

Supplementary Information

Thermoresponsive Silver/Polymer Nanohybrids with Switchable Metal Enhanced Fluorescence

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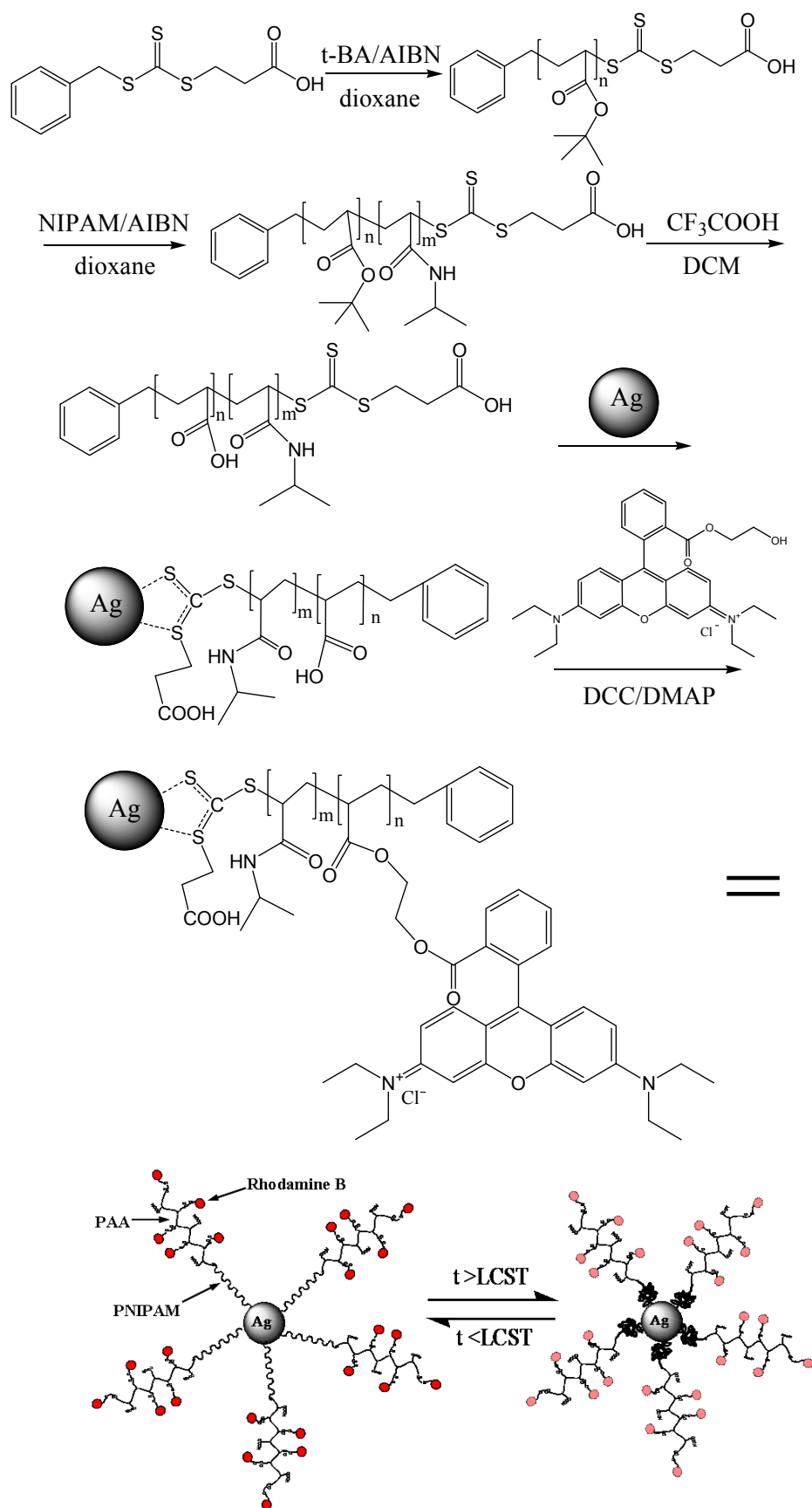
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S1. Materials and Regents

