Polymer Bulletin 60, 581–590 (2008)
DOI 10.1007/s00289-008-0890-1

Polymer Bulletin

Novel Fluorene-based Conjugated Copolymers with Donor-acceptor Structures for Photovoltaic Applications

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Received: 12 August 2007 / Revised version: 24 December 2007 / Accepted: 26 December 2007

Summary

A series of novel copolymers with fluorene and 2-pyran-4-ylidene-malononitrile (PM) moieties were synthesized successfully through Suzuki coupling reactions. The structures and properties of these polymers were characterized using FT-IR, NMR, UV-vis, elemental analysis and cyclic voltametry. All of the copolymers exhibit excellent solubility in common organic solvents. The electrochemical and photophysical properties were investigated, and the results show that the spectral response of these copolymers are extended up to 560nm, 640nm, 625nm and 625nm for P1, P2, P3 and P4, respectively. The PL spectra of the copolymer and TiO_2 bulk-heterojunction films exhibit strong photoinduced electronic interactions. Cyclic voltanmetry studies reveal that the band gaps of these copolymers range from 1.7 to 2.0 eV, implying that they may be promising candidates for solar cells.

Introduction

Polymer solar cells are becoming competitive alternatives to conventional inorganic solar cells due to their low cost, ease of processability, fabrication and the possibility to design the versatility of materials for desirable properties [1-7], their power conversion efficiencies have been improved dramatically from ~0.01% to 5.2% under AM 1.5G (100mWcm^{-2}) [8-11]. By optimizing the device architecture and exploiting better materials, further improvement may be achieved.

Polyfluorenes have attracted much attention in the area of polymer light emitting diodes due to their pure blue and efficient electroluminescene combined with high mobility and stability [12-14]. However, when used as photovoltaic materials, low power conversion efficiencies can be achieved, which may be caused by their large band gap, therefore poor absorption in the red and near IR region. While one of the criterions that efficient solar cell materials should meet with is that its absorption must cover the major visible part of the solar spectrum, i.e., their band gaps should be sufficiently low [15-16]. Therefore we concentrated our efforts on the preparation of chemical modified polyfluorene with extended absorption spectra and low band gaps.

Here, we designed and synthesized a novel series of alternating fluorene copolymers which containing blocks of electron accepting and electron donating moieties along the polymer backbone. The electrochemical and photophysical properties were investigated, and the results suggested that these copolymers may be suitable candidates for solar cells due to their broad optical absorption, low band gaps and possibly high mobility.

Experimental

Materials

All chemicals were purchased from Aldrich and Acros chemical companies and were used without further purification. All the solvents were properly purified before use. All manipulation involving air-sensitive reagents were performed in a dry argon atmosphere. 3-bromocarbazole [17], 3-bro-mo-9-hexyl-9*H*-carbazole [18],3-bromo-9-dodecyl-9*H*-carbazole [18], 3-dodecylthiophene [19], 2-bromo-3-dodecylthiophene [19], 2-hexyloxyl-3-methoxyl-5-bromobenzaldehyde [20], 2-(2,6-dimethylpyran-4-ylidine) malononitrile [21] and 9,9-dihexylflurorene-2,7-bis (trimethylene boronates) [22] were prepared following the published procedures.

Instruments

^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX 400 and Varian Unity INOVA-400 spectrometer operating, respectively, at 400 and 100 MHz. Number-average (M_n) and weight-average (M_w) molecular weights and polydispersity indices(M_w/M_n) of the polymers were measured on a PL-GPC model 210 chromatograph at 25°C, using THF as the eluent and standard polystyrene as the reference. Elemental analysis studies were carried out with Carlo Erba 116 elemental analyzer. UV-vis spectra in solutions and thin films were taken on a Shimadzu UV2100 UV-vis recording spectrophotometer. The PL spectra were measured on a Hitachi 850 fluorescence spectrophotometer. The cyclic voltammograms were recorded on a computer-controlled EG&G potential/galvanostat model 283. The thickness of films was measured by a Dektak surface profilometer.

