

Cyclopentadithiophene–fluorene copolymer for organic solar cells and light emitting diodes

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Synthesis of a conjugated copolymer PF8CPDT10 comprising cyclopentadithiophene and fluorene units, investigation of its optical and electrochemical properties and evaluation of this material in organic bulk heterojunction solar cells and light emitting diodes are reported.

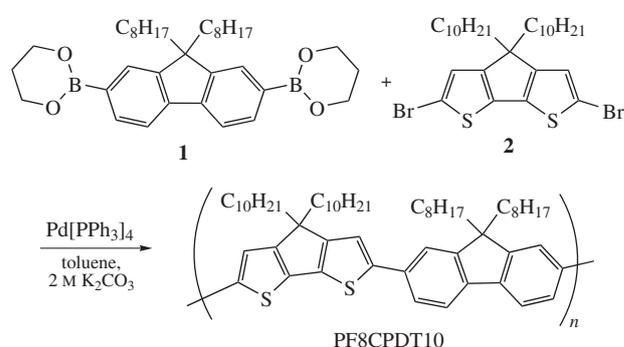
Cyclopentadithiophene and cyclopentadithiophene-based materials have been intensively studied in the context of the synthesis of electrically conductive polymers.¹ Polycyclopentadithiophenes (PCPDTs) show low optical band gaps, and they can be prepared by facile electrochemical² and oxidative chemical³ polymerization. Cyclopentadithiophene can be converted to bisboronic acids or esters,⁴ which can be utilized as functional monomers in Suzuki polycondensation reactions.⁵ Many cyclopentadithiophene-based copolymers have been synthesized recently using this approach.^{6–9}

Multifunctional materials based on PCPDTs demonstrated valuable properties.¹⁰ Copolymers comprising cyclopentadithiophene (CPDT) units are used as semiconductor materials in solar cells,⁷ organic field-effect transistors¹¹ and light emitting diodes.¹²

Here we report the synthesis of a novel copolymer PF8CPDT10 comprising dialkylfluorene and dialkylcyclopentadithiophene units and the optical and electronic properties of this material.

Commercial 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester **1** was used as a precursor for the synthesis of PF8CPDT10 (Scheme 1).[†] The second component, didecyl-substituted CPDT dibromide **2**, was synthesized using previously described methods.^{13–15}

The concentrations of impurities in the monomers should be much lower than 1% to run efficiently the Suzuki polycondensa-



Scheme 1

tion.[‡] The amount of the tetrakis(triphenylphosphine)palladium(0) catalyst has to be as small as possible (1–2 mg) to minimize the contamination of the target polymer.[§] It is well known that palladium nanoparticles are difficult to remove from the polymer. The presence of 10–100 ppm of palladium impurities in the polymer damages its semiconducting properties.¹⁶

To purify the polymer, the crude Suzuki polycondensation product as a toluene solution was washed with warm distilled water and then precipitated in methanol. The precipitate was collected by centrifugation and then dissolved in warm toluene.

[†] 4*H*-Cyclopenta[2,1-*b*:3,4-*b'*]dithiophene has been synthesized according to previously reported methods.^{13–15}

4,4-Didecyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene. A portion of 2 g of 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (11.2 mmol) was dissolved in 50 ml of DMSO in a 100 ml double-neck round-bottom flask under magnetic stirring. The resulting solution was degassed, and decyl bromide (4.3 g, 22.4 mmol) followed with KI (50 mg) were added. The reaction mixture was cooled to 0 °C and 2 g of grounded KOH were added in small portions. The reaction mixture was stirred for 3 days. Then 100 ml of water were added and the product was extracted with diethyl ether. The organic phase was washed three times with the NaCl solution and three times with water and then dried over anhydrous MgSO₄. The dried solution was concentrated *in vacuo* to produce yellow-orange oil which was further purified by column chromatography in light petroleum. The purified product was obtained as a colourless oil (3.84 g) in 85% yield. ¹H NMR (CDCl₃, 600 MHz) δ: 7.14 (d, 2H), 6.93 (d, 2H), 1.84 (m, 4H), 1.14 (m, 20H), 0.94 (m, 4H), 0.84 (t, 6H).

