Supplementary information for

Oxidative desulfurization of dibenzothiophene with hydrogen peroxide catalyzed by selenium(IV)-containing peroxotungstate

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1. Materials

All chemicals were used as received without further purification. Dibenzothiophene (DBT, 99%), Sodium tungstate dihydrate (AR), Selenium dioxide (AR), Stearyl trimethyl ammonium chloride (STAC, 99%), CinnamylAlcohol (CA, AR) and Quinoline (QL, AR) were purchased from Aladdin Reagent Inc.; Hydrogen peroxide (30%, AR) and n-Octane (CP) were obtained from Sinopharm Chemical Reagent Co. Ltd. (SCRC). Chloroform (AR), Acetonitrile (AR), Chlorhydric acid (37%, AR) and Phosphoric acid (85%, AR) were supplied by Nanjing Chemical Reagent Co.,Ltd..

2. Instruments

Infrared spectrum (FTIR) were recorded on Vector 22 spectrometer (Brucker, Germany) by dried KBr pellet. Raman spectrum were measured on HR800 spectrometer (JY, France) with excitation line at 546 nm and a resolution of 1 cm^{-1}. X-ray photoelectron (XPS) pattern was obtained on PHI 5000 VersaProbe (ULVAC-PHI, Japan) using Al K_{α} radiation. X-ray fluorescence (XRF) was performed with ARL-9800 (ARL, Switzerland). Electrospray ionization mass spectra (ESI-MS) was measured on Mat TSQ 7000 (Finnigan, U.S.A.) in positive-ion mode using methanol as the mobile phase. Thermogravimetric (TG) analysis was carried out using STA 499C (NETZSCH, Germany) under N_2 atmosphere, at the heating rate of 10 /min. Mass spectrum was recorded on Time-of-Flight mass spectrometry (TOF-MS, Micromass, U.K.). The elemental analysis were collected on vario EL II (Elementar, Germany).

3. Synthesis of catalysts

$[C_{18}H_{37}N(CH_3)_3]_4[H_2Se^{IV}_3W_6O_{34}]$ (Q_4-$H_2Se^{IV}_3W_6$ for short) was synthesized as follows: H_2WO_4 was prepared by the common way with $Na_2WO_4 \cdot 2H_2O$ and HCl. H_2WO_4 (2.53 g, 10 mmol) was suspended in 30% H_2O_2 (8 mL, 79 mmol). The resulting suspension was stirred at 333 K for 40 min until a pale yellow solution was obtained. Then the solution was centrifuged (15 min, 2000 rpm) to remove insoluble materials with the following addition of 60% H_2SeO_3 (1.12 g SeO_2 dissolved in 1.1 g H_2O, 10 mmol). The mixture was stirred at room temperature for 60 min to get a clear solution (solution A). After that, a solution of $[C_{18}H_{37}N(CH_3)_3]Cl$ (3.52 g, 10 mmol) in 20 mL $CHCl_3$ was added dropwise into the solution A within 5 min, forming a white emulsion under stirring. After 30 min of stirring at room temperature, the emulsion went through phase separation and the organic phase was collected. When the solvent of the organic phase was removed using rotary evaporator, a pale yellow flaky solid was obtained. The crude product was washed with an excess amount of deionized water and anhydrous ethanol followed by drying in vacuum over night.

$[C_{18}H_{37}N(CH_3)_3]_3[PW_4O_{24}]$ (Q_3-PW_4 for short) was synthesized according to the literature procedure[S1].

$[C_{18}H_{37}N(CH_3)_3]_2[W_3O_{17}]$ (Q_2-W_3 for short) was also synthesized by following a similar procedure of Q_4-$H_2Se^{IV}_3W_6$ only in the absence of 60% H_2SeO_3.

4. Characterization of catalysts

XPS analysis to determine the chemical valence of Se in Q_4-$H_2Se^{IV}_3W_6$
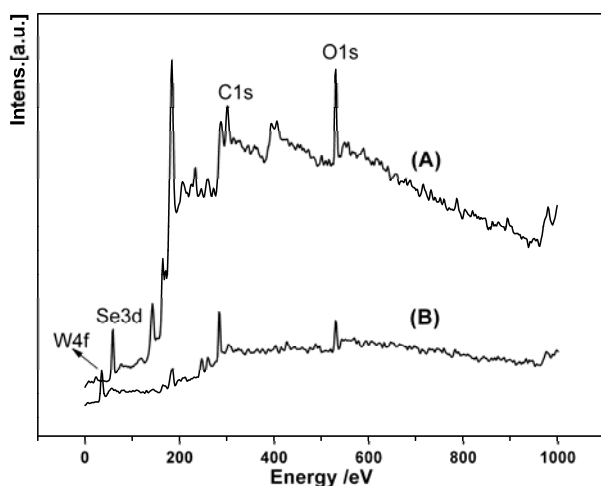
Fig. S1 XPS pattern of (A) SeO_2 (B) Q_4-$H_2Se^{IV}_3W_6$

