Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Reduced Efficiency Roll-off in Light-Emitting Diodes Enabled by Quantum Dot-Conducting Polymer Nanohybrids

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1. Chemicals

CdO (99.9 %), zinc acetate (Zn(acet)$_2$, 99.99 %), oleic acid (OA, 90 %), 1-octadecene (1-ODE, 90 %), trioctylphosphine (TOP, 90 %), anhydrous toluene, methanol, hexane and ethanol was purchased from Sigma-Aldrich. AIBN and cysteamine were purchased from Fluka. TPD monomer was synthesized according to literature by a Buchwald-Hartwig coupling of 4-Iodoanisol with N,N´diphenyl(1,1´biphenyl)4,4´diamin with subsequent Vilsmeyer formylation and Wittig reaction. PFPA was synthesized by esterification of acryloylchloride with pentfluorophenol. THF used for polymerisation was freshly distilled over sodium in a nitrogen atmosphere. All chemicals were used as purchased.

2. Synthesis of CdSe@ZnS QDs

CdSe@ZnS QDs with chemical composition gradient were prepared by single-step synthesis. For the typical synthesis, 0.2 mmol of CdO, 4 mmol of Zn(acet)$_2$ and 4 mmol of OA were loaded in 100 ml flask, evacuated at 150 °C under 100 mTorr pressure for 30 min to form Zn(OA)$_2$. Then the reactor was filled with N$_2$, added with 15 mL of 1-ODE, and heated up to 305 °C. At the elevated temperature, 2 mL of TOP dissolving 0.1 mmol of Se and 3.5 mmol of Se was swiftly injected into the reactor. The reaction temperature was maintained at 300 °C for further growth of CdSe@ZnS QDs. After 10 min of reaction, the reactor was cooled down to room temperature to complete the reaction. The as-prepared QDs were purified by precipitating with ethanol and redispersing in toluene repeatedly (3 times) to remove residual surfactants and unreacted precursors. Final products were dispersed either in hexane or toluene and kept in the refrigerator.

3. Synthesis of poly(TPD-*b*-PFP) and poly(TPD-*b*-SSMe)

Synthesis of poly(TPD-*b*-PFP)

1.2 g of Vinyl-methoxy TPD (2 mmol, 100 eq), 5 mg of benzylbenzodithionate (0.02 mmol, 1eq) and 1 mg of AIBN (0.01 mmol, 0.1 eq) were dissolved in 3 mL dioxane in a Schlenck tube. The reaction vessel was filled with N_2 through repeated freeze-pump-thaw cycles (3 times). Polymerization was carried out at 90 °C for 48 h. The polymer was precipitated three times in methanol and petrolether to yield in 0.67 g (55 %) of polymer (yellow color).

Mn: 3.157×10^4 g mol^{-1},, PDI: 1.10 (PS equivalents)

0.67g (0.02 mmol, 1 eq) homopolymer as a macroinitiator, 0.13 g pentafluorophenolacrylate (0,5 mmol, 50 eq) and 1 mg of AIBN (0.002 mmol, 0.1 eq) were dissolved in 3 mL of dioxane. Polymerization was carried out at 90 °C in N_2 atmosphere for 3 d. The polymer was purified by precipitation with methanol to yield in 0.7 g (%) of the reactive block copolymer PTPA-*b*-PFP. The polymer was stored in refrigerator under N_2 atmosphere.

Mn: 3.871×10^4 g mol^{-1}, PDI: 1.24 (PS equivalents)

^{1}H-NMR(d^8-THF, 300 MHz): 6.84 (m, 25H, ArH), 3.73 (m, 6H, -OMe), 2.54 (m, 1H, CH_2-C*H*), 1.88 (m, 3H, C*H*-C*H*$_2$), 1.21 (m, 2H, CH-C*H*$_2$).

Synthesis of poly(TPD-b-SSMe)

To synthesize PTPD-*b*-SSMe, 0.2 g of PTPD-b-PFP (1eq) was dissolved in tetrahydrofuran, followed by sequential addition with 60 mg of 2-(2-methyldisulfanyl)ethanamine (2 eq according to PFP units) and 0.08 mL of triethylamine. The mixed solution was stirred over night under N_2 atmosphere. The polymer solution was filtered and precipitated in methanol for three times to yield in 0.76 g (96 %) of PTPD-*b*-SSMe.

