Supporting Information

Preparation and Photo/Chemical-Activation of Wormlike Network Micelles of Core-shell Quantum Dots and Block Copolymer Hybrids

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Morphology of PS_{317}-$P4VP_{76}$ micelles at different aging time in the absence of QDs

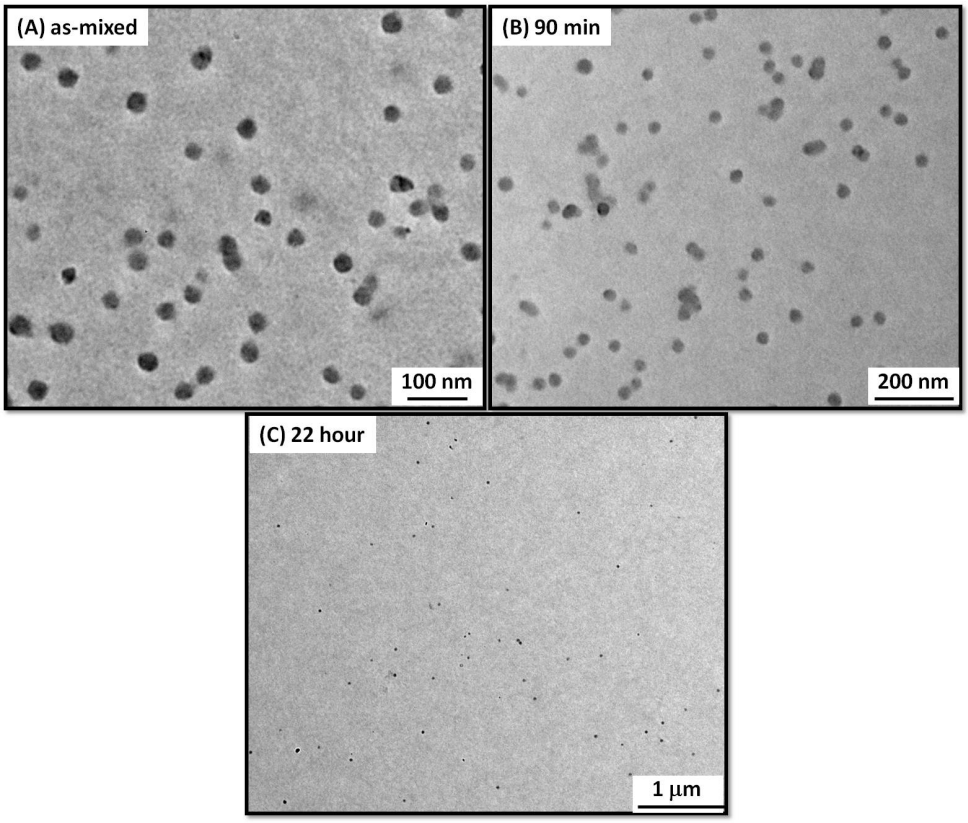

Figure S1. Bright-field TEM images of PS_{317}-*b*-$P4VP_{76}$ micelle prepared in the absence of QDs taken (A) as-mixed, (B) aged for 90 minutes and (C) aged for 22 hours.

TEM analysis of the PS_{317}-$P4VP_{76}$ micelles and QD/PS_{317}-$P4VP_{76}$ hybrid micelles

