

Supporting Information

Fluorescent supracolloidal polymer chains with quantum dots

Seungyong Chae, Sanghwa Lee, Kyungtae Kim, Suk Woo Jang and

Byeong-Hyeok Sohn*

Department of Chemistry, Seoul National University, Seoul 151-747, Korea

*E-mail: bhsohn@snu.ac.kr

Experimental Section

Materials

Polystyrene-*b*-poly(4-vinyl pyridine), PS(51)-*b*-P4VP(18), with a number average molecular weight of 51.0 kg/mol for PS and 18.0 kg/mol for P4VP and a polydispersity index (PDI) is 1.15, was purchased from Polymer Source, Inc.. We used green-emitting quantum dots (QDs) of core-shell CdSe@ZnS capped with oleic acid (green QDs) whose synthetic procedure is described in the literature (W. K. Bae, K. Char, H. Hur and S. Lee, *Chem. Mater.*, 2008, **20**, 531). Red-emitting quantum dots of CdSe@ZnS (red QDs) were purchased from QD Solution Co, LTD. All other solvents and chemicals were purchased from Sigma-Aldrich and used as received.

Crosslinked PS(51)-b-P4VP(18) micelles with quantum dots (QDs)

PS(51)-*b*-P4VP(18) (10.0 mg) and green QDs (2.5 mg) were dissolved in a mixed solvent system of chloroform (3.7 g) and THF (8.8 g) to yield a 0.1 wt% solution. 11-mercapto-1-undecanol (MCU) (1.0 mg, 4.9 μ mol) was then added to this solution (12.5 g), followed by stirring at 40 °C for 12 h. Toluene (4.0 g) was slowly added by a syringe pump to this mixture at a rate of 2.0 ml/h to induce the formation of micelles. After mixing, the

chloroform and THF were evaporated under reduced pressure and the solution (4.0 g) was diluted with toluene (8.5 g) to obtain a 0.1 wt% solution of QD-embedded micelles. To crosslink the P4VP cores, 1,4-dibromobutane (DBB) (2.7 mg, 12 μ mol) was added to this solution (12.5 g) containing PS(51)-*b*-P4VP(18) (10.0 mg), yielding a molar ratio of DBB to 4VP equal to 0.5, which can fully quarternize the 4VP units in the copolymer, followed by stirring at 45 °C for 48 h. PS(51)-*b*-P4VP(18) micelles containing red QDs were prepared employing a similar procedure where red QDs (1.0 mg) and MCU (0.2 mg, 1.0 μ mol) were used.

Patched micelles with QDs

To produce colloidal monomers of patched micelles with QDs, the polarity of the solvent was changed by adding dimethylformamide (DMF) which is 9 times to toluene in weight, to a 0.1 wt% toluene solution of cross-linked PS(51)-*b*-P4VP(18) micelles containing QDs, resulting in a 0.01 wt% solution of colloidal monomers containing QDs with a reorganized corona of two PS patches.

Supracolloidal polymer chains of patched micelles with QDs

The polarity of the solvent was further increased to synthesize supracolloidal polymer chains from colloidal monomers of PS(51)-*b*-P4VP(18) micelles containing QDs. A mixture of DI water and anhydrous DMF (3:7 w/w) was added by a syringe pump at a rate of 10 ml/h to yield 15.0 wt% water in the final solution. The solution was stood without stirring at 30 °C for 48 h.

Supracolloidal random and block copolymer chains

To prepare supracolloidal random copolymer chains, two colloidal monomers containing green and red QDs independently were initially mixed in equal amounts. Then, a

mixture of DI water and anhydrous DMF (3:7 w/w) was added by a syringe pump at a rate of 10 ml/h to the solution to obtain 15 wt% water in the final solution. The solution was kept standing without stirring at 30 °C for 48 hr. To synthesize supracolloidal block copolymer chains, two pre-polymerized chains containing green and red QDs independently were mixed in an equal amount. The mixed solution was kept standing without stirring at 30 °C for additional 24 hr.

