Supporting Information for:

Luminous block copolymer-quantum dots hybrids formed by cooperative assembly in selective solvent

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Materials

Cadmium oxide (CdO, purity 99.95%), myristic acid (MA, purity ≥ 99%), n-trioctylphosphine oxide (TOPO, purity 98%), and thiourea (purity 99%) were purchased from Aladdin. Selenourea (purity 99%) were obtained from Alfa Aesar. PS_{356}-*b*-PEO_{148} (M_n = 37000 for the PS block and M_n = 6500 for the PEO block, PDI = 1.06, where the subscripts indicate the number of average degree of polymerization) and thiol terminated polystyrene (PS-SH, M_n = 2000, PDI = 1.15) were purchased from Polymer Source, Inc., Canada. All of the materials were used after receiving without further purification. All the glassware were cleaned by aqua regia and rinsed with deionized water prior to the experiments.

Synthesis of TOPO-coated CdS QDs

TOPO-coated CdS QDs were synthesized by two-phase approach according to the literature by Pan[1,2] with some modification. Firstly, Cd-MA was prepared through the following procedure: CdO (1.926 g, 15 mmol) and myristic acid (7.500 g, 33 mmol) were loaded into a flask and were heated to 210 ℃ for 10 min. An optically clear solution was obtained. The crude products were recrystallized twice from toluene. The Cd-MA was dried in an oven and was used for further synthesis of CdS and CdSe/CdS core-shell QDs. Secondly, TOPO-coated CdS QDs were obtained by a two-phase approach in the flask using thiourea as the sulfur precursor. As a typical example, Cd-MA (226.8 mg, 0.4 mmol), TOPO (1 g), and toluene (10 mL)

were placed in a flask and the mixture was heated to 100 ℃ for 10 min until an optically clear solution was obtained. Then, a freshly prepared aqueous solution of thiourea (10 mL, 0.05 M) was swiftly injected to the clear solution of cadmium (Cd) precursors. The reaction was kept at 100 ℃ for two hours. Finally, the mixture was kept still and cooled to room temperature. The crude toluene solution of TOPO-coated CdS QDs was precipitated with methanol and was further isolated by centrifugation and decantation. The purified nanocrystals were redispersed in chloroform.

Synthesis of TOPO-coated CdSe/CdS QDs

Similar with the synthesis of TOPO-coated CdS QDs, TOPO-coated CdSe/CdS core-shell QDs were prepared to improve the fluorescent quantum efficiency.[3,4] Firstly, TOPO-coated CdSe cores were obtained by a two-phase approach in the autoclave using selenourea as selenium precursor. In a typical experiment, Cd-MA (113.4 mg, 0.2 mmol), TOPO (500.0 mg), and toluene (10 mL) were placed in a flask and the mixture was heated to 100 ℃ for 10 min until an optically clear solution was obtained. The clear solution of Cd precursors and a freshly prepared aqueous solution of selenourea (10 mL, 0.01 M) were swiftly transferred to a 30 mL Teflon-lined stainless steel autoclave. The autoclave was maintained at 180 ℃ for an hour. Then, the autoclave was cooled to room temperature with tap water. Secondly, about 9 mL of the crude solution of CdSe cores, Cd-MA (113.4 mg, 0.2 mmol), and TOPO (500.0 mg) were put into a flask and the mixture was heated to 100 ℃ for 10 min until an optically clear solution was obtained. The clear solution was cooled down to room temperature and was then transferred with a freshly prepared aqueous solution of thiourea (10 mL, 0.05 M) to an autoclave with capacity of 30 mL. The autoclave was sealed and maintained at 140 ℃ for overnight (about 12 h). Finally, the autoclave was cooled to the room temperature with tap water. The crude toluene solution of TOPO-coated CdSe/CdS QDs was precipitated with methanol and was further isolated by centrifugation and decantation. The purified nanocrystals were redispersed in chloroform.

