Assembly of a coordination polymer with sulphate-capped pentamolybdate units and copper: Synthesis, Structure, Magnetic and Catalytic studies

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SUPPORTING INFORMATION

Table S1: Selected bond lengths (Å) and bond valence sum calculations for compound 1, $[Cu^{II}(C_5H_5N)_4]_3[\{Mo^{VI}_5O_{15}(SO_4)_2\}\{Cu^{II}(C_5H_5N)_3(DMF)(H_2O)\}]$ $[Mo^{VI}_5O_{15}(SO_4)_2]\bullet 2DMF$

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
Mo1-O1A	1.706(4)	1.7215813	
Mo1-O15	1.8969(4)	1.0276733	
Mo1-O15S	2.4504(4)	0.2302364	Σ(Mo1) = 6.0468364
Mo1-O1S	2.3275(4)	0.3209447	
Mo1-O12	1.8871(4)	1.0552564	
Mo1-O1C	1.7126(4)	1.6911443	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
Mo2-O2B	1.7091(4)	1.707275	
Mo2-O2A	1.6977(4)	1.760637	
Mo2-O12	1.8972(4)	1.0268404	Σ(Mo2) = 6.0297979
Mo2-O2S	2.3492(4)	0.3026631	
Mo2-O23S	2.412(4)	0.2554152	
Mo2-O23	1.9156(4)	0.9770248	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
Mo3-O3B	1.6995(4)	1.7520925	
Mo3-O3A	1.7188(4)	1.6630423	
Mo3-O23	1.9107(4)	0.9900498	Σ(Mo3) = 6.0534558
Mo3-O23S	2.2637(4)	0.3813438	
Mo3-O34S	2.4207(4)	0.2494795	
Mo3-O34	1.9006(4)	1.017448	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
Mo4-O4B	1.7035(5)	1.733253	
Mo4-O4A	1.7029(5)	1.736066	
Mo4-O34	1.9153(4)	0.9778173	Σ(Mo4) = 5.9494347
Mo4-O34S	2.4145(4)	0.2536952	
Mo4-O45S	2.4216(4	0.2488734	
Mo4-O45	1.9071(4)	0.9997298	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
Mo5-O5A	1.7004(4)	1.7478359	
Mo5-O45	1.9141(4)	0.9809938	
Mo5-O45S	2.3867(4)	0.273491	Σ(Mo5) = 6.0084316
Mo5-O15S	2.2759(4)	0.3689748	
Mo5-O15	1.9162(4)	0.9754417	
Mo5-O5C	1.7191(4)	1.6616945	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
Mo6-O6A	1.7024(4)	1.7384136	
Mo6-O610	1.895(4)	1.0329641	
Mo6-O61S	2.4667(4)	0.2203137	Σ(Mo6) = 6.045759
Mo6-O6S	2.32(4)	0.3275167	
Mo6-O67	1.8904(4)	1.0458865	
Mo6-O6C	1.7149(4)	1.6806644	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
Mo7-O7A	1.6778(5)	1.8579235	
Mo7-O7B	1.7112(5)	1.6975554	
Mo7-O67	1.8895(4)	1.0484337	Σ(Mo7) = 6.166415
Mo7-O7S	2.3795(4)	0.2788651	
Mo7-O78S	2.3994(3)	0.2642629	
Mo7-O78	1.8999(4)	1.0193745	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
Mo8-O8B	1.7025(4)	1.7379438	
Mo8-O8A	1.7158(4)	1.6765813	
Mo8-O78	1.9296(4)	0.940747	Σ(Mo8) = 5.9651965
Mo8-O78S	2.2695(4)	0.3754125	
Mo8-O89S	2.4402(4)	0.2366718	
Mo8-O89	1.9078(4)	0.9978402	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
Mo9-O9B	1.7037(4)	1.7323164	
Mo9-O9A	1.7026(5)	1.7374742	
Mo9-O89	1.9119(4)	0.9868441	Σ(Mo9) = 5.9405739
Mo9-O89S	2.4459(4)	0.2330537	
Mo9-O91S	2.3862(4)	0.2738609	
Mo9-O910	1.9156(4)	0.9770248	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
Mo10-O10A	1.7022(4)	1.7393535	

Mo10-O910	1.9056(4)	1.003791	
Mo10-O91S	2.4206(4)	0.249547	Σ(Mo10) = 6.0120666
Mo10-O61S	2.2584(4)	0.3868456	
Mo10-O610	1.9214(4)	0.9618287	
Mo10-O10C	1.7171(4)	1.6707009	

Bond	**Bond Length (Å)**	**Bond Valence**	**Bond Valence Sum**
Cu1-O1C	2.3623 (4)	0.157748	
Cu1-O6C	2.3615(4)	0.1580894	
Cu1-N11	2.061(5)	0.432645	Σ(Cu1) = 2.0929649
Cu1-N12	2.0502(5)	0.4454596	
Cu1-N13	2.0473(5)	0.4489648	
Cu1-N14	2.0464(5)	0.4500582	

Bond	**Bond Length (Å)**	**Bond Valence**	**Bond Valence Sum**
Cu2-O10C	2.3752(4)	0.1523429	
Cu2-O8A	2.4447(4)	0.126254	
Cu2-N21	2.0198(4)	0.4836052	Σ(Cu2) = 2.1756362
Cu2-N22	2.0265(5)	0.4749268	
Cu2-N23	2.0247(4)	0.4772429	
Cu2-N24	2.0373(5)	0.4612644	

Bond	**Bond Length (Å)**	**Bond Valence**	**Bond Valence Sum**
Cu3-O3A	2.4757(4)	0.116107	
Cu3-O5C	2.3327(4)	0.1708863	
Cu3-N31	2.0281(5)	0.4728775	Σ(Cu3) = 2.164094
Cu3-N32	2.0264(4)	0.4750552	
Cu3-N33	2.0362(5)	0.4626378	
Cu3-N34	2.0331(4)	0.4665302	

Bond	**Bond Length (Å)**	**Bond Valence**	**Bond Valence Sum**
Cu4-O1W	2.0056(5)	0.4136634	
Cu4-O1D	2.235(6)	0.2225279	
Cu4-O7B	2.8362(5)	0.0438243	Σ(Cu4) = 2.1197235
Cu4-N41	2.0462(7)	0.4503015	
Cu4-N42	1.9937(5)	0.5189509	
Cu4-N43	2.03(5)	0.4704554	

