Quantum Dot–Block Copolymer Hybrids with Improved Properties and Their Application to Quantum Dot Light-Emitting Devices

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ABSTRACT To combine the optical properties of CdSe@ZnS quantum dots (QDs) with the electrical properties of semiconducting polymers, we prepared QD/polymer hybrids by grafting a block copolymer (BCP) containing thiol-anchoring moieties (poly(*para*-methyl triphenylamine-*b*-cysteamine acrylamide)) onto the surfaces of QDs through the ligand exchange procedure. The prepared QD/polymer hybrids possess improved processability such as enhanced solubility in various organic solvents as well as the film formation properties along with the improved colloidal stability derived from the grafted polymer shells. We also demonstrated light-emitting diodes based on QD/polymer hybrids, exhibiting the improved device performance (*i.e.*, 3-fold increase in the external quantum efficiency) compared with the devices prepared by pristine (unmodified) QDs.

KEYWORDS: hybrid materials · quantum dot(s) · light-emitting device(s)

Due to their size in the nanometer range, quantum dots (QDs) show an interesting physical behavior that is totally different from the properties exhibited by bulk material. This effect is known as the quantum confinement effect. For semiconducting QDs such as CdSe or CdTe, fluorescence and emission properties can be varied over a broad range in the electromagnetic spectrum simply by tuning the particle size. High fluorescence quantum yield and high optical stability make the quantum dots potentially important nanomaterials for photovoltaic cells,[1] biosensors,[2] or light-emitting diodes.[3] Compared with their counterparts, such as organic fluorescent small molecules and polymers, quantum dots offer the combination of solution processing with the high efficiency of fluorescent inorganic materials. However, quantum dots do not yet show additional desired properties known from polymers, such as film formation and the possibility for inkjet printing.[4]

Inorganic–organic hybrid materials that combine the unique properties of inorganic and quantum-confined particles with that of polymers are therefore interesting candidates for combining the two desired properties in a synergistic way. Polymers can provide various properties such as solubility in different solvents and film formation. Recently, we could show that the solubility of inorganic nanoparticles can be strongly improved with suitable block copolymers.[5] In these block copolymers, a short anchor block binds strongly to the nanoparticle, while the second block creates a soft shell and acts as a steric stabilization for the inorganic nanoparticle. In addition, properties such as a stimuli-responsive behavior (*e.g.*, for switchable dispersions)[5] are possible. Further, surface functionalization with polymers allows the direct linkage of organic and semiconducting materials[6] to an inorganic core as described in this article. This might improve the injection of electrons and holes into the quantum dot. Like surfactants, polymer chains grafted onto the surface of inorganic nanomaterials protect the inorganic nanomaterials from aggregation and increase the solubility and miscibility of such inorganic nanomaterials in an organic host. In addition, they might improve film formation, an important property that influences the device characteristics of optoelectronic components.

Generally, polymer chains can be introduced by two methods. One is a polymerization from the nanoparticle surface

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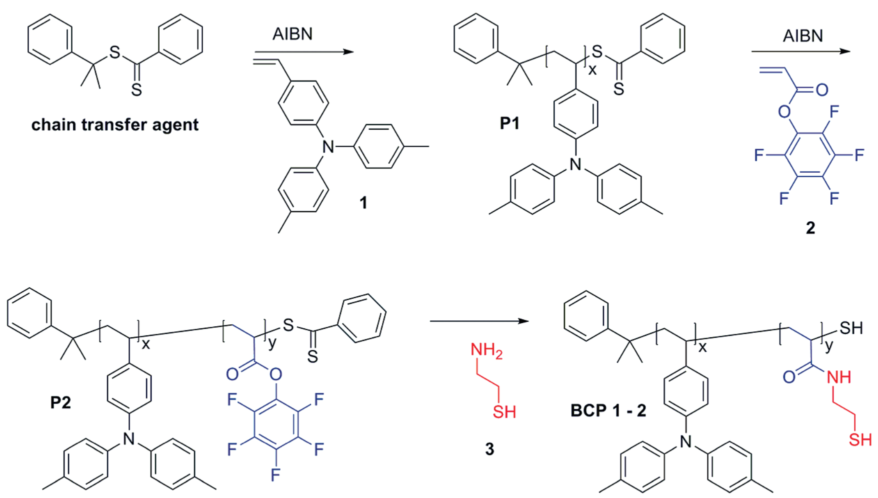

