Supporting information for

Tetrahedral, Octahedral, and Triangular Dipyramidal Microgel Clusters with Thermosensitivity Fabricated from Binary Colloidal Crystals Template and Thiol-Ene Reaction

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Experimental details

Materials. N-isopropylacrylamide (NIPAM), cysteamine hydrochloride, allylamine hydrochloride and tris-carboxyethylphosphine (TCEP) were purchased from Tokyo Chemical Industry Co. 2, 2-diethoxyacetophenone (DEAP) was purchased from Aladdin. Sulfo-Cy3 maleimides was purchased from Lumiprobe Corporation. Sodium dodecyl sulfate (SDS), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC), N,N'-methylenebis(acrylamide) (BIS), acrylic acid (AAc), and potassium persulfate (KPS) were purchased from Tianjin heowns Biochemical Technology Co., Ltd. NIPAM was purified by recrystallization from hexane/acetone mixture and dried in a vacuum prior to use. AAc was distilled under reduced pressure. Other reagents were used as received.

Synthesis of PNIPAM Microgel with Surface Carboxylic Acid Groups. PNIPAM microgel was synthesized by free radical precipitation polymerization. Briefly, NIPAM (4.200 g), BIS (0.097 g) and SDS (0 or 0.087 g) were dissolved in 290.00 mL of deionized water. The reaction mixture was then transferred to a three-necked round-bottom flask equipped with a condenser and a nitrogen line. The solution was purged with nitrogen and heated to 70.0°C. After 1 h, 0.243 g KPS (dissolved in 6.00 mL of deionized water) was added to initiate the reaction. The reaction was allowed to proceed for 3 h. Then 0.303 g of AAc was added using an injector, and the reaction was allowed to proceed for another 2h. The resultant microgel was purified by dialysis against

water with frequent water change for 1 week. The microgel synthesized in the presence of SDS have a small size (D_h ~310 nm at 20 °C), while the one synthesized in the absence of SDS have a large size (D_h ~1000 nm at 20 °C).

Synthesis of Vinyl- and SH-Microgels. To 100.00 mL of purified small-size microgel dispersion, 1.310 g of allylamine hydrochloride and 2.684 g of EDC were added. After being stirred at room temperature for 4 h, the mixture was dialyzed against water with frequent water change for 3 days. The resulting product was named as vinyl-microgels. To 100.00 mL of purified large-size microgel dispersion, 1.591 g of cysteamine and 1.342 g of EDC were added. After being stirred at room temperature for 4 h, the mixture was dialyzed against water with frequent water change for 3 days. The resulting product was named as SH-microgels.

Preparation of Microgel Clusters. Firstly, the large-size SH-microgels dispersions were concentrated by centrifugation at 14000 rpm and 20°C for 2h, followed by decanting the supernatant. The concentration of the resulting opaque, viscous solution was ~4.0 wt%. To avoid large aggregates formed during UV irradiation, mixed dispersions of small vinyl-microgels and large SH-micrgoels with a number ratio of ~ 1: 30 were used to assemble binary colloidal crystals. To 7 mL of the concentrated dispersion, 30 μL of the as-prepared vinyl-microgel dispersion and 70 μL of DEAP (0.24 mol/L in DMSO) were added. The mixed dispersion was then injected into the space between two quartz slides separated by a rubber spacer. The samples were assembled into colloidal crystals simply

by heating to 37°C and then allowing it to cool back to room temperature. Finally the samples were kept in ice bath and irradiated with UV light for 2 h (λ = 365 nm). To separate the particles, a gradient of sucrose solution (4.0-12.0 wt%) was prepared. 400 μL of the dispersion was carefully loaded on top of the gradient and centrifuged for 10 min at 14000 rpm and 10°C. A syringe with pipetting needle was used to pull out individual bands from the sample. The fractions were purified by several centrifugation-redispersion cycles in deionized water.

Characterizations. ^{1}H NMR spectra were recorded on a Varian UNITY-plus 400 NMR spectrometer using D_2O or DMSO-d_6 as solvents. The hydrodynamic diameter (D_h) of the particles were measured by dynamic light scattering (DLS) with a Brookhaven 90Plus laser particle size analyzer using deionized water as solvent. All the measurements were carried out at a scattering angle of 90°. The sample temperature was controlled with a build-in Peltier temperature controller. Optical micrographs and confocal images were obtained on an Olympus IX70 fluorescence microscope and a Leica TCS SP8 Confocal Microscope. To acquire the fluorescence images of clusters, an excess of TCEP reagent was added to the dispersion to reduce disulfide bonds, then keep the mixture for 20 minutes at room temperature. To label the microgels fluorescently, 2 mg/mL solution of sulfo-Cy3 maleimide dye was mixed with the microgels. After overnight reaction at room temperature, the unreacted dye was removed by centrifugation.