Synthesis of monomers

General procedure for the preparation of monoaldehyde intermediates

To a mixture of *N*, *N*-dimethylformamide (30.0 g, 0.41mol) and 30 mL of 1, 2-dichloroethane at 0°C was added dropwise phosphorus oxychloride (52.0 g, 0.34 mol). Then the mixture was heated to 35°C, and (0.02 mol) of **2a**, **2b** or **5** was added. After standing for 24 h at 90°C, the mixture was poured into 300 mL of water, and then extracted with chloroform. The organic phase was washed with water for three times and dried over $MgSO_4$. The solvent was removed and the residue was purified by column chromatography.

6-bromo-9-hexyl-9*H*- carbazole-3-carbaldehyde (**3a**)

Yellow solid Yield: 75%. m.p.: 103-105°C. ^{1}H NMR (400 MHz, $CDCl_3$): 0.86 (t, J = 6.8 Hz, 3H), 1.26-1.89 (m, 8H), 4.31 (t, J = 7.2 Hz, 2H), 7.33 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 8.8 Hz, 1H), 7.61 (dd, J = 8.6, 1.6 Hz, 1H), 8.03 (dd, J = 8.6, 1.4 Hz, 1H), 8.26 (d, J = 2.0 Hz, 1H), 8.55 (d, J = 1.2 Hz, 1H), 10.0 (s, 1H). ^{13}C NMR(100MHz, $CDCl_3$) δ 190.4, 144.5, 139.9, 129.5, 128.4, 127.1, 124.5, 124.3, 123.5, 121.6, 113.2, 110.5, 109.1, 44.5, 32.1, 29.4, 27.2, 22.4, 14.0. Anal.Calcd. for $C_{19}H_{20}BrNO$: C: 63.69, H: 5.59, N: 3.91; Found: C: 63.65, H: 5.54, N: 3.94.

6-bromo-9-dodecyl-9*H*-carbazole-3-carbaldehyde (**3b**)

Yellow solid Yield: 80% m.p.: 89-90°C. ^{1}H NMR (400 MHz, $CDCl_3$): 0.87 (t, J = 6.6 Hz, 3H), 1.22-1.89 (m, 20H), 4.31 (t, J = 7.2 Hz, 2H), 7.32 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 8.8 Hz, 1H), 7.62 (dd, J = 8.4, 1.8 Hz, 1H), 8.03 (dd, J = 8.8, 1.2 Hz, 1H), 8.26 (d, J = 1.6 Hz, 1H), 8.55 (d, J = 0.8 Hz, 1H), 10.0 (s, 1H). ^{13}C NMR(100MHz, $CDCl_3$) δ 191.5, 144.2, 139.8, 129.4 128.8, 127.4, 124.6, 124.4, 123.5, 121.9, 113.1, 110.8, 109.3, 43.6, 31.9, 29.5, 28.9, 27.2, 22.7, 14.1. Anal. Calcd for $C_{25}H_{32}BrNO$: C: 67.87, H: 7.24, N: 3.17; Found: C: 67.83, H: 7.20, N: 3.15.

5-bromo-4-dodecylthiophene-2-carbaldehyde (**6**)

Yellow liquid Yield: 85% ^{1}H NMR (400 MHz, $CDC1_3$): 0.88 (t, J = 6.4 Hz, 3H), 1.26-1.62 (m, 20H), 2.60 (t, J = 7.6 Hz, 1H), 7.49 (s, 1H), 9.75 (s, 1H). ^{13}C NMR(100MHz, $CDCl_3$) δ 182.1, 143.9, 142.9, 139.8, 121.2, 31.93, 29.4, 27.9, 22.7, 14.1. Anal. Calcd for $C_{17}H_{27}BrOS$: C: 56.82, H: 7.52; Found: C: 56.86, H: 7.55

