Electronic Supplementary Information (ESI)

Zn(II) porphyrin based nano-/microscale metal-organic frameworks: morphology dependent sensitization and photocatalytic oxathiolane deprotection

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Experimental details

Materials and methods

All reagents and chemicals were purchased from commercial sources and used as received unless stated otherwise. All solvents used in synthesis and catalysis were purified by standard procedures. The ligand of tetrakis(4-carboxyphenyl)porphyrin (H_2TCPP) was prepared by the literature method.[1]

Scanning electron microscope (SEM) images were taken with a JEOL JSM-7500F scanning electron microscope. The powder X-ray diffraction (PXRD) spectra were recorded on a Rigaku D/Max-2500 diffractometer with Cu Kα radiation (λ = 0.15406 nm) at 40 kV and 100 mA. Elemental analysis (C, H, and N) was carried out using a Perkin-Elmer 240C analyzer. Thermogravimetric analysis (TGA) was performed on a Rigaku standard thermogravimetry-differential thermal analysis instrument from ambient temperature to 700 °C with a heating rate of 10 °C min^{-1} in air, and an empty Al_2O_3 crucible was used as the reference. The ^1H NMR spectra was measured in $CDCl_3$ or DMSO with a Bruker 300 MHz NMR spectrometer. UV–vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Electron spin resonance (ESR) spectra were obtained using a Brucker model EPR 300E spectrometer. GC analysis was performed on a Shimadzu GC-2014 gas chromatograph equipped with a 30 m × 0.53 mm SE-30 capillary column and a FID.

Synthesis of MOF materials

H_2TCPP (180 mg, 0.23 mmol), $ZnNO_3{\cdot}6H_2O$ (200 mg, 0.68 mmol), and 4,4'-bipyridine (86 mg, 0.75 mmol) were dissolved in a mixed solvent of DMF (2 mL) and ethanol (1 mL). After addition of 10 μL ethanol solution of HNO_3 (1 M), the mixture was sealed in a screw-cap vial and heated at 80 °C for 6 h. P-1 was precipitated as rose powder and separated by filtration. The sample of P-1 was washed with DMF and ethanol, and then dried at 60 °C for 12 h. Yield: 53%−59%, based on H_2TCPP. Anal. Calcd. (%) for $Zn_3(TCPP)(bpy)_{1.5}(DMF)_3(H_2O)_4$ (Mw = 1504.54): C, 57.45; H, 4.32; N, 9.30. Found: C, 57.59; H, 4.57; N, 9.24.

P-2 and P-3 were prepared with the same procedure as that of P-1 except that the addition amounts of reactants were decreased. P-2 was synthesized with 60 mg of H_2TCPP, 67 mg of $ZnNO_3{\cdot}6H_2O$ and 29 mg of 4,4'-bipyridine. Yield: 71%−75%. Anal. Calcd. (%) for $Zn_3(TCPP)(bpy)_{1.5}(DMF)_3(H_2O)_4$ (Mw = 1504.54): C, 57.45; H, 4.32; N, 9.30. Found: C, 57.48; H, 4.42; N, 9.28.

P-3 was synthesized with 90 mg of H_2TCPP, 100 mg of $ZnNO_3{\cdot}6H_2O$ and 43 mg of 4,4'-bipyridine. Yield: 65%−70%. Anal. Calcd. (%) for $Zn_3(TCPP)(bpy)_{1.5}(DMF)_3(H_2O)_4$ (Mw = 1504.54): C, 57.45; H, 4.32; N, 9.30. Found: C, 57.36; H, 4.41; N, 9.24.

Synthesis of oxathiolanes

Boron trifluoride diethyl etherate (30 mmol, 3.5 mL) was added to the THF solution (20 mL) containing ketone substrate (40 mmol, ~6 g) and *β*-mercaptoethanol (40 mmol, 2.8 mL). The mixture was stirred at room temperature for 2 h to ensure the completion of the reaction. The reacted solution was diluted by ethyl acetate (50 mL), washed with saturated $KHCO_3$ solution, water and brine in sequence, and dried over $MgSO_4$. The solvent was removed by rotary evaporation. The obtained crude product was purified by column chromatography with hexanes/ethyl acetate or CH_2Cl_2/ethyl acetate as eluent.

