Supporting information

Polyoxometalate-Based Supramolecular Architecture Constructed from Purely Inorganic 1D Chain and Metal-Organic Layers with Efficient Catalytic Activity

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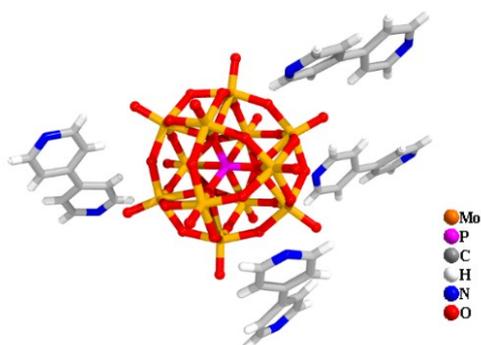
Fig. S1 The structure of $(4,4\text{-bpy})_4[H_3PMo_{12}O_{40}]$ composed of one $[PMo_{12}O_{40}]$ anion

and four 4,4-bpy ligands.

Table S1 The crystal data and structure refinement of $(4,4\text{-bpy})]_4[H_3PMo_{12}O_{40}]\cdot 5H_2O$

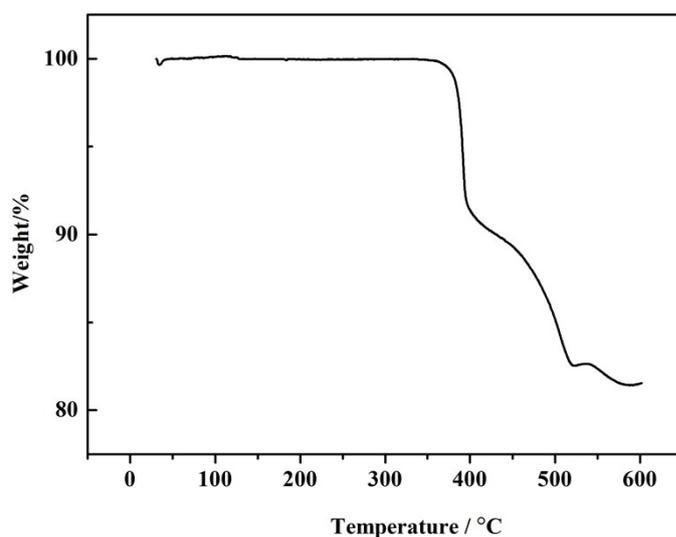| Compound $(4,4\text{-bpy})]_4[H_3PMo_{12}O_{40}]\cdot 5H_2O$	
Formula	$C_{40}H_{42}Mo_{12}N_8O_{45}P$
T (K)	296(2)
F_w	2537.07
Crystal system	monoclinic
Space group	P2(1)/c
a (Å)	18.7596(10)
b (Å)	14.0406(8)
c (Å)	26.5614(14)
$\beta/°$	105.4350(10)
V (Å^3)	6743.8(6)
Z	4.00
μ (mm^{-1})	2.284
λ (Å)	0.71073
R_1, wR_2 [$I>2\sigma(I)$]	0.0670, 0.1819
R_1, wR_2 (all data)	0.0908, 0.2000
$^aR_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; $wR_2 = \Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]^{1/2}$	

Fig. S2 TG curve for compound 1. There is no weight loss up to 356 °C, suggesting no water molecules in the crystal structure, which is consistent the singly crystal X-ray diffraction analysis. Also, this result revealed that the inorganic-organic hybrids polyrotaxane structure exhibited commendably thermal stability. On further heating, there are three weight losses in the TG curve. The first weight loss (8.64%) from 356 to 400°C is attributed to the loss of four Htrz organic ligands (Calcd: 8.56%). The second weight loss (8.54%) and the third weight loss (1.14%) from 400 to 580 °C corresponds to the decomposition of two 4,4-bpy molecules (Calcd: 9.63%).