General procedure for the preparation of intermediates **M1**-**M4**

DCM derivatives (**M1**-**M4**) were synthesized by adaptation of literature [23-26] as depicted in Scheme 1.To a 25mL round-bottom flask fitted with a magnetic stirrer, a condenser, and a nitrogen inlet was added 2-(2, 6-dimethylpyran-4-ylidine)malononitrile (10 mmol), piperidine (1 mL), acetonitrile (10 mL), and 20.0 mmol of **8**, **3a**, **3b**, or **6** in sequence. The reaction solution was stirred at reflux under nitrogen for 24 h, the crude product was collected by filtration, washed with acetonitrile, and purified by recrystallizing from chloroform to afford the resulting products.

2-{2, 6-bis[2-(2-hexyloxyl-3-methoxyl-5-bromophenyl)vinyl]pyran-4-ylidene}malononitrile (**M1**)

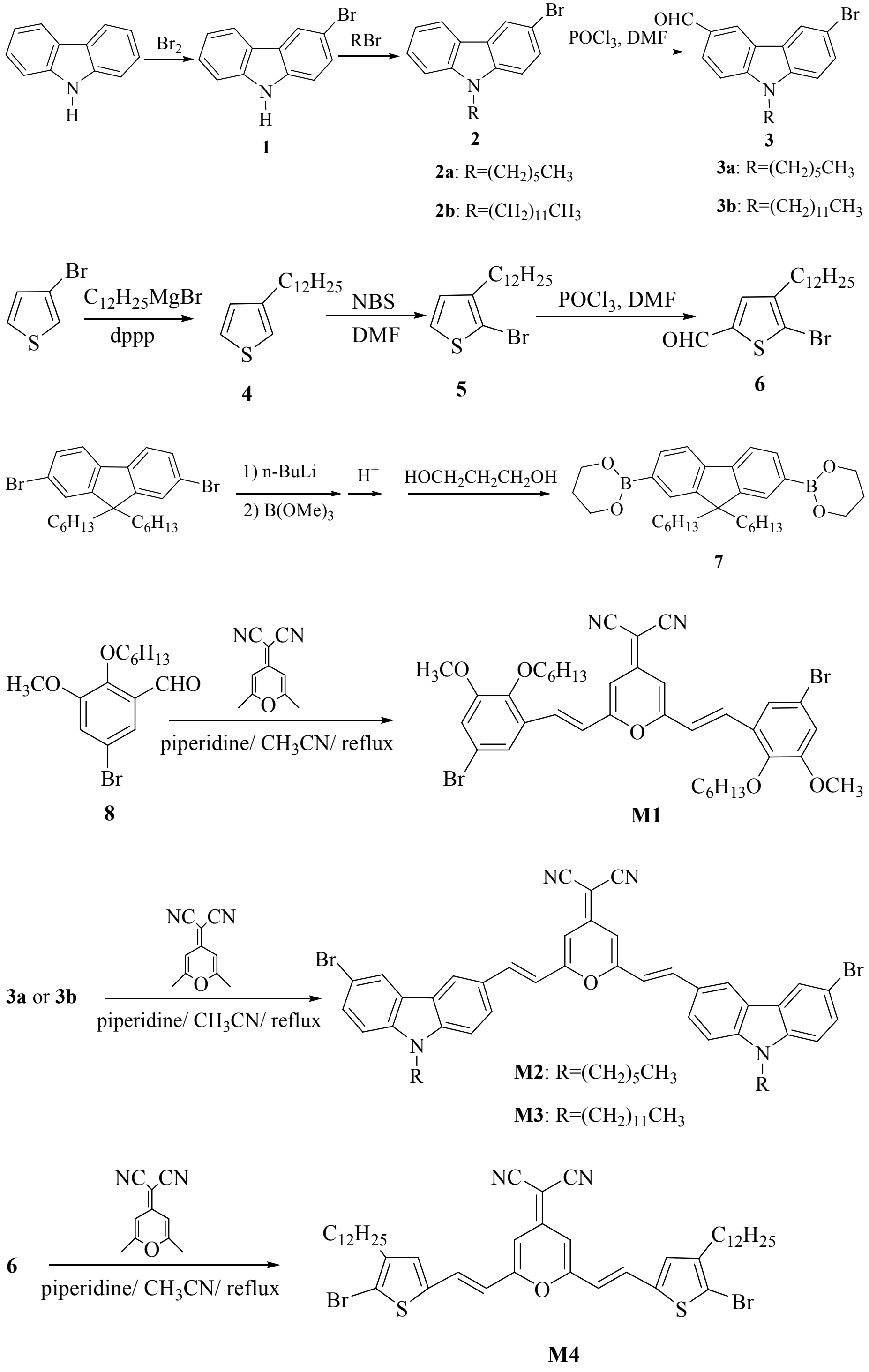
Red solid Yield: 80%. m.p.: 188-191°C ^{1}H NMR (400 MHz, $CDCl_3$): 0.77 (t, J = 6.0 Hz, 6H), 1.19-1.77 (m, 16H), 3.87 (s ,6H), 3.98 (t, J = 6.4 Hz, 4H), 6.69 (s, 2H), 6.83 (d, J = 16.4 Hz, 2H), 7.05 (s, 2H), 7.20 (s, 2H), 7.80 (d, J = 16.4 Hz, 2H). ^{13}C NMR(100 MHz, $CDCl_3$) δ 157.9, 157.6, 155.6, 146.8, 134.2, 132.1, 130.6, 121.6, 120.3, 117.0, 114.8, 108.2, 107.7, 74.3, 56.3, 31.5, 30.2, 25.8, 22.5, 14.0. Anal. Calcd for $C_{38}H_{42}Br_2N_2O_5$: C: 59.53, H: 5.48, N: 3.65; Found: C: 59.49, H: 5.43, N: 3.68

