

Supplementary Information

Dendritic Amphiphile Mediated Porous Monolith for Eliminating Organic Micropollutants from Water

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Experimental Section

Materials: Toluene, AIBN (further purified by recrystallization with ethanol), ethylene oxide, eosin Y (EY), rose Bengal (RB), methyl orange (MO), congo red (CR), sodium dodecylbenzene sulfonate (SDBS), direct blue 80 (DB80) and direct black 71 (DB71) were purchased from SCRC (China). St (99%) and DVB (80%) were acquired from Aladdin and were purified by distillation under vacuum or by passing through neutral chromatographic aluminum oxide to eliminate the inhibitor. PEI ($M_n = 10^4$, degree of branch = 60%) was purchased from Aldrich.

Preparation of PolyHIPE. A HIPE process was conducted with St, DVB, toluene (porogen solvent) and PEI@PS (stabilizer) as the continuous phase and water (4-fold the volume of oil phase, pH 7.4, phosphate buffer (0.01 M)) as the dispersed phase. Typically, to an oil phase composed of components in volume ratio of monomer of St/DVB (60%; St/DVB = 8: 2), toluene (30%), stabilizer (PEI@PS310-3, 10%) and AIBN (1 wt-% with respect to the monomer) under stirring, water was added dropwise to form a HIPE. The HIPE was allowed to stand at 70 °C for 12 h. The resulting polyHIPE was washed with ethanol before dried in vacuum to yield a creamy white solid. PolyHIPE of S5 was prepared from S4 by immersing S4 (0.5 g) in ethanol (20 mL), and ethylene oxide (1 mL) was added in 3-batch with an interval of 2 h. 12 h later, the sample was fully washed with ethanol and followed by drying in vacuum.

Water remediation and recycling of polyHIPE: Typically, a polyHIPE solid of S4 (0.2 g) was ground into powder and packed in a Teflon bag and sewed with Teflon thread, and was dropped into a dye (pyrene, surfactant)-contaminated water (10-200 mL) and allowed to stand for several

days. The residual pollutants was monitored with a UV/vis spectrometer (after concentration), or with a fluorescent spectrometer (without concentration) by detecting aliquots. For detection of pyrene and EY by fluorescence, the excitation wavelengths were 335 and 465 nm, respectively. For recycling of the adsorbent, the dye-loaded S4 was immersed into aqueous NaOH (2 M, 10 ml) with the aid of a heavy object for 3 d and washed with fresh aqueous NaOH and neutral water in sequence.

Saturated adsorbing capacity of a polyHIPE. Typically, to an MO-contaminated water (200 mL, 5×10^{-6} M) charged in a vial, polyHIPE (2 mg, mediated by PEI@PS70-15) was ground into powder and packed in a hydrophilic Teflon bag dropped into the vial. The vial was sealed and placed on a low-frequency oscillator in dark. The aqueous solution was monitored with a UV/vis spectrometer at an interval of 1 d, and a control experiment without polyHIPE was also carried out. When the residual concentration of MO remained intact, the adsorbed amount of MO could be derived from the differential absorbance.

Characterization: UV/vis spectra were recorded on a Mapada UV-6300 spectrophotometer (Shanghai Mapada Instruments Co., Ltd., China). The fluorescence spectra of aqueous samples were recorded on an F-4600 fluorescence spectrometer (Hitachi Co. Ltd., Japan), SEM was conducted by placing the polyHIPE sample on an aluminum stub with an adhesive carbon pad and was imaged using a FEI's QUANTA250FEG Instrument operating at an accelerating voltage of 10 kV and spot size of 2.0 nm. The apparent densities of polyHIPE were measured according to Archimedes principle. Porosity and surface area were determined by mercury intrusion method with a mercury porosimeter of PoreMaster 60-GT at 20 °C.

Synthesis of PEI@PS with different molecular parameters

The molecular weight (chain length) of epoxy terminated PS was controlled by nitroxide mediated living radical polymerization,¹ the molecular weight and polydispersity index were listed in **Table S1**.