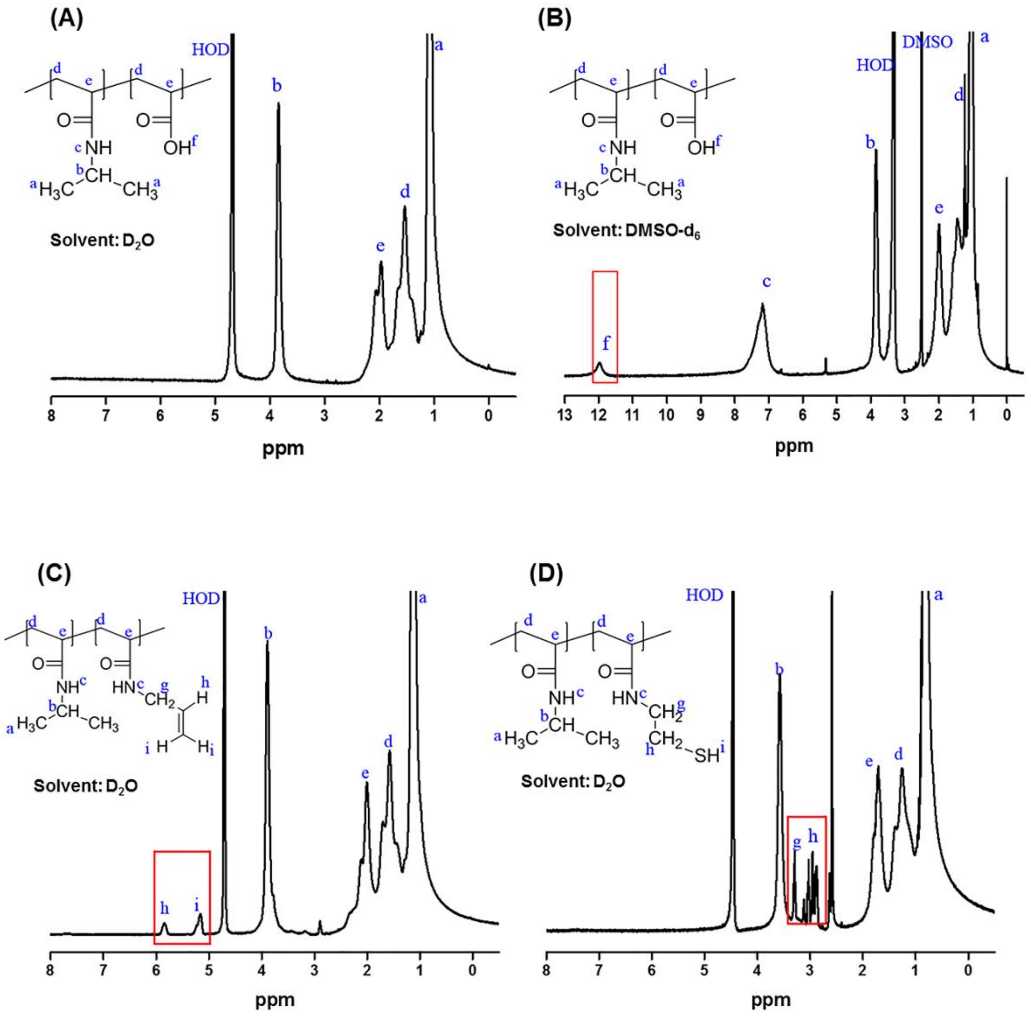

Figure S1. ^{1}H NMR spectra of the parent PNIPAM microgel (A, B), the allylamine-modified vinyl-microgel (C), and the cysteamine-modified SH-microgel (D). The solvent is DMSO-d_6 for B and D_2O for A, C and D, respectively. In DMSO-d_6 PNIPAM microgel presents a peak at 12.10 ppm because of the surface carboxylic acid groups. Successful introduction of vinyl groups is confirmed by the appearance of new peaks at 5.80 and 5.12 ppm (C). The appearance of multiple peaks at 2.5-3.5 ppm (-NH-CH_2-CH_2-S-) confirms the successful coupling of cysteamine with the microgel (D).