Characterizations

Transmission electron microscopy (TEM) was performed on a Hitachi H-7600 at 100 kV. A TEM sample was prepared by dropping a solution of micelles or supracolloidal chains onto a carbon-coated TEM grid with removal of excess solvent using a filter paper. After drying in air, the TEM sample was exposed to iodine or ruthenium tetroxide vapor to stain P4VP or PS. UV-Vis absorption spectra were recorded on a Varian Cary-5000 spectrophotometer. Steady-state fluorescence was measured on an Acton SpectraPro with a He-Cd laser (325 nm) as the excitation source. Dynamic light scattering was performed using a DLS-8000 instrument (Otsuka Electronics Co, Ltd) with a fixed scattering angle of 90°. Structured illumination microscopy (SIM) was performed on a dried sample prepared by spin-coating (6000 rpm, 60 s) a solution of supracolloidal chains onto a glass substrate using an Elyra PS1 microscope system (Carl Zeiss) equipped with an EMCCD camera (Andor Technology) at the National Center for Inter-University Research Facilities. Excitation with an Argon laser at 488 nm was used with emission filters (495~550 nm for green QDs and 570~620 nm for red QDs). A SIM image was acquired from z-stacks containing 5 phase-shifts and 3 rotations per z-slice (100 nm interval) and processed with Zen software (Carl Zeiss). For multicolor imaging, channels were aligned using a multispec calibration slide (170 nm beads, Carl Zeiss) with the channel alignment program in Zen software.

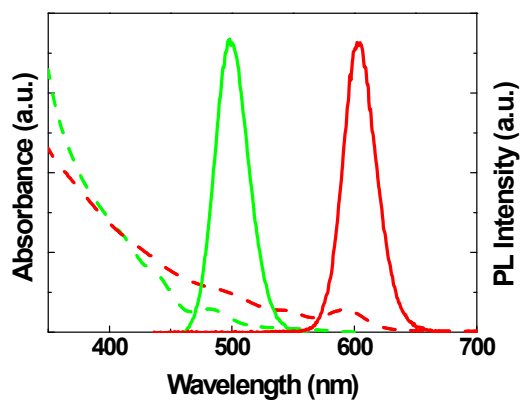


Fig. S1 UV-Vis (dashed) and photoluminescence (solid) spectra of green QDs (green) and red QDs (red).

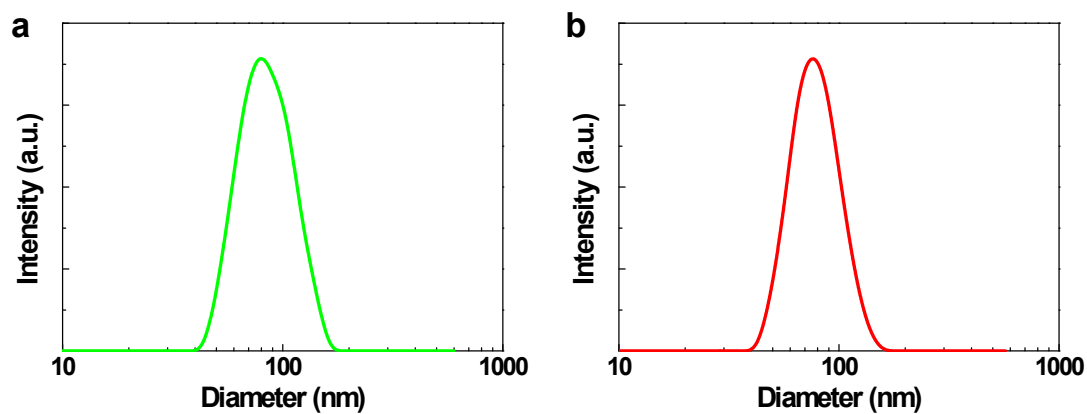


Fig. S2 Dynamic light scattering (DLS) results of PS(51)-*b*-P4VP(18) micelles with QDs: (a) micelles with green QDs; (b) micelles with red QDs.

