Electronic Supplementary Information for

Hollow and Sulfonated Microporous Organic Polymers: Versatile Platforms for Non-Covalent Fixation of Molecular Photocatalysts

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Experimental Sections

Transmission electron microscopy was conducted using a JEOL 2100F. N_2 sorption isotherms (77 K) were measured using a BELSORP II-mini equipment. For pore size analysis, the DFT method was applied. PXRD patterns were obtained using a Rigaku MAX-2200 operating with filtered Cu-Ka radiation. Infrared absorption spectra were recorded using a Bruker VERTEX 70 FT-IR spectrometer. The absorption spectra were obtained from diffuse reflectance spectroscopy which was conducted with a SHIMADZU UN-3600. The UV/vis spectroscopy for the detection of benzoquinone was conducted with a JASCO V-630 spectrofluorometer. The solid phase ^{13}C-NMR spectrum was obtained on a Bruker 400 MHz Solid State DSX NMR spectrometer at the Korea Basic Science Institute (Daegu, South Korea). Elemental analysis was performed using a CE EA1110 elemental analyzer. HPLC was conducted using a Yong Lin HPLC YL9100 equipped with a UV/Vis detector and a Sun Fire C18 column 5 μm (4.6 × 150 mm^2)

Synthetic procedure for HMOP

Silica spheres with 83 ± 4 nm diameters were prepared by the Stöber method. In a 250 mL round-bottomed flask, a mixture of ethanol (200 mL), ammonia solution (28~30%, 3 mL), and water (2.7 mL) was stirred for 30 min. After adding tetrethylorthosilicate (TEOS, 4.4 mL), the mixture was stirred for 18 h at room temperature. The solution was added to a mixture of methylene chloride and hexane (volume ratio: 1:1). The white solid was isolated by centrifugation, washed with ethanol, and dried under vacuum for 24 h.

For the preparation of **HMOP**, silica spheres (600 mg) were dispersed in triethylamine (60 mL). Next, $Pd(PPh_3)_2Cl_2$ (17 mg, 0.024 mmol) and CuI (4.4 mg, 0.024 mmol) were added. The solution was stirred for 1 h at room temperature. Tetrakis(4-ethynylphenyl)methane (0.10 g, 0.24 mmol) and 1,4-diiodobenzene (0.16 g, 0.48 mmol) were then added and the reaction mixture was heated at 90 ℃ for 24 h. The resultant yellow solids (SiO_2@**HMOP**) were retrieved by centrifugation, washed with acetone, methanol, methylene chloride, and diethylether, and dried under vacuum overnight. The SiO_2@**HMOP** (~0.70 g) was added to a HF solution (48%, 15 mL) and the reaction mixture was stirred for 1.5 h. The resultant materials (**HMOP**) were retrieved by centrifugation, washed with water, ethanol, acetone and Hexane, and dried under vacuum for 24 h.

Synthetic procedure for S-HMOP

To an ice-bath-cooled dichloromethane (10 mL) solution of **HMOP** (45 mg), chlorosulfonic acid (0.6 mL, 9 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 1 h. Then, water (1~2 ml) was added to the mixture at 0 °C to quench excess chlorosulfonic acid. Neither extending the reaction time to 3 days nor using more excess amount of chlorosulfonic acid upto 3 mL increased the amount of sulfonic acid groups in the materials. The resultant solid (~48 mg) was retrieved by centrifugation, washed with water and methanol, and dried under vacuum overnight.

Synthetic procedure of dye-loaded S-HMOP (D-HMOP)

For the preparation of **D-HMOP**, the **S-HMOP** (0.10 g) was added to 2.5 mM dye aqueous solution (30 mL) and the reaction mixture was treated by sonication for 30 min. The resultant materials were isolated by centrifugation and washed with water, methanol, and ether. The **D-HMOP** was dried under vacuum overnight. Rhodamine B, methylene blue, acridine yellow G, and $Ru(BPy)_3Cl_2$ are commercially available. TPP,[1,2] ZnTPP,[1] and CuTPP[2] were prepared by the literature method. 1) C. Pavani, A. F. Uchoa, C. S. Oliveira, Y. Isamanoto, and M. S. Baptista, *Photochem. Photobiol. Sci.* 2009, **8**, 233; 2) K. Groves, A. J. Wilson and A. D. Hamilton, *J. Am. Chem. Soc.* 2004, **126**, 12833.