Characterization

TEM measurements were performed on a JEOL JEM-1011 transmission electron microscopy operated at an accelerating voltage of 100 kV. The samples were unstained and prepared by depositing one drop of the dialyzed solution of micelles onto a 300 mesh copper grid coated with a carbon film. After *ca.* 15 min, the excess sample solution was blotted away using a strip of filter paper. Finally, the sample was allowed to

dry in air and at room temperature before observation. UV-vis absorption spectra and PL spectra of samples solution were recorded on a Shimadzu UV-2450 PC spectrometer and a Shimadzu RF-5301 PC fluorometer with a resolution of 1.0 nm, respectively. For the tests of PL spectra, the excitation wavelength of 450 nm and 420 nm were used corresponding to the PS-grafted CdSe/CdS QDs with 3.8 nm and 4.9 nm, respectively.

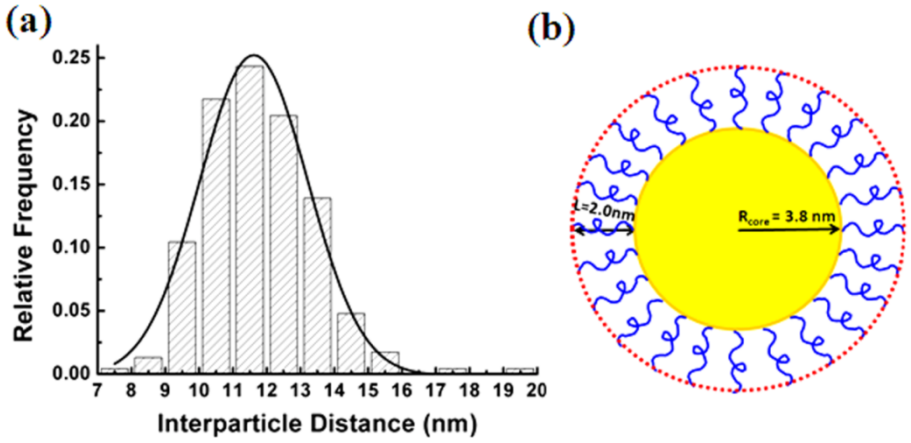

Fig. S1 (a) The interparticle distance histogram and "Gauss Fit" of PS-grafted CdS QDs; (b) Schematic illustration of the PS-grafted CdS QDs. The average interparticle distance and average diameter of PS-grafted CdS QDs was 11.6 nm and 7.6 nm, respectively. Thus, the cartoon figure of PS-grafted CdS quantum dot with radius of 3.8 nm and PS brush thickness of 2.0 nm was depicted easily.

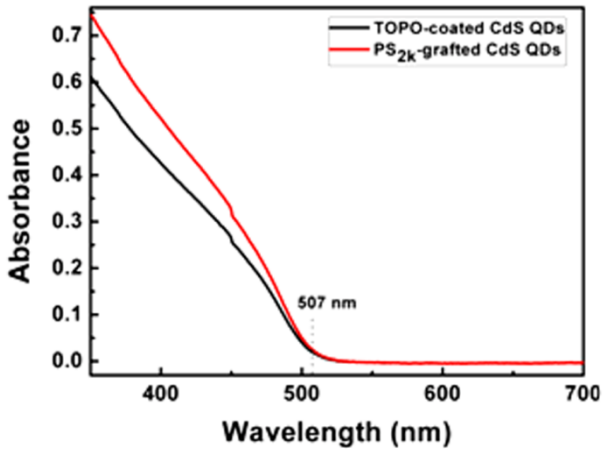

Fig. S2 UV-vis absorption spectra of TOPO-coated (black curve) and PS-grafted (red curve) CdS QDs. They were both dispersed in chloroform, with the absorption band at 507 nm, indicating almost no change of the size of QDs before and after surface modification.

