Synthesis and light emitting properties of sulfide-containing polyfluorenes and their nanocomposites with CdSe nanocrystals: A simple process to suppress keto-defect

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Abstract

A new series of sulfide-containing polyfluorene homopolymers and copolymers (PFS, PF1, PF3 and PF4) comprising 9,9-di[11-(decylsulfanyl)undecyl] fluorene, 9,9-dihexylfluorene, triphenylamine or benzothiadiazole moieties were synthesized by Ni(0)-mediated Yamamoto-coupling and palladium-catalyzed Suzuki polymerizations. Three other polyfluorenes (PF2, PF5 and PFC6) without sulfur atom in the alkyl side chains were also synthesized by a similar method for comparison purpose. These fluorene-based polymers were characterized using FT-IR spectroscopy, elemental analysis, DSC, TGA, photoluminescence (PL) and electroluminescence (EL) spectroscopies. The synthesized polymers PFS and PF1–PF3 emit blue light at around 440–468 nm, while copolymers PF4 and PF5 emit green light at around 540 nm. In annealing experiments, these polymer films show better stability against thermal oxidation than polymer PFC6. Sulfide-containing polymers show not only good electroluminescent color stability, but their EL spectra also remain unchanged at high driving voltage. A multi-layer electroluminescent device with the configuration of ITO/PEDOT/PF1/CsF/Al exhibited a stable sky-blue emission with color coordinates (0.21, 0.23) at 10 V, which showed a maximum brightness of 2991 cd/m² at 8 V (75 mA/cm²) and a maximum efficiency of 1.36 cd/A. Finally, by ligand exchange process, the sulfur element could form coordination bonding with quantum dots, and PLED devices using these new QDs-containing organic/inorganic hybrid materials as light-emitting layers exhibit superior or comparable EL performance compared to those without quantum dots.

Keywords: Polyfluorene; Keto-defect; Light-emitting diodes

1. Introduction

Since the first report of an electroluminescence device based on conjugated polymers by Burroughes et al. [1], this field has been extensively studied. Compared to inorganic or small organic molecules, organic conjugated polymers offer many advantages such as simple processing, high flexibility, potentially low power consumption, and uniformly covering large areas by spin coating in flat panel displays. By properly adjusting the chemical structure, one can fine-tune their optical and electrical properties, and get pure red, green, and blue light-emitting chromophores with narrow emitting spectra.

Polymers based on poly(phenylene vinylene) and poly(di-alkylfluorene) show great promise and have evolved as most well-studied conjugated systems for organic light-emitting diode (OLED) application. Polyfluorenes, with their high photoluminescence (PL) quantum efficiencies, good thermal and chemical stabilities, excellent solubility in common organic solvents, can be used as a good blue-light emitter. By structural modification at the 9-position of the fluorene ring, one can easily synthesize different polyfluorene derivatives which
possess good thermal stability and electroluminescent properties. However, polyfluorene tends to aggregate in the condensed phase and degrade the device performance with n-alkyl side chains resulting in a red-shifted fluorescence and lower PL intensity by exciton relaxation through lowering excimer trap process [2–8]. Spectral instability changes the emission light of polyfluorene from blue to greenish-blue region, and usually results in a broad band emission centered at around 530—540 nm with heat treatment, UV irradiation or applied electrical field. This is imputing to polyfluorene backbone degradation and named ‘keto-defect’ [3,7,9–11]. Continuing efforts have been made to reduce this phenomenon, which involve (1) synthesis of polymers that are thermally more stable [3a,d,12], (2) usage of bulky groups as end cappers to suppress excimer emission [3b,c,5], (3) insertion of the rigid bulky groups to C-9 position to prevent formation of excimers [4a,b,13,14], (4) copolymerization with sterically hindered groups, combining with spiro- or cross-linked hole-transporting materials to prevent aggregation [3c,5,15–18] and (5) bonding covalently with organic—inorganic hybrid materials (e.g. POSS) [19,20] to effectively improve electroluminescent characteristics.

Research on PLEDs has focused on the improvement of the emission efficiency of molecular semiconductors. Utilization of the nanocomposites to enhance the performance of PLEDs was proposed several years ago. Several studies have been carried out to enhance the current density, radiances, and power efficiency properties by mixing oxide nanoparticles (TiO2, SiO2) into electroluminescent polymer materials like MEH–PPV [21]. Moreover, photovoltaic efficiency of PPV derivatives could be improved by the incorporation of C60 nanoparticles [22]. Kim et al. reported the method of blending 5 nm gold nanoparticles in very low amounts into polyfluorene or PPV, resulting in an enhancement in quantum efficiency and oxidation stability [23]. Recently, Chou et al. reported that with the incorporation of surface-modified cadmium sulfide nanoparticles into dendron-substituted polyfluorene, the luminescence could be enhanced by as much as three times [24].

In earlier work, we have already reported the synthesis of sulfide-containing poly(1,4-phenylene vinylene) derivatives, and these polymers have the advantage of permitting the coordinate bonding of sulfur atoms with inorganic crystals (CdSe, ZnS) through ligand exchange process [25]. By incorporating CdSe/ZnS quantum dots onto sulfide-containing conjugated polymer S–PPV, the device performance was significantly improved as compared to the pristine polymers. Herein, we demonstrate the synthesis and characterization of series of fluorene-based copolymers with pendant sulfide groups attached on the C-9 positions of the fluorene unit. The thermal, electrochemical, optical, and other relevant physical properties of the synthesized polymers were also systematically studied. In addition, a series of PLED devices were also fabricated to study the electroluminescent (EL) properties of these polymers. Granting a low percentage of CdSe/ZnS nanocrystals with sulfide-containing polyfluorene as active layers in the light-emitting diodes improved the efficiency of double-layer PLED device.

