

# Supporting Information

## Polymer Brush-Based Erasable and Rewritable Nanostructured Particle Surfaces

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# 1. EXPERIMENTAL SECTION

## 1.1 Materials

Styrene (98%, Tianjin Chemical Reagent Company), DMAEMA (99%, Acros) and methyl methacrylate (MMA, 99%, Sigma Aldrich) were purified by passing through basic alumina columns and distilling under reduced pressure. 2,2-Azoisobutyronitrile (AIBN, Guo Yao Chemical Company) was purified by recrystallization from ethanol. Cyano-4-(dodecylsulfanylthiocarbonyl) sulfanyl pentanoic acid (CDTPA) was synthesized in this laboratory.<sup>1</sup> Silica particles with an average size of 500 nm (99.9%, Alfa Aesar) were dried under reduced pressure at 110 °C before use. Poly(ethylene glycol) monomethyl ether (CH<sub>3</sub>O-PEG-OH,  $M_n = 2000$ , Alfa Aesar), N,N'-dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-(dimethylamino)pyridine (DMAP, 99%, Alfa Aesar), succinic anhydride (99%, Heowns), hydroxyethyl disulfide (98%, Alfa Aesar), 2,2'-disulfanediybis(ethan-1-ol) (Aldrich, technical grade), (3-mercaptopropyl)-trimethoxysilane (95%, Aldrich), DL-dithiothreitol (DTT, 99%, Aldrich), hexylamine (Aladdin, 99%), 2,2'-dipyridyl disulfide (98%, Alfa Aesar), L-glutathione reduced (GSH, Heowns, 97%), Bovine Serum Albumin (BSA, Dingguo, 96%), and fluorescein isothiocyanate (FITC, Alfa Aesar, 95%) were used as received. The synthesis of silica particles with thiol groups on the surfaces (SiO<sub>2</sub>-SH) was described in our previous research.<sup>2</sup> All the solvents used in the chemical reactions or polymerizations were distilled before use.

## 1.2 Experimental Procedures

**Synthesis of Carboxylic Acid Terminated Poly(ethylene glycol) (PEG<sub>44</sub>-COOH).** Poly(ethylene glycol) monomethyl ether (PEG<sub>44</sub>-OH), purchased from Alfa

Aesar, was used in the synthesis of PEG<sub>44</sub>-COOH. PEG<sub>44</sub>-OH (2.0 g, 1.0 mmol), succinic anhydride (150 mg, 1.50 mmol), DMAP (12.2 mg, 0.100 mmol), and dichloromethane (5.0 mL) were added into a 50 mL round-bottom flask. The reaction was performed at room temperature overnight, and after the reaction the solution was poured into 10-fold diethyl ether. After filtration and drying under reduced pressure, white powder polymer was obtained. Yield: 75%.

**Synthesis of Chain Transfer Agent with a Disulfide Bond (CTA-SS-OH).** RAFT chain transfer reagent (RAFT CTA) with a disulfide bond (CTA-SS-OH) was synthesized by an esterification reaction between hydroxyethyl disulfide and the reversible addition-fragmentation chain transfer (RAFT) agent, 4-cyano-4-dodecylsulfanylcarbothioylsulfanylpentanoic acid (CDTPA). To a 100 mL round-bottom flask, hydroxyethyl disulfide (1.4 g, 9.0 mmol), DCC (741.6 mg, 3.600 mmol), DMAP (36.6 mg, 0.300 mmol), and dichloromethane (25.0 mL) were added. CDTPA (1.2 g, 3.0 mmol) dissolved in 5.0 mL of dichloromethane was added by drop to the solution at 0 °C. The reaction was performed at room temperature overnight, and after the reaction the insoluble solids were removed by filtration. The crude product was further purified by column chromatography (hexane/ethyl acetate, 4:1) yielding a yellow liquid (1.0 g). Yield: 64%. <sup>1</sup>H NMR (400 MHz, chloroform-*d*, TMS, ppm): 4.39 (t, 2H), 3.89 (t, 2H), 3.33 (t, 2H), 2.91 (dt, 4H), 2.66 (dd, 2H), 2.60 - 2.48 (m, 1H), 2.44 - 2.32 (m, 1H), 1.89 (s, 3H), 1.68 (dd, 3H), 1.45 - 1.15 (m, 18H), 0.88 (t, 3H). <sup>13</sup>C NMR (101 MHz, chloroform-*d*, TMS, ppm): 216.89, 171.37, 118.99, 62.91, 60.28, 46.33, 41.59, 37.10, 36.81, 33.79, 31.92, 29.75, 29.62, 29.55, 29.43, 29.34, 29.08, 28.94, 27.67, 24.90, 22.70, 14.14.