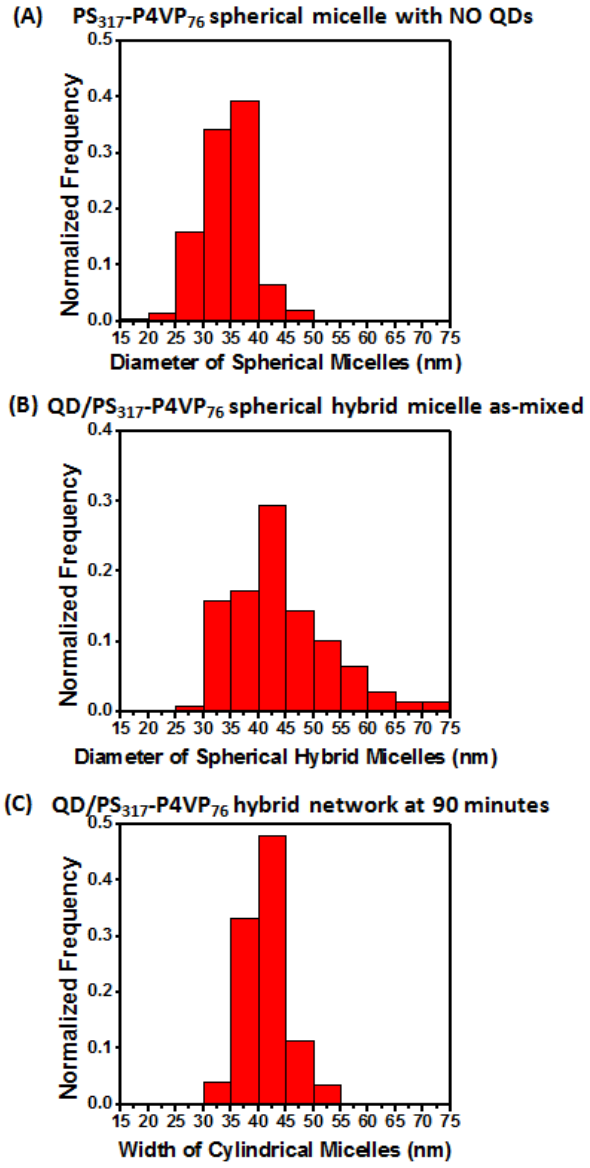

Figure S2. Normalized size distribution of (A) the diameters of spherical micelles of PS_{317}-$P4VP_{76}$ without the presence of QDs, d_{sphere} = 34.2 ± 4.8 nm; (B) the diameters of spherical hybrid micelles of QD/ PS_{317}-$P4VP_{76}$, d_{sphere} = 44.0 ± 8.4 nm formed as-mixed; and C) the widths of cylindrical structures after aging for 90 min, $d_{cylinder}$ = 41.3 ± 3.8 nm. The histograms are constructed based on analysis of dark-field TEM images of 200 hybrid micelles. The analysis of dark-field TEM images shows small, but statistically significant differences, ca. 20% larger mean diameters, than those obtained by analysis of images taken in bright-field.

The Evolution of PL intensity of CdSe/ZnS and CdSe/ZnS/PS-P4VP in chloroform

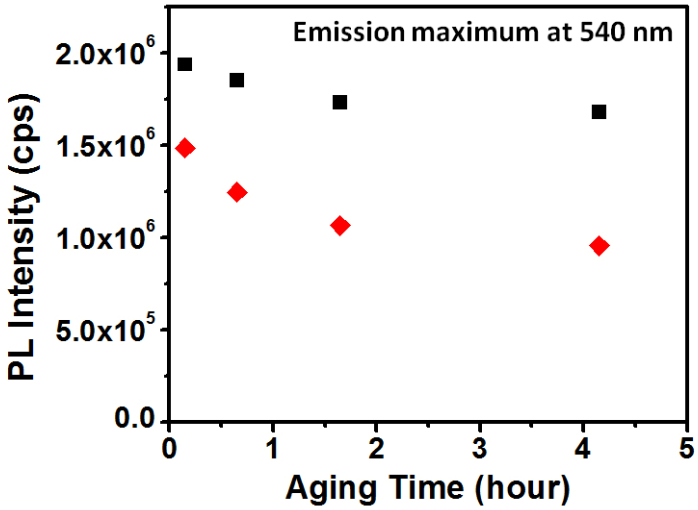

Figure S3. Evolution of the maximum PL intensity of CdSe/ZnS QDs (black squares, 0.03 nmol/mL) and the mixture of CdSe/ZnS/PS_{317}-*b*-$P4VP_{76}$ (red diamonds, 0.03 nmol/mL QDs and 0.0076 mg/mL PS_{317}-*b*-$P4VP_{76}$) in chloroform. The solutions were aged in the dark without stirring. After 4 h aging, the QD solution retained 87 % of the initial PL intensity; while the PL intensity of QD and PS-P4VP hybrids retained 65% of that of the initially formed sample.

To study the evolution of PL intensity of CdSe/ZnS in a good solvent, a chloroform solution of CdSe/ZnS was prepared by diluting an aliquot of 0.1 mL QDs solution (1 nmol/mL, $CHCl_3$) with 3.2 mL $CHCl_3$. The final concentration of QDs was 0.03 nmol/mL. The mixing was promoted by gentle shaking. The 1st data point was recorded 15 minutes after mixing. A gradual decrease in PL intensity was observed in the QDs chloroform solution, while 87 % of the initial emission intensity was retained.

