

*Electronic Supplementary Information (ESI) for*

## **Polyoxometalate LUMO engineering: strategy for visible-light-responsive aerobic oxygenation photocatalysts**

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**Materials:** Acetonitrile (Kanto Chemical), acetone (Kanto Chemical), dimethyl sulfoxide (Kanto Chemical), *N,N*-dimethylacetamide (TCI), *N,N*-dimethylformamide (Kanto Chemical), methanol (Wako), ethanol (Kanto Chemical), trifluorotoluene (TCI), benzonitrile (Kanto Chemical), VO(acac)<sub>2</sub> (Aldrich), V<sub>2</sub>O<sub>5</sub> (Kanto Chemical), NaVO<sub>3</sub> (Nacalai Tesque), Na<sub>3</sub>VO<sub>4</sub> (Aldrich), VOSO<sub>4</sub>·3H<sub>2</sub>O (Wako), thioanisole (TCI), 4-(methylthio)toluene (TCI), 4-methoxythioanisole (TCI), 4-chlorophenyl methyl sulfide (TCI), 4-nitrothioanisole (TCI), ethyl phenyl sulfide (TCI), pentamethylene sulfide (TCI), and *n*-butyl sulfide (TCI) were used as received. H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> were obtained from Wako. TBA<sub>4</sub>[W<sub>10</sub>O<sub>32</sub>],<sup>S1</sup> TBA<sub>3</sub>H<sub>4</sub>[ $\gamma$ -PW<sub>10</sub>O<sub>36</sub>],<sup>S2</sup> TBA<sub>4</sub>[ $\alpha$ -PV<sub>1</sub>W<sub>11</sub>O<sub>40</sub>],<sup>S3</sup> TBA<sub>4</sub>H[ $\gamma$ -PV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>],<sup>S4</sup> TBA<sub>6</sub>[ $\alpha$ -PV<sub>3</sub>W<sub>9</sub>O<sub>40</sub>],<sup>S3</sup> TBA<sub>4</sub>H<sub>2</sub>[ $\gamma$ -SiV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>],<sup>S5</sup> TBA<sub>3</sub>H<sub>3</sub>[V<sub>10</sub>O<sub>28</sub>],<sup>S6</sup> and TBA<sub>6</sub>[Ce<sub>4</sub>L<sub>4</sub>( $\mu_4$ -O)( $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>)<sub>2</sub>]<sup>S7</sup> were synthesized according to the reported procedures.

**Instruments:** IR spectra were measured on JASCO FT/IR-4100 using KCl disks. UV/Vis spectra were measured on Jasco V-570 with a quartz cell of 1 cm path length. GC analyses were performed on Shimadzu GC-2014 with a FID detector equipped with a TC-1 capillary column. GC mass spectra were recorded on Shimadzu GCMS-QP2010 at an ionization voltage of 70 eV. Cyclic voltammetric measurements were carried out with a Solartron SI 1287 Electrochemical Interface. A standard three-electrode arrangement was employed with a BAS glassy carbon disk electrode as the working electrode, a platinum wire as the counter electrode, and a silver wire electrode as the pseudoreference electrode. The voltage scan rate was set at 100 mV s<sup>-1</sup>, and TBAClO<sub>4</sub> was used as an electrolyte. The potentials were measured using Ag/AgNO<sub>3</sub> reference electrode (10 mM AgNO<sub>3</sub>, 100 mM TBAClO<sub>4</sub> in acetonitrile, 0.55 V vs NHE).

