Supporting Information

of

Reversible vesicles of supramolecularly hybrid nanoparticles

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EXPERIMETAL SECTION

Materials. *N*-isopropyl acrylamide (NIPAM) purchased from Tokyo Kasei Kagyo Co. was recrystallized three times from benzene/hexane (65:35 v/v) prior to use. *N,N*-dimethyl acrylamide (DMA) from Tokyo Kasei Kagyo Co. was distilled under reduced pressure before polymerization. 4-Phenylazophenol (97%) was purchased from Alfa Aesar. Azobisisobutyronitrile (AIBN, CP) supplied by Sinopharm Chemical Reagent Co. was recrystallized from ethanol before use. α-CD@AuNP was prepared by reported procedure[1]. Unless specially mentioned, all other chemicals were used as received.

Characterization methods. ^{1}H NMR spectra were recorded with a JEOL ECA-400 spectrometer. Gel permeation chromatography (GPC) analysis was carried out with a Waters Breeze 1515 GPC analysis system with two PL mix-D columns, using DMF with 0.5 M LiBr as eluent at the flow rate of 1 mL/min at 80°C, and PEO calibration kit (purchased from TOSOH) was employed as the calibration standard. UV-vis spectrum was recorded in a conventional quartz cell (light path 10 mm) on a Perkin-Elmer Lambda 35 spectrophotometer. Dynamic light scattering studies were conducted using ALV/5000E laser light scattering (LLS) spectrometers at scattering angle of 90°, CONTIN analysis was used for the extraction of $<R_h>$ data. All the measurements were carried out after incubation at a given temperature for 30 minutes with a typical heating/cooling rate of 2°C/min. The AFM images were acquired in tapping mode by using a Nanoscope IV from Digital Instruments equipped with a silicon cantilever with 125 imand E-type vertical engage piezoelectric scanner. The TEM images were acquired by using a JEOL-2010 instrument. Samples for AFM and TEM observation were prepared in the following way: one drop of solution after incubation of 30 minutes at the given temperature was loaded on mica surface or copper grid and then dried at the same temperature. Thermogravimetric analysis (TGA) measurements were carried out on a Perkin-Elmer Pyris-1 series thermal analysis system under a flowing nitrogen atmosphere at a scan rate of 20°C/min.

Synthesis of chain transfer agent. The synthesis of azobenzene-protected RAFT chain transfer agent (Azo-CTA) has been describe in our previous work[2].

RAFT polymerization of Azo-PNIPAM. Briefly, polymerization was conducted under argon at 70°C in 1,4-dioxane employing Azo-CTA as RAFT agent and AIBN as initiator. A representative polymerization procedure is as follows. NIPAM (1g, 8.85 mmol), CTA (0.045 mmol), AIBN (0.013 mmol) and 3 mL 1,4-dioxane were sealed in a flask equipped with a magnetic stir bar, followed by three freeze-thaw cycles. The reaction flask filled with argon was placed in a preheated oil bath at 70°C. The polymerization was quenched after 5 h by removing the reaction flask from heat followed by cooling in liquid nitrogen immediately. The polymer was precipitated into cold ethyl ether, filtrated and dissolved in THF to be precipitated again. The procedure was repeated for three times and the polymer was obtained as powder after drying under vacuum at room temperature for 12 h. GPC (Figure S4) exhibited satisfactory PDI around 1.22.

RAFT polymerization of Azo-PNIPAM-*b*-PDMA. The same procedure as preparation of Azo-PNIPAM was applied, except that Azo-PNIPAM was used as macro-RAFT chain transfer agent instead of Azo-CTA. GPC (Figure S4) exhibited PDI around 1.24. The polymers were also characterized by ^{1}H NMR (Figure S5).

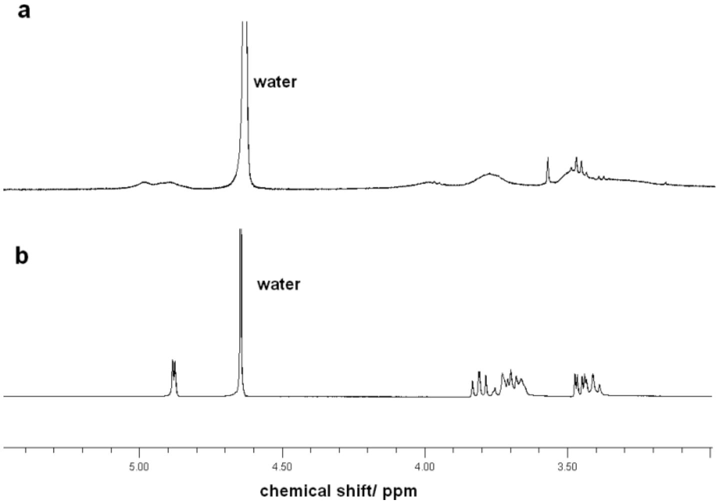

Figure S1. ^{1}H NMR spectrum of a) α-CD@AuNP in D_2O, b) perthiolated α-CD in D_2O