**Synthesis of PEG Macromolecular Chain Transfer Agent with Disulfide Group (PEG<sub>44</sub>-SS-CTA).** PEG<sub>44</sub>-SS-CTA was synthesized by an esterification reaction between PEG<sub>44</sub>-COOH and CTA-SS-OH. CTA-SS-OH (269 mg, 0.500

mmol), DCC (51.5 mg, 0.250 mmol), DMAP (6.1 mg, 0.050 mmol) and dichloromethane (25 mL) were added into a 50 mL round-bottom flask. PEG<sub>44</sub>-COOH (525 mg, 0.250 mmol) dissolved in 5.0 mL of dichloromethane was added by drop to the solution at 0 °C. The reaction was performed at room temperature overnight, and after the reaction the insoluble solids were removed by filtration. The solution was poured into 10-fold of diethyl ether. After filtration and drying under reduced pressure, PEG<sub>44</sub>-SS-CTA was obtained. Yield: 72%.

**Synthesis of PEG<sub>44</sub>-*b*-PS<sub>83</sub> BCP with Disulfide Groups at the Block Points (PEG<sub>44</sub>-SS-PS<sub>83</sub>).** PEG<sub>44</sub>-SS-PS<sub>83</sub> was synthesized by RAFT polymerization of styrene in toluene using PEG<sub>44</sub>-SS-CTA as macro-CTA. To a 10 mL Schlenk flask, PEG<sub>44</sub>-SS-CTA (50 mg, 0.019 mmol), AIBN (0.58 mg, 0.0034 mmol), styrene (596.8 mg, 5.730 mmol), and toluene (0.5 mL) were added. The solution was degassed by three freeze-pump-thaw cycles. After stirring at 90 °C for 12 h, the polymerization was stopped by quenching the solution in an ice bath. The polymer solution was poured into 10-fold of n-hexane, and BCP was precipitated from the solution. After filtration and drying under reduced pressure, PEG<sub>44</sub>-SS-PS<sub>83</sub> was obtained. The average degree of polymerization (DP) of PS block was determined by <sup>1</sup>H NMR.

**Synthesis of PS Brushes on Silica Particles (SiO<sub>2</sub>-PS<sub>80</sub>).** PS<sub>80</sub> were synthesized by RAFT polymerization. A typical procedure was described as follows. Styrene (7.3 g, 70 mmol), AIBN (5.8 mg, 0.035 mmol), CPADB (70 mg, 0.25 mmol), and toluene (10.0 mL) were mixed in a 50 mL Schlenk flask. After three freeze-pump-thaw cycles, the polymerization was performed at 90 °C for 12 h. After the polymerization, PS was precipitated in methanol and dried under reduced pressure. The degree of polymerization (DP) of PS was determined by <sup>1</sup>H NMR. Based on size exclusion chromatography (SEC) results, the number average molecular weight ( $M_n$ ) and molecular dispersity ( $D$ ) of the PS were determined to be 8.6 K and 1.16. Silica

particles with average size of 500 nm were purchased from Alfa Aesar. The details for the synthesis of SiO<sub>2</sub>-ss-py was described in our previous research paper.<sup>2</sup> The RAFT CTA on PS<sub>80</sub> was reduced to thiol groups with hexylamine, and thiol-terminated PS (PS<sub>80</sub>-SH) was obtained. PS brushes on silica particles were prepared by thiol-disulfide exchange reaction between PS<sub>80</sub>-SH and SiO<sub>2</sub>-ss-py. Herein, the silica particles with polymer brushes (SiO<sub>2</sub>-PS<sub>80</sub>) were collected by centrifugation (10000 rpm, 2 min) and washed with THF to remove the excess PS.

**Coassembly of PEG<sub>44</sub>-SS-PS<sub>83</sub> and SiO<sub>2</sub>-PS<sub>80</sub>.** A typical procedure for the surface coassembly was described as follows.<sup>3</sup> SiO<sub>2</sub>-PS<sub>80</sub> (20.0 mg) and PEG<sub>44</sub>-SS-PS<sub>83</sub> BCP (4.0 mg) were dissolved/dispersed in 1.0 mL of THF under sonication. Methanol (7.0 mL) was added into the dispersion through a peristaltic pump. After centrifugation (3500 rpm, 2 min), silica particles at the bottom of the tube were collected and washed with methanol to remove the excess BCP in the solution. The silica particles were dried under reduced pressure.