Another chloroform solution of QDs was prepared in the presence of PS-P4VP block copolymer with an identical QD concentration. Specifically, 0.1 mL QD solution (1 nmol/mL, $CHCl_3$) was mixed with an aliquot of 0.25 mL PS_{317}-*b*-$P4VP_{76}$ solution (0.1 mg/mL, $CHCl_3$). This mixture was adjusted to a total volume of 3.3 mL with $CHCl_3$. The final sample solution consisted of 0.0076 mg/mL PS-P4VP and 0.03 nmol/mL QDs. Mixing was promoted by gentle shaking. The sample was allowed to sit 15 minutes before carrying out the first PL measurement. The PL intensity of QD/PS-P4VP mixture was ca. 25 % lower compared to the freshly prepared QD solution in chloroform without PS-P4VP. The PL intensity decreased over longer aging times. After 4.3 hours, its PL intensity was ca. 50 % of the PL intensity of the freshly prepared QDs solution without diblock copolymer.

The influence of UV-irradiation on the PL of APP/CdSe/ZnS/PS-P4VP

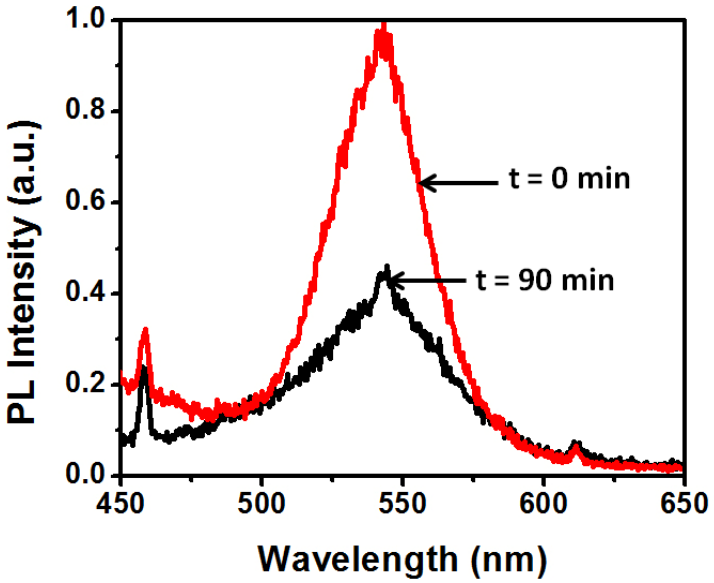

Figure S4. CdSe/ZnS/PS_{317}-*b*-$P4VP_{76}$ wormlike network solution was treated with 2 M of 3-amino-1-proponal (APP) and annealed in the dark for 20 hours. Normalized PL spectra of the mixture measured before and after a 90-mintues UV-irradiation at 365 nm.

The solubility limit of MEH-PPV in 2-PrOH and in 3:8 $CHCl_3$/2-PrOH

Chloroform solutions of MEH-PPV were prepared at a series of concentrations, 0.088, 0.16, 0.22, 0.29 μg/mL. To determine the specific extinction coefficient ε, the maximum absorbance at 480 nm was recorded and plotted against mass concentration as shown in Figure S5. The slope of this line yielded ε = 0.106 mL/μg×cm, of MEH-PPV in chloroform.

To determine the limiting solubility of MEH-PPV in 2-PrOH containing 5 vol % $CHCl_3$ and in a 3:8 v/v mixture of $CHCl_3$/2-PrOH, saturated solutions of MEH-PPV in these solvents were prepared. Specifically, 0.1 mL of 1mg/mL MEH-PPV in chloroform was added to 2 mL 2-PrOH. The solvent consist of 95 vol% 2-PrOH and 5 vol% of chloroform. A red precipitate fell to the bottom of the vial, while the supernatant solution appeared pink. In parallel, 0.75 mL of 1 mg/mL MEH-PPV in chloroform was added to 2 mL 2-PrOH. The final constitution of the solvent is 73 vol% 2-PrOH. Again, a red sediment formed, but the supernatant here was deep yellow in color.

