Thermo-responsive Well-defined Amphiphilic Star Block Copolymer Photosensitizer: Smart BTEX Remover

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Experimental

Materials. 1-dodecanethiol (Aldrich, 98%), tricaprylylmethylammonium chloride (Aldrich, > 97%), acetone (Aldrich, > 99.9%), Sodium hydroxide (Aldrich, > 98%), carbon disulfide (Aldrich, 99.9%), chloroform (Aldrich, > 99%), and 2-propanol (Aldrich, 99.5%) were used as purchased. 5,10,15,20-Tetrakis-(3,5-dihydroxyphenyl)-21H,23H-porphine (TCI, 90%), potassium carbonate (Aldrich, > 99%), tert-butylbromoacetate (Aldrich, 98%), lithium chloride (Aldrich, 99%), potassium borohydride (Aldrich, 99.9%), sodium hydrogen carbonate (Junsei, 99.5%), sodium carbonate (Aldrich, 99%), *N,N*-dicyclohexylcarbodiimide (Daejung, 99%), dimethylformamide (Aldrich, 99.8%), tetrahydrofuran (J.T. Baker, 99.8%) and 4-dimethylamino pyridine (Daejung, 99%) were of commercial grade and used without purification. Styrene (Aldrich, 99%) was dried overnight over calcium chloride, and purified by distillation from calcium hydride prior to use. *N*-Isopropylacrylamide (Aldrich, 97%) and azobisisobutyronitrile (Daejung, 99%) were purified by recrystallization from *n*-hexane and methanol, respectively. 2-dodecylsulfanylthiocarbonylsulfanyl-2-methylpionic acid (CTA) was synthesized according to the literature. [1]

Preparation of multifunctional-CTA with porphyrin (Scheme S1)

5,10,15,20-Tetrakis(3,5-bis(tert-butyl1'-methoxyacetate)phenyl)porphyrin (Porphyrin-*t*BA) (A). 5,10,15,20-Tetrakis-(3,5-dihydroxyphenyl)-21H,23H-porphine(Porphyrin) (1 g, 0.00134 mol) and K_2CO_3 (2.23 g, 0.01615 mol) were added to the 2-neck RB flask, sealed with glass stopper and 3-way cock. The mixture was slowly stirred for 2 hours under vacuum.

After purging with argon, the porphyrin and K_2CO_3 were dissolved in DMF (90 mL) over 20 min. After addition of *tert*-butyl bromoacetate (4.20 g, 0.02154 mol) dropwise, and stirring for 20 min, a reflux condenser was attached and the reaction mixture refluxed. The reaction was monitored by ^{1}H NMR. After 12 hours, the reaction mixture was poured into 100 mL of diethyl ether, which was extracted with 200 mL of distilled water. Drying over $MgSO_4$, followed by concentration of the solvent gave a red liquid. The solution was dropped into n-hexane. The precipitated product was collected by vacuum filtration, followed by drying in a vacuum oven for 48 hours, giving a wine color powder (2.05 g, 90% yield). ^{1}H NMR (300MHz, $CDCl_3$): 8.87 (s, 8H), 7.38 (d, *J*=2Hz, 8H, *o*-aryl H), 6.96 (t, *J*=2Hz, 4H, *p*-aryl H), 4.66 (s, 16H, TPP-OCH_2-), 1.41-1.48 (s, 72H, TPP- $OCH_2COOC(CH_3)_3$). See Fig. S1.

5,10,15,20-Tetrakis(3,5-bis(2'-hydroxy-1'-ethoxy)phenyl)porphyrin (Porphyrin-OH) (B). Porphyrin-*t*BA (1 g, 0.00060 mol) was dissolved in THF (33 mL) and heated to reflux, when KBH_4 (0.52 g, 0.00966 mol) and LiCl (0.41 g, 0.00966 mol) were added under Ar and the mixture was stirred for 12 hours. The reaction was monitored by ^{1}H NMR. The reaction mixture was poured into 66 mL of THF and washed with 20 mL of a 4:1 mixture of brine and 1M $NaHCO_4$, 30 mL of a 4:1 mixture of brine and 1M Na_2CO_3, and 30 mL of brine. After repeating this extraction process 3 times, collection of the organic portions, drying over $MgSO_4$, followed by concentration of the solvent gave a red liquid. This red solution was dropped into n-hexane. The precipitated product was collected, and dried in a vacuum oven overnight to give a wine color powder (0.60 g, 91% yield). ^{1}H NMR (300 MHz, $(CD_3)_2SO$): 9 (s, 8H), 7.42 (d, *J*=2Hz, 8H, *o*-aryl H), 7.05 (t, *J*=2Hz, 4H, *p*-aryl H), 4.99 (s, 8H, TPP-OCH_2CH_2OH), 4.25 (s, 16H, TPP-OCH_2-), 3.86 (m, 16H, TPP-OCH_2CH_2-). See Fig. S1.

5,10,15,20-Tetrakis(3,5-bis(2'-(2-dodecylsulfanylthiocarbonylsulfanyl-2-methylpropionate)-1'-ethoxy)phenyl)porphyrin (Porphyrin-CTA) (C). Porphyrin-OH (0.33 g, 0.0003 mol), CTA (1.76 g, 0.0048 mol) and DMAP (0.29 g, 0.0024 mol) were dissolved in 13 mL of dried THF. DCC (0.5 g, 0.0024 mol) was also dissolved in 1.5 mL of dried THF. The main solution which contained Porphyrin-OH was stirred for 20 min at 0 °C. DCC in THF was dropped into the main solution over 10 min, and followed by stirring for 1hour at 0 ^{o}C. The reaction went for 12 hours at room temperature. After evaporation of the volatiles, 30 mL of methylene chloride was added and washed with 50 mL of distilled water. The organic parts were collected and dried over $MgSO_4$. After filtering off $MgSO_4$, the concentrated reaction mixture was poured into -75 °C methanol. The precipitated red powder was immediately collected by membrane filter paper (1 μm pore size). Precipitations were repeated twice and the obtained products dried in the vacuum oven for 48 hours. At room temperature, the product state turned to a sticky gel (1.05 g, 90% yield). ^{1}H NMR (300MHz, $CDCl_3$, TMS): 8.94 (s, 8H), 7.37 (d, *J*=2Hz, 8H, *o*-aryl H), 6.89 (t, *J*=2Hz, 4H, *p*-aryl H), 4.52 (s, 16H, TPP-OCH_2-), 4.33 (m, 16H, TPP-OCH_2CH_2-), 3.22 (t, 16H), 1.71 (s, 48H), 1.6-0.95 (m,160H), 0.83 (t, 24H).

