Engineering polyoxometalates-based metal organic framework with more exposed active edge sites of Ag for visible light-driven selective oxidation of *cis*-cyclooctene

Supporting Information

Table S1. Selected bond lengths (Å) and bond angles (°) for compound **1**.

Ag(4)-N(6)#2	2.249(17)	Ag(4)-N(5)	2.306(17)
Ag(4)-S(2)#3	2.646(6)	Ag(1)-N(2)	2.27(2)
Ag(1)-N(4)#4	2.33(2)	Ag(1)-O(1W)	2.50(3)
Ag(1)-O(12)	2.544(18)	Ag(1)-S(1)	2.863(6)
Ag(2)-N(8)#2	2.241(19)	Ag(2)-N(1)	2.401(19)
Ag(2)-S(1)	2.564(6)	Ag(3)-N(3)	2.183(18)
Ag(3)-N(7)#5	2.200(19)	Ag(3)-O(22)#6	2.54(2)
N(4)-Ag(1)#2	2.33(2)	N(7)-Ag(3)#7	2.200(19)
N(6)-Ag(4)#4	2.249(17)	N(8)-Ag(2)#4	2.241(19)
O(22)-Ag(3)#8	2.54(2)	S(2)-Ag(4)#9	2.646(6)
N(6)#2-Ag(4)-N(5)	124.6(6)	N(6)#2-Ag(4)-S(2)#3	124.1(5)
N(5)-Ag(4)-S(2)#3	106.3(5)	N(2)-Ag(1)-N(4)#4	128.0(7)
N(2)-Ag(1)-O(1W)	116.1(10)	N(4)#4-Ag(1)-O(1W)	114.7(10)
N(2)-Ag(1)-O(12)	101.2(7)	N(4)#4-Ag(1)-O(12)	81.9(7)
O(1W)-Ag(1)-O(12)	74.2(9)	N(2)-Ag(1)-S(1)	91.5(6)
N(4)#4-Ag(1)-S(1)	96.8(5)	O(1W)-Ag(1)-S(1)	93.0(8)
O(12)-Ag(1)-S(1)	164.9(5)	N(8)#2-Ag(2)-N(1)	118.8(7)
N(8)#2-Ag(2)-S(1)	130.1(5)	N(1)-Ag(2)-S(1)	89.7(4)
N(3)-Ag(3)-N(7)#5	139.6(7)	N(3)-Ag(3)-O(22)#6	84.9(7)
N(7)#5-Ag(3)-O(22)#6	89.6(7)		

Symmetry codes for **1**: #1 -x,-y,-z+1 #2 x, -y+1/2, z-1/2 #3 x+1, -y+1/2, z+1/2 #4 x, -y+1/2, z+1/2 #5 x-1, y, z-1 #6 x, y, z-1 #7 x+1, y, z+1 #8 x, y, z+1 #9 x-1, -y+1/2, z-1/2.

Table S2. Selected bond lengths (Å) and bond angles (°) for compound **2**.

Ag(1)-N(1)	2.167(10)	Ag(1)-S(1)	2.433(3)
Ag(1)-O(4)	2.505(8)	Ag(1)-Ag(1)#2	2.9545(19)
Ag(2)-N(8)#3	2.192(9)	Ag(2)-N(4)	2.224(10)
Ag(2)-N(6)	2.346(10)	Ag(3)-N(5)#4	2.255(9)
Ag(3)-N(7)	2.307(10)	Ag(3)-N(3)	2.358(10)
Ag(4)-N(2)	2.254(10)	Ag(4)-O(1W)	2.414(10)
Ag(4)-S(2)	2.477(4)	N(5)-Ag(3)#3	2.255(9)
N(8)-Ag(2)#4	2.191(9)		
N(1)-Ag(1)-S(1)	170.8(3)	N(1)-Ag(1)-O(4)	103.0(3)
S(1)-Ag(1)-O(4)	81.0(2)	N(1)-Ag(1)-Ag(1)#2	86.4(3)
S(1)-Ag(1)-Ag(1)#2	87.07(8)	O(4)-Ag(1)-Ag(1)#2	158.1(2)
N(8)#3-Ag(2)-N(4)	142.9(4)	N(8)#3-Ag(2)-N(6)	118.9(4)
N(4)-Ag(2)-N(6)	96.4(4)	N(5)#4-Ag(3)-N(7)	121.3(4)
N(5)#4-Ag(3)-N(3)	126.7(4)	N(7)-Ag(3)-N(3)	97.6(4)
N(2)-Ag(4)-O(1W)	113.1(4)	N(2)-Ag(4)-S(2)	139.7(3)
O(1W)-Ag(4)-S(2)	106.3(3)		

Symmetry codes for **2**: #1 -x, y, -z+1/2 #2 -x+1/2, y+1/2, -z+3/2 #3 -x+1/2, y-1/2, -z+3/2 #4 -x, -y+2, -z+1.

