Supplementary material

Characterization, oxidative desulfurization performance evaluation and catalytic reaction mechanism of polyoxometalate-coated, semi-encapsulated heart-shaped metal organic frameworks

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1.Figures

2.Tables

3.References

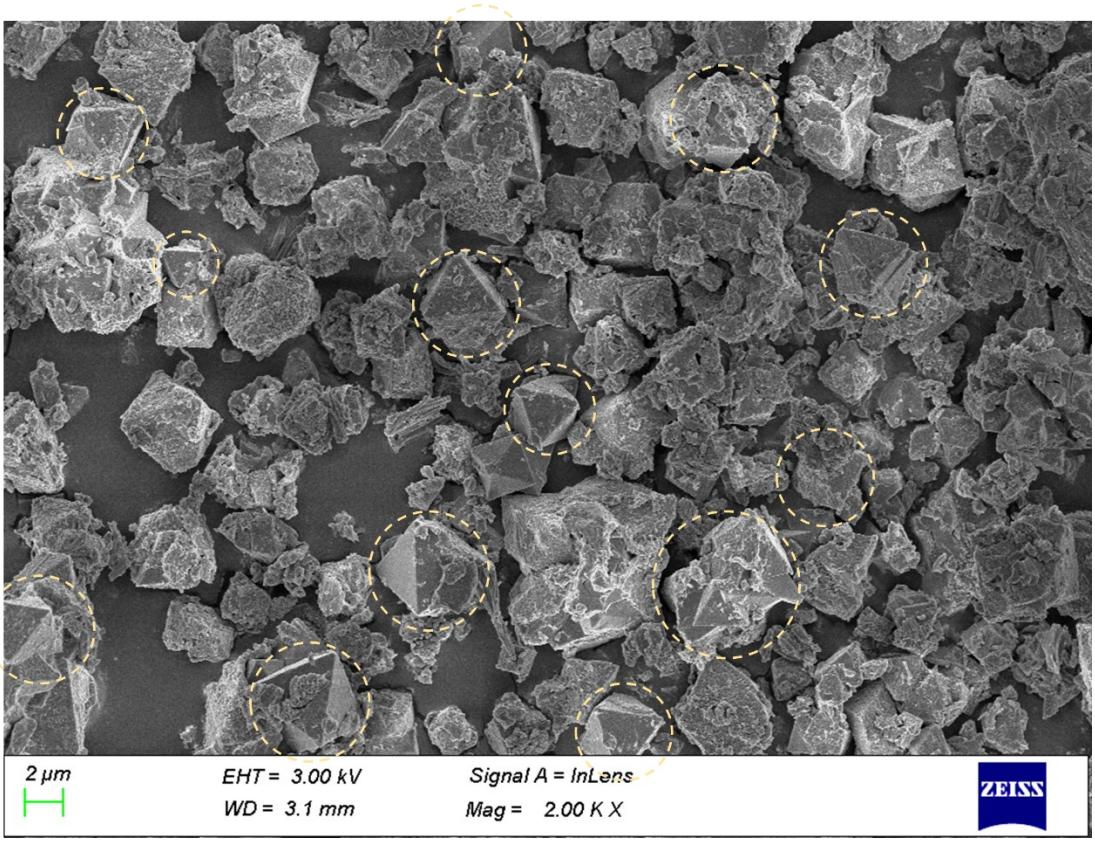

Fig. S1. SEM image of H-POMOF, where the H-POMOF complex with a distinct semi-encapsulated style is labelled within the yellow dashed circle.