We suggest that the valence of Se be not changed during the preparation of Q_4-$H_2Se^{IV}_3W_6$ with SeO_2 because the only used oxidant, 30%H_2O_2, is not strong enough to oxidize Se from +4 to +6 (extra experiment was carried out to confirm the knowledge employing the $AgNO_3$/HNO_3 reagent to examine SeO_4^{2-}). Moreover, the XPS analysis of SeO_2 and Q_4-$H_2Se^{IV}_3W_6$ gave the direct evidence: the E_b of Se3d electron in Q_4-$H_2Se^{IV}_3W_6$ (56eV) was almost the same as in SeO_2 (58eV) while the value in H_2SeO_4 is 62 eV.

ESI-MS of Q_4-$H_2Se^{IV}_3W_6$
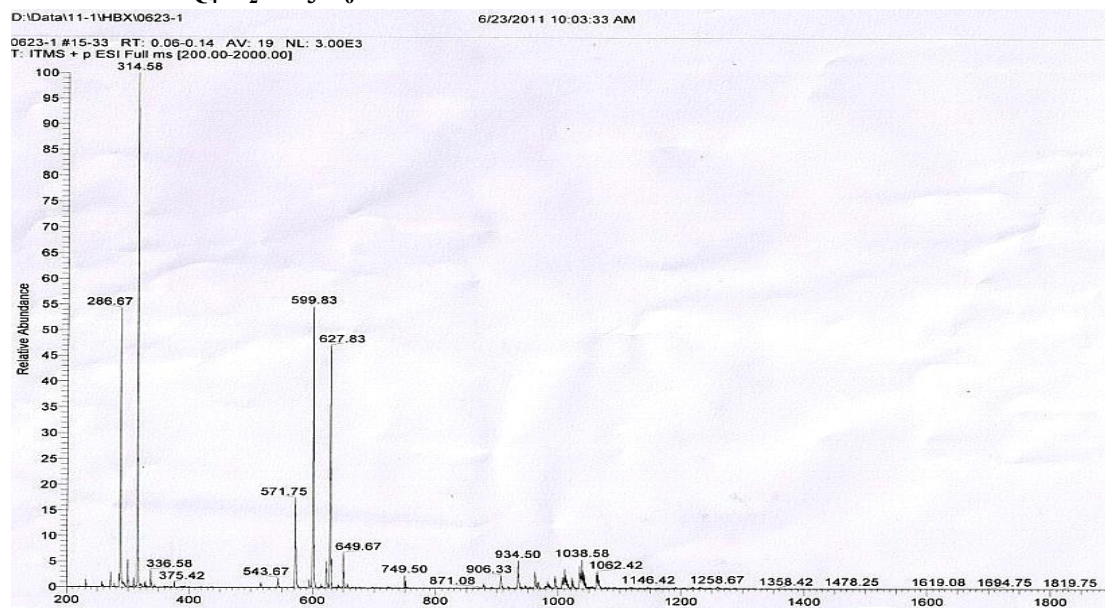
Fig. S2 Positive-ion mode ESI-MS of Q_4-$H_2Se^{IV}_3W_6$

When the ESI-MS of Q_4-$H_2Se^{IV}_3W_6$ was carried out in negative-ion mode, no valid ion flow was observed in the chromatogram while in positive-ion mode, the $[M]^+$ peak of $[C_{18}H_{37}N(CH_3)_3]$ was not found either. So, we presumed that as a kind of non-covalent complex, Q_4-$H_2Se^{IV}_3W_6$ didn't dissociate to $[C_{18}H_{37}N(CH_3)_3]^+$ and $[H_2Se^{IV}_3W_6O_{34}]^{4-}$ but existed as a monolithic molecule during its dissolution course in methanol. What's more, since there are many W=O and W(O)$_2$ in Q_4-$H_2Se^{IV}_3W_6$, the occurrence of high charged ions is possible under acidic condition in positive-ion mode[S2-S6]. Thus, some peaks in ESI-MS can be assigned as follows: 314.58, $[M+10H]^{10+}$; 336.58, $[M+10Na]^{10+}$; 627.83, $[M+5H]^{5+}$; 649.67, $[M+5Na]^{5+}$.