Table S3. Crystal data and structure refinements for compound **1** and **2**.

	1	**2**
formula	$C_8H_{20}Ag_8N_{16}S_4O_{48}PW_{12}$	$C_8H_{18}Ag_8N_{16}S_4O_{42}PMo_{12}$
*F*w	4328.59	3177.79
crystal system	Monoclinic	Monoclinic
space group	P2(1)/c	C2/c
a (Å)	13.0330(19)	24.880(5)
b (Å)	22.665(3)	10.683(2)
c (Å)	11.9449(16)	22.308(4)
β (º)	116.967(2)	106.567(4)
V (Å^3)	3144.8(8)	5683.3(19)
Z	2	4
D_c (g·cm^{-3})	4.571	3.714
μ (mm^{-1})	24.535	5.518
F(000)	3798	5868
R_{int}	0.0408	0.0734
finalR_1^a, wR_2^b (all data)	0.0778 0.2391	0.0612 0.1920
GOF on F^2	1.620	1.095

Table S4. Coordination modes of Ag^{I} ions in compounds **1** and **2**.

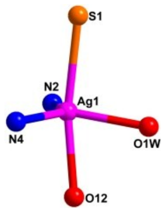
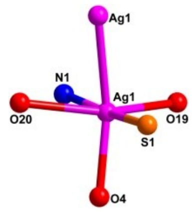
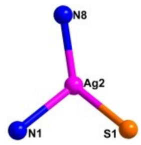
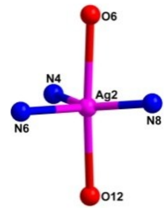
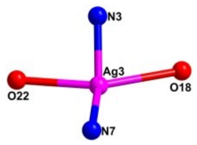
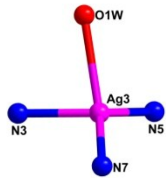
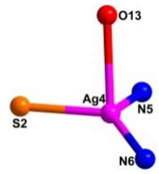
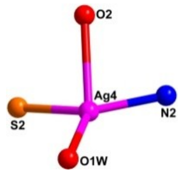
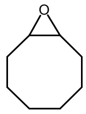
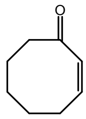
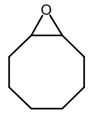
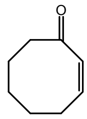
Compound	**1**	**2**
Coordination modes of Silver ions		
		
		
		

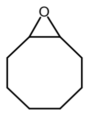
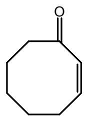
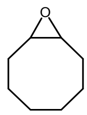
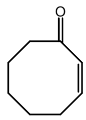
Table S5. Selective oxidation of *cis*-cyclooctene using compounds **1** and Materials of **1** as photocatalysts under visible light irradiation. [a]

Reaction time (h)	Compound **1**				Materials of **1**			
	Conversion (%)	Product selectivity (%)			Conversion (%)	Product selectivity (%)		
				$\Sigma_{sel}C_8$[b] (%)				$\Sigma_{sel}C_8$[b] (%)
0	0	0	0	0	0	0	0	0
8	38.12	99.42	0.56	99.98	11.17	86.45	4.56	91.01
16	45.95	99.57	0.40	99.97	15.39	86.17	4.43	90.60
24	66.52	99.69	0.22	99.91	19.52	85.75	4.23	89.98
32	70.15	99.68	0.15	99.83	22.14	85.58	4.05	89.63

[a]Reaction condition: catalyst (100 mg), *cis*-cyclooctene (10 ml), H_2O_2 (30%, 10 ml), 70°C, under illumination (300 W Xe lamp; λ > 460 nm; light intensity: 80 mW).

[b]Total selectivity to C_8 partial oxidation products.

