Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information for:

Encapsulation of semiconductor quantum dots into the central cores of block copolymer cylindrical and toroidal micelles

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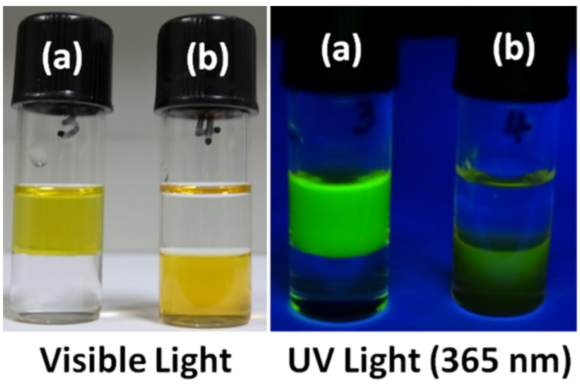

Fig. S1 (a) Photograghs of TOPO-coated CdSe/CdS QDs dispersed in n-hexane (upper layer) before phase transfer to DMF in the down layer; (b) Photograghs of PS-grafted CdSe/CdS QDs well dispersed in DMF (down layer) after modification of TOPO-coated CdSe/CdS QDs with PS-NH_2. Through ligand exchange, the QDs can be readily transferred from n-hexane in the upper layer to DMF in the down layer. The emitting color of TOPO-coated CdSe/CdS QDs (a) and PS-grafted CdSe/CdS QDs (b) in the left and right pictures are under visible light and UV irradiation of 365 nm, respectively.

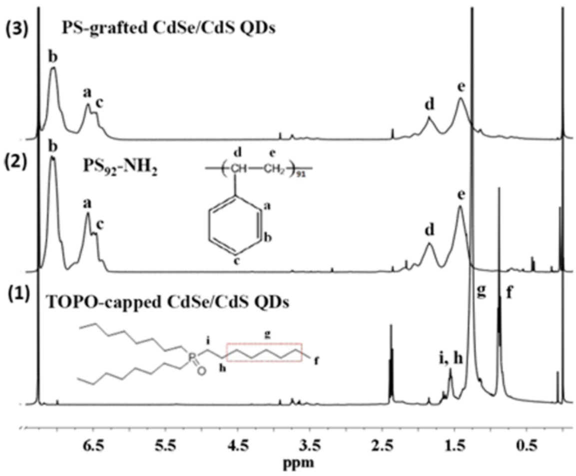

Fig. S2 [1]H NMR spectra of (1) TOPO-coated CdSe/CdS QDs, (2) PS-NH_2 and (3) PS-grafted CdSe/CdS QDs.

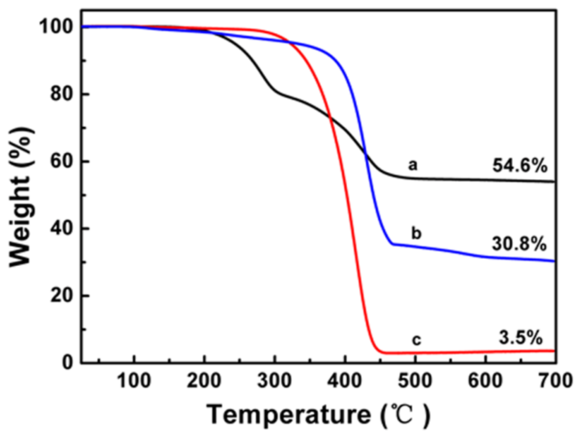

Fig. S3 TGA plot of (a) TOPO-coated CdSe/CdS QDs, (b) PS-grafted CdSe/CdS QDs and (c) PS-NH_2.

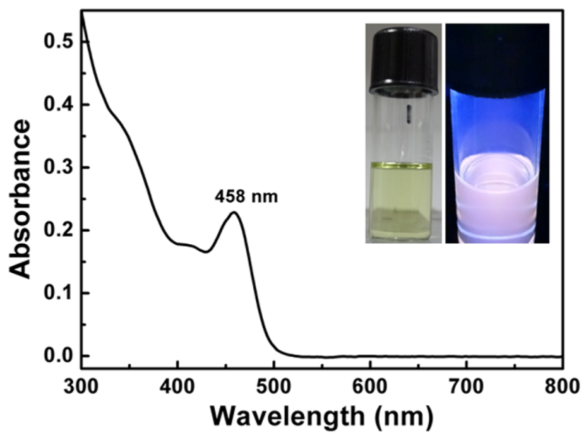

Fig. S4 UV-vis absorption spectra of TOPO-coated CdSe core dispersed in chloroform, with the excitonic absorption peak locating at 458 nm. Upright insert is the photogragh of TOPO-coated CdSe core dispersed in chloroform under visible light and UV irradiation of 365 nm, respectively. Under UV irradiation of 365 nm, the CdSe core emitted brightly violet luminescence.

