Colloidal Molecules with Well-Controlled Bond Angles

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Supporting Information

1. Experimental Section

Synthesis of Monodisperse Crosslinked Polystyrene Spheres

Monodisperse cross-linked (3% w/w divinylbenzene) polystyrene spheres (CPS) with a mean diameter of 226 nm were synthesized by an emulsion polymerization procedure described earlier[26, 27]. All components were used as received. A round bottom flask (1 L) equipped with a PTFE stir bar was charged with deionized water (400 mL) and placed in an 80°C oil bath. Then styrene (47 mL, 99% purity, Merck), divinylbenzene (1.39mL, DVB, 55% mixture of isomers, tech. grade) and sodium dodecylsulfate (0.500g, BDH) dissolved in deionized water (50.0 mL) were added, followed by 50 mL of rinse water. The ingredients were allowed to mix and reach the temperature of the oil bath for one hour. Polymerization was initiated by addition of potassium persulfate (1.55g) dissolved in deionized water (75.0 mL) and allowed to continue for 24h. Two samples of the CPS suspension were consequently coated with vinyl acetate (surface coverage $3.56 \cdot 10^{-21} g/nm^2$) to render the surface more hydrophilic. Despite using the same coating procedure two batches with different wetting angles between the CPS seeds and the swelling styrene were obtained, namely $\theta=23°$and $\theta=30°$. The obtained CPS particles of 111 nm radius (measured by TEM) had a polydispersity of 2.5% and weight fraction of 2.6% w/w in aqueous solution.

Synthesis of Colloidal Molecules

In a typical experiment 5mL of CPS seed suspensions and varying volumes of the swelling monomer were added to a glass flask equipped with a magnetic PTFE-coated stir bar. During swelling all samples were stirred vigorously for about 2-3 days and subsequently placed in an 80°C oil bath. Heating causes the cross-linked polymer network to shrink resulting in the formation of a droplet of the swelling monomer on the colloidal surface[26, 27, 29]. Surface energy between the monomer and the water phase favors the formation of one single protrusion. The hydrophilicity of the surface as well as the surfactant determines the wetting angle between the monomer and the colloidal surface. The less favorable it is for the monomer to wet the surface, the more aspherical the protrusion is to the extent of forming a separate droplet. The samples were left stirring in the oil bath for several days for increasing the number of coalesced colloids. Subsequent polymerization was carried out at 80°C by addition of a water soluble inhibitor, hydroquinone (0.75 mM, 99% purity, Riedel), and initiated with

azobisisobutyronitrile (0.94 mg AIBN dissolved in 0.046 mL styrene per mL of seed suspension). Polymerization was allowed to continue for 24h.

Characterization

Polymerized samples were imaged using a scanning electron microscope (SEM XL FEG 30, Philips). The PS particles were sputter coated with platinum/palladium prior to imaging. Dynamic Light Scattering measurements were done by a Malvern Zetasizer Nano NS at 173°and 13°(wavelength: 620 nm). Electron micrographs were digitally post-processed to optimize brightness and contrast for print.

Density gradient centrifugation

Density gradient centrifugation was performed in a 3 to 9% w/w Ficoll 400 in 1%w/w Pluronic F127 in MilliQ water gradient. Centrifugation was performed for 12 mins at 20,000 rpm in a L60 ultracentrifuge. After having taken out the bands we washed them three times with MilliQ water to remove remains from the density gradient.