Table S6. Selective oxidation of *cis*-cyclooctene using compounds **2** and Materials of **2** as photocatalysts under visible light irradiation. [a]

Reaction time (h)	Compound **2**				Materials of **2**			
	Conversion (%)	Product selectivity (%)			Conversion (%)	Product selectivity (%)		
				$\Sigma_{sel}C_8$[b] (%)				$\Sigma_{sel}C8$[b] (%)
0	0	0	0	0	0	0	0	0
8	28.89	99.27	0.58	99.85	12.12	87.42	2.56	89.98
16	38.84	99.21	0.54	99.75	15.93	87.27	2.53	89.80
24	54.99	99.17	0.44	99.61	18.52	87.35	2.22	89.57
32	63.93	99.35	0.18	99.53	20.14	87.47	2.05	89.52

[a]Reaction condition: catalyst (100 mg), *cis*-cyclooctene (10 ml), H_2O_2 (30%, 10 ml), 70°C, under illumination (300 W Xe lamp; λ > 460 nm; light intensity: 80 mW).

[b]Total selectivity to C_8 partial oxidation products.

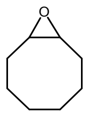
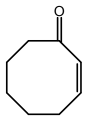
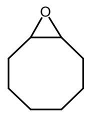
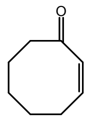
Table S7. The conversion of *cis*-cyclooctene and the selectivity to epoxycyclooctane with different components as catalysts.[a]

Reaction Time (h)	PMo_{12}		PW_{12}	
	Conversion (%)	Product selectivity (%)	Conversion (%)	Product selectivity (%)
0	0	0	0	0
8	6.20	83.67	7.20	77.67
16	6.33	85.95	7.43	85.55
24	7.12	86.73	7.98	86.33
32	7.54	87.26	8.54	88.25
	mttz		Ag^+ ion	
	Conversion (%)	Product selectivity (%)	Conversion (%)	Product selectivity (%)
0	0	0	0	0
8	1.28	93.84	8.67	94.13
16	2.17	94.57	11.16	95.76
24	2.32	95.78	13.34	96.32
32	2.45	95.96	13.82	96.98
	H_2O_2[b]		Ag-PW_{12}	
	Conversion (%)	Product selectivity (%)	Conversion (%)	Product selectivity (%)
0	0	0	0	0
8	1.54	93.54	8.09	93.64
16	1.07	94.53	12.36	95.03
24	1.42	95.28	13.47	95.37
32	1.89	95.36	14.20	95.58
	Ag-mttz		Ag-PMo_{12}	
	Conversion (%)	Product selectivity (%)	Conversion (%)	Product selectivity (%)
0	0	0	0	0
8	7.56	92.44	8.27	94.66
16	10.09	93.57	12.06	95.63
24	11.57	94.05	13.85	96.07
32	11.99	94.12	14.32	96.32

[a]Reaction condition: catalyst (100 mg), *cis*-cyclooctene (10 ml), H_2O_2 (30%, 10 ml), 70°C, under illumination (300 W Xe lamp; λ > 460 nm; light intensity: 80 mW).

[b]Reaction condition: *cis*-cyclooctene (10 ml), H_2O_2 (30%, 20 ml), 70°C, under illumination (300 W Xe lamp; λ > 460 nm; light intensity: 80 mW).

Table S8. Selective oxidation of *cis*-cyclooctene with compounds **1** and **2** as catalysts in dark. [a]

Dark reaction time (h)	Compound **1**				Compound **2**			
	Conversion (%)	Product selectivity (%)			Conversion (%)	Product selectivity (%)		
				$\Sigma_{sel}C_8$[b] (%)				$\Sigma_{sel}C_8$[b] (%)
0	0	0	0	0	0	0	0	0
8	3.25	96.07	3.58	99.65	3.12	95.21	4.34	99.55
16	5.69	95.20	3.52	98.72	5.45	95.28	4.09	99.37
24	9.10	94.22	3.44	97.66	7.52	94.95	3.94	98.89
32	9.24	93.83	3.46	97.29	9.17	95.23	3.37	98.60

[a]Reaction condition: catalyst (100 mg), *cis*-cyclooctene (10 ml), H_2O_2 (30%, 10 ml) 70°C, in dark.

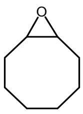
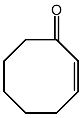
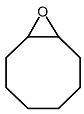
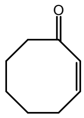
[b]Total selectivity to C_8 partial oxidation products.

