

## Supporting Information

### Photomanipulatable Colloidal Clusters from Aggregation of Azo Molecular Glass Spheres

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## 1. Materials and Synthesis

**Materials.** Isosorbide, 4-nitrobenzoyl chloride, *N,N*-di(hydroxyethyl)aniline, cinnamoyl chloride were purchased from Alfa Aesar and used as received. Concentrated sulfuric acid, glacial acetic acid, tetrahydrofuran (THF), dichloromethane (DCM), chloroform, ethanol and *N,N*-dimethylformamide (DMF) were purchased from commercial sources as analytical pure products and used as received. Deionized water (resistivity >18.0 M $\Omega$ ·cm) was obtained from a Milli-Q water purification system. Other reagents were commercially available products and used as received without further purification. The azo compound (IAC-4) was synthesized according to the method reported by us previously.<sup>[S1]</sup> The details of the synthesis and characterization are given below.

**Isosorbide Bis(4-Nitrobenzoat).** Isosorbide (7.31 g, 0.05 mol) and triethylamine (15 mL) were dissolved in 40 mL CHCl<sub>3</sub>. The mixture was stirred with cooling in an ice-water bath. 4-Nitrobenzoyl chloride (19 g, 0.1 mol) was dissolved in 40 mL CHCl<sub>3</sub> and dropwise added into the mixture. The reaction was carried out at the room temperature for 6 h. After the reaction, the mixture was dropped into 200 mL water. White solid was obtained after rotary evaporation and then washed with hot alcohol.

**Isosorbide Bis(4-aminobenzoat).** Isosorbide *bis*(4-nitrobenzoat) (4.7 g, 10.6 mmol), Na<sub>2</sub>S·9H<sub>2</sub>O (14.4 g, 60 mmol), NH<sub>4</sub>Cl (4.5 g, 84 mmol), 50 mL H<sub>2</sub>O and 80 mL alcohol were added into a 250 mL round bottom flask. The mixture was refluxed with vigorous stirring for 6 h. The precipitated powder was filtered while the solution was hot. The precipitate was dissolved in dilute hydrochloric acid (1 mol/L) and then filtered. The filtrate was adjusted to alkalescency with ammonia and white precipitate was collected by filtration. The crude product was further purified by recrystallization with alcohol.

**Di(hydroxyethyl)aniline Biscinnamate.** *N, N*-di(hydroxyethyl)aniline (1.81 g, 10 mmol) and triethylamine (3.03 g, 30 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and then the mixture was stirred in an ice-water bath. Cinnamoyl chloride (4 g, 24 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and dropwise added into the mixture. After the addition, the reaction was carried out at the room temperature for 24 h. When the reaction was completed, liquid with low boiling point in the reaction mixture was removed by rotary evaporation. The residual mixture was washed with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The solution containing the extract was dried with anhydrous MgSO<sub>4</sub>. The crude product was obtained by distilling the solvent and then purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>, the first component).

**IAC-4 Synthesis.** IAC-4 was prepared by azo-coupling reaction between isosorbide

*bis*(4-aminobenzoat) and *di*(hydroxyethyl)aniline *biscinnamate*. For the synthesis, *di*(hydroxyethyl)aniline *biscinnamate* (0.66 g, 1.5 mmol) was dissolved in DMF (25 mL) and then cooled to 0 °C. Isosorbide *bis*(4-aminobenzoat) (0.19 g, 0.5 mmol) was mixed with sulfuric acid (0.3 mL) and glacial acetic acid (3 mL). The diazonium salt was prepared by adding an aqueous solution of sodium nitrite (0.1 g, 1.44 mmol in 0.3 mL water) into the homogeneous mixture of isosorbide *bis*(4-aminobenzoat). The mixture was stirred at 0 °C until the solid was completely dissolved and then added dropwise into the DMF solution of *di*(hydroxyethyl)aniline *biscinnamate*. The solution was stirred at 0 °C for 12 h. Then the solution was poured into plenty of water and the precipitate was collected by filtration. After repeated wash and dry, the crude product was further purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate = 10:1 (v/v)). After repeated wash and dry, the crude product was further purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>: ethyl acetate = 10:1 (v/v)). Yield: 80%. IR (KBr, cm<sup>-1</sup>): 3060 (=CH-), 3000-2800 (-CH<sub>2</sub>, -CH), 1712 (C=O, str.), 1635 (-CH=CH-), 1597, 1576, 1512 (benzene ring), 1497 (-CH<sub>2</sub>), 1448 (benzene ring). <sup>1</sup>H NMR (CDCl<sub>3</sub>-d<sub>1</sub>): 8.22-8.19 (d, 2H, ArH), 8.15-8.12 (d, 2H, ArH), 7.95-7.88 (m, 8H, ArH), 7.70-7.64 (d, 4H, -CH=CH-), 7.51-7.48 (m, 8H, ArH), 7.38-7.36 (m, 12H, ArH), 7.96-7.94 (d, 4H, ArH), 6.46-6.40 (d, 4H, -CH=CH-), 5.54 (s, 1H, -O-CH-, isosorbide), 5.48-5.46 (m, 1H, isosorbide), 5.14-5.10 (t, 1H, isosorbide), 4.75-4.73 (t, 1H, isosorbide), 4.50-4.46 (t, 8H, -OCH<sub>2</sub>-), 4.18-4.17 (d, 2H, isosorbide), 4.12-4.11 (m, 2H, isosorbide), 3.89-3.85 (t, 8H, -N-CH<sub>2</sub>-). Figure S1 provides the <sup>1</sup>H NMR spectrum and UV-vis spectrum of IAC-4.

