Novel poly(fluorene-alt-squaraine) derivatives having large coverage with solar spectrum

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Abstract: Novel main-chain-conjugated poly(fluorene-alt-squaraine) using vinyl as linkage group were synthesized through direct condensation of 9,9'-dioctylfluorene derivatives and squaric acid. The resulting polyfluorenes were characterized by NMR and FT-IR. They have good solubility in common organic solvents, good thermal stability and electrochemical reversibility. The structure of donor-acceptor-donor interaction in the polymer backbone resulted in much more red-shifted absorption spectra of 500-1000 nm, and extremely low band gaps of ~1.2 eV have been obtained. Their absorption spectra have large coverage with solar spectrum, suggesting that they are potential materials that can be used in photovoltaic devices.

Introduction

Over the last years, there has been an increasing interest in polymer-based photovoltaic devices [1-5]. Conjugated polymers are now recognized as the emerging semiconductors due to their low cost, ease of processing and flexibility; not only polymeric light emitting diodes (PLEDs) [6] are approaching commercial application, but also field effect transistors (FETs)[7], photodiodes[8], and photovoltaic devices[4, 5] are being widely studied. However, compared to inorganic materials, conjugated polymers have some serious limitations for photovoltaic materials because of their relatively low mobility of charge carriers and their narrow absorption bands that have poor coverage with solar spectrum [9, 10]. For this reason, polyfluorenes, although has been well-developed as PLED materials for their high mobility and stability[11, 12], have received less attention due to their relatively short absorption wavelength, i.e. large band gaps, since high absorption coefficient and broad absorption spectra are required for efficient harvesting of the solar energy.

Squaraines, 1,3-disubstituted derivatives of squaric acid, exhibit intense and sharp absorption bands in the visible and near IR regions and high fluorescence quantum yields, which render them attractive for optical switches [13] and dye-sensitized solar cells (DSSCs) [14], and in 2003, Ajayaghosh reported a series of polymers having extremely low optical band gap by incorporation of squaraine units [15]. Herein, we describe an alternative strategy for the design of low-band-gap polymers with a donor-acceptor-structured backbone where squaraines act as acceptor and fluorene units act as donor. The conjugation length of polymers are prolonged by employing double bond linkage between donor and acceptor, thus the absorption bands are much more broadened to the region of 500-1000 nm, while those of the squaraines are narrow and generally fallen into the region of ~700 nm [16]. Furthermore, as many of the squaraines have poor solubility in both polar and non-polar organic solvents, the introduction of 9,9-dialkyl substituted fluorene derivatives has resulted

in much more improved solution properties, and the influence of different alkyl side chains on their absorption properties has been studied in this system as well.

Results and discussion

Polymer synthesis

As shown in Scheme 1, **P1** and **P2** were obtained through direct condensation of monomer **5** and **6** with squaric acid. They have good solubility in common organic solvents such as THF, CHCl_3 , CHCl_2 and toluene due to the introduction of the alkyl substituted fluorene segments into the polymer backbone. GPC results, as listed in Table 1, indicated that the polymers had high weight-average molecular weights (M_w) of 142700 and 254400 with polydispersities around 7.00 and 8.80. The polymers could be easily processed into transparent and uniform thin film by casting or spin-casting from toluene solution, and were found to be air stable in both solution and solid state.

Scheme 1. The synthetic route to the monomers and the polymers.

Tab. 1. GPC and thermal analysis data of **P1** and **P2**.

Polymers	Yield%	M_w^a	M_n^a	M_w/M_n^a	$T_d / ^\circ\text{C}^b$	$T_g / ^\circ\text{C}^b$
P1	72	142700	20400	7.00	421.23	158.66
P2	68	254400	28900	8.80	407.29	116.42

^aGPC (THF), polystyrene standards. ^bTGA and DSC under nitrogen.

These polymers were characterized by their ^1H NMR and ^{13}C NMR and FT-IR. NMR spectra of polymer **P2** as a representative polymer are shown in Figure 1, In the ^1H NMR spectrum of **P2** in CDCl_3 (Figure 1, A), the signals of the alkyl chain dominated in the region of 0.80-2.04 ppm, especially, the signals of the $\alpha\text{-CH}_2$ of octyl group at 9-position of fluorene appeared at 2.01 ppm and the signals of the -NCH_2 and $\text{-N}^+\text{CH}_2$ appeared at 4.00 and 4.89 ppm. The pyrrole unit appeared at 6.18-6.70 ppm. The signals of the vinylic unit were between 6.96 and 7.14 ppm. In the ^{13}C NMR spectrum of **P2** in CDCl_3 (Figure 1, B), the signals of the squaric carbons were dominant in the region of 140.06-176.80 ppm, and the other aromatic carbons appeared in the region

of 115.15-151.54 ppm, The signals of alkyl carbons were between 14.10 and 46.71 ppm. The NMR spectra of polymer **P1** was similar to polymer **P1** and is not shown. The polymers **P1** and **P2** were also characterized by FI-IR spectra, strong absorptions were observed at 1098, 1624, 2851 and 2923 cm^{-1} .