Table S9. The conversion of *cis*-cyclooctene and the selectivity to epoxycyclooctane with different reaction conditions.[a]

photocatalyst	T.	Conv. (%)	Select. (%)	**light intensity**	Conv. (%)	Select. (%)	**wavelength**	Conv. (%)	Select. (%)
compound **1**	25	2.09	84.82	20	26.31	94.42	340	38.12	94.12
	40	5.99	90.23	40	42.03	94.55	460	70.13	99.27
	50	11.85	94.75	60	54.78	95.91	540	20.32	96.55
	60	26.31	96.68	80	70.15	99.58	630	15.39	96.68
	70	70.15	99.68	100	70.16	99.44	700	14.23	96.44
Compound **2**	25	1.99	88.35	20	18.58	89.68	340	13.93	98.35
	40	4.87	89.12	40	38.56	90.05	460	63.55	99.12
	50	10.21	90.21	60	49.99	94.86	540	26.58	99
	60	19.89	96.37	80	63.93	98.87	630	13.55	98.37
	70	63.93	99.35	100	63.98	98.80	700	13.93	98.35

[a]Reaction condition: catalyst (100 mg), *cis*-cyclooctene (10 ml), H_2O_2 (30%, 10 ml), under illumination (300 W Xe lamp; λ > 460 nm; light intensity: 80 mW).

Table S10. The cycle experiment of the selective oxidation of *cis*-cyclooctene using compounds **1** and **2** as photocatalysts.[a]

Recycling times	Compound **1**				Compound **2**			
	Conversion (%)	Product selectivity (%)			Conversion (%)	Product selectivity (%)		
				$\Sigma_{sel}C_8$[b] (%)				$\Sigma_{sel}C_8$[b] (%)
1	70.15	99.68	0.15	99.83	63.93	99.35	0.18	99.53
2	70.01	99.16	0.17	99.33	63.64	98.76	0.12	98.88
3	69.35	99.12	0.16	99.28	59.75	97.75	0.10	97.85
4	68.29	99.08	0.13	99.21	58.49	97.70	0.09	97.79
5	68.04	99.05	0.12	99.17	55.97	97.19	0.01	97.20

[a]Reaction condition: catalyst (100 mg), *cis*-cyclooctene (10 ml), H_2O_2 (30%, 10 ml) 70°C, under illumination (300 W Xe lamp; $\lambda > 460$ nm; light intensity: 80 mW).

[b]Total selectivity to C_8 partial oxidation products.

Table S11. The electrochemical band gaps of compound **1** and **2**.

Catalyst	Cyclic voltammetry		Band-gap/eV
	E_{HOMO}/eV	E_{LUMO}/eV	
Compound **1**	-7.43	-4.43	3.00
Compound **2**	-7.35	-4.38	2.97

$E_{HOMO} = -[E_{ox} - E_{fe} + 4.80]$ eV; $E_{LUMO} = -[E_{re} - E_{fe} + 4.80]$ eV. 4.8 eV is the energy level of ferrocene below the vacuum level. E_{ox} and E_{re} are the onset potentials for oxidation (E_{ox}) and reduction (E_{re}) in the CV curves of compounds **1-2** and the onset of the oxidation potential of ferrocene (E_{fe}).[1]

References

1. D. Patra, C. C. Chiang, W. A. Chen, K. H. Wei, M. C. Wu and C. W. Chu. *J. Mater. Chem. A*, 2013, **1**, 7767-7774.

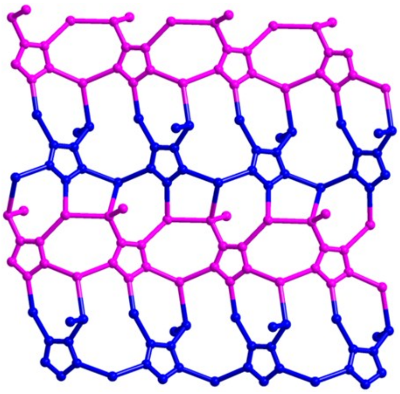


Figure S1. 2D layer in compound **1** constructed by adjacent two chains (blue: A-type chain, pink: B-type chain).

