Supplementary Information

The controllable nanostructure and photocatalytic behaviour of 5,10,15,20-tetra-(3,4,5 trimethoxyphenyl) porphyrin through solvophobic supramolecular self-assembly

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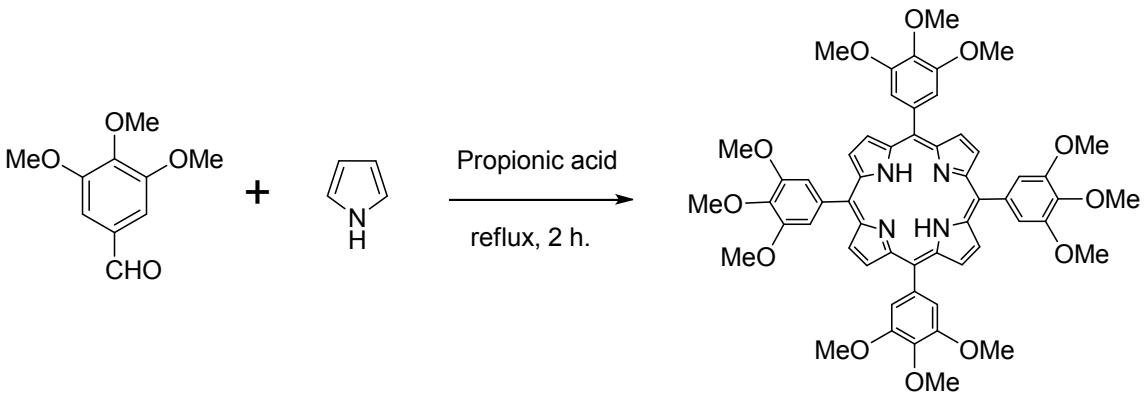
Materials and Methods

Materials

All the chemicals that are involved in order to triphenylamine, pyrrole, propionic acid, POCl3, N,N'-dimethyl formamide (DMF), tetrahydrofuran (THF) and Rhodamine B were purchased from Sigma Aldrich and used as they are without further purification.

Synthesis of TTOP

Synthesis of 5,10,15,20-tetrakis(3,4,5-trimethoxyphenyl)porphyrin (**TTOP**) was synthesized following literature procedure with slight modification.[1] An illustration for the TTOP synthetic reaction is shown as follow:



Scheme 1. Illustration for the **TTOP** synthetic reaction

(3,4,5)-Trimethoxybenzaldehyde (5g, 25 mmol) and propionic acid (60 ml) was taken in a round bottom flask and stirred to get a clear solution, then pyrrole (1.8g, 25 mmol) was added and solution was refluxed for 2 hours at 140 ^{o}C. After completion of reaction, mixture was cooled to room temperature and was filtered under vacuum. The solid obtained was washed with methanol (3x10ml), obtained purple color solid. The product was further purified by column chromatography on silica gel (DCM/PET ether, 5/1 v/v) The shiny purple solid was obtained 2.4 g (9.7%). All the characterisation such as NMR, mass and IR perfectly matches with literature report.[1]

Fabrication of porphyrin microstructures from TTOP monomers

First, 8 mg of **TTOP** porphyrin was dissolved in THF solution. Various fractions of water (0 - 100 v/v %) were added porphyrin solution under stirring at room temperature in the dark for 1 hour. The obtained aggregates were, then, filtered and dried for further characterizations.

Photocatalytic investigation

Photocatalytic performance of **TTOP** porphyrin micro-rod and belt crystals were evaluated by the degradation of dye (rohdamine B, RhB or methylene blue, MB) in aqueous media. In a typical photodegradation measurement, 0.1 mg of both 70, 80 and 90% of assembled **TTOP** porphyrin were dispersed in 20 mL solution of 5 mg L^{-1} of dye separately. The resulted dispersions were stirred in the dark for 30 minutes to establish an adsorption/desorption equilibrium before irradiation. The visible light source for the photocatalytic reaction was a 350 W air cooled Xenon lamp with a UV cut-off filter, which only allowed wavelengths of >

400 nm to penetrate. Every 30 minutes, 1.5 mL of dispersion aliquots were taken out and centrifuged to remove photocatalyst. The photocatalytic performance of the as-fabricated samples for dye degradation were evaluated by recording real-time UV-vis adsorption spectra of dye at a wavelength of 553 nm for RhB and 663 nm for MB, respectively.