2. Supporting Figures

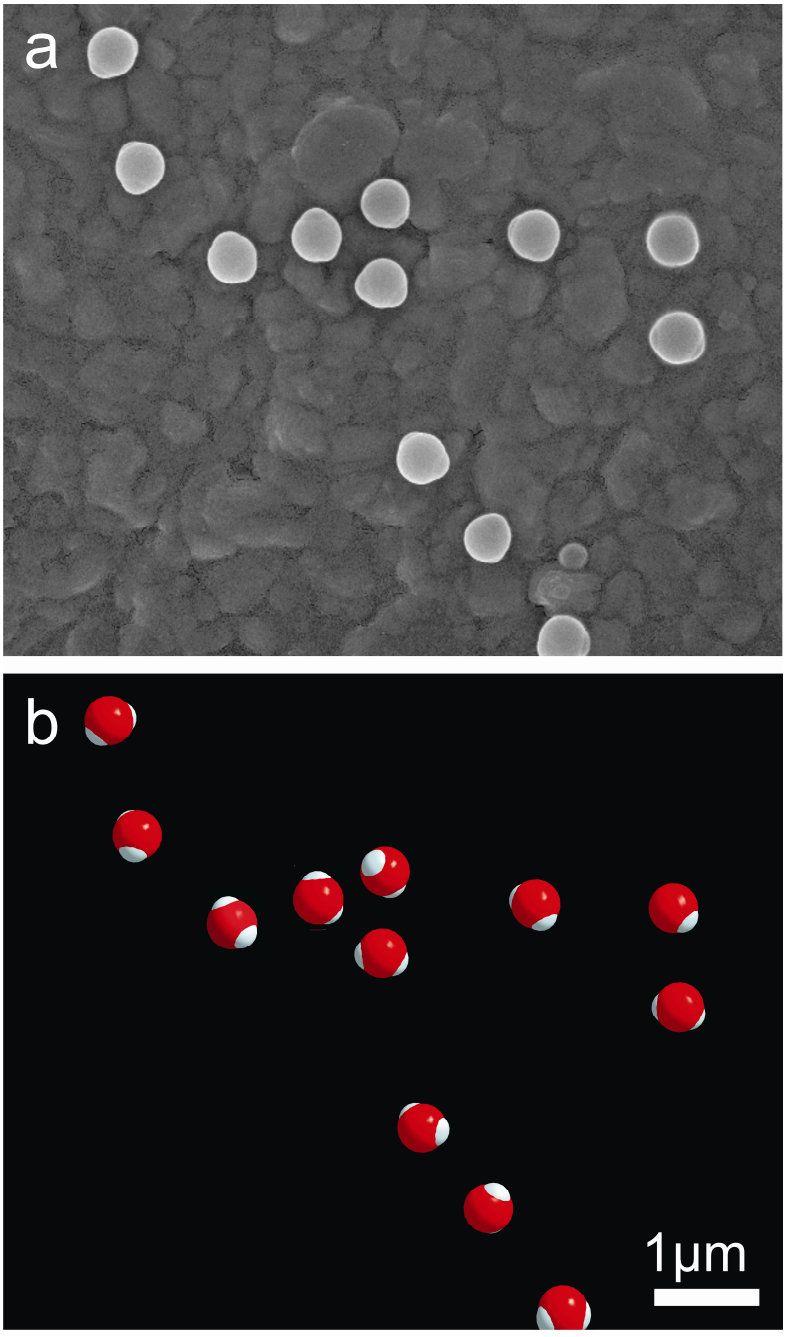

Fig. S1: Water-like colloidal polystyrene particles synthesized by fusion of large liquid protrusions and their corresponding view of a 3D model. The particles were obtained from the second band of a density gradient centrifugation. The angle between the two white seed particles and the red center is 139°. The wetting angle between seed particles and the center is 23°.