2-phenyl-2-methyl-1, 3-oxathiolane (1a). ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 7.45 (2H, d), 7.30 (2H, t), 7.28 (1H, d), 4.34 (1H, m), 4.02 (1H, m), 3.20 (1H, m), 3.09 (1H, m), 1.91 (3H, s).

2-(4-bromophenyl)-2-methyl-1, 3-oxathiolane (1b). ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 7.43 (2H, d), 7.40 (2H, d), 4.33 (1H, m), 3.98 (1H, m), 3.20 (1H, m), 3.08 (1H, m), 1.87 (3H, s).

2-(4-methylphenyl)-2-methyl-1, 3-oxathiolane (1c). ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 7.35 (2H, d), 7.10 (2H, d), 4.32 (1H, m), 4.02 (1H, m), 3.20 (1H, m), 3.08 (1H, m), 2.32 (3H, s), 1.91 (3H, s).

2-(4-methoxylphenyl)-2-methyl-1, 3-oxathiolane (1d). ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 7.40 (2H, d), 6.84 (2H, d), 4.31 (1H, m), 4.02 (1H, m), 3.20 (1H, m), 3.09 (1H, m), 1.8 (3H, s).

2-(4-acetoxylphenyl)-2-methyl-1, 3-oxathiolane (1e). ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 7.47 (2H, d), 7.02 (2H, d), 4.33 (1H, m), 4.00 (1H, m), 3.21 (1H, m), 3.06 (1H, m), 2.28 (3H, s), 1.89 (3H, s).

2-(4-acetylaminophenyl)-2-methyl-1, 3-oxathiolane (1f). ^{1}H NMR (DMSO, 300 MHz): *δ* 9.98 (1H, s), 7.61 (2H, d), 7.33 (2H, d), 4.26 (1H, m), 4.00 (1H, m), 3.19 (1H, m), 3.06 (1H, m), 2.02 (3H, s), 1.80 (3H, s).

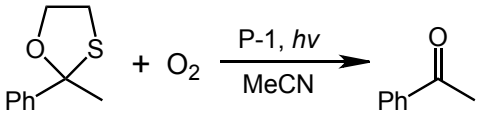
1-oxa-4-thiaspiro[4,5]decane (1g). ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 4.17 (2H, t), 3.02(2H, t), 1.80(6H, m), 1.40 (4H, m).

2-(*n*-amyl)-2-methyl-1, 3-oxathiolane (1h). ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 4.14 (2H, m), 3.06 (2H, m), 1.81 (2H, m), 1.57 (3H, s), 1.30 (8H, m), 0.88 (3H, m).

Photocatalytic deprotection of oxathiolanations

In a typical photocatalytic experiment, P-1 (2 mg), oxathiolane substrate (0.1 mmol) and 10 μL bromobenzene (used as internal standard) was dispersed in acetonitrile (2 mL) and placed in a 10 mL Pyrex glass bottle. This container was sealed with a rubber stopper wrapped in aluminum foil using a hand crimper, and filled with pure O_2 (1 atm). The reaction proceeded with continuous stirring under the irradiation of a 300 W Xe lamp, and a light filter was used to cut off light with wavelength below 420 nm. After the reaction, the suspension was centrifuged and the supernatant was analyzed with GC.

Table S1 Results of the cyclic experiment for the photocatalytic deprotection of **1a**[a]



Cycle	Time (min)	Conv. (%)	Sel. (%)
1	90	100	95
2	90	99	94
3	90	96	99
4	90	99	95
5	90	100	95
6	90	99	96

[a] 2 mg P-1, 50 mM **1a**, 2 mL acetonitrile, 1 atm of O_2, 300 W Xe lamp cut off below 420 nm. At the end of each cycle, the used photocatalyst was separated and reused to the next run.

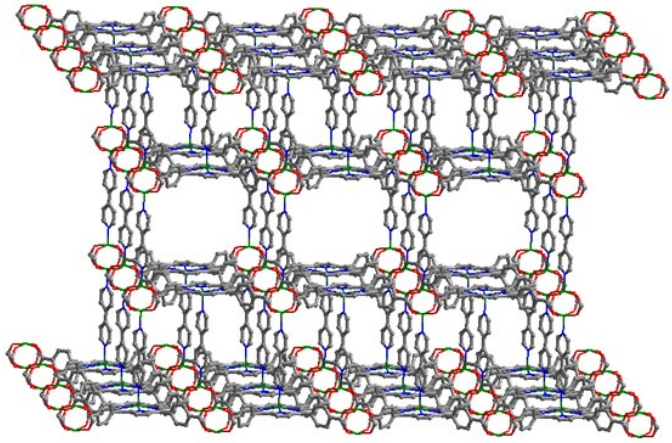


Fig. S1 Framework structure of $Zn_3(TCPP)(bpy)_{1.5}$.