Figure 1. Synthetic scheme for poly(*para*-methyl triphenylamine-*b*-cysteamine acrylamide) (PTPA-*b*-CAA) (P3) derived from triphenylamine (1) and pentafluoroacrylate (PFA) (2) through RAFT polymerization followed by the polymer analogous conversion with cysteamine (3) (P1: poly-TPA, P2: poly-TPA-*b*-PFA).

(grafting-from approach). For this purpose, an initiator like a radical or ROMP starter,[7] a dithioester for RAFT polymerization,[8,9] or a halogen-containing surfactant for ATRP[10] has to be linked to the particle surface. It is also possible to anchor premade polymers containing anchor groups at the chain end(s)[11] or an anchor block by simple ligand exchange. This grafting-to approach will be used here. It has the advantage that the polymer for surface modification can be characterized very well before grafting.

In this article, we describe the synthesis of a block copolymer (BCP) containing a semiconducting block based on triphenylamine (TPA) moieties and a short reactive ester block, which allows introduction of the desired anchor groups.[12] Triphenylamine polymers and small molecule TPA derivatives are known to show good hole conducting properties in the bulk state. They are easy to process and relatively well-known materials for applications in OLEDs[13] and photovoltaics.[14] The short multidentate anchoring block binds to the particle surfaces effectively. In this case, we used thiol-based anchor groups to bind to Zn-chalcogenide-based QDs (*i.e.*, CdSe@ZnS QDs). The resulting inorganic−organic hybrid materials consist of the inorganic core, wrapped by the short anchoring block and surrounded by the shell of triphenylamine polymers. With regard to light-emitting devices, the semiconducting polymer brushes also improve the hole injection into the quantum dots. By the simultaneous injection of electrons from a counter electrode, excitons will be formed within QDs, and photons with a characteristic wavelength relevant to the QDs will be emitted. By testing such hybrid materials for QLED devices, we could demonstrate that the turn-on voltage and the efficiency of QLEDs could be improved by employing such QD/polymer hybrid materials in multilayered devices.

RESULTS AND DISCUSSION

To prepare semiconducting block copolymers with anchor groups for CdSe@ZnS QDs, RAFT polymerization was chosen for the controlled radical polymerization, as this method can be applied to many radically polymerizable monomers. *para*-Methylated vinyltriphenylamine (TPA) was used as a hole conducting species. It can be polymerized in a controlled radical way by NMRP and RAFT polymerization.[6,15] We used 2-phenylpropan-2-yl benzodithioate as a chain transfer agent, as already described in previous work.[16] By using pentafluorophenol acrylate as a monomer for the second block, it is possible to introduce various types of anchor groups for inorganic materials (see Figure 1). The reactive ester blocks can be converted with any kind of primary amines to introduce functionality to such blocks.[6] For binding to the QD surfaces, the reactive esters were treated with cysteamine and thus transformed into poly(*para*-methyl triphenylamine-*b*-cysteamine acrylamide) (PTPA-*b*-CAA) block copolymers. Because of the thiol-containing anchor blocks with multiple binding sites, the adsorption of such BCPs at QD surfaces is much more efficient than the adsorption efficiency of end-functionalized polymers or monodentate surfactants often used for the synthesis of well-defined nanoparticles.

The block copolymerization can be monitored by GPC and NMR. The conversion of the reactive ester block can be followed by ^{19}F NMR and IR spectroscopy, showing the split-off of pentafluorophenole (PFP) moieties followed by the appearance of the absorption characteristic for amides at 1680 cm^{-1} after the reaction with cysteamine. Both methods demonstrate the conversion to be quantitative.[17] Due to the controlled radical polymerization, block copolymer **P2** could be prepared with a low polydispersity (PDI ~1.2; see Supporting Information S1). We prepared two block copolymers with different molecular weights. Table 1 gives the analytical data of GPC analysis (PS equivalents). The GPC traces of the BCP show a shoulder at higher molecular weights due to oxidative disulfide bridges between the thiol groups in the anchor block. The tested polymers (50 and 100 repeating units of TPA;

TABLE 1. Analytical Data for the Prepared Block Copolymers (Based on GPC Data (PS Equivalents))

	M_n (P1)	*x*	M_n (P2)	*y*	PDI (P2)
BCP 1	15000	50	17000	10	1.16
BCP 2	30000	100	32000	10	1.23

see Table 1) showed similar properties in the hybrid case.