Bond	**Bond Length (Å)**	**Bond Valence**	**Bond Valence Sum**
S1-O1S1	1.4332(4)	1.6747697	
S1-O2S	1.4822(4)	1.4670348	Σ(S1) = 5.8269783
S1-O34S	1.514(4)	1.3462155	
S1-O15S	1.5160(4)	1.3389583	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
S2-O1S2	1.4284(4)	1.696638	
S2-O1S	1.4563(4)	1.5734069	Σ(S2) = 5.9869669
S2-O23S	1.5101(4)	1.3604804	
S2-O45S	1.5112(4)	1.3564417	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
S3-O1S3	1.4333(4)	1.6743171	
S3-O6S	1.4665(4)	1.5306243	Σ(S3) = 5.9182152
S3-O91S	1.5096(4)	1.3623201	
S3-O78S	1.5127(4)	1.3509537	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
S4-O1S4	1.4303(4)	1.6879479	
S4-O7S	1.4831(4)	1.4634707	Σ(S1) = 5.901076
S4-O89S	1.5014(4)	1.3928491	
S4-O61S	1.5111(4)	1.3568083	

Table S2: List of Hydrogen-bond interactions present in compound 1

S No	Donor --- H … Acceptor	D H (Å)	H ... A (Å)	D ... A (Å (°))	D H ... A (°)
1.	O1W --- H1WA ... O2D$^{\#1}$	0.89	1.91	2.6749(1)	142
2.	O1W --- H1WB ... O7S	0.88	1.95	2.6911(1)	141
3.	C4D --- H4D2 ... O9A$^{\#2}$	0.98	2.56	3.3648(1)	139
4.	C111 --- H111 ... O1C	0.95	2.49	3.0429(1)	117
5.	C112 --- H112 ... O5A$^{\#3}$	0.95	2.48	3.127(1)	125
6.	C114 --- H114 ... O7A	0.95	2.49	3.2609(1)	138
7.	C115 --- H115 ... O6C	0.95	2.55	3.1276(1)	119
8.	C121 --- H121 ... O1C	0.95	2.40	3.0068(1)	122
9.	C123 --- H123 ... O1S3$^{\#4}$	0.95	2.41	3.1067(1)	130
10.	C125 --- H125 ... O6S	0.95	2.46	3.0364(1)	119
11.	C131 --- H131 ... O6C	0.95	2.45	3.0572(1)	122
12.	C132 --- H132 ... O10A$^{\#5}$	0.95	2.50	3.0511(1)	117
13.	C134 --- H134 ... O2B	0.95	2.45	3.2298(1)	139
14.	C135 --- H135 ... O1C	0.95	2.52	3.1409(1)	123
15.	C141 --- H141 ... O6C	0.95	2.32	2.9412(1)	122
16.	C143 --- H143 ... O1S2$^{\#6}$	0.95	2.38	3.0218(1)	125
17.	C144 --- H144 ... O1S2$^{\#6}$	0.95	2.55	3.1004(1)	117
18.	C145 --- H145 ... O1C	0.95	2.52	3.1455(1)	123
19.	C145 --- H145 ... O1S	0.95	2.36	3.0695(1)	131'
20.	C211 --- H211 ... O8A$^{\#7}$	0.95	2.51	3.0814(1)	118
21.	C211 --- H211 ... O8B$^{\#7}$	0.95	2.56	3.2734(1)	132'
22.	C212 --- H212 ... O1S4$^{\#8}$	0.95	2.59	3.3551(1)	138
23.	C213 --- H213 ... O8B$^{\#8}$	0.95	2.59	3.2657(1)	128
24.	C221 --- H221 ... O8A$^{\#7}$	0.95	2.46	2.9977(1)	116
25.	C231 --- H231 ... O12$^{\#5}$	0.95	2.32	3.2622(1)	169
26.	C225 --- H225 ... O10C	0.95	2.56	3.0821(1)	115
27.	C231 --- H231 ... O10A	0.95	2.45	3.2887(1)	147
28.	C232 --- H232 ... O10A$^{\#5}$	0.95	2.52	3.1621(1)	125
29.	C245 --- H245 ... O78$^{\#7}$	0.95	2.54	3.3075(1)	138
30.	C311 --- H311 ... O5C	0.95	2.547	3.0542(1)	112
31.	C313 --- H313 ... O67$^{\#3}$	0.95	2.58	3.4912(1)	161
32.	C315 --- H315 ... O3A$^{\#7}$	0.95	2.51	3.0539(1)	117
33.	C321 --- H321 ... O5A	0.95	2.39	3.2779(1)	155
34.	C331 --- H331 ... O5C	0.95	2.56	3.150(1)	117
35.	C335 --- H335 ... O23$^{\#9}$	0.95	2.43	3.1636(1)	133
36.	C341 --- H341 ... O5C	0.95	2.55	3.1456(1)	121
37.	C343 --- H343 ... O3B$^{\#10}$	0.95	2.50	3.1667(1)	127
38.	C344 --- H344 ... O1S1$^{\#10}$	0.95	2.57	3.3941(1)	145
39.	C345 --- H345 ... O3A$^{\#9}$	0.95	2.46	3.0931(1)	124

40.	C345 --- H345 ... O3B[#9]	0.95	2.52	3.2496(1)	134'
41.	C411 --- H411 ... O7B	0.95	2.33	3.1517(1)	144
42.	C412 --- H412 ... O4A[#3]	0.95	2.39	3.2391(1)	149
43.	C414 --- H414 ... O23[#11]	0.95	2.39	3.1536(1)	137
44.	C415 --- H415 ... O1D	0.95	2.46	3.1188(1)	126
45.	C415 --- H415 ... O2S[#11]	0.95	2.54	3.3266(1)	140'
46.	C421 --- H421 ... O78	0.95	2.42	3.1576(1)	134
47.	C424 --- H424 ... O9A[#12]	0.95	2.56	3.1848(1)	124
48.	C425 --- H425 ... O2A[#11]	0.95	2.39	3.2930(1)	160
49.	C432 --- H432 ... O6A	0.95	2.43	3.1875(1)	137
50.	C434 --- H434 ... O3B	0.95	2.40	3.1756(1)	139

Symmetry transformations used to generate equivalent atoms:

[#1] = x, y, 1+z

[#2] = 2-x, 1/2+y, 3/2-z

[#3] = 1-x, -y, 2-z

[#4] = 2-x, -y, 2-z

[#5] = 2-x, 1-y, 2-z

[#6] =1-x, 1-y, 2-z

[#7] = x, 1+y, z

[#8] = 2-x, 1/2+y, 5/2-z

[#9] = x, -1+y, z

[#10] = 1-x, -1/2+y, 3/2-z

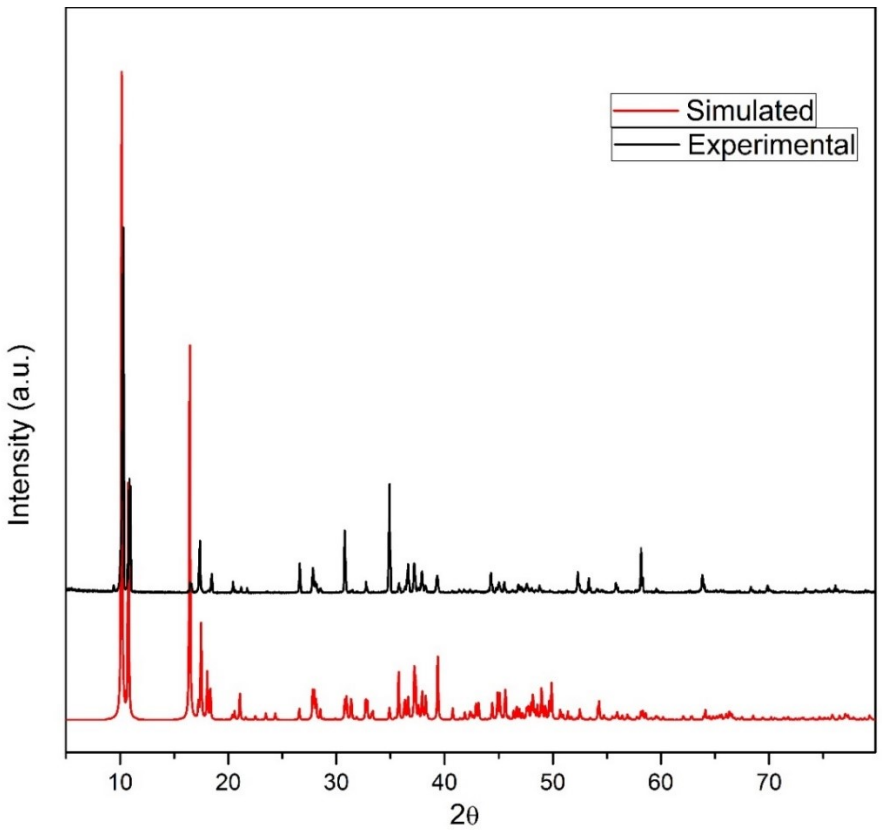
[#11] = x, 1/2-y, 1/2+z

[#12] = 2-x, -1/2+y, 5/2-z

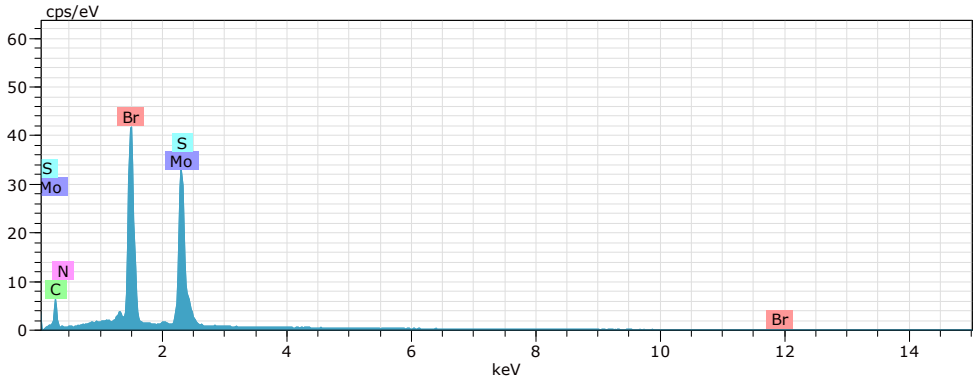
Table S3: Comparision of literature reports of oxidative desulfurization process studied with dibenzothiophene and polyoxomolybdates as catalysts.

Sl. No.	Catalyst	Oxidant	Temperature (°C)	% Removal	References
1.	$H_6P_2Mo_{18}O_{62}$	H_2O_2/HCOOH	70	60	104
2.	$H_6PMo_9V_3O_{40}$	H_2O_2/HCOOH	70	83	104
3.	$[Co(BBPTZ)_3][HPMo_{12}O_{40}]\cdot 24H_2O$	TBHP	50	99.1	105
4.	$[Omim]_3PMo_{12}O_{40}$	TBHP	60	100	106
5.	$[Cu^{II}(C_5H_5N)_4]_3[\{Mo^{VI}_5O_{15}(SO_4)_2\}\{Cu^{II}(C_5H_5N)_3\{DMF\}(H_2O)\}][Mo^{VI}_5O_{15}(SO_4)_2]\bullet 2DMF$	TBHP	60	100	This article

BBPTZ: 4,4′-bis(1,2,4-triazol-1-ylmethyl)biphenyl]; Omim: 1-octyl-3-methylimidazolium, TBHP: Tetrabutyl hydroperoxide



(a)



Compound	Elements	Atomic weight (%)	Approx. mol ratio (approx.)
$(NEt_4)_2Mo_3S_7Br_6$	Mo	5.88	1
	S	11.24	2.2
	Br	10.02	2
	C	25.11	5
	N	7.01	1

(b)

Figure S1: (a) Comparative P-XRD data for $(NH_4)_2Mo_3S_{13}$, and (b) EDX analysis data for $(NEt_4)_2Mo_3S_7Br_6$ with elemental percentage distribution shown in table.