**Cleavage of Disulfide Bonds with DTT.** A typical procedure for the cleavage reaction of disulfide bonds between the PS and PEG blocks was described as follows. SiO<sub>2</sub>-PS-PEG (20.0 mg) and DTT (10.0 mg) were dissolved/dispersed in 1.0 mL of MeOH under sonication in a 10 mL Schlenk flask. The solution was degassed by three -pump-thaw cycles. After stirring at room temperature for 24 h, SiO<sub>2</sub>-PS-SH were collected by centrifugation (10 000 rpm, 4 min), washed with degassed methanol and dried under reduced pressure.

**The determination of the grafting density.** The thiol-disulfide exchange reaction yields equivalent 2-mercaptopyridine, which has a specific absorption at 375 nm. The concentration of 2-mercaptopyridine in the solution was determined by equation 1, where,  $A$  represents the measured UV-vis absorption value, and  $c$  represents the

concentration of 2-mercaptopyridine (mg/mL) in the solution.

$$A = 56.3c + 0.008 \dots \dots \dots (1)$$

$$\delta = (c\rho_{Si}DVN_A)/(6mM_n) \dots \dots \dots (2)$$

The grafting density ( $\delta$ ) can be calculated by using equation 2. In the equation,  $\rho_{Si}$  is the density of SiO<sub>2</sub> (2.6 mg/cm<sup>3</sup>),  $D$  is the average diameter of SiO<sub>2</sub> (500 nm),  $V$  is the volume of the solution,  $N_A$  is Avogadro's constant,  $m$  is the weight of SiO<sub>2</sub>, and  $M_n$  represents the molecular weight of 2-mercaptopyridine. Based on the equation, the grafting density of pyridyl disulfide was calculated to be around 0.5 chains/nm<sup>2</sup>.

### 1.3 Characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra of CTA-SS-OH, homopolymers and block copolymers were collected on Bruker Avance III 400 MHz spectrometer. The analysis on the apparent molecular weights and dispersities of the linear BCP and the precursors were performed on a size exclusion chromatograph (SEC). The details about the equipment can be found in our previous paper.<sup>4</sup> HRMS analysis of CTA-SS-OH was performed on Varian 7.0 T Fourier transform ion cyclotron resonance mass spectrometer. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum was collected on Bruker Autoflex III spectrometer using  $\alpha$ -cyano-4-hydroxycinnamic acid as the matrix. UV-vis spectra were recorded on a Shimadzu UV-2450 spectrophotometer at room temperature. X-ray photoelectron spectroscopy (XPS) spectra of the silica particles with surface nanostructures were collected on a Kratos Axis Ultra DLD spectrometer equipped with a monochromated Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV). Survey spectra and high-resolution scans were collected after the samples were treated with toluene or water. Transmission electron microscopy (TEM) measurements were performed on a Tecnai G2 20 S-TWIN electron microscope operated at 200 kV. The TEM specimens were prepared by depositing diluted

solutions on Formvar-coated copper grids at room temperature, and the solvents were evaporated at room temperature. Field emission scanning electron microscopy (FE-SEM) images were collected on a SEM (Apreo S LoVac Thermo Scientific), and the samples were coated with Pt for 40 s on a Cressington 108 auto sputter coater. Confocal laser scanning fluorescence microscopy (CLSM) was performed on a LSM 800 with Airyscan at excitation wavelengths of 488 nm. Contact angles were determined on a JC2000D1 contact angle goniometer (Shanghai Zhongchen Digital Technic Apparatus Co.) equipped with an environmental chamber.