Tert-butyl acrylate (t-BA, Aladdin, 99%), 2,2'-azobis(isobutyronitrile) (AIBN, 98%, Sigma-Aldrich), dioxane (Tianjin, AR), n-hexane (Fuyu, AR), N-isopropylamide (NIPAM, Aladdin, 99%), dichloromethane (DCM, Yongda, AR), diethyl ether (Laiyang, AR), trifluoroacetic acid (Kefeng in Shanghai, AR), tetrahydrofuran (THF, Guangcheng, AR), ethanol (Laiyang, AR), N,N'-dicyclohexyl carbodiimide (DCC, Adamas-beta, 99%), 4-dimethylamino pyridine (DMAP, Aldrich, 99%), ethylene glycol (Fuyu, AR), Rhodamine B (Adamas-beta, 99%), polyvinylpyrrolidone (PVP, Ruijinte in Tianjin, AR), glucose monohydrate (Guangfu in Tianjin, AR), sodium citrate dihydrate (Dengke in Tianjin, AR), ammonia solution (Sanhe in Yantai, AR), silver nitrate (Sinopharm Chemical Regent, AR), RAFT agent (3-(Benzylsulfanylthiocarbonylsulfanyl)-propionic Acid, BSPA) was synthesized using an published procedure.^{1,2}

S2. Preparation of Fluorescent Silver Nanohybrids

The preparation of fluorescent silver nanohybrids is summarized in Scheme s1.



Scheme S1. Schematic of the synthesis of di-block copolymer PAA-*b*-PNIPAM by RAFT polymerization and hydrolysis, and use it to modify AgNPs and the subsequent attachment of fluorescent Rhodamine B.

S2.1. Syntheses of silver nanoparticles and Rhodamine B ethanol ester

Synthesis of Silver Nanoparticles

AgNPs was synthesized using a citrate reduction according to the published procedures.³

Synthesis of Rhodamine B ethanol ester

Ethylene glycol (0.647g, 1.04×10^{-2} mol), DCC (0.516 g, 2.5×10^{-3} mol) and DMAP (0.031g, 2.5×10^{-4} mol) were dissolved in DCM (20ml), followed by the dropwise addition of Rhodamine B (1g, 2.1×10^{-3} mol) DCM solution. The mixture was stirred at room temperature for 12 h. The resulting product was washed by diluted hydrochloric acid for three times to remove excessive ethylene glycol. ¹HNMR confirmed the expected structure as shown in Figure S1.

¹HNMR (CDCl₃, 298K, 600MHz), δ (ppm from TMS): 8.41-8.46 (1H, a), 7.7-7.8 (2H, b and c), 7.48 (1H, d), 7.10 (2H, e), 6.87(2H, f), 6.85(2H, g), 4.10 (2H, l), 3.45-3.66 (10H, m and j), 0.99-1.33 (12H, k).

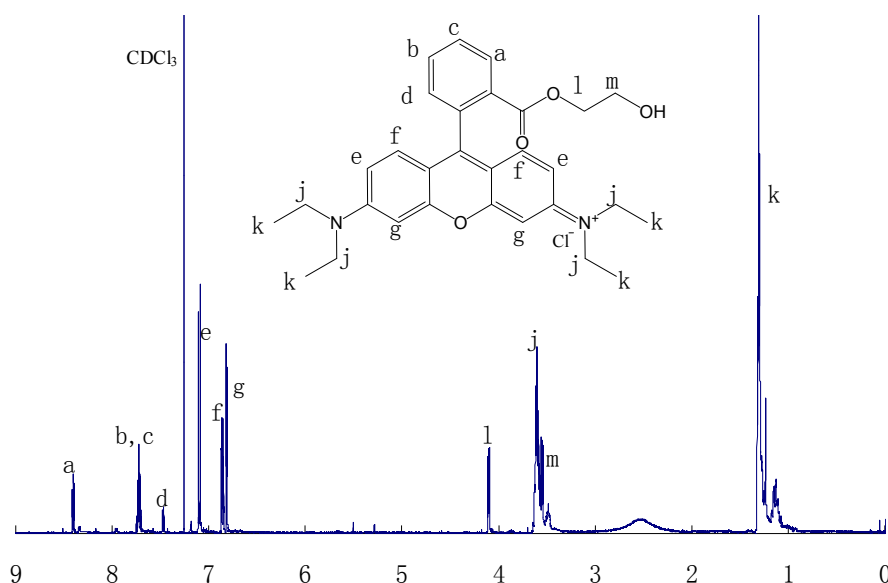


Figure S1. ¹HNMR spectrum of Rhodamine B ethanol ester in CDCl₃ (298K, 600MHz).

S2.2. RAFT Polymerizations

Homopolymerization of Pt-BA Controlled by the 3-(Benzylsulfanylthiocarbonylsulfanyl)-propionic Acid (BSPA) as RAFT Agent

A solution of Pt-BA (5 g, 0.039 mol), RAFT agent (BSPA, 0.106 g, 3.9×10^{-4} mol), and AIBN (21.3 mg, 1.30×10^{-4} mol) in dioxane (20mL) was prepared, followed by the deoxygenation with nitrogen for 30 min. The resulting mixture was then incubated in a preheated oil bath at 75 °C for 7 hours to afford expected poly(Pt-BA), which was purified by repeated precipitation in hexane and dried under vacuum.