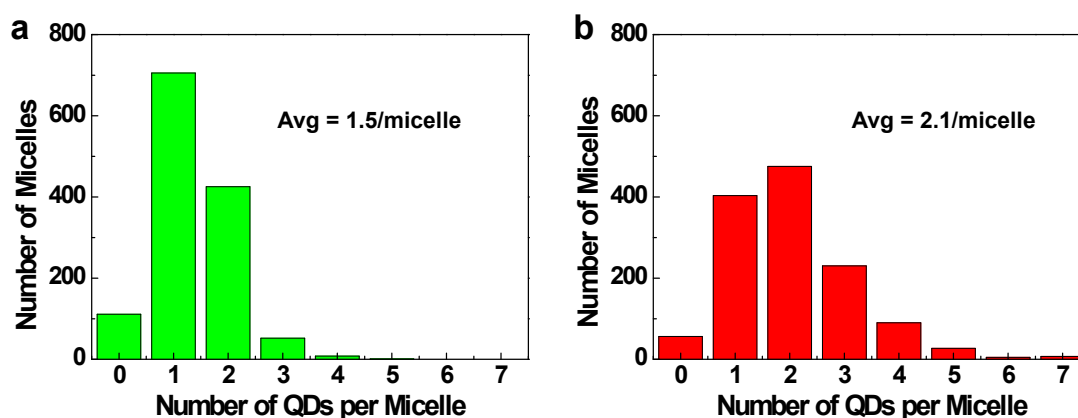


Fig. S3 Histograms of the number of QDs per micelle: (a) green QDs; (b) red QDs.