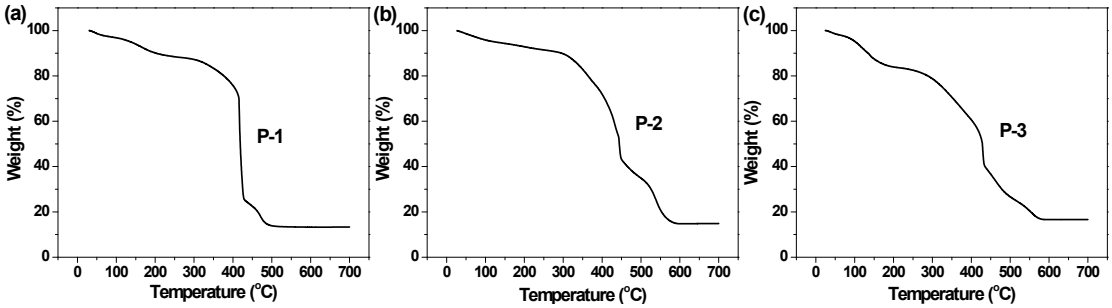


Fig. S2 TGA curves of (a) P-1, (b) P-2 and (c) P-3.

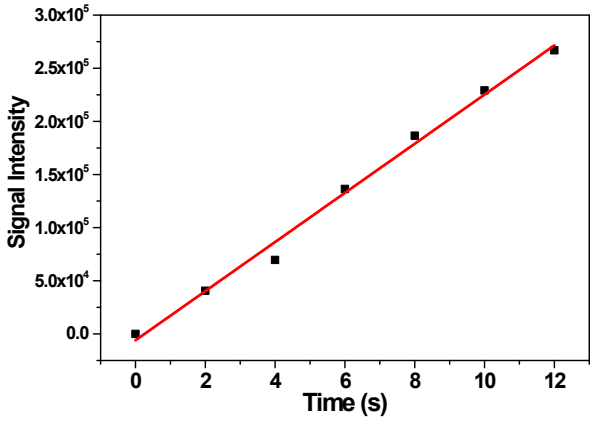


Fig. S3 Intensity change of the resonance signal of TMPO with irradiation time. 1 g L^{-1} P-1, 40 mM TMP, dispersed in acetonitrile, 355 nm laser.

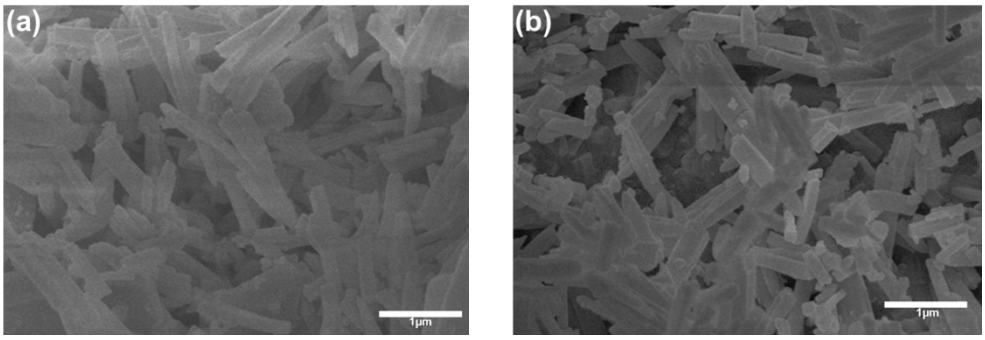


Fig. S4 Comparison between the SEM images of (a) as-prepared and (b) used sample of P-1.

Fig. S5 ^{1}H NMR spectrum of 2-phenyl-2-methyl-1,3-oxathiolane.