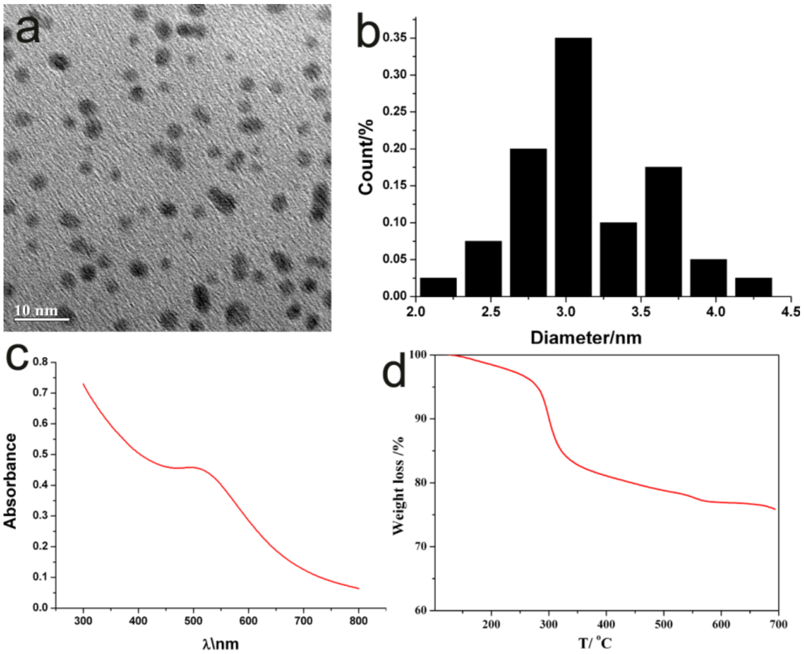

Figure S2. Characterization results of α-CD@AuNPs: a) TEM image, b) size distribution calculated from TEM observation, c) UV-vis absorption spectrum (0.1 mg/mL aqueous solution), d) thermogravimetric analysis (TGA).

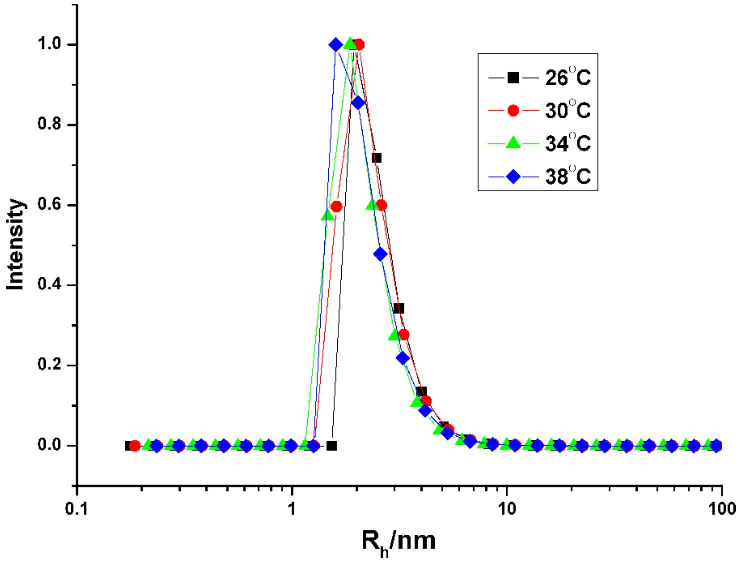

Figure S3. Size distribution (<R_h>) of α-CD@AuNP (0.1 mg/mL in water).

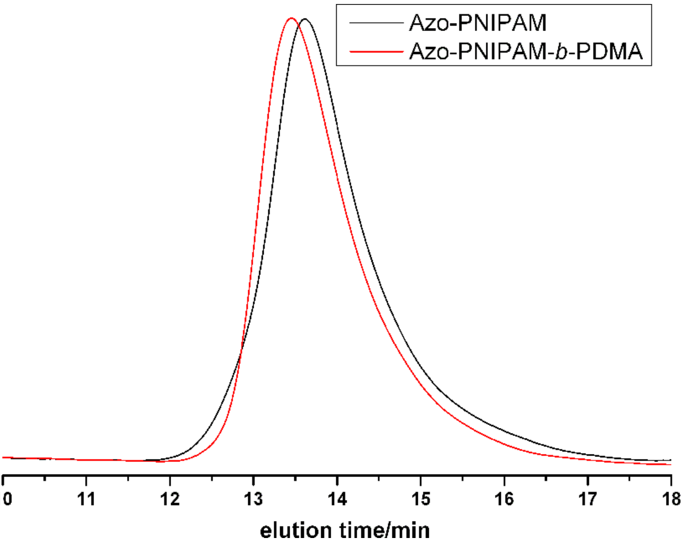

Figure S4. GPC results of Azo-PNIPAM (PDI 1.22) and Azo-PNIPAM-*b*-PDMA (PDI 1.24).