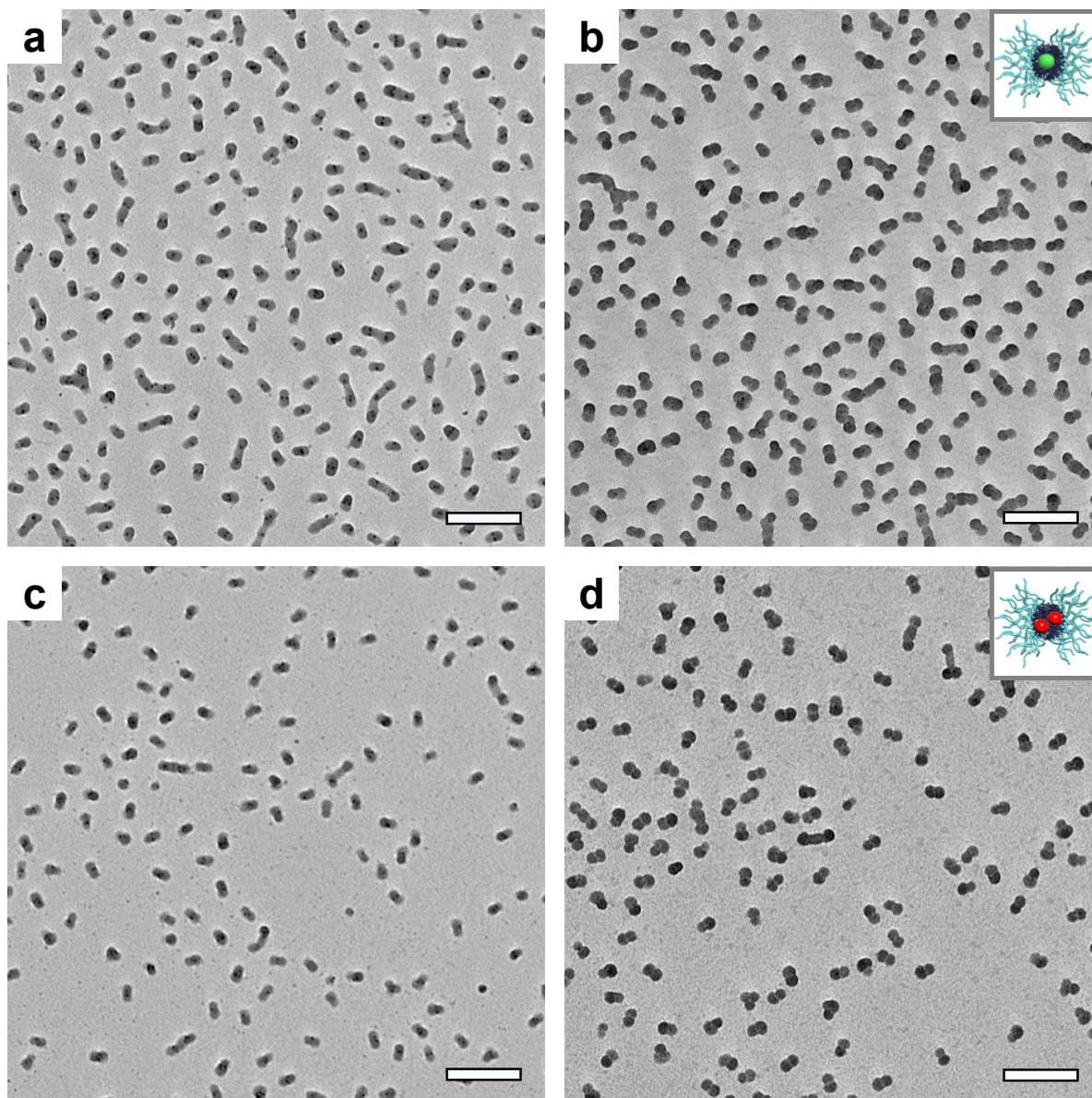


Fig. S4 Large-area TEM images of patched micelles with green QDs (a,b) and with red QDs (c,d). Left images (a,c) were stained with I_2 whereas right images (b,d) were stained with RuO_4 . All scale bars are 100 nm.

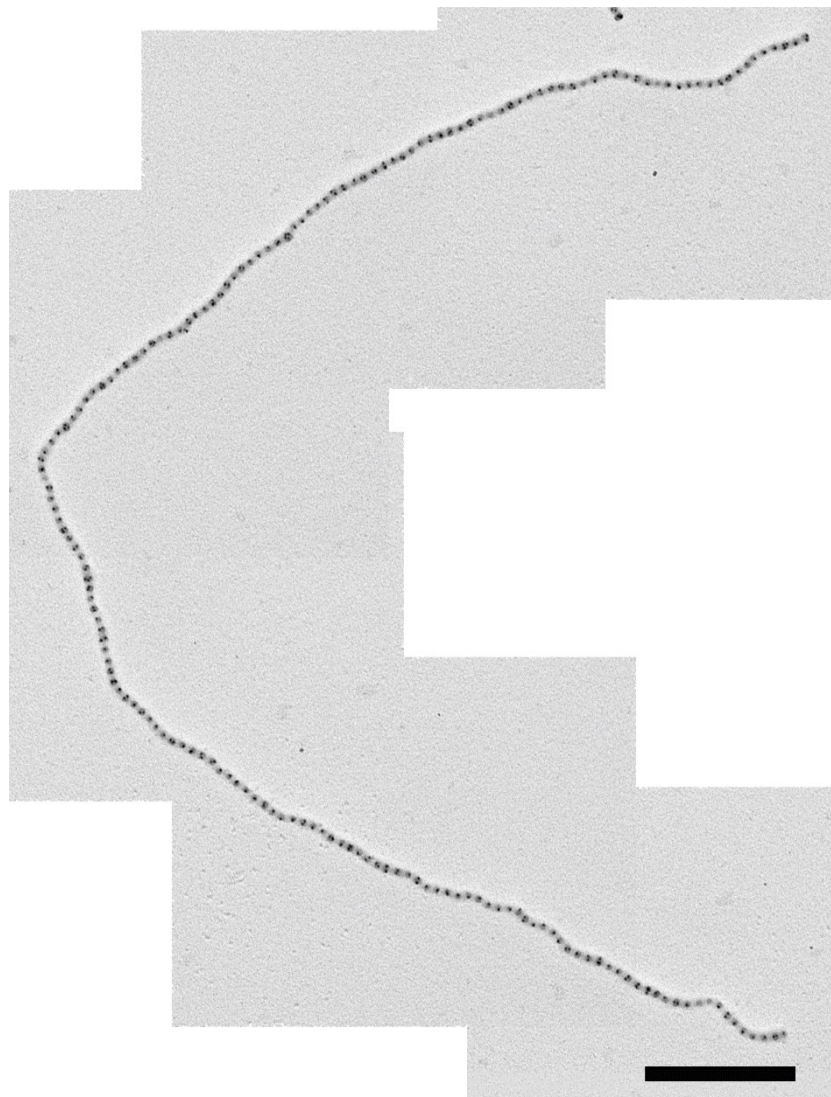


Fig. S5 TEM image of a supracolloidal polymer chain with green QDs shown in the inset of Figure 2a. The scale bar is 500 nm.

