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[*Electronic Supplementary Information (ESI)*]

Photodeformable microspheres from an azo molecule containing 1,4,3,6-dianhydrosorbitol core and cinnamate peripheral groups

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1. Materials

Deionized water (resistivity >18 MΩ·cm) was obtained from a Milli-Q water purification system. Other reagents and solvents were obtained from commercial sources and used as received without further purification. The azo molecule (IAC-4) was prepared by azo-coupling reaction between 1,4,3,6-dianhydrosorbitol bis(4-aminobenzoat) and di(hydroxyethyl)aniline biscinnamate as described below.

To prepare 1,4,3,6-dianhydrosorbitol bis(4-aminobenzoat), 4-nitrobenzoyl chloride was first obtained by the chlorination reaction between 4-nitrobenzoic acid and thionyl chloride. 1,4,3,6-Dianhydrosorbitol bis(4-nitrobenzoat) was then obtained by the Schotten-Baumann reaction between 4-nitrobenzoyl chloride and 1,4,3,6-dianhydrosorbitol. After that, 1,4,3,6-dianhydrosorbitol bis(4-nitrobenzoat) was reduced with Na_2S to obtain 1,4,3,6-dianhydrosorbitol bis(4-aminobenzoat). Di(hydroxyethyl)aniline biscinnamate was obtained by the esterification reaction between di(hydroxyethyl)aniline and cinnamoyl chloride. To synthesize IAC-4, di(hydroxyethyl)aniline biscinnamate (0.66 g, 1.5 mmol) was dissolved in DMF (25 mL) and then cooled to 0 °C. 1,4,3,6-Dianhydrosorbitol bis(4-aminobenzoat) (0.19 g, 0.5 mmol) was mixed with 0.3 mL of sulfuric acid and 3 mL of glacial acetic acid. The diazonium salt was obtained by adding an aqueous solution of sodium nitrite (0.1 g, 1.44 mmol in 0.3 mL water) into the homogeneous mixture of 1,4,3,6-

dianhydrosorbitol 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 it was poured into plenty of water and the precipitate was collected by filtration. After repeated wash with water and dry, the crude product was further purified by column chromatography (CH_2Cl_2: ethyl acetate=10:1 (v/v)). Yield: 80%. EA (%): C 70.37 (calcd 70.79), H 5.31 (calcd 5.32); N 6.53 (calcd 6.52). MS: MW 1288.47 (calcd 1288.48). IR (KBr, cm^{-1}): 3060 (=CH-), 3000-2800 ($-CH_2$, -CH), 1712 (C=O, str), 1635 (-CH=CH-), 1597, 1576, 1512 (benzene ring), 1497 ($-CH_2$), 1448 (benzene ring). ^{1}H NMR ($CDCl_3$-d1): 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, $-OCH_2-$), 4.18-4.17 (d, 2H, isosorbide), 4.12-4.11 (m, 2H, isosorbide), 3.89-3.85 (t, 8H, $-N-CH_2-$). T_g: 63 ^oC.

The more details about preparation and characterization of IAC-4 can be seen in our previous paper.[1]

2. Experiment and Characterization

2.1 Critical water content (CWC)

A THF solution with predetermined concentration was prepared and an appropriate amount of deionized water was added into the THF solution (1 mL) under mildly stirring for 5 min in the closed environment in order to mix completely. The scattered light intensity was measured following each step addition of the deionized water into the solution. The same procedure was carried out for a series of THF solutions with different concentrations to investigate the relationship between CWC and the initial concentration of IAC-4 in THF.

2.2 Self-assembly experiment

A THF solution with predetermined concentration was prepared and an appropriate amount of water (such as 2 mL) was dropwise added into the THF solution (1 mL) at the rate of 7.2 mL/h under mildly stirring. Then, excess water (20 mL) was added into the solution to “quench” the structure formed in the dispersion. The colloidal spheres were finally obtained by slow evaporation of THF under the ambient conditions at room temperature for 3 days.

2.3 Transmission electron microscopy (TEM)

TEM images were obtained on a JEOL-JEM-1200EX electron microscope with an accelerating voltage of 80 kV. The TEM samples were prepared by casting diluted sphere dispersions onto the copper grids which were exposed in the air to evaporate water for 24 h and then dried under vacuum for 12 h at room temperature. No staining treatment was performed for the measurements.