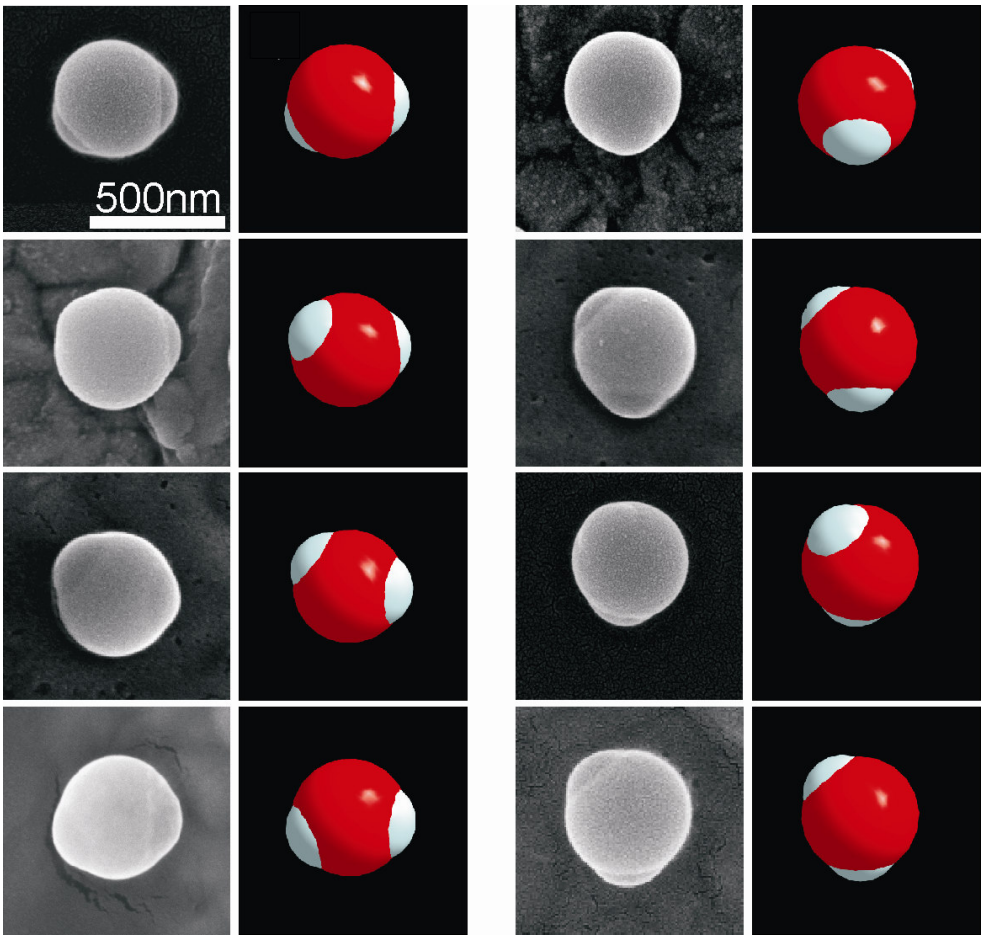

Fig. S2: Water-like colloidal polystyrene particles synthesized by fusion of large liquid protrusions and their corresponding view of a 3D model. The angle between the two white seed particles and the red center is 139°. The wetting angle between seed particles and the center is 23°.

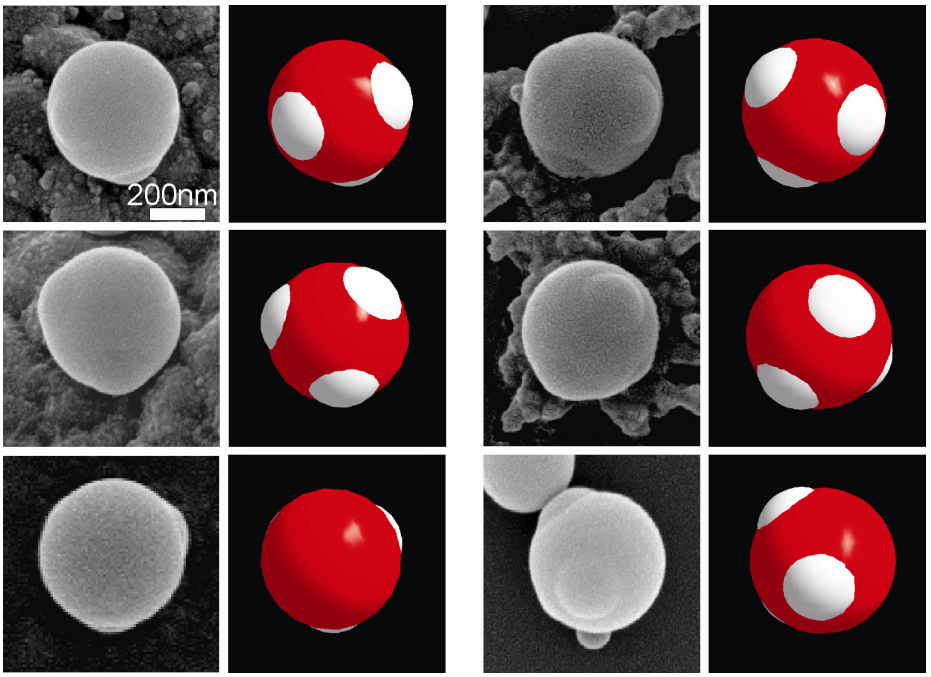

Fig. S3: Colloidal polystyrene particles with three patches resembling ammonia molecules and their respective view of the 3D model. The angle between any two seed particles (white) and the center (red) is 101°. The wetting angle between seed particles and the center is 23°.

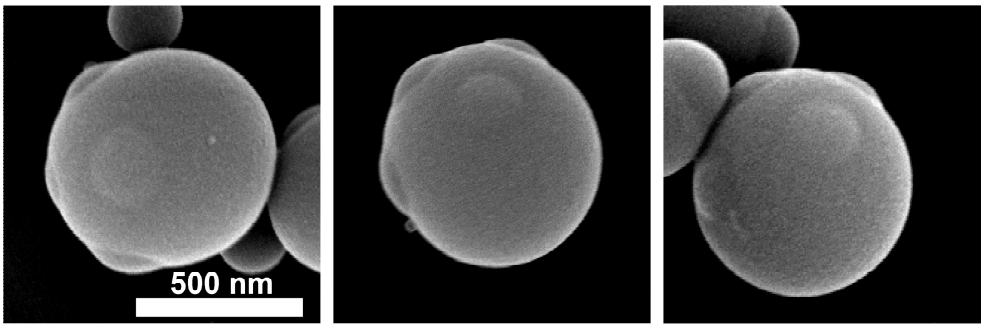

Fig. S4: Colloidal molecules with four integrated seed particles also show uniform shapes.

