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ARTICLE

CdSe/ZnS Nanoparticle Composites with Amine-Functionalized Polyfluorene Derivatives for Polymeric Light-Emitting Diodes: Synthesis, Photophysical Properties, and the Electroluminescent Performance

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ABSTRACT: A series of amine-functionalized poly(9,9-dihexylfluorene) (**PFH**) derivatives, **PFH-NH$_2$F-39-1** (**P1**), **PFH-NH$_2$F-19-1** (**P2**), **PFH-NH$_2$F-9-1** (**P3**), and **PFH-NH$_2$F-17-3** (**P4**), and **PFH-NH$_2$F-4-1** (**P5**), were developed to form organic/inorganic hybrid composites with CdSe/ZnS nanoparticle for polymeric light-emitting diodes (LEDs). The structures and purities of all desired polymers were fully characterized by ^{1}H and ^{13}C NMR, UV−vis and photoluminescent spectroscopy, gel permeation chromatography, elemental analyses. The hybrid nanocomposites were in situ formed through these amino-functionalized polyfluorene derivatives doped with core−shell CdSe/ZnS quantum dots (QDs). The detailed characterizations of their photophysical properties revealed that rapid Förster energy transfer from the conjugated polymers to the red-emitting QDs afforded an efficient red color emission. The preliminary polymeric LEDs fabrication with the configuration of ITO/DB/nanocomposites/Al achieved red emission for the in situ prepared hybrid nanocomposites. The investigation of device performance indicates that these nanocomposites are promising red light-emitting polymeric LED materials with good performance in providing excellent color purity, stability, and robustness. Such strategy provides us a platform to achieve red-emitting hybrid nanocomposites as the active materials for LEDs.

Introduction

π-Conjugated polymers have attracted considerable interest because of their electronic and optoelectronic applications, such as in organic light-emitting diodes (OLEDs),[1] organic field effect transistors (OFETs),[2] photovoltaics,[3] and other optoelectronic devices. Polyfluorene derivatives (PFs) have emerged as promising blue-emitting materials for OLEDs because of their good blue electroluminescence (EL) performance, high thermal stability, large band gap, and good processability.[4] Even though there have been significant innovations on both polymer structure and device architecture design to improve the lifetime, the stability, and color purity of OLED devices, using PFs as the active materials still presents a big challenge to the display industry.[5−8]

Recently, hybrid nanocomposites based on semiconducting quantum dots (QDs) and conjugated polymers have attracted substantial attention for their applications in flexible electronics, light-emitting displays,[9] and photovoltaics,[10] which benefit from their spectral tunability, color purity, and photostability. These hybrid nanocomposites are prepared by mixing the formed or grown in situ QDs (PbS, CdTe, or CdSe) within a polymer matrix[11] or directly growing QD colloids within a polymer matrix that is formed in situ from polymer precursor materials.[12a]

In most of the previous QD-polymer nanocomposite materials, the QDs are merely physically mixed with the polymer matrix rather than chemically attached (through chemical bonds or chemical complexes) to the polymer material. Such QD-polymer hybrid nanocomposites might be unstable, and the phase segregation may occur between QDs and the polymer matrix material, thereby hindering the formation of QD-polymer nanocomposites having uniform distributions of nanocrystals within the polymer matrix. Skaff et al. achieved red-emission from hybrid QDs tailored with poly(*para*-phenylene vinylene) (PPV),[12a] in which a phosphine oxide group is located at the end of the PPV chain; Wolf and Advincula synthesized conjugated oligothiophenes-capped CdSe nanoparticles and realized energy transfer from oligothiophenes to CdSe nanoparticles.[12b,c] Herein we present the synthesis and the photophysical properties of amine-functionalized poly(9,9-dialkylfluorene) (PF) derivatives that can interact with QDs to form well-dispersed QD-polymer hybrid nanocomposites. A series of characterizations including photoluminescence (PL), photoluminescence excitation (PLE), and preliminary electroluminescent (EL) measurements reveal that efficient Förster energy transfer from PFH derivatives to the core−shell CdSe/ZnS QDs results in an efficient red emission purely from the QDs. The EL devices have been fabricated using such hybrid core−shell CdSe/ZnS QDs-PFH nanocomposites as the emissive layer by facile spin-casting technology to achieve the good red-emission EL performance.