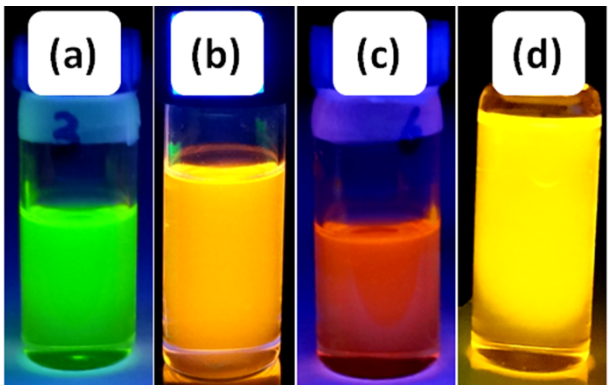

Fig. S3 (a)-(c) Photograghs of PS-grafted CdSe/CdS QDs with average diameter of 3.8 nm, 4.9 nm and 5.8 nm, respectively; (d) Photogragh of TOPO-coated CdSe/CdS QDs with average diameter of 4.9 nm. All the photograghs of QDs dispersed in chloroform were taken under 365 nm UV light irradiation.

Table S1. Characteristics of QDs/PS-*b*-PEO hybrid micelles

QDs Weigh Fraction (*f*)	0.27	0.33	0.43	0.50	0.62	0.67
Micelles Diameter/nm	66.1±6.9	69.8±7.0	75.3±7.3	61.7±6.0	56.8±6.2	55.4±8.7
PS Shell Thickness/nm	14.2±1.6	15.5±1.7	17.9±2.0	12.7±1.6	11.2±1.8	8.1±1.9
The QDs Number per Micelle	33	49	83	56	57	58
QDs Volume Fraction per Micelle/%	17.13	22.49	30.34	37.21	48.55	53.24

The statistical values of micelles diameters and PS shell thicknesses were obtained by measuring at least 200 spherical QDs/BCP micelles. The average QDs number and QDs volume fraction per micelle can be calculated by using the following equations:

$$N_{\mathrm{QDs/micelle}} = \frac{m(\mathrm{QDs})}{\dfrac{\frac{4}{3}\pi {R_{\mathrm{core}}}^3 \times \rho_{\mathrm{CdS}} + \left[\frac{4}{3}\pi (R_{\mathrm{core}} + L)^3 - \frac{4}{3}\pi {R_{\mathrm{core}}}^3\right] \times \rho_{\mathrm{PS}}}{\mathrm{m(BCP)} \times \frac{37000}{37000 + 6500}} \times \left[\frac{4}{3}\pi {R_{\mathrm{micelle}}}^3 - \frac{4}{3}\pi (R_{\mathrm{core}} + L)^3 \times N_{\mathrm{QDs/micelle}}\right] \times \rho_{\mathrm{PS}}}$$

The $N_{\mathrm{QDs/micelle}}$ can be simplified and calculated as follows:

$$N_{\mathrm{QDs/micelle}} = \frac{m(\mathrm{QDs}) \times {R_{\mathrm{micelle}}}^3 \times \rho_{\mathrm{PS}}}{m(\mathrm{QDs}) \times (R_{\mathrm{core}} + L)^3 \times \rho_{\mathrm{PS}} + 0.85 \times \mathrm{m}(\mathrm{BCP}) \times \left\{ {R_{\mathrm{core}}}^3 \times \rho_{\mathrm{CdS}} + \left[(R_{\mathrm{core}} + L)^3 - {R_{\mathrm{core}}}^3 \right] \times \rho_{\mathrm{PS}} \right\}}$$

Where $N_{\mathrm{QDs/micelle}}$ is the QDs loading number per micelle; m(QDs) and m(BCP) are the mass of PS-grafted CdS QDs and PS-b-PEO, respectively. In our experiments, the BCP initial concentration was 0.2 wt%, m(BCP) =1 mg. R_{micelle}, R_{core} are L express the radius of hybrid micelle not containing the corona layer of PEO, the radius of CdS core and the thickness of PS grafts layer, respectively, all of which are obtained from the TEM statistical values. Here, for the PS-grafted QDs, the radius (R_{core}) and PS grafts thickness (L) are 3.8 nm and 2.0 nm, respectively. ρ_{PS} and ρ_{CdS} are the density of PS and CdS, respectively. $\rho_{\mathrm{PS}} = 1.05\ \mathrm{g/cm^3}$, $\rho_{\mathrm{CdS}} = 4.82\ \mathrm{g/cm^3}$.

