Electronic Supplementary Information

Two Titanium(IV)-Oxo-Clusters: Synthesis, Structures, Characterization and Recycling Catalytic Activity in Oxygenation of Sulfide

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Table S1 Selected bond lengths (Å) and angles (°) for TOC-1

Lengths			
Ti2-Ti1	3.397(2)	Ti2-Ti3	3.340(2)
Ti1-N1	2.273(8)	Ti1-N2	2.202(8)
Ti2-N3	2.235(7)	Ti2-N4	2.242(8)
Ti3-N5	2.254(7)	Ti3-N6	2.232(7)
Ti-(μ_2-O)		Ti- O($OR_{terminal}$)	
Ti1-O8	1.796(6)	Ti1-O1	2.004(7)
Ti2-O10	1.8327(17)	Ti- O($O_2CR_{terminal}$)	
Ti2-O7	1.837(6)	Ti1-O3	1.924(6)
Ti2-O11	1.822(6)	Ti-O($OH_{terminal}$)	
Ti3-O13	1.824(2)	Ti1-O7	1.807(6)
Ti3-O8	1.839(6)	Ti3-O12	2.092(6)
Ti3-O11	1.825(6)		
Angles			
Ti1-O7-Ti2	137.6(4)	Ti1-O8-Ti3_2	168.9(4)
Ti2-O11-Ti3	132.6(3)	Ti2-O10-Ti2_2	171.8(5)
Ti3-O13-Ti3_2	155.0(5)	O8-Ti1-O3	97.6(3)
O8-Ti1-O7	99.5(3)	O8-Ti1-O1	166.9(3)
O7-Ti1-O3	103.1(3)	O3-Ti1-O1	85.3(3)
O7-Ti1-O1	92.2(3)	O7-Ti1-N2	93.0(3)
O8-Ti1-N2	90.0(3)	O1-Ti1-N2	83.5(3)
O3-Ti1-N2	160.8(3)	O7-Ti1-N1	164.9(3)
O8-Ti1-N1	88.1(3)	O1-Ti1-N1	79.2(3)
O3-Ti1-N1	88.6(3)	O11-Ti2-O7	98.4(3)
N2-Ti1-N1	73.9(3)	O7-Ti2-O10	103.28(19)
O11-Ti2-O10	105.0(3)	O7-Ti2-O9	164.5(2)
O11-Ti2-O9	90.0(3)	O11-Ti2-N3	89.1(3)
O10-Ti2-O9	86.88(19)	O10-Ti2-N3	158.5(3)
O7-Ti2-N3	90.3(3)	O11-Ti2-N4	161.2(3)
O9-Ti2-N3	76.8(3)	O10-Ti2-N4	91.0(3)
O7-Ti2-N4	87.1(3)	N3-Ti2-N4	72.9(3)
O9-Ti2-N4	81.0(3)	O13-Ti3-O8_1	100.5(2)
O13-Ti3-O11	104.8(3)	O13-Ti3-O12	93.0(2)
O11-Ti3-O8_1	97.4(3)	O8_1-Ti3-O12	163.3(3)
O11-Ti3-O12	88.5(3)	O11-Ti3-N6	163.3(3)
O13-Ti3-N6	88.5(3)	O12-Ti3-N6	80.7(3)
O8_1-Ti3-N6	89.7(3)	O11-Ti3-N5	92.3(3)
O13-Ti3-N5	162.0(3)	O12-Ti3-N5	81.8(3)
O8_1-Ti3-N5	82.4(3)	N6-Ti3-N5	73.6(3)

Table S2 Selected bond lengths (Å) and angles (°) for TOC-2

Lengths			
Ti1-N1	2.278(6)	Ti1-N2	2.197(7)
Ti-(μ_2-O)		Ti- O($OR_{terminal}$)	
Ti1-O7	1.766(5)	Ti1-O3	1.874(5)
Ti1-O7_1	1.836(5)	Ti- O($O_2CR_{terminal}$)	
		Ti1-O1	2.026(5)
Angles			
Ti1-O7-Ti1_2	161.3(3)	O7-Ti1-O7_1	100.0(3)
O7-Ti1-O3	105.8(3)	O7_1-Ti1-O3	94.4(2)
O7-Ti1-O1	93.0(2)	O7_1-Ti1-O1	166.5(2)
O3-Ti1-O1	85.3(2)	O7-Ti1-N2	88.9(3)
O7_1-Ti1-N2	90.0(3)	O3-Ti1-N2	163.7(3)
O1-Ti1-N2	86.8(3)	O7-Ti1-N1	161.8(3)
O7_1-Ti1-N1	82.9(2)	O3-Ti1-N1	91.7(3)
O1-Ti1-N1	83.7(2)	N2-Ti1-N1	73.2(3)