The procedure for oxidative desulfurization:

A mixture of catalyst (15 μmol), thiophene sulfides (80 μmol) and TBHP (240 μmol) in 2 mL CH_2Cl_2 was stirred at 60 ˚C. The identity of the product was confirmed by FTIR and GC-MS, while the yield was achieved by HPLC analysis with a UV-Vis detector at λ = 254 nm using a Inertsil SIL-100A C18 column. All analyses were obtained with the mobile phase: CH_3CN : H_2O = 90 : 10 at an operating flow rate of 1 mL min^{-1}.

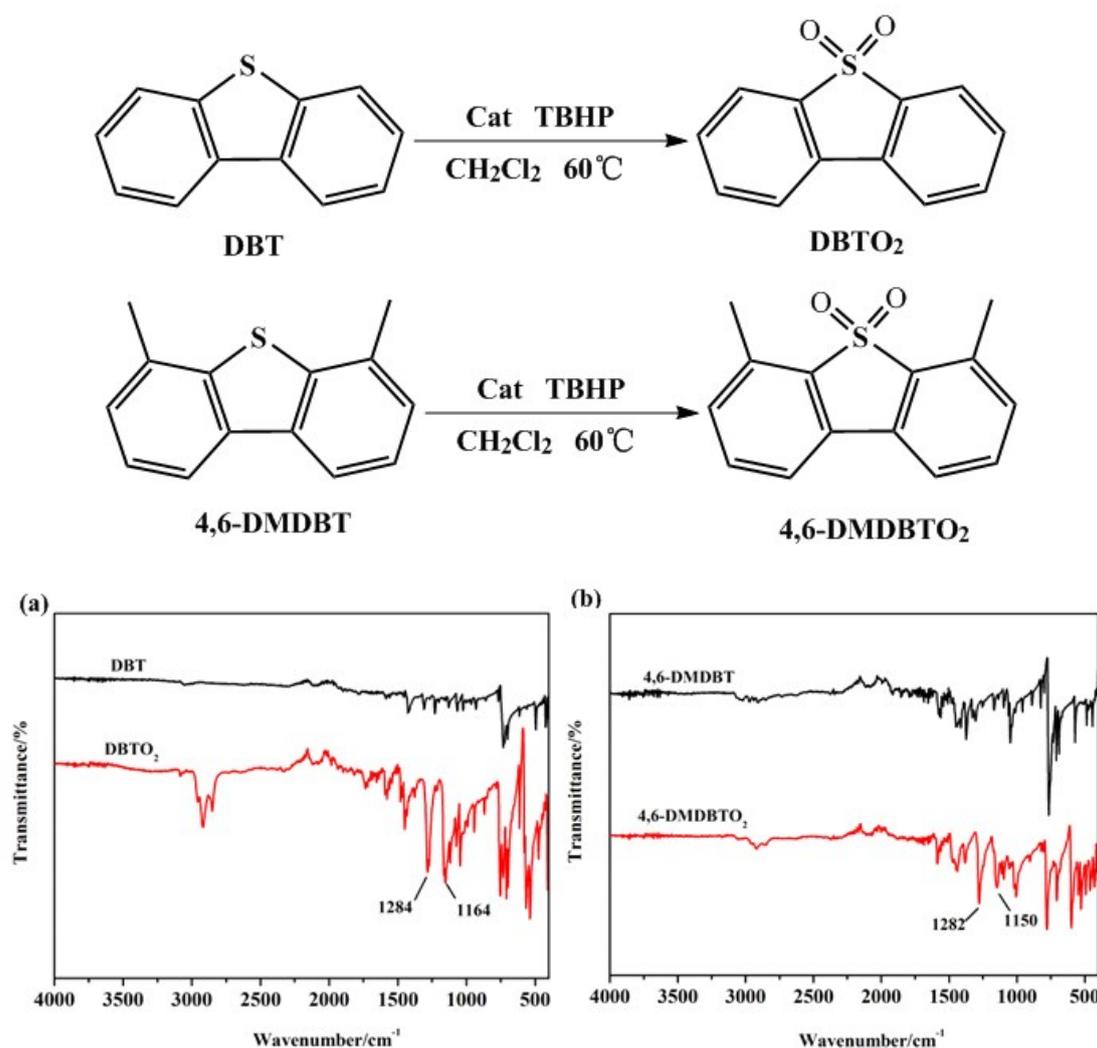**Scheme S1 Oxidation reaction of sulfide to corresponding sulfones.**