Synthetic procedure of control materials, ZnTPP-S-nonhollow-MOP

For the preparation of ZnTPP-**S**-nonhollow-**MOP**, MOP materials were prepared by the procedure used for HMOP without using and etching the silica template. According to SEM analysis, the nonhollow MOP materials had a broad size range in ~ 0.5~1 μm and irregular granular shape. The surface area was measured as 529 m^2/g. For the preparation of **S**-nonhollow-**MOP**, the same procedure used for S-HMOP was applied. According to elemental analysis (S: 4.76 %), the content of sulfonic acid was calculated as 1.48 mmol/g. For the preparation of ZnTPP-**S**-nonhollow-**MOP**, the same procedure used for ZnTPP-**S-HMOP** was applied. According to N_2 isotherm curve analysis, the surface area was measure as 38 m^2/g. According to the elemental analysis (N: 0.468 %), the content of ZnTPP in ZnTPP-**S**-nonhollow-**HMOP** was calculated as 41.8 μmol/g.

The procedure of photocatalytic studies

ZnTPP-**S-HMOP** (13.4 mg, ZnTPP: 0.0931 mmol/g based on 1.04% N contents) was added to 1 mM 4-chlorophenol (4-CP) aqueous solution (25 mL) in a 50 mL Pyrex tube. Initial pH of reaction mixture was 5.0. The aqueous solution was stirred for 30 min in the dark to allow the equilibrium adsorption of substrates on the ZnTPP-**S-HMOP**. The Pyrex tube was opened to the air. The mixture was stirred during irradiation. A 200 W Xe lamp (4.6 mW/cm^2, $\lambda > 420$ nm) combined with a cutoff filter ($\lambda > 420$ nm) was used as a light source. Sample aliquots (0.40 mL) were taken. The ZnTPP-**S-HMOP** was filtered by a 0.45 μm PTFE filter (Millipore) and washed with 2 mL of MeOH to extract 4-CP. The concentrations of 4-CP were analyzed using a high-performance liquid chromatography (HPLC, Yong Lin YL9100 series) equipped with a UV/Vis detector and a Sun Fire C18 column 5 μm (4.6 × 150 mm^2) and an eluent of MeOH and water (v/v 1:1). For the recovery tests, the catalytic system was irradiated for 4 h. The catalysts were retrieved by centrifugation, washed with water, MeOH, acetone and hexane, dried under vacuum, and used for the next run. For the photocatalytic studies of ZnTPP-**S**-nonhollow-**MOP** in Fig. S7, 29.8 mg of catalyst (ZnTPP: 0.0418 mmol/g based on 0.47% N contents) was used.

Fig. S1 Low magnification TEM images of **HMOP**, **S-HMOP**, and ZnTPP/**S-HMOP**.

