

Supporting Information

Polyelectrolyte Nanocages via Crystallized Miniemulsion Droplets

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Experimental Section

Measurements. ^1H NMR (500 MHz) spectra were acquired in CDCl_3 using a Varian INOVA-500 spectrometer at 25 °C. Tetramethylsilane (TMS) was used as an internal reference for ^1H NMR spectroscopy. FT-IR spectra were obtained on a Bruker Tensor 27 system using attenuated total reflectance (ATR) sampling accessories. High resolution mass spectra were obtained on a ThermoFinnigan MAT XL spectrometer.

Atomic force microscopy (AFM) measurements were performed on an Asylum Research MFP-3D AFM instrument operating in tapping mode. The AFM samples were prepared from dilute sample solutions (0.1 mg/mL in water) by solvent casting on fresh cleaved mica. The measurements were conducted in air at ambient conditions by using Si cantilevers with a spring constant of ca. 20-95 N/m and a resonance frequency of about 145-230 kHz, with image resolution of 512×512 points and a scan rate of 1 Hz. The AFM tip was purchased from Nanoscience Instruments with a tip radius smaller than 10 nm.

Transmission electron microscopy (TEM) images were obtained by using a JEOL 2010 microscope. TEM samples were prepared by solvent casting on 300 mesh carbon-coated copper grids from dilute sample solutions (0.1 mg/mL in water). The TEM samples were stained with saturated uranyl acetate aqueous solution for 10 minute prior to TEM measurements.

Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q200 system with a RCS-90 cooling device under nitrogen in the temperature range of 10-60 °C, with a heating rate of 5 °C/min.

Dynamic light scattering (DLS) measurements were performed using a Nano ZS90 Zetasizer (Malvern Instruments). A 4 mW 633 nm HeNe laser was used as the light source and all experiments were performed at a temperature of 25.0 °C at a measuring angle of 90° to the incident laser beam. The correlation decay functions were analyzed by cumulants method to obtain size distribution. All determinations were repeated five times.

Materials. 2,2-Diphenyl-1-picryl-hydrazyl (DPPH), 2-(dimethylamino)ethyl acrylate (98%), 1-bromodocosane (96%), and acryloyl acid (99%) were purchased from Aldrich. 2,2-Dimethoxy-2-phenylacetophenone (DMPA, 99%), n-docosane (n-DS; 99%), *N,N*-dimethanolmethylamine (99+%), 4-dimethylaminopyridine (DMAP; 99+%), and *N,N'*-dicyclohexyl-carbodiimide (DCC, 99%) were purchased from Acros. Dichloromethane (DCM; HPLC), Tetrahydrofuran (THF; HPLC), diethyl ether (HPLC), methanol (HPLC), toluene (HPLC), and acetonitrile (HPLC) were purchased from Fisher. Uranyl acetate dihydrate was purchased from Ted Pella. All other chemicals were used without further purification unless stated otherwise.

Synthesis of Monoacryloyl-Functionalized Monomer Surfactant. 1-Bromodocosane (2.80 g, 7.20 mmol) and 2-(dimethylamino)ethyl acrylate (0.86 g, 6.00 mmol) were dissolved in 15 mL of 30% methanol-acetonitrile. With the presence of a catalytic amount of DPPH, the reaction was conducted at reflux condition for 48 h. After evaporation to remove solvent, the product was purified by flash chromatography on silica gel using 15% methanol-DCM as eluent ($R_f \sim 0.3$) to give 1.98 g of the monomer surfactant as a slightly yellow solid (yield: 73%). IR (cm^{-1}): 2915 (strong), 2847 (strong), 1729 (strong), 1632 (weak), 1473 (medium-strong), 1416 (medium), 1297 (medium), 1191 (strong), 1174 (strong), 1063 (weak), 1040 (weak), 995 (medium), 947 (medium),

910 (medium), 870 (weak), 844 (weak), 816 (medium), 802 (medium), 733 (medium), 719 (medium), 665 (weak). ^1H NMR (500 MHz, CDCl_3 , 25 °C, TMS): δ 0.88 (t, 3H, $\text{CH}_3\text{-CH}_2$), 1.25-1.35 (m, 38H, CH_2), 1.75 (m, 2H, CH_2), 3.53 (s, 6H, $\text{CH}_3\text{-N}^+\text{-CH}_3$), 3.61 (t, 2H, $\text{CH}_2\text{-N}^+$), 4.17 (m, 2H, $\text{N}^+\text{-CH}_2\text{-CH}_2\text{-O}$), 4.67 (m, 2H, $\text{N}^+\text{-CH}_2\text{-CH}_2\text{-O}$), 5.95 (m, 1H, $\text{CH}=\text{CH}_2$), 6.15 (m, 1H, $\text{CH}=\text{CH}_2$), 6.51 (m, 1H, $\text{CH}=\text{CH}_2$). HRMS (ESI) calcd. for $[\text{M}]^+$ $\text{C}_{29}\text{H}_{58}\text{NO}_2$: 452.4462; found: 452.44519.

