Supporting Information

Suppression of electron trapping by quantum dot emitters using a grafted polystyrene shell

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**Ligand exchange procedure:** During this procedure, weakly coordinated oleic acid ligands, which are used as the initial small molecule ligands for pristine QDs, possessing weaker affinity to the QDs surface than the disulfide functionalities and can be replaced by the disulfide anchoring functionalities chemically grafting to the QDs surface leading to polymer functionalized QDs.

The ligand exchange is monitored by the solubility change of the QDs as the QDs show altered solubility properties acquired from the ligands attached to their surface\textsuperscript{[1–4]}. The bare QDs with initial oleic acid ligands are well soluble in hexanes and just poorly soluble in \textit{o}-dichlorobenzene, while the QDs functionalized with polymer (QD/PS-hybrids) become well soluble in \textit{o}-dichlorobenzene and are no longer soluble in hexanes acquiring the insolubility of the polymer attached onto the QDs surface (see Fig. S1)

**Fig. S1** Solubility change from pure QDs to QD/PS-hybrids, normal (left) and UV light (right). Pure QDs, coated by oleic acid, are soluble in hexanes. QD/PS-hybrids, coated by polymer, are insoluble in hexanes, resulting in precipitation. In a biphase system of hexanes (upper phase) and \textit{o}-dichlorobenzene (lower phase), pure QDs are soluble in upper hexanes phase, QD/PS-hybrids are soluble in lower \textit{o}-dichlorobenzene phase.

In addition, the attachment of the polymer onto the QDs surface was also confirmed by IR spectroscopy as signals of the polymer can be observed in the IR spectra of the QD/polymer
hybrids and thermogravimetric analysis (TGA) was also conducted revealing successful coating of the polymer onto the QDs surface (see Fig. S2).

**Fig. S2** IR spectra of QD/PS-hybrids and polymer and TGA spectra of pure QDs and QD/PS-hybrids. (left) IR spectra of QD/PS-hybrids and polymer, signals at 3000 cm\(^{-1}\) attributed to -CH-vibrations and signals at 1650 cm\(^{-1}\) and 1520 cm\(^{-1}\) attributed to the disulfide anchor group are observed in the IR spectra of QD/PS-hybrid, (right) TGA spectra of QD/PS-hybrids, coated with polymer, weight loss 25 wt%.

**Polymer synthesis:** The synthesis of the diblock copolymer poly(styrene-\textit{block}-cysteaminemethyldisulfide) (P(S-\textit{b}-SSMe) via RAFT polymerization and post-polymerization modification is shown in Fig. 2 The reactive ester block allows the introducing of desired functionalities by a polymer analogous reaction with a primary amine\textsuperscript{[5,6]} and the successful conversion can be easily monitored by \(^{19}\text{F}-\text{NMR}\) or IR spectroscopy. The quantitative replacement of the pentafluorophenyl groups with cysteaminemethyldisulfide was confirmed by disappearance of the C=O band of the ester at 1786 cm\(^{-1}\) and appearance of the C=O band of the corresponding amide at 1654 cm\(^{-1}\) in the IR spectroscopy (see Fig. S3) as well as by disappearance of the pentafluorophenyl peaks in the \(^{19}\text{F}-\text{NMR}\) spectroscopy (see Fig. S4). Also, SEC and 2D-DOSY-NMR measurements are shown in Fig. S5 and Fig. S6.
Fig. S3 IR spectra of P(S-b-PFPA) and after post-polymerization modification of P(S-b-SSMe). IR spectra of P(S-b-PFPA) shows characteristic signal at 1786 cm$^{-1}$ attributed to reactive ester block before post-polymerization modification and IR spectra of P(S-b-SSMe) shows characteristic signal at 1654 cm$^{-1}$ attributed to the amide group of the disulfide anchor block, the signal at 1786 cm$^{-1}$ vanished after post-polymerization modification.