Preparation of amphiphilic PNIPAM-PS star block copolymer with porphyrin core.

Synthesis of polystyrene star polymer precursor with porphyrin core by bulk polymerization. Porphyrin-CTA (100 mg, 0.0258 mmol) and AIBN (0.42 mg, 0.00258 mmol) were added into the 50 mL RB flask and dried under vacuum for one hour. Styrene (4.3 g, 0.0413 mol) was injected under argon atmosphere and stirred until the solution gave a clear color. The reaction solution was degassed 3 times by freeze-pump-thaw method. The prepared solution was started the reaction by immersing into the 80 ^{o}C oil bath. After a predetermined time, a small amount of reaction solution was collected from the solution which was on the reaction at the several points of the polymerization to monitor the monomer conversion. Obtained the reaction solutions were precipitated with pouring into methanol after dilution with THF. Precipitated wine colored powder was filtered and then dried under vacuum oven. The conversion was determined by ^{1}H NMR spectroscopy and listed in Table S1.

Synthesis of polystyrene star polymer precursor with porphyrin core by solution polymerization.

Porphyrin-CTA (30 mg, 0.00775 mmol) and AIBN (0.127 mg, 0.000775 mmol) were added into the 30 mL RB flask and dried under vacuum for one hour. Toluene 1.68 mL and styrene (1.29 g, 0.0124 mol) was injected under argon atmosphere and stirred until the solution gave a clear color. The reaction solution was degassed 3 times by freeze-pump-thaw method. The prepared solution was started the reaction by immersing into the 80 ^{o}C oil bath. After a predetermined time, a small amount of reaction solutions were collected from the solution which was on the reaction at the several points of the polymerization to monitor the monomer conversion. Obtained the reaction solution was precipitated with pouring into methanol after dilution with THF. Precipitated wine colored powder was filtered and then dried under vacuum oven. The conversion was determined by ^{1}H NMR spectroscopy and listed in Table S1.

Synthesis of poly(N-isopropylacrylamide) amphiphilic starpolymer with Porphyrin-styrene macro-initiator (Porphyrin-PSN). The polystyrene star polymer precursor (200 mg, 0.0177 mmol), AIBN (0.29 mg, 0.00177 mmol) and NIPAM (800 mg, 0.0070 mmol) were added and dried under vacuum for one hour. DMF (3.5 mL) was injected under argon atmosphere and stirred until the solution showed a clear color. The reaction solution was degassed 3 times by freeze-pump-thaw method. After a predetermined time, a small amount of reaction solution was collected from the solution which was on the reaction at the several points of the polymerization to monitor the monomer conversion. Obtained the reaction solutions were precipitated with pouring into n-hexane after dilution with THF. Precipitated wine colored powder was filtered and then dried under vacuum oven. The conversion was determined by ^{1}H NMR spectroscopy and listed in Table 1.

Low critical solution temperature (LCST). The thermal responsive property was confirmed in Fig. S8. A water solution of P-PSN star copolymer was placed in a 32 ^{o}C oil bath stirred for 5 min. (Fig. S8, (B)). The clear P-PSN water solution turned turbid. This behavior was supported by the transmittance curves in Fig. 3. The transmittance critically changed due to the aggregation of the P-PSN star copolymers at the cloud temperature. The degree of aggregation of the P-PSN star copolymers increased with the elapse of time. After 60 min. passed, a large precipitate was observed on the bottom of the vial and transmittance of the solution seemed to be increase. After 120 min. passed, the precipitate and water were looked as if it were perfectly phase-separated. The size of precipitate could be easily filtered using fine mesh. These results definitively supported that the transmittance increased despite the solutions being at a temperature above that of the cloud point.

Encapsulation of benzene using PNIPAM-PS star block copolymer with porphyrin core. PNIPAM-PS star block copolymer as materials of encapsulation for benzene was prepared for equilibrium batch experiment. The PNIPAM-PS (0.001 g) was allowed to react with 100 mL of benzene solution, with various initial concentrations (10, 30, 50 and 100 mg L^{-1}) in 125 mL wide neck bottles. The flasks were placed on an orbital shaker at 150 rpm. Triplicate samples were obtained from each flask using a syringe needle to measure the aqueous benzene concentrations during the reactions. Benzene was quantified using direct immersion SPME (solid-phase-micro-extraction), where the extraction was performed in a 0.7 mL micro-tube by immersion of the SPME fiber into the liquid sample and removal of the fiber in order to increase the accuracy of measurements. After the direct extraction, the SPME fiber was immediately inserted into GC-FID (Agilent 6890, Agilent Tech co.). Controlled experiments, where there were no reactions with the PNIPAM-PS star block copolymer (run 10), were also conducted to confirm that the decreases in the benzene concentration were actually caused by encapsulation into the P-PSN rather than by adsorption onto the walls of the glass bottles or from volatilization.

Photocatalytic degradation of BTEX using PNIPM-PS star block copolymer with porphyrin core. Photoreactor vessels containing 500 mL of individual aqueous solution of BTEX (100 ppm) were placed in a photoreactor chamber with visible or UV light, a cooling fan for adjusting the air temperature, a stirrer, and a darkroom. The temperature in the photoreactor was controlled to 25 °C using the cooling fan. The star block copolymer solution (2.85×10^{-7} mol/L) was injected into each of BTEX solution and stirred at 300 rpm. After a predetermined time, 1 mL samples were withdrawn from the reactors and filtered through a syringe filter (Puradisc Nylon 25 nm; 0.45 μm) to measure the residual BTEX concentrations by HPLC. In addition, the quantity of CO_2 as a byproduct was determined at regular 1 h intervals (Fig. S6). Analysis of CO_2 was performed by gas chromatography.