Synthesis of Diol-Functionalized Quaternary Ammonium Bromide. 1-Bromodocosane (5.00 g, 12.8 mmol) and *N,N*-dimethanolmethylamine (15.4 g, 128 mmol) were dissolved into 140 mL of 50% toluene-acetonitrile. The reaction was conducted at 100 °C for 24 h. The organic solvent was evaporated under reduced pressure. The precipitated product was filtered, washed with cold diethyl ether and dried in vacuum oven at 50 °C, to give 6.29 g of the targeted compound as a white solid (yield: 97%). IR (cm^{-1}): 3500-3100 (strong), 2915 (strong), 2848 (strong), 1485 (medium-strong), 1476 (medium), 1461 (strong), 1416 (medium-strong), 1086 (medium-strong), 1054 (medium-strong), 1028 (medium), 917 (medium), 902 (medium), 887 (weak), 858 (weak), 801 (medium), 729 (medium), 718 (medium). ^1H NMR (500 MHz, CDCl_3 , 25 °C, TMS): δ 0.89 (t, 3H, CH_3), 1.22-1.42 (m, 38H, CH_2), 1.76 (m, 2H, CH_2), 3.31 (s, 3H, $\text{CH}_3\text{-N}^+$), 3.52 (m, 2H, $\text{CH}_2\text{-N}^+$), 3.83 (m, 4H, $\text{HO-CH}_2\text{-CH}_2\text{-N}^+$), 4.18 (m, 4H, $\text{HO-CH}_2\text{-CH}_2\text{-N}^+$). HRMS (ESI) calcd. for $[\text{M}]^+$ $\text{C}_{27}\text{H}_{58}\text{NO}_2$: 428.4462; found: 428.44611.

Synthesis of Diacryloyl-Functionalized Cross-Linker Surfactant. The diol-functionalized quaternary ammonium bromide (1.00 g, 1.96 mmol), acryloyl acid (0.35 g, 4.91 mmol), DCC (1.01 g, 4.91 mmol) and DMAP (0.05 g, 0.39 mmol) were dissolved in DCM (20 mL). The reaction was conducted for 24 h at room temperature under nitrogen.

The reaction mixture was filtered and the organic solvent was evaporated. After purification by flash chromatography on silica gel using 15% methanol-DCM as eluent ($R_f \sim 0.3$), 0.93 g of the cross-linker surfactant was obtained as a slight yellow solid (yield: 77%). IR (cm^{-1}): 2920 (strong), 2850 (strong), 1728 (strong), 1639 (weak), 1470 (medium-strong), 1408 (medium), 1362 (weak), 1297 (medium), 1267 (medium-strong), 1187 (strong), 1070 (medium), 981 (medium), 806 (medium), 723 (medium). ^1H NMR (500 MHz, CDCl_3 , 25 °C, TMS): δ 0.89 (t, 3H, $\text{CH}_3\text{-CH}_2$), 1.22-1.42 (m, 38H, CH_2), 1.78 (m, 2H, CH_2), 3.53 (s, 3H, $\text{CH}_3\text{-N}^+$), 3.61 (m, 2H, $\text{CH}_2\text{-N}^+$), 4.20-4.32 (m, 4H, $\text{N}^+\text{-CH}_2\text{-CH}_2\text{-O}$), 4.75 (m, 4H, $\text{N}^+\text{-CH}_2\text{-CH}_2\text{-O}$), 5.95 (m, 2H, $\text{CH}=\text{CH}_2$), 6.15 (m, 2H, $\text{CH}=\text{CH}_2$), 6.51 (m, 2H, $\text{CH}=\text{CH}_2$). HRMS (ESI) calcd. for $[\text{M}]^+$ $\text{C}_{33}\text{H}_{62}\text{NO}_4$: 536.4673; found: 536.46606.