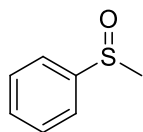
**Quantum calculations:** The calculations were performed with Gaussian 09 software.<sup>S8</sup> Anionic parts of **I** and TBA<sub>3</sub>H<sub>4</sub>[ $\gamma$ -PW<sub>10</sub>O<sub>36</sub>] were optimized at the B3LYP functional<sup>S9</sup> with 6-31++G\*\* (for C, H, and O), 6-31G\* (for Si), and LanL2DZ (for W)<sup>S10</sup> by using conductor-like polarizable continuum model (CPCM)<sup>S11</sup> with the parameters of the United Atom Topological Model (UAHF) for acetonitrile. TD-DFT calculations were performed with CAM-B3LYP exchange–correlation energy functional.<sup>S12</sup>

**Photocatalytic oxygenation of sulfides:** A typical procedure for photocatalytic oxygenation of sulfides is as follows: Into a Pylex schlenk flask (volume: ca. 20 mL), **I** (4  $\mu$ mol, 2 mol% with respect to **1a**), **1a** (0.2 mmol), biphenyl (0.1 mmol), acetonitrile (2 mL), and a Teflon-coated magnetic stir bar were successively

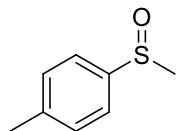
placed under O<sub>2</sub> (1 atm). The reaction was initiated by irradiation with visible light ( $\lambda > 400$  nm) with a Xe-lamp equipped with a 400 nm cut off filter at 30 °C. The detailed reaction conditions are shown in the footnotes of Tables. The products were confirmed by comparison of their GC retention times and GC-MS spectra with those of authentic chemical standards data. The yields of products were periodically determined by GC analysis using an internal standard technique.

**A possible reaction mechanism:** When the photocatalytic oxygenation of **1a** by POM I in the presence of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO; 1 equivalent with respect to **1a**) as a radical scavenger, the yield of **2a** (after 24 h) significantly decreased from 92% to 16%. Although a free radical-adduct to TEMPO was not directly detected by MS spectra, the significant suppression of the reaction indicated the involvement of radical species in the reaction. In addition, we also confirmed that peroxy species hardly existed in the reaction solution. Based on these results as well as the discussion in the previous reports (ref 18, (a) *J. Am. Chem. Soc.*, 1997, **119**, 243; (b) *J. Am. Chem. Soc.*, 2006, **128**, 17033; (c) *J. Am. Chem. Soc.*, 2010, **132**, 11678), we proposed the possible mechanism of this present photocatalytic oxygenation of sulfides as stated in the manuscript.

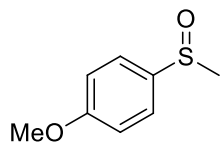
#### Compound data:



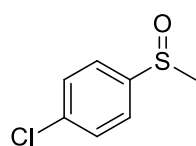
**Methyl phenyl sulfoxide (2a):** MS (EI) m/z (%): 140 (24) [M<sup>+</sup>], 126 (6), 125 (32), 124 (100), 123 (8), 109 (39), 108 (5), 97 (18), 91 (40), 79 (6), 78 (41), 77 (24), 69 (10), 65 (22), 63 (5), 51 (29), 50 (12). GC (TC-1 capillary column, 0.32 mm × 30 m, GL-science): carrier gas inlet pressure (N<sub>2</sub>, 115 kPa), initial column temperature (353 K), intermediate column temperature (423 K), progress rate (10 K min<sup>-1</sup>) final column temperature (523 K), progress rate (20 K min<sup>-1</sup>), injection temperature (523 K), detection temperature (523 K), retention time (5.2 min).



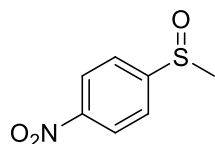
**Methyl p-tolyl sulfoxide (2b):** MS (EI) m/z (%): 155 (6), 154 (63) [M<sup>+</sup>], 141 (5), 140 (9), 139 (100), 138 (17), 123 (6), 122 (4), 121 (5), 111 (14), 108 (11), 107 (7), 95 (4), 92 (5), 91 (41), 90 (4), 89 (11), 79 (10), 78 (12), 77 (35), 67 (17), 65 (27), 63 (15), 62 (5), 51 (9), 50 (5). GC (TC-1 capillary column, 0.32 mm × 30 m, GL-science): carrier gas inlet pressure (N<sub>2</sub>, 115 kPa), initial column temperature (353 K, maintained for 3 min), intermediate column temperature (423 K), progress rate (10 K min<sup>-1</sup>) final column temperature (523 K), progress rate (20 K min<sup>-1</sup>), injection temperature (523 K), detection temperature (523 K), retention time (9.3 min).



