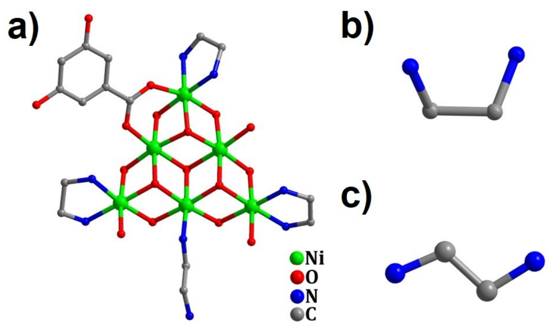

Fig. S4 The coordination environment of the $\{Ni_6\}$-oxo cluster in **1A** (a); The two conformations of ethylenediamine in compound **1** are located in **1A** (b) and **1B** (c).

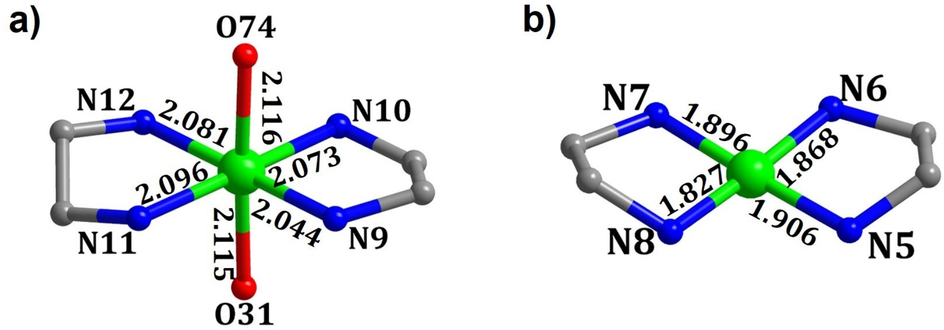

Fig. S5 Ethylenediamine exists in six-coordinate in compound **1** (a) and four-coordinate forms in compound **2** (b).

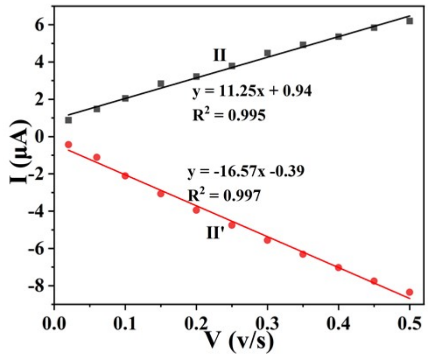

Fig. S6 The relationship diagram between scan rate and peak current.

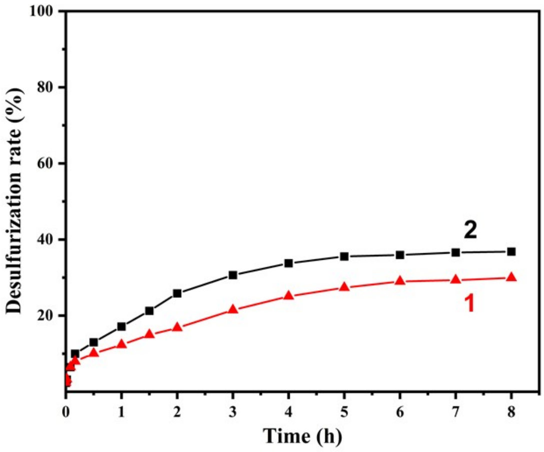

Fig. S7 Oxidative desulfurization performance of **1**-**2**. Reaction conditions: oxidant/oil volume ratio = 1:1, T = 60 ℃, t = 8 h.

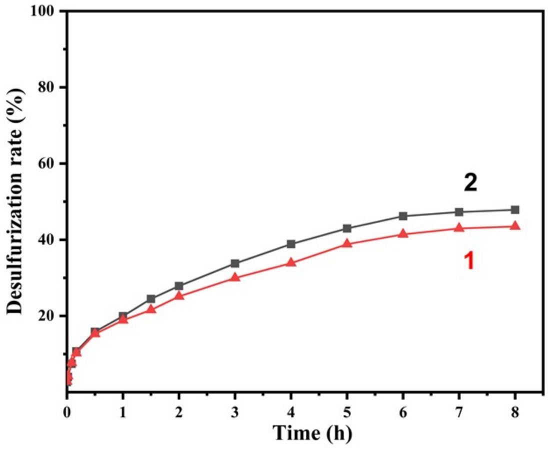

Fig. S8 Oxidative desulfurization performance of **1**-**2**. Reaction conditions: oxidant/oil volume ratio = 1:1, T = 80 ℃, t = 8 h.

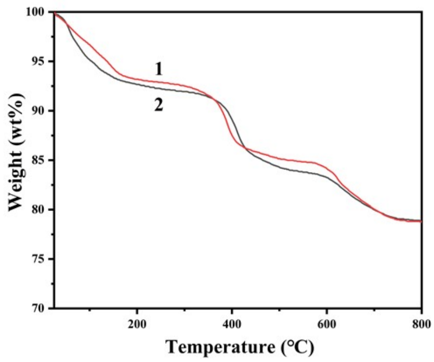

Fig. S9 The TG curves of compounds **1-2**.

TG curves indicate that the weight loss of **1-2** can be divided into regarded as a continuous process in the range of 25-800 ˚C (Fig. S9). From 25 to 800 °C, the reduction of 21.2% for the mass of compound **1** was attributed to the loss of 9 adsorbed water molecules, 8 lattice water molecules, 5 coordination water molecules, 9 en ligands and one Ac ligand， two 3,5-DDB ligands, 1 proton (dehydrated as 0.5 H_2O), and 6 hydroxyl groups (dehydrated as 3 H_2O). From 25 to 800 °C, the reduction of 21.0% for the mass of compound **2** was attributed to the loss of 12 adsorbed water molecules, 3 lattice water molecules, 4 coordination water molecules, 4 en ligands, one 3,5-DDB ligands and 6 hydroxyl groups (dehydrated as 3 H_2O).

Table S1. Bond Valence Sum (BVS) calculations for Compound **1**.

Atom	BVS	Atom	BVS	Atom	BVS
Ni1	2.0234	Ni12	2.0666	W8	6.101
Ni2	2.0678	Ni13	1.9711	W9	6.0304
Ni3	2.0036	P1	4.8999	W10	6.034
Ni4	1.9286	P2	4.9171	W11	6.0448
Ni5	1.9566	W1	6.0753	W12	6.0763
Ni6	1.9027	W2	6.0069	W13	6.0623
Ni7	2.0324	W3	6.0848	W14	6.0373
Ni8	1.9627	W4	6.0056	W15	6.1489
Ni9	1.9713	W5	6.0815	W16	6.0204
Ni10	2.0201	W6	6.1478	W17	6.0965
Ni11	1.9709	W7	6.0938	W18	6.1082

Table S2. BVS calculations for Compound **2**.

Atom	BVS	Atom	BVS	Atom	BVS
Ni1	1.7214	Ni7	2.4847	W5	6.6446
Ni2	2.023	P1	4.8988	W6	5.886
Ni3	1.8711	W1	6.0146	W7	6.3811
Ni4	1.8771	W2	6.3255	W8	6.1216
Ni5	2.0136	W3	6.554	W9	6.3359
Ni6	2.0763	W4	6.0022		