(A) ^1H NMR spectrum of **P2**

(B) ^{13}C NMR spectrum of **P2**

Fig. 1. NMR spectrum of polymer **P2** in CDCl_3 .

The thermal properties of the polymers that determined by TGA and DSC measurements were shown in Table 1 and Figure 2. According to Figure 2, little weight loss was observed at temperatures below 400 $^{\circ}\text{C}$, and the curves fall rapidly, which suggest the polymer backbones have decomposed, at onset decomposition (T_d) temperature of 407.29-421.23 $^{\circ}\text{C}$ under nitrogen, indicating that the target polymers exhibit good thermal stability. The glass transition temperature (T_g) of the polymers range from 116.42 $^{\circ}\text{C}$ to 158.66 $^{\circ}\text{C}$, and these T_g values are much higher than that of poly (9,9-dioctylfluorene) (POF) (51 $^{\circ}\text{C}$). It is obvious that the incorporation of squarain units into the main chain of polyfluorene can result in remarkable increase in T_g , which is very important for photovoltaic materials in organic solar cells.

Fig. 2. Thermal gravimetric analysis (TGA) curves of the polymers under nitrogen (10 °C/min).

Fig. 3. Differential scanning calorimetry (DSC) curves of the polymers under nitrogen (10 °C/min).

Optical and electrochemical analysis

The UV-Vis-NIR absorption spectral data of polymers **P1** and **P2** in toluene solution are summarized in Table 2, and their spectra are shown in Figure 4(A). Their absorption band of 380~390 nm, which is a little red-shifted compared to that of poly(9,9-dialkylfluorene) (376 nm), can be assigned to the π - π^* transition of the conjugated polymer backbone. However, the target polymers **P1** and **P2** have broad visible and NIR absorption bands of 500~1000 nm, as the characteristic absorption of squaraine dyes is generally a sharp and intense absorption at ~700 nm, the much broadened absorption bands are attributed to the exciton interaction and the extended conjugated length.

Fig. 4. (A) UV-Vis-NIR spectra of polymers in toluene; (B) The solid-state (film) absorption spectra of polymers and its overlap with solar spectrum.

Tab. 2. Optical and electrochemical properties of the polymers P1 and P2 in solution and film state.

Polymer	Solution in toluene			Solid state film			CV date		
	$\lambda_{\max}$ (nm)	λ_{onset} (nm)	E_g^a (eV)	$\lambda_{\max}$ (nm)	λ_{onset} (nm)	E_g^a (eV)	$E_{\text{ons}}^{\text{red}}$ (eV)	$E_{\text{ons}}^{\text{ox}}$ (eV)	E_g^b (eV)
P1	784	1035	1.20	796	1104	1.12	-0.62	0.52	1.14
P2	688	993	1.25	702	1015	1.22	-0.68	0.55	1.23

^aCalculated from the onset of absorption. ^bEstimated from the onset potentials of the oxidation and reduction processes.

The **P1** with *n*-hexyl side-chain shows broader absorption in 500-1100 nm, whereas **P2** with *n*-hexadecyl group showed relatively narrow spectra with 60 nm blue shifted absorption with considerable differences in the ratio of intensities of the shoulder bands. This could be assigned to an enhanced exciton coupling due to the relatively rigid and planar conformation in P1. The solid-state (film) absorption maxima, onset of absorption, and the corresponding band gaps of polymers **P1** and **P2** are summarized in Table 2. In general, the electronic properties such as absorption and emission of polymers are considerably different in the solid-state when compared to their solution behavior. This is mainly due to the formation of well-ordered self-assemblies of the macromolecular backbone in the case of poly(*p*-phenylene-ethynylene)s [20] and regioregular poly(3-alkylthiophenes) [21]. The solid-state band gaps of **P1** and **P2** were calculated from the onset of the solid-state absorption spectra, which are 0.1-0.2 eV less, when compared to the band gap calculated from the onset of the solution absorption spectra (Table 2). Comparison of the UV-Vis-NIR absorption spectra of **P1** and **P2** (Figure 4) revealed that the absorption maxima and the vibronic features are significantly influenced by the length of the hydrocarbon side chains.