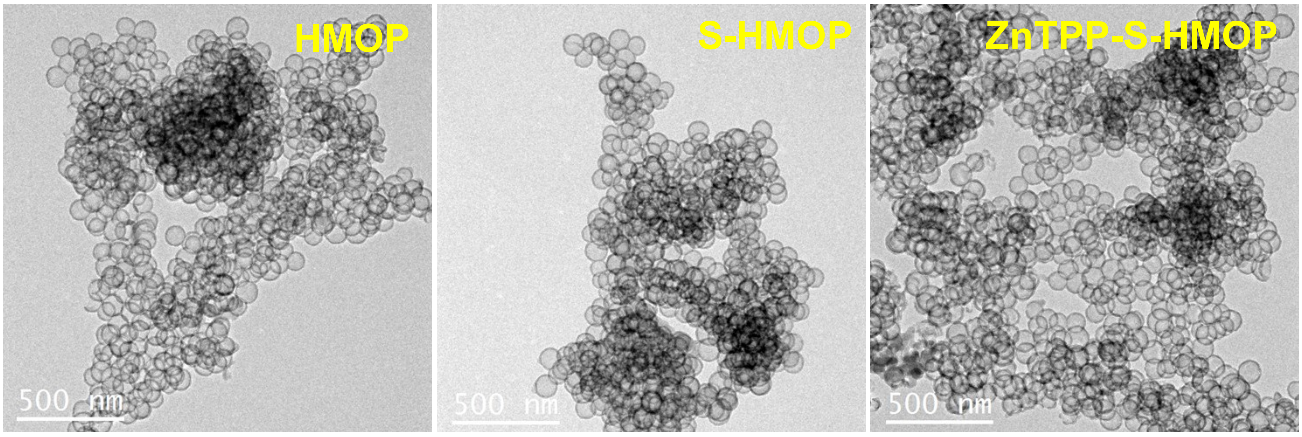


Fig. S2 Powder XRD patterns of **HMOP**, **S-HMOP**, and dye loaded **S-HMOP**.

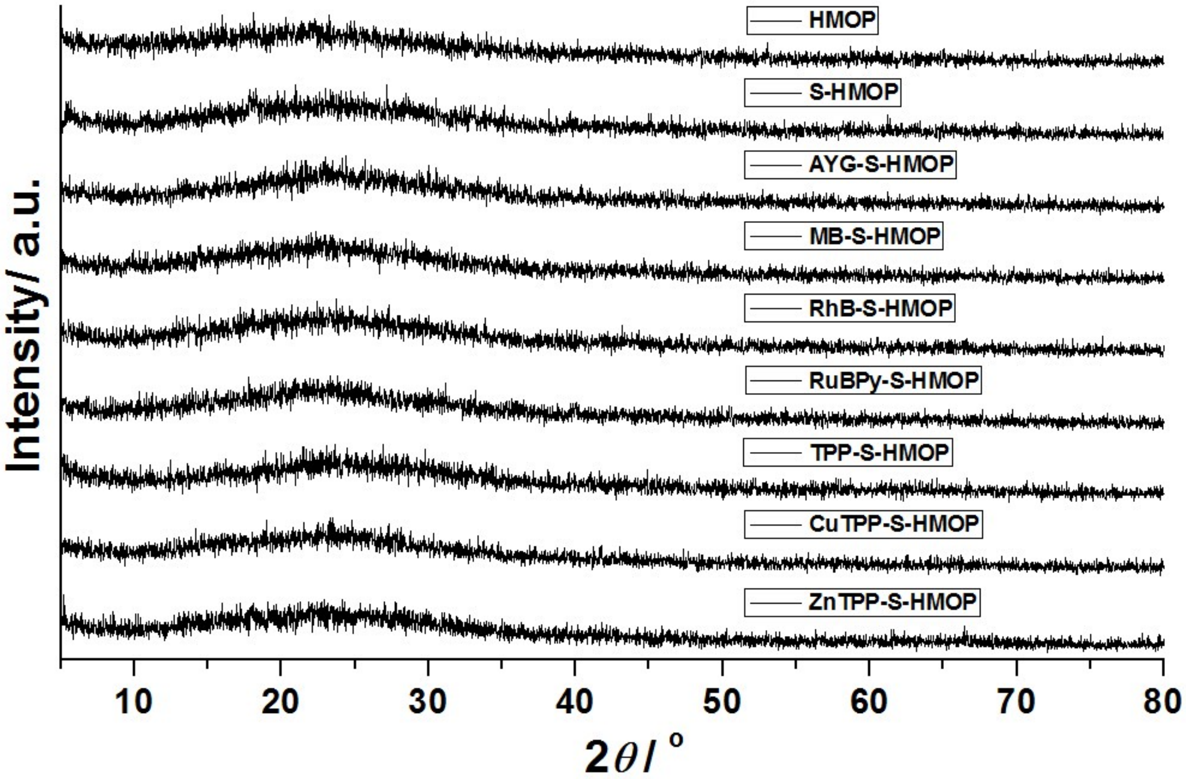


Fig. S3 IR spectra of dye-loaded **S-HMOP**.