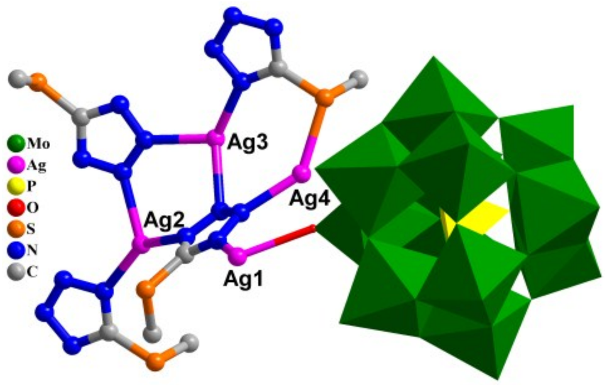


Figure S2. Ball and stick view of the asymmetric unit of compound **2** (hydrogen atoms are omitted for clarity).

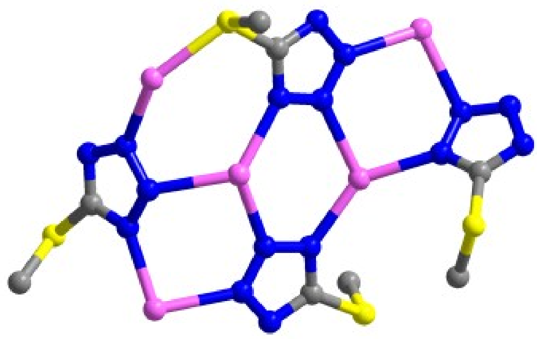


Figure S3. Ball and stick view of the $[Ag_5mttz_4]$ subunit in compound **2**.

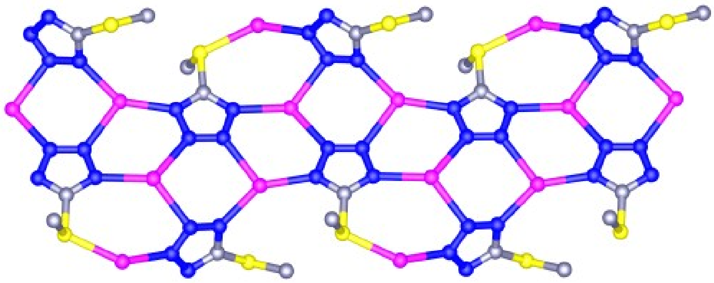


Figure S4. 1D Ag ribbon is formed by [Ag_5mttz_4] subunit in compound **2**.

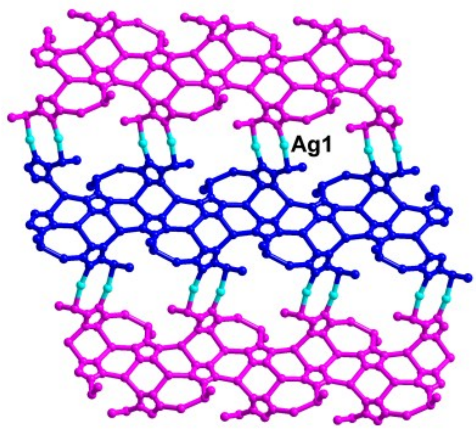


Figure S5. 2D layer in compound **2** constructed by adjacent 1D Ag ribbons with S1-Ag1-N1 subunits (pink and blue: 1D Ag ribbon)

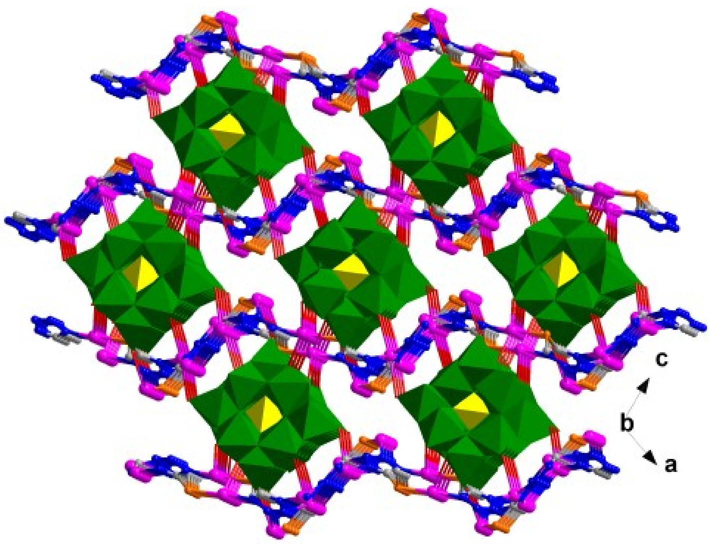


Figure S6. The schematic view of the 3D framework in compound **2**.