XRF analysis to determine the molar ratio between Se and W in Q_4-$H_2Se^{IV}_3W_6$

Q_4-$H_2Se^{IV}_3W_6$: WO$_3$, 80.37 wt%; SeO$_2$, 17.75 wt%; W/Se = 2.16 (molar ratio).

Q_4-$H_2Se^{IV}_3W_6$ after 6h calcination at 200℃: WO$_3$, 81.66 wt%; SeO$_2$, 17.35 wt%; W/Se = 2.25.

Q_4-$H_2Se^{IV}_3W_6$ after 6h calcination at 400℃: WO$_3$, 98.44 wt%; SeO$_2$, 0.06 wt%.

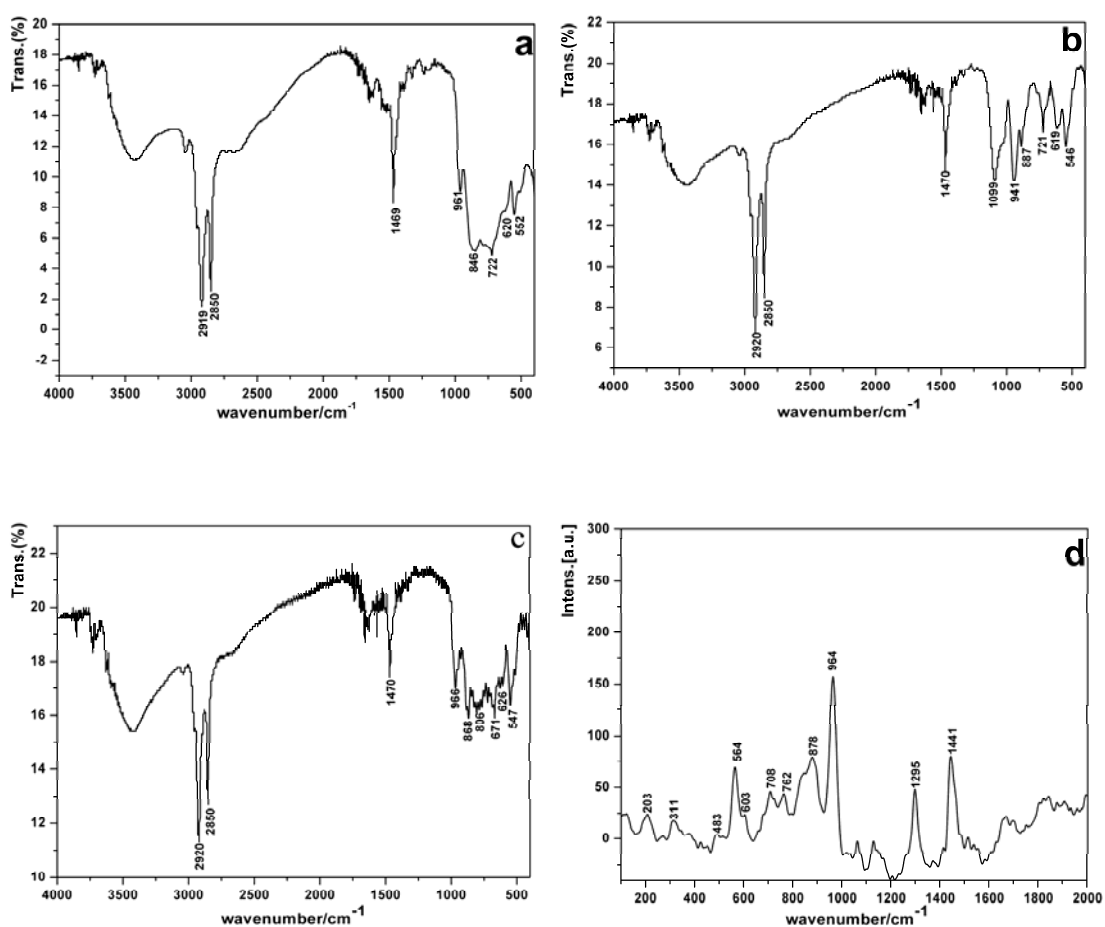## C H N elemental analysis of catalysts

Q_4-$H_2Se^{IV}_3W_6$, Found: C, 32.41; H, 5.84; N, 1.75. Calc.: C, 32.17; H, 5.98; N, 1.79 %.

Q_3-PW$_4$, Found: C, 36.42; H, 6.75; N, 1.90. Calc.: C, 36.22; H, 6.61; N, 2.01 %.