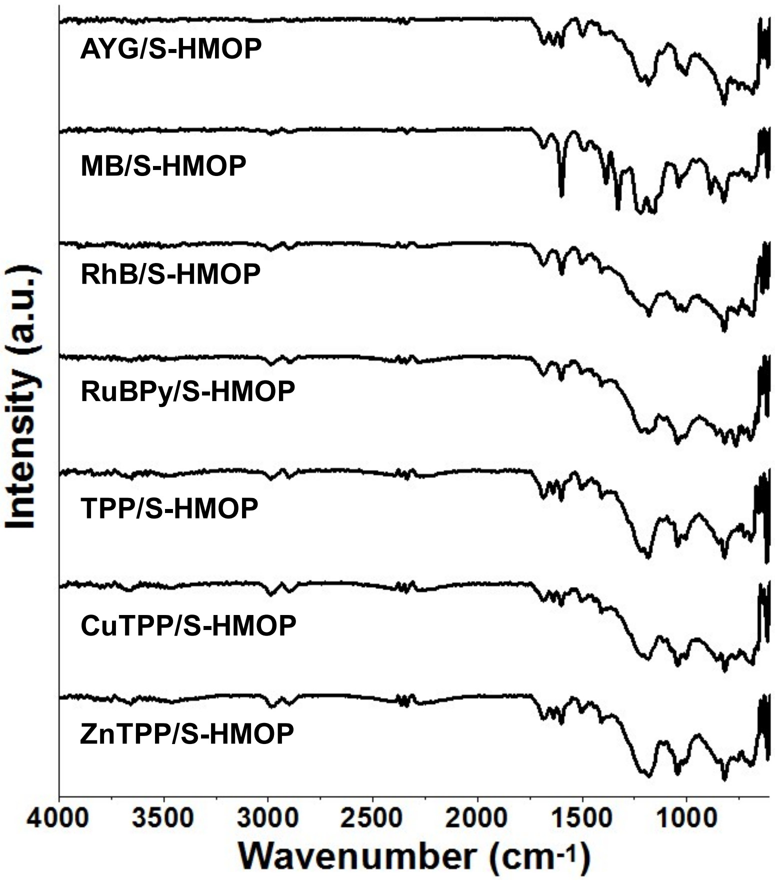


Fig. S4 N_2 adsorption and desorption isotherms at 77K and pore size distribution diagram (DFT method) of **HMOP**, **S-HMOP**, and dye loaded **S-HMOP**.