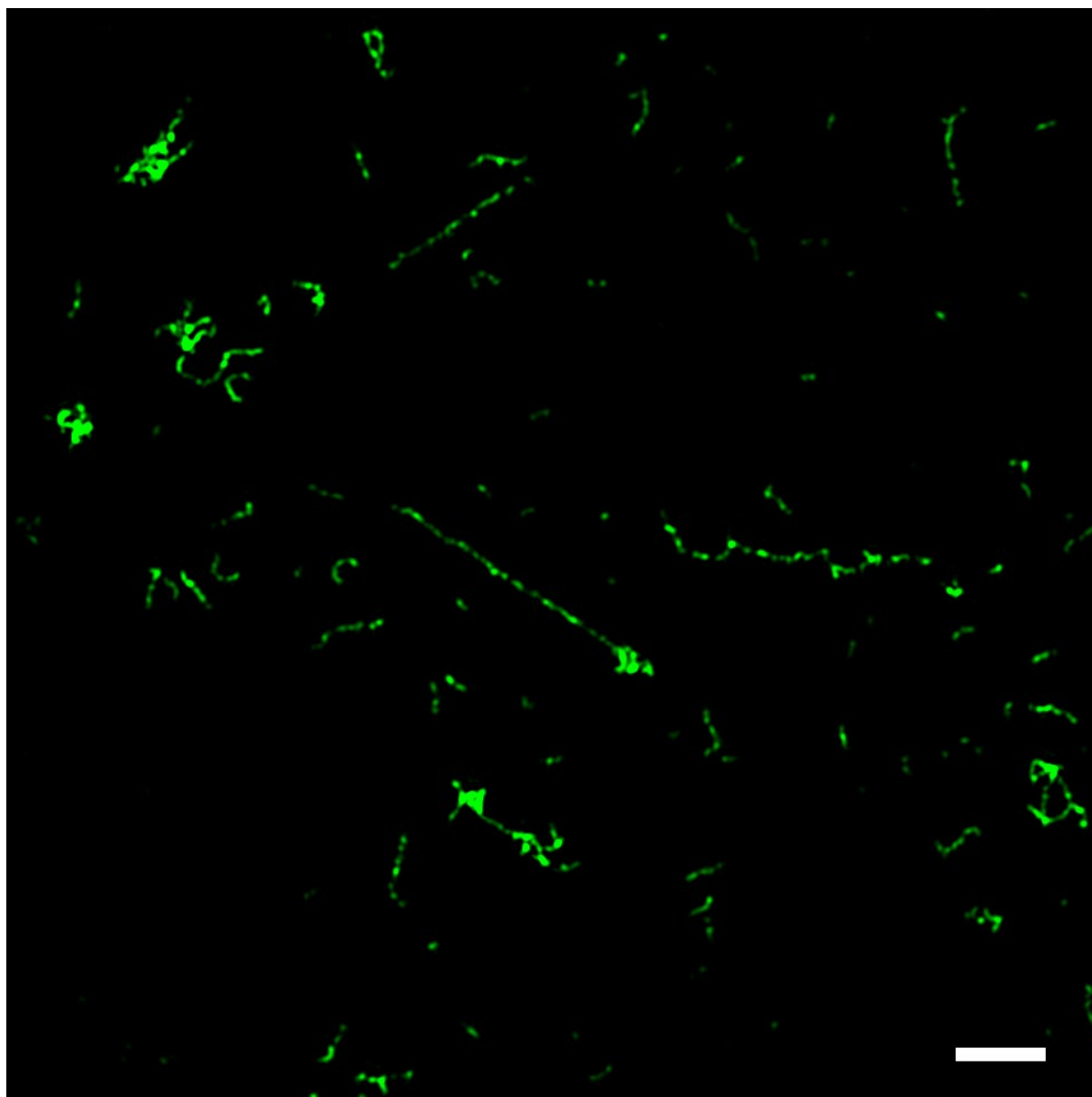


Fig. S6 Large-area SIM image of supracolloidal chains functionalized with green QDs. The scale bar is 1 μm .