IR: ν_{max}/cm^{-1}: 3027 (CH), 1658 (CONH), no ester band

^{19}F-NMR: no signal

4. Characterization

Sample Characterization

NMR spectra were obtained with a Bruker AC 300MR. IR spectroscopy was performed with a Bruker Vector 22. Gel permeation chromatography (GPC) was carried out in THF as solvent and the detector system contained refractive index (Jasco), UV-Vis (Jasco) and light scattering (Wyatt) detectors. The values given here were calculated in relation to PS standards. UV-Vis. absorption spectra were measured with an Agilent 8454 UV-Vis. diode array spectrometer. Photoluminescence (PL) spectra were collected on an ACTON spectrometer.

QD density calculation

From the center-to-center distance for pristine QDs and QD-polyTPD nanohybrids (Figure 6S), we could calculate nominal QD number densities per unit area for devices I & device II. The center-to-center distances for pristine (oleic acid capped) QDs and QD-poly(TPD-b-SSMe) hybrids were estimated as 10.3 nm (±0.8 nm) and 11.7 nm (±0.8 nm), respectively. Assuming that both QDs are randomly packed (80 % of hexagonal close packing), we estimate the QD number density for a monolayer of pristine QDs (8.0×10^{11} cm^{-2}) and QD-poly(TPD-b-SSMe) hybrid films (6.2×10^{11} cm^{-2}). The number density of QDs in the active layer per unit area are 1.2×10^{12} cm^{-2} for 1.5 ML QD films and 5.0×10^{12} cm^{-2} for 8 ML poly(TPD-b-SSMe) hybrid films, respectively.

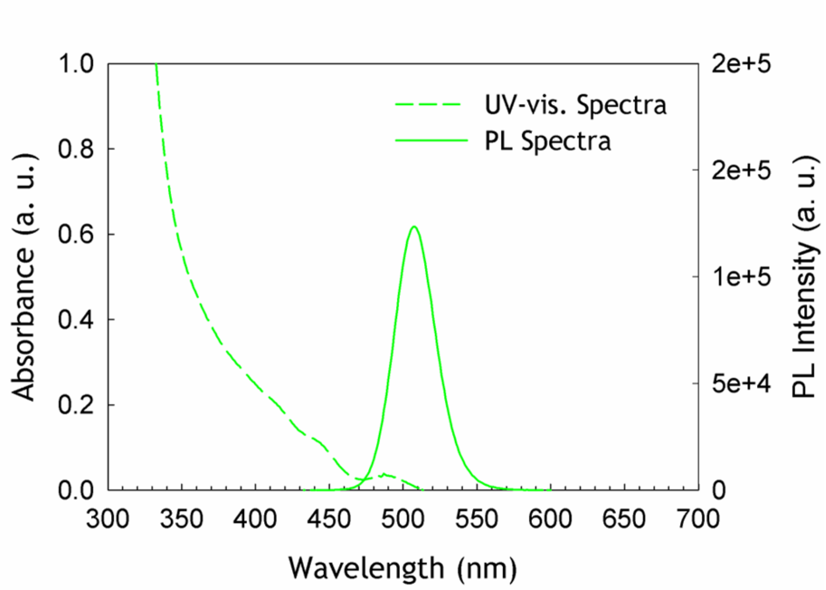

Figure S1. UV-Vis. and PL spectra of CdSe@ZnS QDs with chemical composition gradient.