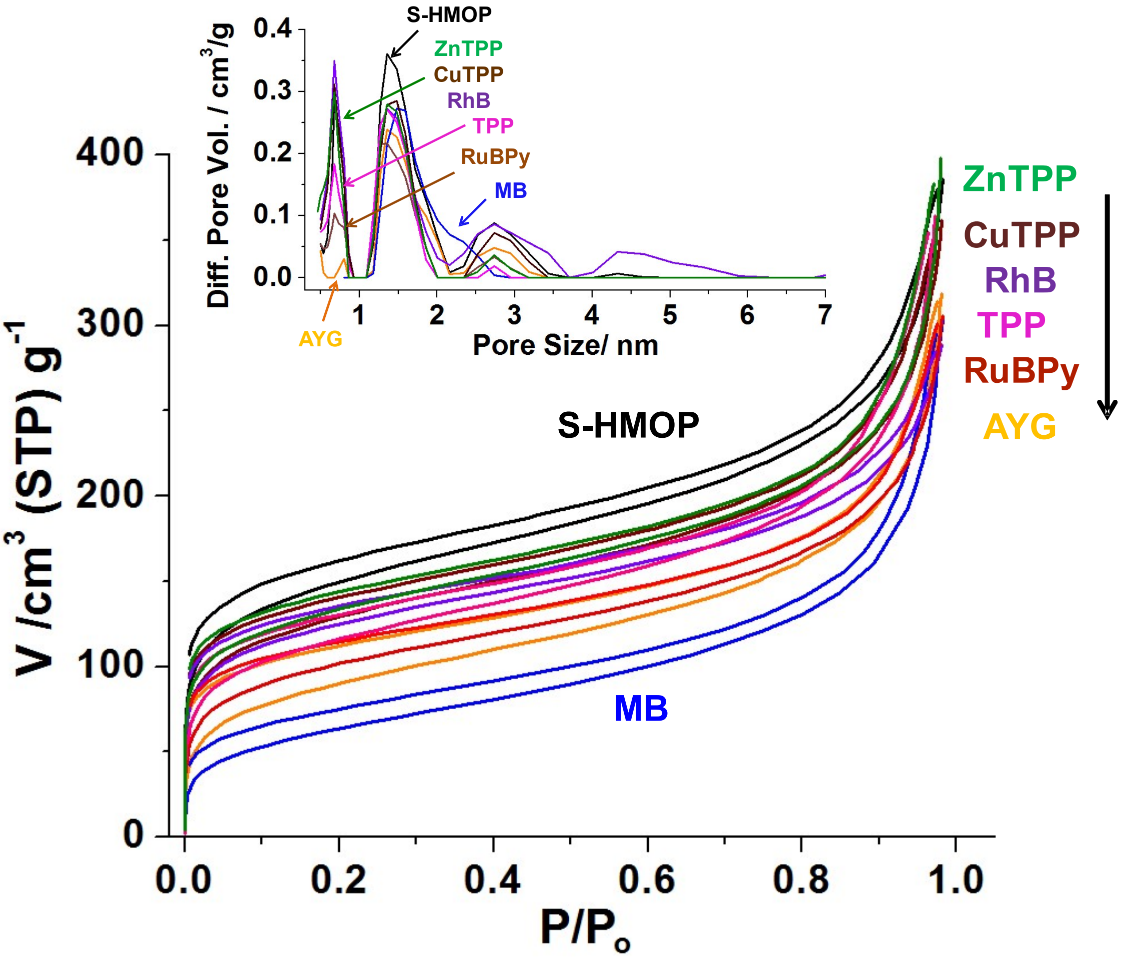


Fig. S5 Water contact angle measurement of **HMOP**, **S-HMOP**, and ZnTPP/**S-HMOP.** The water contact angles of pellet samples were measured using the Theta Optical Tensiometer model (KSV instruments, Ltd.) and lectrooptics comprising a CCTV camera connected to a computer (software Attension Theta).