Characterizations. The number averaged molecular weight (M_n) and the molecular weight distributions (M_w/M_n) of the samples were measured using a JASCO PU-2080 plus SEC system equipped with RI-2031 and a UV-2075 (254 nm detection wavelength) using THF as an eluent at 40 °C with a flow rate of 1 mL/min. The samples were separated through four columns: Shodex-GPC KF-802, KF-803, KF-804, and KF-805. ^{1}H-NMR spectra were taken in $CDCl_3$ and DMSO at 25 °C on a 300 MHz Varian Unity INOVA. FTIR spectrum was measured with a Thermo Nicolet iS10 using solvent cast film on KBr pallet. UV–vis absorption spectra were measured in air with JASCO V-670 spectrophotometer with a thermal controller accessary. HPLC elution was carried out using 20:80 v/v of 1% phosphoric acid : acetonitrile at a flow rate of 1 mL/min. The temperature of oven for column was kept at 40 ºC. Photoreactor vessels containing 500 mL of individual aqueous solution of the BTEX (100 ppm) were placed in a photoreactor chamber (Fig. S9), with UV or visible light lamps, a cooling fan for adjusting the air temperature at RT, a stirrer and a darkroom (W 20 cm, D 25 cm, H 30 cm). At predetermined intervals, the obtained samples were measured for the residual BTEX concentration by HPLC (PerkinElmer, Massachusetts, USA), equipped with a C18 column (Zorbax Eclipse XDB-C18; 4.6 mm x 150 mm; 3.5 μm) and fluorescence detector at an excitation wavelength of 254 nm. Analysis of CO_2 by gas chromatography was performed in glass packed columns (Porapak R (100 Mesh)) of 3.6 m length. The carrier gas used was helium and flowed 30 mL/min. The thermal conditions were set inlet = 100 ^{o}C, thermostat = 50 ^{o}C, and detector = 100 ^{o}C. The gas analysis was executed with thermal conductivity detection (Agilent 7890, Agilent Tech, Korea).

Table S1. Synthesis of polystyrene star polymer precursor with a porphyrin core in bulk and in toluene solution at 80 °C by RAFT process.

	run	reaction time (h)	conversion (%)	Mn (SEC)	Mn (Cal.)	PDI (SEC)
in bulk	1[1]	3	15	26,500	28,800	1.11
	2[1]	18	35	47,200	62,200	1.2
	3[1]	40	60	82,900	103,800	1.34
	4[1]	89	72	95,700	124,000	1.33
in toluene	5[2]	3	10	19,500	20,500	1.09
	6[2]	18	17	30,800	32,100	1.12
	7[2]	43	26	37,000	47,000	1.13
	8[2]	86	32	41,500	57,000	1.16
	9[2]	134	44	59,100	77,200	1.18

[1] [Porphyrin-CTA]/ [Styrene]/ [AIBN] = 0.0054/ 8.7/ 0.00054 = 1/ 1600/ 0.1.

[2] [Porphyrin-CTA]/ [Styrene]/ [AIBN] = 0.0025/ 4/ 0.0025 = 1/ 1600/ 0.1, Toluene = 1.68 mL

Table S2. Maximum adsorption capacities of the Langmuir isotherm for benzene of various adsorbents.

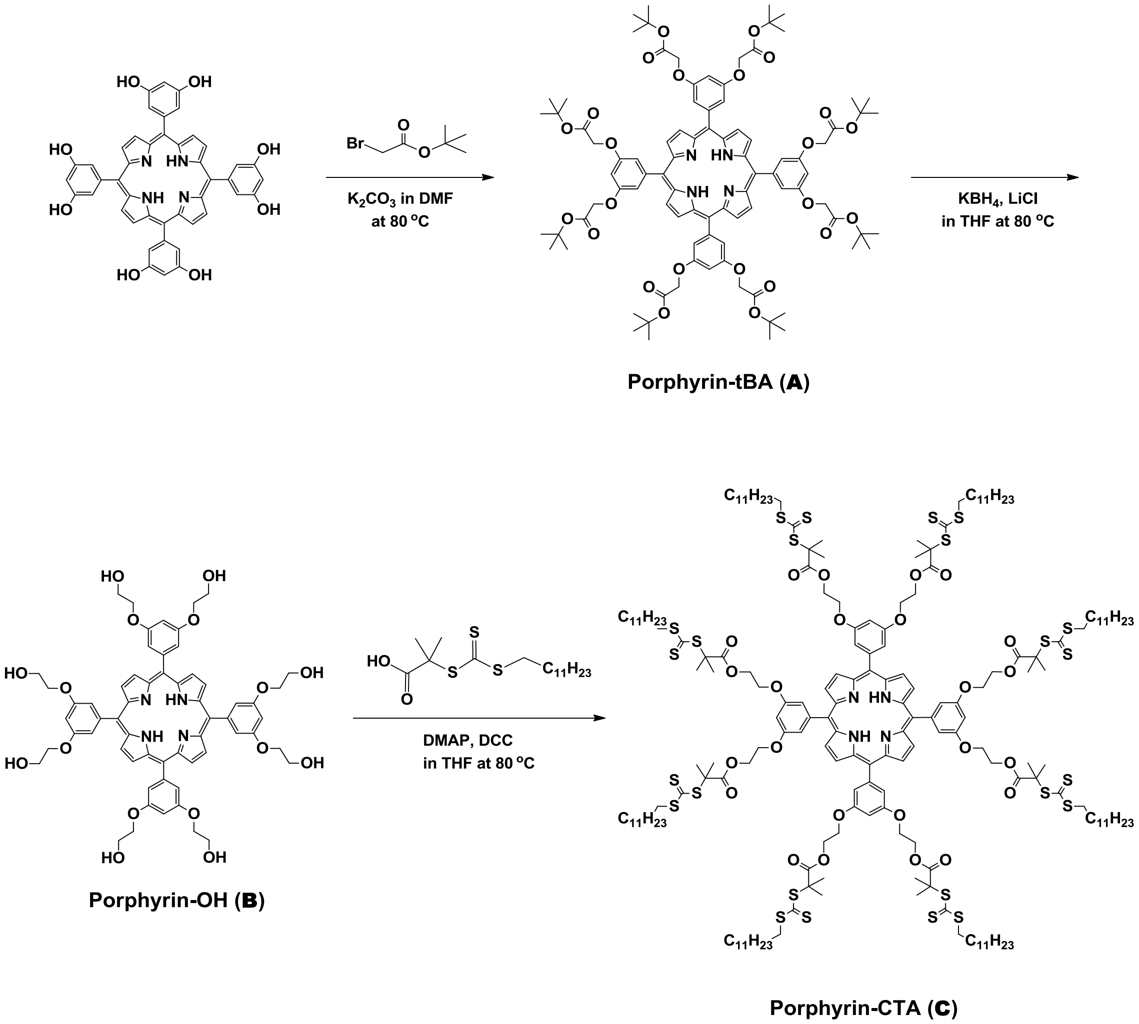
Langmuir Equation	Chars (Zhou et al., 2010)	Surfactant modified zeolite (Ghiaci et al., 2004)	Modified clinoptilolite (Ghiaci et al., 2004)	Star block copolymer (This study, run 10)
α (L/mg)	0.022	0.019	0.061	0.014
β (mg/g)	79.04	95.49	77.97	194.53

(run 10) M_n = 270,000, 85 wt.% of PNIPAM

Table S3. Maximum adsorption capacities of the Langmuir isotherm for benzene of various star block copolymers with different molecular weights and weight fractions.