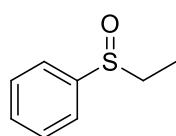
**1-Methylsulfinyl-4-methoxybenzene (2c):** MS (EI) m/z (%): 170 (25) [M<sup>+</sup>], 156 (10), 155 (100), 154 (26), 139 (33), 127 (7), 123 (12), 11 (8), 96 (7), 95 (9), 92 (9), 77 (15), 69 (6), 65 (10), 64 (12), 63 (17), 50 (7). GC (TC-1 capillary column, 0.32 mm × 30 m, GL-science): carrier gas inlet pressure (N<sub>2</sub>, 115 kPa), initial column temperature (353 K, maintained for 3 min), intermediate column temperature (423 K), progress rate (10 K min<sup>-1</sup>) final column temperature (523 K), progress rate (20 K min<sup>-1</sup>), injection temperature (523 K), detection temperature (523 K), retention time (11.1 min).



**1-Chloro-4-(methylsulfinyl)benzene (2d):** MS (EI) m/z (%): 176 (17), 175 (11), 174 (48) [M<sup>+</sup>], 161 (34), 160 (28), 159 (100), 158 (54), 145 (12), 143 (39), 131 (36), 128 (18), 127 (12), 125 (12), 112 (15), 111 (22), 108 (32), 76 (11), 75 (35), 74 (17), 69 (14), 63 (11), 50 (24), 45 (32). GC (TC-1 capillary column, 0.32 mm × 30 m, GL-science): carrier gas inlet pressure (N<sub>2</sub>, 115 kPa), initial column temperature (353 K, maintained for 3 min), intermediate column temperature (423 K), progress rate (10 K min<sup>-1</sup>) final column temperature (523 K), progress rate (20 K min<sup>-1</sup>), injection temperature (523 K), detection temperature (523 K), retention time (9.9 min).

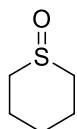


**1-Nitro-4-(methylsulfinyl)benzene (2e):** MS (EI) m/z (%): 187 (6), 186 (9), 185 (100) [M<sup>+</sup>], 170 (42), 169 (17), 140 (27), 139 (15), 124 (16), 123 (6), 112 (18), 111 (10), 110 (5), 108 (11), 96 (14), 95 (8), 92 (12), 84 (16), 82 (11), 79 (8), 77 (13), 75 (22), 74 (14), 70 (13), 69 (11), 65 (6), 64 (10), 63 (22), 58 (6), 51 (8), 50 (31). GC (TC-1 capillary column, 0.32 mm × 30 m, GL-science): carrier gas inlet pressure (N<sub>2</sub>, 115 kPa), initial column temperature (353 K, maintained for 3 min), intermediate column temperature (423 K), progress rate (10 K min<sup>-1</sup>) final column temperature (523 K), progress rate (20 K min<sup>-1</sup>), injection temperature (523 K), detection temperature (523 K), retention time (10.7 min).