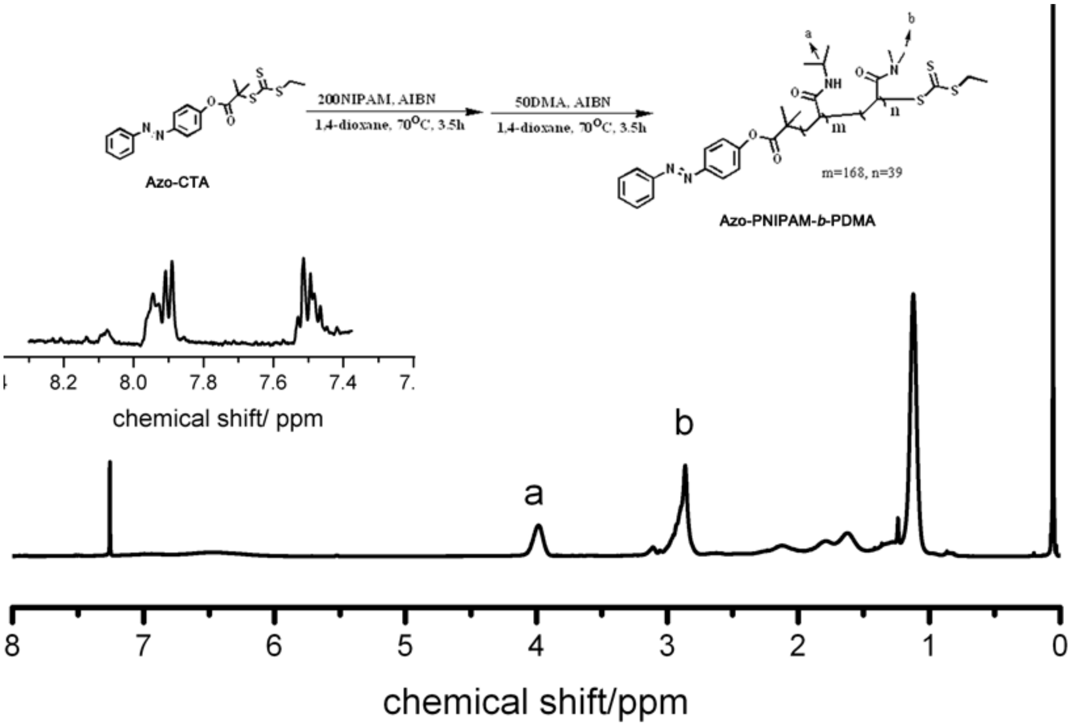

Figure S5. (top) Preparation of Azo-PNIPAM-*b*-PDMA from Azo-CTA. (bottom) ^{1}H NMR results of Azo-PNIPAM-*b*-PDMA (the inserted image shows the signals of Azo group).

Calculation detail of theoretical organic content of HIC

Mass of AuNP: M_1

Mass of α-CD: $M_1 \times 20\%$

Mass of Azo-PNIPAM-*b*-PDMA : $M_2 = (M_1 \times 20\% \div M_{\alpha\text{-CD}}) \times M_{block}$

Organic content of HIC: $a=(M_2+ M_1 \times 20\%) \div (M1+M2)$

$\because M_{\alpha\text{-CD}}=1068$ g/mol

$M_{block}=23000$ g/mol

$\therefore a=85\%$

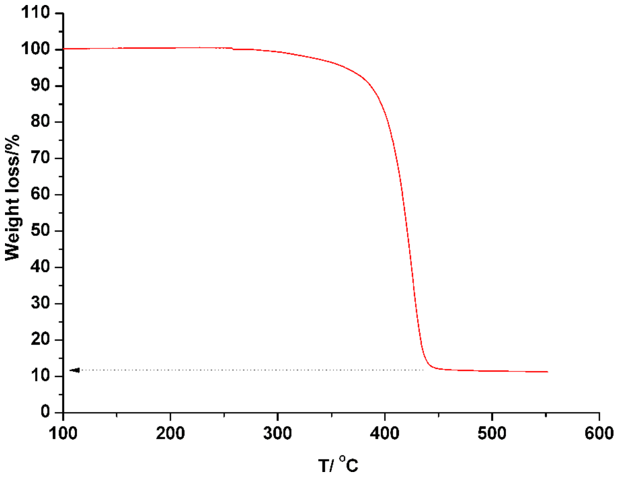

Figure S6. TGA result of HIC.

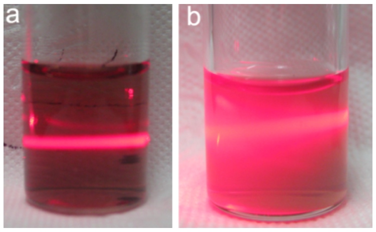

Figure S7. Pictures taken under laser pointer: a) transparent solution of HIC-vesicle at 42°C, showing strong Tyndall effect; b) precipitation of HIC-homo consisting of Azo-PNIPAM in aqueous solution at 32°C.

Reference:

1) Liu J, Alvarez J, Ong W, Roman E, and Kaifer AE. Journal of the American Chemical Society 2001;123(45):11148-11154.

2) Liu JH, Chen GS, Guo MY, and Jiang M. Macromolecules 2010;43(19):8086-8093.