Langmuir Equation	Star block Copolymer (run 2)	Star block Copolymer (run 7)	Star block Copolymer (run 10)
α (L/mg)	0.155	0.082	0.014
β (mg/g)	20.07	30.32	194.53

(run 2) M_n = 16,800, 52.5 wt.% of PNIPAM,
(run 7) M_n = 38,000, 64 wt.% of PNIPAM
(run 10) M_n = 270,000, 85 wt.% of PNIPAM.



Scheme S1. Syntheses of Porphyrin-*t*BA (**A**), Porphyrin-OH (**B**), and Porphyrin-CTA) (**C**).

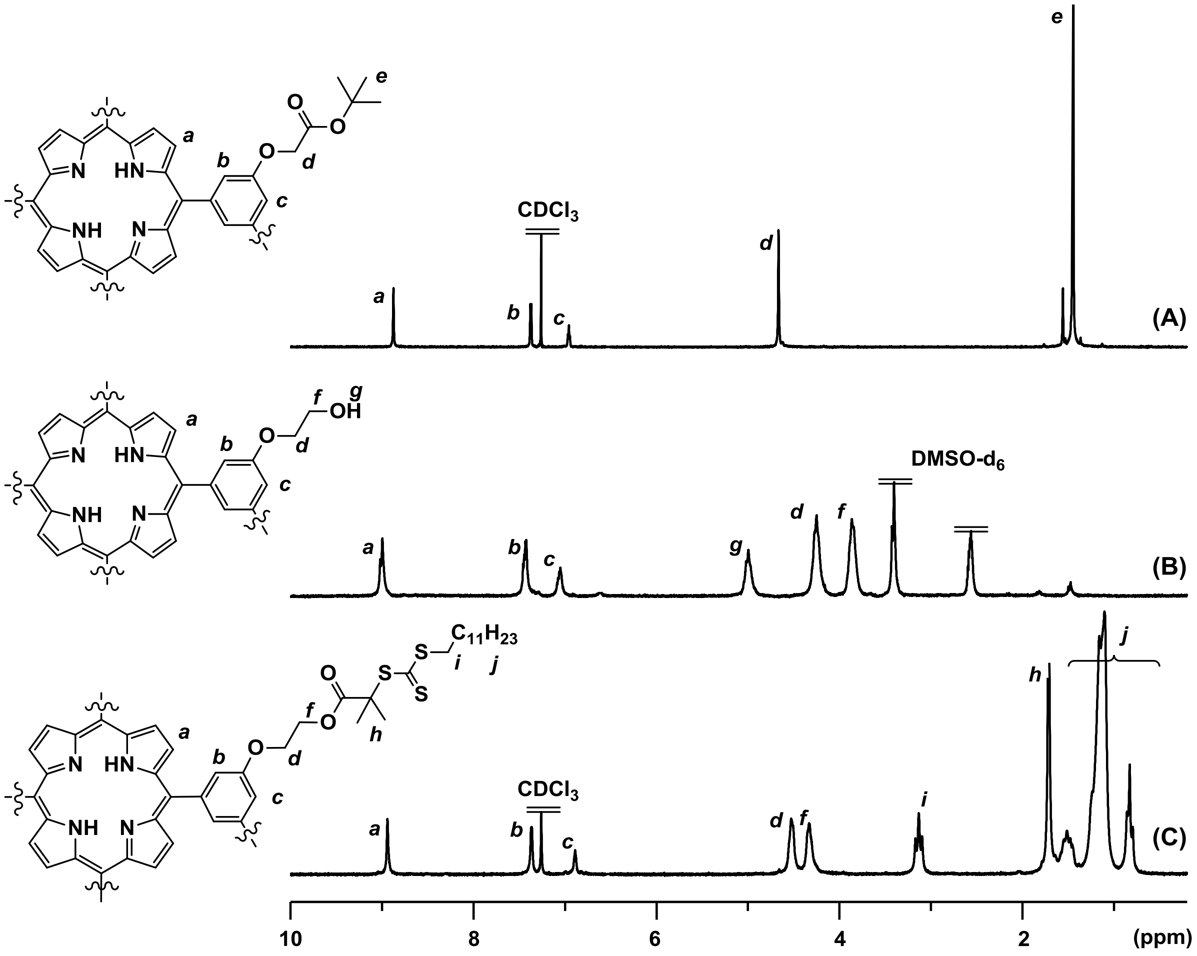


Fig. S1 ^{1}H NMR spectra of (A) Porphyrin-*t*BA in $CDCl_3$, (B) Porphyrin-OH (**B**) in DMSO-d_6, and (C) Porphyrin-CTA in $CDCl_3$ at room temperatures.