## 2. Characterization

<sup>1</sup>H NMR spectra were acquired on a JEOL JNM-ECA 600 spectrometer with CDCl<sub>3</sub> as the solvent. The UV-vis spectra of samples in DMF were obtained using an Agilent 8453 UV-vis spectrophotometer. A field-emission scanning electron microscope (SEM, Zeiss Merlin, 5.0 kV) was used to investigate the morphologies of colloidal spheres, colloidal clusters, deformed spheres and clusters. The TEM observations of colloidal spheres and clusters were realized via Hitachi H-7650B with the electron beam of 80 kV. Light scattering experiment was performed on a LLS instrument (ALV/DLS/SLS-5022F), which was equipped with a multi- $\tau$  digital time correlator (ALV/LSE-5003) and a solid-state laser (Uniphase, output power = 17 mW at  $\lambda$  = 633 nm). All the LLS measurements were carried out at 25  $\pm$  0.1 °C. DLS analysis was carried out by the following procedure.<sup>[S2]</sup> An intensity-intensity time correlation function  $G^{(2)}(t, \theta)$  was measured, which has the following form,

$$G^{(2)}(t, \theta) = A[1 + \beta |g^{(1)}(t, \theta)|^2] \quad (1)$$

where  $A$  is a measured baseline,  $\beta$  is a parameter depending on the coherence of the

detection,  $t$  refers to the delay time,  $g^{(1)}(t, \theta)$  is the first-order electric field correlation function. For polydispersed particles in dispersion,  $g^{(1)}(t, \theta)$  is related to the line-width distribution function  $G(\Gamma)$  by the following equation.

$$|g^{(1)}(t, \theta)| = \int_0^\infty G(\Gamma) e^{-\Gamma t} d\Gamma \quad (2)$$

Both the cumulant analysis and the CONTIN analysis were used for data processing. The analysis of the cumulant expansion of the correlation function was performed by fitting a polynomial up to the third order for the function  $\ln[G^{(2)}(t, \theta) - 1]$ . The polynomial coefficients were converted into the coefficients of the cumulant expansion of the field correlation function by the equation,

$$\ln[g^{(1)}(t, \theta)] = \ln(a) - \bar{\Gamma}t + \frac{\mu_2}{2}t^2 - \frac{\mu_3}{6}t^3 \quad (3)$$

where  $a$  is the amplitude, the first cumulant ( $\bar{\Gamma}$ ) yields the  $z$ -averaged diffusion coefficient and the second cumulant ( $\mu_2$ ) is a measure of polydispersity. The widely accepted Laplace inversion procedure (CONTIN analysis) was also employed to calculate  $G(\Gamma)$  from the measured  $G^{(2)}(t, \theta)$ . For a diffusive relaxation,  $\Gamma$  is related to the translational diffusion coefficient ( $D$ ) of particles by,

$$\Gamma = Dq^2 \quad (4)$$

where  $q [= (4\pi n/\lambda_0) \sin(\theta/2)]$  is the scattering vector,  $\theta$  is the scattering angle,  $n$  is the solvent refractive index, and  $\lambda_0$  is the wavelength of the incident light.  $G(\Gamma)$  obtained was converted to a hydrodynamic radius distribution  $f(R_h)$  by the CONTIN program equipped in the instrument, according to the Stokes-Einstein equation,

$$\langle R_h \rangle = \frac{k_B T}{6\pi\eta D} \quad (5)$$

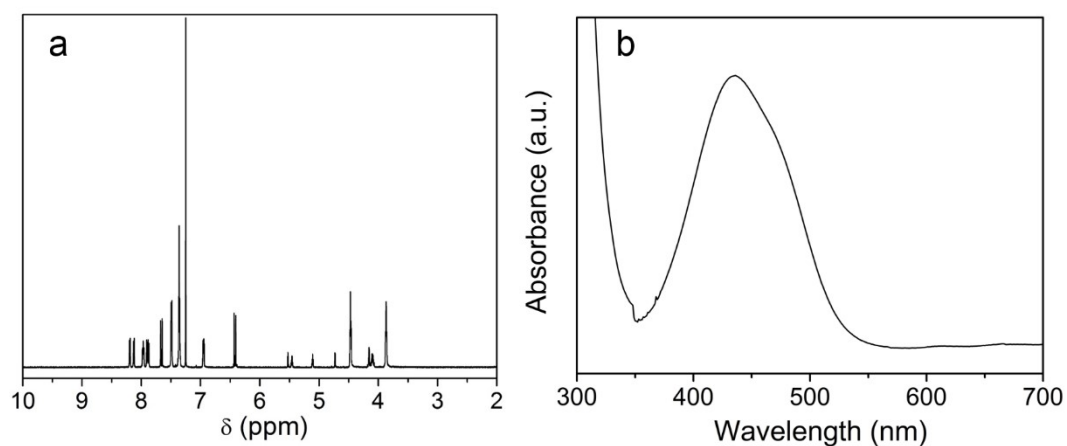
where  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\eta$  is the viscosity of the solvent.

