

Electronic Supplementary Information (ESI) for

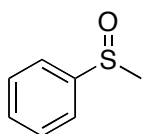
Photoredox catalysis for oxygenation/deoxygenation between sulfides and sulfoxides by visible-light-responsive polyoxometalates

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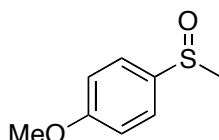
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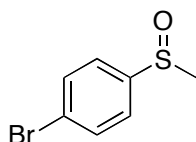
Compound data



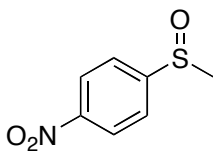
Methyl phenyl sulfoxide (2a): MS (EI) m/z (%): 140 (24), 126 (6), 125 (32), 124 (100), 123 (8), 109 (39), 108 (5), 97 (18), 91 (40), 79 (6), 78 (41), 77 (24), 69 (10), 65 (22), 63 (5), 51 (29), 50 (12). GC (Rtx-1 capillary column, 0.32 mm \times 30 m, Restek): carrier gas inlet pressure (N_2 , 175 kPa), initial column temperature (373 K), final column temperature (553 K), progress rate (10 K min^{-1}), injection temperature (553 K), detection temperature (553 K), retention time (7.6 min).



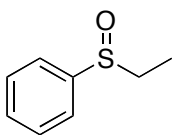
1-Methylsulfinyl-4-methoxybenzene (2b): MS (EI) m/z (%): 170 (25), 156 (10), 155 (100), 154 (26), 139 (33), 127 (7), 123 (12), 11 (8), 96 (7), 95 (9), 92 (9), 77 (15), 69 (6), 65 (10), 64 (12), 63 (17), 50 (7). GC (Rtx-1 capillary column, 0.32 mm \times 30 m, Restek): carrier gas inlet pressure (N_2 , 175 kPa), initial column temperature (373 K), final column temperature (553 K), progress rate (10 K min^{-1}), injection temperature (553 K), detection temperature (553 K), retention time (11.5 min).



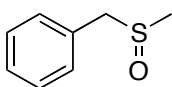
1-Bromo-4-(methylsulfinyl)benzene (2c): MS (EI) m/z (%): 221 (5), 220 (60), 219 (5), 218 (59), 206 (8), 205 (100), 204 (14), 203 (99), 202 (6), 177 (15), 175 (16), 174 (11), 173 (9), 172 (11), 171 (10), 157 (14), 155 (15), 145 (6), 143 (6), 139 (12), 124 (8), 111 (9), 108 (18), 96 (45), 77 (7), 76 (33), 75 (40), 74 (22), 69 (8), 63 (13), 51 (8), 50 (39). GC (Rtx-1 capillary column, 0.32 mm \times 30 m, Restek): carrier gas inlet pressure (N_2 , 175 kPa), initial column temperature (373 K), final column temperature (553 K), progress rate (10 K min^{-1}), injection temperature (553 K), detection temperature (553 K), retention time (11.4 min).



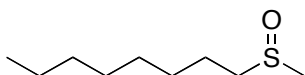
1-Methylsulfinyl-4-nitrobenzene (2d): MS (EI) m/z (%): 187 (6), 186 (9), 185 (100), 170 (42), 169 (17), 140 (27), 139 (15), 124 (16), 123 (6), 112 (18), 111 (10), 110 (5), 108 (11), 96 (14), 95 (8), 92 (12), 84 (16), 82 (11), 79 (8), 77 (13), 75 (22), 74 (14), 70 (13), 69 (11), 65 (6), 64 (10), 63 (22), 58 (6), 51 (8), 50 (31). GC (Rtx-1 capillary column, 0.32 mm \times 30 m, Restek): carrier gas inlet pressure (N_2 , 175 kPa), initial column temperature (373 K), final column temperature (553 K), progress rate (10 K min^{-1}), injection temperature (553 K), detection temperature (553 K), retention time (12.8 min).