The size of CdSe core can be calculated by using the equation as follows:[1]

$$D=\left(1.6122\times10^{-9}\right)\lambda^{4}-\left(2.6575\times10^{-6}\right)\lambda^{3}+\left(1.6242\times10^{-3}\right)\lambda^{2}-0.4277\lambda+41.57$$

Where $D(\text{nm})$ is the size of the given CdSe quantum dots, and $\lambda(\text{nm})$ is the wavelength of the first excitonic absorption peak of the corresponding sample. Here, the first excitonic absorption peak of CdSe core is 458 nm and the size is calculated to be 2.0 nm.

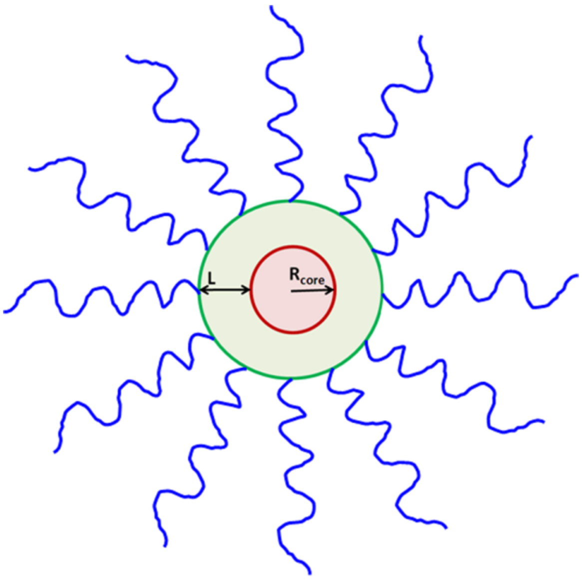

Fig. S5 Schematic illustration of the PS-grafted CdSe/CdS QDs. R_{core} represents the radius of CdSe core, which can be calculated based on UV-vis Absorption Spectra of TOPO-coated CdSe core in Figure S4. L expresses the shell thickness of CdS layer. The blue coronas on the surface of CdSe/CdS QDs denote the PS brushes. Here, the average diameter of bare QDs was 4.6 nm. R_0, the root-mean-square end-to-end distance of PS brushes on the surface of QDs, was estimated by the equivalent freely jointed chain model: $R_0=bN^{1/2}$, where b is the Kuhn monomer length, with b=1.8 nm for PS block, and N is the degree of polymerization which can be obtained based on the molar mass of Kuhn monomer M_0 (M_0=720 g/mol for PS).[2]

$$R_0=b\cdot N^{1/2}=1.8\times\sqrt{\frac{9700}{720}}=6.6\ \text{nm}$$

$R_{core} = 1.0\ \text{nm}$; $L = 1.3\ \text{nm}$; $\omega_{PS} = 0.692$; $\omega_{QDs} = 0.308$; $\rho_{CdSe} = 5.81\ \text{g/cm}^3$;

$\rho_{CdS} = 4.82\ \text{g/cm}^3$; $M_n(\text{PS}) = 9700\ \text{g/mol}$; $N_A = 6.02\times10^{23}\ \text{mol}^{-1}$

Where ω_{PS} and ω_{QDs} are the mass fraction of PS grafts and QDs, respectively, which are obtained from TGA in Figure S3, $\omega_{PS} + \omega_{QDs} = 1$; ρ_{CdSe} and ρ_{CdS} are the density of CdSe and CdS; $M_n(\text{PS})$ is the molecular weight of PS; N_A is the Avogadro Number.

$$V_{\text{CdSe core}} = \frac{4}{3}\pi R_{core}{}^3 = \frac{4}{3}\times3.14\times1.0^3 = 4.19\ \text{nm}^3$$

$$V_{\text{CdS shell}} = \frac{4}{3}\pi\left(R_{core}+L\right)^3 - \frac{4}{3}\pi R_{core}{}^3 = \frac{4}{3}\times3.14\times(1.0+1.3)^3 - \frac{4}{3}\times3.14\times1.0^3 = 46.75\ \text{nm}^3$$

$$m_{QD} = V_{\text{CdSe core}}\cdot\rho_{CdSe} + V_{\text{CdS shell}}\cdot\rho_{CdS} = 4.19\times10^{-21}\times5.81 + 46.75\times10^{-21}\times4.82 = 249.68\times10^{-21}\ \text{g}$$

$$N_{\text{PS grafts per QD}} = \frac{\dfrac{\omega_{PS}}{M_n(\text{PS})}\cdot N_A}{\dfrac{\omega_{QDs}}{m_{QD}}} = \frac{\dfrac{0.692}{9700}\times6.02\times10^{23}}{\dfrac{0.308}{249.68\times10^{-21}}} = 35\ \text{chains/QD}$$

$$\sigma = \frac{N_{\text{PS grafts per QD}}}{4\pi\left(R_{core}+L\right)^2} = \frac{35}{4\times3.14\times(1.0+1.3)^2} = 0.53\ \text{chains/nm}^2$$

In the above equations, $V_{\text{CdSe core}}$ and $V_{\text{CdS shell}}$ represent the volumes of CdSe core and CdS shell per QD, respectively; m_{QD} represents the mass per QD; $N_{\text{PS grafts per QD}}$ means the number of PS chains on the surface of a single CdSe/CdS QD; σ expresses the grafting density of PS chains on the surface of QDs.