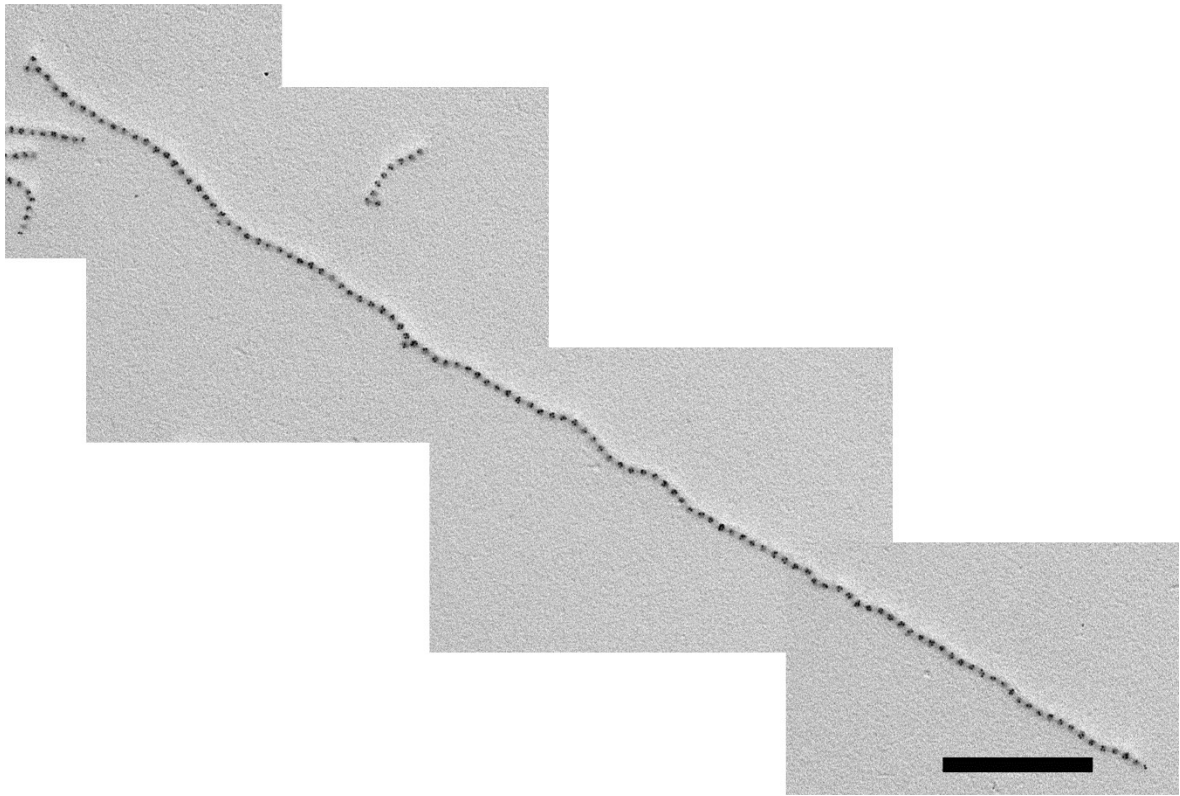


Fig. S7 TEM image of a supracolloidal polymer chain with red QDs shown in the inset of Figure 2d. The scale bar is 500 nm.