Table S3 BVS calculations for O atoms in TOCs 1-2 [a]

TOC-1							
u2-O/total valence	**Bonded atoms**	**distance**	**BVS**	**Aqua-O**	**Bonded atoms**	**distance**	**BVS**
O7/2.123	Ti1	1.818	0.997	O9	Ti2	2.156	0.3979
	Ti2	1.792	1.064	O12	Ti3	2.103	0.451
O8_01/2.033	Ti1	1.792	1.064				
	Ti3_01	1.827	0.969				
O11/1.966	Ti2	1.818	0.997				
	Ti3	1.827	0.969				
O13/1.984	Ti3	1.823	0.992				
	Ti-3	1.823	0.992				
TOC-2							
O7/1.976	Ti1	1.771	0.984				
	Ti1_01	1.832	0.992				

[a] Bond valence calculations were performed using Bond Valence Calculator (Version 2.0, February 1993), and default parameters provided by Bond Valence Calculator were used, i.e., R_0 = 1.815 and B = 0.370.

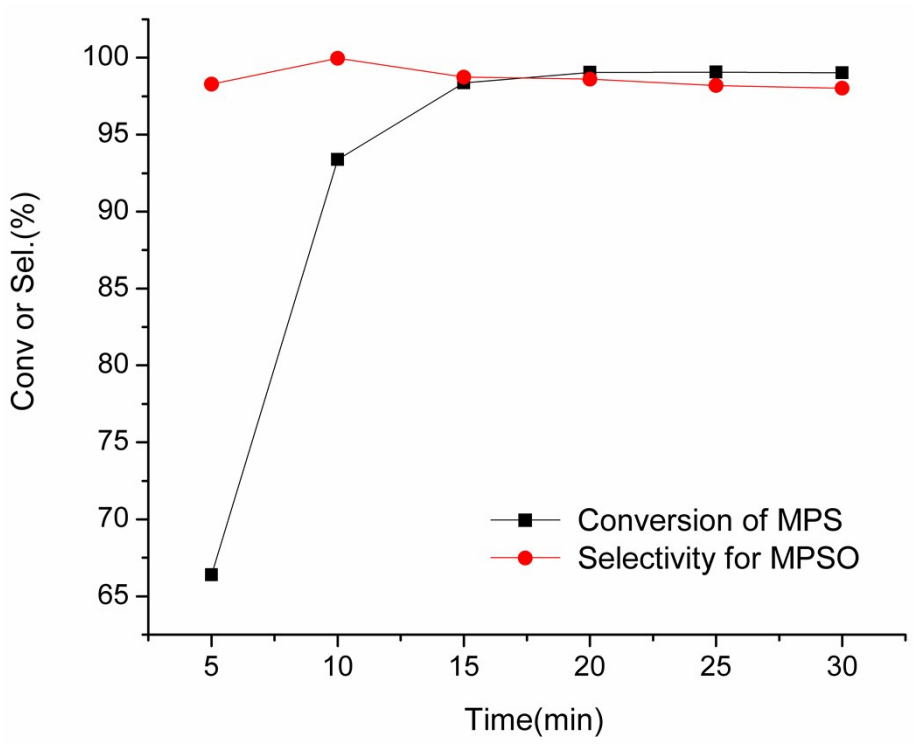

Fig S1. A time dependent profile of the oxidation of MPS by aqueous H_2O_2 by TOC-1.