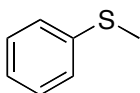
Ethyl phenyl sulfoxide (2e): MS (EI) m/z (%): 154 (19), 138 (15), 127 (5), 126 (58), 125 (15), 123 (10), 110 (12), 109 (7), 97 (13), 91 (8), 79 (10), 78 (100), 77 (25), 69 (5), 66 (6), 65 (9), 51 (23), 50 (8). GC (Rtx-1 capillary column, 0.32 mm \times 30 m, Restek): carrier gas inlet pressure (N_2 , 175 kPa), initial column temperature (373 K), final column temperature (553 K), progress rate (10 K min^{-1}), injection temperature (553 K), detection temperature (553 K), retention time (9.7 min).



Benzyl methyl sulfoxide (2f): MS (EI) m/z (%): 154 (2), 138 (10), 92 (8), 91 (100), 89 (4), 65 (15), 63 (5). GC (Rtx-1 capillary column, 0.32 mm \times 30 m, Restek): carrier gas inlet pressure (N_2 , 175 kPa), initial column temperature (373 K), final column temperature (553 K), progress rate (10 K min^{-1}), injection temperature (553 K), detection temperature (553 K), retention time (9.7 min).

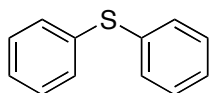


1-(Methylsulfinyl)-heptane (2g): MS (EI) m/z (%): 161 (6), 160 (17), 159 (90), 145 (7), 83 (7), 78 (10), 71 (56), 70 (10), 69 (31), 64 (43), 63 (15), 61 (23), 57 (100), 56 (17), 55 (45), 53 (6). GC (Rtx-1 capillary column, 0.32 mm \times 30 m, Restek): carrier gas inlet pressure (N_2 , 175 kPa), initial column temperature (373 K), final column temperature (553 K), progress rate (10 K min^{-1}), injection temperature (553 K), detection temperature (553 K), retention time (10.5 min).

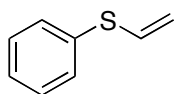


Thioanisole (1a): MS (EI) m/z (%): 125 (9), 124 (100), 123 (7), 109 (38), 91 (37), 79 (5), 78 (38), 77 (9), 69 (8), 65 (16), 51 (15), 50 (7). GC (Rtx-1 capillary column, 0.32 mm \times 30 m, Restek): carrier gas inlet pressure (N_2 , 175 kPa), initial column temperature (373 K), final column temperature (553 K),

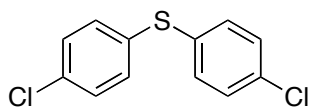
progress rate (10 K min⁻¹), injection temperature (553 K), detection temperature (553 K), retention time (4.6 min).



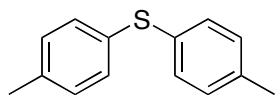
Diphenyl sulfide (1h): MS (EI) *m/z* (%): 188 (5), 187 (17), 186 (100), 185 (73), 184 (31), 171 (6), 152 (11), 109 (7), 92 (9), 77 (16), 69 (7), 65 (14), 51 (31), 50 (8). GC (Rtx-1 capillary column, 0.32 mm × 30 m, Restek): carrier gas inlet pressure (N₂, 175 kPa), initial column temperature (373 K), final column temperature (553 K), progress rate (10 K min⁻¹), injection temperature (553 K), detection temperature (553 K), retention time (11.5 min).



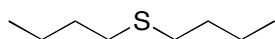
Phenyl vinyl sulfide (1i): MS (EI) *m/z* (%): 137 (12), 136 (84), 135 (100), 134 (8), 109 (10), 92 (5), 91 (53), 77 (13), 69 (8), 66 (9), 65 (16), 59 (6), 58 (8), 51 (21), 50 (9). GC (Rtx-1 capillary column, 0.32 mm × 30 m, Restek): carrier gas inlet pressure (N₂, 175 kPa), initial column temperature (373 K), final column temperature (553 K), progress rate (10 K min⁻¹), injection temperature (553 K), detection temperature (553 K), retention time (5.1 min).