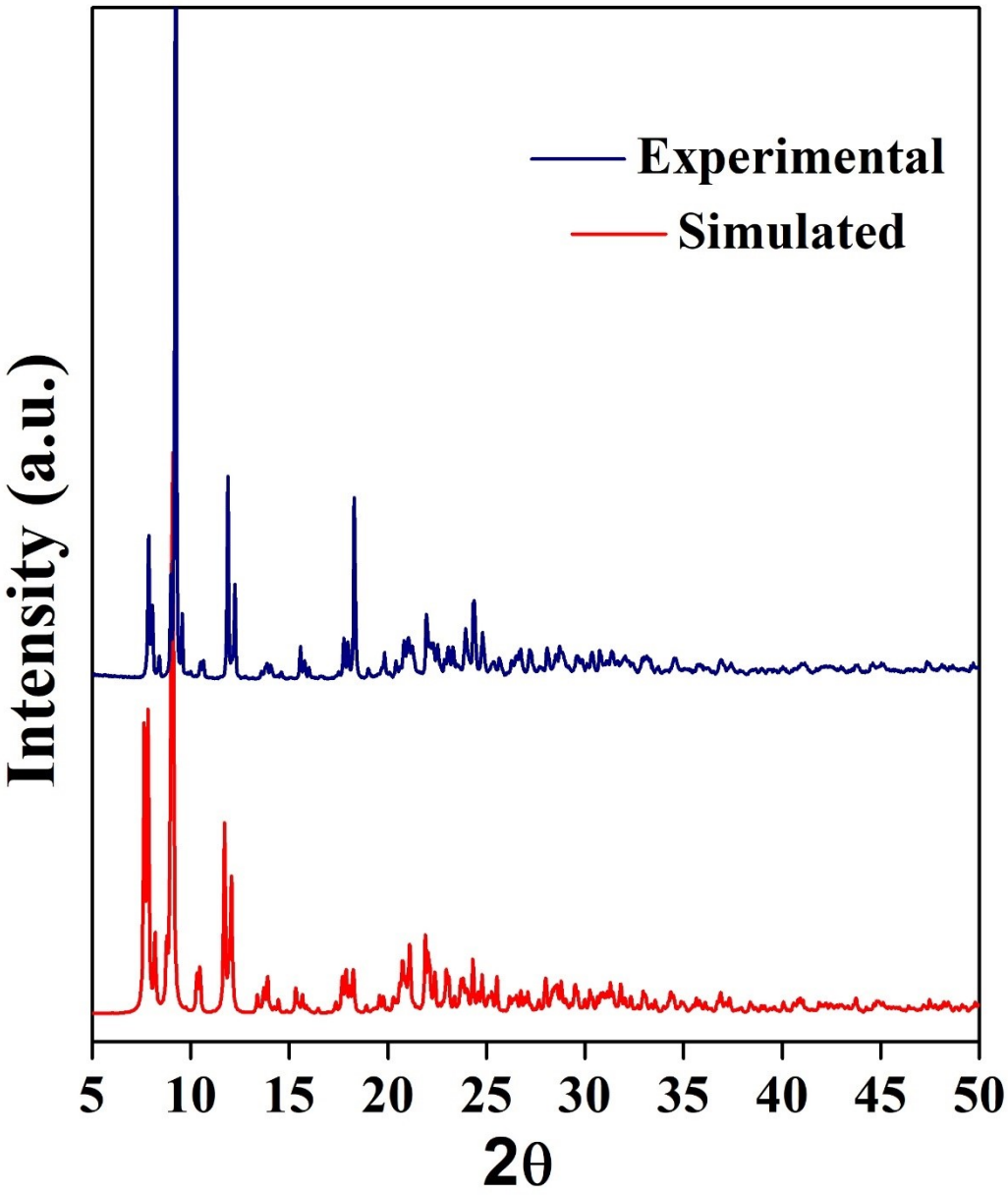


Figure S2: Comparative simulated and experimental P-XRD of compound **1**.

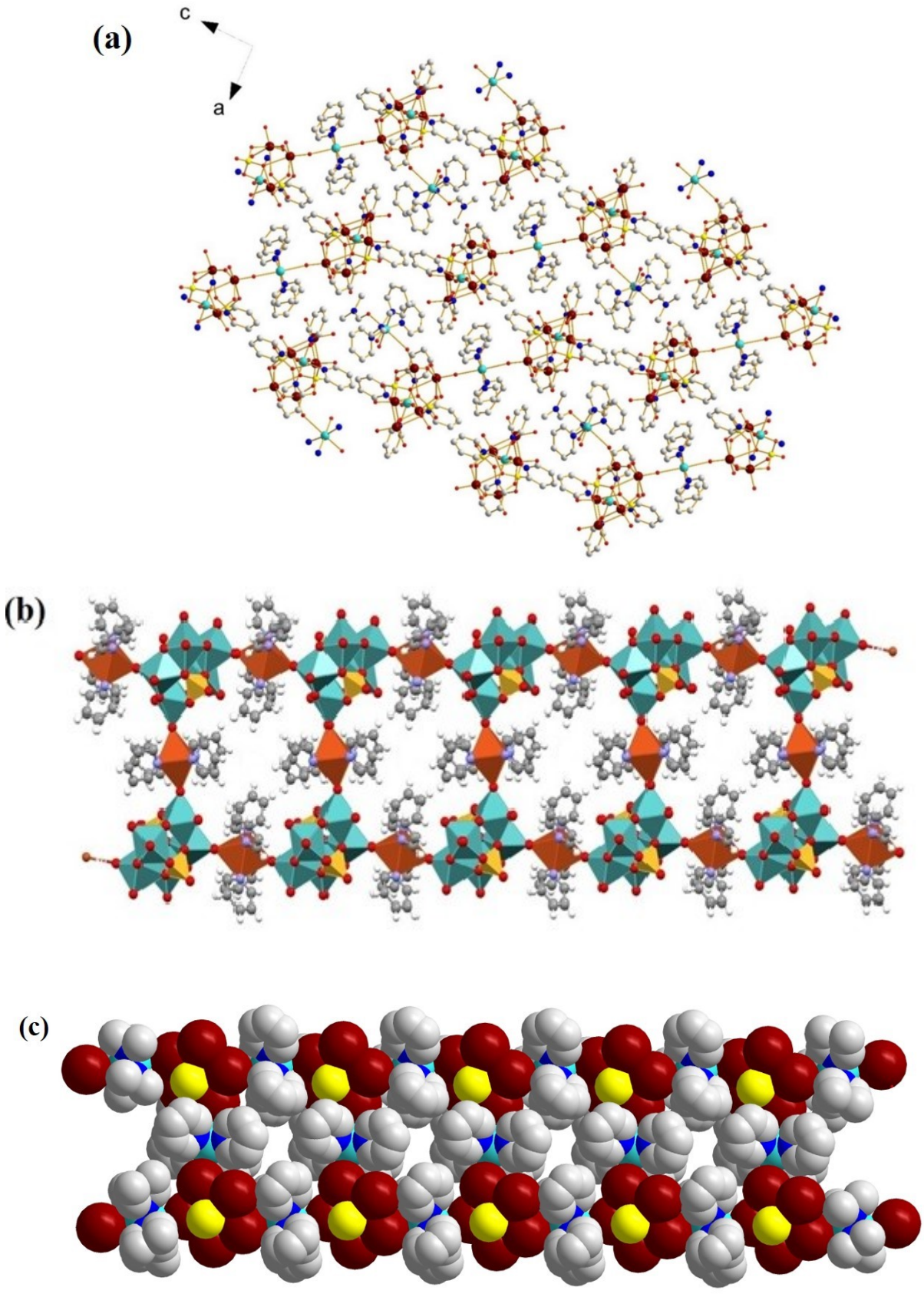


Figure S3: (a) Ball and stick, (b) Polyhedral, and (c) Space-filling model of interdigitated architecture of **1**; (Colour code: Mo: Dark red, Cu: Turquoise, S: Yellow, O: Red, N: Blue, C: Grey, H: white).