## 2. REFERENCES

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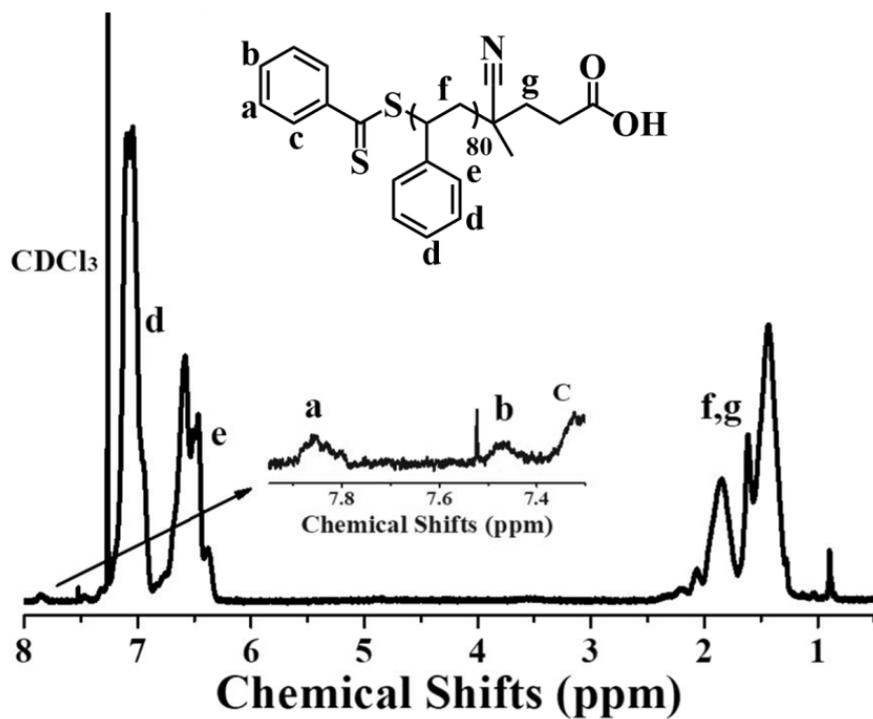
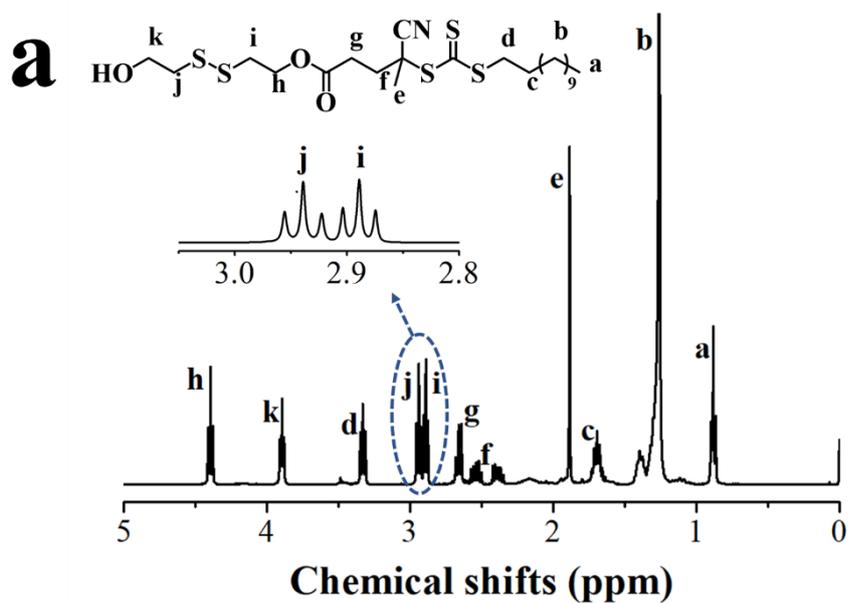
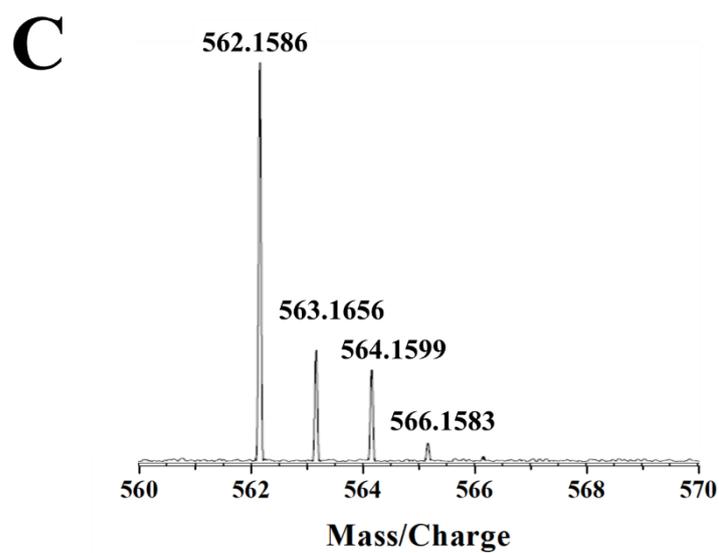
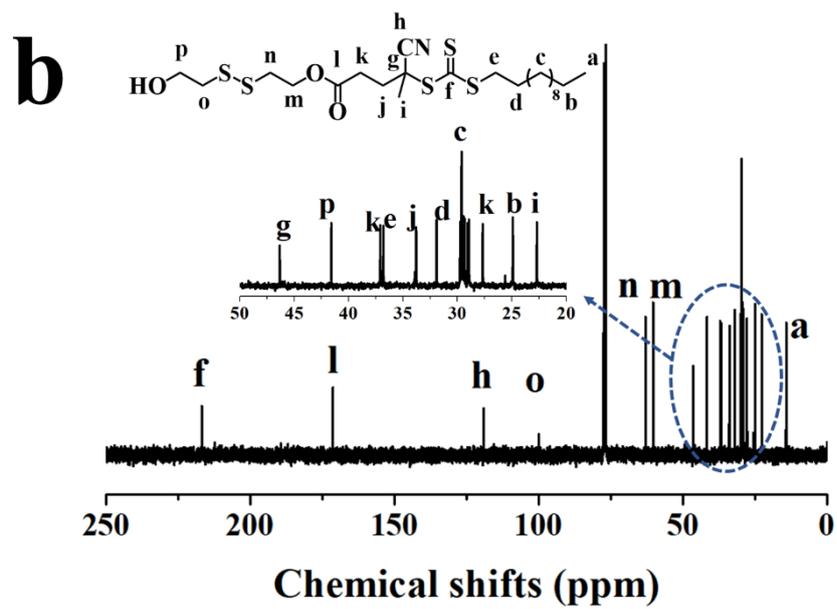