Bis(4-chlorophenyl) sulfide (1j): MS (EI) *m/z* (%): 258 (13), 257 (10), 256 (68), 254 (100), 222 (6), 221 (9), 220 (10), 219 (24), 218 (18), 186 (10), 185 (14), 184 (93), 183 (13), 152 (5), 143 (6), 139 (10), 111(5), 110 (8), 109 (20), 108 (26), 99 (6), 91 (13), 75 (22), 74 (6), 69 (7), 63 (8), 50 (8). GC (Rtx-1 capillary column, 0.32 mm × 30 m, Restek): carrier gas inlet pressure (N₂, 175 kPa), initial column temperature (373 K), final column temperature (553 K), progress rate (10 K min⁻¹), injection temperature (553 K), detection temperature (553 K), retention time (15.9 min).



Bis(4-methylphenyl) sulfide (1k): MS (EI) *m/z* (%): 216 (6), 215 (18), 214 (100), 213 (14), 200 (5), 199 (30), 198 (13), 197 (7), 184 (17), 181 (11), 165 (8), 105 (10), 91 (19), 65 (10). GC (Rtx-1 capillary column, 0.32 mm × 30 m, Restek): carrier gas inlet pressure (N₂, 175 kPa), initial column temperature (373 K), final column temperature (553 K), progress rate (10 K min⁻¹), injection temperature (553 K), detection temperature (553 K), retention time (14.1 min).



Dibutyl sulfide (1l): MS (EI) *m/z* (%): 146 (36), 117 (6), 103 (14), 91 (16), 90 (25), 89 (12), 75 (6), 61 (91), 60 (6), 57 (29), 56 (100), 55 (26), 47 (14), 46 (7), 45 (10). GC (Rtx-1 capillary column, 0.32 mm × 30 m, Restek): carrier gas inlet pressure (N₂, 175 kPa), initial column temperature (373 K), final column

temperature (553 K), progress rate (10 K min⁻¹), injection temperature (553 K), detection temperature (553 K), retention time (4.7 min).