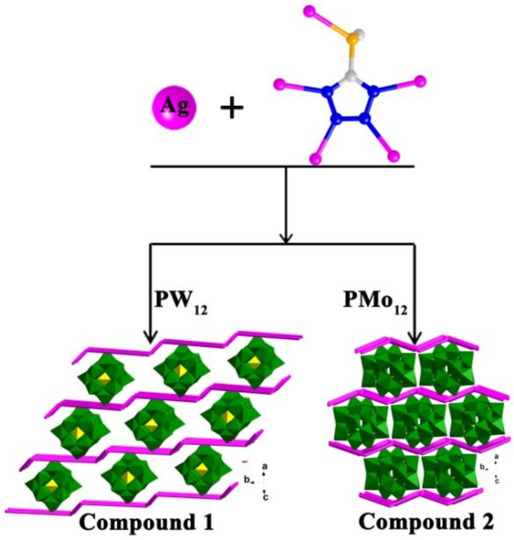
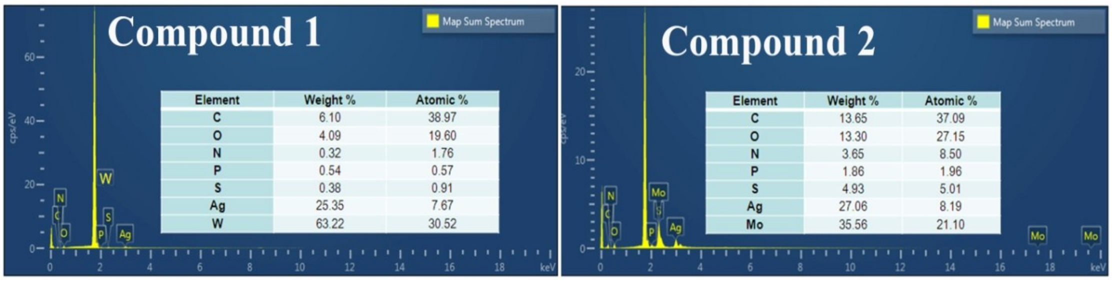


Figure S7. Schematic of synthetic route for compounds **1-2**.



Element	Weight %	Atomic %
C	6.10	38.97
O	4.09	19.60
N	0.32	1.76
P	0.54	0.57
S	0.38	0.91
Ag	25.35	7.67
W	63.22	30.52

Element	Weight %	Atomic %
C	13.65	37.09
O	13.30	27.15
N	3.65	8.50
P	1.86	1.96
S	4.93	5.01
Ag	27.06	8.19
Mo	35.56	21.10

Figure S8. EDS spectra of compounds **1** and **2**.

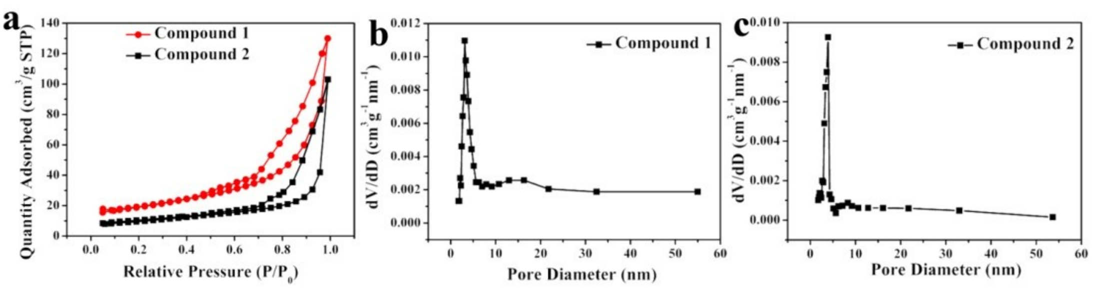


Figure S9. The N_2 adsorption-desorption isotherms and pore size distribution curves of compound **1** and **2.**