2. Experimental section

2.1. Characterization methods

IR spectra were recorded on a Perkin–Elmer 16PC FT-IR spectrometer. The chemical structures were confirmed using 1H and 13C NMR spectra measured on a Varian VXR-300 spectrometer (300 MHz). Differential scanning calorimetry (DSC) thermograms were recorded on a Perkin–Elmer Pyris Diamond DSC unit using a heating rate of 20 °C/min and a cooling rate of 50 °C/min. TGA thermograms were obtained on a Perkin–Elmer Pyris 1 TGA instrument with a heating rate of 10 °C/min. UV–Vis spectra were measured with an HP 8453 diode array spectrophotometer. PL spectra were obtained on a Hitachi F-4500 luminescence spectrometer, and the PL external quantum efficiencies were measured using an integrating sphere. Cyclic voltammetry (CV) measurements of the polymers were done in acetonitrile (CH3CN) with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) as the supporting electrolyte at a scan rate of 50 mV/s. Platinum wires were used as both the counter and working electrodes, silver/silver ions (Ag in 0.1 M AgNO3 solution, from Bioanalytical Systems, Inc.) were used as the reference electrode, and ferrocene as an internal standard.

2.2. Fabrication and characterization of PLEDs

Double-layer PLED devices were fabricated as sandwich structures between cathode (Ca) and indium-tin oxide (ITO) anodes. ITO-coated glass substrates were cleaned sequentially in ultrasonic baths of detergent, 2-propanol/deionized water (1:1 volume) mixture, toluene, deionized water, and acetone. A 50 nm thick hole injection layer of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) was prepared by spin-coating on the ITO from a dispersion. Thin films of polymers from a 1.5 wt% toluene solution were spin-coated upon the PEDOT layer and dried at 70 °C under vacuum for 1 h. The film thickness obtained was ca. 45 nm, which was measured using an Alpha-Step 500 surface profilometer. The coating thickness of PEDOT and polymers together was about 1000 Å, and the active areas were 0.04 cm2, defined by the area overlapped by the anode and the cathode. The TPBI layer was grown by thermal sublimation under vacuum (3 × 10–6 Torr) and was used as an electron transporting layer, which would also block holes and confine excitons. The CsF layer was also grown by thermal sublimation under vacuum (3 × 10–6 Torr) and was used as an electron injection layer. Finally, 35 nm Ca and 100 nm Al electrodes were thermally evaporated through a shadow mask onto the polymer films using an AUTO 306 vacuum coater (BOC Edwards, Wilmington, MA); typical evaporations being carried out at base pressure lower than 2 × 10–6 Torr. The PLED characterization was carried out by a Keithley 2400 source-measure unit. The brightness was further measured using a Photo Research PR650 spectrophotometer.
2.3. Materials

Starting materials such as fluorene, n-butyllithium were purchased from TCI. The Suzuki-coupling catalyst, tetrakis(triphenylphosphine)palladium(0) and Yamamoto polymerization catalyst, bis(1,5-cyclooctadienyl)nickel(0), 2,2'-bipyridinyl, and 1,5-cyclooctadiene were purchased from Aldrich and handled under inert argon atmosphere. All other chemicals were used as received from commercial sources without further purification, except tetrahydrofuran (THF) and toluene which were distilled over sodium/benzophenone and calcium hydride, respectively. The synthesis of monomers M1–M6 is shown in Scheme 1. 2,7-Dibromofluorene (1), 2,7-dibromo-9,9-dihexylfluorene (M1) [26], 11-bromoundecyl decyl sulfide (2) [27] and 4,7-dibromo-1,2,3-benzothiadiazole (M6) [28] were prepared following the published procedures. (1): white crystal, yield 91%, mp = 161–163 °C. M1: white crystal, yield 89%, mp = 64–65 °C. (2): white solid, yield 83%, mp = 25–26 °C. M6: yellow needle crystals, yield 98%, mp = 187–188 °C.

2.3.1. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (M2)

M2 was prepared following the modified procedure from 2,7-dibromo-9,9-dihexylfluorene (M1). White solid, yield 81%, mp = 185–186 °C. 1H NMR (300 MHz, CDCl3, δ ppm): 7.78 and 7.71 (d, 4H, fluorene ring), 7.68 (s, 2H, fluorene ring), 1.98 (t, 4H, H-alkyl), 1.36 (s, 24H, CH3), 1.11–0.98 (m, 16H, CH2), 0.72 (t, 6H, CH3). 13C NMR (75 MHz, CDCl3, δ ppm): 150.44, 143.30, 133.62, 129.29, 119.34 (fluorene ring), 83.61 (C-alkyl), 55.15 (C 9, fluorene ring), 40.49, 31.48, 29.58, 24.31, 23.54, 22.53, 13.48 (C-alkyl). MS (EI-MS) m/z: 586.4. Elemental Anal. Calcd. for C37H60B2O4: C, 75.7; H, 9.62. Found: C, 75.62; H, 9.73.

2.3.2. 2,7-Dibromo-9,9-di[11-(decylsulfanyl)undecyl]-fluorene (M3)

To a solution of t-BuOK (5.2 g, 46.3 mmol) and 11-bromoundecyl decyl sulfide (2) [27] and 4,7-dibromo-1,2,3-benzothiadiazole (M6) [28] were prepared following the published procedures. (1): white crystal, yield 91%, mp = 161–163 °C. M1: white crystal, yield 89%, mp = 64–65 °C. (2): white solid, yield 83%, mp = 25–26 °C. M6: yellow needle crystals, yield 98%, mp = 187–188 °C.