Fig. S2.  $^1\text{H}$  NMR spectrum of  $\text{PS}_{80}$  synthesized by RAFT polymerization.





**Fig. S3.** (a) <sup>1</sup>H NMR, (b) <sup>13</sup>C NMR and (c) high-resolution mass spectra of CTA-SS-OH.

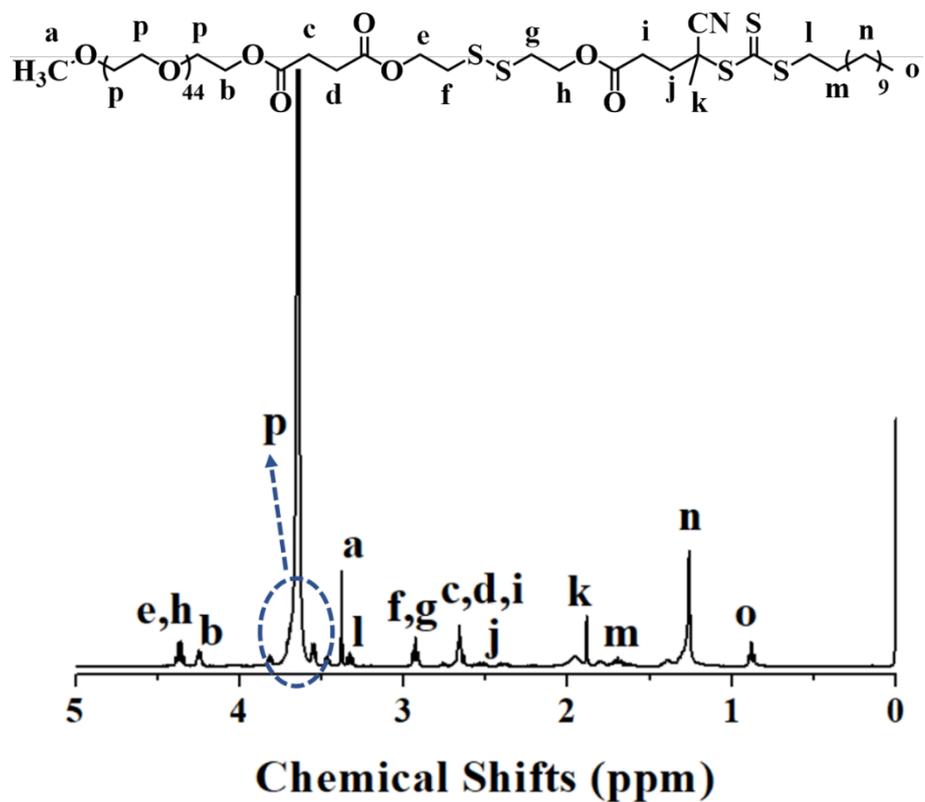
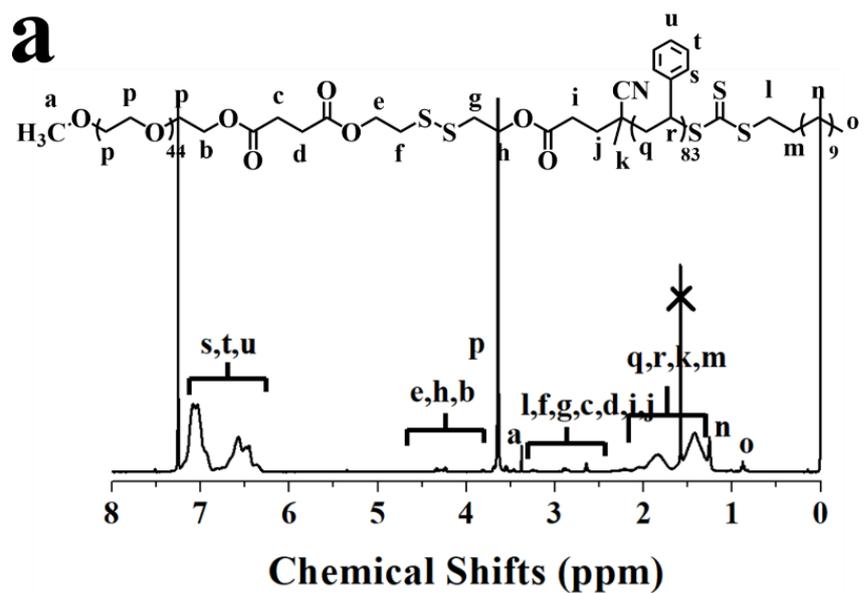
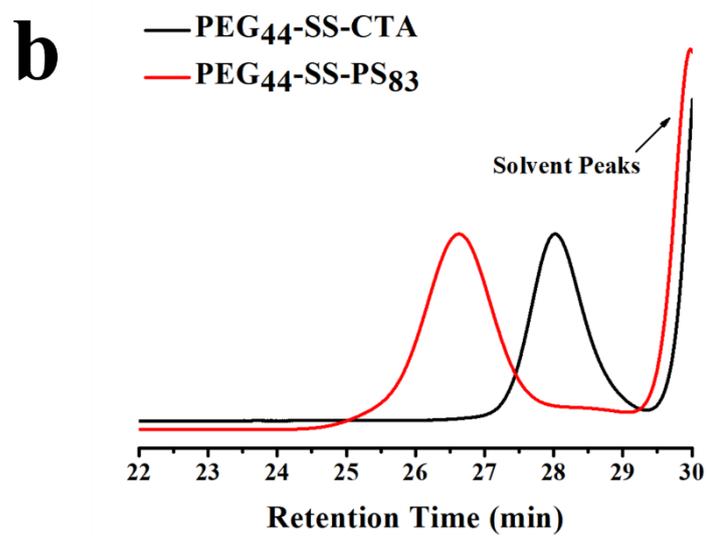
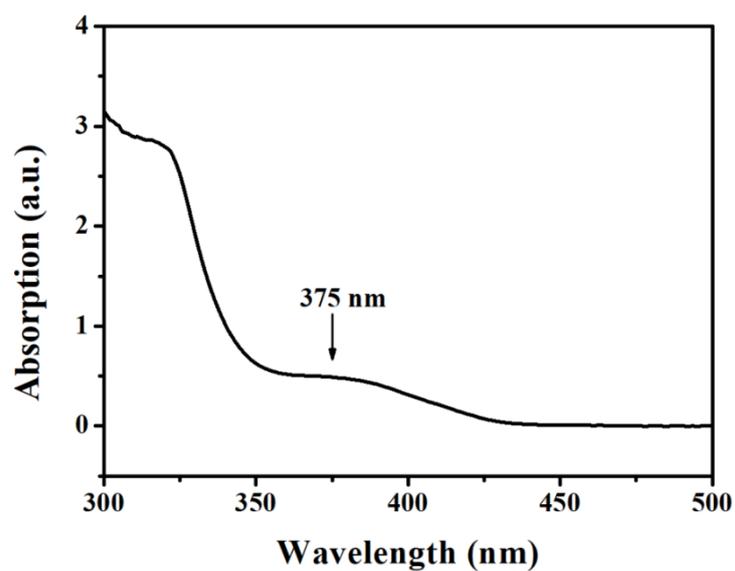