2.4 Laser light scattering (LLS)

The laser light scattering experiments were performed on a commercial LS instrument (ALV/DLS/SLS-5022F) equipped with a solid-state laser (Uniphase, output power = 22 mW at λ = 632.8 nm) and a multi-τ digital time correlator (ALV/LSE-5003). Before LLS experiment, the samples were filtered for removing the impurities. The dynamic light scattering (DLS) was applied to measure the hydrodynamic radius (R_h) and polydispersity of colloidal spheres formed in the THF solutions with different initial concentrations at 25 ± 0.1 ^{o}C. The scattering angle used for the DLS measurement was fixed to be 90^{o}.

2.5 Laser irradiation experiment

A linearly polarized beam from a solid state laser (488 nm) was used as the light source. The intensity of the laser beam was 100 mW cm^{-2} and the solid microspheres on the TEM grid were exposed to the perpendicularly incident light. The microspheres were irradiated for different time periods at room temperature under an ambient condition. The deformation of the microspheres was monitored by TEM observations.

3 Additional Characterization Data

2.1 Spectra of IAC-4

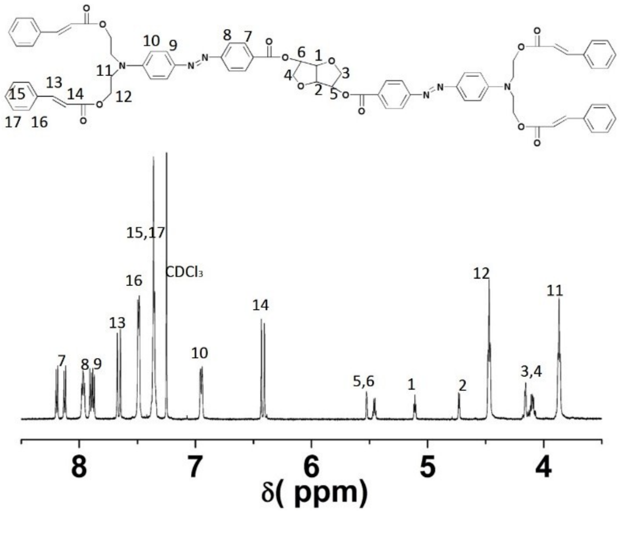

Figure S1. ^{1}H NMR spectrum of the azo compound IAC-4.

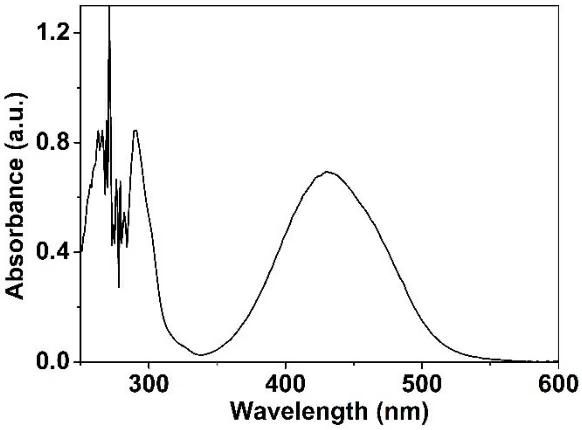

Figure S2. UV-vis spectrum of the azo compound IAC-4 in THF solution.

Table S1. DLS experimental results of THF solutions with the initial concentrations (C_0) of 0.2 and 0.8 mg/mL, after adding the deionized water to reach different water contents.

C_0	Water Content (v %)	$\langle R_h \rangle$ (nm)	$R_{h\,min}$ (nm)	$R_{h\,max}$ (nm)
0.2 mg/mL	45%	232.6	164.1	344.9
	50%	600.3	439.8	834.6
	55%	955.9	690.1	1298
	60%	1332	882.9	2341
	65%	1187	785.8	1898
	70%	703.6	420.3	1167
	75%	569.8	388.0	815.5
0.8 mg/mL	40%	425.5	251.9	767.4
	45%	529.7	374.4	816.7
	50%	1053	908.0	1234
	55%	845.0	677.1	1057
	60%	828.3	648.7	1051
	65%	766.9	577.7	1008
	70%	579.8	381.4	863.3
	75%	532.2	356.4	777.3

Table S2. DLS experimental results of the colloidal spheres obtained from THF solutions with different initial concentration.