Chain Extension Using MacroRAFT in the presence of NIPAM

A solution of NIPAM (0.530 g, 4.7×10^{-3} mol), macro-RAFT agent [poly(Pt-BA)] (0.303 g, 2.37×10^{-3} mol), and AIBN (1.28 mg, 7.81×10^{-6} mol) in 5 mL dioxane was prepared to afford a homogeneous solution. After deoxygenation with nitrogen for 30 min, the resulting mixture was incubated in a preheated oil bath at 75 °C for 7 hours. The obtained block copolymer was purified by repeated precipitation in cold diethyl ether for three times. The different di-block copolymers with different PNIPAM polymerization degrees (DP) were synthesized with the same macro-RAFT agent [poly(Pt-BA)] via RAFT polymerization via manipulation of the portion of NIPAM. The purified copolymer was characterized by the ^1H NMR as shown in Figure S2a.

Hydrolysis of PNIPAM-block-Pt-BA

The obtained block copolymer (0.7 g) was dissolved in THF (10 ml) completely, and then trifluoroacetic acid (0.5 g, 4.4×10^{-3} mol) was added. The resulting mixture was slowly stirred for 48 hours and then precipitated in cold diethyl ether for three times to obtain the expected PNIPAM-*b*-PAA, which was characterized by ^1H NMR as shown in Figure S2b.

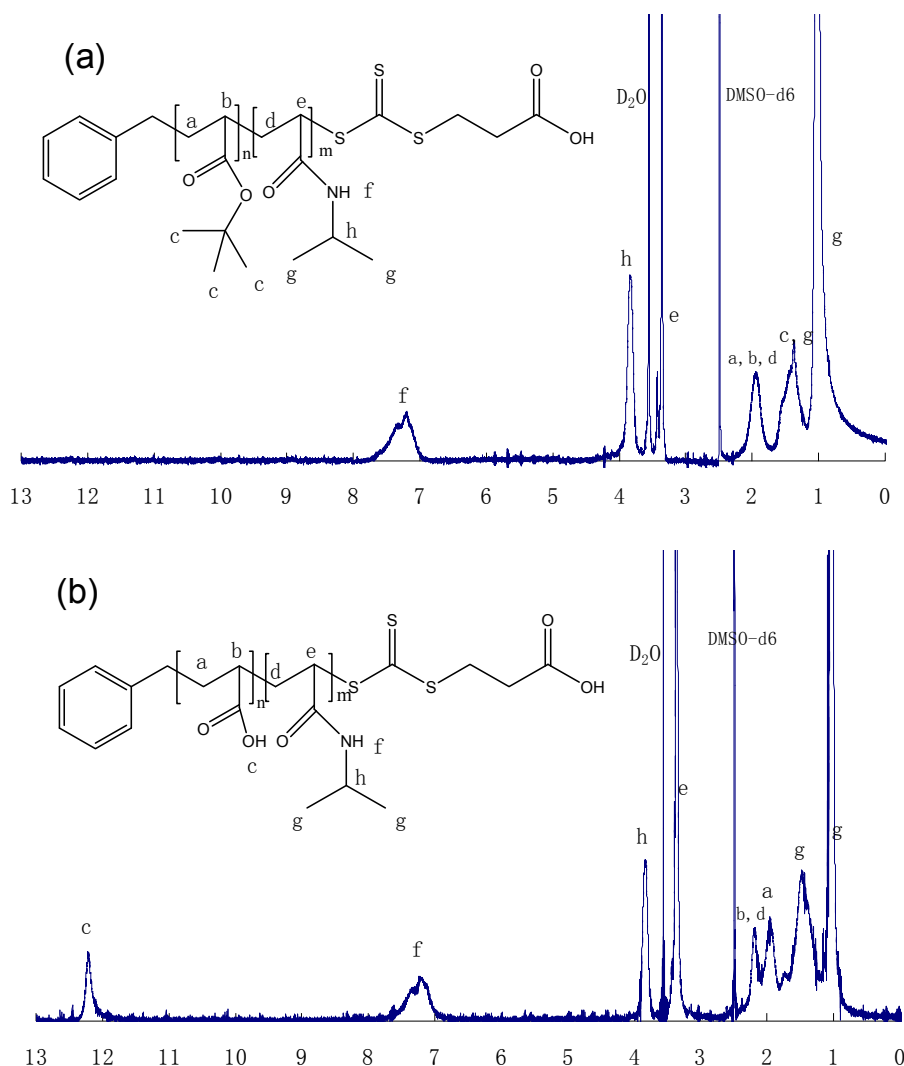


Figure S2. ^1H NMR spectra of block polymers before and after hydrolysis in DMSO- d_6 (298K, 600KMz): (a) block polymer PNIPAM-*b*-Pt-BA, and (b) PNIPAM-*b*-PAA.