Fig. S4 $^{19}$F-NMR spectra of P(S-b-PFPA) (top) and after post-polymerization modification of P(S-b-SSMe) (bottom). $^{19}$F-NMR spectra of P(S-b-PFPA) shows characteristic signal of reactive ester block before post-
polymerization modification and after post-polymerization modification the signals of the reactive pentafluorophenyl ester vanished.

Fig. S5 SEC curves of all reaction steps. Measured in THF, polystyrene standards (UV-vis detector).

Fig. S6 DOSY 2 D NMR spectrum of P(S-b-SSMe). Only one diffusing species demonstrates the successful post-polymerization modification step.
Fig. S7 EL spectrum of a device based on PFO with 3% QD-Hybrid versus energy. The FWHM linewidth of the red QD emission is significantly smaller as compared to the blue PFO emission.
**Fig. S8** Voltage dependence of normalized EL spectra for PLED with 100nm PFO:5% QD/PS-hybrid blend active layer a) second up-scan, b) consecutive down-scan, c) third up-scan and d) corresponding down-scan, e) fourth up-scan and f) corresponding down-scan.
**Fig. S9** Photoluminescence spectra of PFO: oa-QD blend and QD/PS-hybrid blend for 5% QD concentrations. An excitation wavelength of 390 nm was used.

**Fig. S10** Normalized electroluminescence spectra of PFO with 5% QD/PS hybrids with shell thickness of a) 3nm b) 6nm. The relative contribution of red QD emission to blue PFO emission strongly decreases with increasing PS shell thickness.
Morphology of PFO: QD/polymer-hybrids films: To further prove the well-distribution of the QDs not only on the surface but also in the bulk of the film, additional cross-section SEM image of PLED active layer with PFO:5% QD/PS-hybrids is shown in Fig. S11.

![Cross-sectional SEM image of PLED active layer with PFO:5% QD/PS-hybrids](image)

**Fig. S11** Cross-sectional SEM image of PLED active layer with PFO:5% QD/PS-hybrids.

In order to find the optimal concentration of QD/PS-hybrid in PFO matrix, we made series of films with PFO as host with different concentrations of the QD as guest. For low loading of QDs, although the QDs are single-by-single separated in PFO matrix, the PFO emission has still considerable contribution in EL spectra. Increasing the QD concentration to 5% is sufficient to have dominant red QD emission in EL spectra and still having well-distributed QDs in polymer matrix. By further increasing the QD content of about 7% we found that for the QD/PS-hybrid phase separation starts to occur, as shown in Fig. S12.
Fig. S12 Voltage dependence of normalized EL spectra and SEM images for PLED with 100nm. a) PFO:3% QD/PS-hybrid b) PFO:5% QD/PS-hybrid c) PFO:7% QD/PS-hybrid blend active layer.

**Hole only devices:** The hole only devices characterization with PFO as host and QD/PS-hybrid as guest are shown in Fig. S13. The incorporation of low loading QD/PS-hybrids does not significantly affect the hole transport properties compared to unblended PFO.

Fig. S13 Hole current density of devices with 110nm active layer for unblended PFO and blend of PFO with 5% QD/PS-hybrid.
Fig. S14  a) Chemical structure of the PSF-TAD polymer. The composition copolymers are $m = 50\%$ and $n = 37.5\%$ (PSF) and $o = 12.5\%$ (TAD) b) schematic energy diagram of blend of PSF-TAD with QD with high injection barrier for holes from host to guest. c) Electroluminescence spectra of PSF-TAD with 5% QD/PS-Hybrid d) electron current density of devices with 110nm active layer for unblended PSF-TAD and blend of PSF-TAD with 5% and 10% QD/PS-hybrid and 10% of oa-QD.
Fig. S15 Lifetimes of devices with 110nm active layer for unblended PFO and blend of PFO with 5% QD/PS-hybrid under constant-current over time.

References