Q_2-W$_3$, Found: C, 34.68; H, 6.54; N, 1.89. Calc.: C, 34.82; H, 6.40; N, 1.93 %.
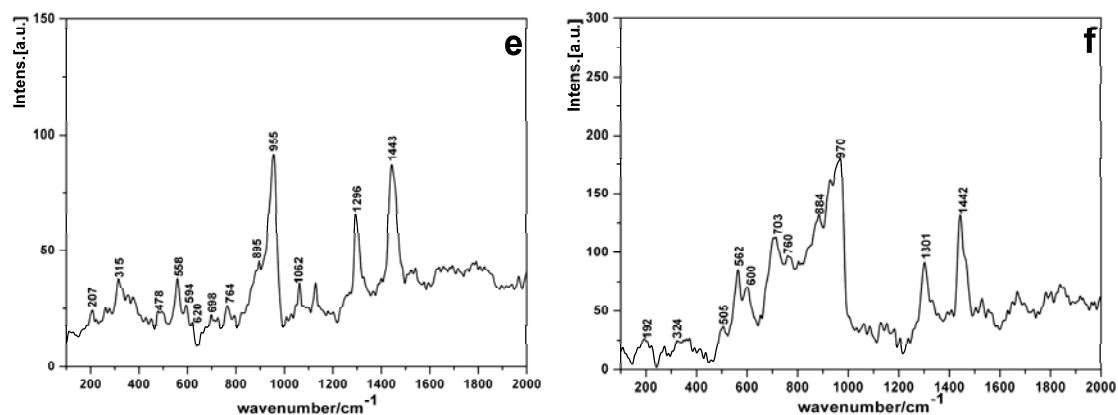
FTIR and Raman spectrum

Fig. S3 FTIR spectrogram of Catalyst (a) $Q_4\text{-}H_2Se^{IV}_3W_6$ (b) $Q_3\text{-}PW_4$(c) $Q_2\text{-}W_3$;
Raman spectrogram of Catalyst (d) $Q_4\text{-}H_2Se^{IV}_3W_6$ (e) $Q_3\text{-}PW_4$(f) $Q_2\text{-}W_3$.

Table S1. Assignment in FTIR and Raman spectrogram of three catalysts[S7-S10]

Assignment*		Catalyst		
		$Q_4\text{-}H_2Se^{IV}_3W_6$	$Q_3\text{-}PW_4$	$Q_2\text{-}W_3$
$\nu(W=O)$	IR	961	941	966
	Raman	964	955	970
$\nu(O\text{-}O)$	IR	846	887	868
	Raman	878	895	884
$\nu_{asym}[W(O)_2]$	IR	620	619	626
	Raman	603	594	600
$\nu_{sym}[W(O)2]$	IR	552	546	547
	Raman	564	558	562
$\nu(P\text{-}O)$ or $\nu(Se\text{-}O)$	IR	722	1099	-
	Raman	762,706	1062,620	-

* Assignment resulting from quaternary ammonium cation and adsorbed water are not listed.
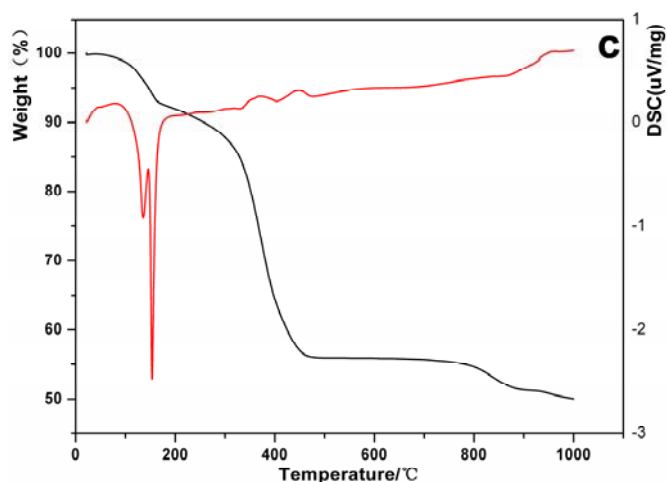
TG analysis:
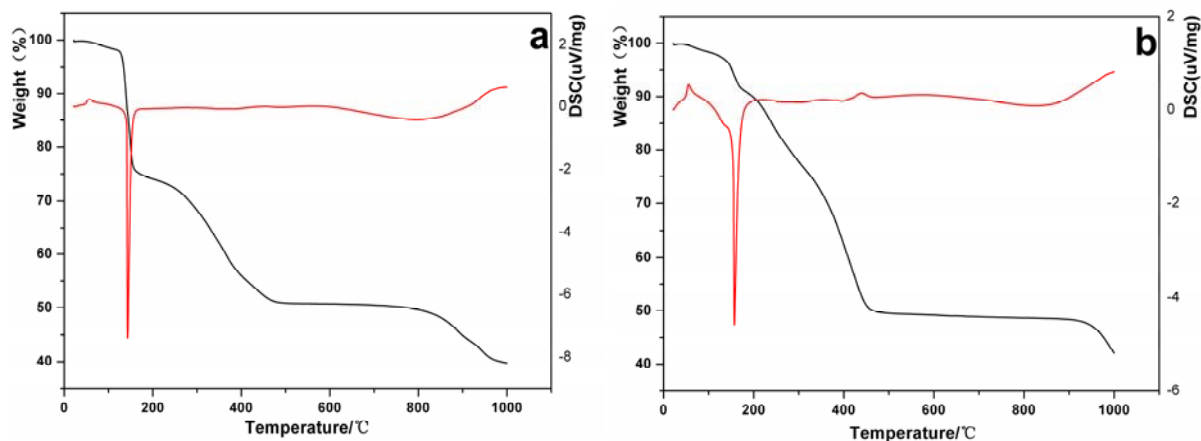
Fig. S4 TG curves for (a) Q_4-$H_2Se^{IV}_3W_6$ (b) Q_3-PW_4 (c) Q_2-W_3