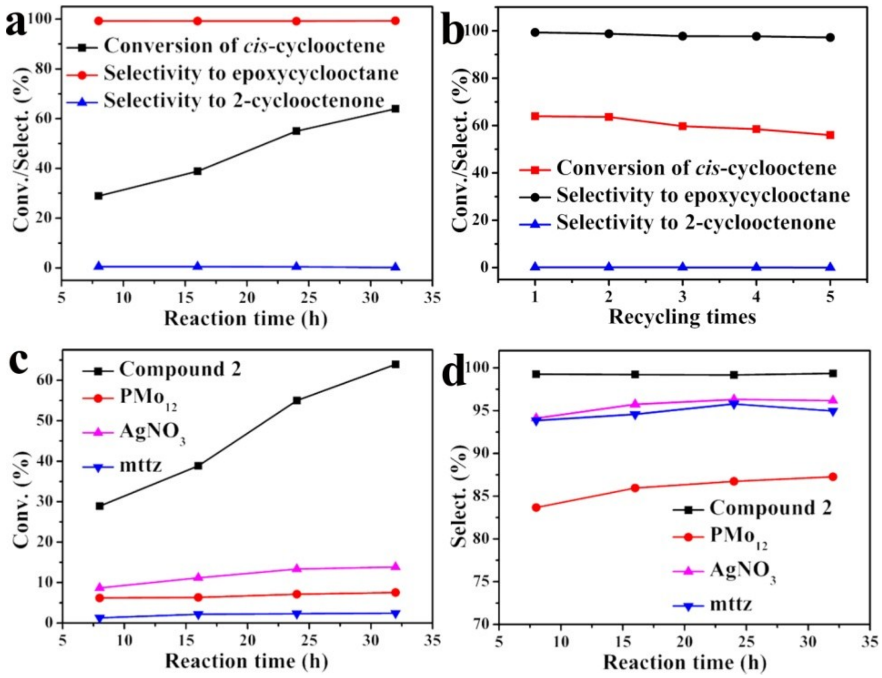


Figure S10. (a) The relationship between the conversion of *cis*-cyclooctene/selectivity to oxidative products (2-cyclooctenone and epoxycyclooctane) and reaction time with compound **2** as photocatalyst. (b) The relationship between the conversion/selectivity to oxidative products and recycling times with compound **2** as photocatalyst for five times. (c and d) The relationship between the conversion/selectivity and reaction time with compound **2**, PMo_{12}, mttz and metal ion (Ag^{+}) as photocatalysts.

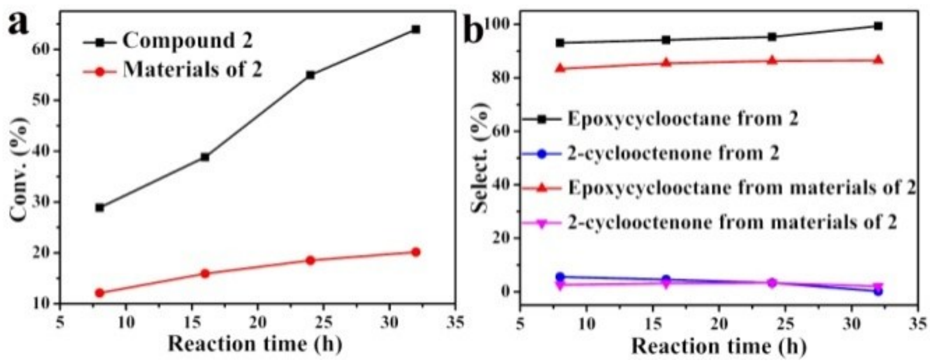


Figure S11. (a and b) The relationship between the conversion of *cis*-cyclooctene/selectivities to oxidation productions and reaction time with compound **2** and Materials of **2** as photocatalysts.