The QDs volume fraction per micelle (ϕ_{QDs}) can be calculated according to the following equation[5]:

$$\phi_{\mathrm{QDs}} = \frac{\frac{4}{3}\pi (R_{\mathrm{core}} + L)^3 \times N_{\mathrm{QDs/micelle}}}{\frac{4}{3}\pi {R_{\mathrm{micelle}}}^3} = \left(\frac{R_{\mathrm{core}} + L}{R_{\mathrm{micelle}}} \right)^3 \times N_{\mathrm{QDs/micelle}}$$

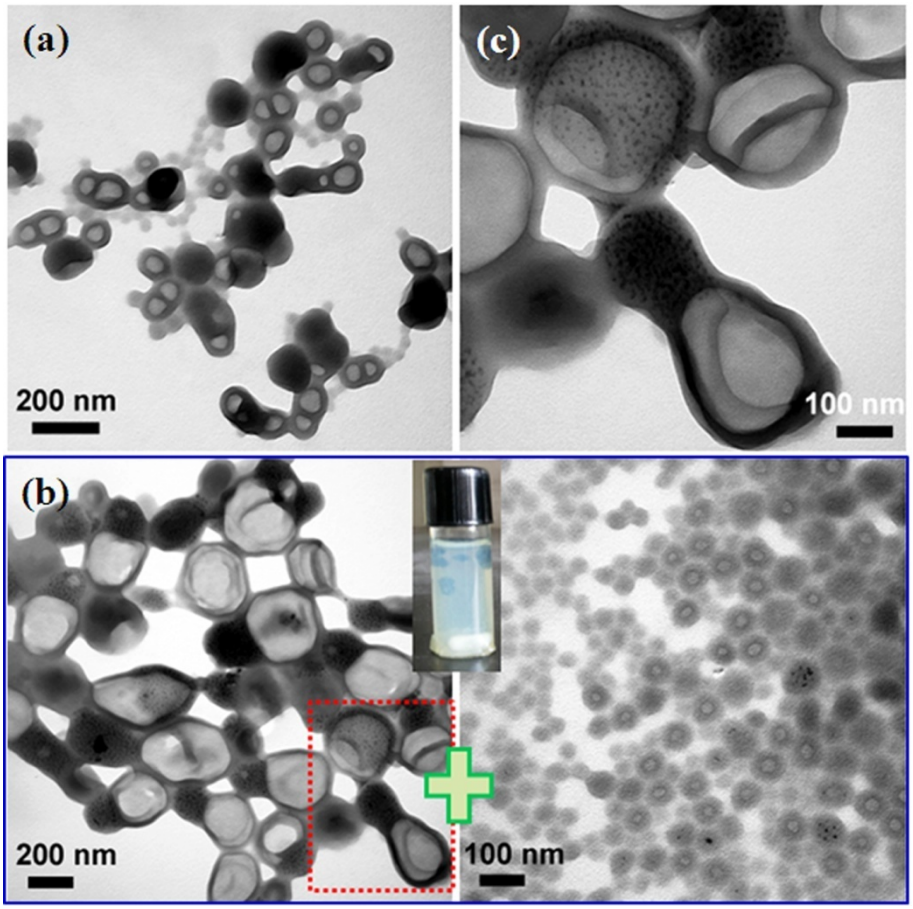

Fig. S4 Bright-field TEM images of hybrid assemblies formed from PS-*b*-PEO (0.2 wt %) and PS-grafted CdS QDs (7.6 nm) at water content of 6 wt % and stirring time of one day with different QDs weight fraction: (a) f = 0; (b) f = 0.06. (c) The magnified image of the red dashed rectangular area in (b). The insert in (b) is the photogragh of the corresponding sample dispersed in water.