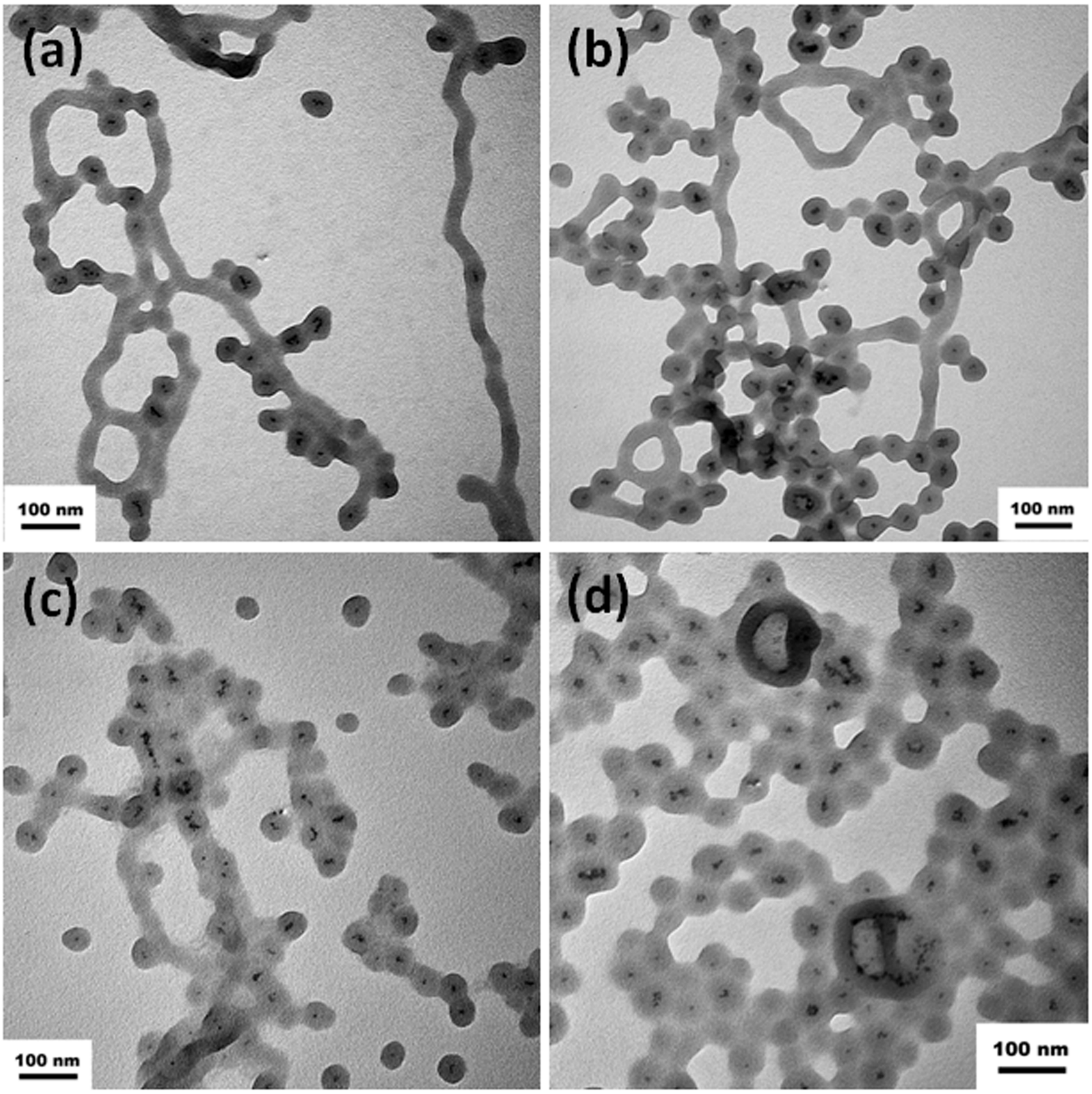

Fig. S6 Bright-field TEM images of hybrid assemblies formed from PS_{356}-*b*-PEO_{148} (2 wt %) and PS_{92}-grafted CdSe/CdS QDs (size 4.6 nm, f = 0.1) with water content of 5 wt % in different stirring time before purification: (a) t = 1 day; (b) t = 3 days; (c) t = 5 days; (d) t = 7 days.