S2.3. Grafting of Block Copolymer PNIPAM-*b*-PAA to AgNPs

Copolymer PNIPAM-*b*-PAA was dissolved in ethanol (10 ml), followed by the addition of previously prepared AgNPs solution (5 ml, 0.03 mg/ml), the resulting mixture was kept stirring for 24 hours. The particles were purified by repeated centrifugation below 10°C and re-dispersed in acetone for attachment of Rhodamine B.

S2.4. Preparation of Fluorescent AgNPs/polymer Nanoparticles

The polymer-coated AgNPs were re-dispersed in acetone (6ml), followed by the addition of Rhodamine B ethanol ester (0.167 g, 3.19×10^{-4} mol), DCC (0.079g, 3.83×10^{-4} mol) and DMAP (0.0053g, 3.83×10^{-5} mol). The resulting mixture was stirred for 12 hours and then subject to dialysis in acetone to afford fluorescence functionalized silver nanoparticles, which was then characterized by fluorescence spectrometer, polarizing microscope, DLS and TEM.

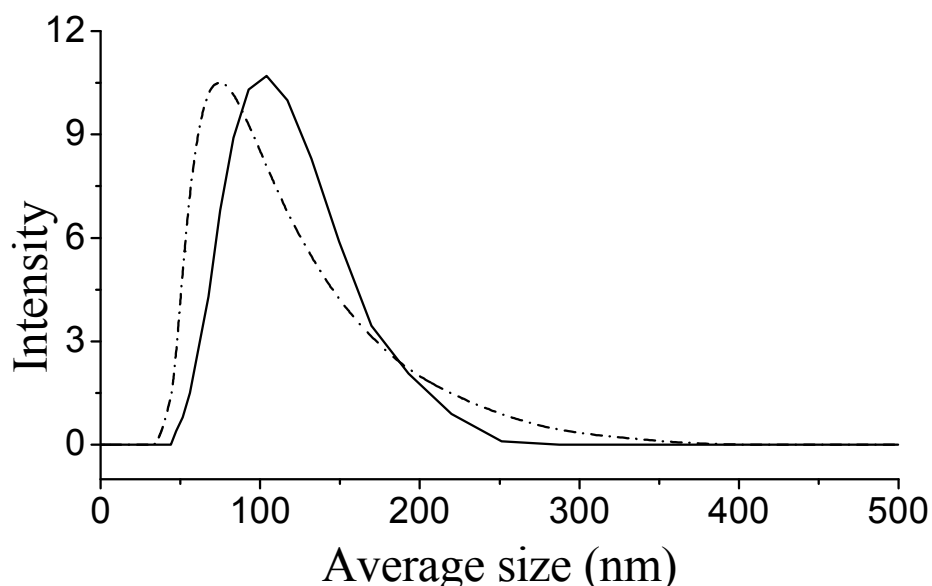


Figure S3. The average size of fluorescent nanohybrids at different solution temperature. (The broken line represent the size at 40 °C and the continuous line the size at 20 °C.

S3. Analyses

S3.1. Gel permeation chromatography.

Gel permeation chromatography (GPC) was performed in N,N-dimethylacetamide (DMAc) (0.03%w/v LiBr, 0.05% BHT stabilizer) at 50°C (flow rate: 0.85 ml min^{-1}) using a Shimadzu modular system comprised of a DGU-12A solvent degasser, an LC-10AT pump, a CTO-10A column oven, and an RID-10A refractive index detector. The system was equipped with a Polymer Laboratories 5.0 mm bead-size guard column ($50 \times 7.8 \text{ mm}^2$) followed by four $300 \times 7.8 \text{ mm}^2$ linear PL columns (10^5 , 10^4 , 10^3 , and 500 g mol^{-1}). Calibration was performed with low polydispersity polystyrene standards ranging from 500 to 10^6 g mol^{-1} .

S3.2 NMR spectroscopy. ^1H NMR spectra of Rhodamine B ethanediol ester and copolymers were obtained using a JNM-ECP 600 (600MHz) spectrometer, with CDCl_3 or DMSO-d_6 used as deuterated solvent.