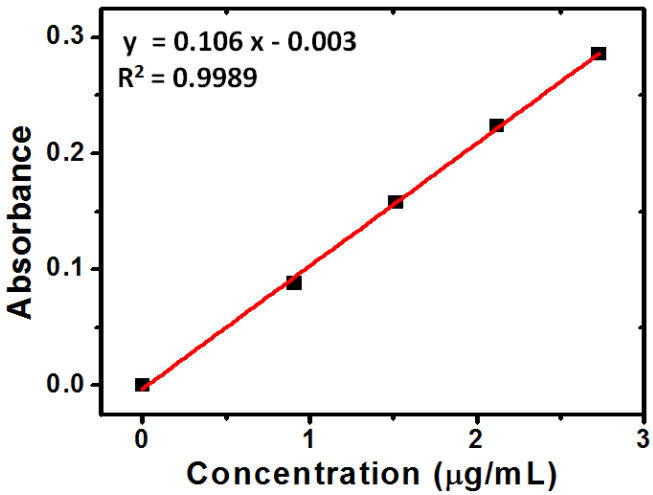

Figure S5. The absorbance at 480 nm ($A_{480\ nm}$) of MEH-PPV chloroform solutions plot against their mass concentrations. These data was fitted to a linear plot (red). The extinction coefficient of MEH-PPV in chloroform is determined to be 0.106 mL/μg×cm.

Both samples were aged in the dark for 1 day and then subjected to 15 min centrifugation at 3,000 rpm. An aliquot of 2.0 mL of each supernatant was removed and dried by rotary evaporation. The residues were dissolved in 2.0 mL chloroform for UV-Vis measurements. The solubility limit for each solvent was estimated by the Beer-Lambert law based on the measured absorbance and the value ε = 0.106 mL/μg×cm for MEH-PPV in

chloroform. These values are 0.96 µg/mL in 5:95 $CHCl_3$/2-PrOH and 8.7 µg/mL in the 3:8 mixture of $CHCl_3$/2-PrOH.

Comparison of the PL intensity in chloroform of MEH-PPV, and of CdSe/ZnS QDs

Figure S6 compares separately the PL spectra of a solution of MEH-PPV in $CHCl_3$ (red curve), a spectrum of CdSe/ZnS in the presence of PS-P4VP (denoted CdSe/ZnS/PS-P4VP) (blue curve) and that of a solution containing all three components at the same concentrations (green curve). The black dashed line represents the sum of the PL intensity contributions of the red and blue curves and is essentially identical to the green curve. This establishes that the components do not interact in chloroform at this low concentration.

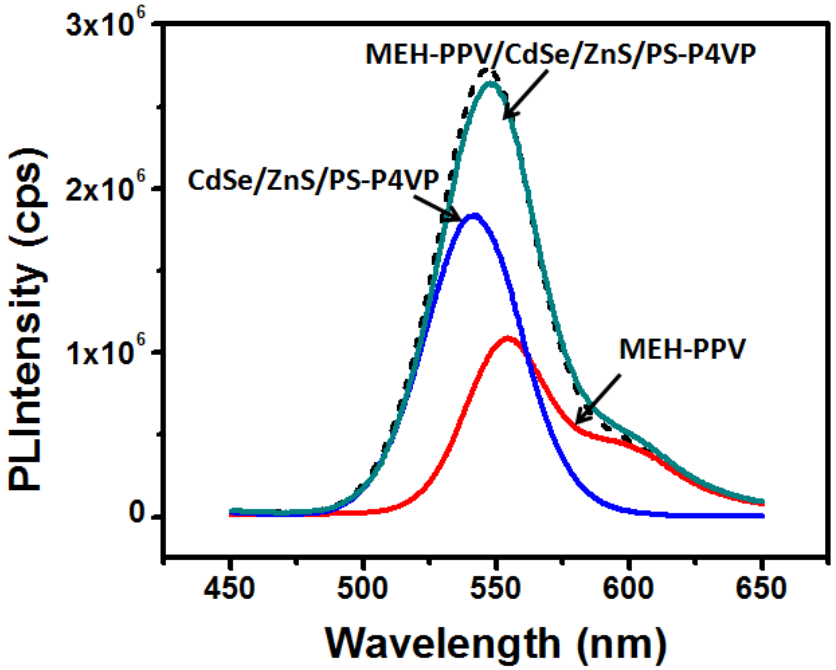

Figure S6. The PL emission of a chloroform solution of CdSe/ZnS/PS-P4VP (blue-plot; 0.03 nmol/mL QD; 0.0076 mg/mL PS-P4VP); and a chloroform solution of MEH-PPV (red-plot, 0.67 µg/mL MEH-PPV) in chloroform. The green plot represents the PL spectra of a chloroform solution of MEH-PPV/QD/PS-P4VP (0.03 nmol/mL QD; 0.0076 mg/mL PS-P4VP; 0.67 µg/mL MEH-PPV). In comparison, the sum of the plots of the spectra of CdSe/ZnS/PS-P4VP and MEH-PPV is drawn as the black dashed line.