For the hybridization with inorganic nanomaterials, CdSe@ZnS quantum dots were employed, which were prepared by the one-pot synthesis from our laboratory[18] and already investigated in QLEDs.[19] Since oleic acid was used as a surfactant for the QDs, oleic acid chains are bound to the QD surface during the synthesis. By variation of the size and the composition of the core, the emission colors can be varied over a wide range of the spectrum.[18] The results presented here were obtained with green-emitting QDs, while stability tests were performed with blue-emitting QDs.

The quantum dots were functionalized with the block copolymers (**BCP1** and **2**) by the ligand exchange procedure, which is driven by the strong enthalpic binding of multiple thiols in the anchoring blocks, displacing the weakly bound carboxylic acid groups derived from oleic acid. The exchange reaction was performed under phase transfer conditions. The oleic acid capped QDs are soluble in chloroform, tetrahydrofurane, and hexane but are insoluble in dimethylformamide (DMF) and water. An immiscible solvent pair of hexane (a good solvent for QDs) and DMF (a good solvent for TPA polymer) was chosen for monitoring the phase transfer of QDs from hexane to DMF as a proof for the functionalization of QD surfaces (see Figure 2a,b).

To cover the QD surfaces with semiconducting triphenylamine polymers, 6 mg of PTPA-*b*-CAA (**P3**) was dissolved in 1 mL of DMF and 20 mg of green QDs was dissolved in 1 mL of hexane. Due to the immiscibility between hexane and DMF as well as the insolubility of QDs in DMF and of the block copolymers in hexane, this combination gives a two-phase system. By ultrasonication, it is possible to transfer the QDs to the DMF phase by displacing oleic acids with the block copolymer brushes. Due to the excess amount of QDs in the two-phase mixture, all of the block copolymer chains in the DMF phase should be bound to the QD surfaces while residual unmodified QDs remain in hexane after the surface modification procedure. The hexane phase can be thus separated, and the QDs transferred to the DMF phase can be purified for further experiments. The QDs functionalized with the block copolymers show the same solubility behavior as the block copolymer itself, providing the evidence for sufficient surface modification of QDs (see Figure 2). The functionalized QDs were then precipitated in methanol three times to remove displaced oleic acids and were washed with hexane to eliminate unmodified QDs (capped with oleic acid) which might be accidentally transferred to the DMF phase during the ultrasonication process.

In order to determine the degree of substitution of oleic acid with block copolymer, NMR spectroscopy and thermal gravimetric analysis (TGA) were used. NMR spectra reveal that the QDs still retain oleic acid on the surface to some extent. Comparing the signals of the oleic acid double bond with the aromatic protons from triphenylamine, a relative ratio of 1:5 was estimated (one oleic acid to five triarylamine moieties). Consequently, a complete exchange of oleic acids was not possible, but the majority of the bound organic material is now polymeric. Therefore, block copolymers anchoring to the QDs mostly influence the solubility and the properties of the hybrid materials.

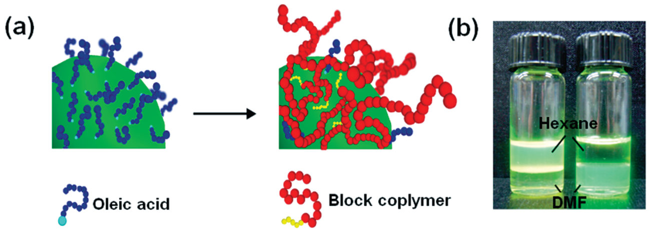

Figure 2. (a) Schematic presentation of QD functionalization and (b) photograph showing the hybridization of QDs with PTPA-*b*-CAA through the phase transfer method (hexane on top and DMF at the bottom in immiscible mixture). Left vial: QDs dissolved in hexane over DMF. Right vial: QDs functionalized with BCP in DMF.