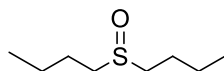


**Ethyl phenyl sulfoxide (2f):** MS (EI) m/z (%): 154 (19) [M<sup>+</sup>], 138 (15), 127 (5), 126 (58), 125 (15), 123

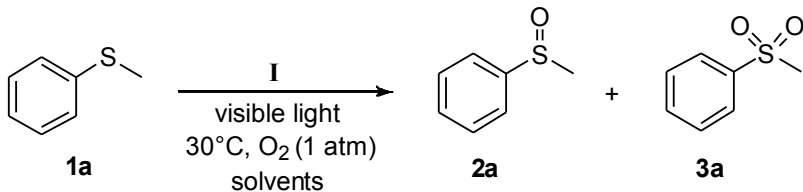
(10), 110 (12), 109 (7), 97 (13), 91 (8), 79 (10), 78 (100), 77 (25), 69 (5), 66 (6), 65 (9), 51 (23), 50 (8). GC (TC-1 capillary column, 0.32 mm × 30 m, GL-science): carrier gas inlet pressure (N<sub>2</sub>, 115 kPa), initial column temperature (353 K, maintained for 3 min), intermediate column temperature (423 K), progress rate (10 K min<sup>-1</sup>) final column temperature (523 K), progress rate (20 K min<sup>-1</sup>), injection temperature (523 K), detection temperature (523 K), retention time (8.8 min).



**Thiane 1-oxide (2g):** MS (EI) m/z (%): 120 (3), 119 (4), 118 (66) [M<sup>+</sup>], 102 (10), 101 (23), 90 (18), 87 (10), 85 (3), 77 (4), 76 (5), 73 (6), 70 (7), 69 (100), 68 (28), 67 (28), 65 (6), 64 (8), 63 (73), 62 (3), 61 (8), 60 (5), 59 (12), 58 (3), 57 (4), 56 (21), 54 (4), 53 (10), 51 (3), 50 (4). GC (TC-1 capillary column, 0.32 mm × 30 m, GL-science): carrier gas inlet pressure (N<sub>2</sub>, 115 kPa), initial column temperature (353 K, maintained for 3 min), intermediate column temperature (423 K), progress rate (10 K min<sup>-1</sup>) final column temperature (523 K), progress rate (20 K min<sup>-1</sup>), injection temperature (523 K), detection temperature (523 K), retention time (4.0 min).



**Dibutyl sulfoxide (2h):** MS (EI) m/z (%): 162 (1) [M<sup>+</sup>], 154 (8), 153 (3), 152 (3), 148 (3), 147 (5), 146 (44), 145 (8), 117 (5), 106 (7), 103 (13), 91 (15), 90 (28), 89 (33), 88 (4), 75 (6), 63 (9), 62 (5), 61 (93), 60 (5), 59 (3), 58 (3), 57 (44), 57 (4), 56 (100), 55 (32), 54 (3), 53 (4). GC (TC-1 capillary column, 0.32 mm × 30 m, GL-science): carrier gas inlet pressure (N<sub>2</sub>, 115 kPa), initial column temperature (353 K, maintained for 5 min), intermediate column temperature (423 K), progress rate (10 K min<sup>-1</sup>) final column temperature (523 K), progress rate (20 K min<sup>-1</sup>), injection temperature (523 K), detection temperature (523 K), retention time (10.6 min).