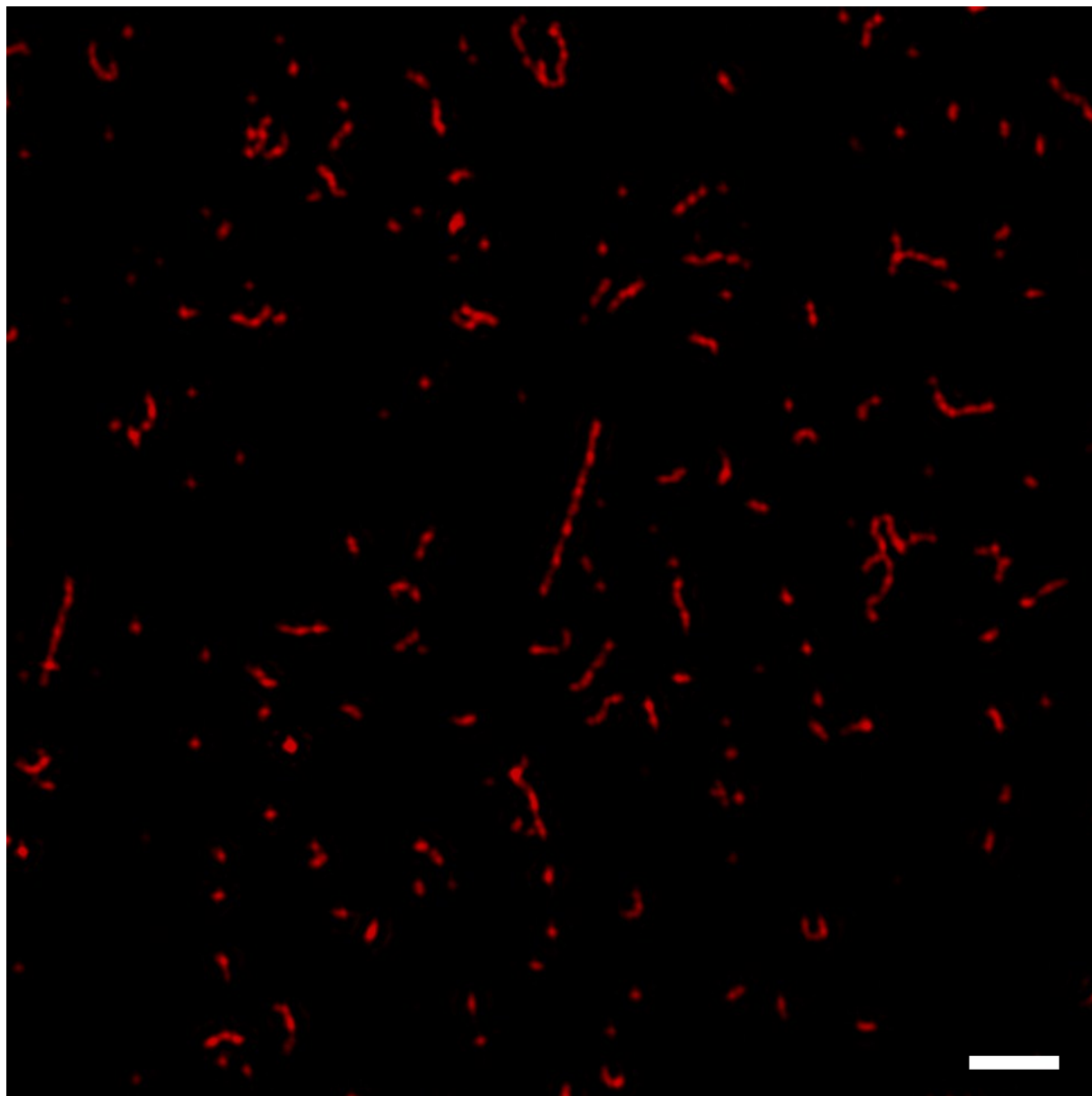


Fig. S8 Large-area SIM image of supracolloidal chains functionalized with red QDs. The scale bar is 1 μm .