TGA analysis could also be used to determine the content of organic species attached to the QD surface. Data were taken at a heating rate of 20 K/min in nitrogen atmosphere. For the oleic acid capped QDs, the degradation temperature, which is defined as the temperature at which 5 wt % of organic species is burned off, is determined to be 388 °C. The weight loss shows that about 20 wt % of the oleic acid coated QDs consist of the organic surfactants. For the triphenylamine-containing block copolymer, the degradation temperature was found to be 350 °C, and we also found that the block copolymer depolymerizes almost completely (~4 wt % solid content left). The organic species in the QD/polymer hybrid material shows the degradation temperature at 350 °C, which is the same as the temperature found for the BCP. A second step around 388 °C was not observed. In the hybridized QDs 30−40 wt % is organic material, composed of a mixture of the semiconducting block copolymer and oleic acid. The increase in the organic materials attached to the QD surface and the reduced degradation temperature indicates that the QD surfaces are covered mainly by block copolymer chains (see Supporting Information Figure S2).

A photoluminescence spectrum of the QD/polymer hybrid material shows that 80% of the PL intensity remains after grafting the QD surfaces with block copolymer. This is a high intensity value compared with other functional QDs in which fluorescence drops mostly after surface modification (see Supporting Information Figure S3).

The hybridized QDs consist—in analogy to earlier work[5]—of an inorganic core (CdSe@ZnS) around which the short anchor block is wrapped, while the triarylamine polymer acts as a polymeric shell. To determine the nature of the colloidal state of the hybridized QDs,

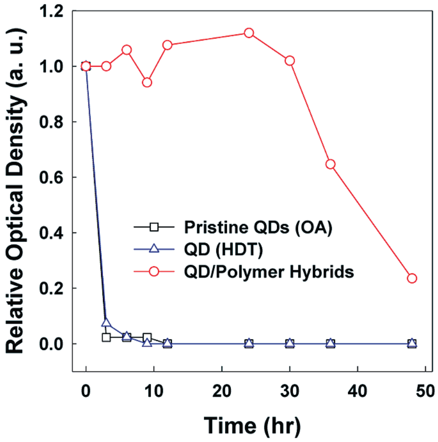

Figure 3. Test for colloidal stability of the QD/polymer hybrid (blue-emitting QDs) under illumination in comparison with oleic acid and hexandecane thiol (HDT) coated QDs in $CHCl_3$. While pristine QDs and HDT coated agglomerate during illumination (365 nm, 2 mW/cm^2), QD/polymer hybrids are stable for more than 30 h.

dynamic light scattering and AFM measurements were performed. AFM measurements show mostly individual QDs in combination with small aggregates. Dynamic light scattering gives a z-averaged hydrodynamic radius $\langle R_h \rangle_z$ of the hybridized QDs of 18 nm, which is a bit larger than the one of the pristine QDs (6 nm). As the z-averaged weighs aggregates much stronger than the individual QDs, this result is coincident with the AFM measurements (number majority of individual QDs plus small aggregates; see Supporting Information Figure S4).

Experiments to test the colloidal stability of QDs demonstrate the improved stability of the QD/polymer hybrids in comparison with pristine QDs with oleic acids bound to the surface or QDs covered with hexadecylthiol (prepared by ligand exchange).[19] We used blue-emitting QDs, which are unstable under continuous UV illumination. It was noted that QDs covered with small molecules massively agglomerate under UV illumination (at 365 nm with 2 mW/cm^2) for 2 h, while QD/polymer hybrids show extended stability under the continuous illumination for more than 30 h in chloroform (see Figure 3). The reasons for such improved colloidal stability are due to two reasons: at first, longer polymer brushes attached to QD surfaces provide the enhanced steric stabilization of the colloidal QD dispersions, preventing agglomeration of QD particles. Second, we can also assume that the UV illumination breaks the bonds between small molecule surfactants and the QD surfaces. The unprotected QDs tend to agglomerate massively. In the case of the multidentate ligands, the probability that all the anchoring bonds are broken is quite unlikely. As a result, the QD/polymer hybrids are quite stable in dispersion due to the strongly bound steric stabilization layers.