Fig. S3 IR spectrum of DBT (a), 4,6-DMDBT (b) and the products DBTO$_2$ and 4,6-DMDBTO$_2$ after the oxidation reaction. The appearance of characteristic frequencies at 1284 cm^{-1} (v_{as}, SO$_2$) and 1164 cm^{-1} (v_s, SO$_2$) confirms the occurrence of sulfones in the product.
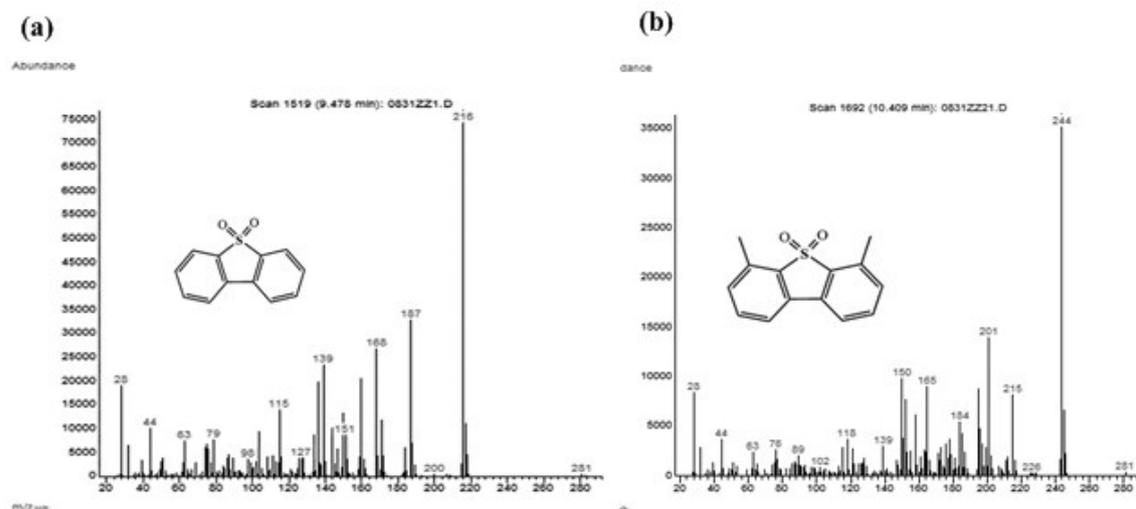
Fig. S4. MS spectra for the oxidation product of DBT (a) and 4,6-DMDBT (b) at 120 min and 200min, respectively.
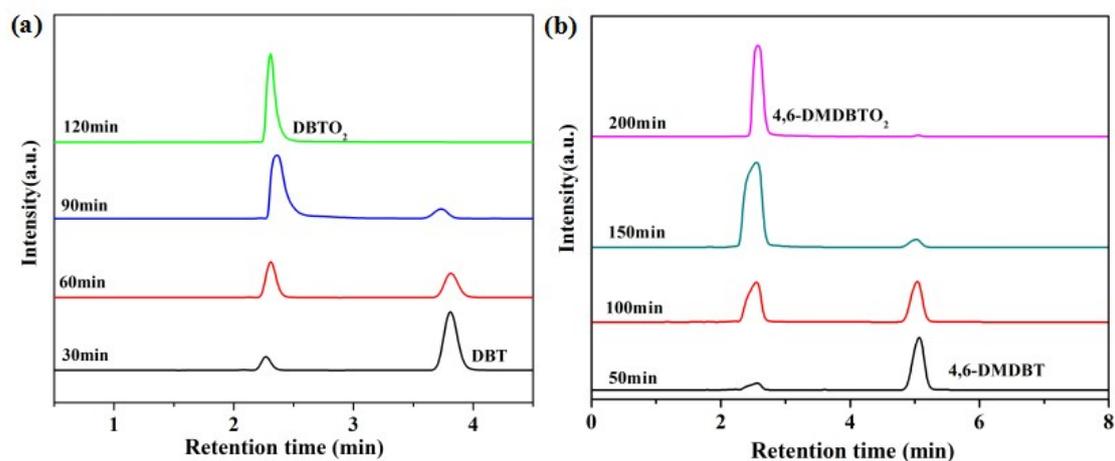