C_0	$\langle R_h \rangle$ (nm)	$R_{h\,min}$ (nm)	$R_{h\,max}$ (nm)
0.2	280.4	204.4	384.4
0.5	277.2	193.4	387.9
0.8	262.4	170.5	372.0
1.0	247.6	185.7	324.1

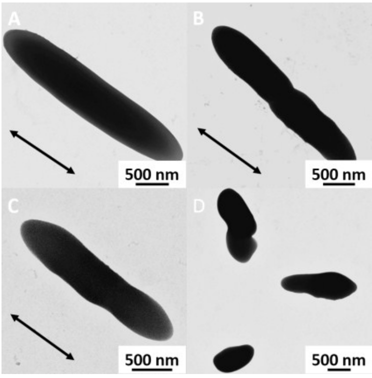

Figure S3. TEM images of the microspheres prepared from the THF solution with the concentration of 0.2 mg/mL, after irradiated for 10 min (488 nm, 100 mW/cm^2). The microspheres were fabricated from the IAC-4 solution with C_0 = 0.2 by firstly dropwise adding 2 mL water into the solutions (1 mL) and then adding excess water (20 mL) to quench the structures formed in the dispersion.

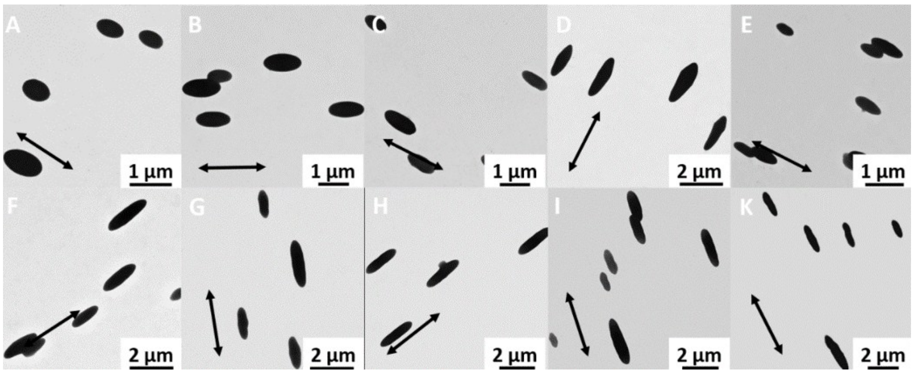

Figure S4. TEM image of the microspheres prepared from the THF solution with the concentration of 0.2 mg/mL, after irradiated for 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 min (A-K). The microspheres were fabricated by the same procedure as described above.

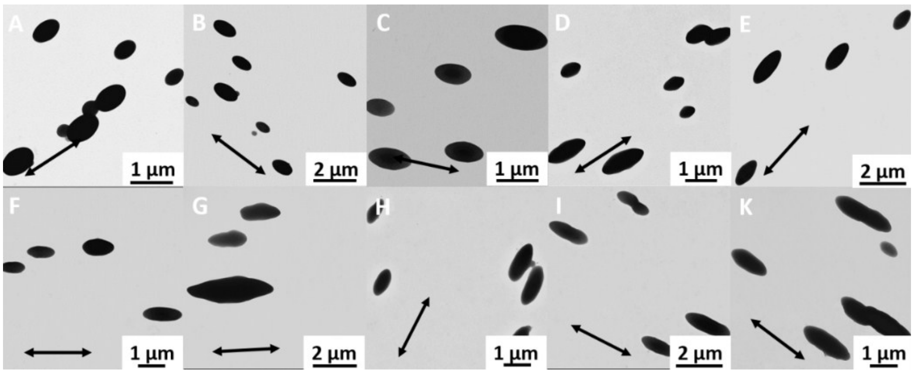

Figure S5. TEM image of the microspheres prepared from the THF solution with the concentration of 0.8 mg/mL, after irradiated for 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 min (A-K). The microspheres were fabricated by the same procedure as described above.

References:

1. M. C. Guo, Z. D. Xu and X. G. Wang, *Langmuir*, 2008, 24, 2740-2745.