The proposed structure of the anion part of Q_4-$H_2Se^{IV}_3W_6$:

Based on our characterizations of the catalyst, the proposed structure of the anion part of Q_4-$H_2Se^{IV}_3W_6$ was given out as follows[S1, S7-S11]:
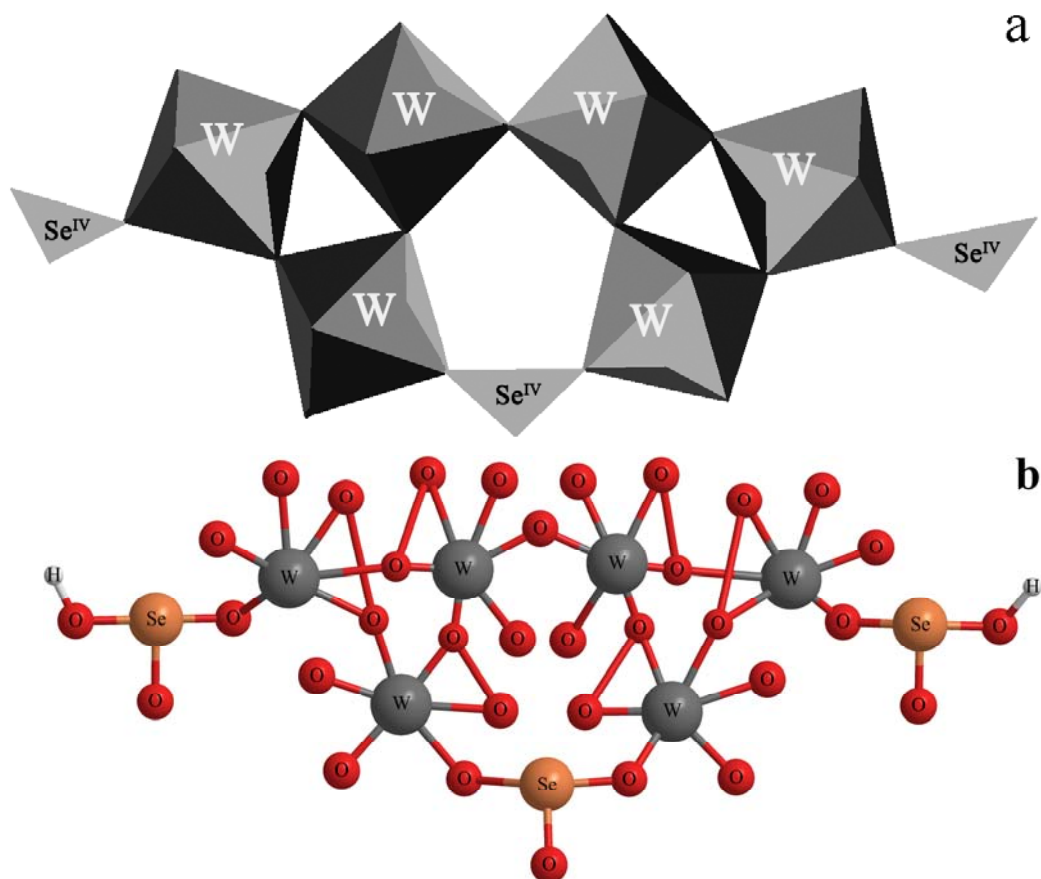