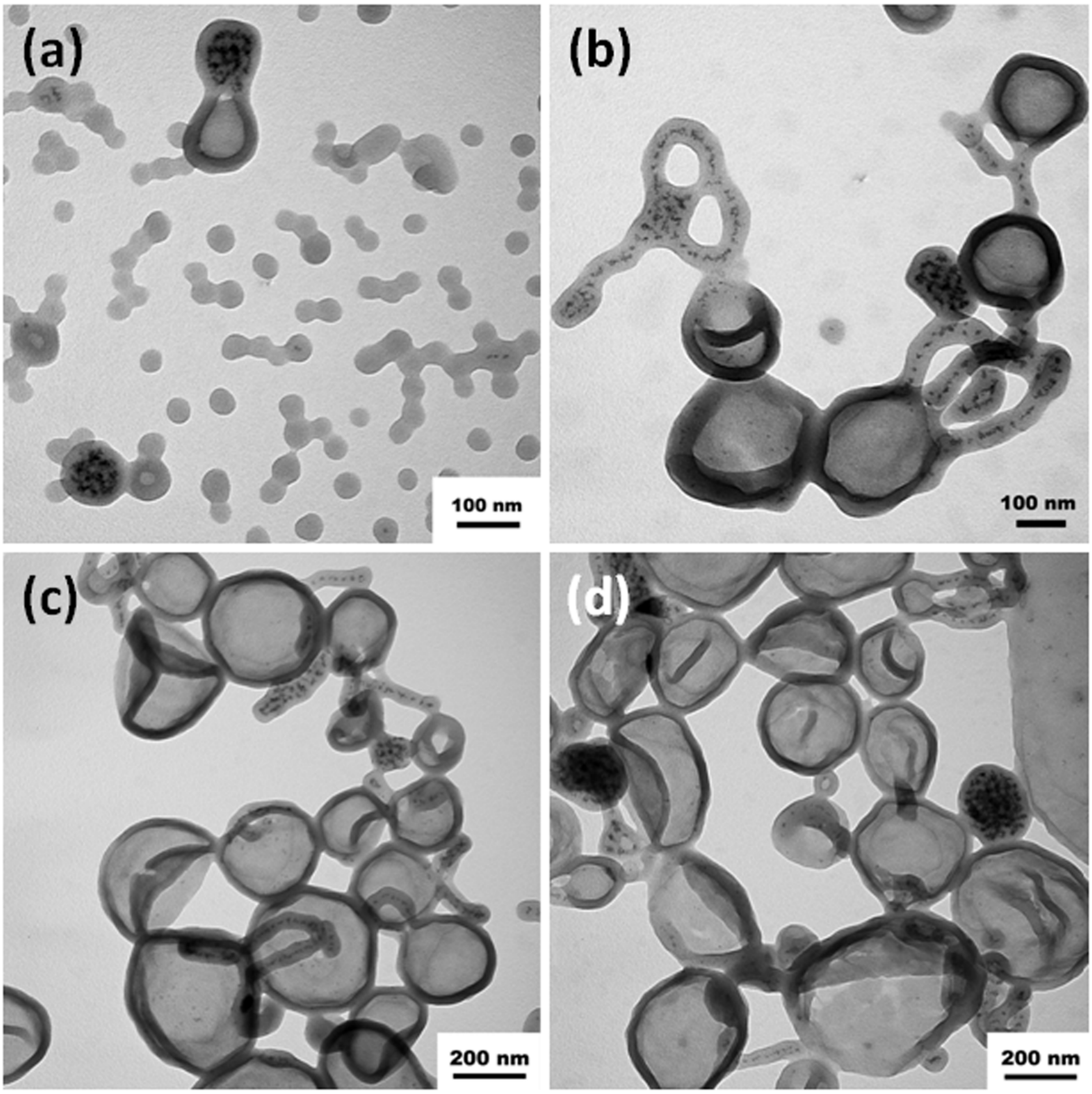

Fig. S7 Bright-field TEM images of hybrid assemblies formed from PS_{356}-*b*-PEO_{148} (2 wt %) and PS_{92}-grafted CdSe/CdS QDs (size 4.6 nm, $f = 0.1$) with water content of 7 wt % in different stirring time before purification: (a) t = 1 day; (b) t = 3 days; (c) t = 5 days; (d) t = 7 days.

References

1 W. W. Yu, L. H. Qu, W. Z. Guo and X. G. Peng, *Chem. Mater.*, 2003, **15**, 2854.

2 W. K. Li, S. Q. Liu, R. H. Deng and J. T. Zhu, *Angew. Chem. Int. Edit.*, 2011, **50**, 5865.