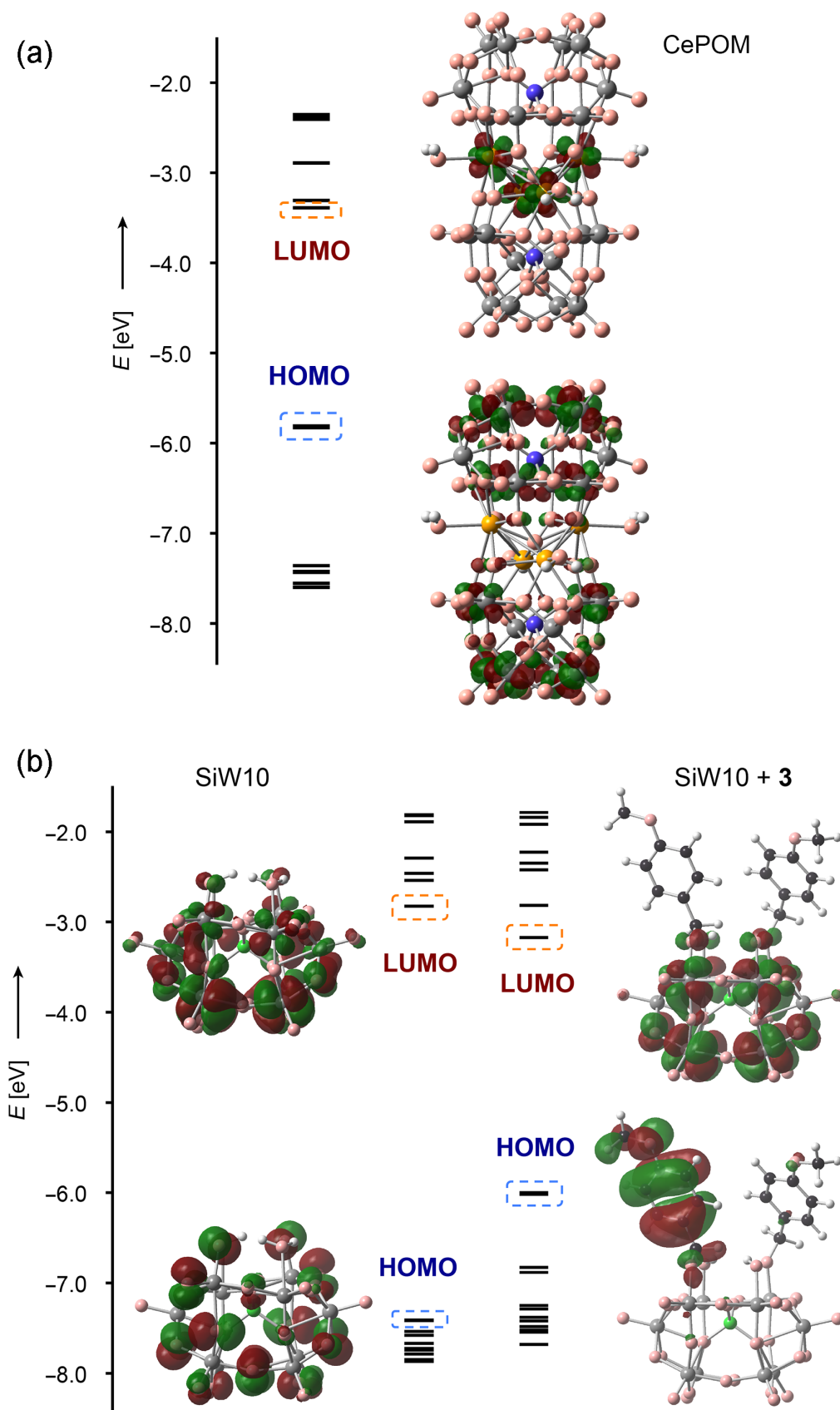


Fig. S1 Energy diagram and molecular orbitals of a) CePOM and b) SiW10 (left) and the complex of SiW10 and **3** (right). The orbitals are represented by dark red and green lobes. The atoms are represented by spheres: Ce, yellow; W, gray; Si, blue; O, pink; C, black; H, light gray.