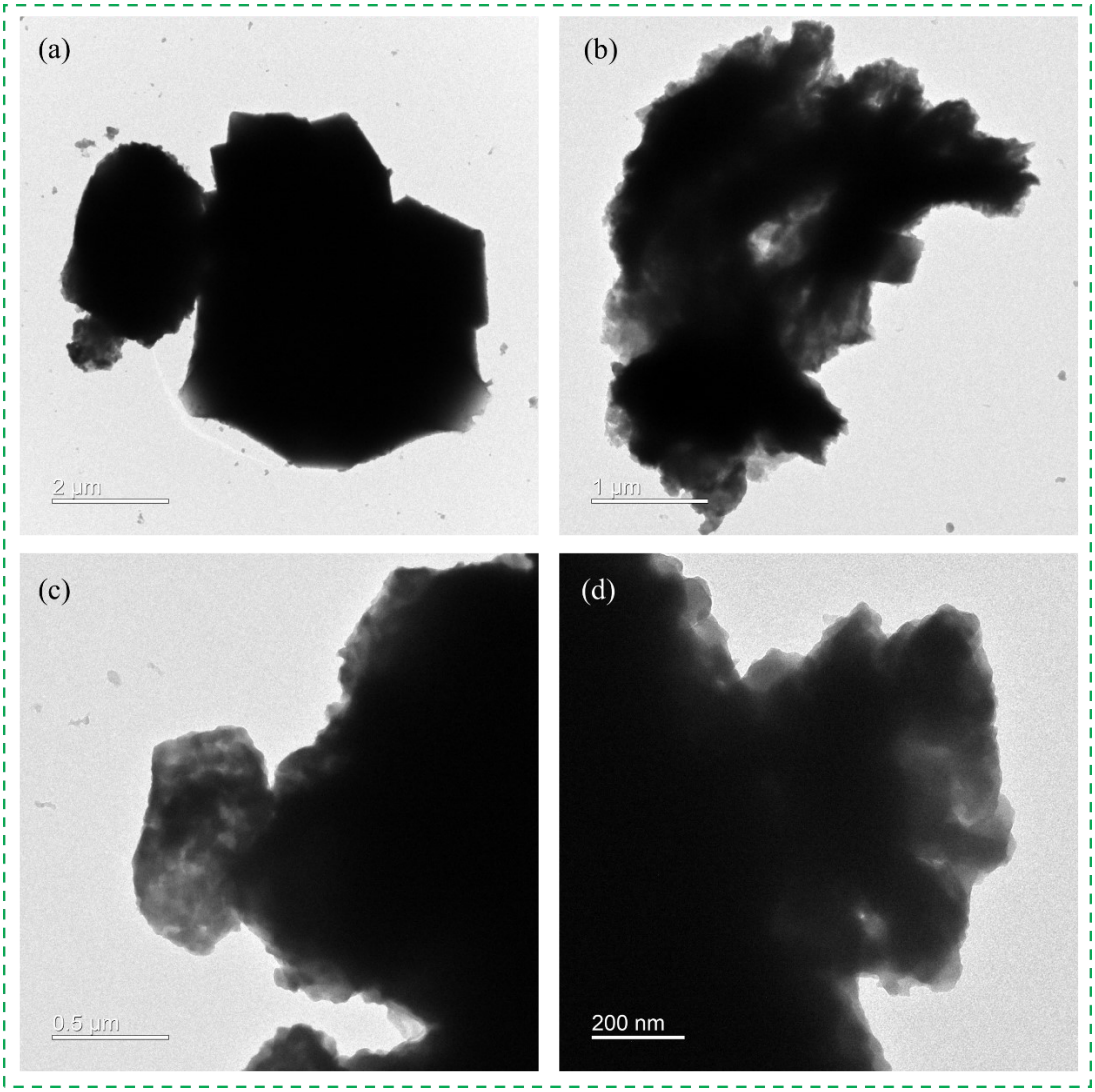

Fig. S2. TEM image of H-POMOF from 1 μm to 200 nm.

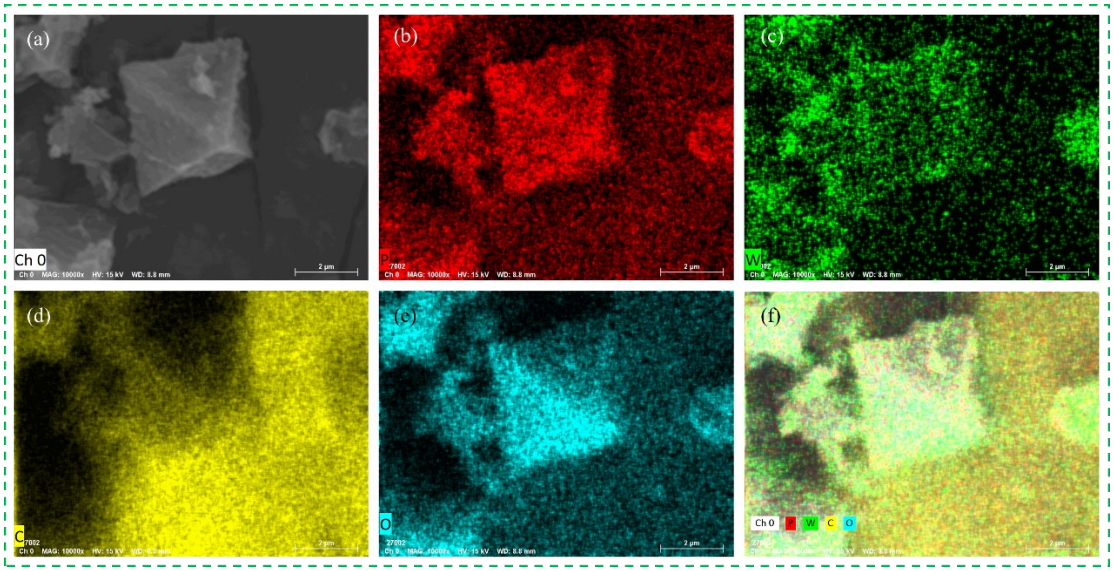

Fig. S3. SEM mapping of P, W, C and O elements of H-POMOF.

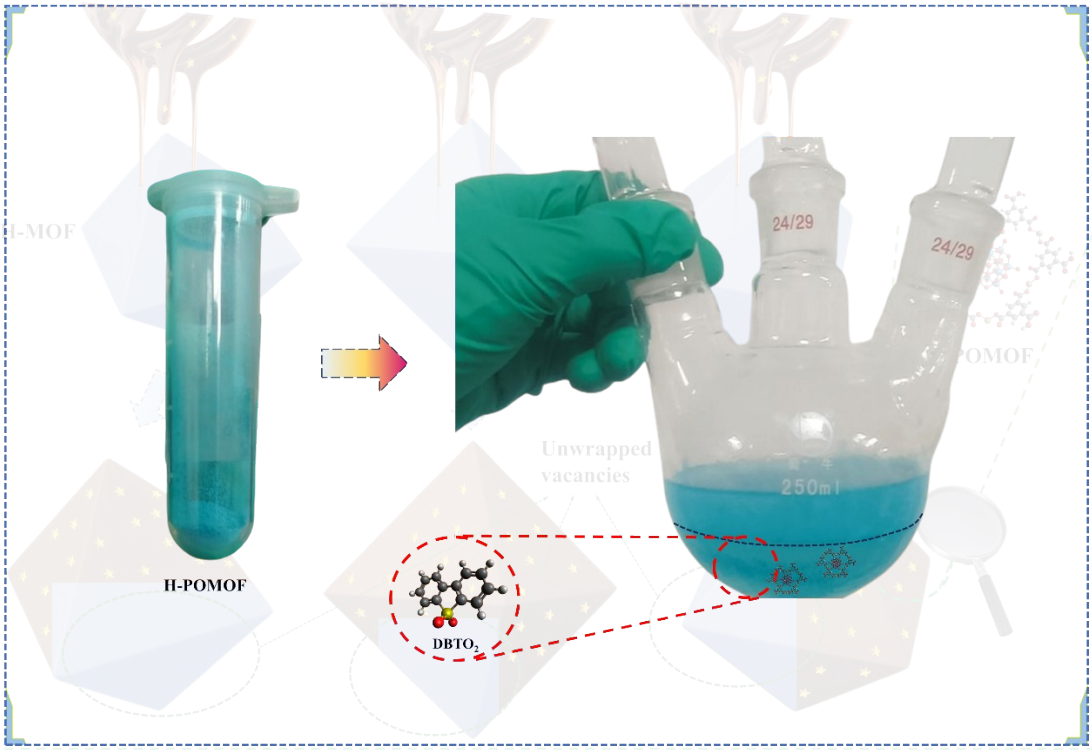

Fig. S4. Delamination occured when the medium was left to stand at the end of the ODS reaction.