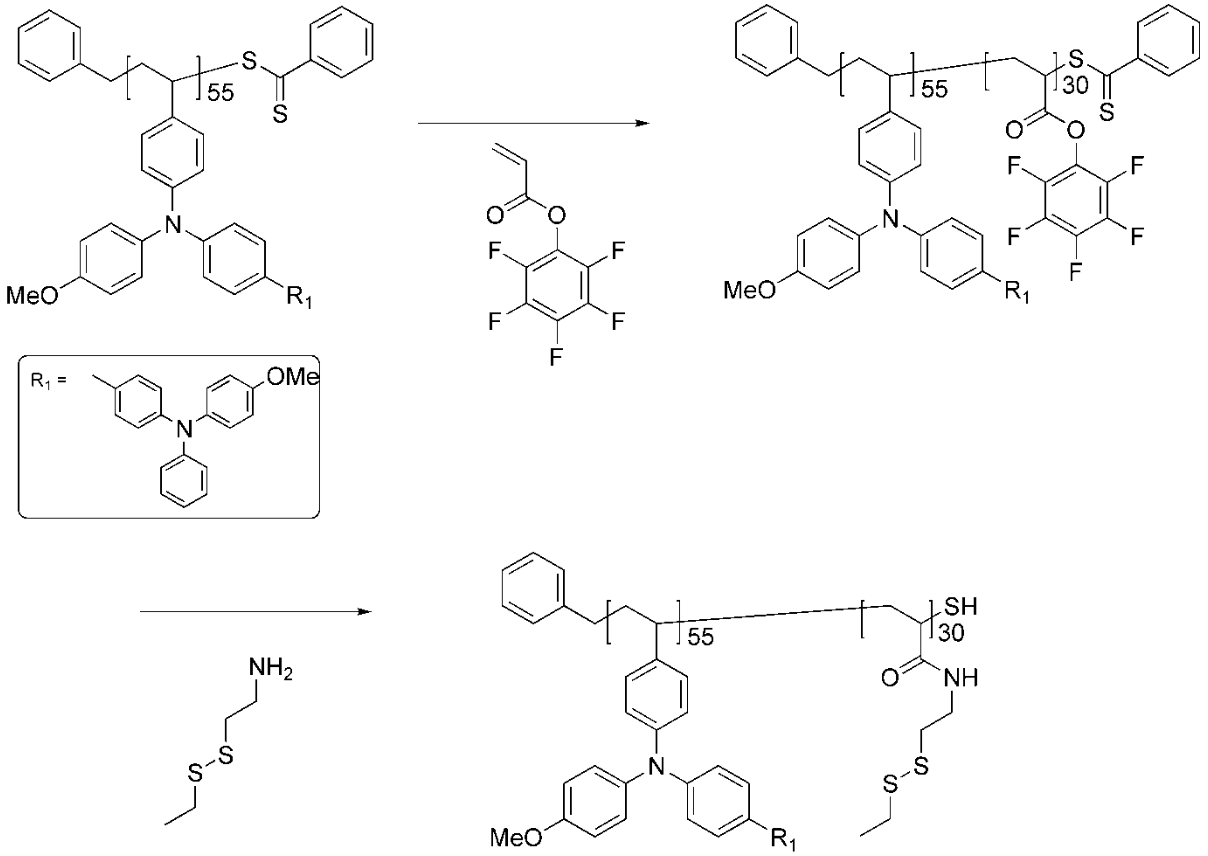

Figure S2. A synthetic route to prepare poly(TPD-*b*-SSMe).