Fig. S5 (a) Polyhedral representation of the anion of Q_4-$H_2Se^{IV}_3W_6$; The [WO_6] unit and [SeO_3] unit are shown as octahedron and triangle respectively. (b)the proposed 3D structure of the anion part of Q_4-$H_2Se^{IV}_3W_6$

5. Experimental details for oxidative desulfurization of dibenzothiophene

In a typical run, 20.4 mg dibenzothiophene (DBT) dissolved in 10mL n-octane (S:500 ppm), 0.5 mL CH_3CN, 26 mg 30%H_2O_2 and a certain amount of catalyst were added into a 50 mL flask with reflux condenser. The reaction was timed from putting the flask into a 318 K water bath and starting the magnetic stirring. The reaction progress was promptly examined with sulfur-specific GC-FPD by sampling the upper phase (200 ul) at different time intervals. When the reaction finished after 2h, the mixture went through phase separation by centrifugation (2000 rpm, 10 min) and the oil phase as well as CH_3CN phase was respectively analyzed by GC. The residual white solid in the reaction vessel was collected, dried and analyzed by FTIR and GC.

6. Analysis of sulfur content

The oxidation progress of DBT was analyzed by a sulfur-specific gas chromatography coupled with a flame photometric detector (GC-FPD). Capillary column: SE-30,50m x 0.53mm,id x 0.5um; injector temperature:240℃; column temperature:180 ; detector temperature, 220℃; carrier gas: ultra-purity nitrogen, column flow, 1.0 mL/min; reagent gases: air,60 mL/min, ultra-purity hydrogen,60 mL/min; injection volume:1ul.

The contents of DBT in samples was quantified by GC-FPD according to the following equation:

$$\ln C_{DBT}(\text{ppm}) = n \ln A + m \tag{1}$$

Where C_{DBT} is the concentration of DBT, A is the peak area of DBT, m and n are constant for a determinate sulfur-containing compound. According to equ.(1), we could adopt the standard curve method to determine the sulfur content as follows:

A series of standard samples (DBT dissolved in n-octane) were prepared and each sample was analyzed by GC-FPD for at least three times keeping the A deviation of each other less than 2%. The average values of A were recorded and $\ln A$ was plotted versus $\ln C_{DBT}$ in Fig. S5.
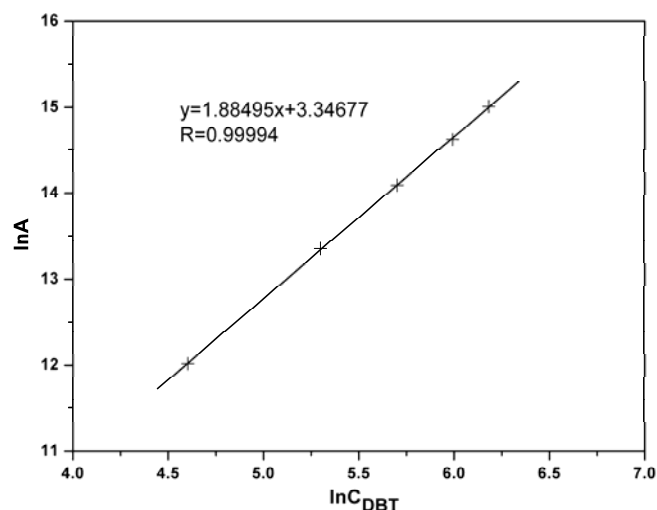

Fig. S6　Standard curve of $\ln A$-$\ln C_{DBT}$

In fact, the standard curve method was operated on GC workstation and it is very convenient to immediately obtain the contents of DBT following the GC analysis. Detection limit: 0.5 ppm.