Results and Discussion

Synthesis. Scheme 1 depicts the synthetic approach to amino-functionalized monomer **3**[13] and monomer **5**. The

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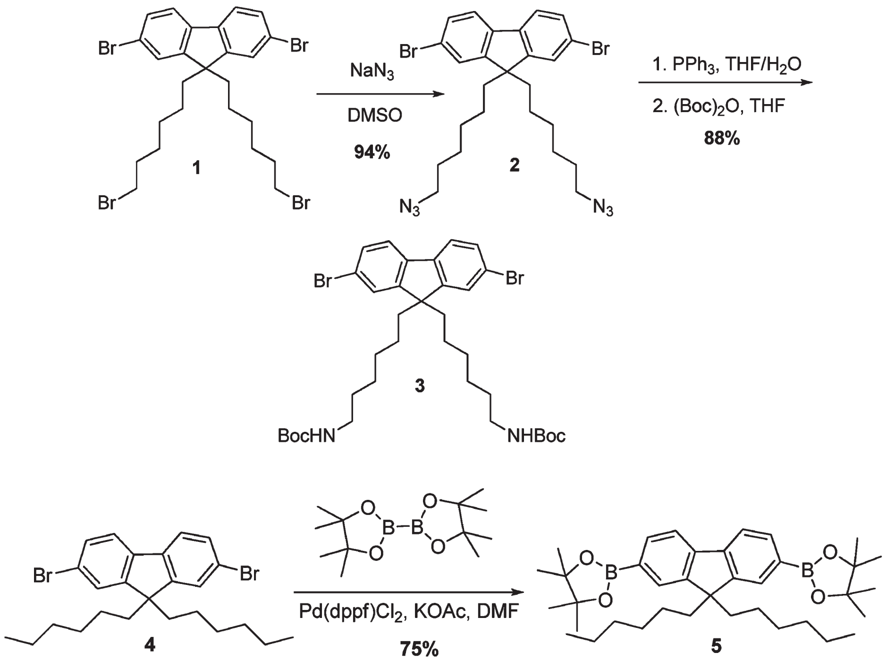
Scheme 1



reaction of 2,7-dibromo-9,9-bis(6′-bromohexyl)fluorene (**1**) with sodium azide gave 2,7-dibromo-9,9-bis(6′-azidohexyl)-fluorene (**2**) with a 94% yield. Reduction of **2** by PPh_3 in THF/H_2O, followed by protection of the amine groups with $(Boc)_2O$, afforded 2,7-bibromo-9,9-bis(6′-butoxylcarbonyl-aminohexyl)fluorene (**3**) with an 88% overall yield.[14] 2,7-Dibromo-9,9-dihexylfluorene (**4**) reacted with 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bi(1,3,2-dioxaborolane) to afford 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (**5**) with a 75% yield.

Monomers **3** and **4** with different ratios were polymerized with monomer **5** via palladium-mediated Suzuki cross-coupling reaction to afford five corresponding amino-functionalized polymers **6a**–**6e**, respectively, as shown in Scheme 2. The crude polymers were washed with methanol, water, and methanol again, successively, and were placed in a Soxhlet apparatus and extracted with refluxed acetone for 48 h, and then were dried at 60 °C in a vacuum oven. These polymers were readily soluble in common organic solvents, such as THF, $CHCl_3$, and toluene. Therefore, their basic chemical structures were clearly determined by ^1H and ^{13}C NMR, FT-IR, and elemental analysis. The molecular weights of these polymers were determined by gel permeation chromatography (GPC) with THF as the eluent, calibrated against polystyrene standards. As shown in Table 1, the GPC analysis indicated that the number-average molecular weight (M_n) and polydispersity index (PDI) of these polymers were in the ranges from 16 280 to 19 275 and from 2.1 to 2.4, respectively.

These conjugated polymers were converted to their quaternary ammonium salts, **7a**–**7e**, respectively, by treatment with 37% hydrochloric acid. Finally, quaternary ammonium salts were neutralized by 50% KOH aqueous solution to yield neutral amino-functionalized copolymers **PFH-NH$_2$F-39–1 (P1)**, **PFH-NH$_2$F-19–1 (P2)**, **PFH-NH$_2$F-9–1 (P3)**, **PFH-NH$_2$F-17–3 (P4)**, and **PFH-NH$_2$F-4–1 (P5)**. The thermal stability of amino-functionalized polymers **P1**–**P5** was investigated by thermogravimetric analysis (TGA) under a nitrogen atmosphere. The degradation onset temperature of the polymers was above 220 °C under a nitrogen atmosphere. The thermally induced phase transition behaviors of these polymers were examined by differential scanning calorimetry (DSC) under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. However, no obvious T_g of the polymers was observed in the temperature range from 0 to 220 °C.

Photophysical Properties. Figure 1 shows normalized UV–vis absorption and PL spectra of polymers **P1**, **P2**, **P3**, **P4**, and **P5** in dilute THF solutions in a concentration of 1×10^{-5} M based on the polymer repeat unit. These polymers showed the same absorption and emission features in dilute solution as homopolymer poly(9,9-dihexylfluorene). The photophysical properties of these polymers in dilute solutions are summarized in Table 2. As illustrated in Figure 1a, polymers **P1**–**P5** exhibited similar absorption maximum λ_{max} (388 nm for **P1**, 390 nm for **P2**, 389 nm for **P3**, 390 nm for **P4**, and 382 nm for **P5**), which was not affected by the ratio of free amine groups in these polymers.