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\[ {\text{NiCl} \cdot \text{ammonia}} \] was added to the mixture for 6 h. The solution was cooled to room temperature and then the solvent was removed by evaporation. The collected organic layer was mixed with 50 mL of ethyl acetate and extracted with 50 mL of water. The organic layer was dried over anhydrous magnesium sulfate. After the solvent was removed by rotary evaporator, the crude product was isolated by filtration, and further purified by column chromatography using silica gel by eluting with ethyl acetate/hexane 1:5 to yield 3.81 g (40%) white crystals, mp \( 57-58 °C \). \[^{1}H\ NMR (300 MHz, CDCl}_3, \delta ppm): 7.50-7.41 (m, 6H, fluorene ring), 2.49-2.42 (t, 8H, \( CH_2S \), 1.90-1.85 (t, 4H, H-alkyl), 1.56-1.17 (m, 68H, \( CH_2 \), 0.87 (s, 12H, \( CH_3 \)). \[^{13}C\ NMR (75 MHz, CDCl}_3, \delta ppm): 152.49, 139.02, 130.11, 126.14, 121.43, 121.08 (fluorene ring), 55.64 (C9, fluorene ring), 40.09, 32.15, 31.86, 29.79, 29.70, 29.53, 29.50, 29.42, 29.29, 29.23, 29.19, 29.12, 28.92, 28.90, 23.57, 22.65, 14.08 (C-alkyl). MS (El-MS) \( m/z \): 977.2. Elemental Anal. Calcd. for \( C_{55}H_{92}Br_2S_2 \): C, 67.6; H, 9.49. Found: C, 67.72; H, 9.53.

2.3.3. \( N,N\)-Di(4-bromophenyl)-N-(4-pentylphenyl)amine (M4)
A mixture of 1-bromo-4-iodobenzene (13.32 g, 47 mmol), 4-pentanil (3.5 g, 21.4 mmol), 1,10-phenanthroline (0.385 g, 2.14 mmol), CuCl (0.212 g, 2.14 mmol) and KOH (12 g, 214 mmol) in 120 mL toluene was refluxed at 120 °C for 12 h. The solution was cooled to room temperature and then the solvent was removed by evaporation. The collected organic layer was mixed with 50 mL of ethyl acetate and extracted with 50 mL of water. The organic layer was dried over anhydrous magnesium sulfate. After the solvent was removed by rotary evaporator, the crude product was isolated by filtration, and further purified by column chromatography using silica gel by eluting with ethyl acetate/hexane 1:5 to yield 7.3 g (72%) white crystals, mp \( 57-58 °C \). \[^{1}H\ NMR (300 MHz, CDCl}_3, \delta ppm): 8.68-7.32 (m, 12H, aromatic protons). 2.54 (t, 2H, \(-CH_2-(CH_2)_3-CH_3 \), 1.23-1.59 (m, 6H, \(-CH_2-(CH_2)_3-CH_3 \). 0.88 (t, 3H, \(-CH_3 \). \[^{13}C\ NMR (75 MHz, CDCl}_3, \delta ppm): 147.52, 144.40, 139.72, 132.59, 128.23, 124.21, 121.37, 114.28 (aromatic ring). 36.92, 31.66, 31.02, 22.43, 14.29, (C-alkyl). MS (El-MS) \( m/z \): 473.2. Elemental Anal. Calcd. for \( C_{23}H_{35}Br_2N \): C, 58.37; H, 4.9; N, 2.96. Found: C, 58.67; H, 5.06; N, 2.90.

2.3.4. 4,4'-Bis[(N-p-bromophenyl)-N-phenylamino]biphenyl (M5)
The procedures for the synthesis of M5 were similar to that of M4, using 1-bromo-4-iodobenzene (9.25 g, 32.69 mmol), \( N,N\)-diphenyl benzidine (5 g, 14.86 mmol), 1,10-phenanthroline (0.385 g, 2.14 mmol), CuCl (0.212 g, 2.14 mmol) and KOH (12 g, 214 mmol) in 120 mL toluene. Polymerization was carried out using Pd(PPh3)4 as a catalyst in a mixture of toluene and aqueous \( K_2CO_3 (2.0 M) \) in the presence of aliquat 336 as a phase transfer reagent. The solution was first put under the protection of argon and refluxed with vigorous stirring at 85 °C for 4 days. After polymerization was complete, each polymer was precipitated from a mixture of concentrated HCl, methanol, and acetone with equal volume. The isolated polymers were dissolved in acetone solution to remove oligomers and catalyst residues. The precipitate was collected by filtration, re-dissolved in acetone solution to remove oligomers and catalyst residues. The yields of these two homopolymers were 73% and 85%, respectively.

2.4. Polymerization
2.4.1. The synthetic procedures for homopolymers PFS and PFC6
Homopolymers (PFS and PFC6) were synthesized by nickel(0)-catalyzed polymerizations [29] (Scheme 2). A typical synthetic procedure of PFS is given as follows. A mixture of bis(1,5-cyclooctadiene)nickel(0) (560 mg, 2.05 mmol), 2,2'-bipyridinyl (320 mg, 2.05 mmol), and 1,5-cyclooctadiene (220 mg, 2.05 mmol) was added to a 50 mL flask containing 10 mL of DMF and 10 mL of toluene. The solution was preheated at 60 °C under nitrogen atmosphere for 30 min, and then 5 mL of anhydrous toluene was added to the mixture. M2 (500 mg, 1.02 mmol) was added to the flask and polymerization temperature was maintained at 80 °C for 72 h. \( N,N\)-Bis(4-methylphenyl)-N-(4-bromophenyl)amine was used as an end-capping reagent [30]. After polymerization was completed, each polymer was precipitated from a mixture of concentrated HCl, methanol, and acetone with equal volume. The isolated polymers were dissolved in toluene and further precipitated in methanol and dried under vacuum. Dialysis of the obtained polymers was done by immersing the polymer in acetone solution to remove oligomers. The yields of these two homopolymers were 73% and 85%, respectively.