### 3. Supplementary Table

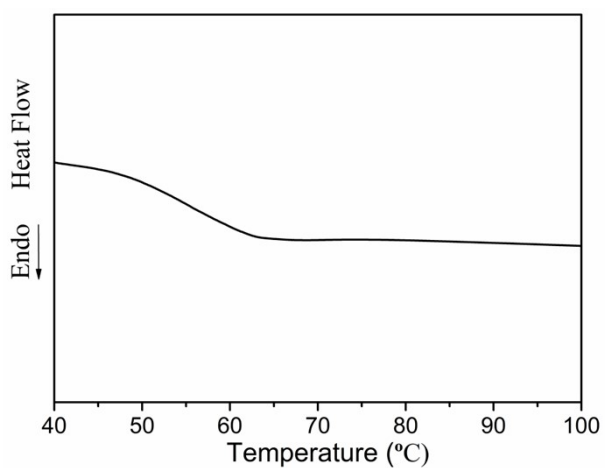
**Table S1.** The average hydrodynamic radius ( $\langle R_{hc} \rangle$ ), average volume of the compound spheres formed via colloidal fusion with the stirring time of 80 min, and the average number of spheres included in each colloidal cluster from SEM ( $\langle N \rangle$ ) and DLS ( $\langle n \rangle$ ).

Stirring Rate (rpm)	N/A	1300	1400	1500	1600	2400
$\langle N \rangle$	1.0	2.1	2.9	4.2	4.8	>10
$\langle R_{hc} \rangle$ (nm)	260±4	334±4	380±3	413±5	447±4	657±8
Average vol.( $\mu\text{m}^3$ )	0.074	0.156	0.230	0.295	0.370	1.187
$\langle n \rangle$	1.0	2.1	3.1	4.0	5.1	16.0

#### 4. Supplementary Figures and Interpretation



**Figure S1.** The characterization of IAC-4, (a)  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3\text{-d}_1$ ; (b) UV-vis spectrum of its solution in DMF.



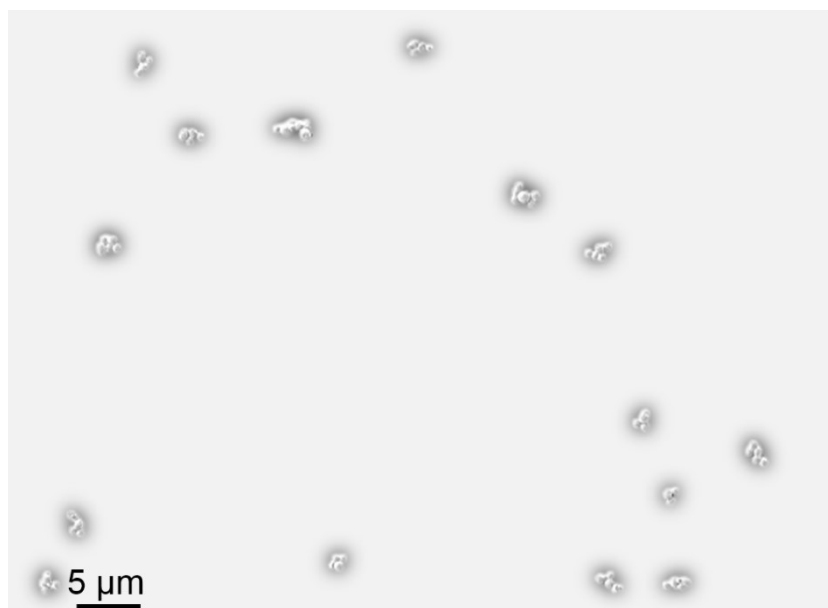
**Figure S2.** The DSC curve of IAC-4 with the glass transition temperature of about 56  $^{\circ}\text{C}$ .



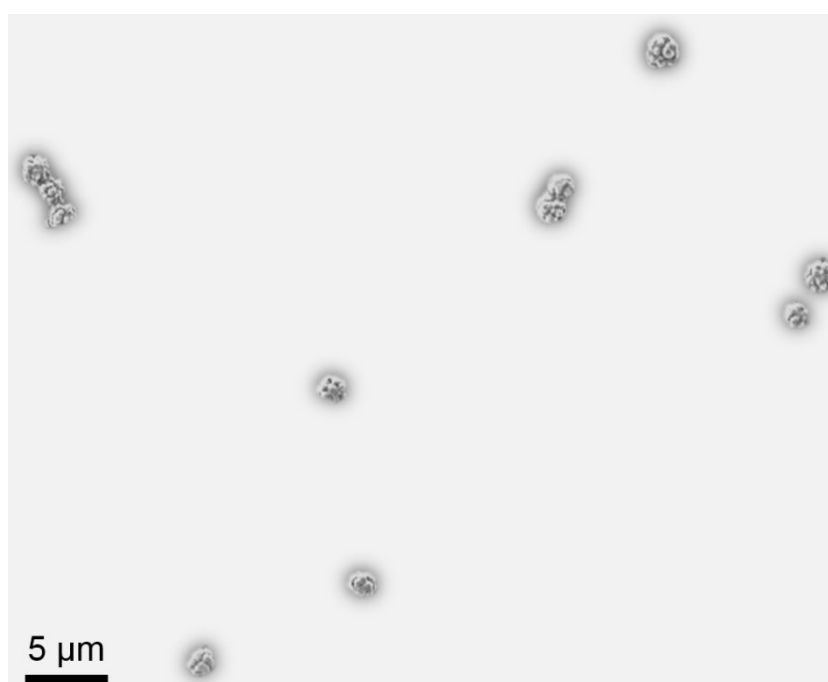
**Figure S3.** SEM images of the colloidal clusters with  $\langle N \rangle = 2.9$ . The colloidal clusters were obtained by first adding an appropriate amount of ethanol (4.2 mL) into the THF solution of IAC-4 (2.0 mg/mL, 1 mL) with the adding rate of 86.4 mL/h and meanwhile the dispersion was stirred with a rate of 1800 rpm. After adding ethanol, the stirring was continued for 15 min with the stirring rate of 1400 rpm. Finally, 20 mL ethanol was quickly added into the dispersion to quench the formed structures. The dispersions were placed for 3 days before fabricating samples for SEM observations.