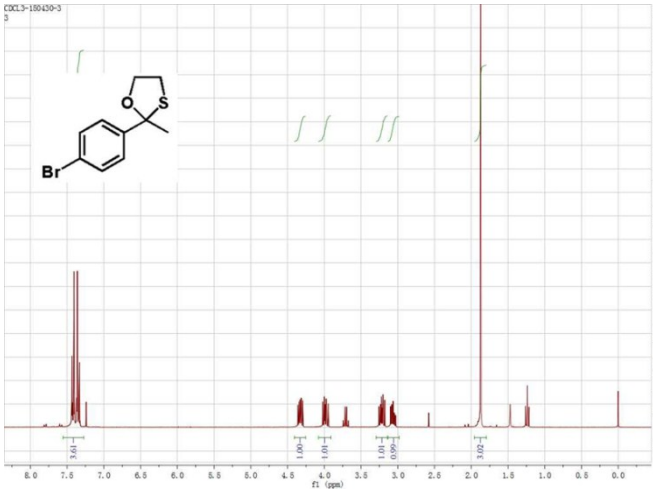


Fig. S6 ^{1}H NMR spectrum of 2-(4-bromophenyl)-2-methyl-1,3-oxathiolane.

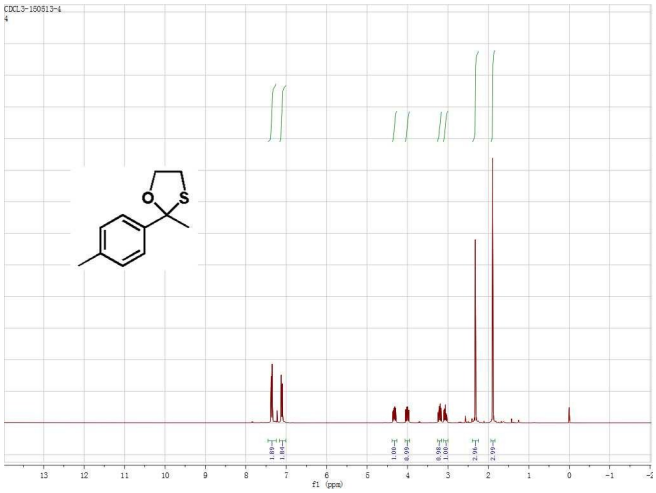


Fig. S7 ^{1}H NMR spectrum of 2-(4-methylphenyl)-2-methyl-1,3-oxathiolane.

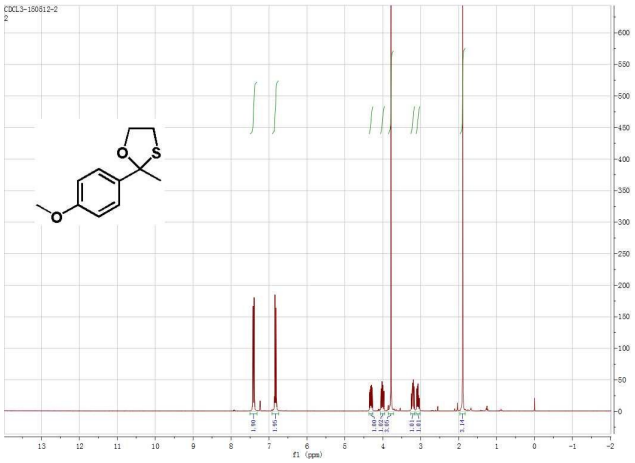


Fig. S8 ^{1}H NMR spectrum of 2-(4-methoxyphenyl)-2-methyl-1,3-oxathiolane.

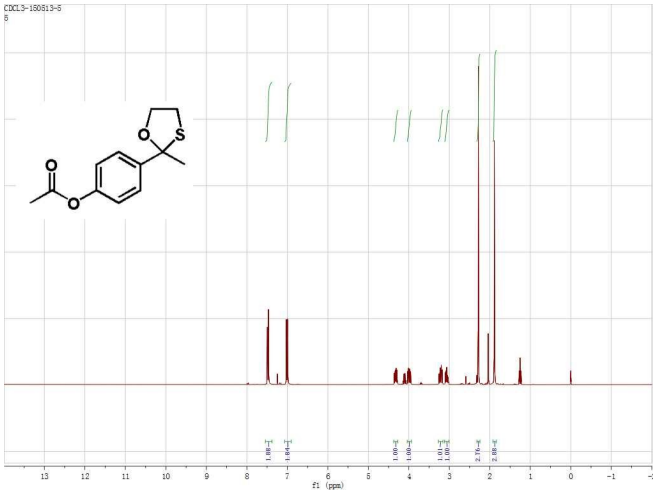


Fig. S9 ^{1}H NMR spectrum of 2-(4-acetoxylphenyl)-2-methyl-1,3-oxathiolane.