Fig. S4. <sup>1</sup>H NMR spectrum of PEG<sub>44</sub>-SS-CTA.

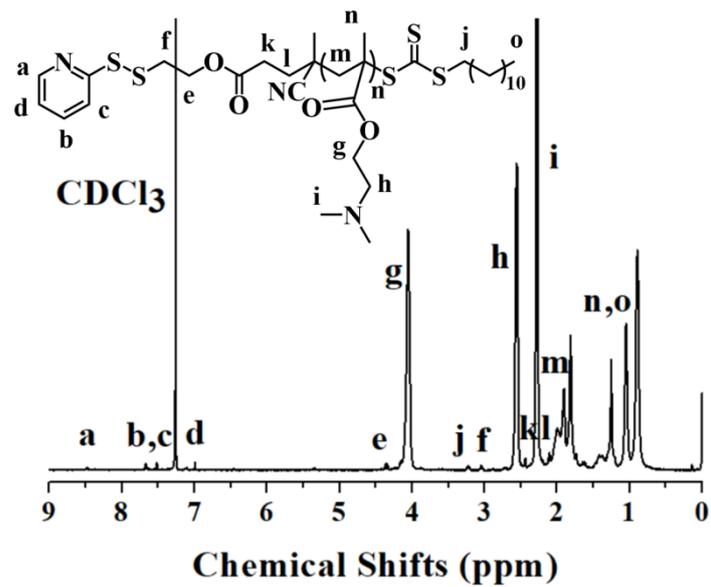




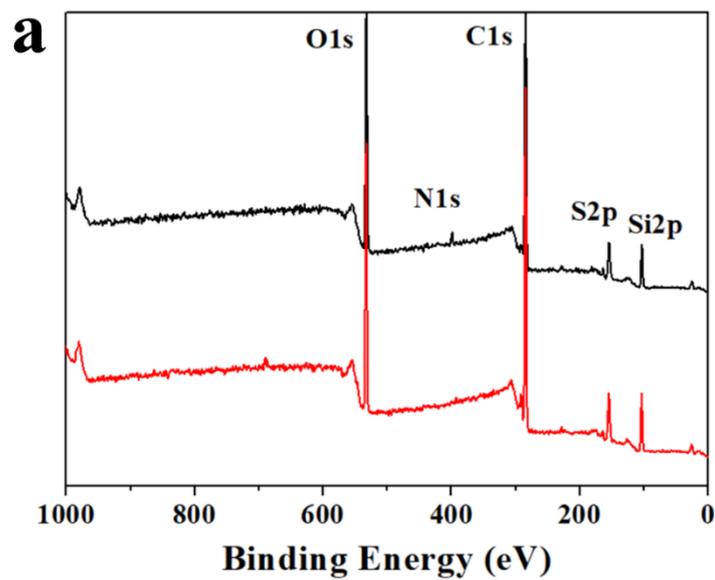
**Fig. S5.** (a) <sup>1</sup>H NMR spectrum of PEG<sub>44</sub>-SS-PS<sub>83</sub> BCP and (b) SEC curves of PEG<sub>44</sub>-SS-CTA and PEG<sub>44</sub>-SS-PS<sub>83</sub>.

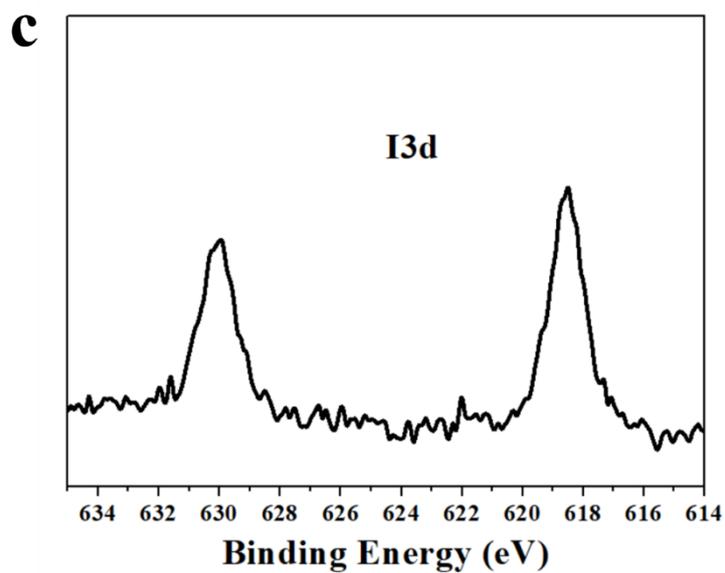
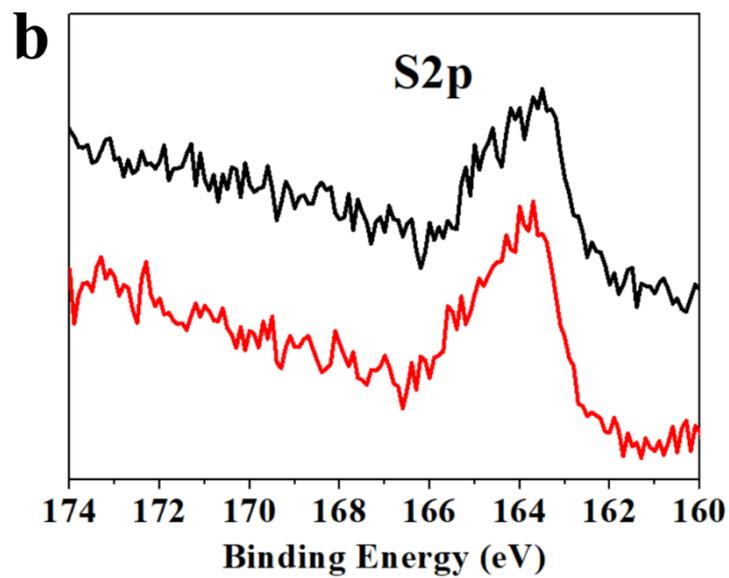


**Fig. S6.** UV-vis absorption of 2-mercaptopyridine produced in the thiol–disulfide reaction between SiO<sub>2</sub>-PS-SH and 2,2'-dipyridyl disulfide.