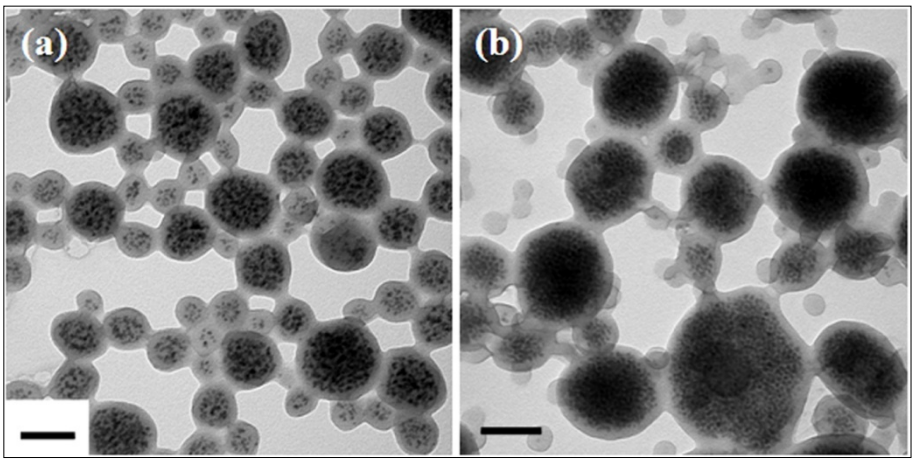

Fig. S5 Bright-field TEM images of QDs/BCP hybrid assemblies formed at the QDs weight fraction of 0.30, water content of 6 wt% and stirring time of one day but with different BCP initial concentration of (a) C_0 = 0.5

wt% and (b) C_0 = 1.0 wt%, respectively. Both of the samples were quenched by a lot of water and then dialyzed against water for 2 days and finally directly used for TEM tests without further purification. Both scale bars are 100 nm.

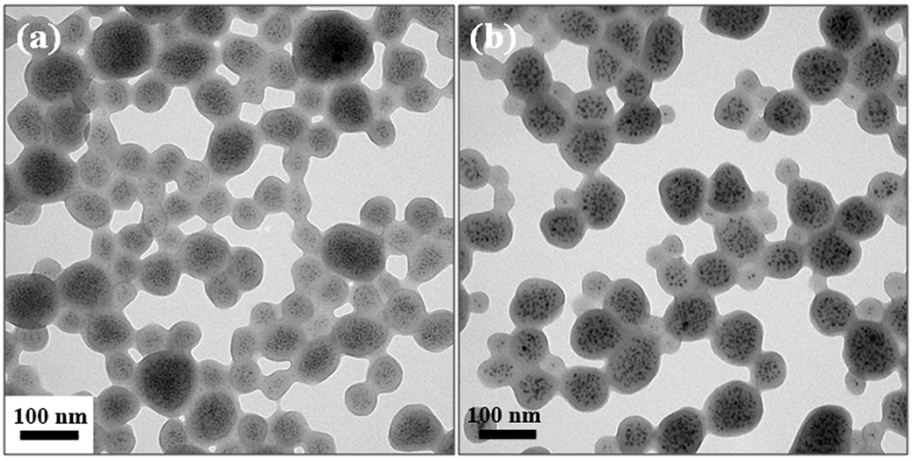

Fig. S6 Bright-field TEM images of hybrid QDs/BCP assemblies formed at C_0 = 0.2 wt%, f = 0.30, water content of 6 wt% and t = 1 day but varied sizes of PS-grafted CdSe/CdS QDs: (a) 3.8 nm and (b) 4.9 nm.

References

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