The PL spectra of **P1**, **P2**, **P3**, **P4**, and **P5** in dilute THF solutions, excited at the absorption maximum wavelength, are illustrated in Figure 1b. These polymers showed almost identical PL behaviors. Their emission features peaked at ~416 nm with a clear vibronic shoulder at 441 nm, which indicated that these polymers exhibited well-extended chain conformation because of their good solubility in THF.[15] These five polymers also showed very small Stokes shifts (about 30 nm) between the 0–0 transition of absorption and emission, indicating a little structural reorganization in the excited state.[16] We also measured their absorption and emission properties in thin solid films, which also exhibited the same features as that of homopolymer poly(9,9′-dihexylfluorene).

Electrochemical Properties. The electrochemical behavior of these polymers, as shown in Figure 2, was investigated by cyclic voltammetry (CV). The CV was performed in a solution of n-Bu_4NPF_6 (0.1 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under the atmosphere of nitrogen. A carbon electrode coated with a thin polymer film was used as the working electrode. A platinum wire was used as the counter electrode, and all potentials were recorded versus Ag/AgCl (saturated) as a reference electrode. The oxidation and reduction peaks appeared at 1.2 to 1.4 and −2.1 to −2.3 V, respectively, which were attributed to the oxidation and

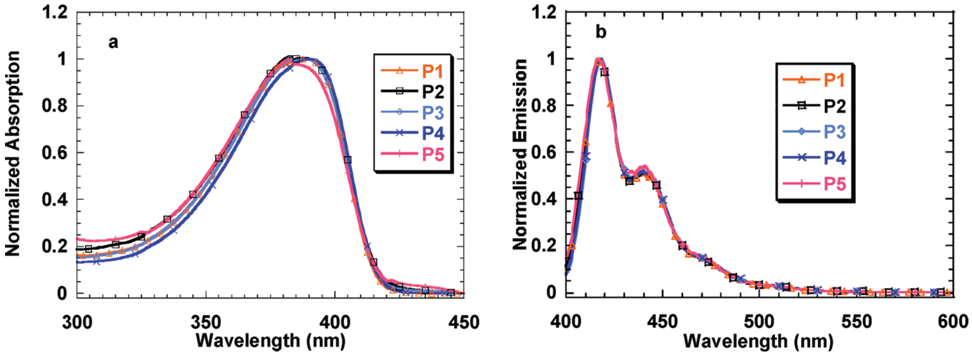


Figure 1. Normalized UV−vis absorption and PL spectra of **P1**, **P2**, **P3**, **P4**, and **P5** in dilute THF solutions. (1×10^{-5} M based on the polymer repeat unit): (a) UV−vis absorption spectra and (b) PL spectra.