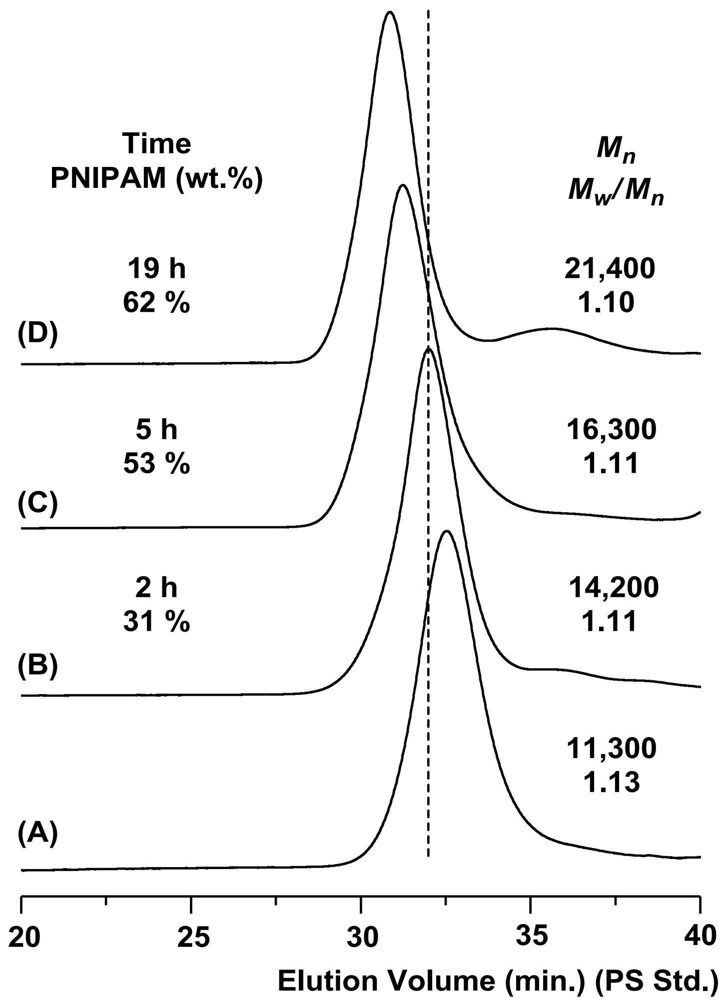


Fig. S2 SEC curves of (A) PS star polymer precursor with porphyrin core and (B-D) PNIPAM-PS star block copolymers with porphyrin cores. See Table 1, run 1-4.

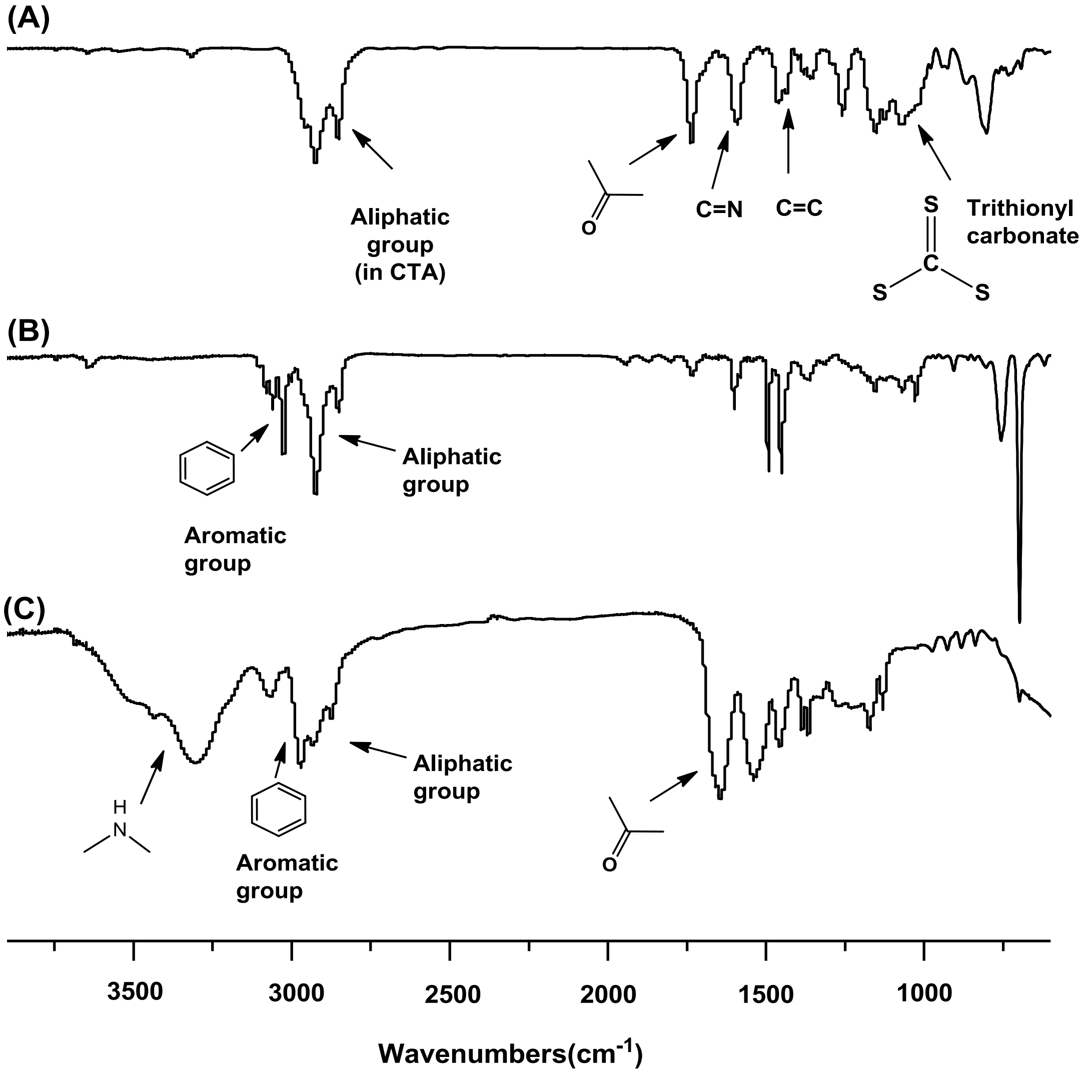


Fig. S3 FTIR spectra of (A) Porphyrin-CTA, (B) PS star polymer precursor with porphyrin core, and (C) PNIPAM-PS star block copolymer with porphyrin core.