2.4.2. The synthetic procedures for copolymers PFI–PFS
The copolymers of PFI–PFS were prepared via palladium-catalyzed Suzuki-coupling reaction [31] of the diboric ester monomer M2 with dibromo monomers M1, M3–M6 (Scheme 3). The monomer feed ratios used in the polymerization are also given in Scheme 3. A typical synthetic procedure of PFI is given as follows. A mixture of M2 (0.40 g, 0.68 mmol), M3 (0.33 g, 0.34 mmol), and M4 (0.16 g, 0.34 mmol) was added to a 50 mL flask containing 10 mL of toluene. Polymerization was carried out using Pd(PPh3)4 as the catalyst in a mixture of toluene and aqueous K2CO3 (2.0 M) in the presence of aliquat 336 as a phase transfer reagent. The solution was first put under the protection of argon and refluxed with vigorous stirring at 85 °C in oil bath for 4 days. \( N,N\)-Bis(4-methylphenyl)-N-(4-bromophenyl)amine was added for end-capping the boronic ester for 6 h. \( N,N\)-Di-(4-methylphenyl)-N-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]amine was then added into the mixture for end-capping the bromo active site for additional 6 h. After cooling, the reaction mixture was precipitated from methanol to get polymers. This was followed by immersing the solid material in acetone solution to remove oligomers and catalyst residues. The precipitate was collected by filtration, re-dissolved in acetone solution to remove oligomers and catalyst residues.
in THF, and then reprecipitated in methanol, and finally dried under vacuum oven. The yields of these five copolymers were in the range of 62–90%.

2.4.3. Homopolymer PFS

Yield of PFS: 73%. 1H NMR (300 MHz, CDCl3, δ ppm): 7.53–7.39 (m, aromatic protons), 2.50–2.41 (t, CH₂S), 1.90–0.88 (m, alkyl protons). Elemental Anal. Calcd. for C₅₅H₉₂S₂: C, 80.88; H, 11.27. Found: C, 79.12; H, 10.35.

2.4.4. Homopolymer PFC6

Yield of PFC6: 85%. 1H NMR (300 MHz, CDCl₃, δ ppm): 7.64–7.38 (m, aromatic protons), 1.88–0.76 (m, alkyl protons). Elemental Anal. Calcd. for C₂₅H₃₂: C, 90.36; H, 9.64. Found: C, 89.82; H, 10.42.

2.4.5. Copolymer PF1

Yield of PF1: 82%. 1H NMR (300 MHz, CDCl₃, δ ppm): 7.62–6.85 (m, aromatic protons), 2.84–2.30 (m, –CH₂–), 1.48–0.83 (m, alkyl protons). Elemental Anal. Calcd. for C₁₂₈H₁₇₀NS₂: C, 85.6; H, 10.05; N, 0.78. Found: C, 83.87; H, 9.70; N, 0.80.

2.4.6. Copolymer PF2

Yield of PF2: 78%. 1H NMR (300 MHz, CDCl₃, δ ppm): 7.68–6.82 (m, aromatic protons), 2.82–2.25 (m, –CH₂–), 1.49–0.81 (m, alkyl protons). Elemental Anal. Calcd. for C₉₈H₁₁₀N: C, 89.78; H, 9.15; N, 1.07. Found: C, 88.1; H, 8.21; N, 1.21.

2.4.7. Copolymer PF3

Yield of PF3: 67%. 1H NMR (300 MHz, CDCl₃, δ ppm): 8.10–6.85 (m, aromatic protons), 2.85–2.28 (m, –CH₂–), 1.46–0.83 (m, alkyl protons). Elemental Anal. Calcd. for C₁₅₀₃H₂₁₅NS₅: C, 84.68; H, 10.15; N, 0.656. Found: C, 85.23; H, 9.05; N, 0.82.

2.4.8. Copolymer PF4

Yield of PF4: 90%. 1H NMR (300 MHz, CDCl₃, δ ppm): 8.12–6.96 (m, aromatic protons), 2.86–2.32 (m, –CH₂–), 1.42–0.84 (m, alkyl protons). Elemental Anal. Calcd. for C₂₉₄H₄₁₆N₄S₅: C, 84.77; H, 10.05; N, 1.34. Found: C, 82.74; H, 9.55; N, 1.26.
2.4.9. Copolymer PF5
Yield of PF5: 88%. 1H NMR (300 MHz, CDCl3, δ ppm): 8.05—8.63 (m, aromatic protons), 2.84—2.28 (m, −CH2−), 1.46—0.83 (m, alkyl protons). Elemental Anal. Calcd. for C439H536N12S3: C, 89.05; H, 9.06; N, 1.89. Found: C, 88.0; H, 8.54; N, 1.68.

2.5. Synthesis of PF1 and CdSe/ZnS nanocomposites
CdSe/ZnS nanocrystals were prepared following the published procedures [25], and the size of the nanocrystals was about 7.0 nm as determined by TEM. Generally, the procedure for ligand exchange reaction was described as follows. A solution of the sulfide-containing ligand PF1 (20 mg in 1 mL of toluene) was added to the colloidal solution of CdSe nanocrystals (10 mg in 1 mL of toluene). The mixture was then stirred at constant temperature. The reaction status was confirmed by FT-IR. After ligand exchange process [25,37], the solution was poured into methanol to give the final polymer. The yields of obtained nanocomposites were in the range of 75—90%. TEM images of the nanocomposites also showed that CdSe nanocrystals were mono-dispersed with a diameter of about 7 nm. It indicates that QDs exactly exist inside the polymers.