Scheme 2

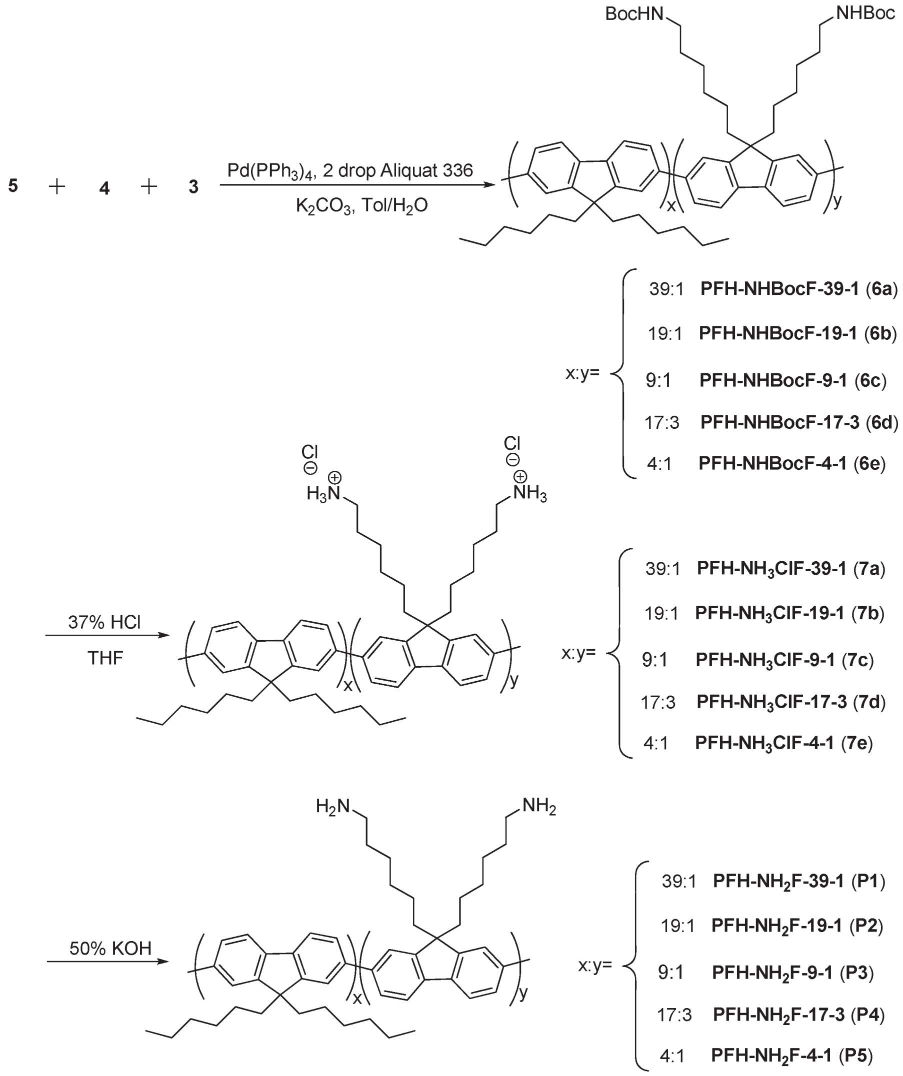


Table 1. Molecular Weight of the Polymers

polymers	M_n	M_w	PDI
6a	18 692	45 209	2.4
6b	19 275	43 464	2.2
6c	17 680	41 738	2.3
6d	18 318	39 714	2.1
6e	16 280	38 356	2.3

reduction potentials for the polymers' backbones. The HOMO and LUMO levels calculated according to an empirical formulas, $E_{\mathrm{HOMO}} = -e(E_{\mathrm{ox}} + 4.4)$ (eV) and $E_{\mathrm{LUMO}} = -e(E_{\mathrm{red}} + 4.4)$ (eV),[17] are listed in Table 2. From the electrochemical data, it was estimated that the band gap of these functionalized polymers was around 2.70 to 3.07 eV for **P1**−**P5**, which made them good candidates as host materials for polymer-QD hybrid nanocomposites.

Hybrid Polymer-Quantum Dot (QD) Nanocomposites. As mentioned above, these amine-functionalized PFs are good candidates to form polymer-QD nanocomposites. The amino groups can bind to the QD surfaces and help to

Table 2. Electrochemical Properties of Polymers P1−P5 in Dilute Solution and in Thin Film

polymers	UV−vis λ_{max} (nm)[a]	PL λ_{max} (nm)[a]	E_{ox} (V)[b]	E_{red} (V)[b]	HOMO (eV)[b]	LUMO (eV)[b]	E_{gap} (eV)[b]
P1	388	418, 440	1.05	−1.90	−5.45	−2.50	2.95
P2	390	418, 440	1.28	−1.79	−5.68	−2.61	3.07
P3	389	418, 440	1.18	−1.78	−5.58	−2.62	2.96
P4	390	418, 441	1.05	−1.65	−5.45	−2.75	2.70
P5	382	416, 441	1.14	−1.82	−5.54	−2.58	2.96

[a] In dilute THF solutions (1.0×10^{-5} M) at room temperature. [b] In thin film.

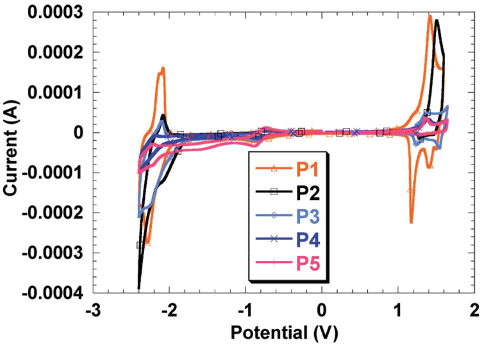


Figure 2. Cyclic voltammograms of polymers **P1**−**P5** in thin film coated on carbon electrodes in a solution of n-Bu_4NPF_6 (0.1 M) in acetonitrile.

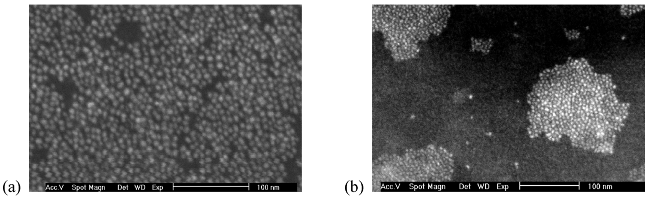


Figure 3. SEM images of (a) hybrid **PFH-NH$_2$F-39-1**-QDs and (b) TOPO-QDs-PFO mixture.

achieve good exciton energy transfer from the backbones to the QDs. For proof-of-concept, polymer **PFH-NH$_2$F-39-1** (**P1**) was mixed with CdSe/ZnS core−shell nanocrystals with pyridine ligands, in which pyridine ligand was exchanged by the amine functional groups of our PFs to form hybrid polymer-QD nanocomposites. Although there was no strong chemical information collected as evidence of polymers directly attaching to QDs, scanning electron microscopy (SEM) images shown in Figure 3 revealed that this amine functionalized copolymer helps QDs well dispersed throughout the thin film, compared with an example of the simple physical mixture of trioctylphosphine oxide (TOPO)-covered CdSe/ZnS in poly(9,9-dioctylfluorene) (PFO).