Ultraviolet Fluorescence method according to ASTM D545309 (Multi EA 3100, Analytik Jena, Germany) was adopted for quantitative estimation of total sulfur concentration in the model

fuel. Oven temperature: 1050℃; reagent gas: oxygen(≥99.9%), 500 mL/min; carrier gas: ultra-purity argon, 150 mL/min; injection volume:40 ul; detection limit: 0.1 ppm.
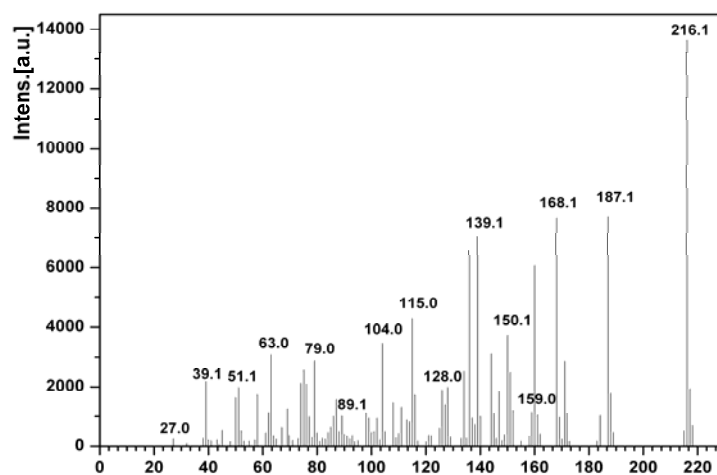
7. Analysis of oxidation product

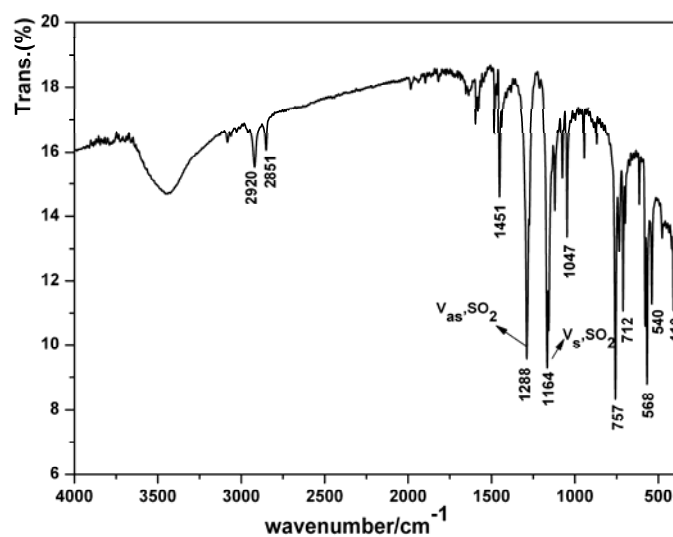**Fig. S7** GC-MS spectrogram for oxidation product present in n-octane

Fig. S8 FTIR spectrogram for the residual solid in the reaction vessel
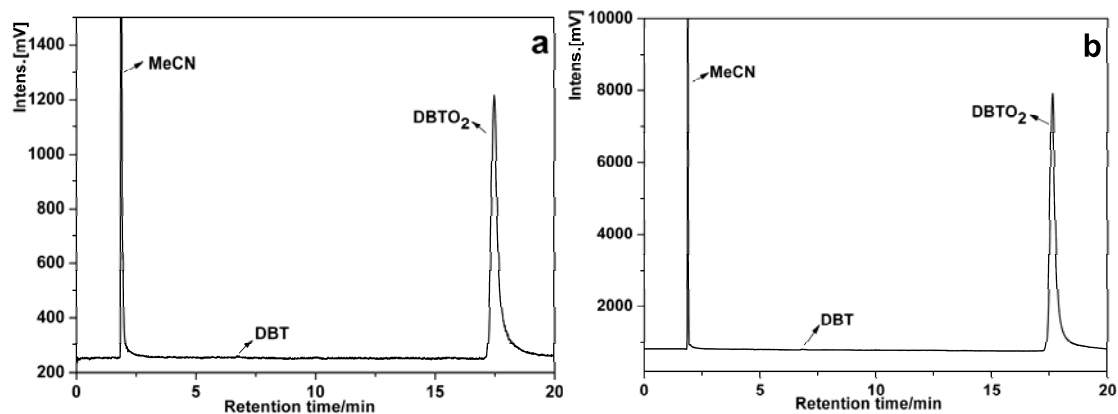

Fig. S9 The megascopic GC-FPD spectrogram of (a) MeCN phase after reaction; (b)the solution of solid product in the vessel bottom dissolved in MeCN