To investigate the involvement of free radicals in the RhB degradation by TTOP, isopropanol, ammonia oxalate, and benzoquinone were added as trapping agents to trap ·OH, h^+, and $\cdot O_2$ radicals, respectively. Trapping experiments were conducted as the same as removing RhB without the addition of trapping agents.

Characterization

UV-Vis Spectrophotometer

Ultraviolet-visible (UV-vis) absorption measurements of samples in solution and in solid state were carried out using a Cary 50 Bio spectrophotometer with a cell of 1 cm path length. Furthermore, UV-vis absorption measurements were also employed to record the photocatalytic performance for dye degradation.

Fluorescence Spectrofluorophotometer

Horiba JobinYvonFluoroMax®-4 Spectrofluorometer was used to record fluorescence emission spectra of **TTOP** in THF/H_2O mixtures. All experiments were performed in a quartz cell with a 1 cm path length upon excitation at 420 nm wavelength.

Scanning Electron Microscope

The supramolecular self-assembled nanostructure morphology of **TTOP** in THF/H_2O mixtures were studied by scanning electron microscopy (SEM) using Hitachi S-4600 equipped with energy dispersive spectrometer for elemental analysis.

X-ray diffraction

X-ray diffraction (XRD) was analyzed by X'Pert PRO PANalytical with 0.15405 nm Cu-Kα radiation source.

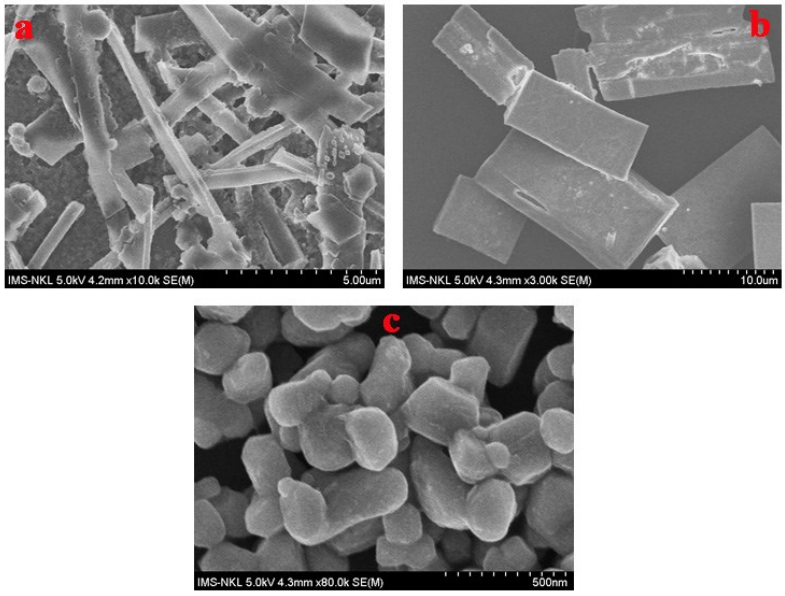


Figure S1. SEM images of TTOP aggregates after catalysis; aggregates prepared from H_2O/HF mixture with water fraction of 70% (a), 80% (b), and 90% (c).

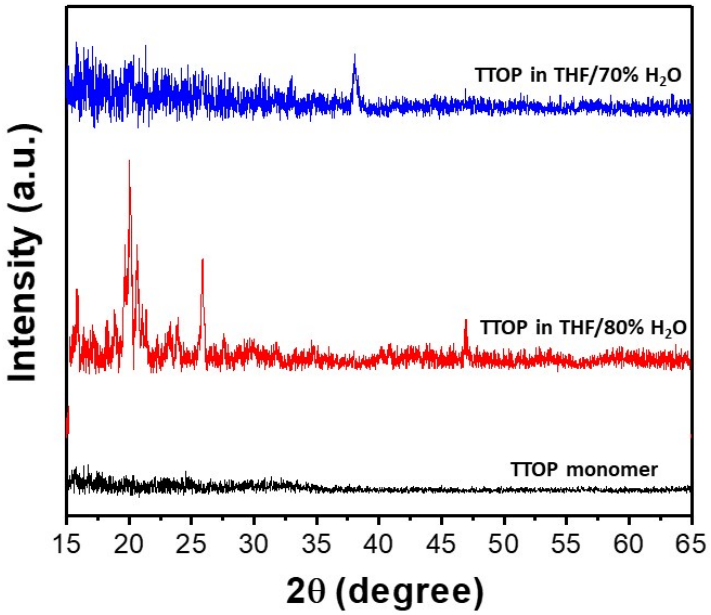


Figure S2. XRD patterns of the monomeric TTOP molecules (black line) and TTOP aggregates in the THF/H_2O mixtures with the water fraction of 70% (blue line) and 80% (red line).