3. Results and discussion
3.1. Synthesis and characterization
The synthesis of monomers M1—M5 is shown in Scheme 1. Monomer M3 was synthesized by reaction between 2,7-di-bromofluorene and 11-bromoundecyl decyl sulfide in the presence of excess base. The sulfur atom in M3 can serve as the ligand for CdSe/ZnS quantum dots which can be attached via simple ligand exchange procedure. The properties of these QD-related nanocomposites will be discussed later. Homopolymers PF5 and PFC6 were synthesized via Yamamoto-coupling method; this is to compare the thermal and electroluminescent properties with different alkyl chains. However, the EL performance of fluorene-based homopolymer is usually not high because of the charge imbalance, and the homopolymer only emits light in the blue region. For these reasons, we synthesized some other copolymers PF1—PF5 via Suzuki-coupling, with triphenylamine (TPA) containing monomers and BTDZ to balance the charge ability and tune emissive colors of these polyfluorenes. TPA compounds are well-known hole-transporting materials. Two TPA-containing monomers (M4 and M5) were synthesized by the Wittig—Horner reaction between N-(4-bromophenyl)-N-(4-formylphenyl) aniline and 4,4′-bis(diethylphosphinatymethyl)triphenylamine. These two TPA derivatives could fine-tune the EL emission wavelength of polyfluorenes in the range 450—470 nm and substantially improve the EL performance. Monomer M6 (BTDZ) is used as comonomer in the polyfluorene backbone. Yellow-green light is emitted via energy transfer from fluorene to BTDZ. The chemical structures of the resulting polymers utilizing Yamamoto and Suzuki-coupling methods were further confirmed by 1H NMR and elemental analyses. The actual ratio calculated from elemental analyses of C, H and N was in good agreement with the feeding ratios of the monomers, as stated above. Slight deviations might be caused by two end-capping reagents (N,N-bis(4-methylphenyl)-N-(4-bromophenyl)amine and N,N-di(4-methylphenyl)-N-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]amine). The obtained copolymers are completely soluble in common organic solvents, such as toluene, THF, and chloroform. The Mn and Mw of these polymers determined by GPC were in the range from 1.03 × 104 to 3.09 × 104 g/mol and from 2.02 × 105 to 3.43 × 105 g/mol, respectively, with the polydispersity index less than 3.01 (see Table 1).

3.2. Thermal properties
Good thermal stability is very important for the application of conjugated polymers in flat panel displays. The thermal stability of these polymers was evaluated by DSC and TGA under nitrogen atmosphere. Table 1 lists the thermal decomposition temperatures (Td, 5% weight loss) and the glass transition temperatures (Tg) of these six polymers. Polymers PF1—PF5 show glass transition temperature at around 80 °C, which is much higher than that of poly(9,9-dioctyfluorene) (Tg = 51 °C) [32]. As revealed by TGA, these polymers also exhibit good thermal stability with 5% weight loss occurring at 350 °C.

3.3. Photoluminescence properties
The fluorescent wavelength of a polymer film fundamentally depends on the band gap between the HOMO and LUMO, which depends on delocalization of π-electrons along the polymer backbone. The characteristic peak in the emission spectrum arises as an excited electron relaxes into vibronic energy level of the HOMO. The optical spectra of conjugated polymers are typically broad, which is due to the coupling of several different vibronic modes. Fig. 1 reveals the normalized absorption and photoluminescence spectra of polymers in dilute toluene solutions. The absorptions located in the range

<table>
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<th>Table 1</th>
<th>Average molecular weights and thermal properties of polymers PF5, PF1—PF5 and PFC6</th>
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Notes:
- Determined by GPC by eluting with THF, by comparison with polystyrene standards.
- Temperature at which a 5% weight loss occurred was determined at a heating rate of 10 °C/min under a nitrogen atmosphere.
- The value of Tg was determined at a heating rate of 20 °C/min under a nitrogen atmosphere.
from 372 to 386 nm were due to \(\pi-\pi^*\) transition of conjugated polyfluorene backbone. The blue emission of polyfluorene around 430 nm could be effectively quenched by introducing BTDZ group into the main chain of polyfluorene copolymer and dominated by a green light peaked at 540 nm for PF4 (see Fig. 1(B)). It also reveals the effective energy transfer from photo-generated excitons on the polyfluorene segment to BTDZ groups. The wavelengths of UV-vis absorption and PL emission maxima of these polymers in dilute toluene solution (10\(^{-5}\) M) and in solid state are summarized in Table 2. For comparison purpose, we synthesized PF2 and PF5 which have very similar chemical structures with PF1 and PF4, except that both PF2 and PF5 contain alkyl side groups without sulfur atoms. It is no surprise that both polymers show no difference in their UV absorption and PL emission spectra because of the similar polymer backbone. In comparison with dilute solutions, the emission spectra of polymers in film state are slightly red-shifted and can be attributed due to the aggregation of polymer chains. Table 2 also outlines PL quantum efficiencies of polymers in both solution and film states as measured by the integrating sphere. These polymers exhibit very high PL efficiencies from 56% to 82% in toluene solution.

### 3.4. Annealing experiment

According to the previous literature [33], when the temperature inside PLED devices exceeds 86 \(^\circ\)C, the optical properties, especially luminescence and color stability of light-emitting material are strongly affected. The origin of the green emission in polyfluorene-based conjugated polymers has been mostly attributed to aggregation and/or excimer formation or keto defects caused due to formation of fluorenone units in the PF backbone [3,7,9–11]. The utility of polyfluorenes is limited because of their tendency to undergo interchain aggregation. Furthermore, when the solid films of the polymers are maintained under the higher temperature above \(T_g\), the keto-defect would appear and emit green light around 540 nm. In order to investigate the thermal stability and the keto defects of the prepared polymers, thin films were annealed in the oven at 200 \(^\circ\)C for 20 h in air.

Fig. 2(A) and (B), shows the normalized photoluminescence (PL) spectra of homopolymers PFC6 and PFS films at room temperature 25 \(^\circ\)C and thermally annealed at 200 \(^\circ\)C for