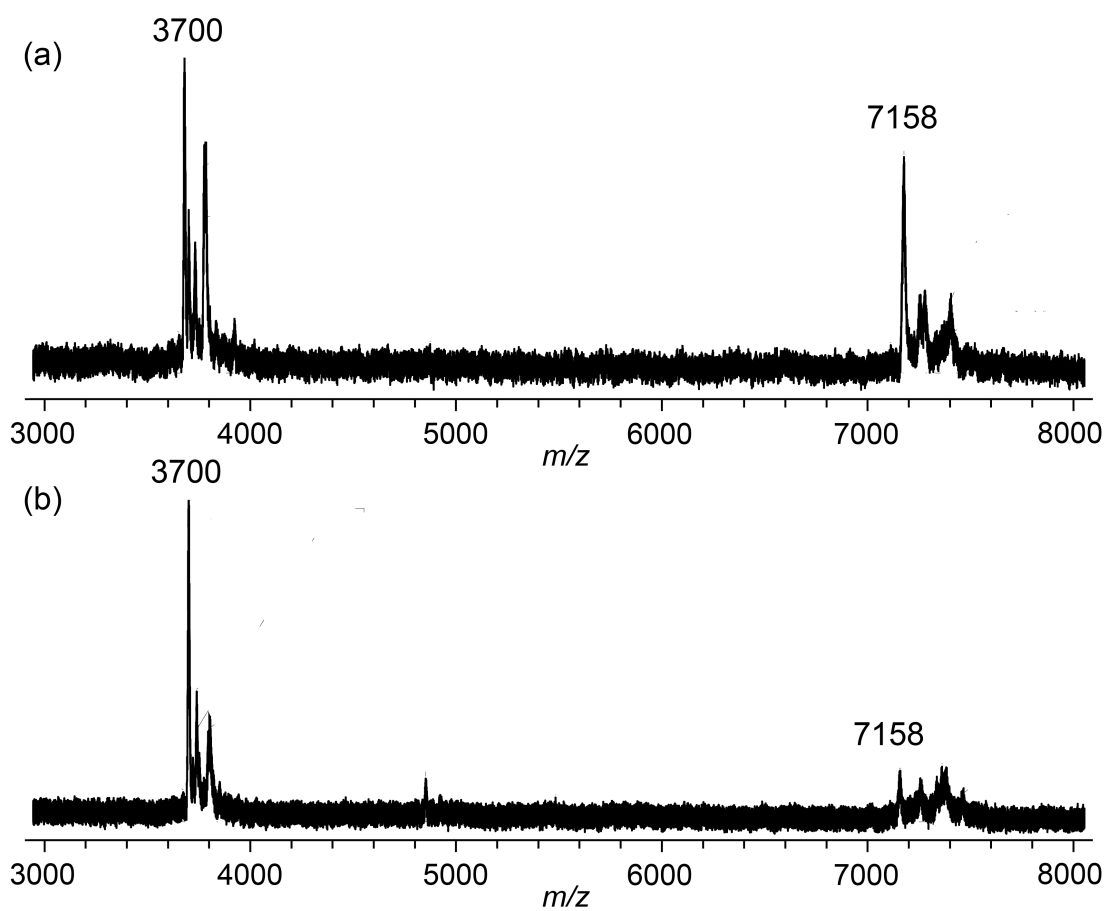


Fig. S2 CSI-mass spectra of (a) the mixture of SiW10 and Ce(acac)₃ (1:2 molar ratio) in the mixed solvent of acetonitrile and methanol (2/1 v/v) and (b) the retrieved catalyst after the photocatalytic oxygenation of thioanisole (**1a**) in acetonitrile. The signal sets at m/z 3700 and 7158 were assignable to $[\text{TBA}_8\text{Ce}_4\text{O}(\text{SiW}_{10}\text{O}_{36})_2]^{2+}$ and $[\text{TBA}_7\text{Ce}_4\text{O}(\text{SiW}_{10}\text{O}_{36})_2]^+$, respectively. Several unknown signals were also observed.