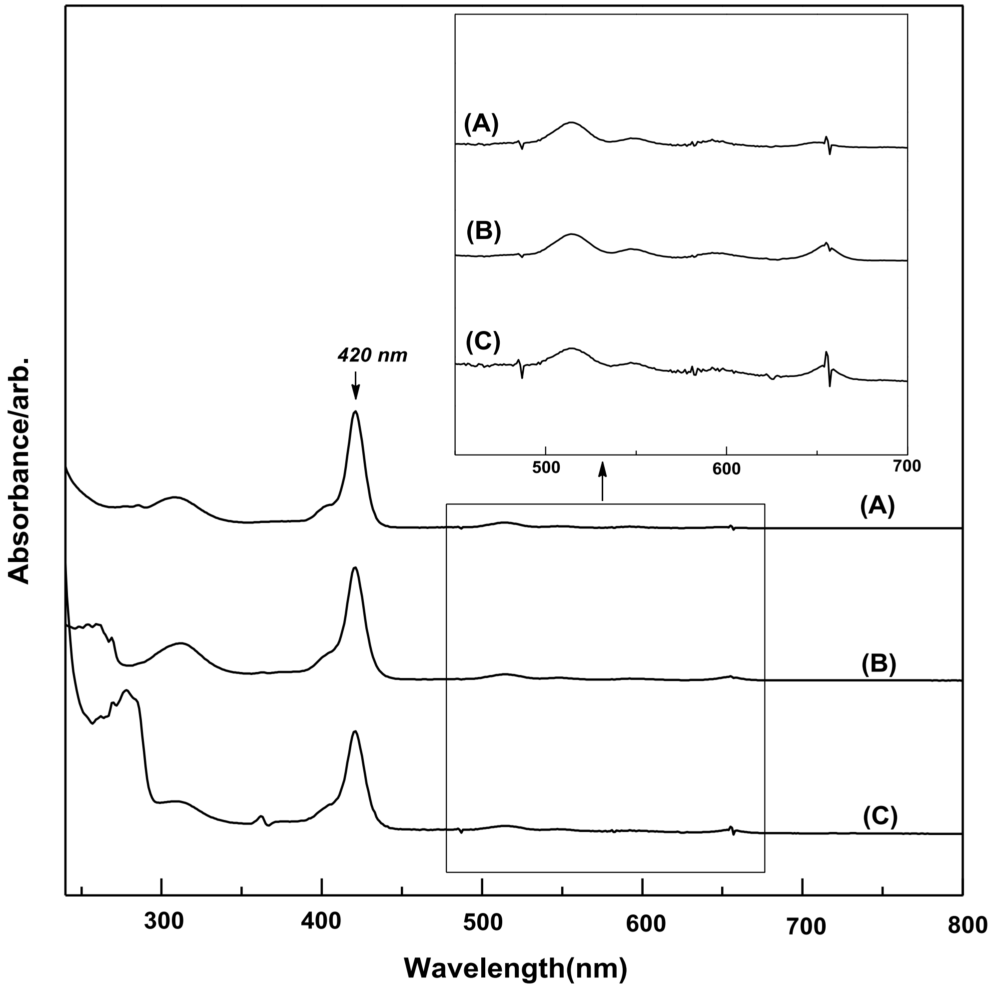


Fig. S4 UV Transmittance curves in THF solutions: (A) Porphyrin-CTA, (B) PS star polymer precursor with porphyrin core, and (C) PNIPAM-PS star block copolymer with porphyrin core.

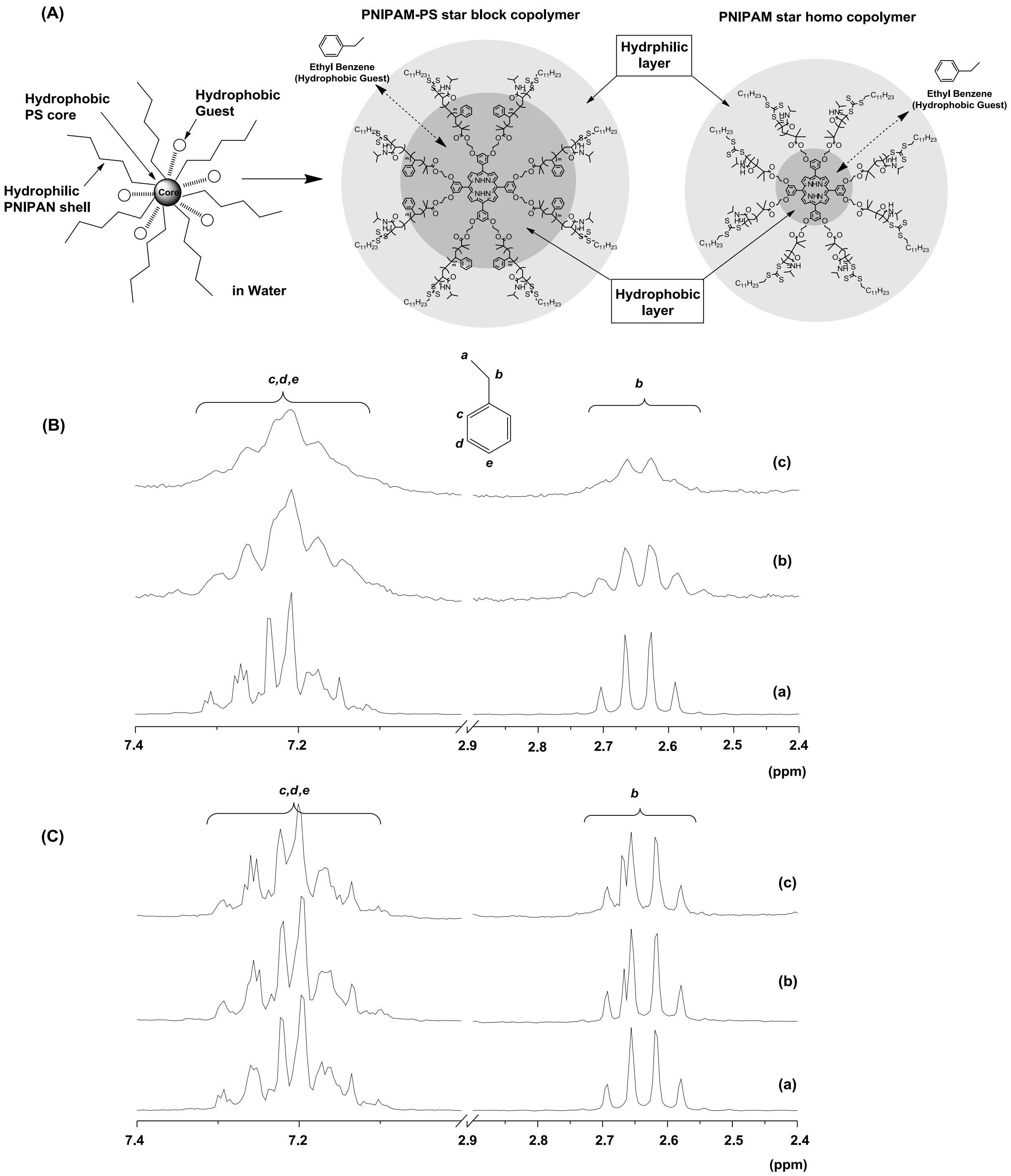


Fig. S5 Host-guest interaction of hydrophobic guest ethyl benzene with PNIPAM-PS star block copolymer host or PNIPAM star homo polymer host: (A) schematic diagrams and ^{1}H NMR spectra of ethyl benzene (0.06M in CD_3OD) with increase of (B) PNIPAM-PS the star block copolymer (run 10) and (C) PNIPAM the star homo polymer (M_n = 33,300; PDI = 1.3) at (a) 0 mg/mL, (b) 47 mg/mL, and (c) 90 mg/mL.