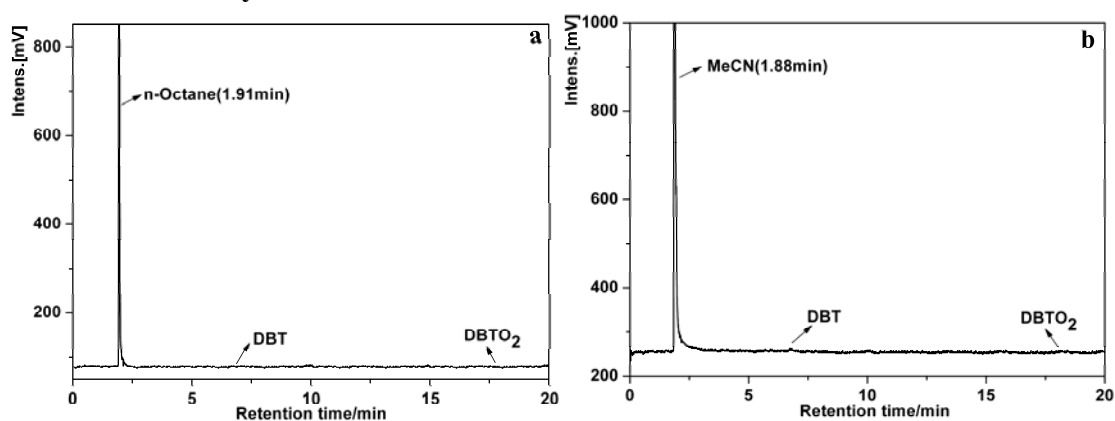## 8. GC-FPD analysis of the solvent used in the reaction

Fig. S10   The megascopic GC-FPD spectrogram of (a) n-Octane (CP) (b) Acetonitrile (AR)

The GC-FPD analysis of the solvent used in the reaction, n-Octane and Acetonitrile, has been carried out to verify the presence of sulfur impurity in the solvent. The results above demonstrate that the solvent used in the oxidation reaction is sulfur-free.

9. Catalytic oxidation reaction kinetics study

Kinetic equations:

$$\ln\left(\frac{C_t}{C_0}\right) = -kt$$

$$C_t = C_0 e^{-kt}$$

Where,

C_0 = initial concentration of reactant

C_t = concentration of reactant at a later time
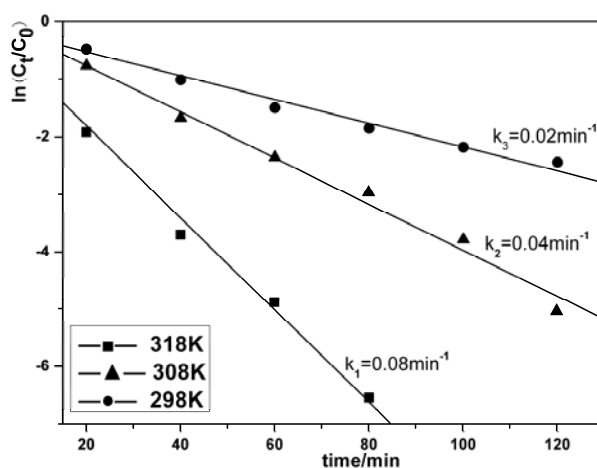

Fig. S11 $\ln(C_t/C_0)$ versus time catalyzed by $Q_4\text{-}H_2Se^{IV}{}_3W_6$ at different temperatures. (Reaction conditions: 20.4 mg DBT in 10mL n-octane, 0.5 ml CH_3CN, 6 mg $Q_4\text{-}H_2Se^{IV}{}_3W_6$, O/S = 2.0, 1 atm..)

10. The value calculation of catalytic selectivity

Under the same reaction conditions catalyzed by Q_4-$H_2Se^{IV}_3W_6$:

When only dibenzothiophene (DBT) was added in n-octane, 99.9% removal of DBT was obtained; when equimolar DBT and Cinnamyl Alcohol (CA) were added in n-octane, 95.6% removal of DBT was obtained. 4.3% removal of DBT was reduced because of the adding of CA. That is to say, 4.3% of the H_2O_2 was consumed by the reaction of CA. So, the proportion of H_2O_2 consumed by DBT and CA was 95.6% : 4.3% which was used to judge the catalytic selectivity. Therefore, the reaction selectivity between DBT and CA catalyzed by Q_4-$H_2Se^{IV}_3W_6$ was 22.2:1.

Similarly, the values of catalytic selectivity were calculated as follows:

Q_4-$H_2Se^{IV}_3W_6$: DBT and Quinoline (QL), 88.5% : (99.9%-88.5%) = 7.8 : 1.

Q_3-PW_4: DBT and CA, 83.0% : (99.9%-83.0%) = 4.9 : 1; DBT and QL, 78.6% : (99.9% -78.6 %) = 3.7 : 1.

Q_2-W_3: DBT and CA, 73.0% : (88.2%-73.0%) = 4.8 : 1; DBT and QL, 70.6% : (88.2%-70.6%) = 4.0 : 1.

References:

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