<table>
<thead>
<tr>
<th>Polymer</th>
<th>UV absorption ((\lambda_{\text{max}}) (nm))</th>
<th>PL ((\lambda_{\text{max}}) (nm))</th>
<th>PL eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Toluene</td>
<td>Film</td>
<td>Toluene</td>
</tr>
<tr>
<td>PFS</td>
<td>381</td>
<td>387</td>
<td>422</td>
</tr>
<tr>
<td>PF1</td>
<td>383</td>
<td>383</td>
<td>431</td>
</tr>
<tr>
<td>PF2</td>
<td>384</td>
<td>386</td>
<td>430</td>
</tr>
<tr>
<td>PF3</td>
<td>375</td>
<td>376</td>
<td>424</td>
</tr>
<tr>
<td>PF4</td>
<td>373</td>
<td>377</td>
<td>425, 532</td>
</tr>
<tr>
<td>PF5</td>
<td>372</td>
<td>377</td>
<td>418, 527</td>
</tr>
</tbody>
</table>
20 h. In Fig. 2(A), the PFC6 film annealed at 200 °C for 1 h shows a strong green emission at a longer wavelength of about 537 nm, which is attributed to the excimer emission in comparison with the fresh films while the absorption \( \lambda_{\text{max}} \) remained at 425 nm. Compared to PFC6, the PL spectrum of PFS shows a small shoulder under similar heating conditions. The unchanged emission \( \lambda_{\text{max}} \) before and after heating suggests that the polymer did not change its conjugated structure during the thermal treatment. The 537 nm peak showed in Fig. 2(A) is due to the combination effect of keto-defect and polymer chain aggregation. The defect phenomena are generally appeared in alkyl-substituted polyfluorene. This unchanged PL curve of polymer PFS strongly hints that the polymer did not change its conjugated structure under thermal annealing. Fig. 3 shows the FT-IR spectra of PFC6 and PFS films after annealed at 200 °C for 20 h. No obvious fluorenone (C=O) characteristic IR peak at around 1720 cm\(^{-1}\) peak was found for PFS; however, for polymer PFC6, the keto peak at 1721 cm\(^{-1}\) appears. This result suggests that the existence of sulfur moiety could effectively suppress the keto formation and aggregation of polymer chains.

### 3.5. Electrochemical properties

The electrochemical behaviors of these polymers were investigated by cyclic voltammetry (CV). The corresponding highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) energy levels were estimated from the onset of the redox potentials. HOMO and LUMO levels of the chromophores were calculated according to empirical formulae \( E_{\text{HOMO}} = -(E_{\text{ox}} + 4.4) \) (eV) and \( E_{\text{LUMO}} = -(E_{\text{red}} + 4.4) \) (eV) [34]. From the difference of the onset potentials and the optical band gaps \( (E_g) \) calculated from the onsets of UV absorption spectra, the energy levels, the oxidation and reduction potentials were determined and are summarized in Table 3. The reversible oxidation curve of PFS with onset around 1.29 V could be assigned to the p-doping oxidation potential of polyfluorene main chains. Meanwhile, the electrochemical oxidation of polymers PF1–PF3 all exhibit similar two peaks at 0.81 and 1.08 V vs Ag/Ag\(^+\), and these characteristic peaks are originated from triphenylamine and fluorene units, respectively [35]. However, the BTDZ
(M6) moiety in PF4 and PF5 is more electron-deficient and easier to be reduced as compared with another system (PF1–PF3) having M3–M5 components. Since BTDZ has a smaller gap than polyfluorene, the excitation energy on the fluorene segments can transfer to the BTDZ unit with highly efficient green light.

### 3.6. Electroluminescence properties

To evaluate the electroluminescent properties of these sulfide-containing polyfluorenes, different types of light-emitting devices were fabricated and the device performances were examined. The energy diagram of these polymers and a general device architecture ITO/PEDOT:PSS/polymer (40 nm)/Ca (35 nm)/Al (100 nm) are shown in the Fig. 4(A) and (B), respectively. In the double-layer device A, poly(3,4-ethylene-dioxythiophene) (PEDOT) was used as the hole-injecting layer. The device performances of PF1–PF5 are shown in Table 4. After introducing the sulfide-containing long alky side chain into the polyfluorene, no noticeable difference in the maximum luminance and yield was observed (PF1/PF2, PF4/PF5). The relevant results showed a maximum brightness of 990 cd/m² at (10 V) and a maximum yield of 0.15 cd/A (330 mA/cm²) for PF1, while a maximum brightness of 700 cd/m² (at 11 V) and a maximum yield of 0.11 cd/A (636 mA/cm²) for PF3, whereas PF4 showed a maximum brightness of 1743 cd/m² (at 11 V) and a maximum yield of 0.60 cd/A (220 mA/cm²). The EL spectra of PF1 and PF4 were also very similar to those of PF2 and PF5, respectively. It also suggests that the incorporation of sulfur atom into the polymers does not influence the conjugation length of these polymers.

In order to improve the EL efficiencies of these sulfide-containing polyfluorene devices, we fabricated device B with the detailed structure ITO/PEDOT:PSS/polymer (40 nm)/CsF (2 nm)/Al (100 nm). A thin layer of CsF introduced between the light-emitting polymer and Al electrode enhances electron injection and leads to a higher electroluminescence [36]. With the CsF as the electron-donator, efficiency and luminance could be effectively enhanced, by improving the electron-hole recombination of the materials. Table 4 summarizes the electroluminescent performance of PF5 and sulfide-containing polyfluorene (PF1, PF3 and PF4) in device B. The maximum luminance of PF1 was increased from 990 to 2991 cd/m², and the maximum efficiency was also improved from 0.15 (330 mA/cm²) to 1.36 cd/A (75 mA/cm²). In the PF4-based systems, the maximum brightness also increased from 1743 cd/m².

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optical band gap (eV)</th>
<th>E&lt;sub&gt;ox&lt;/sub&gt; (V)</th>
<th>E&lt;sub&gt;red&lt;/sub&gt; (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF5</td>
<td>2.48 (500)</td>
<td>1.23</td>
<td>-1.25</td>
<td>-5.63</td>
<td>-3.15</td>
</tr>
<tr>
<td>PF4</td>
<td>2.92 (511)</td>
<td>1.26</td>
<td>-1.16</td>
<td>-5.66</td>
<td>-3.24</td>
</tr>
<tr>
<td>PF3</td>
<td>2.95 (420)</td>
<td>1.08</td>
<td>-1.87</td>
<td>-5.48</td>
<td>-2.53</td>
</tr>
<tr>
<td>PF2</td>
<td>2.93 (423)</td>
<td>1.08</td>
<td>-1.85</td>
<td>-5.48</td>
<td>-2.54</td>
</tr>
<tr>
<td>PF1</td>
<td>2.91 (426)</td>
<td>1.09</td>
<td>-1.82</td>
<td>-5.49</td>
<td>-2.58</td>
</tr>
</tbody>
</table>

* a The optical band gap estimated from the onset wavelength (value in parentheses) of UV–vis spectra of the polymer film.