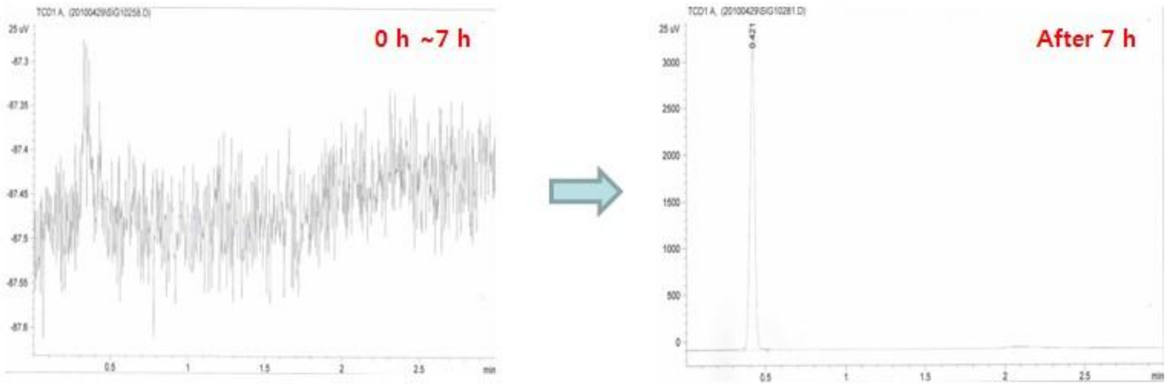


Fig. S6 CO_2 detection after the photooxidation reaction of benzene with PNIPAM-PS star block copolymer.

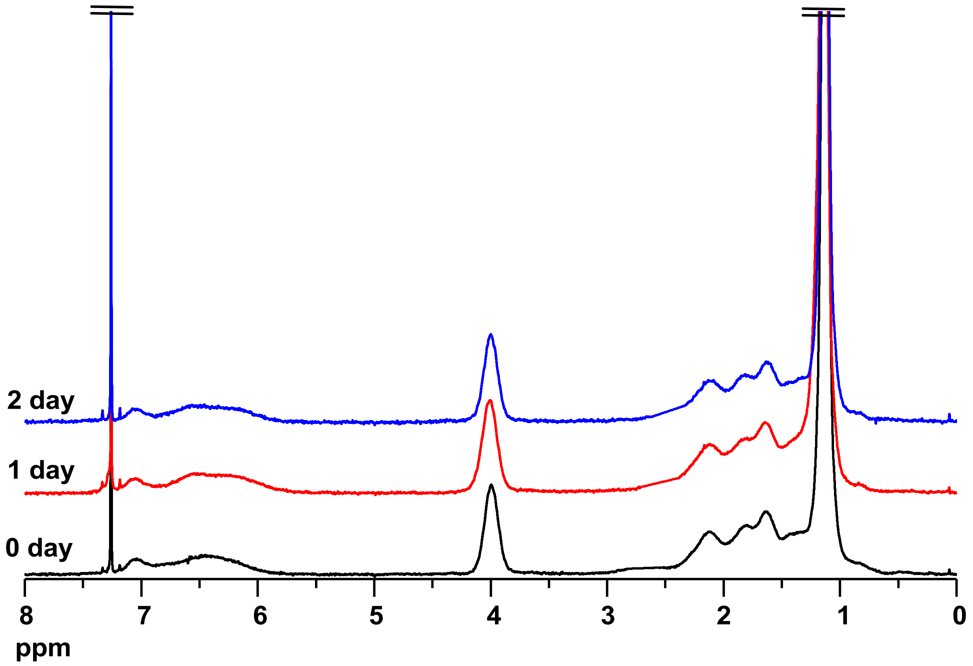


Fig. S7 ^{1}H NMR spectra of the PNIPAM-PS star block copolymer before and after 1 day and 2 days under UV irradiation in $CDCl_3$ at room temperatures.

