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Preparation of Quantum Dot/Polymer Light Conversion Films with Alleviated Förster Resonance Energy Transfer Redshift

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1. Synthesis of QDs

Chemical. Cadmium oxide (CdO, 99%, Showa), zinc oxide (ZnO, average size 300 nm, Sigma-Aldrich) cadmium acetate dihydrate (Cd-AC, 99%, J. T. Baker), zinc acetate dihydrate (Zn-AC, 99%, Showa), selenium oxide (SeO_2, 99.8%, Strem), zinc diethyldithiocarbamate (ZDC, 99%, Aldrich), sodium diethyldithiocarbamate (99%, Aldrich), 1-dodecanethiol (DDT, 98%, Acros), hexadecylamine (HDA, 98%, Acros), oleylamine (OLA, 70%, Aldrich), oleic acid (OA, 90%, Showa), 1-octadecene (ODE, 90%, Acros), poly(methyl methacrylate) (PMMA, M_w ~ 35000, 99%, Aldrich), and poly(methyl methacrylate-co-methacrylic acid) (PMMA-co-MA, Mn ~ 15000, M_w ~ 34000, Aldrich) were used in an as-received condition without further purification.

Stock solution of Se. SeO_2 (8 mmol, 0.88 g) and ODE (10 mL) were loaded into a 100 mL three-neck flask and heated at 200℃ for 2 hr under ambient conditions to obtain a clear solution. DDT (0.8 mmol, 0.19 mL) was then added to the hot ODE-Se solution for later hot injection.

Synthesis of $Cd(OA)_2$. CdO (50 mmol, 6.42 g) and OA (100 mmol, 36 mL) were loaded into a 100 mL three-neck flask and heated at 240°C for 30 min to obtain a clear solution. The solution was then cooled to room temperature to obtain a yellow-white solid product. The product was further ground into a powder form for further reaction.

Stock solution of CDC and ZDC. Cadmium diethyldithiocarbamate (CDC) was prepared via the reaction of Cd-AC and sodium diethyldithiocarbamate in an aqueous solution.[16c] CDC (1 mmol),

OLA (5 mL) and ODE (5 mL) were loaded into a 25 mL flask and sonicated for 10 min under ambient conditions. ZDC solution was prepared using the same method.

Synthesis of CdSe NCs. CdSe nanocystals (NCs) were synthesized using a modified literature method.[15] Specifically, a mixture of Cd-oleate (4 mmol, 2.7 g), ODE (10 mL) and HDA (1 mmol, 0.241 g) was loaded into a 100 mL three-neck flask and degassed at 100°C for 30 min under a N_2 flow. The mixture was then further heated to 240°C and 10 mL hot stock solution of Se was injected into the flask. The temperature was then reduced to 220 °C. Following the injection of the Se stock solution, the color of the reactant changed from clear colorless to green, yellow and finally dark orange as the reaction proceeded. CdSe NCs with wavelengths of 506 nm and 564 nm were synthesized using reaction times of 0.5 min and 20 min, receptively. In each case, the resulting product was diluted with hexane and ethanol and then centrifuged at a speed of 5000 rpm. Finally, the precipitate was washed three times by a mixed hexane/ethanol solvent in order to obtain powder samples. The phases of the precipitates were checked using XRD. TEM samples were prepared by dropping a hexane suspension containing the precipitated NCs onto a copper grid (200 mesh) coated with a carbon film. The size of the products was determined by averaging the lengths of the major and minor axes of a minimum of 500 different particles using Sigmascan Pro 5 software.

Overcoating CdS and ZnS shells on CdSe NCs. CdS or ZnS shells were overcoated on the CdSe NCs using a modified literature method.[16] To prepare red-emitting CdSe/CdS QDs, a mixture of purified CdSe NCs (0.1 mmol, 0.02 g), OLA (2 mL) and ODE (4 mL) was loaded into a 100 mL three-neck flask and degassed at 100°C for 30 min under a N_2 flow. A CDC solution (0.65 mL) was added to the reaction mixture via a syringe and the temperature was increased to 150°C for 20 min to initiate the growth of a CdS shell. The temperature was then increased to 210°C and maintained for a further 10 min in order to obtain a homogeneous shell. Finally, the solution was allowed to cool naturally to room temperature. In practice, the thickness of the CdS shell depends on the amount of CDC used. In the present study, CdSe nanoparticles with one, two and three CdS monolayers were synthesized using 0.65, 0.85 and 1.08 mL CDC solution, respectively. Green-

emitting CdSe/ZnS QDs were synthesized using an equivalent method as that used for the CdSe/CdS QDs. In synthesizing the QDs, 1.42, 2.11 and 2.95 mL of ZDC solution were added to the reaction mixture in order to grow ZnS overcoats comprising one, two and three monolayers, respectively.