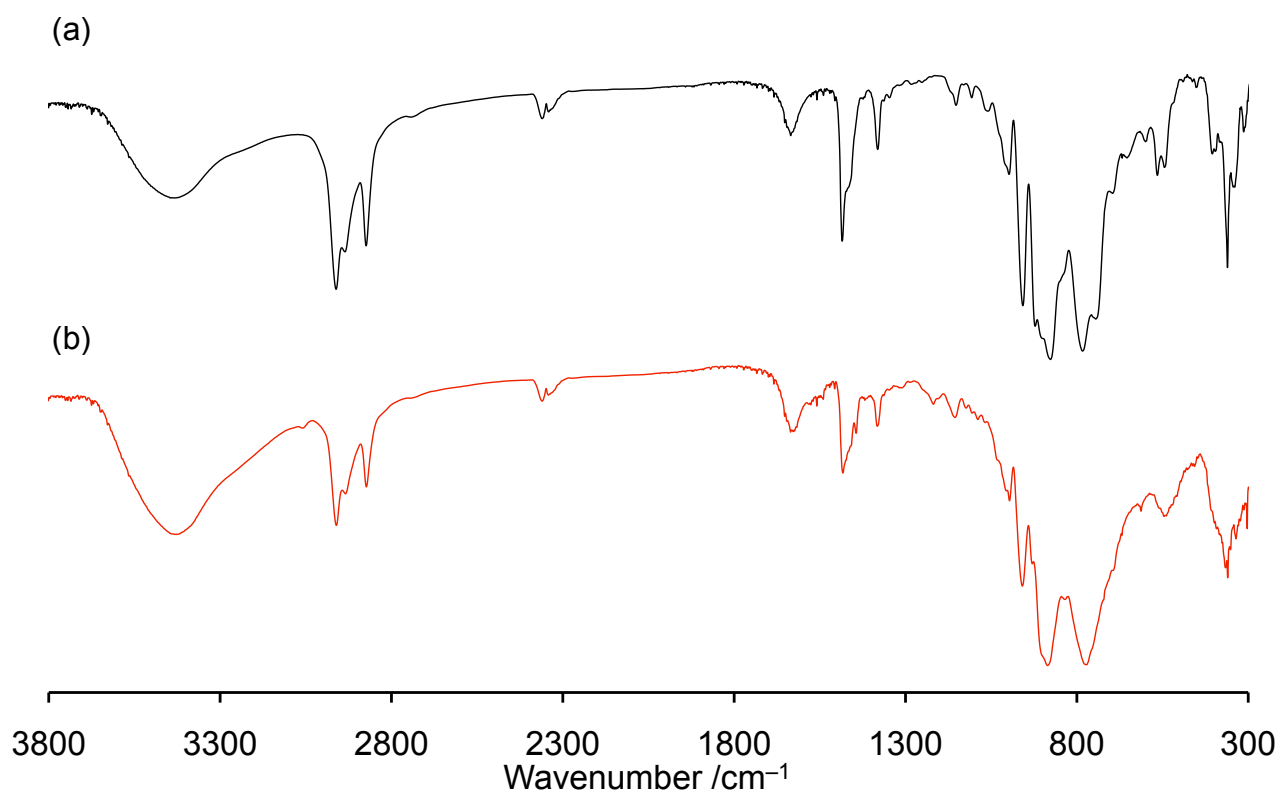


Fig. S3 IR spectra of (a) SiW10 and (b) the retrieved catalyst after the photocatalytic oxygenation of thioanisole (**1a**).

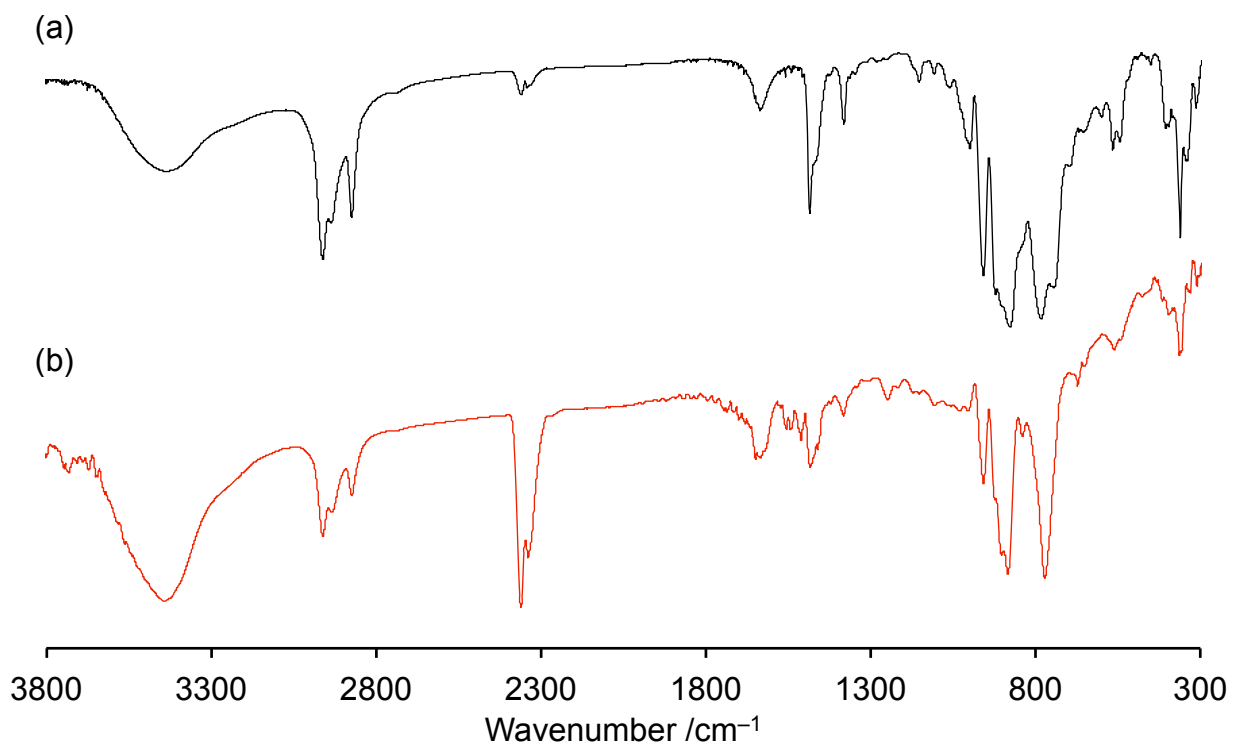


Fig. S4 IR spectra of (a) SiW10 and (b) the retrieved SiW10 after the photocatalytic deoxygenation of methyl phenyl sulfoxide (**2a**).