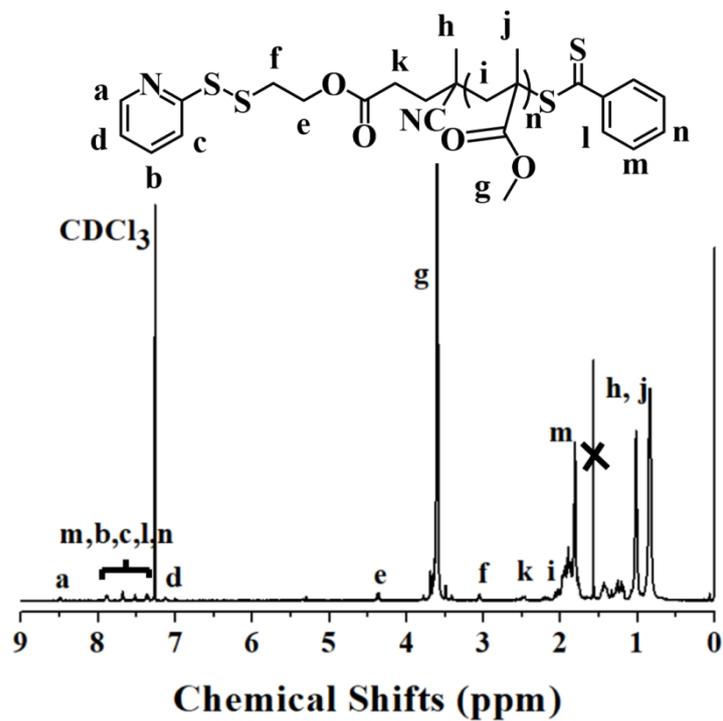


**Fig. S7.**  $^1\text{H}$  NMR of PDMAEMA<sub>91</sub>-SS-py synthesized by RAFT polymerization.

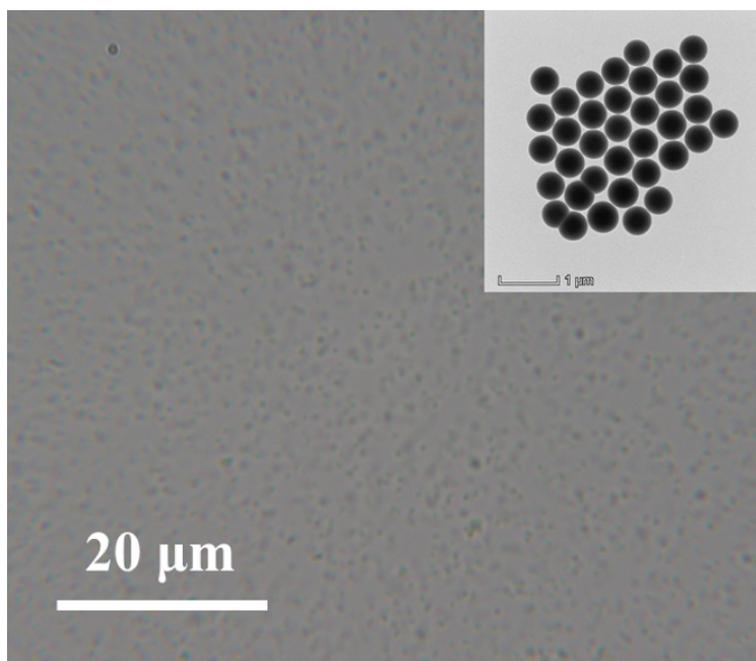




**Fig. S8.** XPS wide-scan (a) and high-resolution S2p scan of SiO<sub>2</sub>-PS-PDMAEMA<sub>91</sub> (dark) and SiO<sub>2</sub>-PS-SH (red), and (c) high-resolution I3d scan of SiO<sub>2</sub>-PS-PDMAEMA<sub>91</sub> after quaternization of PDMAEMA.



**Fig. S9.**  $^1\text{H}$  NMR spectrum of  $\text{PMMA}_{45}\text{-SS-py}$ .



**Fig. S10.** Optical microscopy image of the  $\text{SiO}_2\text{-PS-PMMA}_{45}$  particles dispersed in acetone. The inset shows the TEM image of the  $\text{SiO}_2\text{-PS-PMMA}_{45}$  particles prepared from the acetone dispersion.