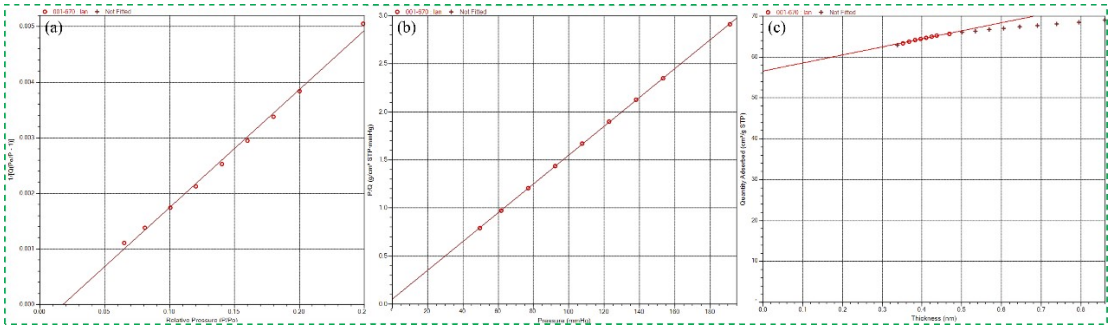

Fig. S5. (a) BET Surface Area Plot, (b) Langmuir Surface Area Plot and (c) t-Plot (Harkins and Jura) of H-POMOF.

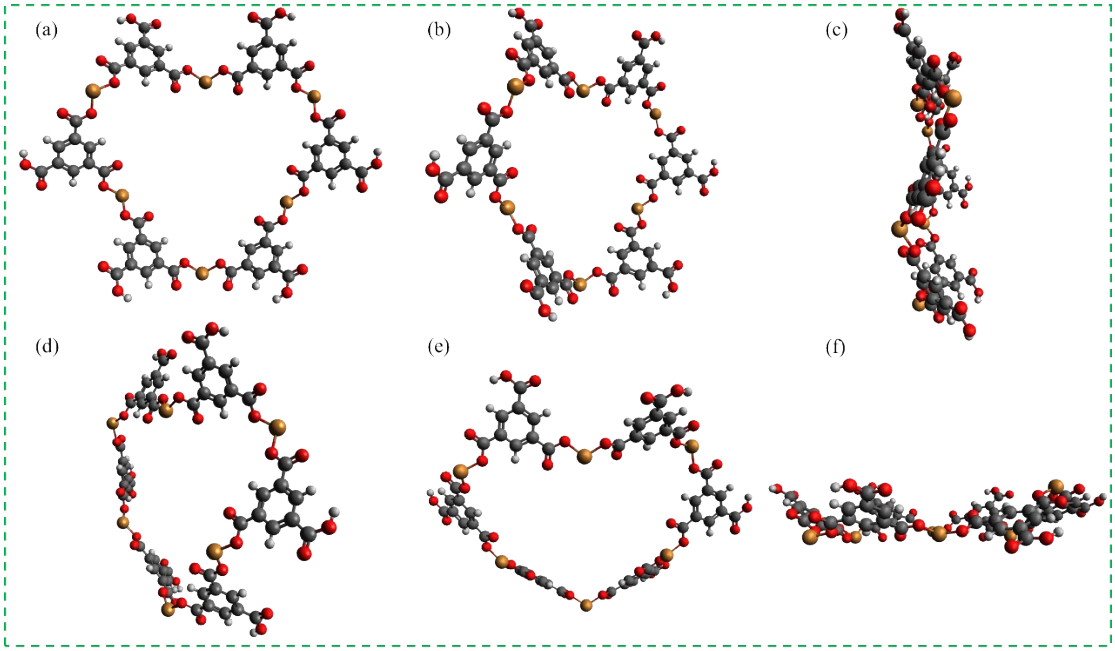

Fig. S6. Illustrations of the heart-shaped MOF (H-MOF) from different perspectives after DFT structure optimization.

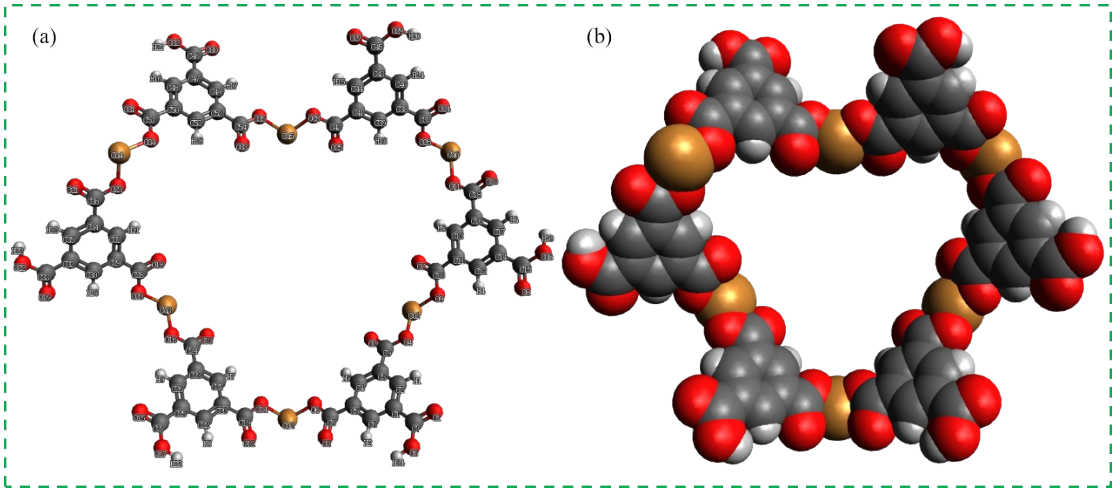

Fig. S7. Front view and van der Waals spheres morphology of the heart-shaped MOF (H-MOF) after DFT structure optimization.