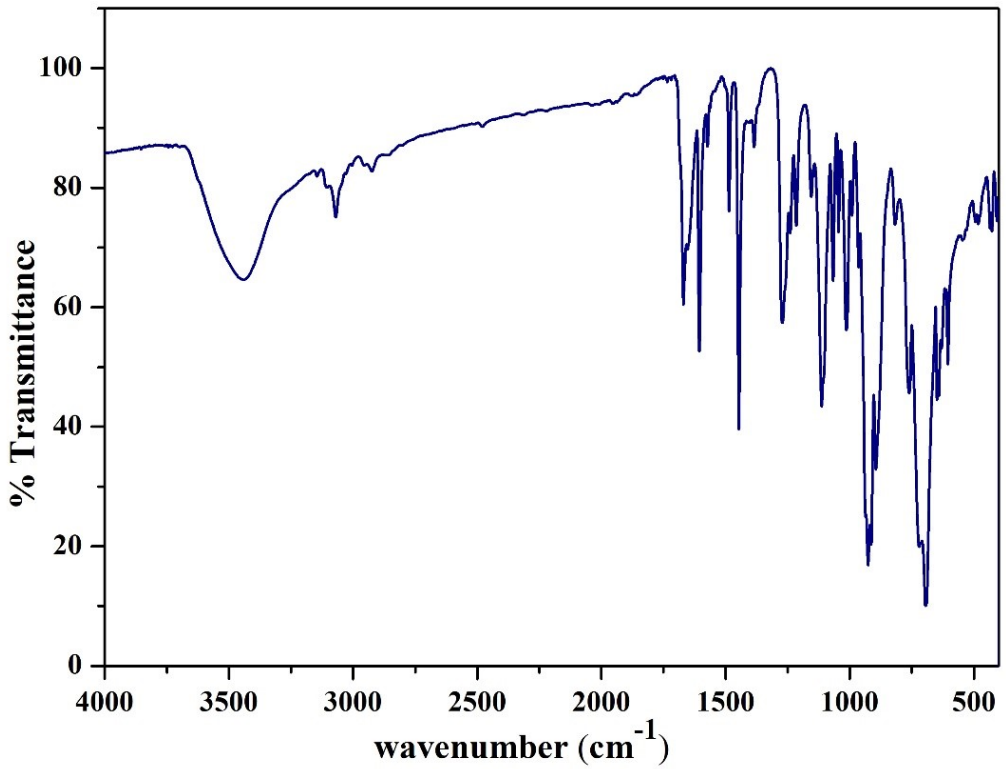


Figure S4: Infrared spectrum of compound **1**.

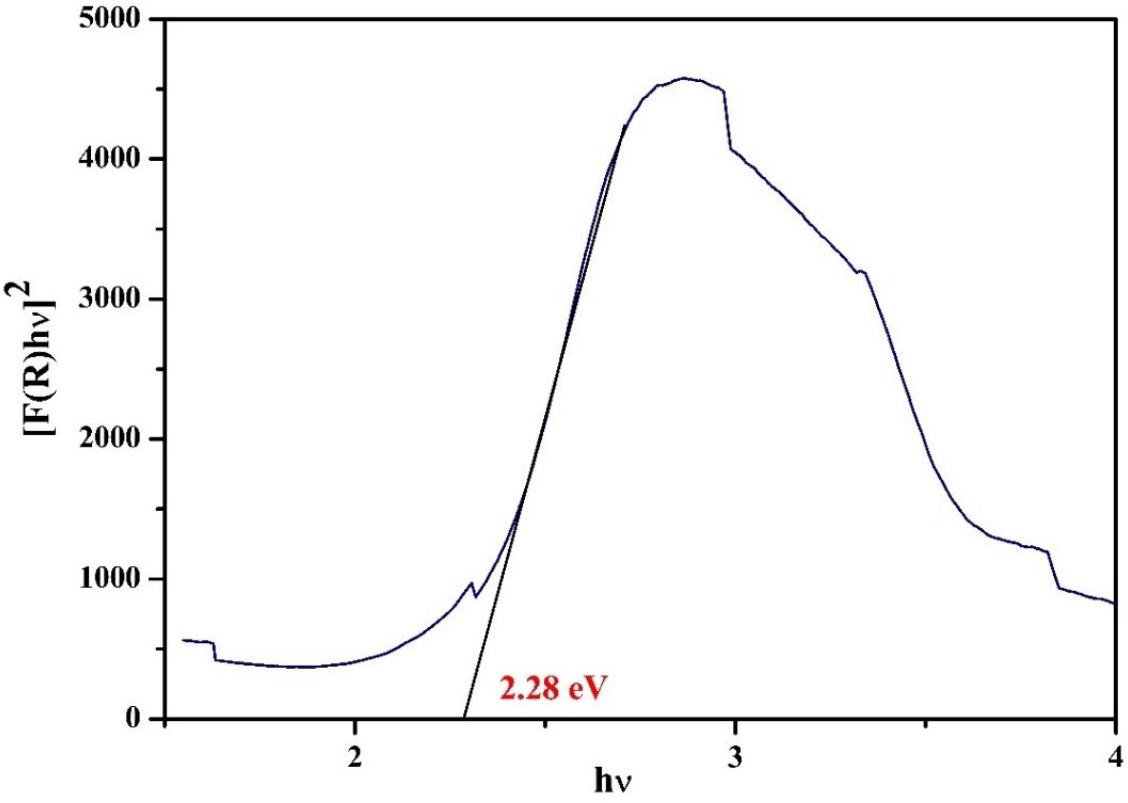
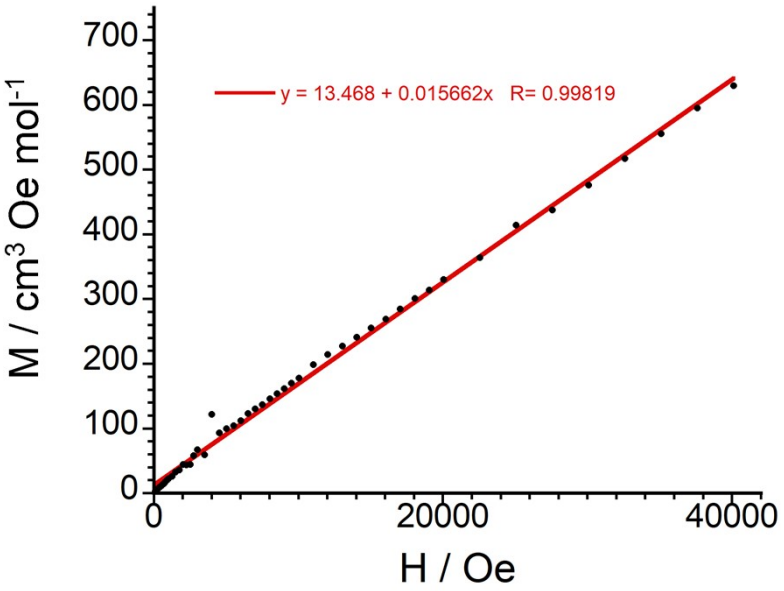
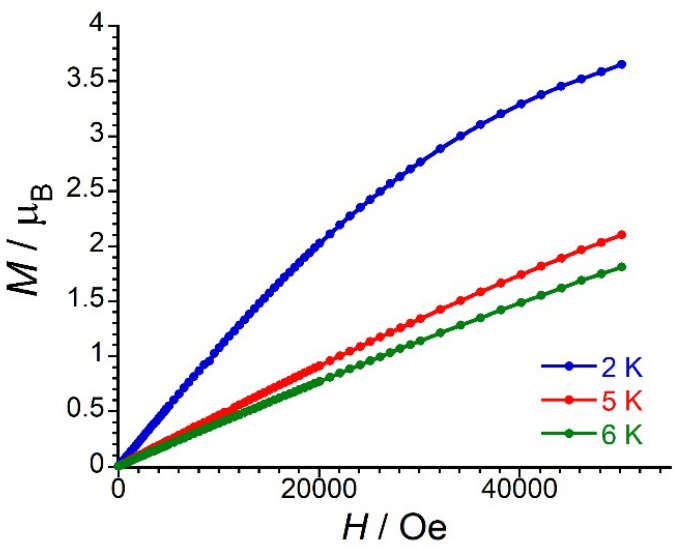