2,6-Dibromo-4,4-didecyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene **2**. Fresh NBS (1.8 g, 10 mmol) was added portionwise to 2 g of 4,4-didecyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (4.97 mmol) dissolved in 90 ml of freshly distilled DMF. The solution was magnetically stirred for 3 days in dark. The addition of 100 ml of water, extraction with 100 ml of diethyl

ether, washing the extract with 1% aqueous HCl and three times with water and finally drying over MgSO₄ was used to isolate the crude product. The obtained brown oil was purified by column chromatography using light petroleum as eluent. The title product was obtained as a transparent colourless oil (yield 2.31 g, 83%). ¹H NMR (CDCl₃, 600 MHz) δ: 6.93 (s, 2H), 1.74 (m, 4H), 1.14 (m, 24H), 0.90 (m, 4H), 0.84 (t, 6H).

[‡] Suzuki polycondensation reaction. The 9,9-dioctyl-2,7-diboronic acid bis(1,3-propanediol) ester **1** (300 μmol), 2,6-dibromo-4,4-didecyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene **2** (300 μmol), freshly distilled toluene (15 ml), one drop of Aliquat 336 and 1 ml of 1 M aqueous solution of Na₂CO₃ were introduced into a 50 ml two-neck round-bottom flask equipped with a condenser and argon inlet. The mixture was deaerated and 1 mg of Pd(PPh₃)₄ was added. The mixture was heated at reflux for 40 h, then cooled down to the room temperature and precipitated in 150 ml of MeOH. The precipitated polymer was separated by filtration, redissolved in warm toluene and precipitated again with methanol. The crude polymer was further purified by continuous washing with methanol and then light petroleum in a Soxhlet apparatus. The purified polymer was dried in air and stored inside argon glove box. The yield of the polymer was 120 mg (47%).

[§] High activity of the palladium catalyst can be preserved by storing it in an inert atmosphere below 0 °C avoiding its exposure to light.

Table 1 Optoelectronic properties of PF8CPDT10.

Parameter	Value	Parameter	Value
M_w /kDa mol ⁻¹	14.0	$E_{1/2(ox)}$ /V vs. Ag/Ag ⁺	0.84
PDI	1.9	$E_{onset(ox)}$ /V vs. Ag/Ag ⁺	0.72
Absorption, λ_{max} /nm	404	$E_{onset(red)}$ /V vs. Ag/Ag ⁺	-1.18
Absorption, λ_{onset} /nm	570	$E_g(EC)$ /eV	1.90
PL, λ_{max} /nm	561	E_{HOMO} /eV	-5.42
$E_g(opt.)$ /eV	2.17		

Addition of an excessive amount of methanol precipitated the polymer again. The precipitation–dissolving cycle was repeated three times. Finally, the precipitated polymer flakes were dried in air and then stored in an argon glove box.[‡]