Fig. S5 The reaction progress of DBT (a) and 4,6-DMDBT (b) was monitored over time by HPLC chromatograms in the presence of compound **1**.
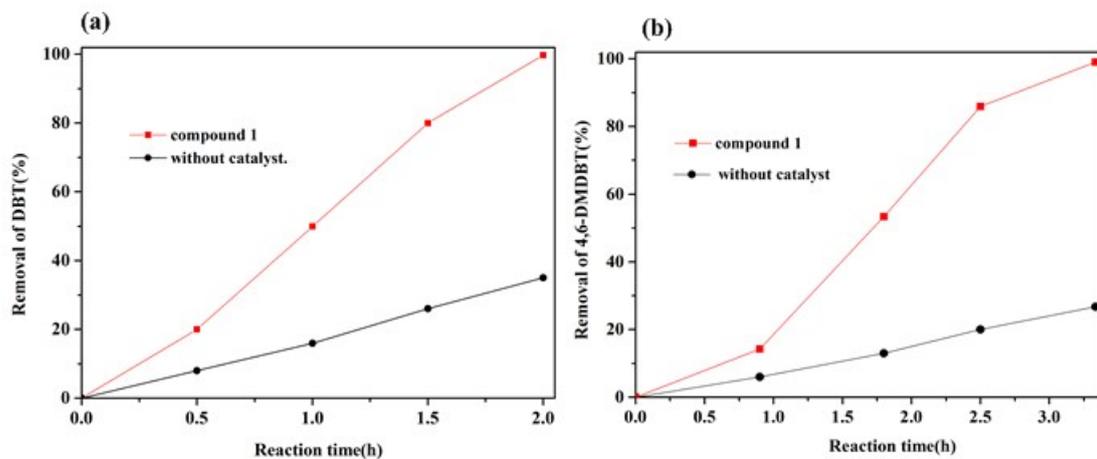
Fig. S6 Removal of DBT (a) and 4,6-DMDBT (b) versus reaction time with the compound **1** as catalyst (■); without catalyst (●). Reaction conditions: thiophene sulfides (80 μmol), TBHP (240 μmol), catalyst (1.5 μmol), CH_2Cl_2 (2mL) and T = 60 ℃.
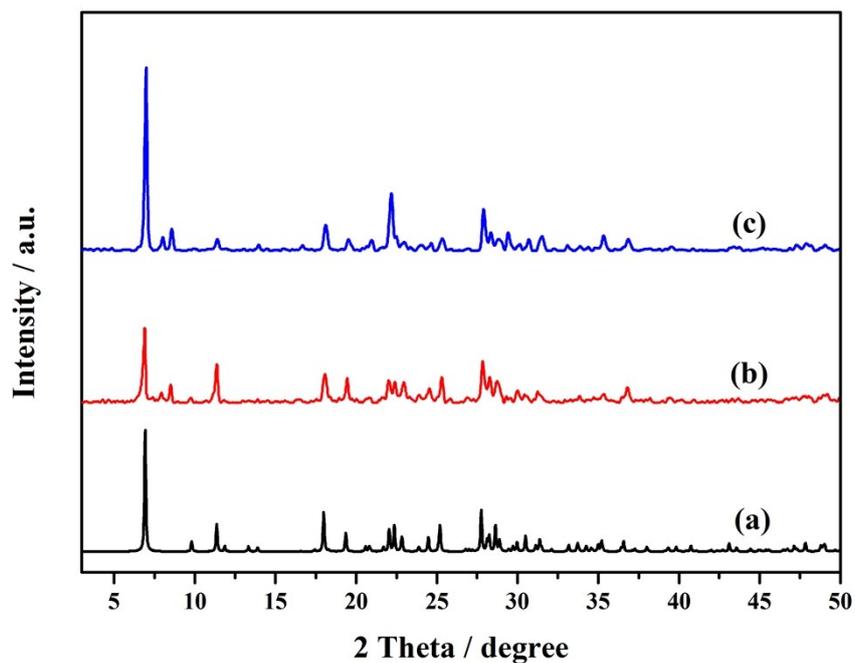