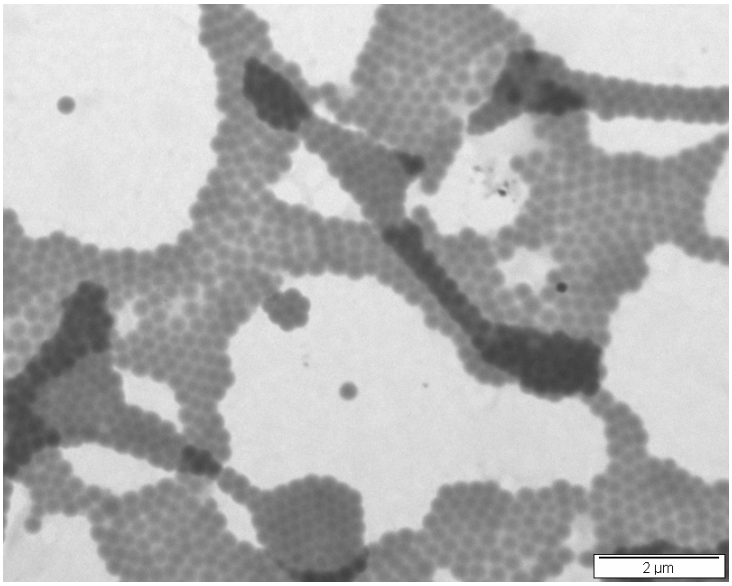

Fig. S5: Transmission electron micrograph of cross-linked polystyrene seed particles in styrene. The particles form 2D layers indicating that no 3D aggregation takes place upon transfer to styrene.

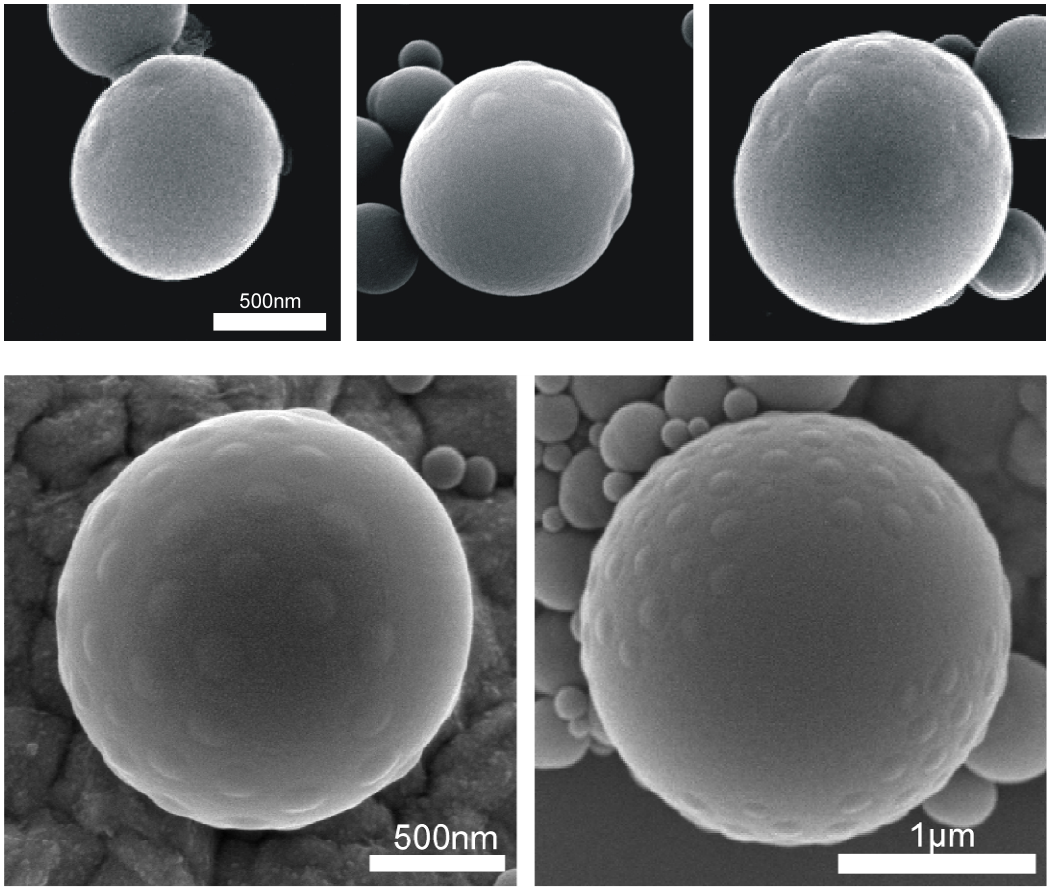

Fig. S6: Assemblies of seed particles intermediate in size between the colloidal molecules (consisting of only few seeds) and the large assembly shown in Fig. 5. On the surface of the droplets consisting of the fused protrusions seed particles aggregate due to polymerization. With an increase in droplet size particle aggregation gradually changes from a global to a local.