**Figure S4.** SEM images of the colloidal clusters with  $\langle N \rangle = 4.2$ . The colloidal clusters were obtained by first adding an appropriate amount of ethanol (4.2 mL) into the THF solution of IAC-4 (2.0 mg/mL, 1 mL) with the adding rate of 86.4 mL/h and meanwhile the dispersion was stirred with a rate of 1800 rpm. After adding ethanol, the stirring was continued for 15 min with the stirring rate of 1500 rpm. Finally, 20 mL ethanol was quickly added into the dispersion to quench the structures. The dispersions were placed for 3 days before fabricating samples for SEM observations.

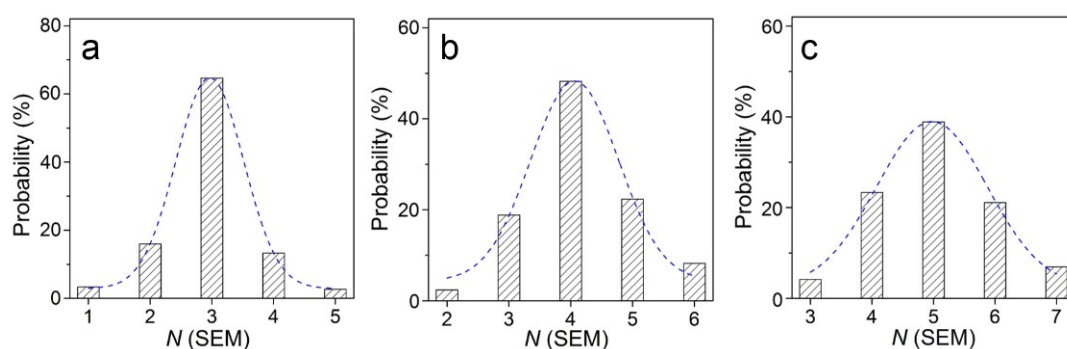


**Figure S5.** SEM images of the colloidal clusters with  $\langle N \rangle = 4.8$ . The colloidal clusters were obtained by first adding an appropriate amount of ethanol (4.2 mL) into the THF solution of IAC-4 (2.0 mg/mL, 1 mL) with the adding rate of 86.4 mL/h and meanwhile the dispersion was stirred with a rate of 1800 rpm. After adding ethanol, the stirring was continued for 15 min with the stirring rate of 1600 rpm. Finally, 20 mL ethanol was quickly added into the dispersion to quench the structures. The dispersions were placed for 3 days before fabricating samples for SEM observations.

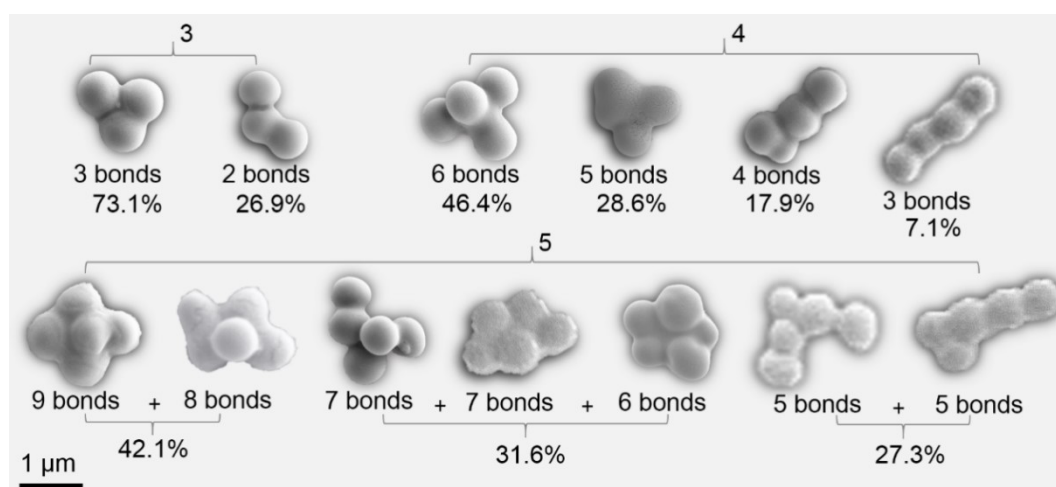


**Figure S6.** SEM images of the colloidal clusters with  $N > 10$ . The colloidal clusters were obtained by first adding an appropriate amount of ethanol (4.2 mL) into the THF solution of IAC-4 (2.0 mg/mL, 1 mL) with the adding rate of 86.4 mL/h and meanwhile the dispersion was stirred with a rate of 1800 rpm. After adding ethanol, the stirring was continued for 15 min with stirring rate of 2400 rpm. Finally, 20 mL ethanol was quickly added into dispersion to quench the formed structures. The dispersions were placed for about 7 days before fabricating samples for SEM

observations.