To demonstrate the energy transfer within these nanocomposites in thin films, the pure polymer **P1** (3 mg/mL) and the nanocomposite with a polymer/QD weight ratio of 1.5:1 (3 mg/mL for polymer and 2 mg/mL for QDs) were deposited by spin coating from chloroform solutions on quartz substrates. Figure 4a shows that the PL intensity of **P1** in this nanocomposite significantly decreases (to < 10% of the pure polymer's emission). Note that the PL emission from the QDs may result not only from the expected energy transfer from the polymer but also from direct excitation. As illustrated in Figure 4b, the PL excitation spectrum of the nanocomposite thin film recorded at the maximum of the QD emission (626 nm) exhibits the absorption characteristic features (as shown in Figure 4a inset). The correspondence between the absorption by the polymer and increased emission by the QDs confirms that when exciting at ~380 nm, the majority of the QD emission results from energy transfer from blue-emitting polymer **P1** to the red QDs.

OLEDs Performance from Hybrid QD-P1 Nanocomposite. A mixture of **P1** (4.5 mg) and CdSe/ZnS with pyridine ligands (3 mg) in a mixture (1.5 mL) of toluene and chloroform was stirred overnight at room temperature in a glovebox (Ar atmosphere), which was used to prepare thin films by spin-casting on quartz substrates for PL and PLE measurements. PLE measurements were taken on Cary 6000i UV−vis-NIR spectrometer with some customized modification. A solution of **P1** (3 mg/mL) in the mixture of toluene/chloroform was used to spin-cast polymer-only thin films as control samples. The polymer and hybrid QD-polymer LEDs were fabricated under clean room conditions, using patterned ITO/glass substrates as bottom electrode. A DuPont buffer (DB) layer (~45 nm) was deposited by spin coating and annealed at 100 °C in clean room for 1 h and in the glovebox for another hour. Subsequently, the emissive polymer **P1** or QD-**P1** was deposited from a mixture of toluene and chloroform by spin coating in the glovebox. The Al metal layer as cathode was then deposited by vacuum evaporation with a base pressure of 10^{-5} Pa. The device area was 0.04 cm^2. PL spectra were recorded on a JobinYvon Triax 550 spectrometer. The EL spectra shown in Figure 5 were recorded from simple proof-of-concept hybrid OLED devices with the architecture of glass/indium tin oxide (ITO)/DB (45 nm)/QD-**P1** (or polymer only (40−60 nm))/Al at an applied voltage of 6 V. According to preliminary results, the EL behavior of the hybrid polymer-QD nanocomposites in devices is similar to their PL behavior. The QD-dominated emission with current efficiency of 0.36 Cd/A was consistent with efficient energy transfer from the polymer to QDs in the EL devices (as shown in Figure 5 inset). Optimization using more sophisticated device architectures and more detailed characterization of hybrid QD-OLED performance are in progress and will be published in due course.

Conclusions

In conclusion, we have developed five new alcohol-soluble amino-functionalized **PFH** derivatives **P1**, **P2**, **P3**, **P4**, and **P5** through the facile approaches. These polymers are the first examples of synthesis of **PF** copolymer derivatives with free amine groups on the side chain. These polymers and core−shell CdSe-ZnS QDs were used to fabricate emissive layers with QDs as the key emissive element. All layers of the device have been deposited by a facile spin-coating technique. Preliminary results from a series of characterizations including PL and PLE measurements on composite films and EL experiments on proof-of-concept hybrid QD-OLED devices revealed efficient energy transfer from the PFH derivatives to the red-emitting QDs. More detailed work on optimizing devices and device performance is in progress.

Experimental Section

General Methods. Chemicals were purchased and used as received. All air- and water-sensitive reactions were performed under a nitrogen atmosphere. Toluene was distilled from sodium. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz or Mercury plus 300 MHz using $CDCl_3$ as