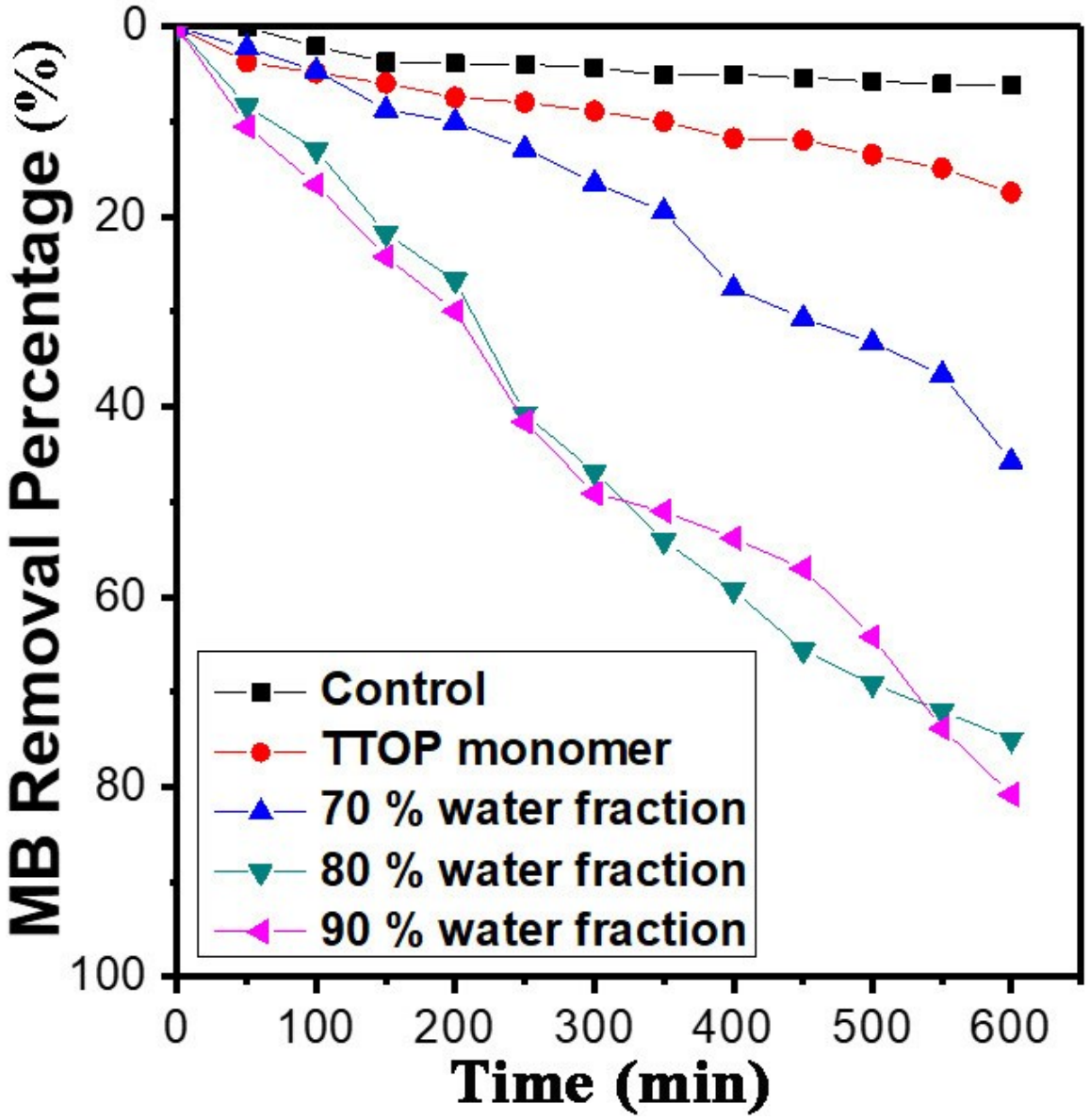


Figure S3. Photocatalytic behaviour of **TTOP** porphyrin aggregates toward Methylene blue dye

References:

1. X. Zhang, B. Zhu, L. Zhou, P. Liu and W. *Deng,* Synthesis of Novel Porphyrin Derivatives with Mesogenic Properties Syn. Commun.*2015,45, 2730-2739.*