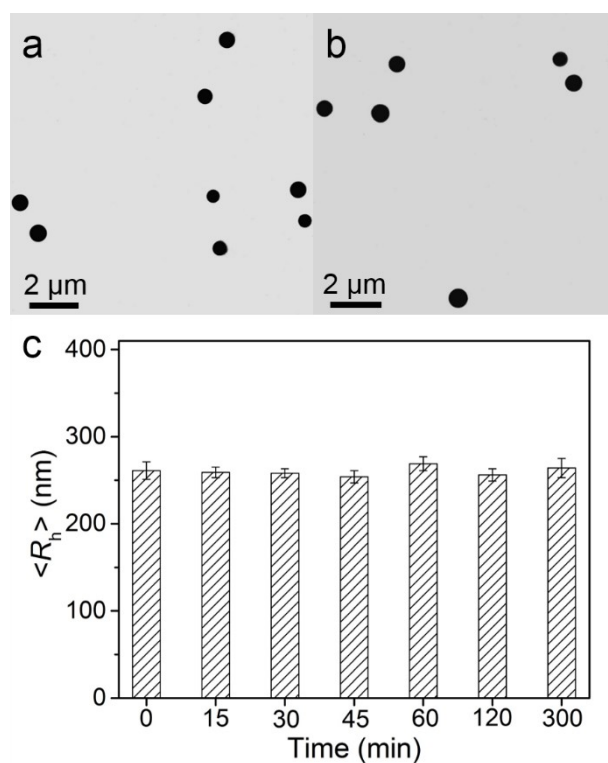


**Figure S7.** Distribution of  $N$  in each colloidal cluster statistically estimated from 100 clusters. The  $\langle N \rangle$  of the clusters are 2.9 (a), 4.2 (b) and 4.8 (c), respectively. The colloidal clusters were obtained by first adding an appropriate amount of ethanol (4.2 mL) into the THF solution of IAC-4 (2.0 mg/mL, 1 mL) with the adding rate of 86.4 mL/h and meanwhile the dispersion was stirred with a rate of 1800 rpm. After adding ethanol, the stirring was continued for 15 min with the stirring rate of 1400 rpm (a), 1500 rpm (b) and 1600 rpm (c), respectively. Finally, 20 mL ethanol was quickly added into the dispersion to quench the formed structures.

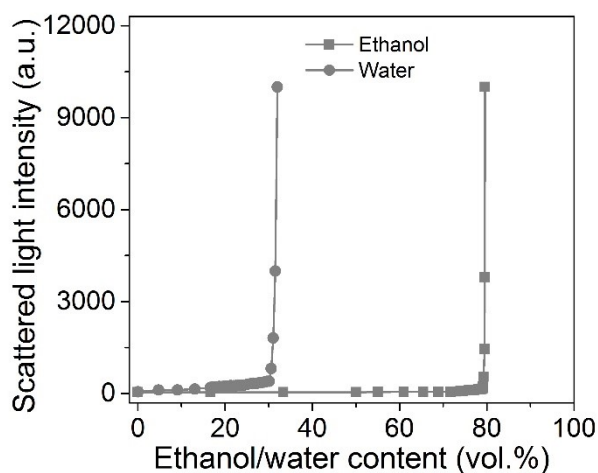


**Figure S8.** (a) Typical colloidal clusters ( $N = 3, 4$  and  $5$ ) with different morphologies, which are selected from SEM images of the clusters formed with the different stirring rates. For  $N = 3$ , there are 73.1 % of clusters with the triangular morphology (3 bonds) that is most favorable. For  $N = 4$ , the majority clusters (46.4%) are the tetrahedral morphology (6 bonds) that is most favorable. For  $N = 5$ , the clusters with 8 and 9 bonds are 42.1% (favorable).

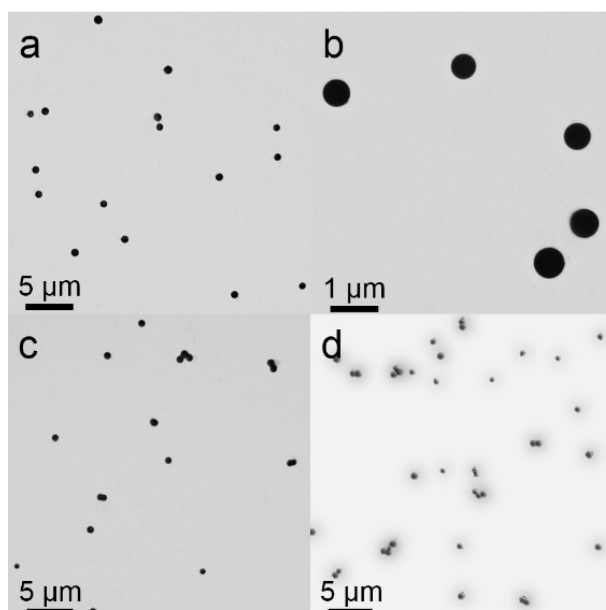




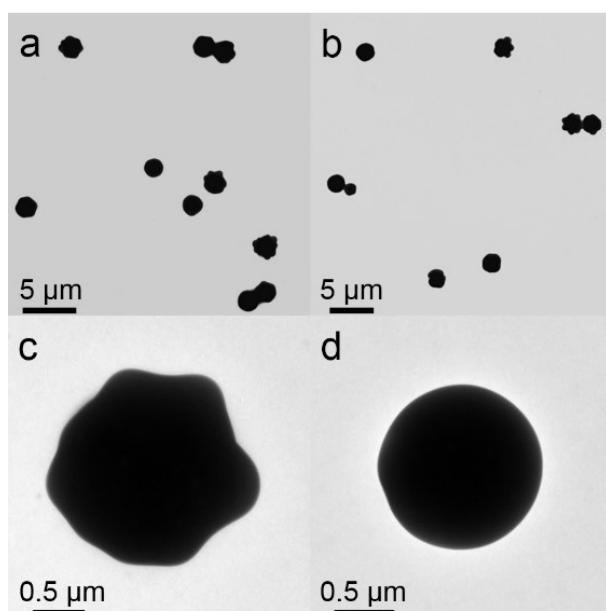
**Figure S9.** (a) TEM image of the colloidal spheres obtained via dropwise adding 4.2 mL ethanol with the adding rate of 86.4 mL/h into the THF solution of IAC-4 (1 mL, 2.0 mg/mL), immediately followed by adding 20 mL ethanol into the mixture under the stirring with the rate of 1800 rpm for 15 min; (b) TEM image of the colloidal spheres obtained as described in (a) were dispersed in the ethanol/THF (24.2/1, v/v) mixture under the stirring with the rate of 1800 rpm for 300 min; (c) the average hydrodynamic radius of colloidal spheres dispersed in the ethanol/THF (24.2/1, v/v) medium for different stirring time periods as was obtained from DLS.