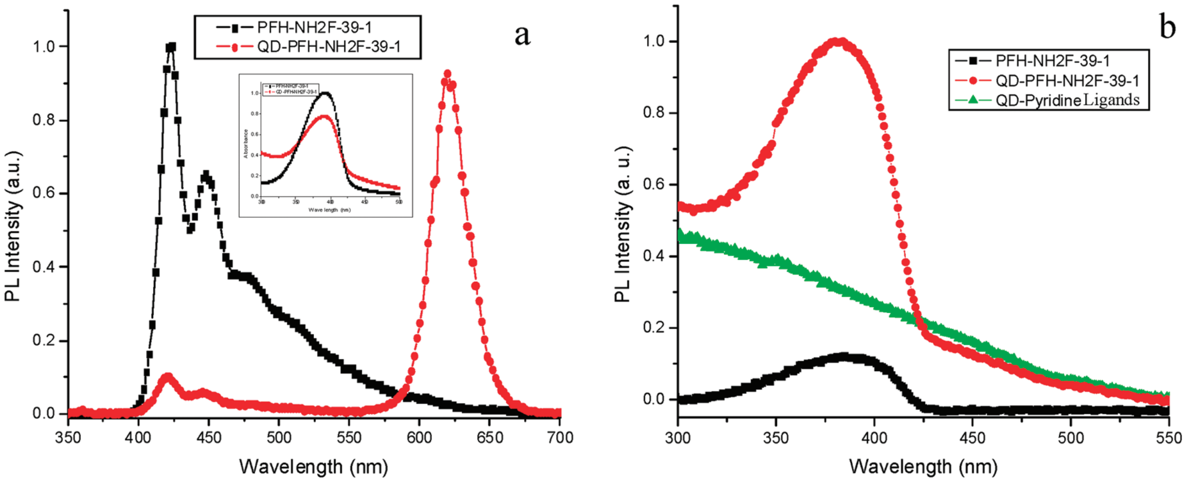


Figure 4. (a) PL spectra of the pure polymer (**P1**) and polymer-QD nanocomposite (QD-**P1**) thin films on quartz substrates. Inset shows the absorption spectra of both thin films. (b) PL excitation spectra of **P1** film, QD-**P1** film, and a pure QD film on quartz substrates.

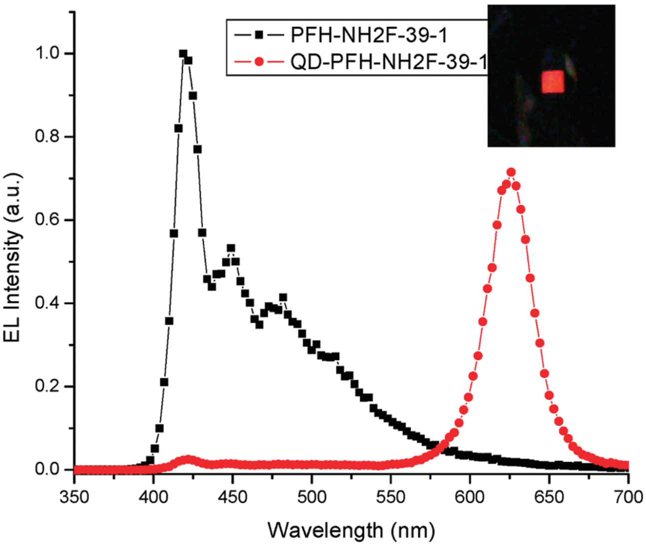


Figure 5. EL spectra of ITO/DB/**P1**/Al (■) and ITO/DB/QD-**P1**/Al (●) collected at 6 V (Inset: EL picture when the device was operating at 3 V).

solvent unless otherwise noted. All chemical shifts were reported in parts per million (ppm), ^{1}H NMR chemical shifts were referenced to TMS (0 ppm) or $CHCl_3$ (7.26 ppm), and ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77.23 ppm). Absorption spectra were recorded on PerkinElmer Lambda 35 UV−vis spectrometer. PL spectra were carried out on a PerkinElmer LS55 luminescence spectrometer. MALDI-TOF mass spectra were recorded on a Bruker BIFLEX III or AUTOFLEX III time-of-flight (TOF) mass spectrometer (Bruker Daltonics, Billerica, MA) using a 337 nm nitrogen laser with dithranol as matrix. Elemental analyses were performed using a German Vario EL III elemental analyzer. DSC analyses were performed on a Mettler Toledo instrument DSC822^e calorimeter. GPC was obtained through a Waters GPC 2410 with a refractive index detector in THF using a calibration curve of polystyrene standards. Thermal gravimetric analyses (TGAs) were measured on Thermal Analysis SDT2960. CV was performed using a BASI Epsilon workstation, and measurements were carried out in acetonitrile containing 0.1 M nBu$_4$NPF$_6$ as a supporting electrolyte. Carbon electrode was used as a working electrode, and a platinum wire was used as a counter electrode; all potentials were recorded versus Ag/AgCl (saturated) as a reference electrode. The scan rate was 100 mV s^{-1}.

The synthesis of monomer **3** has been reported elsewhere.[13]

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (5). A mixture of 2,7-dibromo-9,9-dihexylfluorene (15 g, 30.5 mmol), KOAc (18 g, 183 mmol), bis(pinacolato)diborane (16.4 g, 64 mmol), and Pd(dppf)Cl_2 (1.8 g, 0.22 mmol) in 150 mL of degassed 1,4-dioxane was stirred for 12 h at 80 °C. After cooled to room temperature, water and chloroform were added to the mixture, and the separated organic layer was washed with brine and water and dried over anhydrous Na_2SO_4. After the removal of the solvent under reduced pressure, the residue was purified over silica gel column chromatography with petroleum as the eluent to give **5** as a white solid (13.4 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.70−7.81 (m, 6H), 1.39 (s, 24H), 1.01−1.11 (m, 12H), 0.72−0.76 (t, 6H, $J = 6.9$ Hz).