S3.3. Dynamic Light Scattering (DLS).

Dynamic light scattering studies of fluorescence functionalized silver nanoparticles at 1 mg/ml in aqueous media were conducted using MALVERN-HPPS Dynamic Light Scattering at different temperatures. The sizes of fluorescence functionalized silver nanoparticles were measured by changing temperature with DLS which was performed using a Malvern Zetasizer Nano Series running DTS software and operating a 4mW He-Ne laser at 633 nm. AgNPs (or AgNPs/polymer) solution was prepared in distilled water with AgNPs/polymer concentration of 1 mg/ml. The solution was filtered through Millipore nylon filters (pore size 0.45 μ m) to eliminate dust and large contaminants. The size measurements were carried out in quartz cuvette and the temperature changing from 20 $^{\circ}$ C to 40 $^{\circ}$ C was allowed to equilibrate for 5 min.

S3.4 Fluorescent Spectroscopy.

Fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer at the excitation wavelength of 559 nm. The excitation/emission slits were set at 5.0 nm for both excitation and emission.

S3.5 Polarizing Microscope.

Samples were coated onto glass slide by spincoating and the images of fluorescent AgNPs were obtained using a Nikon Eclipse E600 microscope equipped with a Nikon DXN1200 digital camera and a Nikon Plan Fluor 50 \times objective (Nikon, Tokio, Japan). The excitation laser was reflected by a polarized mirror to a high numerical aperture (NA) oil objective (50 \times) and focused to a diffraction limited spot (\sim 300 nm) on the sample surface. Fluorescence emission from Rhodamine B modified nanoparticles was collected by an avalanche photodiode through the polarized beam splitter and a band-pass filter.

S3.6 Transmission Electron Microscopy (TEM).

The images of the fluorescent nanoparticles were obtained using a transmission electron microscopy JEOL JEM-1200EX TEM at an accelerating voltage of 100 kV. The particles were dispersed in acetone (1mg/mL) and deposited onto 200 mesh, holey film, carbon grid and allowed to air-dry at room temperature. Phosphotungsten acid was used as contrast agent to observe the polymer corona of the fluorescent AgNPs.

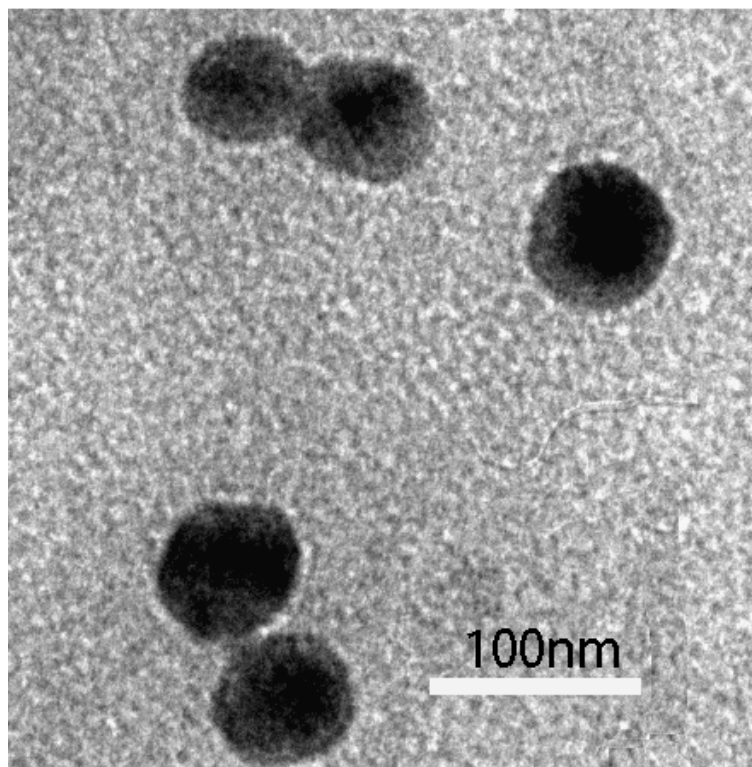


Figure S4. Transmission electron microscopy (TEM) image of the fluorescent silver nanohybrids

References:

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- (2) Boyer, C.; Bulmus, V.; Davis, T. P. *Macromolecular Rapid Communications* **2009**, *30*, 493-497.
- (3) Munro, C. H.; Smith, W. E.; Garner, M.; Clarkson, J.; White, P. C. *Langmuir* **1995**, *11*, 3712-3720.