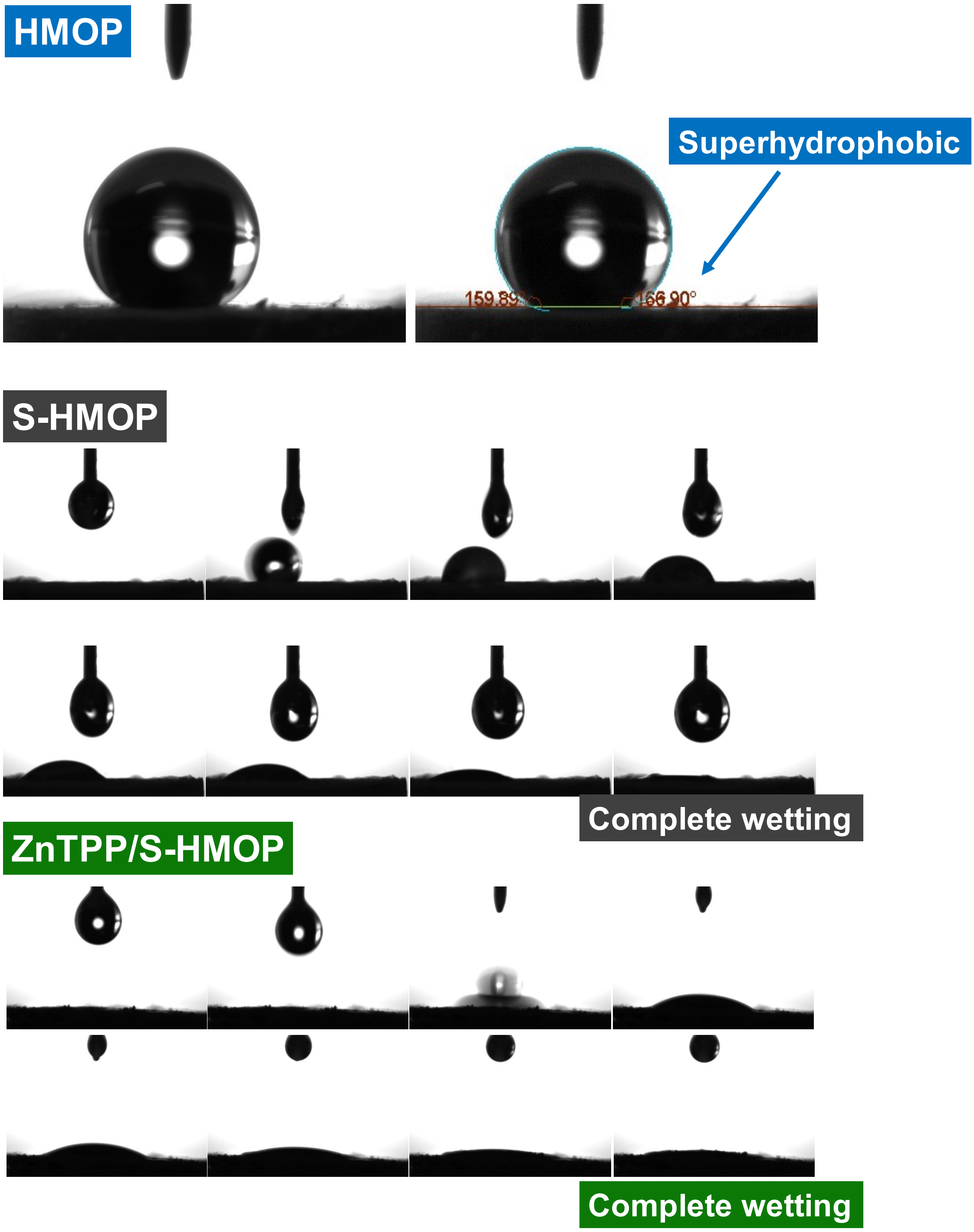
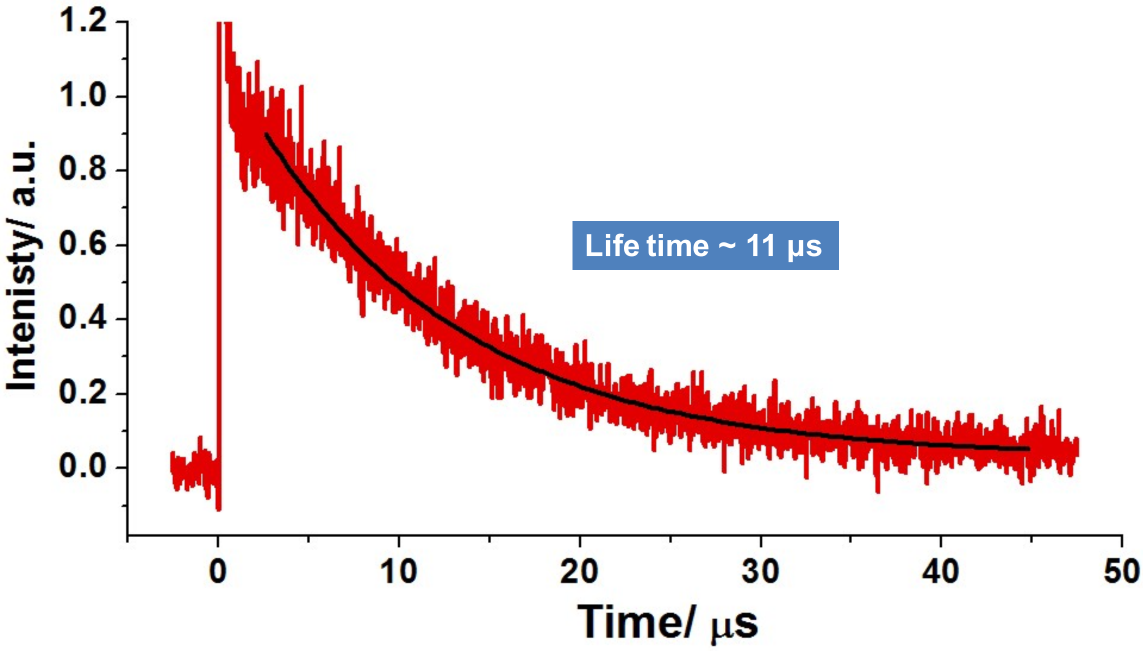


Fig. S6 Singlet oxygen detection in the photocatalytic reaction by ZnTPP/**S-HMOP**: The decay curve of singlet oxygen ($^1O_2$) phosphorescence at 1270 nm.