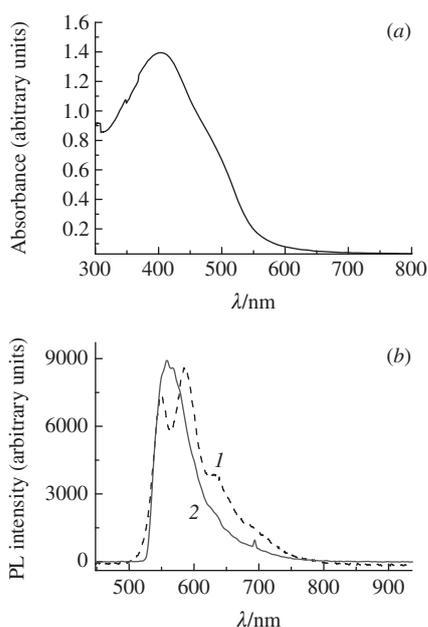
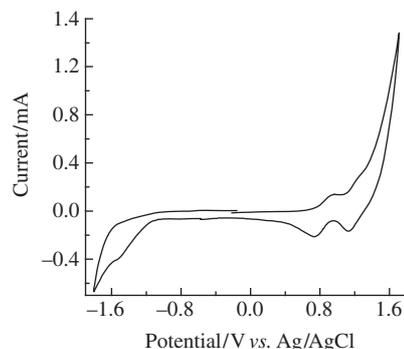
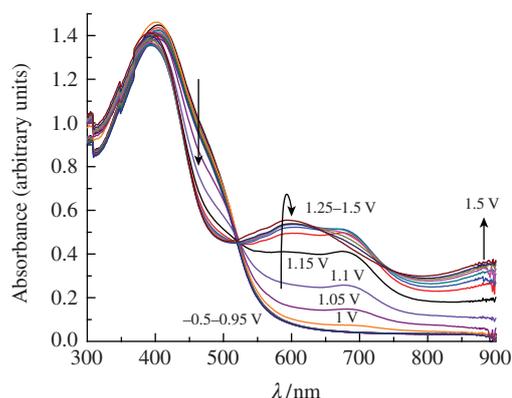
The molecular weight and polydispersity of the PF8CPDT10 polymer were calculated using the gel penetration chromatography (GPC) data (Phenomenex 7.8×300 mm column filled with a Phenogel sorbent; pore sizes of 10³ and 10⁴ Å; THF eluent flow rate, 0.4 ml min⁻¹). The GPC column was calibrated against polystyrene standards.

The absorption spectrum of the polymer shows the main band with $\lambda_{max} = 404$ nm. The optical band gap of PF8CPDT10 (2.17 eV) is larger than that of polydialkylcyclopentadithiophenes ($E_g = 1.8$ – 1.9 eV).¹⁴ This is due to the presence of fluorene units in the polymer chain of PF8CPDT10.

Larger optical bandgap of the PF8CPDT10 polymer leads to the appearance of intense visible orange fluorescence ($\lambda_{max} = 570$ nm) in solution and solid film (Figure 1). The observed differences between the PL spectra of the polymer solution and thin film strongly suggest the formation of exciplex states in the solid PF8CPDT10. These exciplexes cause the splitting of the PL band and the formation of distinct features with maxima at 550, 588, 631 and 650 nm, which can be observed in the spectrum of the solid film.

Figure 2 outlines a cyclic voltammogram of PF8CPDT10. The electrochemical band gap was calculated from the onsets of the first oxidation and reduction waves. $E_g(EC) = 1.90$ eV is smaller than the optical band gap of 2.17 eV. The HOMO energy of -5.42 eV was calculated for PF8CPDT10 using a known approach.¹⁷

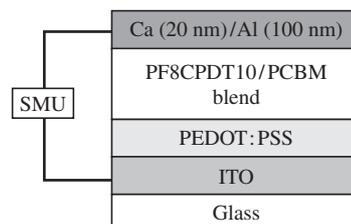
Cyclopentadithiophene-containing polymers undergo reversible electrochemical oxidation and irreversible reduction.^{18–22} We

**Figure 1** (a) Absorption and (b) fluorescence spectra of PF8CPDT10: (1) thin film and (2) solution.**Figure 2** Cyclic voltammogram for a solid film of PF8CPDT10 deposited on ITO electrode. The 0.1 M TBAHFP₆ solution in acetonitrile was used as a supporting electrolyte, scanning speed was 50 mV s⁻¹, Ag/AgCl couple was used as a reference electrode.**Figure 3** Absorption spectra of PF8CPDT10 polymer under different applied potentials.

performed a spectral electrochemistry study for PF8CPDT10 polymer. Figure 3 shows that a thin film of PF8CPDT10 changes its optical properties at applied positive potentials between 0.9 and 1.25 V. The neutral form of PF8CPDT10 has intense absorption bands in the visible range (300–570 nm), while the oxidized form also absorbs in the near infrared region (600–900 nm). The observed electrochromic effect might be useful in manufacturing coatings that require control of infrared light transmission.

The synthesized polymer has been studied as an electron donor material in bulk heterojunction solar cells. Fullerene derivative PC₆₁BM was used as an acceptor counterpart. The layout of the bulk heterojunction solar cell is shown in Figure 4.