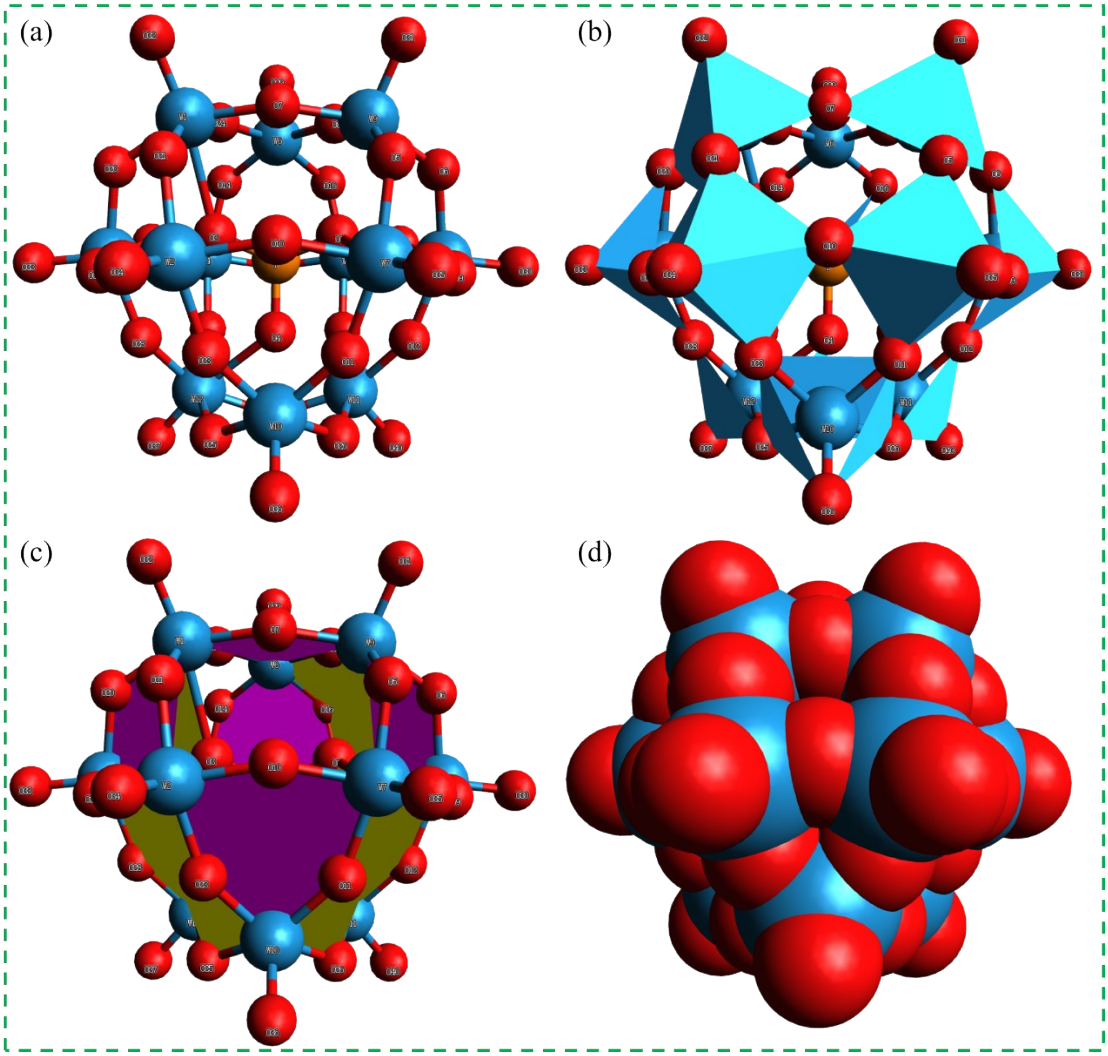

Fig. S8. The label diagram, Polygon diagram, Ring diagram, and Van der Waals Spheres diagram of POM.

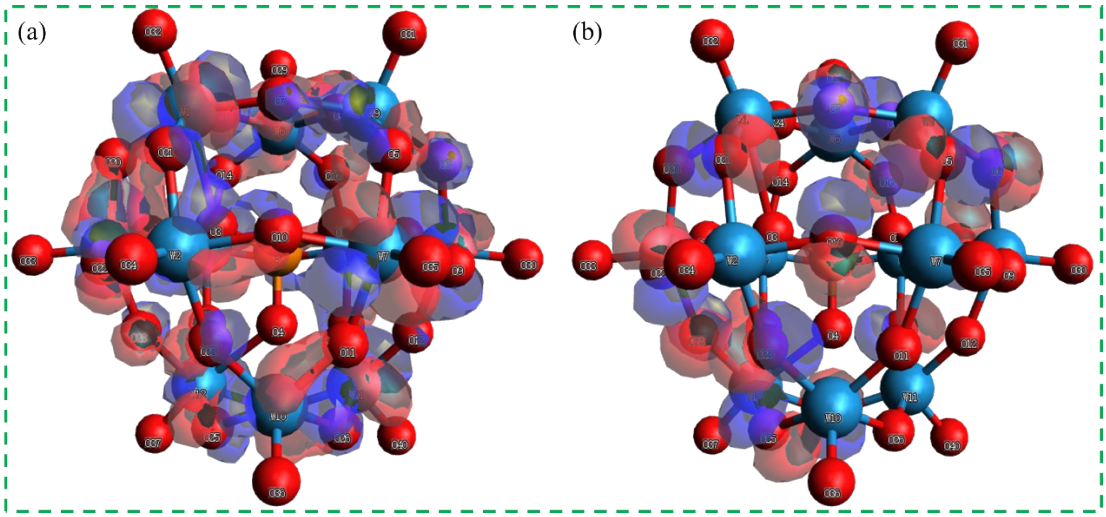

Fig. S9. Illustration of the (a) LUMO and (b) HOMO of POM.