6a. A mixture of 2,7-dibromo-9,9-dihexylfluorene (467 mg, 0.95 mmol), 2,7-bibromo-9,9-bis(6′-butoxylcarbonylaminohexyl)fluorene (36.1 mg, 0.05 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (586 mg, 1 mmol), Pd$(PPh_3)_4$ (24 mg, 0.02 mmol), 2 to 3 drops of Aliquat 336, and 1.66 g of K_2CO_3 was added to a two-necked flask and degassed by N_2; then, degassed toluene (11 mL) and deionized water (6 mL) were injected by syringe. The reaction mixture was stirred under nitrogen purge at 95 °C for 48 h. After cooling to room temperature, water and chloroform were added, and the separated organic layer was washed with brine and water and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was added to stirred methanol to give a precipitate. The precipitate was dissolved in chloroform and purified over a short silica gel column chromatography to remove Pd and reprecipitated from methanol. The resulting precipitate was placed in a Soxhlet apparatus and extracted with refluxed acetone for 48 h and then was dried at 60 °C in vacuum oven to give **6a** as a white solid (540 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.47−7.86 (m, 8H), 3.37−3.40 (m, 0.27H), 3.31 (m, 0.12H), 2.12 (m, 4H), 1.82 (m, 0.88H), 1.41 (m, 1H), 0.59−1.25 (m, 40H). ^{13}C NMR (50 MHz, $CDCl_3$, δ): 152.1, 140.8, 140.3, 126.5, 121.8, 120.3, 55.5, 40.6, 31.6, 29.9, 24.0, 22.75, 22.7, 14.2, 14.1. FT-IR (KBr): 2956, 2926, 2850, 1717, 1458, 1437, 1260, 1095, 1022, 812. Anal. Calcd: C, 89.38; H, 10.22; N, 0.12. Found: C, 87.29; H, 10.26; N, 0.32.

6b. This polymer was prepared following procedures similar to those used to prepare **6a**. A white solid (566 mg, 82%) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.30−7.86 (m, 8H), 3.39−3.44 (m, 0.37H), 3.31 (m, 0.15H), 2.99 (m, 0.11H), 2.12 (m, 4H), 1.82 (m, 0.88H), 1.41 (m, 2H), 0.59−1.35 (m, 32H). ^{13}C NMR (50 MHz, $CDCl_3$, δ): 152.1, 140.8, 140.3, 126.5, 121.8, 120.3, 55.5, 40.5, 31.8, 31.6, 29.8, 29.5, 29.4, 29.3, 28.6, 26.5, 24.0, 22.7, 14.2, 14.1. FT-IR (KBr): 2957, 2928, 2850, 1723, 1458, 1260, 1093, 1068, 910, 813, 802. Anal. Calcd: C, 88.99; H, 10.19; N, 0.25. Found: C, 86.74; H, 10.14; N, 0.51.

6c. This polymer was prepared following procedures similar to those used to prepare **6a**. A yellow solid (556 mg, 78%) was obtained. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.34−7.86 (m, 10H), 3.38 (m, 0.06H), 2.99 (m, 0.3H), 2.12 (m, 4H), 1.41 (m, 3H), 0.59−1.26 (m, 40H). ^{13}C NMR (75 MHz, CDCl$_3$, δ): 156.1, 152.5, 152.0, 151.8, 140.8, 140.2, 132.4, 132.3, 132.1, 128.9, 128.7, 128.6, 127.4, 126.4, 121.8, 121.0, 120.2, 79.2, 61.7, 55.6, 40.5, 32.1, 32.0, 31.8, 31.7, 30.2, 29.9, 29.6, 29.5, 29.4, 29.3, 29.2, 28.6, 26.8, 26.5, 24.1, 22.8, 14.3, 14.2. FT-IR (KBr): 2954, 2918, 2849, 1723, 1458, 1438, 1402, 1260, 1093, 1069, 1020, 951, 813. Anal. Calcd: C, 88.23; H, 10.14; N, 0.50. Found: C, 86.56; H, 10.01; N, 0.63.