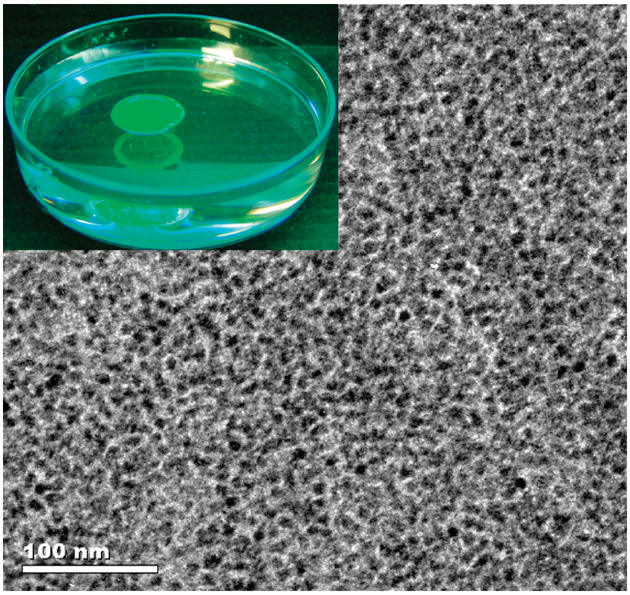

Figure 4. (Top left) QD/PTPA-*b*-CAA hybrid film (size about 1 cm) floated on water surface (from KBr pellet; optical picture) and a TEM image of the corresponding thin free-standing film.

The QD/polymer hybrids show, due to the polymer brushes (~40 wt %) attached to QD surfaces, good film formation properties, similar to QDs carrying cross-linkable ligands.[20] The surface morphology of thin films was tested by AFM measurements with regard to the chain length of the grafted polymer. The rms roughness varies slightly with the molecular weight. While films of QD functionalized with BCP **1** (50 TPA units) exhibit a roughness of 2.7 nm, BCP **2** grafted QDs have a slightly higher rms roughness of 4.1 nm, due to the increased radius with higher molecular weight soluble blocks added to the QD surface. Also thin layers of QD/polymer hybrids spun coated on a mica substrate can be floated on water surface, yielding a free-standing film of the quantum dots. From thicker layers (around 500 nm), large films can be floated off intact (Figure 4). By varying solution concentration, thin free-standing films from polymer hybridized QDs could be prepared. Thin layers (<100 nm) allow the direct visualization by TEM (Figure 4). This is not possible with pristine QDs capped only with oleic acids. Ellipsometric measurement of the film deposited on a silicon wafer shows the average film thickness of about 60 nm from 0.5 wt % solution of the QD/polymer hybrids dissolved in toluene and spun at 4000 rpm. This value showed to be the best for device application in terms of low turn-on voltage and EQE at moderate current density, as experiments with different concentrations for device preparation demonstrated. This value was taken as an ideal standard film thickness for the preparation of light-emitting devices.

QLEDs with a multilayer structure of ITO/PEDOT:PSS (40 nm)/QDs or QD/PTPA-*b*-CAA hybrids/TPBI (40 nm)/LiF (0.5 nm)/Al (1000 nm) were prepared as test devices (Figure 5a,b for the corresponding band diagram). The QLED based on QD/PTPA-*b*-CAA hybrids for the emitting layer shows improved device performance in terms of device efficiency compared with the QLED based on pristine (or unmodified) QDs (Figure 5c,d). These improvements in device performance are mainly attributed to the electrical and physical properties of PTPA-*b*-CAA encapsulating the QDs. The HOMO energy level of PTPA-*b*-CAA resides between the valence band edge energy level of QDs (~6.8 eV) and the HOMO energy level of PEDOT:PSS (5.0 eV). Consequently, the block copolymer shell facilitates the hole injection from PEDOT:PSS into the QDs, increasing the possibility of exciton formation within (or exciton migration to) the QDs. Moreover, the PTPA-*b*-CAA brushes guarantee the uniform coating of the QD-emitting layer, filling up voids between adjacent QDs due to the spherical geometry of QDs or the imperfection of QD layering process (as discussed in Figure 3). In addition, this uniform coating of the emitting hybrid layer suppresses the current leakage, which can result from the direct contact between TPBI and PEDOT:PSS layers through interstitial voids or defects in the case of pristine QD layers. Owing to these combined effects (*i.e.*, facilitated carrier injection as well as the uniform film formation), the QLED with an emitting layer based on QD/PTPA-*b*-CAA hybrids exhibits 3-fold higher device efficiency despite the comparable photoluminescent quantum efficiency (or slightly lower PL QY) of the hybrid materials when compared with unmodified QDs used as an emitting layer.