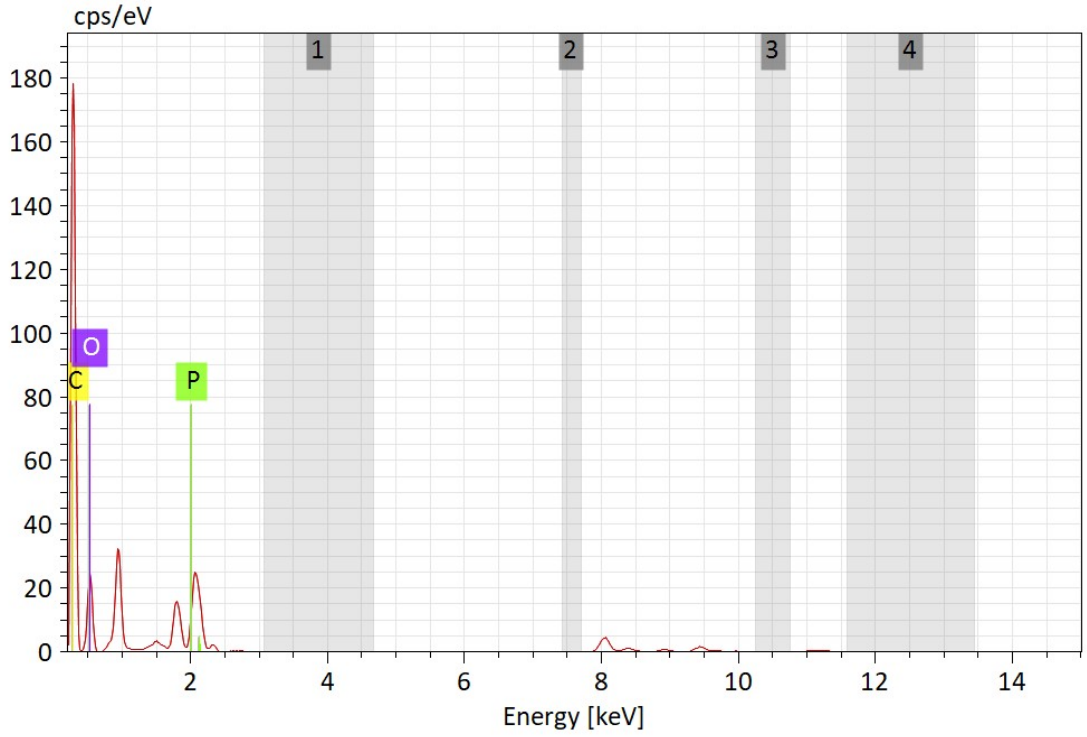

Fig. S10 EDX spectrum analysis of H-POMOF composite material.

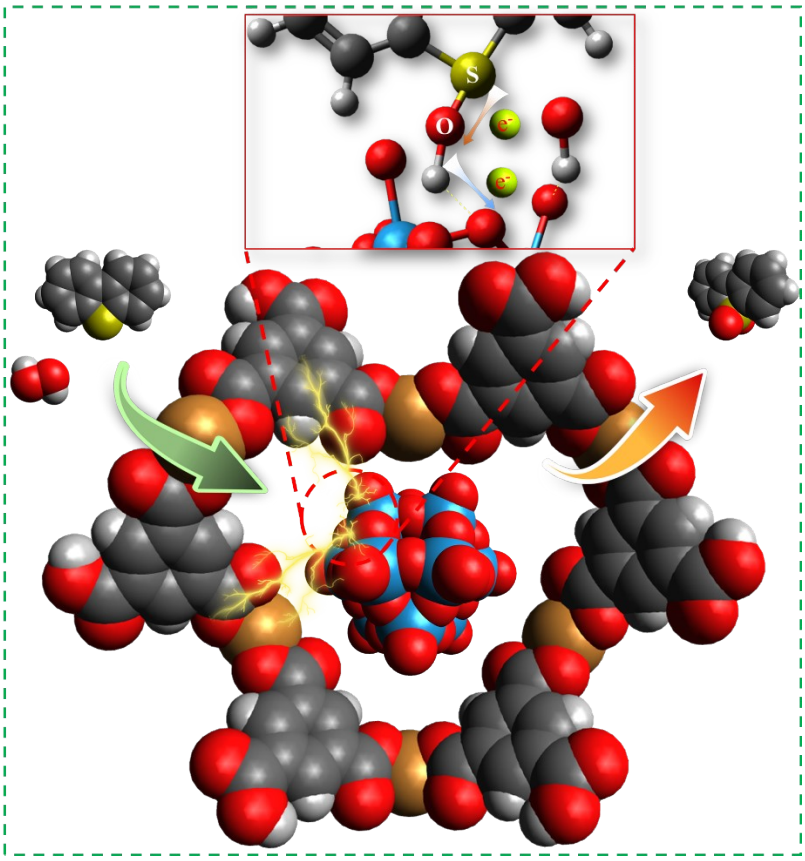

Fig. S11 Schematic diagram of electron transfer and metal oxidation state in the ODS catalytic reaction of H-POMOF.

Table S1 Elemental composition and atomic mass obtained by SEM mapping.

Elements	Atomic number	net worth	Mass (%)	Normalized quality	Atom	Abs. error (%)	Abs. error (%) (3 sigma)	rel. error (%) (3 sigma)
C	6	362611	29.50	71.54	82.02	3.15	9.44	31.99
O	8	53057	7.54	18.29	15.74	0.89	2.66	35.21
P	15	57935	1.65	3.99	1.78	0.06	0.19	11.49
W	74	4545	2.55	6.18	0.46	0.10	0.30	11.70
Total			41.24	100.00	100.00			

Table S2 Mesoporous BET related parameters of H-POMOF.