**Figure S10.** Critical water content (CWC) and critical ethanol content (CEC) for the solution of IAC-4 in THF (2.0 mg/mL).

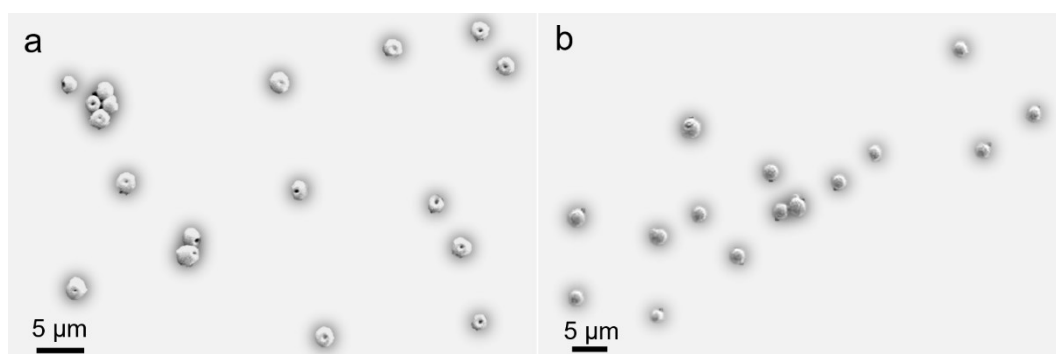


**Figure S11.** Typical TEM (a-c) and SEM (d) images of the colloidal spheres and clusters, (a) and (b) obtained by dropwise adding 9 mL ethanol with the adding rate of 86.4 mL/h into 1 ml THF solution of IAC-4 (2.0 mg/mL) under the stirring with the rate of 1800 rpm for 15 min, followed by adding 20 mL ethanol into the mixture; (c) and (d) obtained by dropwise adding 4.2 mL ethanol with the adding rate of 86.4 mL/h into 1 ml THF solution of IAC-4 (0.2 mg/mL) under the stirring with the rate of 1400 rpm for 15 min, followed by adding 20 mL ethanol into the mixture.

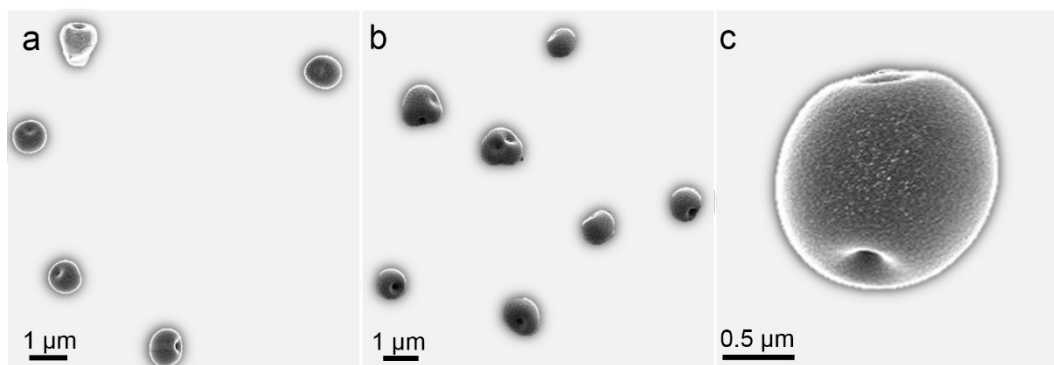


**Figure S12.** Typical TEM images of the colloidal clusters obtained via dropwise adding 4.2 mL ethanol with different adding rates into 1 ml THF solution of IAC-4 (2.0 mg/mL) under the stirring with the rate of 1800 rpm for 15 min, followed by adding 20 mL ethanol into the mixture. (a) and (b) The adding rates of ethanol were 3.6 mL/h and 7.2 mL/h, respectively; (c) and (d) colloidal particles with different morphologies.