The I - V characteristics of the solar cells were measured in the dark and under standard illumination conditions (simulated AM 1.5 solar light, 100 mW cm⁻²). The best output parameters were provided by the blends composed of the polymer and PC₆₁BM mixed in a 1:2 weight ratio. The I - V measurements revealed the short-circuit current density (I_{SC}) of 4.5 mA cm⁻², the open circuit voltage (V_{OC}) of 760 mV, the fill factor (FF) of 44% and overall power conversion efficiency (η) of 1.5%. The efficiency of 1.5% was reached as a compromise of the reasonably

**Figure 4** Bulk heterojunction solar cell architecture.

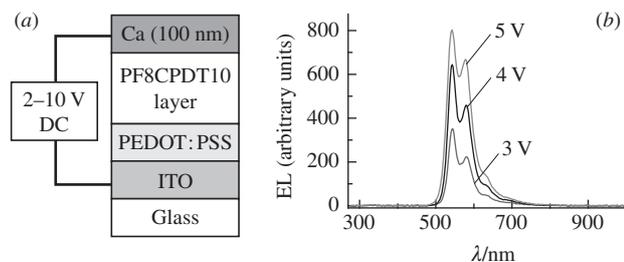


Figure 5 (a) OLED architecture and (b) electroluminescence spectra of the device.

high open circuit voltages characteristic of fluorene-containing polymers and low short-circuit current densities arising from a wide optical band gap. The conjugated polymer PF8CPDT10 is very similar to the well-known material MDMO-PPV in terms of its optical and electronic properties. The best-performing MDMO-PPV/PCBM solar cells yielded power conversion efficiencies of 2.5–2.7%. Similar efficiencies should be reachable for PF8CPDT10/PCBM solar cells after optimization of the polymer properties and the device fabrication procedure. In particular, improved fill factors might be achieved by optimizing the morphology of the fullerene derivative/polymer blend.

The organic light emitting diodes (OLEDs) have been designed using PF8CPDT10 polymer as an electroluminescent material [Figure 5(a)]. The ITO glass was coated with the PEDOT:PSS (PH-100) hole injecting layer, which was further annealed at 150 °C for 15 min. The electroluminescent layer of the PF8CPDT10 polymer was spin-coated from a chlorobenzene solution (10 mg ml⁻¹) at 900 rpm. A calcium cathode (100 nm) was thermally evaporated on the top of the polymer films in a vacuum (10⁻⁶ mBar). The current-brightness-voltage characteristics of the OLED were measured in a nitrogen glove box. The *I*–*V* curve for a fabricated OLED device shows a clear diode behaviour with an opening at 2.5–3.0 V (Figure 6). The OLED produced weak orange luminescence under an applied bias of 2.0–2.5 V. The luminescence intensity reached 5000 cd m⁻² at 4.0–5.0 V and 20000 cd m⁻² at 10.0 V. The maximum current efficiency of the designed OLED was about 2 cd A⁻¹.

The electroluminescence spectra of the OLED comprising PF8CPDT10 polymer showed three maxima at 542, 578 and 628 nm [Figure 5(b)]. Note that the positions of these maxima are slightly shifted compared to the solid state PL spectrum. Small variations (3–10 nm) in the band positions might be attributed to the different mechanism of exciton generation in OLEDs (which might lead to the formation of so called ‘electroplexes’) or to

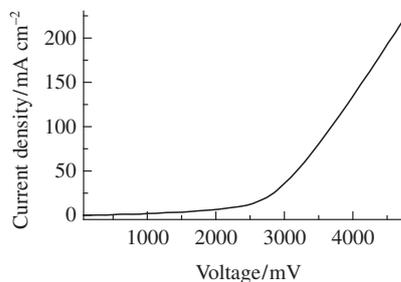


Figure 6 *I*–*V* characteristic of the OLED.

the presence of additional layers (e.g. PEDOT:PSS and metal cathode), which can also affect the spectral characteristics of the device. The PF8CPDT10-based OLED showed very promising performance compared to published data for similar single-layer polymer devices.

In conclusion, we found that the cyclopentadithiophene and fluorene copolymer PF8CPDT10 is a promising semiconductor material for OLEDs and solar cells.

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