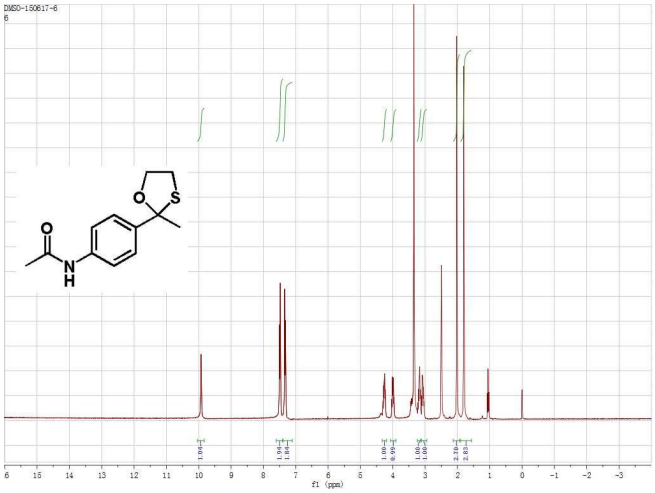


Fig. S10 ^{1}H NMR spectrum of 2-(4-acetylaminophenyl)-2-methyl-1,3-oxathiolane.

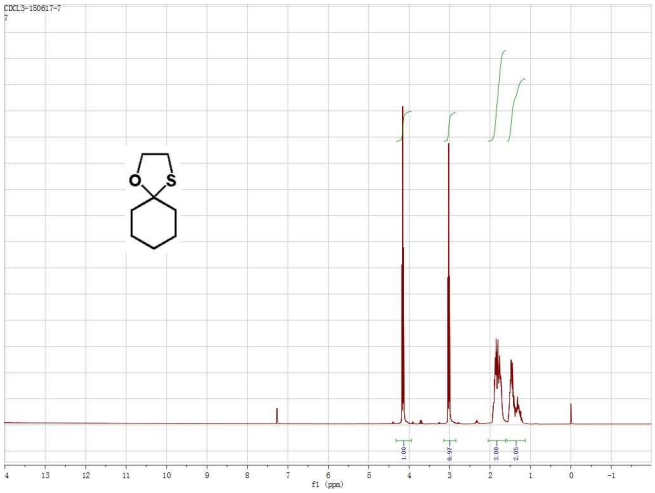


Fig. S11 ^{1}H NMR spectrum of 1-oxa-4-thiaspiro[4,5]decane.

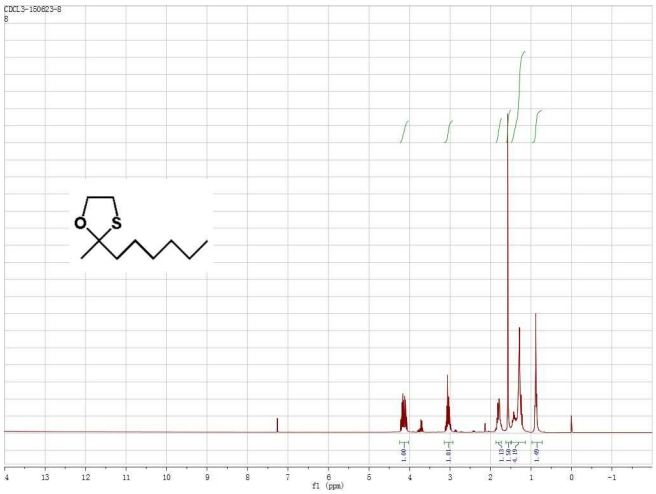


Fig. S12 ^{1}H NMR spectrum of 2-(*n*-amyl)-2-methyl-1,3-oxathiolane.

References

1 D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei and H.-C. Zhou, *Angew. Chem. Int. Ed.*, 2012, **51**, 10307-10310.