Synthesis of Nanocages. The monomer surfactant (30 mg), the cross-linker surfactant (30 mg), docosane (71 mg, 2 wt%), and photoinitiator DMPA (1 mg) were added into water (3.53 g). The mixture was ultrasonicated for 30 min at 50 °C. The resulting transparent miniemulsion was cooled down to 21 °C (r.t.), and purged with nitrogen for 10 min. Polymerization was induced by UV irradiation ($\lambda_{\text{max}} = 365$ nm) of the miniemulsion for 30 min. The dispersion was dialyzed against THF for 3 days and followed by deionized water for another 3 days.

Supporting Figures

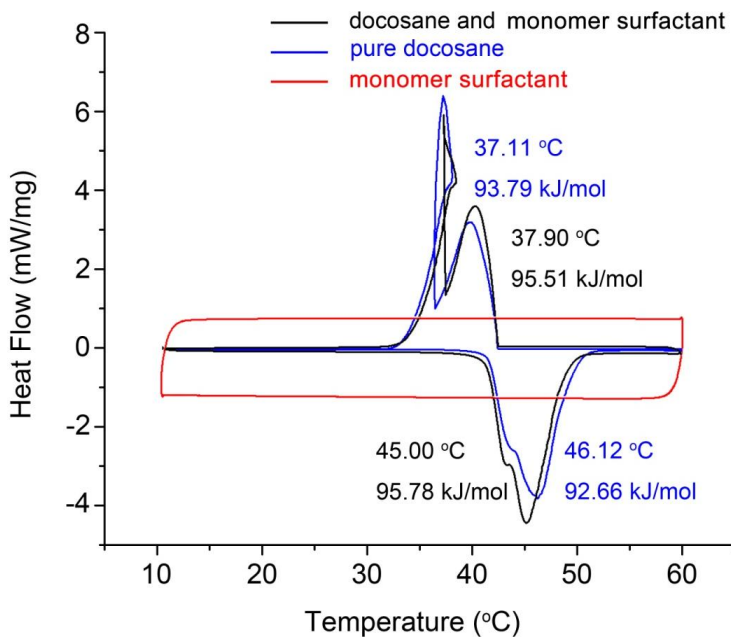


Fig. S1 DSC measurements for monomer surfactant, pure n-DS, and their mixture.

Note: All of the DSC measurements were conducted in the temperature range of 10-60 °C. No obvious melting or crystallization peak for the monomer surfactant was observed. The super-cooling state of pure n-DS was detected. The DSC measurement suggested that the enthalpy changes of pure n-DS were 92.66 kJ/mol by heating and 93.79 kJ/mol by cooling, respectively. The enthalpy changes of the mixture of n-DS (54 wt%) with the monomer surfactant (46 wt%) were 95.78 kJ/mol (of n-DS) by heating and 95.51 kJ/mol (of n-DS) by cooling, respectively. Relative to the enthalpy changes with pure n-DS, the larger enthalpy changes for mixture of n-DS and the monomer surfactant suggested the occurrence of co-crystallization of the alkane tail of the monomer surfactant with n-DS.¹

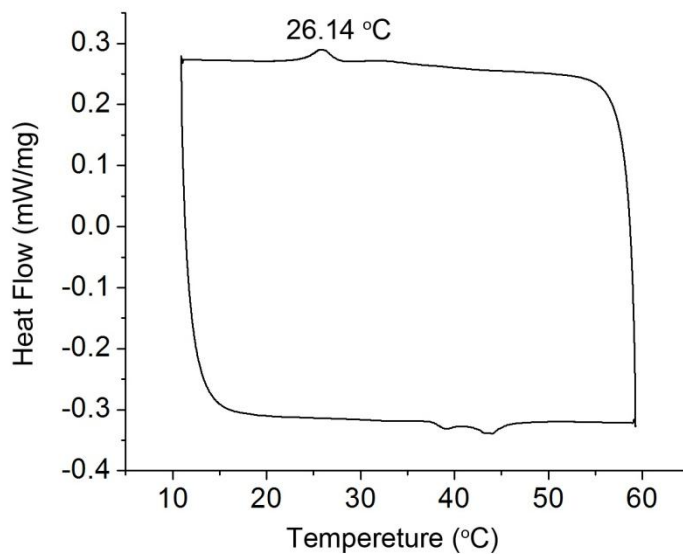


Fig. S2 DSC measurement of miniemulsion.

Note: The DSC measurement indicated that the crystallization temperature of miniemulsion was around 26 °C. The reaction temperature of 21 °C (r.t.) was lower than the crystallization temperature. Therefore, the reaction was conducted with crystallized miniemulsion droplets as templates.

Reference:

1. M. A. Oliveira, M. L. Peterson, and R. J. Davey, *Cryst. Growth Des.*, 2011, **11**, 449-457.