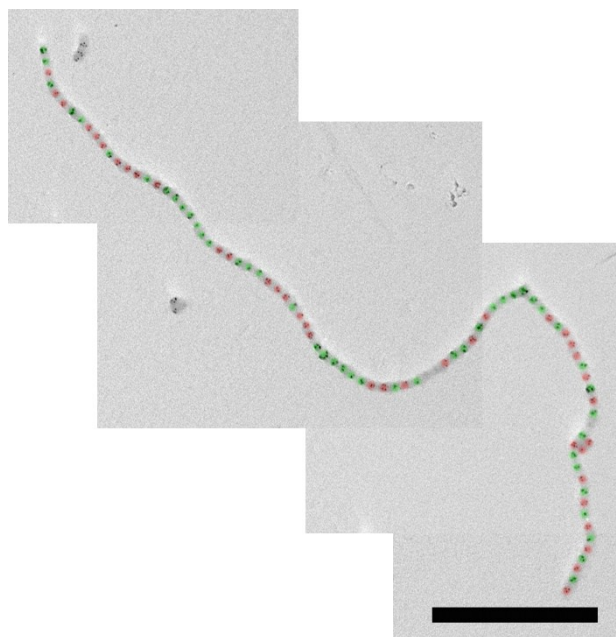


Fig. S9 TEM image of a supracolloidal random copolymer chain with green and red QDs shown in the inset of Figure 3a. Green and red false colors were applied to the cores containing green and red QDs, respectively. The scale bar is 500 nm.

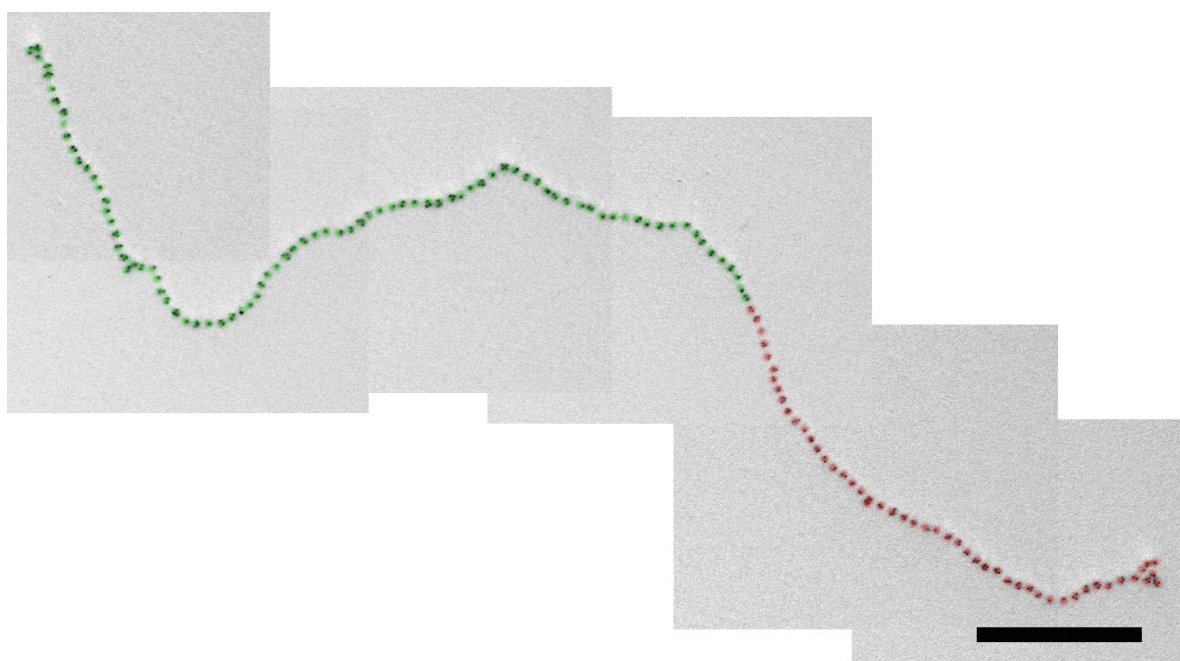


Fig. S10 TEM image of a supracolloidal block copolymer chain with green and red QDs shown in the inset of Figure 3d. Green and red false colors were applied to the cores containing green and red QDs, respectively. The scale bar is 500 nm.