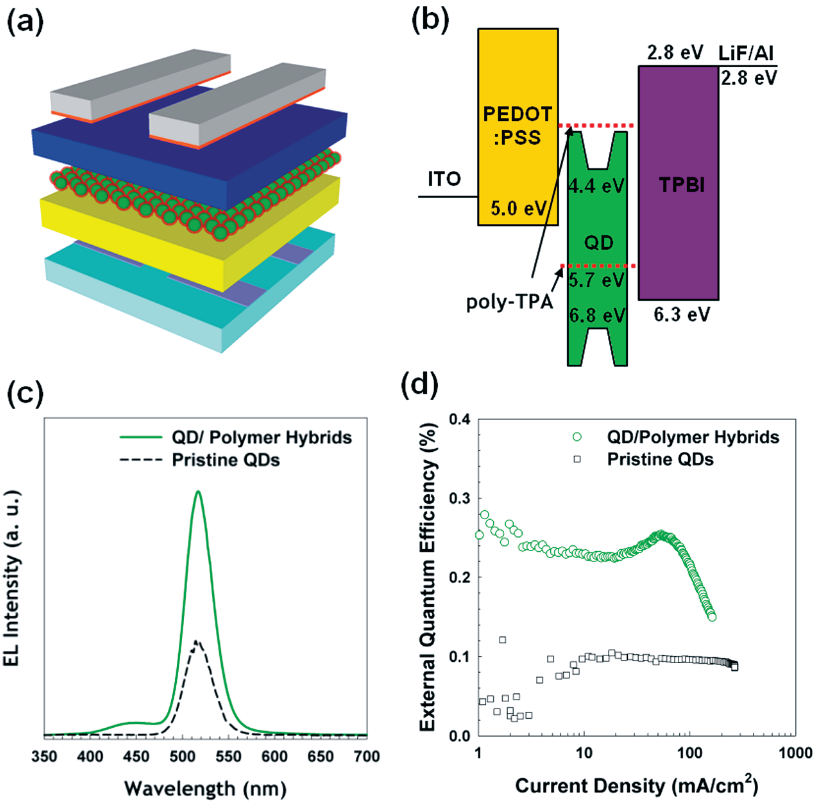

Figure 5. (a) Schematic for the test QLED device structure and (b) the energy band diagram of QLEDs prepared, and (c) electroluminescence spectra and (d) external quantum efficiencies of QLEDs based on pristine QDs (black open squares) and QD/PTPA-*b*-CAA hybrids (green open circles).

The EL spectra, shown in Figure 5c, represent the enhanced emission from the QLED based on QD/polymer hybrids. The QLED-containing QD/polymer hybrids exhibit a weak parasitic shoulder below 460 nm (presumably originating from the emission from PTPA-*b*-CAA itself; also see Supporting Information Figure S5) on top of a strong emission from the QDs. However, the contribution to the emission from PTPA-*b*-CAA remains still quite low (less than 10% of the total EL emission), and the enhancement of the QD band edge emission is truly remarkable (increased by three times in the EL intensity). This underlines the benefits and advantages of QD/PTPA-*b*-CAA hybrids as an emitting layer for efficient QLEDs. We are confident that the QLED device can be even further improved in terms of device efficiency and color purity by introducing both hole-transporting moieties and electron-transporting moieties to copolymers (with either random or block copolymer structure) bound to QD surfaces (for further OLED characteristics, see Supporting Information Figure S6).