Fig. S7 PXRD patterns of compound **1**: (a) calculated, (b) as-synthesized, (c) recovered after catalytic reaction of DBT.
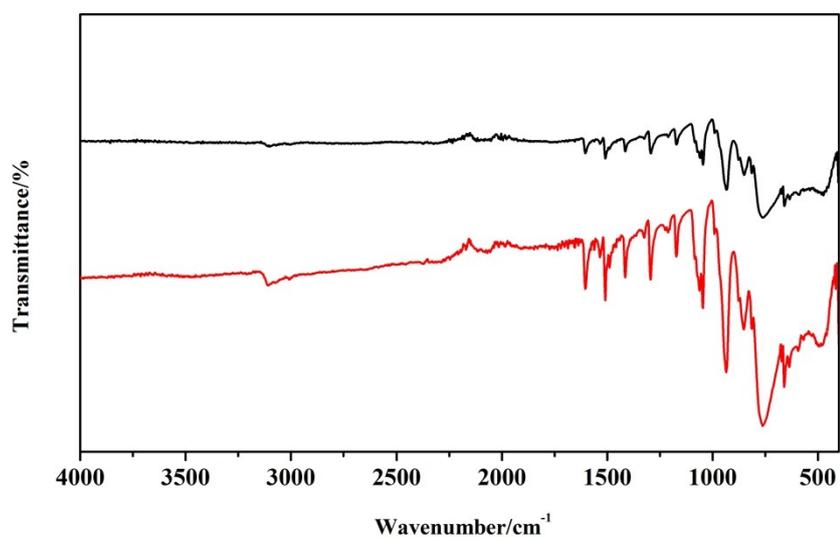
Fig. S8 IR spectrum for as-synthesized catalyst (black line) and recovered catalyst after catalytic reaction (red line).
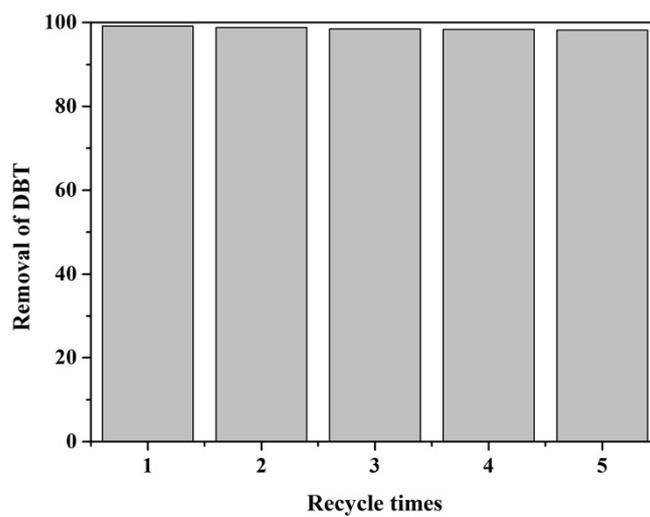

Fig. S9 The recycle experiments for catalytic removal of DBT with **1** as the catalyst.

Table S2 The desulfurization efficiency of polyoxometalates.