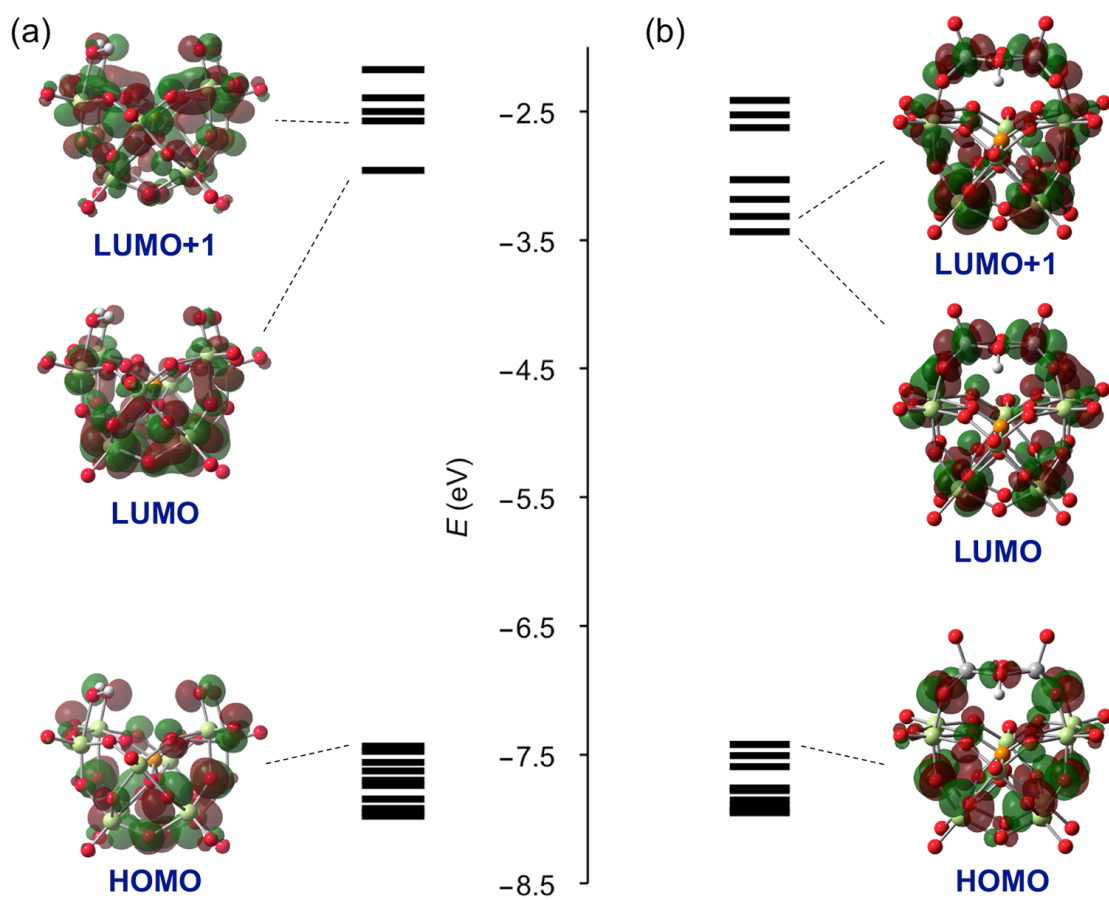
**Table S1.** Effect of solvents on the photocatalytic oxygenation of **1a**<sup>a</sup>

Entry	Solvent	Yield (%)	
		<b>2a</b>	<b>3a</b>
1	<b>Acetonitrile</b>	<b>92</b>	<b>6</b>
2	Acetone	48	7
3	<i>N,N</i> -Dimethylformamide	<1	<1
4	<i>N,N</i> -Dimethylacetamide	<1	<1
5	Dimethyl sulfoxide	<1	<1
6	Ethanol	<1	<1
7	Methanol	54	5
8	Trifluorotoluene	1	<1
9	Benzonitrile	17	<1

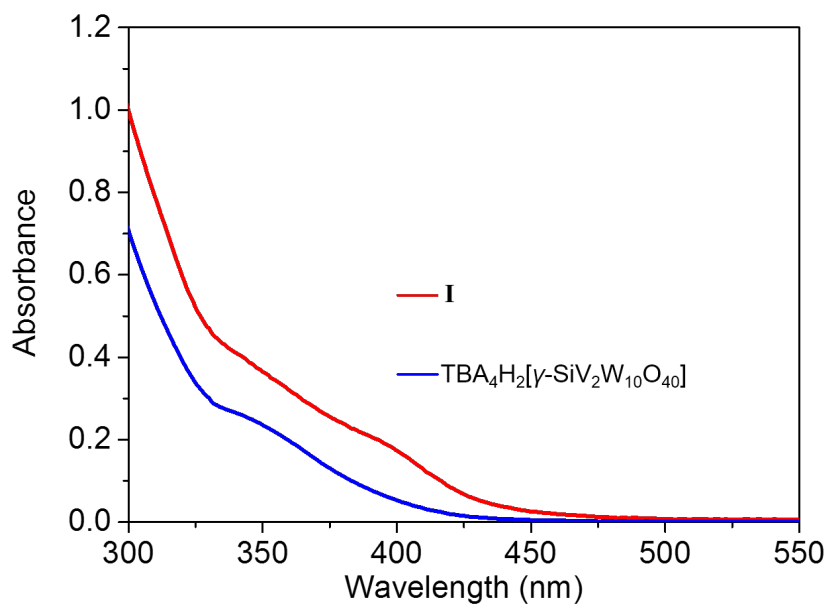
<sup>a</sup> Reaction conditions: **1a** (0.2 mmol), **I** (2 mol%), solvent (2 mL), 30°C, xenon lamp ( $\lambda > 400$  nm), O<sub>2</sub> (1 atm), 24 h. Yields were determined by GC using biphenyl as an internal standard.