The cyclic voltammograms (CV) was employed to investigate the electrochemical behavior of the polymers as well as estimate the HOMO and LUMO energy levels of the materials. **P1** and **P2** films deposited on a platinum plate electrode were scanned as both positive and negative separately in 0.10 M tetrabutylammonium perchlorate

(Bu₄NClO₄) in anhydrous acetonitrile by using platinum wires as a counter electrode and Ag/AgNO₃ (0.10 M) as reference electrode. As shown in Figure 5, the curves showed broad redox bands which may due to their polydisperse nature and intrinsic aggregation behavior.

Fig. 5. Cyclic voltammograms of polymers **P1** and **P2** recorded at a scan rate of 50 mV/s at room temperature.

From the onset potentials of the oxidation and reduction processes, the band gaps of polymers were estimated to be 1.14 and 1.23 eV for polymer **P1** and **P2** respectively. The values are quite close to those obtained by the optical method. According to the equations [22] $E_{\text{HOMO}} = IP = -([E_{\text{onset}}]^{\text{ox}} + 4.4)$ eV and $E_{\text{LUMO}} = EA = -([E_{\text{onset}}]^{\text{red}} + 4.4)$ eV, where $[E_{\text{onset}}]^{\text{ox}}$ and $[E_{\text{onset}}]^{\text{red}}$ are the onset potentials for oxidation and reduction of the polymer vs. the reference electrode, the LUMO and HOMO of the polymers were estimated to be -3.78, -3.72 eV and -5.54, -5.63 eV for **P1** and **P2**.

Conclusions

By modulating the electronic absorption properties of polymers toward low optical band gap regions and strengthening the donor-acceptor interactions, a series of extremely low E_g polyfluorenes with intense NIR absorption have been synthesized. The incorporation of a 9,9'-dioctylfluorene as bridging unit with squaraine moieties can not only change the stabilities and solubility of the resulting polymers, but also adjust their optical and electronic properties. The broad and strong NIR absorption spectra of the new polymers suggest that there exists high conjugation degree and coplanarization in the polymer backbone. The absorption spectra of these novel polymers have large coverage with the solar spectrum, indicating that they are potential candidates as optical active and transition materials in solar cells. Further studies on the application as photovoltaic materials are now in progress.

Experimental part

Materials

All the chemicals were purchased from Aldrich or Fluka Organics and were used as received unless specified. All the solvents such as THF and benzene were dried with appropriate drying agents, and distilled under reduced pressure.

Measurements

^1H NMR and ^{13}C NMR spectra of the samples were recorded with 400 MHz Bruker Advance 400 instrument in CDCl_3 with TMS as an internal standard. The weight-average molecular weights (M_w) and polydispersity indices (M_w/M_n) for the polymers were determined via PL-GPC model 210 chromatograph at 25°C , using THF as the eluent and standard polystyrene as reference. TGA analysis was performed on Perkin-Elmer series 7 thermal analysis system under nitrogen at a heating rate of 10°Cmin^{-1} . DSC measurements were performed on a Perkin-Elmer DSC 7 under nitrogen at a heating rate of 10°Cmin^{-1} . The FT-IR spectra were obtained on a Perkin-Elmer 2000 infrared spectrometer as KBr pellets. The UV-Vis-NIR spectra were recorded on a Shimadzu UV-3101 PC NIR scanning spectrophotometer. The cyclic voltammograms (CV) were recorded on a computer-controlled EG&G potential/galvanostat model 283.

Synthesis of the monomers

9,9'-Di-*n*-octylfluorene(**1**) was synthesized following the previous reported procedure [17], and *N*-alkylpyrrole-2-carboxaldehyde(**6**) was prepared according to literature methods[18].