6d. This polymer was prepared following procedures similar to those used to prepare **6a**. A yellow solid (475 mg, 64%) was obtained. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.47−7.86 (m, 14H), 4.39 (m, 0.40H), 2.99−3.01 (m, 1.28H), 2.05−2.12 (m, 8H), 1.41 (m, 7H), 0.59−1.26 (m, 47H). ^{13}C NMR (75 MHz, CDCl$_3$, δ): 156.1, 152.0, 151.8, 140.8, 140.3, 132.4, 132.3, 129.0, 128.7, 127.4, 126.4, 121.8, 120.2, 79.2, 55.6, 40.6, 31.7, 30.2, 29.9, 28.6, 26.8, 24.1, 22.8, 14.3, 14.2. FT-IR (KBr): 2926, 2849, 1709, 1458, 1260, 1172, 1099, 1069, 1014, 813. Anal. Calcd: C, 87.46; H, 10.09; N, 0.74. Found: C, 86.29; H, 9.79; N, 0.85.

6e. This polymer was prepared following procedures similar to those used to prepare **6a**. A yellow solid (510 mg, 67%) was obtained. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.34−7.86 (m, 14H), 4.39 (m, 0.40H), 3.29−3.38 (m, 0.3H), 2.99−3.01 (m, 1.38H), 2.12 (m, 8H), 1.41 (m, 10H), 0.59−1.26 (m, 50H). ^{13}C NMR (75 MHz, CDCl$_3$, δ): 156.1, 152.0, 151.8, 140.8, 140.6, 140.2, 132.4, 132.3, 128.9, 128.7, 127.4, 126.4, 121.7, 120.2, 79.1, 61.8, 55.5, 40.6, 32.9, 32.1, 31.8,31.7, 30.2, 29.9, 29.6, 29.3, 29.2, 28.6, 26.8, 26.5, 24.0, 22.9, 22.8, 14.2. FT-IR (KBr): 2958, 2927, 2855, 1715, 1504, 1458, 1260, 1172, 1095, 1021, 812. Anal. Calcd: C, 86.69; H, 10.05; N, 0.99. Found: C, 85.06; H, 9.88; N, 1.19.

7a. To a solution of **PFH-NHBocF-39-1** (130 mg) in 15 mL of THF, 5 mL of 37% hydrochloric acid was added, and the reaction mixture was stirred 3 days at room temperature. Solvent was evaporated under vacuum, 50 mL of acetone was added to give a precipitate, and the precipitate was filtered to give **7a** as a yellow powder (105 mg, 82%). ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.59−7.86 (m, 11H), 2.12 (m, 4H), 0.77−1.25 (m, 44H). FT-IR (KBr): 3439, 2922, 2852, 1641, 1453, 1249, 810.

7b. This polymer was prepared following procedures similar to those used to prepare **7a**. A yellow powder (103 mg, 81%) was obtained. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.61−7.86 (m, 18H), 2.12 (m, 4H), 0.77−1.25 (m, 50H). FT-IR (KBr): 3432, 2923, 2853, 1638, 1455, 1250, 811.

7c. This polymer was prepared following procedures similar to those used to prepare polymer **7a**. A yellow powder (98 mg, 78%) was obtained. FT-IR (KBr): 3441, 2923, 2852, 1642, 1454, 1248, 810.

7d. This polymer was prepared following procedures similar to those used to prepare **7a**. A yellow powder (85 mg, 69%) was obtained. FT-IR (KBr): 3448, 2924, 2854, 1636, 1455, 1252, 811.

7e. This polymer was prepared following procedures similar to those used to prepare polymer **7a**. A yellow powder (82 mg, 68%) was obtained. FT-IR (KBr): 3450, 2923, 2853, 1639, 1455, 1252, 810.

P1 (PFH-NH$_2$F-39-1). To a solution of **PFH-NH$_3$ClF-39-1** (100 mg) in 30 mL of THF was added 20 mL of 50% KOH aqueous solution; the reaction mixture was stirred at room temperature for 1 h. The separated organic layer was washed with water and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent under reduced pressure, 50 mL of acetone was added to give a precipitate, and the precipitate was filtered to give **P1** as a yellow powder (75 mg, 77%). FT-IR (KBr): 3448, 2923, 2855, 1641, 1453, 1250, 811.

P2 (PFH-NH$_2$F-19-1). This polymer was prepared following procedures similar to those used to prepare **P1**. A yellow powder (72 mg, 74%) was obtained. FT-IR (KBr): 3450, 2924, 2854, 1641, 1455, 1250, 811.

P3 (PFH-NH$_2$F-9-1). This polymer was prepared following procedures similar to those used to prepare **P1**. A yellow powder (68 mg, 72%) was obtained. FT-IR (KBr): 3445, 2924, 2854, 1690, 1455, 1249, 813.

P4 (PFH-NH$_2$F-17-3). This polymer was prepared following procedures similar to those used to prepare **P1**. A yellow powder (67 mg, 73%) was obtained. IR (KBr): 3452, 2926, 2855, 1636, 1451, 812.

P5 (PFH-NH$_2$F-4-1). This polymer was prepared following procedures similar to those used to prepare **P1**. A yellow powder (58 mg, 65%) was obtained. FT-IR (KBr): 3444, 2926, 2856, 1635, 1444, 881, 812.

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