Surface Area		Pore Volume		Pore Size	
Single point surface area at P/P_0 = 0.249298624:	214.5538 m^2/g	Single point adsorption total pore volume	0.125631 cm^3/g	Adsorption average pore diameter	2.4065 nm
BET Surface Area:	208.8232 m^2/g	t-Plot micropore volume	0.132558 cm^3/g	Desorption average pore diameter	2.5391 nm
Langmuir Surface Area:	290.1607 m^2/g	BJH Adsorption cumulative volume	0.048298 cm^3/g	BJH Adsorption average pore diameter	9.4722 nm

Table S3 Energy values and changes from the initial state (POM, H_2O_2) to the transition state (POM-H_2O_2) to the final state (POM-OH).

State	Final single point energy (Hartree)	△ Energy (Hartree)	△E (kcal/mol)
POM、H_2O_2	-4309.4716	0	0
POM-H_2O_2	-4309.1159	0.3557	223.2
POM-OH	-4309.499	-0.3831	-240.4

Table S4 Representative synthetic strategies and characteristics of POMOF-based materials.

POMOFs	POM	MOF	Diameter pf porous cage (Å)	Organic ligands (linkers)	Synthetic methods	Application	Ref.
POM@ZIF-67	$H_3PW_{12}O_{40}\cdot 18H_2O$	ZIF-67	11.6	2-methylimizole	Encapsulation	Photocatalytic water splitting	1
$(CH_3NH_2CH_3)[Cu_2(TPB)_2(PW_{12}O_40)]\cdot 4DMF\cdot 6H_2O$	$H_3PW_{12}O_{40}$	–	12	1,2,4,5-tetra(4-pyridyl)benzene (TPB)	Encapsulation	Dye adsorption	2
POM@MOF@SBA-15	$H_4[PMo_9V_3O_40]\cdot {}_xH_2O$	MOF-199	–	1,3,5-trihydroxybenzene (BTC)	Encapsulation	Hydroxylation of benzene	3
POM@ MIL101(Cr)	$H_3PW_{12}O_{40}\cdot xH_2O$	MIL101(Cr)	12~16	Terephthalate	Bottle-around-ship	Esterification reaction	4
$Pd_{13}Se_8$@ MIL-101	$[Pd_{13}Se8O_{32}]_6^-$ ($Pd_{13}Se^-$)	MIL-101	12~16	–	Impregnation	Suzuki−Miyaura cross-coupling reaction	5
SRL-POM@MOF-199@MCM-41	$H_3PMo_6W_6O_{40}$	MOF-199 and MCM-41	–	1, 3, 5-benzenetricarboxylic (BTC)	Impregnation	Oxidative desulfurization	6
$PMoV_2$@ MIL-101	$PMoV_2$	MIL-101	12~16	Terephthalic acid	Encapsulation	Aerobic Iodination of Arenes	7
ZZULI-1	$[W_{12}O_40]_8^-$ and $[W_6O1_9]_2^-$	$Cu^I{}_2X$2-basedM	10	1,2,4,5-tetra(4-pyridyl)benzene (TPB)	Immobilization	Photocatalytic water splitting	8
CoW_{12}@ZIF-8	$K_6[CoW_{12}O_{40}]\cdot 6H_2O$	ZIF-8	–	2-methylimidazole	Encapsulation	Hydrogen evolution reaction	9
$Co_3O_4/CoMoO_4$	$H_3PMo_{12}O_{40}\cdot nH_2O$	ZIF-67	11.6	2-methylimidazole	Encapsulation	Hydrogen evolution reaction	10
H-POMOF	$H_3PW_{12}O_{40}\cdot xH_2O$	H-MOF	15.1~16.5	Benzene-1,3,5-tricarboxylic acid	Semi-encapsulation	Oxidative desulfurization (ODS)	This work

Table S5 Comparison of oxidative desulphurisation performance of recently reported representative POMOF matrix composites.

Catalyst	*n*(catalyst)	Sulfur compound	Conc. (ppm)	Oxident	O/S	T (°C)	Time (min)	Conv. (%)	Ref.
PMo_{12}@NH_2-MIL-101(Cr)	4 mol/L	Real diesel	2300	H_2O_2	6	50	120	80	[11]
ZIF-8@{Mo_{132}}	0.15 g/L	DBT	500	TBHP	1	80	720	92	[12]
$Mo_{11}V_1$	12 g/L	DBT	1000	H_2O_2	12	70	50	90	[13]
$Mo_{10}V_2$	12 g/L	DBT	1000	H_2O_2	12	70	50	92	[13]
HPA@MOF@CA-3	1.8 g/L	Thiophene	1000	O_2		25	180	84.91	[14]
HPA@MOF@CA-4	1.8 g/L	Thiophene	1000	O_2		25	180	93.24	[14]
PTA@UiO-66	0.6mol%	BT	950	H_2O_2	4	70	60	94.8	[15]
PTA@MIL-100(Fe)	0.6mol%	4,6-DMDBT	950	H_2O_2	4	70	60	92.8	[15]
POM−PAF-1	8 g/L	DBT	500	H_2O_2	6	30	30	98.5	[16]
SRL-1-POM@MOF-199@MCM-41	1.0 g/L	DBT	2000	O_2		60	150	87.3	[6]
SRL-2-POM@MOF-199@MCM-41	1.0 g/L	DBT	2000	O_2		60	150	92.8	[6]
SRL-4-POM@MOF-199@MCM-41	1.0 g/L	DBT	2000	O_2		60	150	90.5	[6]
Fe_3O_4@UiO-66-PMoW	0.5 g/L	DBT	2000	O_2		60	75	91.6	[17]
H-POMOF	3.5 g/L	DBT	500	H_2O_2	5	60	150	98	This work

Table S6 Langmuir adsorption isotherm parameters at 50°C.