-Synthesis of 2,7-bis(bromomethyl)-9,9'-di-*n*-octylfluorene, **2**

A mixture of 9,9'-di-*n*-octylfluorene (**1**, 3.80g, 10mmol), paraformaldehyde (3.00g, 100mmol), and 30% of hydrobromic acid in acetic acid (16mL) was stirred at 65°C for 24 h. After the reaction mixture was cooled to room temperature, it was slowly poured into saturated sodium bicarbonate solution (100 mL). The mixture was extracted three times with dichloromethane (100 mL) and washed sequentially with water and saturated sodium bicarbonate solution and brine. The combined organic extracts were dried over anhydrous magnesium sulfate and filtered. After removal of the solvent, a viscous liquid **2** was obtained by column chromatography with a yield of 81%. ^1H NMR (CDCl_3 , δ , ppm): 7.63 (d, $J=8.4\text{Hz}$, 2H, Ar-H), 7.34 (d, $J=6.2\text{Hz}$, 4H, Ar-H), 4.59 (s, 4H, $-\text{CH}_2\text{Br}$), 1.92 (m, 4H, $\alpha\text{-CH}_2$ of octyl group at 9-position of fluorene), 1.06-0.75 (30H, $-\text{CH}_2$ and $-\text{CH}_3$). Anal Calcd for $\text{C}_{31}\text{H}_{44}\text{Br}_2$: C, 64.59; H, 7.69. Found: C, 64.61; H, 7.64.

-Synthesis of (9,9'-di-*n*-octyl)-2,7-bis(fluorenylmethylene)-phosphonate, **3**

The synthesis of compound **3** was carried out by heating a mixture of triethyl phosphite (6.64g, 40mmol) and **2** (7.18, 12.5mmol) at 160°C under nitrogen for 16 h. After cooling, the unreacted triethylphosphite was removed under vacuum and the residue was passed through a short column of silica gel using a mixture of hexane and acetone (3:1) to afford 7.32 g (yield 85%) of compound **3** as a viscous oil. ^1H NMR (CDCl_3 , δ , ppm): 7.64-7.57 (m, 2H, Ar-H), 7.29-7.22 (m, 4H, Ar-H), 4.10-4.00 (m, 8H, $-\text{OCH}_2$), 3.98-3.20 (m, 4H, $-\text{PCH}_2$), 1.94 (m, 4H, $\alpha\text{-CH}_2$ of octyl group at 9-

position of fluorine), 1.36-0.79 (m, 42H, $-\text{CH}_2$ and $-\text{CH}_3$). Anal Calcd for $\text{C}_{39}\text{H}_{64}\text{O}_6\text{P}_2$: C, 67.80; H, 9.34. Found: C, 67.85; H, 9.30.

-Synthesis of (E,E)-2,7-bis[2-(1-hexylpyrrol-2-yl)vinyl]-9,9'-di-n-octylfluorene, **4**

A solution of t-BuOK (1.68 g, 15 mmol) in anhydrous THF (10 mL) was added drop wise at ambient temperature under nitrogen to a mixture of **3** (3.45 g, 5 mmol) and the corresponding *N*-hexylpyrrole-2-carboxaldehyde (1.79 g, 10 mmol) in 20 mL THF. After the sample was refluxed for 12 h, the reaction mixture was cooled, and THF was removed under reduced pressure. The residue was neutralized with 5% hydrochloric acid and extracted with chloroform. The extraction was washed with water, saturated NaHCO_3 , and brine, then dried over anhydrous magnesium sulfate. Evaporation of solvent afforded the crude product; it was purified by column chromatography with a mixture of hexane and ethyl acetate (3:1) as eluent, yield: 65%; M.p. 43-44 $^\circ\text{C}$; IR (KBr pellet, cm^{-1}): 3059, 3029, 2921, 2851, 1463, 1310, 1227, 1205, 1065, 947, 810; ^1H NMR (CDCl_3 , δ , ppm): 7.62 (d, $J=16.2\text{Hz}$, 2H, Ar-H), 7.47 (m, 4H, Ar-H), 7.38 (s, 4H, vinylic), 6.98 (s, 2H, pyrrole-H), 6.64 (s, 2H, pyrrole-H), 6.14 (m, 2H, pyrrole-H), 4.01 (t, $J=2.82\text{Hz}$, 4H), 3.87 (t, $J=6.26\text{Hz}$, 4H), 1.97 (m, 4H, $\alpha\text{-CH}_2$ of octyl group at 9-position of fluorine), 1.86-1.25 (m, 36H, CH_2), 0.88-0.85 (m, 12H). Anal Calcd for $\text{C}_{53}\text{H}_{76}\text{N}_2$: C, 85.89; H, 10.34; N, 3.78. Found: C, 85.98; H, 10.28; N, 3.74.