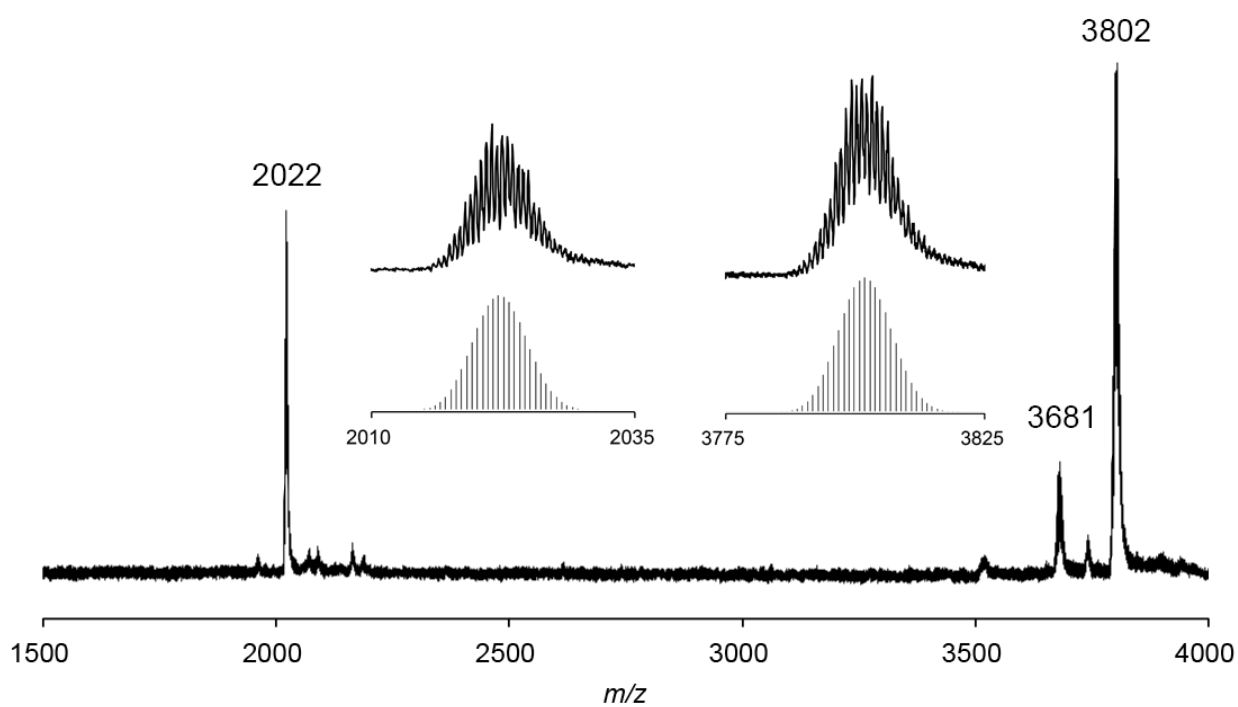


Fig. S5 CSI-mass spectrum of the retrieved SiW10 after the photocatalytic deoxygenation of methyl phenyl sulfoxide (**2a**) in acetonitrile. The sets of signals at m/z 2022, 3681, and 3802 were assignable to $[\text{TBA}_6\text{HSiW}_{10}\text{O}_{34}(\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{O})(\text{CH}_3\text{CN})]^{2+}$, $[\text{TBA}_5\text{SiW}_{10}\text{O}_{34}(\text{CH}_3\text{CN})(\text{H}_2\text{O})]^+$, and $[\text{TBA}_5\text{HSiW}_{10}\text{O}_{34}(\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{O})(\text{CH}_3\text{CN})]^+$, respectively ($\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{OH}$ = 4-methoxybenzyl alcohol (**3**)).