C_a	C_0	C_t	C_T	C_e	C_E	q_e	C_e/q_e
3.5	250	7.4	5.18	242.6	169.82	48.52	0.10676
	500	37	25.9	463	324.1	92.6	0.279698
	750	98.6	69.02	651.4	455.98	130.28	0.529782
	1000	338	236.6	662	463.4	132.4	1.787009

Table S7 Langmuir adsorption isotherm parameters at 60°C.

C_a	C_0	C_t	C_T	C_e	C_E	q_e	C_e/q_e
3.5	250	6.75	4.725	243.25	170.275	48.65	0.097122
	500	10	7	490	343	98	0.071429
	750	65.25	45.675	684.75	479.325	136.95	0.333516
	1000	303	212.1	697	487.9	139.4	1.521521

Table S8 Langmuir adsorption isotherm parameters at 70°C.

C_a	C_0	C_t	C_T	C_e	C_E	q_e	C_e/q_e
3.5	250	7.1	4.97	242.9	170.03	48.58	0.102305
	500	11	7.7	489	342.3	97.8	0.078732
	750	82.4	57.68	667.6	467.32	133.52	0.431995
	1000	322	225.4	678	474.6	135.6	1.662242

C_a——Adsorbent concentration (g/L)

C_0——Initial sulfide concentration (ppm)

C_t——Equilibrium concentration (ppm)

C_T——Equilibrium concentration (mg/L)

C_e——Adsorbed concentration (ppm)

C_E——Adsorbed concentration (mg/L)

q_e——Adsorbent unit adsorption capacity (mg/g)

Table S9 Adsorption thermodynamic parameters at 50°C.

C_e (mg/L)	$K_d=q_e/C_e$	$\ln K_d$	△G (J/mol)
5.18	9.366795367	2.237171	-4778.17
25.9	3.575289575	1.274046	
69.02	1.887568821	0.63529	
236.6	0.559594252	-0.58054	

Table S10 Adsorption thermodynamic parameters at 60°C.

C_e (mg/L)	$K_d=q_e/C_e$	$\ln K_d$	△G (J/mol)
4.725	10.2962963	2.331784	-6419.741566
7	14	2.639057	
45.675	2.998357964	1.098065	
212.1	0.657237152	-0.41971	

Table S11 Adsorption thermodynamic parameters at 70°C.

C_e (mg/L)	$K_d=q_e/C_e$	$\ln K_d$	△G (J/mol)
4.97	9.774647887	2.279792	-6386.1
7.7	12.7012987	2.541704	
57.68	2.314840499	0.839341	
225.4	0.601597161	-0.50817	

Table S12 Cartesian Coordinates (A.U.) of POM by DFT.

NO	LB	ZA	FRAG	MASS	X	Y	Z
0	P	15.0000	0	30.974	2.253757	-0.972047	-2.458035
1	O	8.0000	0	15.999	-0.581771	-1.550797	-3.132544
2	O	8.0000	0	15.999	3.671425	-3.514408	-1.857107
3	O	8.0000	0	15.999	2.361763	0.803755	-0.077468
4	O	8.0000	0	15.999	3.565273	0.372731	-4.761686
5	W	14.0000*	0	183.85	0.624262	-0.185108	4.150262
6	W	14.0000*	0	183.85	0.475777	5.094995	0.194926
7	W	14.0000*	0	183.85	6.256770	2.430787	1.937837
8	W	14.0000*	0	183.85	8.187925	-3.896399	-0.658733
9	W	14.0000*	0	183.85	4.184969	-7.119554	-4.798246
10	W	14.0000*	0	183.85	2.553910	-6.515510	1.560741
11	W	14.0000*	0	183.85	-3.826011	1.615472	-4.264548
12	W	14.0000*	0	183.85	-2.042799	-4.258174	-6.675810
13	W	14.0000*	0	183.85	-3.679378	-3.660892	-0.309437
14	W	14.0000*	0	183.85	2.241268	4.442165	-6.657478
15	W	14.0000*	0	183.85	4.028446	-1.435701	-9.061506
16	W	14.0000*	0	183.85	8.022669	1.788864	-4.917272
17	O	8.0000	0	15.999	-5.252176	-0.702595	-1.805565
18	O	8.0000	0	15.999	-3.888297	-5.178724	-3.643854
19	O	8.0000	0	15.999	-2.216481	-1.506930	2.259613
20	O	8.0000	0	15.999	-0.875297	-5.873343	0.458507
21	O	8.0000	0	15.999	-3.999235	-1.157346	-6.657692
22	O	8.0000	0	15.999	-2.349909	3.536422	-1.523261
23	O	8.0000	0	15.999	-1.131582	3.087447	-6.257065
24	O	8.0000	0	15.999	0.573870	-2.527285	-8.556037
25	O	8.0000	0	15.999	0.681488	-6.455440	-5.611757
26	O	8.0000	0	15.999	6.174022	-5.944366	1.627430
27	O	8.0000	0	15.999	7.418415	-6.405438	-3.221107
28	O	8.0000	0	15.999	3.124572	-8.406023	-1.530533
29	O	8.0000	0	15.999	7.488614	-0.978424	1.435587