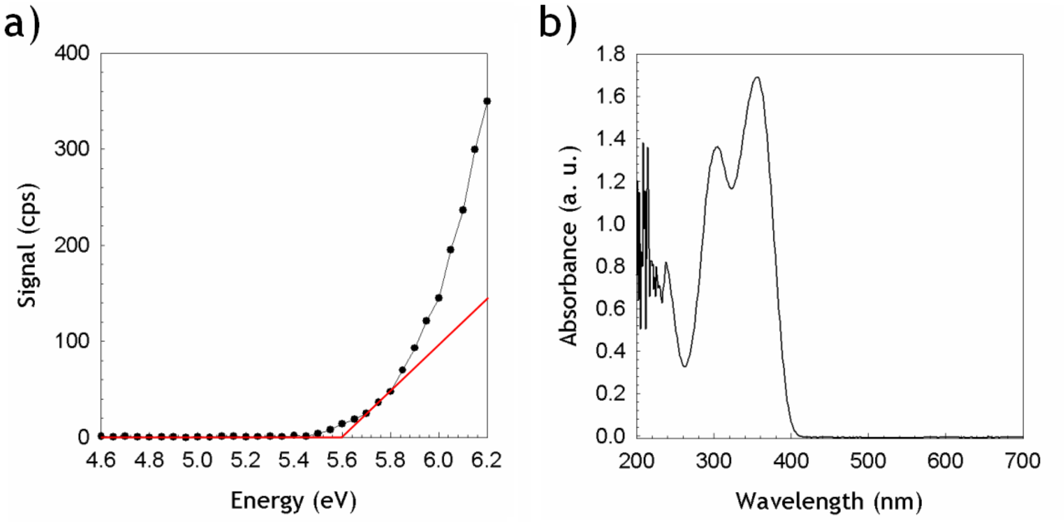

Figure S3. a) Ultraviolet photoelectron spectroscopy (UPS) and b) UV-vis. spectra of poly(TPD-*b*-SSMe). The HOMO and LUMO energy levels of poly(TPD-*b*-SSMe) are determined to be 5.6 eV and 2.6 eV, respectively.