* b The E<sub>ox</sub> and the E<sub>red</sub> are the onset potentials of oxidation and reduction, respectively.

* c Calculated from the empirical formula, E<sub>(HOMO)</sub> = -(E<sub>ox</sub> + 4.40) (eV), E<sub>(LUMO)</sub> = -(E<sub>red</sub> + 4.40) (eV).

### Table 4

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Device structure</th>
<th>L&lt;sub&gt;max&lt;/sub&gt; (cd/m²) at voltage (V)</th>
<th>Yield&lt;sub&gt;max&lt;/sub&gt; (cd/A)</th>
<th>EL λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>CIE coordinate 1931 (X, Y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF5</td>
<td>A</td>
<td>450 at 10 V</td>
<td>0.19</td>
<td>444</td>
<td>0.18, 0.20</td>
</tr>
<tr>
<td>PF5</td>
<td>B</td>
<td>804 at 10 V</td>
<td>0.27</td>
<td>448</td>
<td>0.20, 0.20</td>
</tr>
<tr>
<td>PF5</td>
<td>C</td>
<td>521 at 11 V</td>
<td>0.72</td>
<td>444</td>
<td>0.18, 0.20</td>
</tr>
<tr>
<td>PF4</td>
<td>A</td>
<td>990 at 10 V</td>
<td>0.15</td>
<td>464</td>
<td>0.21, 0.25</td>
</tr>
<tr>
<td>PF4</td>
<td>B</td>
<td>2991 at 8 V</td>
<td>1.36</td>
<td>468</td>
<td>0.21, 0.23</td>
</tr>
<tr>
<td>PF4</td>
<td>C</td>
<td>1832 at 10 V</td>
<td>1.49</td>
<td>464</td>
<td>0.21, 0.23</td>
</tr>
<tr>
<td>PF3</td>
<td>A</td>
<td>1002 at 10 V</td>
<td>0.23</td>
<td>472</td>
<td>0.24, 0.27</td>
</tr>
<tr>
<td>PF3</td>
<td>B</td>
<td>700 at 11 V</td>
<td>0.12</td>
<td>464</td>
<td>0.20, 0.26</td>
</tr>
<tr>
<td>PF3</td>
<td>C</td>
<td>800 at 10 V</td>
<td>0.34</td>
<td>464</td>
<td>0.22, 0.26</td>
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<tr>
<td>PF3</td>
<td>C</td>
<td>686 at 10 V</td>
<td>1.65</td>
<td>464</td>
<td>0.20, 0.26</td>
</tr>
<tr>
<td>PF3</td>
<td>A</td>
<td>1743 at 11 V</td>
<td>0.60</td>
<td>540</td>
<td>0.41, 0.57</td>
</tr>
<tr>
<td>PF3</td>
<td>B</td>
<td>2640 at 10 V</td>
<td>1.23</td>
<td>540</td>
<td>0.39, 0.54</td>
</tr>
<tr>
<td>PF4</td>
<td>A</td>
<td>2868 at 10 V</td>
<td>2.47</td>
<td>540</td>
<td>0.40, 0.54</td>
</tr>
<tr>
<td>PF4</td>
<td>A</td>
<td>1962 at 10 V</td>
<td>0.85</td>
<td>544</td>
<td>0.43, 0.55</td>
</tr>
</tbody>
</table>

Device A: ITO/PEDOT:PSS/polymer (40 nm)/Ca (35 nm)/Al (100 nm), device B: ITO/PEDOT:PSS/polymer (40 nm)/CsF (2 nm)/Al (100 nm), device C: ITO/PEDOT:PSS/polymer (40 nm)/TPBI (2 nm)/CsF (2 nm)/Al (100 nm).
to 2868 cd/m² and the maximum efficiency could be increased from 0.60 (220 mA/cm²) to 1.23 cd/A (57 mA/cm²).

In device C, a thin TPBI layer that acts as an electron transport and hole-blocking layer, was deposited between emitting layer and CsF by a thermal-evaporation method. The detailed device structure is ITO/PEDOT:PSS/polymer (40 nm)/TPBI (2 nm)/CsF (2 nm)/Al (100 nm). Fig. 5, in parts A, B and C, shows the current—voltage, luminescence—voltage and current—efficiency characteristics, respectively, of PF1 based on the different devices. Obviously, the one with the electron transporting TPBI layer shows the highest efficiency of 1.49 cd/A (20 mA/cm²). Similar results were also seen in the PF3 and PF4-based devices, for which the maximum efficiency was improved from 0.12 (636 mA/cm²) to 1.65 cd/A (21 mA/cm²) and from 0.60 (220 mA/cm²) to 2.47 cd/A (11 mA/cm²), respectively (Table 4). Fig. 6 shows the EL spectra of PF1 which emitted sky-blue light under different voltages in device A. The EL spectrum is nearly identical with respect to position and curve shape, indicating that both PL and EL originate from the same radiative decay process of the single exciton. However, under device operation, the undesirable low energy emission band (between 500 and 600 nm) does not appear in the PF1 device. Similar phenomenon was also observed in the case of PF3. These sulfide-containing blue-light polyfluorene polymers exhibit a voltage-independent and stable EL spectrum. This finding was also in consistence with the annealing test mentioned above—that sulfur atom suppresses the keto formation and polymer chain aggregation.