| Entry	Substrate	Catalyst	TBHP	t , min	Removal%	Reference
1	DBT (0.08 mmol)	Compound **1** (0.0015 mmol)	0.24mmol	120	99.8	This work
2	DBT (0.4 mmol)	$La_2MnV_{13}O_{38}$ (0.075 mmol)	2.0 mmol	180	99.5	*Chem. Commun.,* [S1] 2013, **49**, 3673
3	DBT (0.4 mmol)	$Co(BBPTZ)_3][HPMo_{12}O_{40}]$ (0.003 mmol)	1.5 mmol	480	99.16	*Chem. Eur. J.,* [S2] 2015, **21**, 3778
4	DMDBT (0.08 mmol)	Compound 1 (0.0015 mmol)	0.24mmol	200	99.1	This work
5	DMDBT (0.4 mmol)	$La_2MnV_{13}O_{38}$ (0.075 mmol)	2.0 mmol	360	99.1	*Chem. Commun.,* [S1] 2013, **49**, 3673
6	DMDBT (0.4 mmol)	$Co(BBPTZ)_3][HPMo_{12}O_{40}]$ (0.003 mmol)	1.5 mmol	480	99.14	*Chem. Eur. J.,* [S2] 2015, **21**, 3778
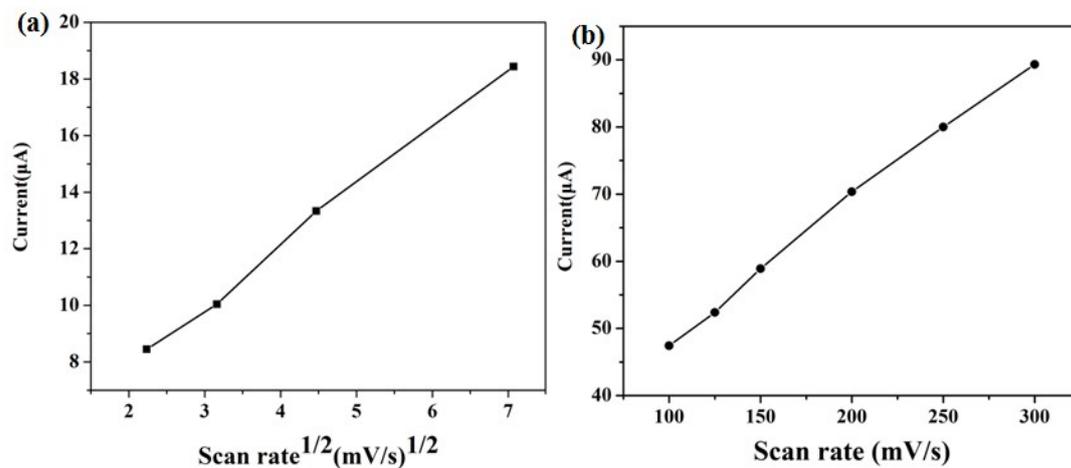
Fig. S10 The relationship of peak currents and scan rate, (a) 5, 10, 20, 50 mV s^{-1} (b) 100, 125, 150, 200, 250, 300 mV s^{-1}.
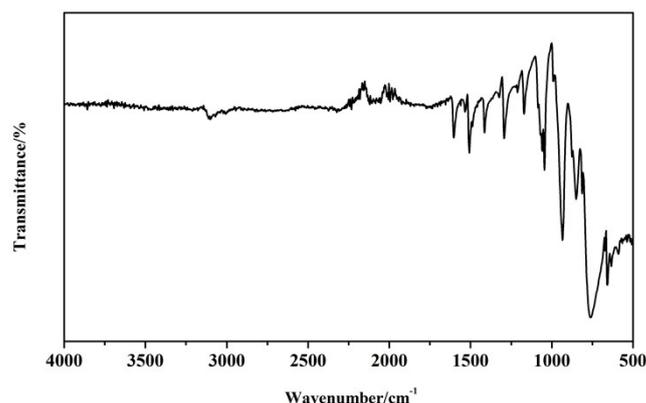

Fig. S11 IR spectrum of compound **1**. There are four characteristic bands at 1045, 932, 876 and 814 cm^{-1}, which corresponded to the characteristic asymmetric vibrations of v(P-Oa), v(Mo-Od), v(Mo-Ob) and v(Mo-Oc). The other absorption bands at 1603, 1508, 1413, 1296, 1170, 762 and 658 cm^{-1}, are attributed to characteristic peaks of the organic ligands.

References

S1 D. Liu, Y. Lu, H. Q. Tan, W. L. Chen, Z. M. Zhang, Y. G. Li and E. B. Wang, *Chem. Commun.*, 2013, **49**, 3673.

S2 X. L. Hao, Y. Y. Ma, H. Y. Zang, Y. H. Wang, Y. G. Li, E. B. Wang, *Chem. Eur. J.*, 2015, **21**, 3778.