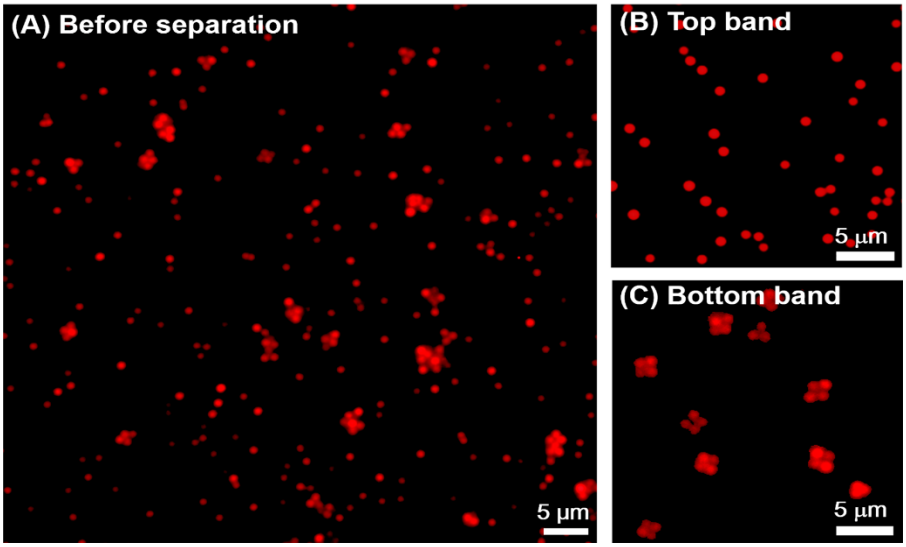

Figure S2. Fluorescence microscopy images of a microgel solution after UV irradiation. (A) Before separation. (B, C) After being separated by density gradient centrifugation. The top (B) and bottom bands (C) correspond to unreacted single SH-microgels and microgel clusters, respectively.

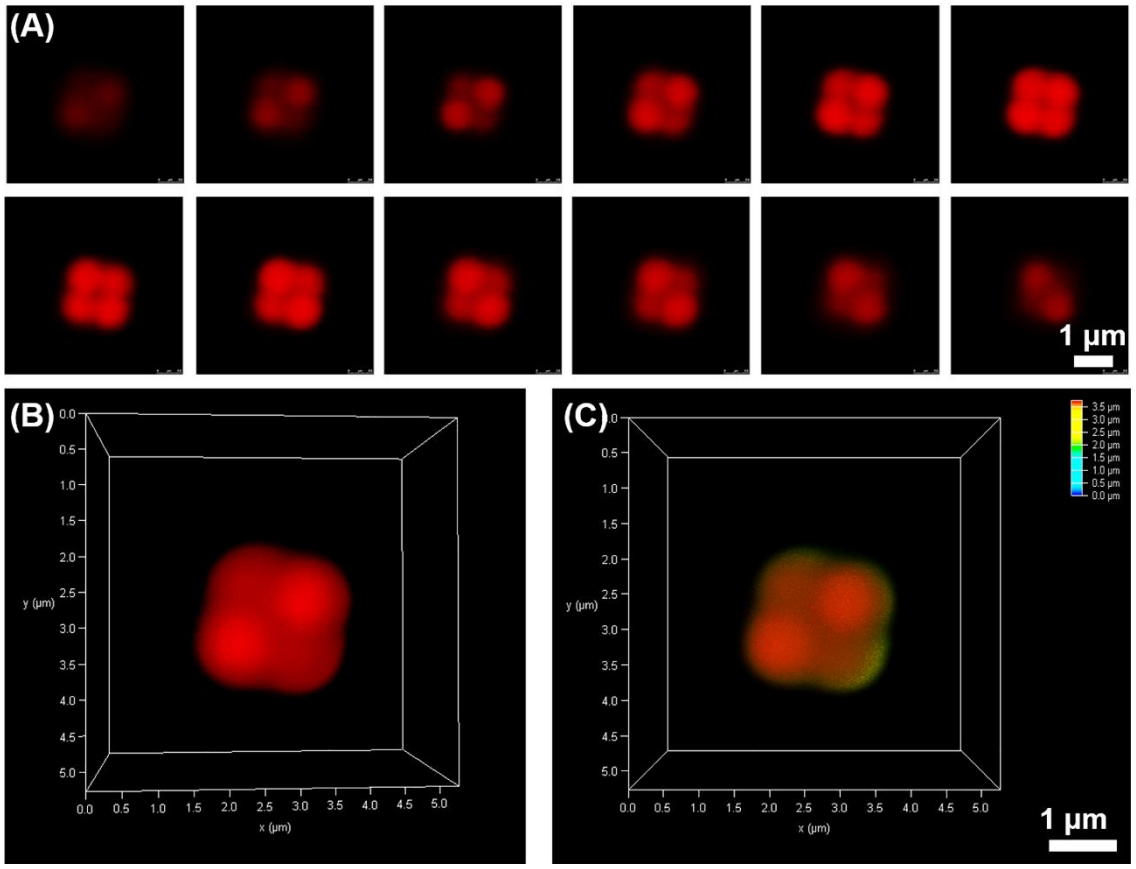

Figure S3. Characterization of a tetrahedral cluster from (100) direction. (A) Cross-section confocal images of the cluster observed from the (100) direction. (B-C) Reconstructed 3D confocal images of the cluster in volume mode (B) and depth mode (C), respectively.