30	O	8.0000	0	15.999	8.689687	-1.426749	-3.303796
31	O	8.0000	0	15.999	4.873273	-4.501213	-7.256893
32	O	8.0000	0	15.999	4.004642	1.183628	4.547336
33	O	8.0000	0	15.999	-0.402769	3.210816	3.217267
34	O	8.0000	0	15.999	3.891051	5.204810	1.527406
35	O	8.0000	0	15.999	1.845875	5.484034	-3.172827
36	O	8.0000	0	15.999	2.091792	-3.480546	3.551415
37	O	8.0000	0	15.999	5.881030	4.479748	-6.191961
38	O	8.0000	0	15.999	2.834073	2.020403	-9.346967
39	O	8.0000	0	15.999	7.241656	-0.003831	-8.021172
40	O	8.0000	0	15.999	7.364326	2.947546	-1.512323
41	O	8.0000	0	15.999	2.190819	-8.893360	3.763216
42	O	8.0000	0	15.999	-3.565509	-6.007430	-8.969298
43	O	8.0000	0	15.999	-6.180216	-5.072096	1.236896
44	O	8.0000	0	15.999	-0.395998	-0.376263	7.242193
45	O	8.0000	0	15.999	8.631956	3.824066	3.685909
46	O	8.0000	0	15.999	-0.631779	8.081441	0.896836
47	O	8.0000	0	15.999	-6.424713	3.400524	-5.100528
48	O	8.0000	0	15.999	1.734626	7.203860	-8.317287
49	O	8.0000	0	15.999	11.010422	2.947699	-5.524275
50	O	8.0000	0	15.999	11.231475	-4.704798	0.191002
51	O	8.0000	0	15.999	4.822924	-9.863655	-6.441495
52	O	8.0000	0	15.999	4.611640	-2.217451	-12.173926

Table S13 Mayer Population Analysis of POM by DFT.

ATOM	NA	ZA	QA	VA	BVA	FA
0 P	13.6543	15.0000	1.3457	4.9293	4.9293	-0.0000
1 O	8.6307	8.0000	-0.6307	2.0446	2.0446	0.0000
2 O	8.6320	8.0000	-0.6320	2.0431	2.0431	-0.0000
3 O	8.6320	8.0000	-0.6320	2.0428	2.0428	-0.0000
4 O	8.6320	8.0000	-0.6320	2.0424	2.0424	-0.0000
5 W	12.6857	14.0000	1.3143	6.4591	6.4591	0.0000
6 W	12.6878	14.0000	1.3122	6.4605	6.4605	0.0000
7 W	12.6857	14.0000	1.3143	6.4592	6.4592	0.0000
8 W	12.6869	14.0000	1.3131	6.4601	6.4601	0.0000
9 W	12.6860	14.0000	1.3140	6.4591	6.4591	-0.0000
10 W	12.6862	14.0000	1.3138	6.4595	6.4595	0.0000
11 W	12.6858	14.0000	1.3142	6.4597	6.4597	0.0000
12 W	12.6876	14.0000	1.3124	6.4611	6.4611	0.0000
13 W	12.6880	14.0000	1.3120	6.4616	6.4616	0.0000
14 W	12.6864	14.0000	1.3136	6.4598	6.4598	-0.0000
15 W	12.6866	14.0000	1.3134	6.4595	6.4595	-0.0000
16 W	12.6861	14.0000	1.3139	6.4592	6.4592	-0.0000
17 O	8.5618	8.0000	-0.5618	2.2645	2.2645	0.0000
18 O	8.5619	8.0000	-0.5619	2.2645	2.2645	-0.0000
19 O	8.5827	8.0000	-0.5827	2.2432	2.2432	-0.0000
20 O	8.5825	8.0000	-0.5825	2.2432	2.2432	-0.0000
21 O	8.5612	8.0000	-0.5612	2.2653	2.2653	0.0000
22 O	8.5830	8.0000	-0.5830	2.2427	2.2427	-0.0000
23 O	8.5828	8.0000	-0.5828	2.2432	2.2432	0.0000
24 O	8.5828	8.0000	-0.5828	2.2429	2.2429	0.0000
25 O	8.5829	8.0000	-0.5829	2.2428	2.2428	-0.0000
26 O	8.5617	8.0000	-0.5617	2.2646	2.2646	0.0000
27 O	8.5615	8.0000	-0.5615	2.2651	2.2651	0.0000
28 O	8.5618	8.0000	-0.5618	2.2646	2.2646	-0.0000
29 O	8.5832	8.0000	-0.5832	2.2426	2.2426	0.0000

30 O	8.5826	8.0000	-0.5826	2.2432	2.2432	-0.0000
31 O	8.5827	8.0000	-0.5827	2.2431	2.2431	-0.0000
32 O	8.5616	8.0000	-0.5616	2.2649	2.2649	0.0000
33 O	8.5619	8.0000	-0.5619	2.2645	2.2645	0.0000
34 O	8.5616	8.0000	-0.5616	2.2649	2.2649	-0.0000
35 O	8.5827	8.0000	-0.5827	2.2430	2.2430	-0.0000
36 O	8.5828	8.0000	-0.5828	2.2431	2.2431	0.0000
37 O	8.5616	8.0000	-0.5616	2.2648	2.2648	-0.0000
38 O	8.5616	8.0000	-0.5616	2.2648	2.2648	-0.0000
39 O	8.5618	8.0000	-0.5618	2.2647	2.2647	0.0000
40 O	8.5831	8.0000	-0.5831	2.2428	2.2428	-0.0000
41 O	8.3204	8.0000	-0.3204	2.4524	2.4524	0.0000
42 O	8.3206	8.0000	-0.3206	2.4519	2.4519	-0.0000
43 O	8.3205	8.0000	-0.3205	2.4520	2.4520	0.0000
44 O	8.3204	8.0000	-0.3204	2.4525	2.4525	0.0000
45 O	8.3204	8.0000	-0.3204	2.4525	2.4525	-0.0000
46 O	8.3206	8.0000	-0.3206	2.4518	2.4518	-0.0000
47 O	8.3205	8.0000	-0.3205	2.4525	2.4525	0.0000
48 O	8.3206	8.0000	-0.3206	2.4522	2.4522	0.0000
49 O	8.3205	8.0000	-0.3205	2.4523	2.4523	0.0000
50 O	8.3205	8.0000	-0.3205	2.4521	2.4521	-0.0000
51 O	8.3205	8.0000	-0.3205	2.4523	2.4523	-0.0000
52 O	8.3205	8.0000	-0.3205	2.4521	2.4521	-0.0000

NA - Mulliken gross atomic population

ZA - Total nuclear charge

QA - Mulliken gross atomic charge

VA - Mayer's total valence

BVA - Mayer's bonded valence

FA - Mayer's free valenc

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