CONCLUSION

We have presented QD/polymer hybrids by grafting a block copolymer containing thiol-anchoring groups (poly(*para*-methyl triphenylamine-*b*-cysteamine acrylamide)) onto the surfaces of CdSe@ZnS QDs through the ligand exchange procedure. The QD/polymer hybrids possess both optical properties of QDs (*i.e.*, high photoluminescence with narrow spectral bandwidth) as well as good processability based on the grafted block copolymers (*i.e.*, enhanced solubility in typical organic solvents as well as good film forming property) along with improved colloidal stability compared with unmodified QDs (capped with oleic acid). We have also fabricated light-emitting diodes based on the new QD/polymer hybrid material, exhibiting the improved device performance (increased EL intensity at 50 mA/cm^2 and 3-fold increase in EQE) compared with the QLED device based on unmodified QDs due to the uniform deposition of the QD/polymer hybrid layer for the emitting layer as well as the facilitated hole injection into the QDs. Since the approaches taken and results presented here prove positive process capability along with new functionality on QDs, these approaches can be extended to other functional nanomaterials (such as rod, wires, tubes, and sheets) for further practical applications.

EXPERIMENTAL METHODS

Solvents and chemicals for preparation of the hybrids and film preparation were purchased from Sigma-Aldrich and Fisher Scientific in analytical grade and used without further purification. TPA monomer and PTPA-*b*-CAA were synthesized as described in previous work,[6] and cysteamine (Sigma-Aldrich) was used as a reagent for the conversion of the reactive ester. QDs were synthesized in a one-pot method as described in previous work.[18] Thermogravimetry was carried out in a TGA 2050 instrument (TA Instruments Inc.) under nitrogen atmosphere. NMR spectra were obtained in a Bruker AC 400. Transmission electron microscopy was performed on a CM-20 Philipps operated at 200 kV. QD/polymer hybrid films for TEM investigations were spin coated on mica from a 0.5 wt % solution in toluene at 4000 rpm, floated on a water surface, and investigated on a TEM grid without additional layer. Thicker films were prepared by spin coating a 10 wt % solution on a KBr pellet, which was afterward dissolved in water. A variable-angle multiwavelength ellipsometer (Gaertner L2W16C830) was used to measure the thickness of the films.

Colloidal Stability Test: For the investigation of the stability of QD/polymer hybrid against UV, blue QDs were used, which are less stable against external environment. Three samples were prepared with different ligands (QDs capped with oleic acids, hexadecane thiol, QDs, **P3**). All samples were dissolved in $CHCl_3$ and were irradiated by UV light with $\lambda = 356$ nm continuously. UV−vis spectra were measured every 3 h. The stability of QDs against UV irradiation was characterized by analyzing the transmission of the UV−vis spectra after exposure of UV irradiation.

Device Preparation: A QD−polymer hybrid LED was fabricated by the following sequence: The ITO substrate (sheet resistance of about 10 Ω/□) was cleaned ultrasonically in organic solvents (isopropyl alcohol, acetone, and methanol), rinsed in deionized water, and dried in an oven at 120 °C for more than an hour. The substrate was cleaned with a UV-ozone cleaner prior to spin-coating PEDOT:PSS (CLEVIOS P VP AI 4083, H.C. Starck) and QD−hybrid material. TPBI, LiF, and Al electrodes were deposited under a base pressure of 3×10^{-6} Torr by thermal evaporation, and the evaporation speed was 1−1.5 Å/s for TPBI and 4−5 Å/s for the metals. The current−voltage (*I*−*V*) and electroluminescence (EL) characteristics were measured by using a Keithley-236 source measurement unit, Si photodiode (Hamamatsu), and a photomultiplier tube combined with a monochromator (Acton Spectropro-275). The measurement of the EL device was conducted under vacuum.

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Supporting Information Available: Analytical data, photoluminescence spectra, thermal gravimetric analysis data, electroluminescence spectra of poly-TPA (**P1**), DLS and AFM data, *I*−*V* and *L*−*V* characteristics of QLED. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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