3.7. Formation and characterization of the nanocomposites

The sulfur atom in monomer M3 can serve as the ligand for CdSe/ZnS quantum dots (QDs) in the final nanocomposites obtained via ligand exchange procedure. These nanocomposites are also soluble in common organic solvents, such as toluene, THF, and chloroform. The FT-IR spectroscopy technique was applied to verify the chemical structure of the organic/inorganic hybrid material. Fig. 7(A) shows the FT-IR spectra of PF1, PF1 grafted with CdSe/ZnS nanocomposite and CdSe/ZnS quantum dots. The FT-IR spectrum of CdSe/ZnS quantum dots around 3000 cm⁻¹ is attributed to the C—H stretching of the outer shell alkyl surfactant, trioctylphosphine oxide (TOPO). It is obvious that two new bands were formed around 1000—1100 cm⁻¹ after ligand exchange process, which are attributed to the force formation between sulfur and CdSe/ZnS. Similar observations were also found for other nanocomposites. This finding is consistent with the literature reports [24,25]. The TGA measurements were made up to 750 °C, and the residue was considered to be char (from polymers) and CdSe/ZnS. By subtracting the char content, the CdSe/ZnS content in the polymer was determined to be 10.1 and 6.6 wt% for PF1—CdSe and PF4—CdSe. By grafting CdSe with polyfluorenes, a hard block of phase-separated graft copolymer would form that effectively suppresses the chain mobility and packing ability, and thus slightly improves the thermal stability. The decomposition temperatures of polyfluorene derivatives and their nanocomposites with QDs are in the range from 344 to 373 °C, as shown in Fig. 7(B). All the QDs-containing polymers exhibit better thermal stability over the original, pristine polymers. The higher $T_d$ values obviously suggest that the incorporation of inorganic QDs into polyfluorenes could effectively enhance the thermal stability. Fig. 8 shows the normalized photoluminescence (PL)
spectra of the PF1–CdSe nanocomposite films before and after thermally annealed at 200 °C for 20 h. First of all, the emission curve of PF1–CdSe nanocomposite is similar to pristine polymer PF1 without CdSe moiety, with a longer wavelength at 440 nm. This phenomenon also suggests that inserting CdSe component does not affect the optical properties of polymer backbone. It is obvious that the PL spectrum of PF1–CdSe nanocomposite shows a small shoulder under heating conditions, this is similar to the case of homopolymer PF4. The unaltered emission λ_{max} in the annealing test deeply indicates that sulfide-containing polyfluorene effectively restrains the ketone formation and aggregation of polymer chains under thermal annealing.

To identify the EL properties of the nanocomposite, both the pristine polymers and QDs-containing polymers were used as the emitting layers in a double-layer light-emitting device of ITO/PEDOT:PSS/polymer/Ca/Al configuration. Fig. 9 shows the current–voltage, luminescence and yield–voltage characteristics of the devices based on PF1–CdSe and pristine PF1. It is seen that the current densities of PF1–CdSe devices are much lower than that of pristine PF1. The luminance was increased from 990 to 1536 cd/m², and the efficiency was also be improved from 0.15 (330 mA/cm²) to 0.78 cd/A (65 mA/cm²). The similar results were also seen in the PF4-based devices, for which the maximum brightness was also increased from 1743 to 2847 cd/m² and the maximum efficiency was increased from 0.60 (220 mA/cm²) to 1.74 cd/A (61 mA/cm²). Polyfluorene is a well-known hole-dominating material, and the mobility of holes and electrons is not very much balanced. To consider direct charge injection, holes were blocked at CdSe owing to the relatively low-lying HOMO energy level. This can also be verified from the decreased current density under the same driving voltage. The blocked holes were accumulated and recombined with electrons to form excitons in the emitting layer. This suggests that incorporation of CdSe restrains the charge flow substantially throughout the device and increases the probability of excitons’ formation. Balanced hole and electron transports are thus achieved; the performance and efficiency of the device are also improved.

3.8. Hole-only and electron-only devices

In general devices, holes are injected from the PEDOT:PSS contact into the polyfluorene emitting layer and transported
toward the cathode. Hole-only and electron-only devices were prepared to characterize the current transport properties of the nanocomposites [38,39]. In Fig. 10, the $J$–$V$ characteristics of several ITO/PEDOT/polymer/Au “hole-only” and ITO/Al/polymer/Ca/Al “electron-only” devices were presented; the current was reduced substantially in both cases. It also indicates that QDs decrease the charge mobility and result in higher efficiency for these nanocomposite devices. The hole-blocking ability of QDs is stronger than the electron trapping ability. For these nano-sized QDs-containing devices, some of the injected holes were blocked by QDs in the light-emitting layer, resulting in better recombination of carriers in the polymer layer than that without QDs.

4. Conclusions

In this paper, we have established synthetic approaches to four sulfide-containing polyfluorene derivatives (PFS, PF1–PF3). These polymers show higher $T_g$ and $T_d$ values than their corresponding alkyl-substituted polyfluorenes. FT-IR and PL spectral studies of thermal annealing tests demonstrate that the incorporation of the sulfur atom into the polyfluorene could effectively suppress the ‘keto-defect’ which is commonly observed in polyfluorenes. This means that sulfur-containing polymers are less susceptible to oxidation. The CdSe/ZnS was grafted to the sulfur atoms by the ligand exchange reaction. FT-IR spectra display two new peaks around 1000–1100 cm$^{-1}$, indicating new force formation between sulfur from polyfluorene and CdSe. As CdSe/ZnS was incorporated onto polymers via chemical bonding, the device performance was significantly increased as compared to their parent polymers alone. The electrical characteristics of the diodes reveal that QDs could effectively increase the luminance and reduce the current density of devices. Hole-only and electron-only devices fabricated from these nanocomposites demonstrate that CdSe/ZnS QDs exactly block the hole and trap the electron in the light-emitting layer, respectively. Consequently, the electroluminescent efficiency of the light-emitting materials was effectively improved. The present chemical bonding process of nano-sized materials and conjugated polymers may offer a general strategy for fabricating high-performance light-emitting materials.

Fig. 9. (A) Voltage–current density, (B) luminescence–voltage efficiency characteristics of the PF1 and nanocomposite LED devices.

Fig. 10. $J$–$V$ characteristic of (A) ITO/PEDOT/polymer or nanocomposite/Au hole-only device, (B) ITO/Al/polymer or nanocomposite/Ca/Al electron-only device with a thickness around $L=0.040–0.045$ μm.
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