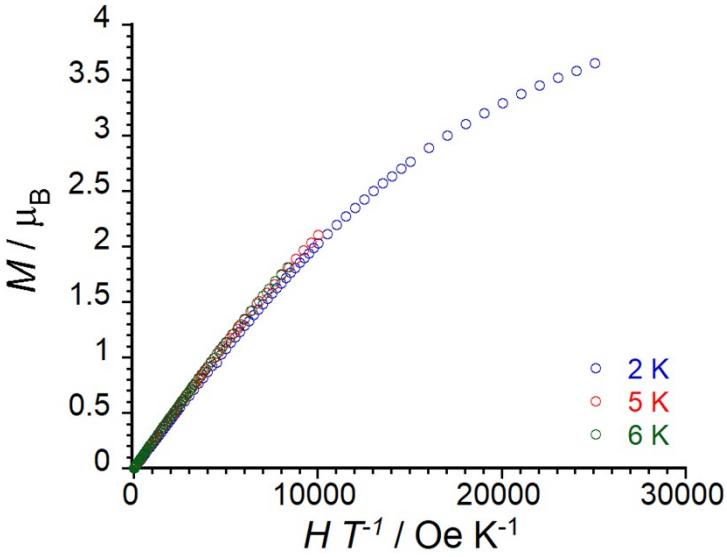
Figure S5: Kubelka-Munk plot of UV-DRS spectra of compound **1** showing direct band energy gap (Eg).



(a)

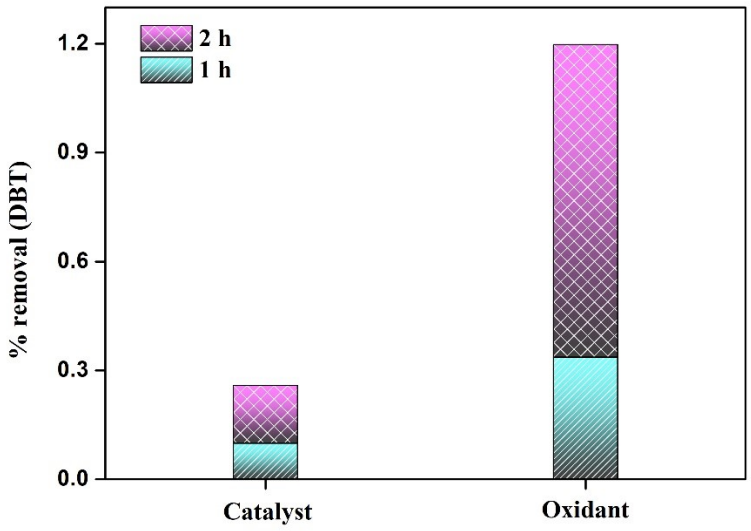


(b)

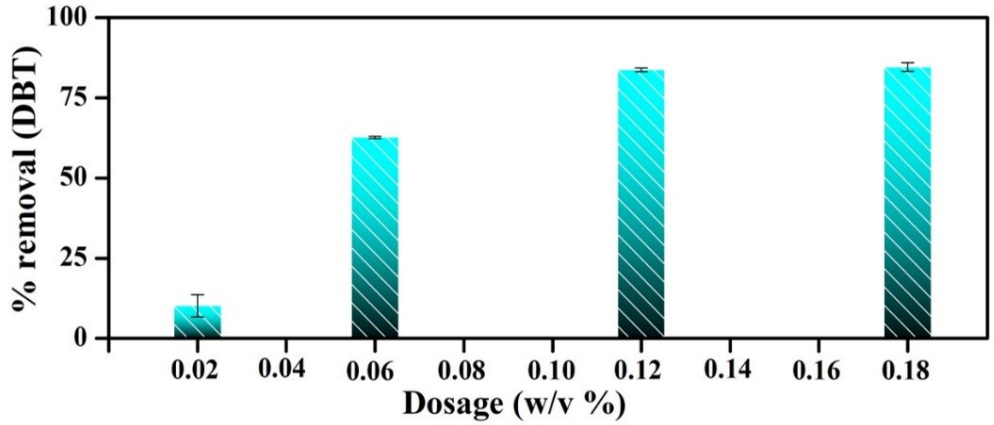


(c)

Figure S6: (a) Field dependence of the magnetization plotted as *M vs H* for **1** at 100 K. The solid lines represent the best fit. Field dependence of the magnetization as **(b)** *M vs H* (left) and, **(c)** *M vs H/T* (right) plots for **1** at 2, 5, and 6 K. The solid lines are guide for the eyes.



(a)



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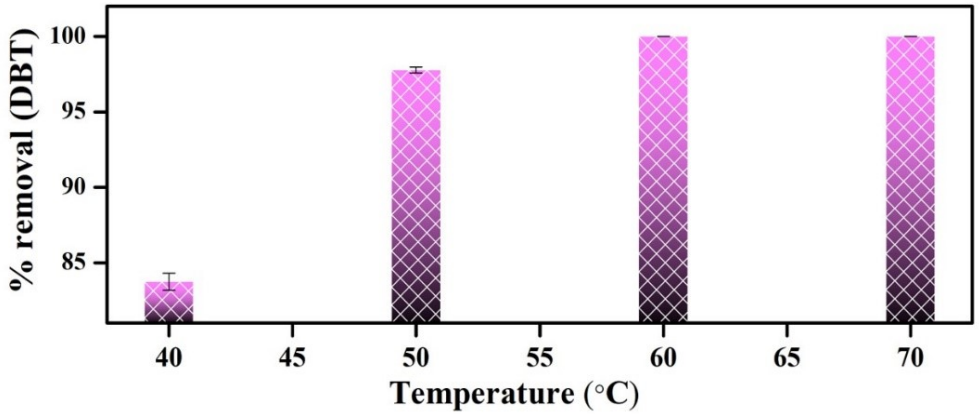

(c)

Figure S7: (a) Control catalysis experiment(s) without catalyst or oxidant. Bar-chart illustrating the optimization of ODS parameters with respect to **(b)** catalyst dosage, **(c)** temperature.