**Table S2.** Transition energy ( $E$ ), oscillator strength ( $f$ ), and the major transitions for **I**

$E$ (eV)	$f$	Major transitions
3.45	0.0025	HOMO-4 $\rightarrow$ LUMO (22%); HOMO-4 $\rightarrow$ LUMO+1 (40%)
3.63	0.0240	HOMO-3 $\rightarrow$ LUMO+1 (21%); HOMO-7 $\rightarrow$ LUMO (34%)
3.73	0.0036	HOMO-4 $\rightarrow$ LUMO+3 (27%); HOMO-4 $\rightarrow$ LUMO+2 (29%)
3.86	0.0127	HOMO $\rightarrow$ LUMO+1 (16%); HOMO-7 $\rightarrow$ LUMO+3 (19%)
3.90	0.0275	HOMO-5 $\rightarrow$ LUMO+1 (23%); HOMO $\rightarrow$ LUMO+1 (33%)

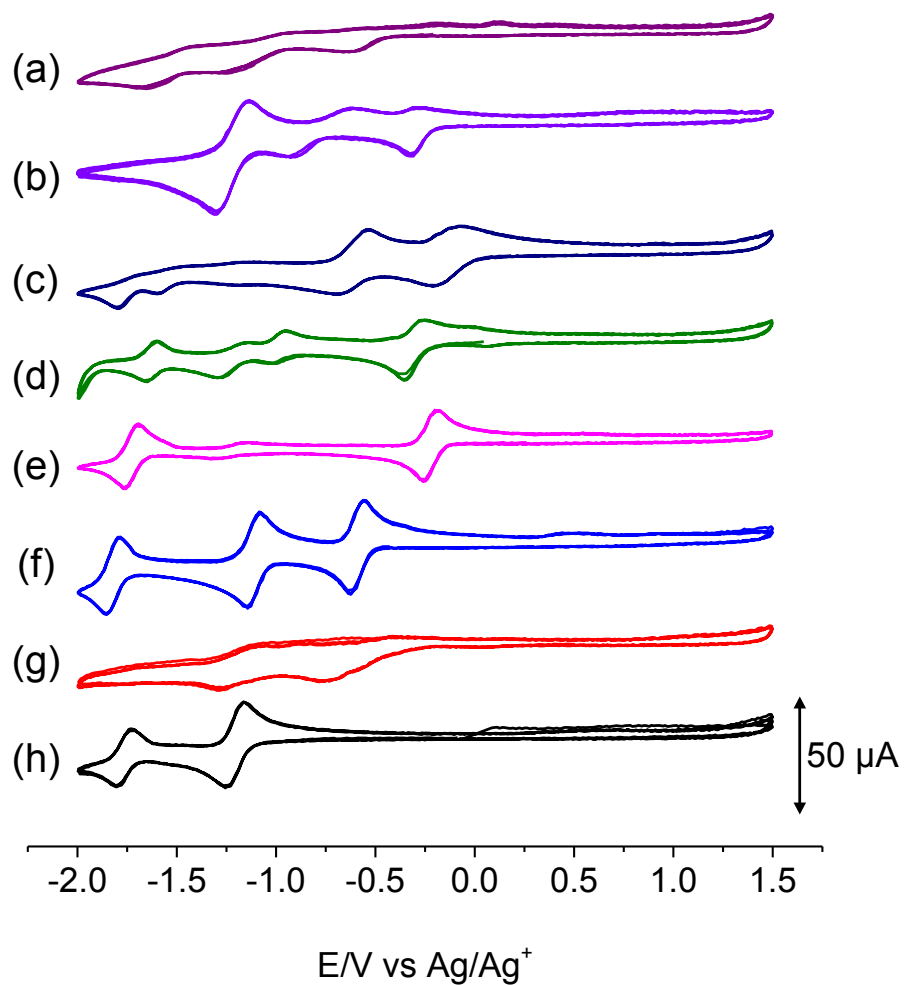


**Fig. S1** Energy diagrams and molecular orbitals of (a) TBA<sub>3</sub>H<sub>4</sub>[ $\gamma$ -PW<sub>10</sub>O<sub>36</sub>] and (b) **I**. The orbitals are represented by dark red and green lobes. The atoms are represented by spheres: W, light green; V, gray; P, orange; O, red; H, light gray.

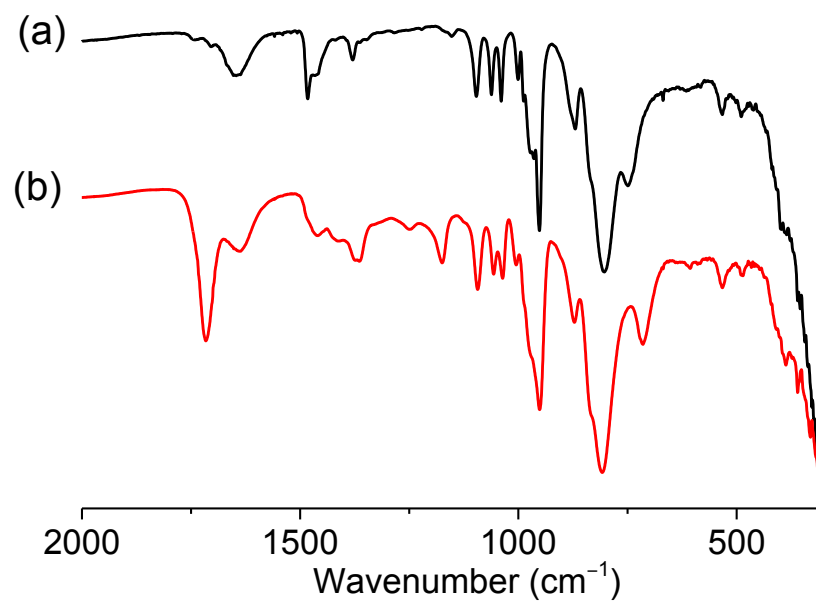


**Fig. S2** UV-Vis spectra of I and TBA<sub>4</sub>H<sub>2</sub>[γ-SiV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>] in acetonitrile (0.05 mM, 1 cm cell).





**Fig. S3** Cyclic voltammogram of (a)  $\text{TBA}_3\text{H}_3[\text{V}_{10}\text{O}_{28}]$ , (b)  $\text{TBA}_4\text{H}_2[\gamma\text{-SiV}_2\text{W}_{10}\text{O}_{40}]$ , (c)  $\text{TBA}_6[\alpha\text{-PV}_3\text{W}_9\text{O}_{40}]$ , (d) **I**, (e)  $\text{TBA}_4[\alpha\text{-PV}_1\text{W}_{11}\text{O}_{40}]$ , (f)  $\text{TBA}_3[\alpha\text{-PW}_{12}\text{O}_{40}]$ , (g)  $\text{TBA}_3\text{H}_4[\gamma\text{-PW}_{10}\text{O}_{36}]$ , and (h)  $\text{TBA}_4[\text{W}_{10}\text{O}_{32}]$  in acetonitrile (100 mM  $\text{TBAClO}_4$ ).



**Fig. S4** IR spectra of (a) **I** and (b) the retrieved **I** after the photocatalytic reaction.

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