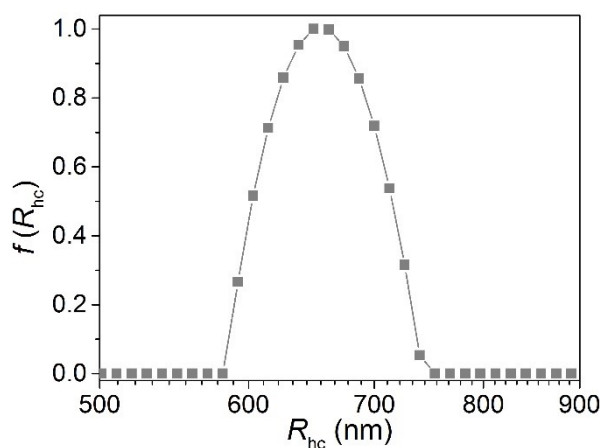
As shown in **Figure S10-S12**, the colloidal fusion of spheres is closely related to the ethanol content. As the ethanol content is increased to 90 vol.%, the spheres are hard and cannot coalesce with each other (**Figure S11a** and **S11b**). Therefore, it is important to select the suitable amount of ethanol for controlling the aggregation of colloidal spheres. In order to obtain soft colloidal spheres, the amount of ethanol added into the system should be carefully selected. The CEC for the solution of IAC-4 in THF (2.0 mg/mL) is 80 vol.% (**Figure S10**). Therefore, the amount of ethanol added into THF solution cannot be less than 80 vol.%. The study shows that 4.2 mL ethanol for 1 mL THF solution (80.8 vol.%) is the optimized condition for aggregation and colloidal fusion of the IAC-4 spheres. The yield of clusters depends on the collision probability between the colloidal spheres, which is influenced by the concentration of the soft spheres in the dispersion. As shown in **Figure S11c** and **S11d**, there are many isolated spheres compared to the results given in **Figure S3**, where the initial IAC-4 concentration in THF was 2.0 mg/mL. The average radius of the colloidal spheres is  $261 \pm 18$  nm (**Figure S11c** and **S11d**), which is nearly equal to that of spheres obtained with the initial IAC-4 concentration of 2.0 mg/mL. Therefore, the concentrations of the colloidal spheres in the dispersions should be determined by the initial IAC-4 concentration for the same volume of ethanol/THF (5.2 mL) mixture. The collision probability in the case for the low concentration (such as 0.2 mg/mL) is too low, and the soft spheres are difficult to collide with each other. Therefore, IAC-4 with the initial concentration of 2.0 mg/mL in THF was employed to study the fabrication of colloidal clusters via colloidal fusion. If the adding rate of ethanol is too slow, it is almost impossible to control the size and number of the spheres included in the colloidal clusters and the architectures of colloidal particles (**Figure S12**). In this case, the colloidal sphere formation from IAC-4 molecules and the aggregation of the soft spheres take place at the same time. Therefore, it is important to add ethanol with the relatively fast rate (86.4 mL/h), for which soft spheres can be formed in the short time period and then coalesce into colloidal clusters with the particular architectures.



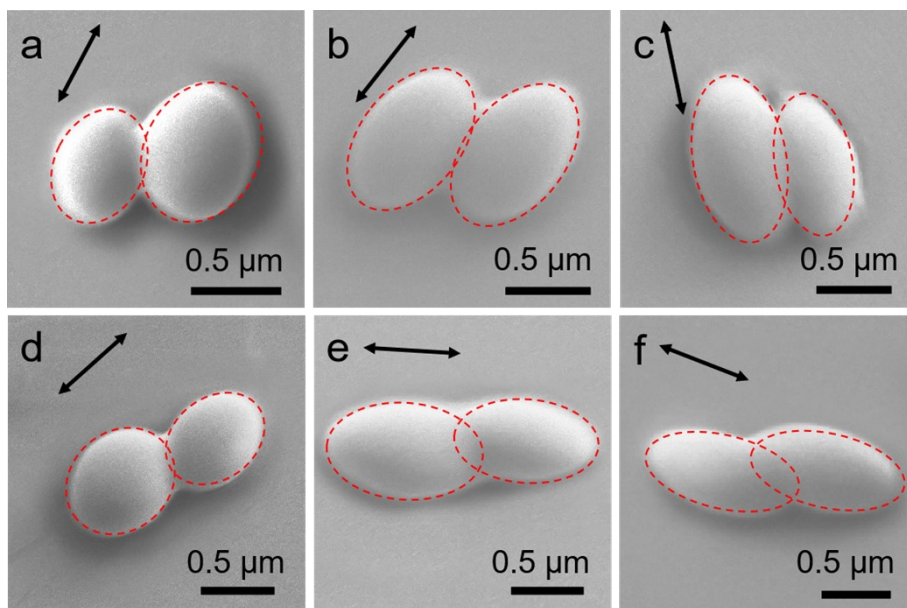
**Figure S13.** Typical SEM images of the colloidal clusters after fusion, (a) colloidal clusters with the average sphere number of 16.0 (estimated from DLS) fuse into the apple-shaped particles, (b) fuse into the compound spheres. For the preparations, the appropriate amount of ethanol (4.2 mL) was dropwise added into the THF solution of IAC-4 (2.0 mg/mL, 1 mL) with the adding rate of 86.4 mL/h and meanwhile the dispersion was stirred with a rate of 1800 rpm. After adding ethanol, the stirring was continued with the stirring rate of 2400 rpm for 60 min (a) and 80 min (b), respectively. Finally, 20 mL ethanol was quickly added into the dispersion to quench the formed structures.