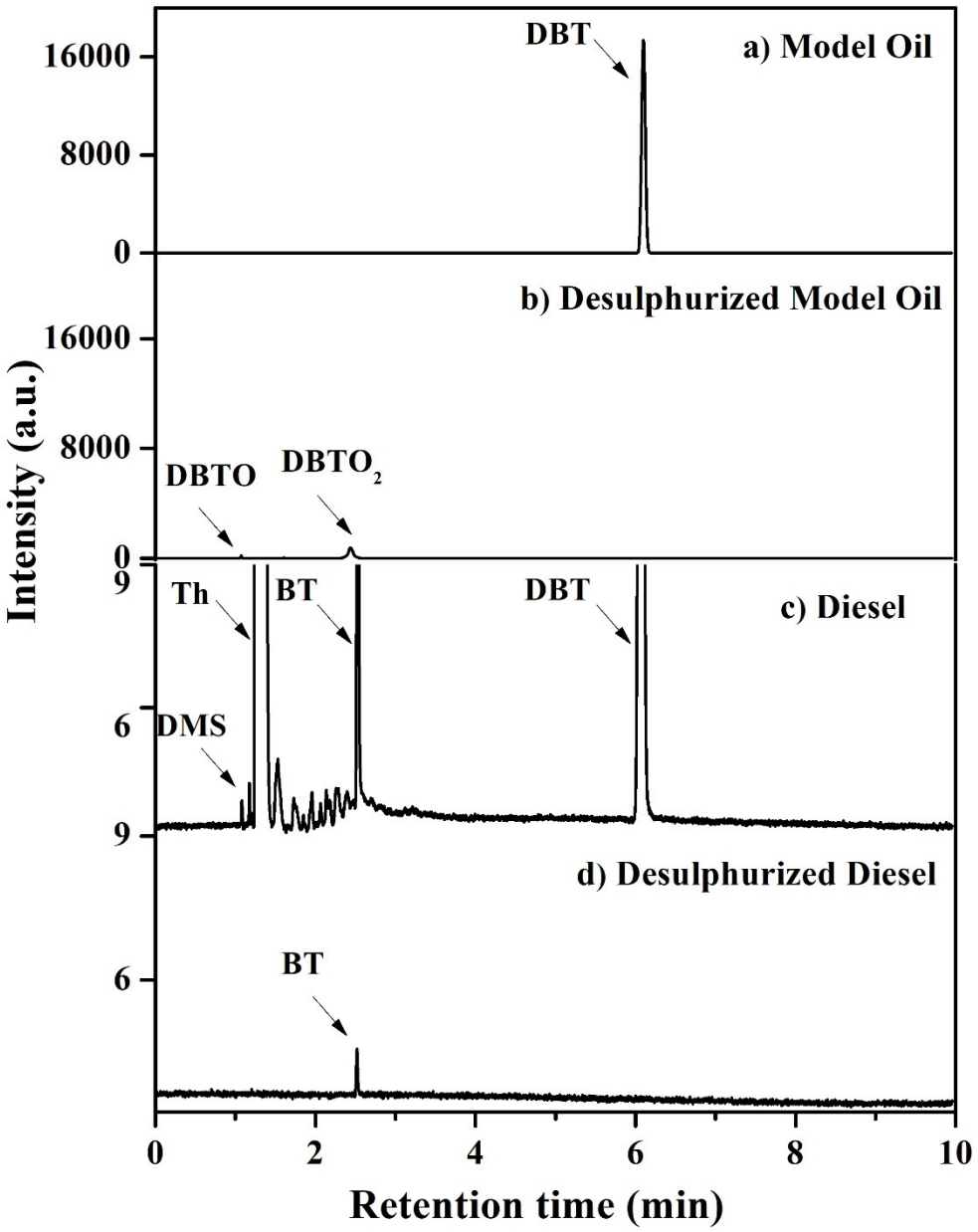

Figure S8: GC-FPD chromatograms of aliquots extracted during ODS process of **(a)** fresh model oil, **(b)** desulphurized model oil, **(c)** fresh diesel, and **(d)** desulphurized diesel.

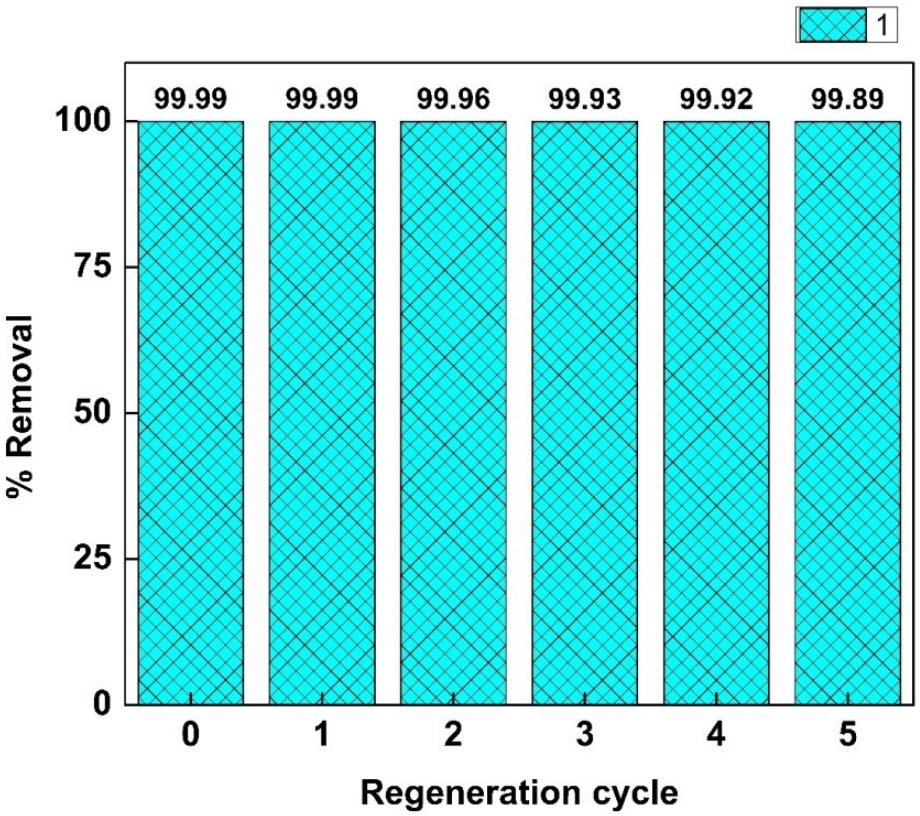

Figure S9: Bar-chart showing regeneration and reusability of compound **1** for ODS catalysis.