-Synthesis of (E,E)-2,7-bis[2-(1-hexadecylpyrrol-2-yl)vinyl]-9,9'-di-n-octylfluorene, **5**

The yellow solid was synthesized with the similar synthetic procedure for **4** from the reaction of **3** with *N*-hexadecylpyrrole-2-carboxaldehyde, yield, 73%; M.p. 26-28 $^\circ\text{C}$; IR (KBr pellet, cm^{-1}): 3046, 3027, 2923, 2856, 1468, 1388, 1299, 1230, 1037, 947, 809; ^1H NMR (CDCl_3 , δ , ppm): 7.60 (d, $J=8.0\text{Hz}$, 2H, Ar-H), 7.44 (m, 4H, Ar-H), 7.34 (s, 4H, vinylic), 6.98 (s, 2H, pyrrole-H), 6.65 (s, 2H, pyrrole-H), 6.17 (m, 2H, pyrrole-H), 4.01 (t, $J=8.0\text{Hz}$, 4H), 3.86 (t, $J=7.2\text{Hz}$, 4H), 1.96 (m, 4H, $\alpha\text{-CH}_2$ of octyl group at 9-position of fluorine), 1.86-1.25 (m, 76H, CH_2), 0.89-0.84 (m, 12H). Anal. Calcd for $\text{C}_{73}\text{H}_{116}\text{N}_2$: C, 85.81; H, 11.44; N, 2.74. Found: C, 85.92; H, 11.36; N, 2.71.

Synthesis of the target polymers

-The general polymeric procedure of P1 and P2

The polymers were synthesized by an adapted literature procedure [19]. Squaric acid (1 mmol), monomer **4** or **5** (1 mmol) and a mixture of *n*-butanol (20 mL) and toluene (40 mL) were added to a flask equipped with an azeotropic reflux condenser and refluxed under nitrogen atmosphere for 24 h. The reaction mixture was cooled and concentrated under reduced pressure, then poured into petroleum ether to afford crude product. The precipitate obtained was collected by filtration, washed thoroughly with diethyl ether and methanol, then Soxhlet extracted with methanol and acetone for 24 h respectively, which afforded the polymers **P1** and **P2**.

P1: dark-blue powder, yield 72%, IR (KBr pellet, cm^{-1}): 3046, 3027, 2923, 2852, 1628, 1468, 1385, 1301, 1183, 1099, 948, 810; ^1H NMR (CDCl_3 , δ , ppm): 8.02-7.38 (m, broad, Ar-H), 7.13-6.98 (m, broad, vinylic), 6.72 (s, 2H), 6.48 (s, 2H), 6.45 (s, 2H), 6.20 (s, 2H), 4.92 (s, broad, $-\text{N}^+\text{CH}_2$), 4.03 (s, broad, NCH_2), 2.04 (m, broad, $\alpha\text{-CH}_2$ of octyl group at 9-position of fluorine), 1.80-1.09 (m, 76H, CH_2), 0.87-0.79 (m, 12H). ^{13}C NMR (CDCl_3 , δ , ppm): 179.32, 170.25, 154.46, 143.62, 141.32, 139.88, 138.76,

128.44, 125.78, 124.05, 116.03, 55.41, 46.75, 46.26, 34.23, 31.95, 31.84, 30.16, 29.88, 29.62, 29.54, 29.48, 29.42, 29.25, 28.87, 26.51, 22.72, 22.61, 21.20, 14.13, 13.09. Anal. Calcd for (C₅₇H₇₄N₂O₂•H₂O): C, 81.77; H, 9.15; N, 3.35. Found: C, 81.84; H, 9.14; N, 3.38.

P2: dark-blue powder, yield 68%, IR (KBr pellet, cm⁻¹): 3046, 3027, 2922, 2849, 1623, 1465, 1383, 1297, 1180, 1098, 947, 809; ¹H NMR (CDCl₃, δ, ppm): 7.35-7.98 (m, broad, Ar-H), 6.96-7.14 (m, broad, vinylic), 6.70 (s, 2H), 6.45 (s, 2H), 6.44 (s, 2H), 6.18 (s, 2H), 4.89 (s, broad, -N⁺CH₂), 4.00 (s, broad, NCH₂), 2.01 (m, broad, α-CH₂ of octyl group at 9-position of fluorine), 1.09-1.80 (m, 76H, CH₂), 0.80-0.88 (m, 12H). ¹³C NMR (CDCl₃, δ, ppm): 176.80, 169.22, 151.54, 141.59, 140.06, 139.87, 138.90, 128.26, 125.54, 123.98, 115.15, 55.32, 46.71, 46.24, 34.24, 31.96, 31.64, 30.06, 29.74, 29.71, 29.64, 29.59, 29.41, 29.28, 28.86, 26.52, 22.73, 22.63, 21.22, 14.16, 14.10. Anal. Calcd for (C₇₇H₁₁₄N₂O₂•H₂O): C, 82.74; H, 10.46; N, 2.51. Found: C, 82.78; H, 10.46; N, 2.54.

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