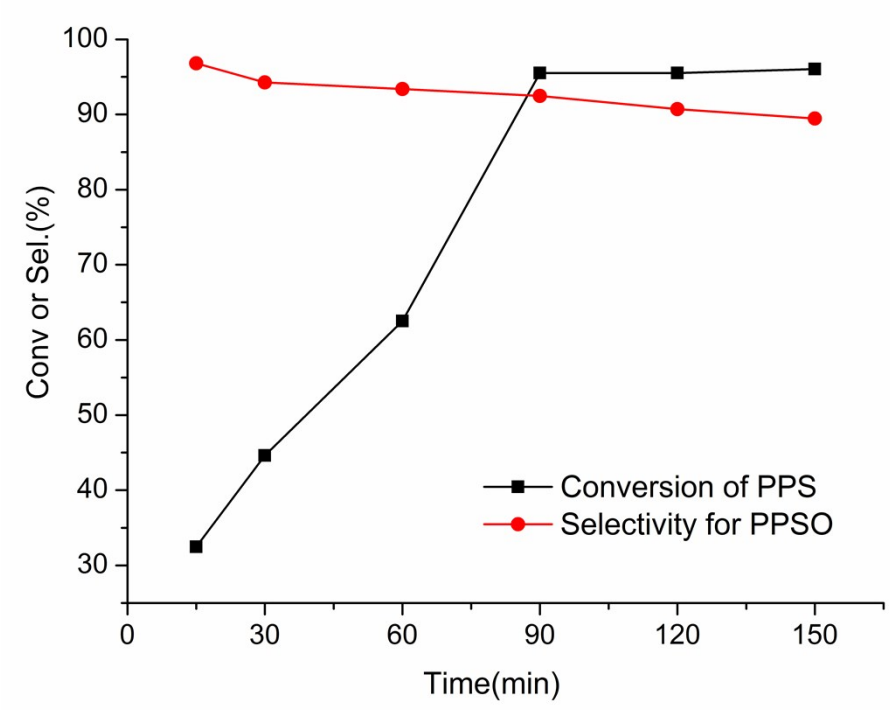

Fig S2. A time dependent profile of the oxidation of PPS by aqueous H_2O_2 by TOC-1.

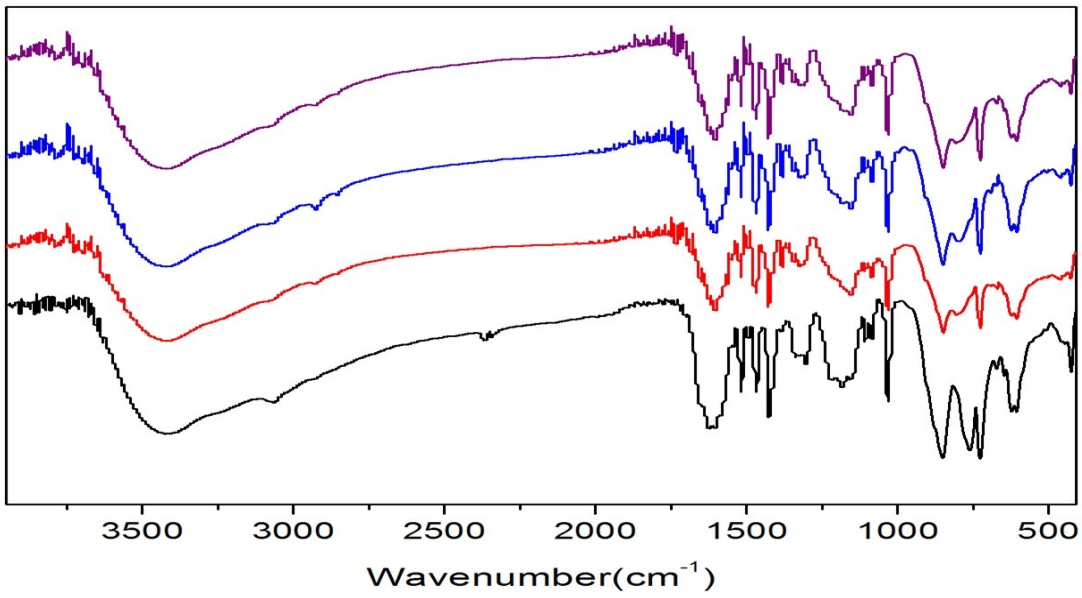

Fig S3. The IR spectrum of three recycling runs for TOC-1. Black represent original IR spectrum, red, blue and purple repensent IR spectrum after catalytic reaction one time, second time and fourth time.

Table S4 Crystallographic data and refinement parameters for TOCs 1-2.

TOC	**1**	**2**
Empirical formula	$C_{86}H_{110}N_{12}O_{49}Ti_6S_2$	$C_{76}H_{96}N_{12}O_{46}Ti_4S_4$
Mr	2446.96	2232.96
Crystal system	monoclinic	tretragonal
Space group	C 2/c	I-4
Size(mm^3)	0.38×0.34×0.30	0.40×0.40×0.32
habit/color	yellow/block	yellow/block
a(Å)	25.875(4)	13.5404(3)
b(Å)	29.103(2)	13.5404(3)
c(Å)	23.050(2)	27.7844(10)
α(°)	90.00	90.00
β(°)	121.355(8)	90.00
γ(°)	90.00	90.00
V($Å^3$)	14823(3)	5094(2)
Z	4	2
D_c($Mg·m^{-3}$)	0.895	1.200
μ(mm^{-1})	0.385	0.453
θ range	3.2-29.5	3.0-29.4
Unique reflections	17533	6231
Observed reflections	7839	4586
parameters	594	271
F(000)	4272	1872

T(K)	170	293
R_1 $wR_2[I>2\sigma(I)]$	0.0982,0.2621	0.0540, 0.1664
R_1 wR_2[all data]	0.1631,0.2992	0.0726, 0.189
GOF	0.947	0.703
Largest peak and hole(e· $Å^{-3}$)	1.177, -1.123	0.29, -0.20