Table S1. Molecular weight and molecular weight distribution of several PS samples.^a

PS (polymerization degree)	$M_n/10^3$	M_w/M_n
PS21	2.3	1.23
PS70	7.5	1.49
PS310	32.5	1.48
PS520	54.3	1.49

^a The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC) using a Waters 150-C, calibrated with standard poly(styrene); eluent: chloroform.

The PEI@PS (**Fig. S1**) samples were prepared by quantitative reaction between PEI and epoxy PS. A control experiment by dialysis of PEI@PS towards chloroform ((spectro/por, molecular weight cut off: 8000–14,000) for 24 h) showed that all PS chains were attached to PEI and dialysis was not necessary if the functional degree of PEI was below 60%.

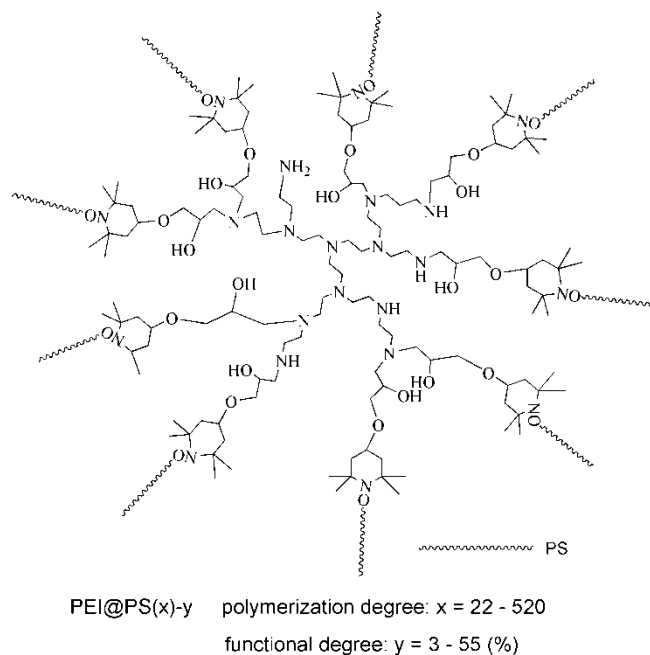


Fig. S1. Dendritic amphiphile of PEI@PS samples with different molecular parameters. (PEI has 232 repeat units on average but only several are shown here for clarity; x represents the polymerization degree of PS; y represents the functional degree of amino protons of PEI.

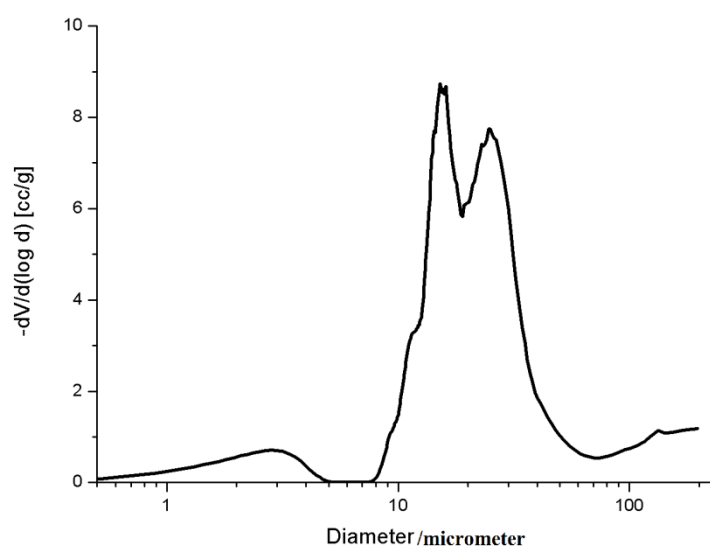


Fig. S2. Pore distribution of a sample (Fig. 2b) measured by mercury intrusion porosimeter.