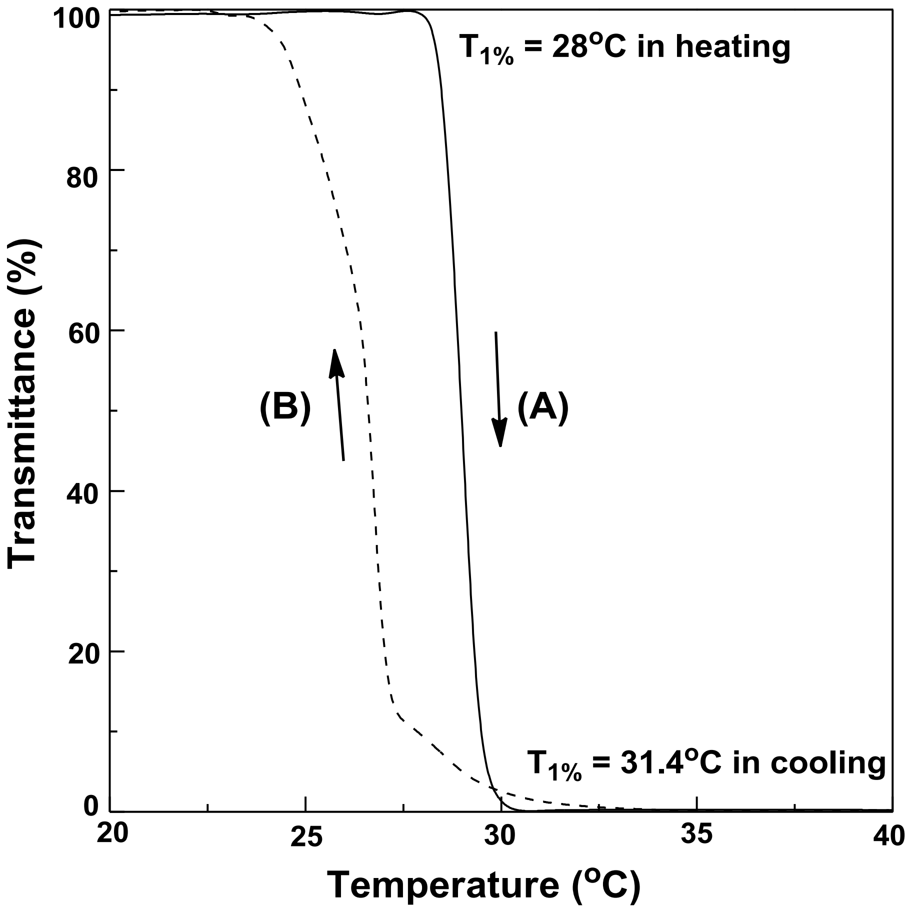


Fig. S8 Transmittance curves of aqueous solutions of PNIPAM-PS star block copolymer (5 mg/mL in water) at different temperatures with a heating/cooling rate of 0.5 °C/min using a UV-vis spectrophotometer at λ = 800 nm: (A) heating curve and (B) cooling curve. ($T_{1\%}$ = 1% transition in transmittance).

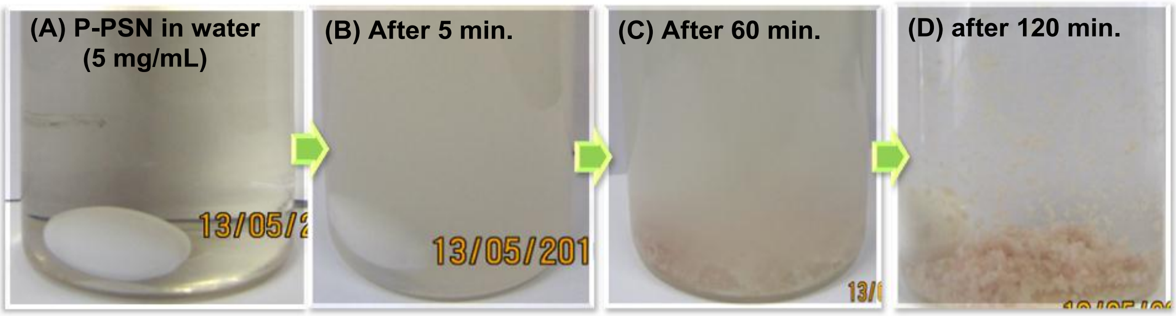


Fig. S9 Pictures of aqueous solution of PNIPAM-PS star block copolymer with porphyrin core (5 mg/mL in water) with increase of temperature: (A) room temperature, (B) 32 °C for 5 min., (C) 32 °C for 60 min., and (D) 32 °C for 120 min.

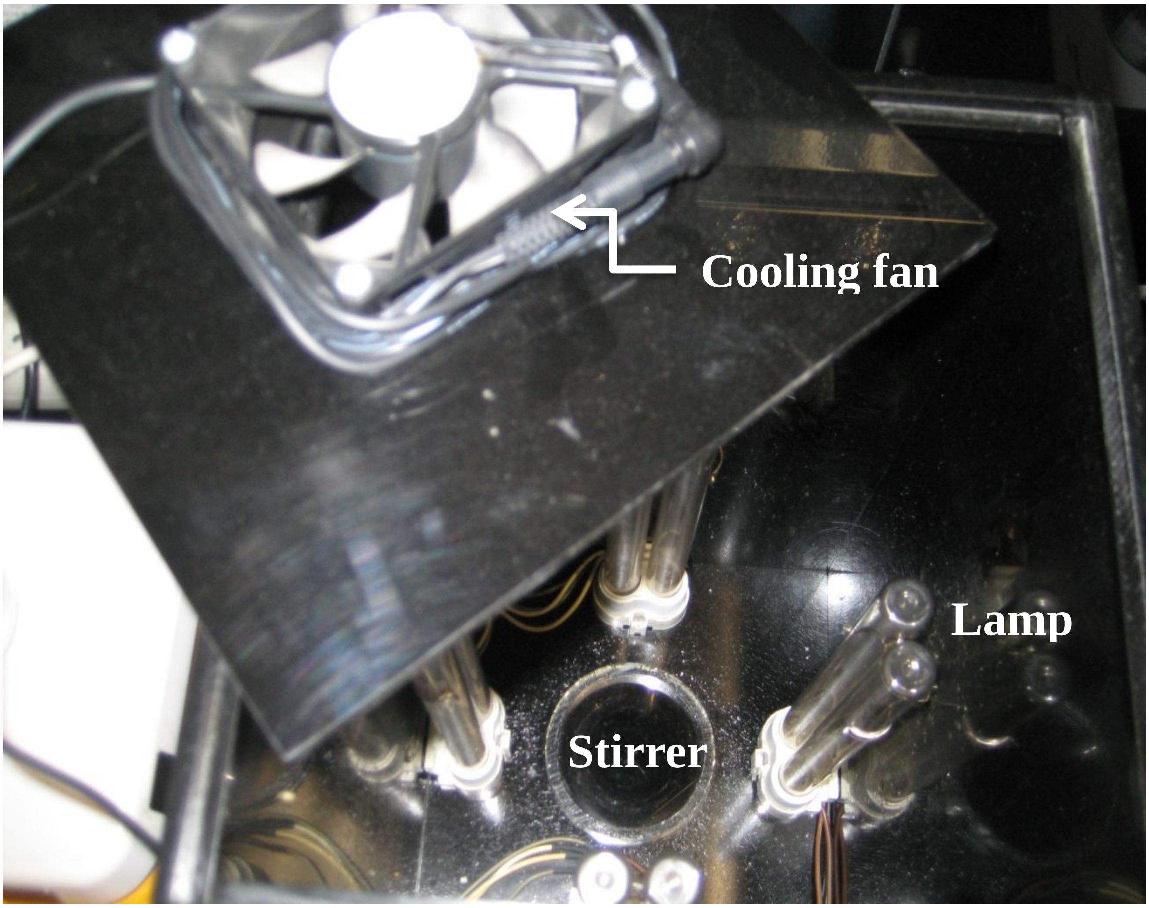


Fig. S10 Actual image of the photoreactor for the photooxidation reaction of BTEX with PNIPAM-PS star block copolymer.

Reference

[1] J. T. Lai, F. Debby, R. Shea, *Macromolecules* 2002, **35**, 6754.

[2] J. W. Choi, S. Y. Lee, K.Y. Park, K. B. Lee, D. J. Kim, S. H. Lee. *Desalination*, 2011, **266**, 281.