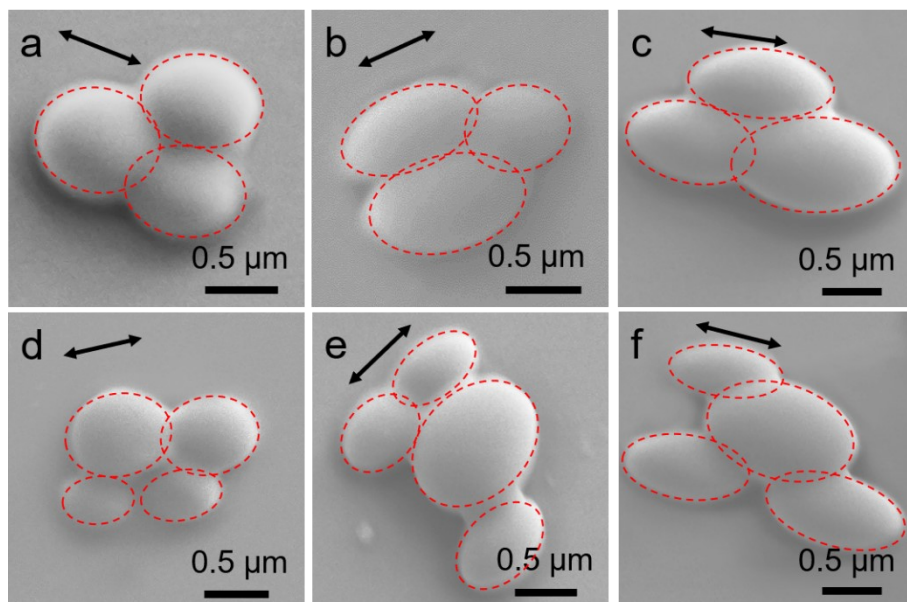
**Figure S14.** SEM images of the apple-shaped particles viewing from different angles, (a) the direction of the electron beam was perpendicular to the surface plane of silicon substrate; (b) the angle between the electron beam and surface plane of silicon substrate was 45°; (c) the magnified image of a typical apple-shaped particle. The apple-shaped particles were obtained by first adding an appropriate amount of ethanol (4.2 mL) into the THF solution of IAC-4 (2.0 mg/mL, 1 mL) with the adding rate of 86.4 mL/h and meanwhile the dispersion was stirred with a rate of 1800 rpm. After adding ethanol, the stirring was continued for 60 min with the stirring rate of 2400 rpm. Finally, 20 mL ethanol was quickly added into the dispersion to quench the formed structures.



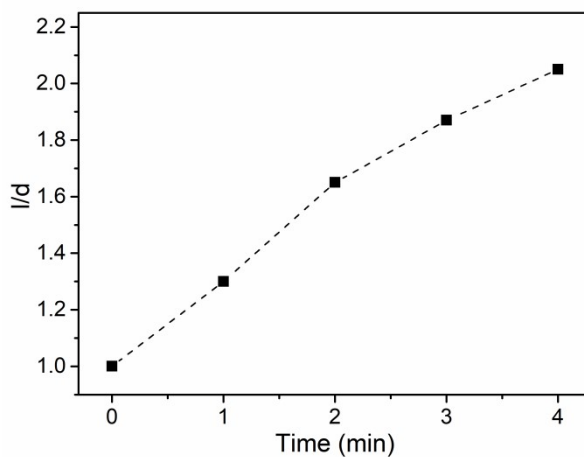
**Figure S15.** The distribution of the hydrodynamic radius of the compound spheres formed via colloidal fusion of the clusters. The compound spheres were obtained by first adding an appropriate amount of ethanol (4.2 mL) into the THF solution of IAC-4 (2.0 mg/mL, 1 mL) with the adding rate of 86.4 mL/h and meanwhile the dispersion was stirred with a rate of 1800 rpm. After adding ethanol, the stirring was continued for 80 min with the stirring rate of 2400 rpm. Finally, 20 mL ethanol was quickly added into the dispersion to quench the formed structures.



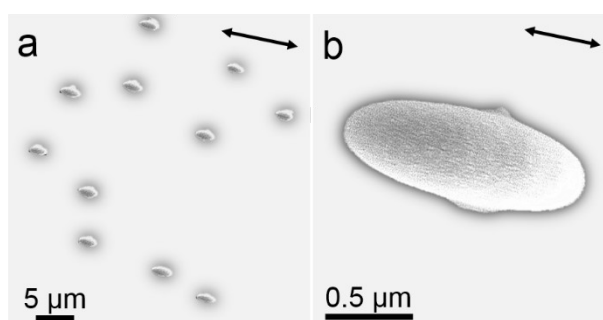
**Figure S16.** SEM images of the colloidal clusters (dimer) after the linearly polarized light irradiation with different irradiation time and stretched direction; the stretched direction perpendicular to the direction of the bond between the two spheres: (a) the irradiation time of 1 minute, (b) the irradiation time of 2 minutes, (c) the irradiation time of 3 minutes; the stretched direction parallel to the direction of the bond between the two spheres: (d) the irradiation time of 1 minute, (e) the irradiation time of 2 minutes, (f) the irradiation time of 3 minutes.



**Figure S17.** SEM images of the colloidal clusters (trimer and tetramer) after the linearly polarized light irradiation with different irradiation time; trimer: (a)-(c) the irradiation time of 1, 2 and 3 minutes, respectively; tetramer: (d)-(f) the irradiation time of 1, 2 and 3 minutes, respectively.



**Figure S18.** The average axial ratio of ellipsoidal particles statistically estimated from 100 ellipsoidal particles in the stretched clusters after the linearly polarized light irradiation with different irradiation time.



**Figure S19.** (a) and (b) SEM images of the stretched spheres (the SEM image before the light irradiation can be seen in Figure 2a), after the irradiation with a linearly polarized laser beam (488 nm, 100 mW/cm<sup>2</sup>) for 4 min. The spheres were obtained by dropwise adding ethanol (4.2 mL) into a THF solution of IAC-4 (1 mL, 2.0 mg/mL) with the adding rate of 86.4 mL/h and the stirring rate of 1800 rpm. Immediately after the addition, 20 mL ethanol was quickly added into the dispersion.

## Reference

- [S1] Guo, M. C.; Xu, Z. D.; Wang, X. G. Photofabrication of two-dimensional quasi-crystal patterns on UV-curable molecular azo glass films. *Langmuir* **2008**, *24*, 2740–2745.
- [S2] Chu B. *Laser Light Scattering*, Academic Press, New York, 1991.