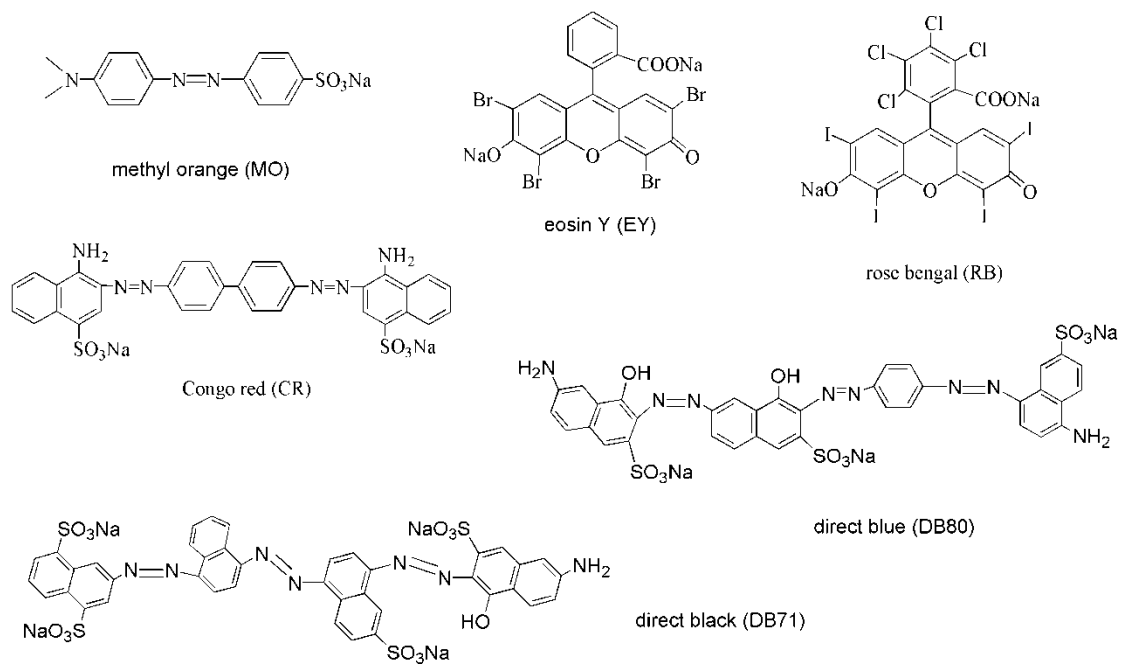


Chart S1. Chemical structures of dyes.

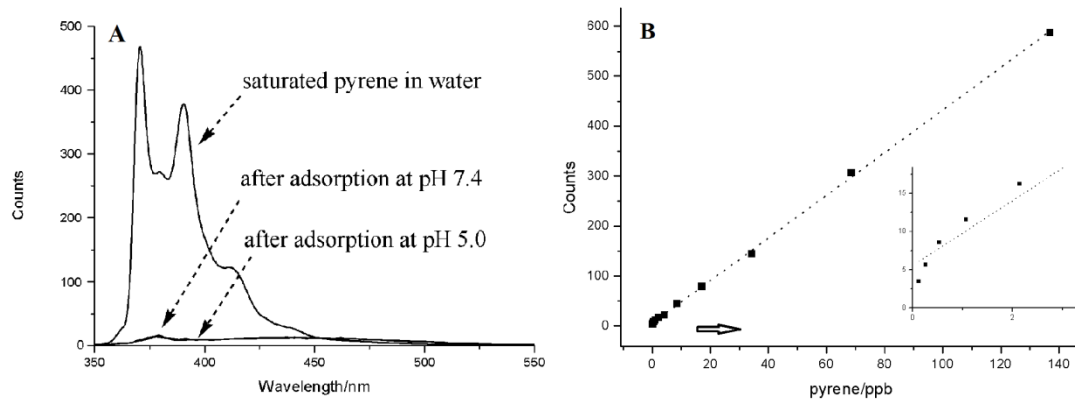


Fig. S3. Fluorescent detection of aqueous pyrene before and after treatment with polyHIPE S4 (A) and the fluorescent intensity-concentration calibration curve of pyrene.

Ref:

- (1) Wan, D.; Yuan, J.; Pu, H. *Macromolecules* **2009**, *42*, 1533–1540.