To obtain the decay curve of singlet oxygen phosphorescence, optical parametric oscillator (OPO) laser (Spectra-Physics, basiScan) pumped by Nd-YAG (Spectra-Physics, INDI-40-10) was used as an excitation source (ex 460 nm). The time duration (FWHM) of the excitation pulse was 7 ns, and the pulse energy was controlled by neutral density filter set from 1.0 to 0.1 mJ/pulse. Phosphorescence of $^1O_2$ was investigated by the characteristic peak at 1270 (1268) nm using by a monochromator (Princeton Instruments, SP2300) equipped with a NIR-PMT (Hamamatsu, H10330-75). The output signal from a NIR-PMT was recorded with a 500 MHz digital oscilloscope (Agilent, DSO-X 3054A). A cut-off filter was used to remove scattered excitation light. The phosphorescence of $^1O_2$ generated by Zn-TPP-**S-HMOP** in water was observed at 1270 nm. The decay curve of phosphorescence of $^1O_2$ matched well with that in the literature. (See the Figure 6 in A. S. Stasheuski, V. A. Galievsky, A. P. Stupak, B. M. Dzhagarov, M. J. Choi, B. H. Chung and J. Y. Jeong, *Photochem. Photobiol.* 2014, **90**, 997.)

Fig. S7 Comparison of photocatalytic activities of ZnTPP/**S**-nonhollow-**MOP** and ZnTPP/**S-HMOP**. (For the preparation of ZnTPP/**S**-nonhollow-**MOP** and procedure for photocatalytic studies, please refer to Experimental Sections. The k_{obs} values were obtained by plotting ln C/C_o versus t based on the equation, ln $C/C_o = -k_{obs}t$.)

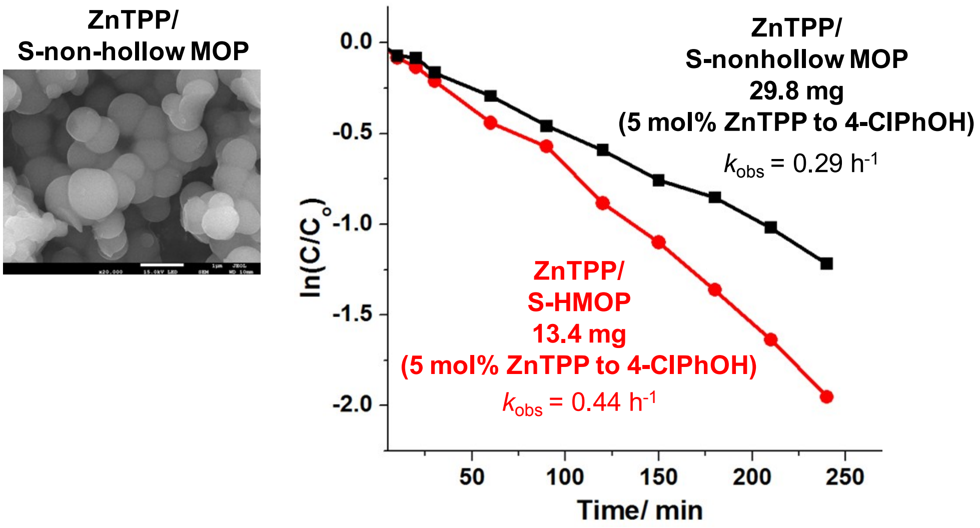


Fig. S8 TEM image and N_2 isotherm curve of the recovered ZnTPP/**S-HMOP** after three cycles.