2. Calculation of chain length and MA number in PMMA-co-MA Copolymer.

PMMA-co-MA copolymer with average molecular weight of M_n ~ 15,000 and an MMA-to-MA ratio of 1:0.016 was purchased from Sigma-Aldrich. The repetition (x) of the MMA_1-co-$MA_{0.016}$ monomers in the polymer chain was calculated as

$$M_n = 15000 = \left[(MMA)_1{:}(MA)_{0.016}\right] \cdot x$$

$$= (100.12 \times 1 + 86.09 \times 0.016) \cdot x = 101.497 \cdot x$$

$$x = \frac{15000}{101.497} = 147.8,$$

where the molecular weight of MMA is equal to 100.12 g/mol and the M_n of MA is equal to 86.09 g/mol. The number of MA in the polymer chain was obtained as

$$y = 147.8 \times 0.016 = 2.36.$$

The total number (z) of monomers in the chain was therefore calculated as

$$z = x + y = 147.8 + 2.36 = 150.16.$$

Finally, the chain length (L) of the PMMA-co-MA matrix was computed as

$$L = (2z - 1) \times 0.126\ nm = (2 \times 150.16 - 1) \times 0.126\ nm = 37.67\ nm.$$

The carbon-to-carbon (C-C) bond length and bond angle were equal to 0.154 nm and 109.5°, respectively. Given the assumption of a zig-zag structure, the projecting length of the C-C chain was thus determined to be 0.126 nm.

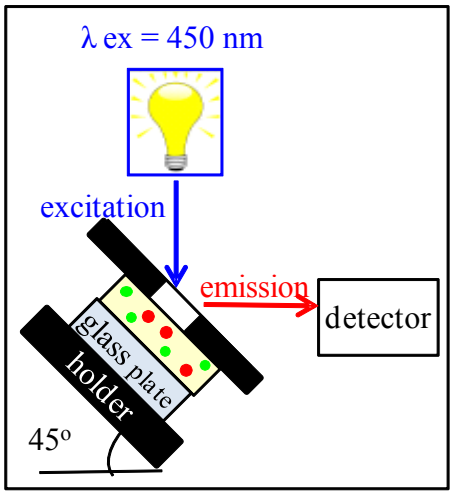

Figure S1. Schematic illustrations of: (a) experimental setup used to measure emission spectra of QDPLC films, and (b) interaction between emission light (including both extraction light and guiding light) and QD.

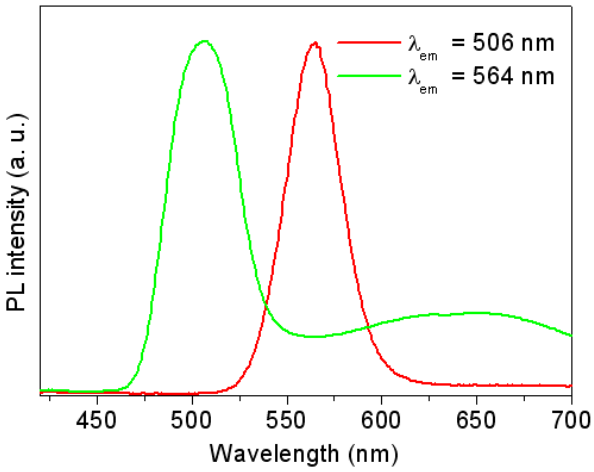

Figure S2. PL spectra of as-prepared CdSe core NCs dispersed in toluene.

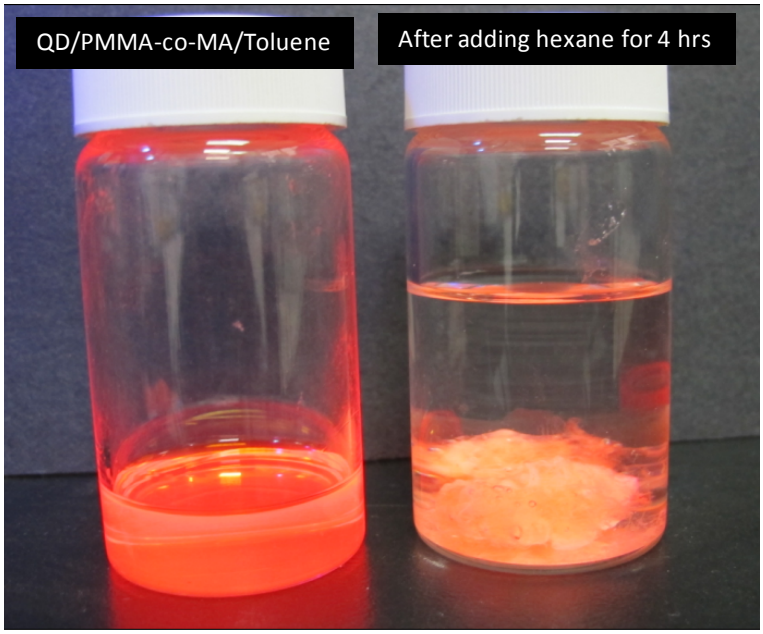

Figure S3. Photographs of (left) original QD/PMMA-co-MA/toluene solution and (right) precipitation of QD nanocomposites following addition of hexane.

Figure S4. Photographs of red and green QDP powders under natural lighting (upper) and UV irradiation (lower).