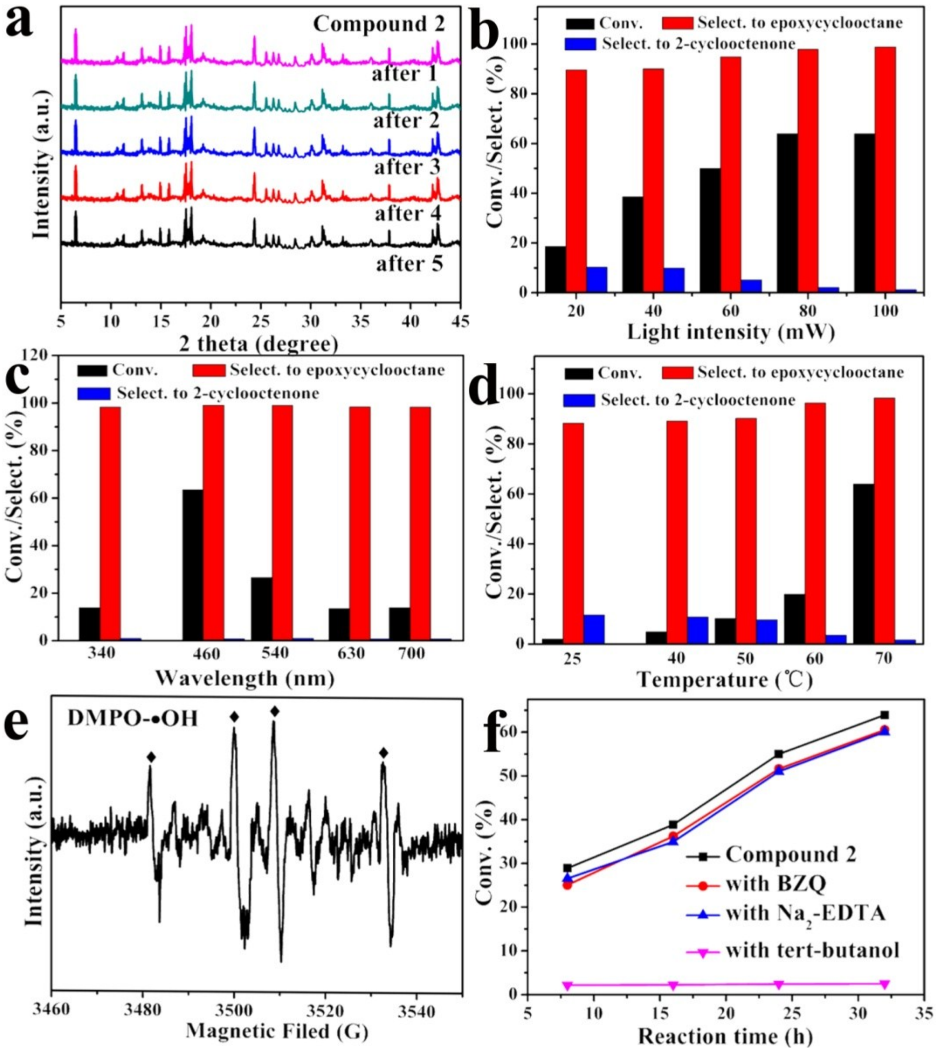


Figure S12. (a) XRD patterns of compound **2**: after 1, 2, 3, 4 and 5 times recycling. (b, c and d) The relationship between the conversion/selectivity and light intensity, wavelength, and reaction temperature with compound **2** as photocatalyst, respectively. (e) The ESR signals of the DMPO-•OH adducts in aqueous solution and compound **2** system. (f) The species trapping experiments for selective oxidation of *cis*-cyclooctene over compound **2** as photocatalyst under visible light irradiation.

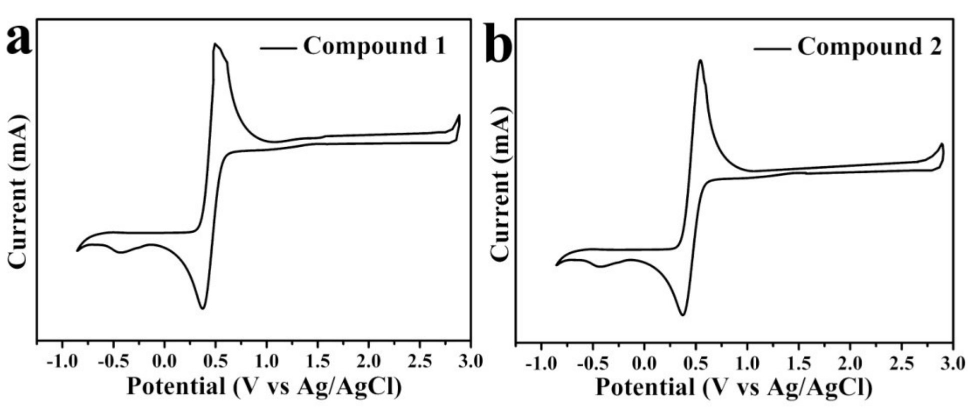


Figure S13. CV curves of compound **1** (a) and **2** (b).