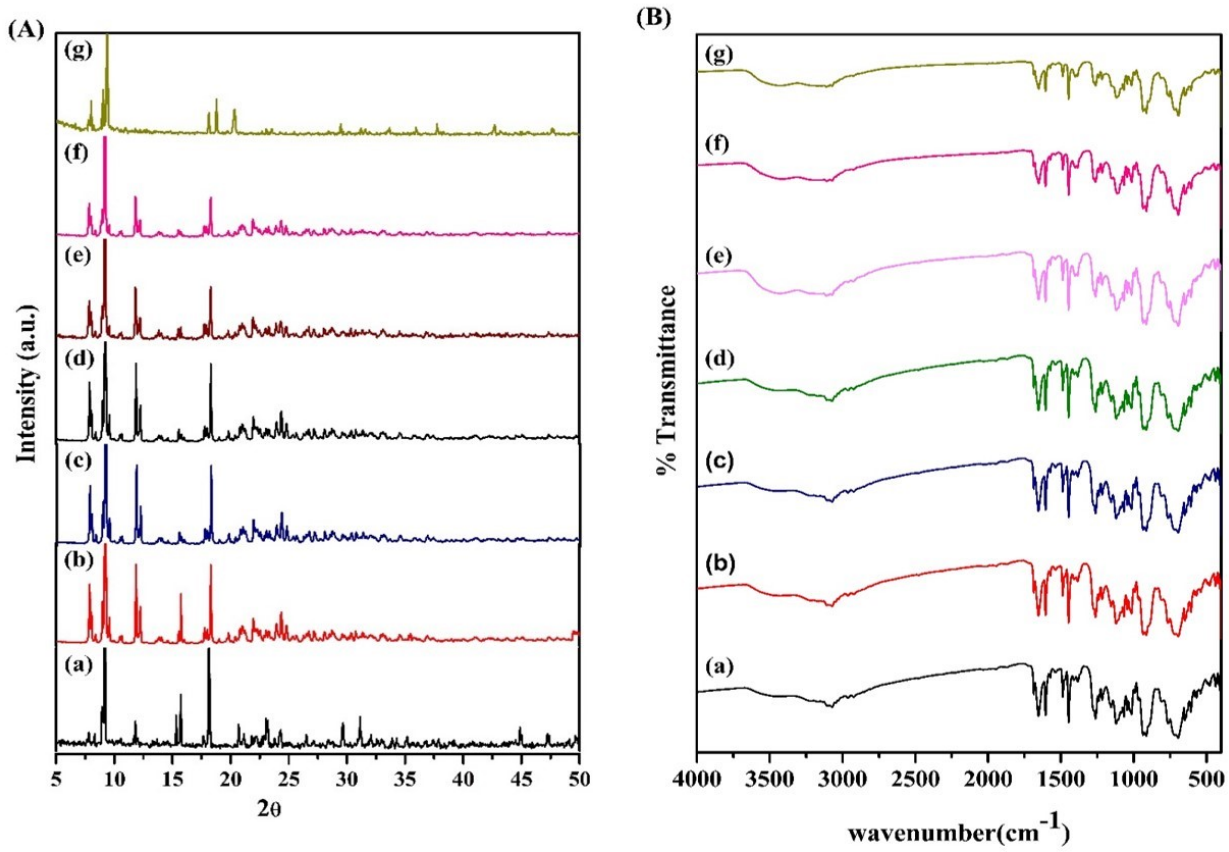

Figure S10: Comparative **(A)** P-XRD and, **(B)** IR spectra of compound **1** during ODS studies along multiple cycles; **(a)** pristine catalyst, **(b)** after initial cycle of oxidative desulphurization **(c)** after regeneration - cycle 1; **(d)** after regeneration - cycle 2; **(e)** after regeneration - cycle 3; **(f)** after regeneration - cycle 4; **(g)** after regeneration - cycle 5.

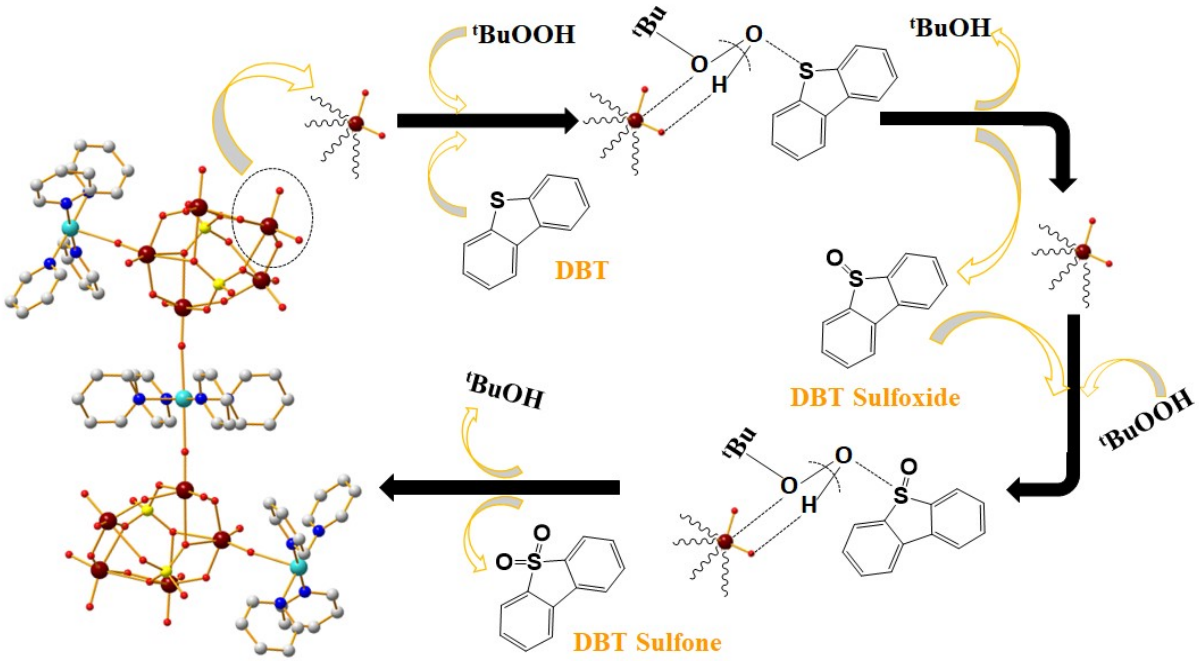

Figure S11: Proposed mechanism of catalytic ODS for DBT with compound **1** as catalyst.