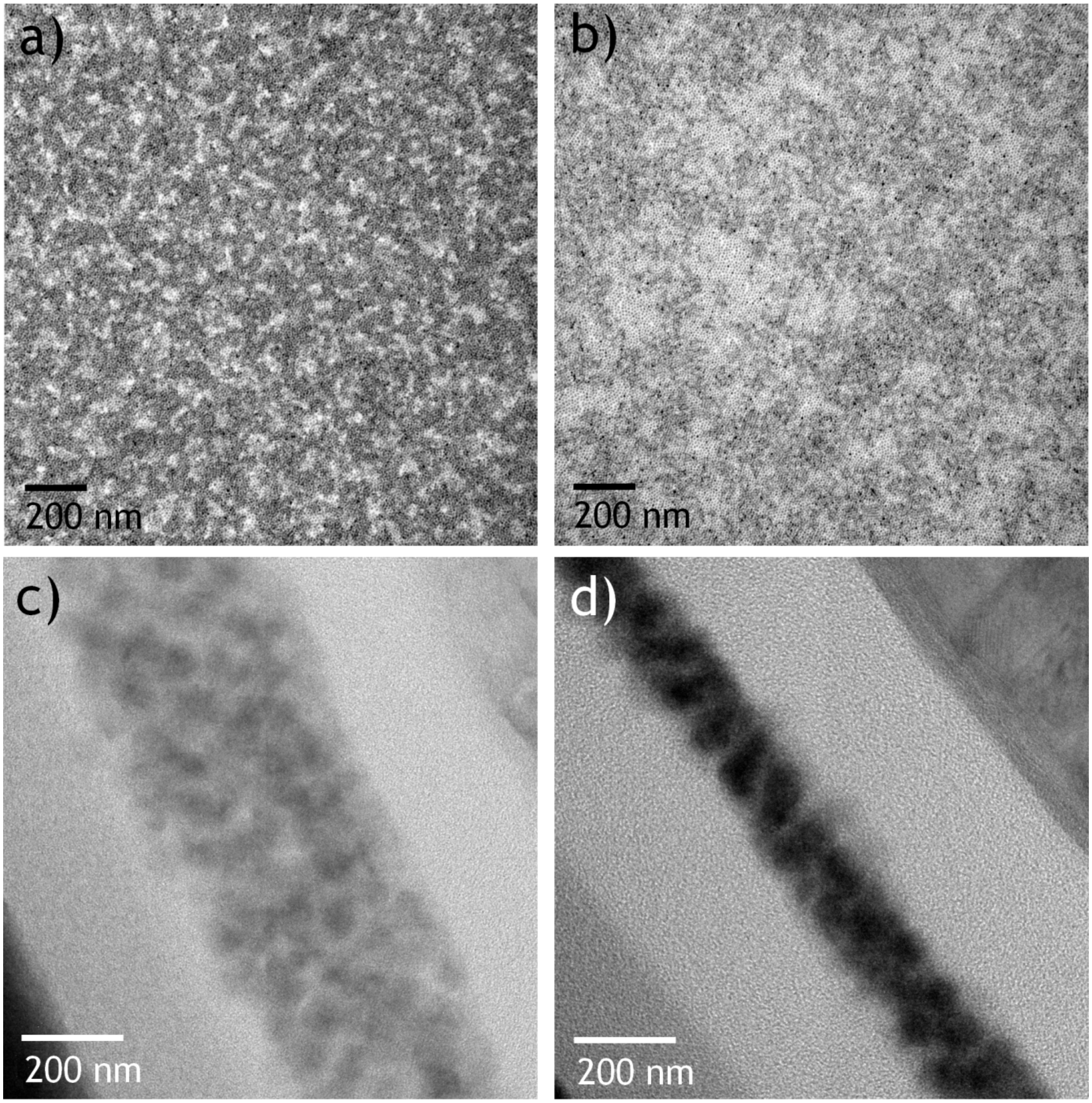

Figure S4. Plane view and cross-sectional TEM images of a QD-poly(TPD-*b*-SSMe) hybrid film ((a) and (c)) and a QD/polyTPD bilayer film with 1.5 QD monolayers ((b) and (d)).

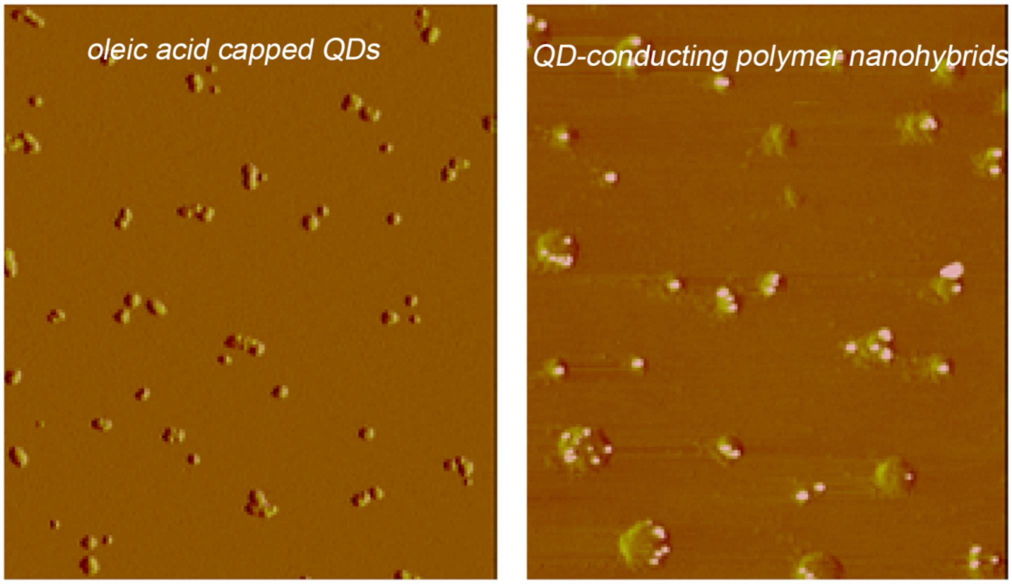

Figure S5. AFM images of a) oleic acid capped QDs and b) QD-conducting polymer nanohybrids.

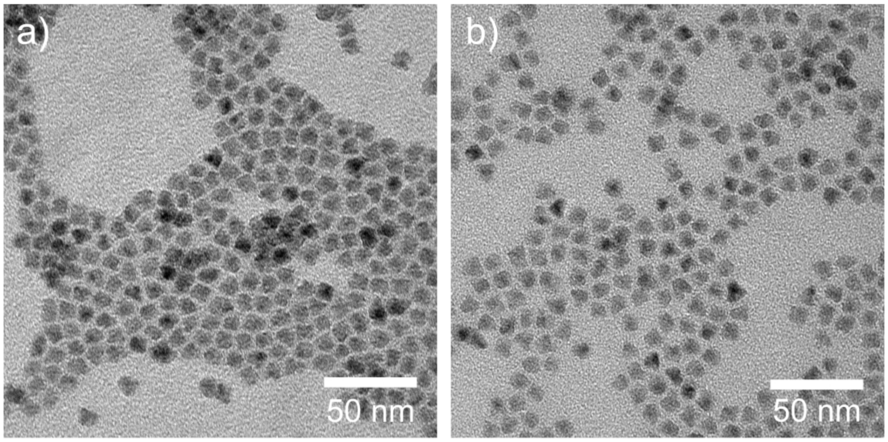

Figure S6. TEM images of a) oleic acid capped QDs and b) QD-poly(TPD-b-SSMe) nanohybrids assembled on substrates.