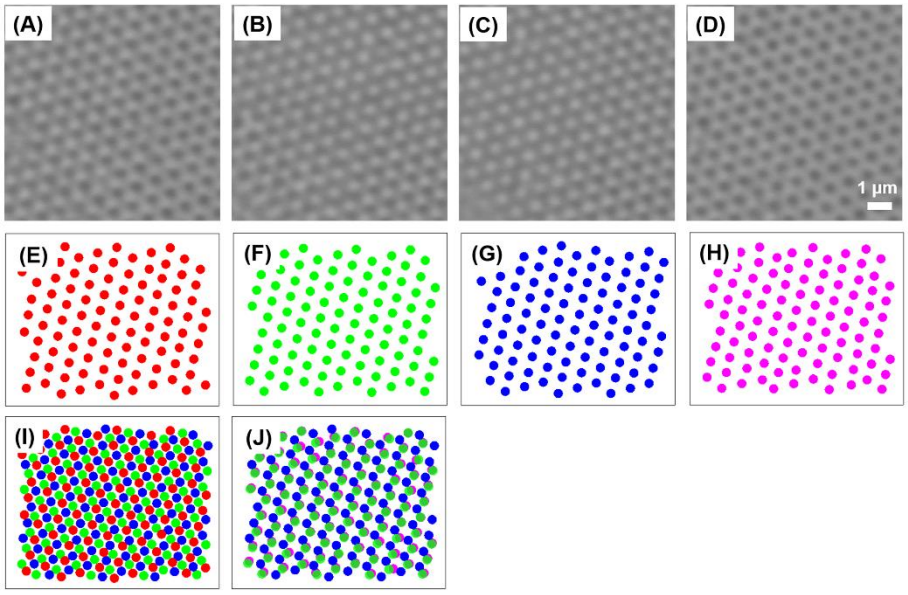

Figure S4. Stacking structures in microgel colloidal crystals. (A-D) Confocal micrographs of 4 consecutive 111 plane in the crystal. (E-H) The corresponding images assigned with pseudocolor red, green, blue and magenta, respectively. (I, J) Images obtained by merging consecutive three layers. I is obtained from E, F and G, indicating an fcc structure; while J is obtained from F, G and H, suggesting a hcp structure.

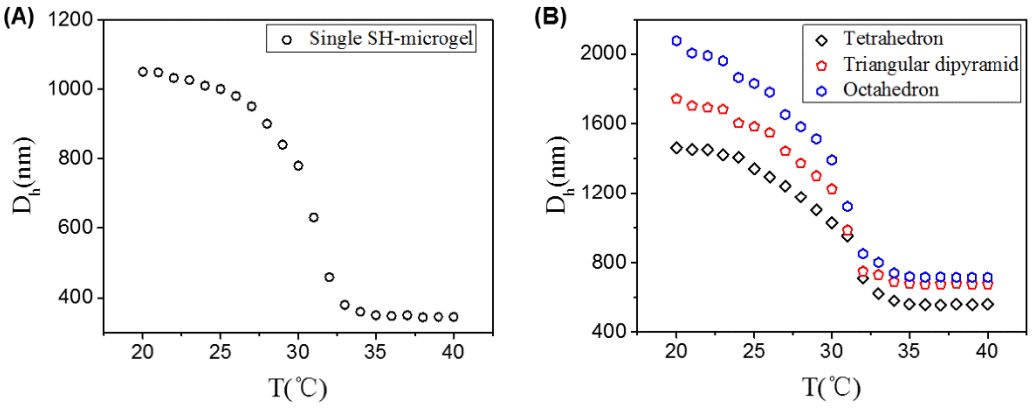

Figure S5. Hydrodynamic diameter (D_h) of single SH-microgel (A) and the three microgel clusters (B) as a function of temperature.

Movie S1. 3D structure of a tetrahedral cluster observed from (111) direction.

Movie S2. 3D structure of a tetrahedral cluster observed from (100) direction.

Movie S3. 3D structure of an octahedral cluster.

Movie S4. 3D structure of a triangular dipyramidal cluster.