2-{2, 6-bis [2-(6-bromo-9-hexyl-9*H*-carbazol-3-yl) vinyl] pyran-4-ylidene}-malononitrile (**M2**)

Dark red solid Yield: 78%. m.p.: 272-274°C ^{1}H NMR (400 MHz, $CDCl_3$): 0.87 (t, J = 7.2 Hz, 6H), 1.27-1.89 (m, 16H), 4.30 (t, J = 6.8 Hz, 4H), 6.60 (s, 1H), 6.77 (d, J = 15.6 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.60 (dd, J = 8.8, 2.0 Hz, 1H), 7.71 (d, J = 16 Hz, 2H), 7.78(d, J = 8.8 Hz, 2H), 8.25 (d, J = 2.0 Hz, 4H). ^{13}C NMR(100MHz, $CDCl_3$) δ 158.5, 157.2, 141.9, 139.6, 138.5, 129.1, 126.1, 125.9, 124.3, 123.3, 122.4, 121.2, 115.7, 115.6, 112.6, 110.7, 109.8, 106.2, 43.5, 31.5, 28.9, 26.9, 22.5, 13.9. Anal. Calcd for $C_{48}H_{44}Br_2N_4O$: C: 67.61, H: 5.16, N: 6.57; Found: C: 67.57, H: 5.13, N: 6.50

2-{2, 6-bis [2-(6-bromo-9- dodecyl -9*H*-carbazol-3-yl) vinyl] pyran-4-ylidene}-malononitrile (**M3**)

Dark red solid Yield: 75%. m.p.: 196-198°C ^{1}H NMR (400 MHz, $CDCl_3$): 0.87 (t, J = 6.8 Hz, 6H), 1.24-1.89 (m, 40H), 4.30 (t, J = 6.8 Hz, 4H), 6.59 (s, 2H), 6.77 (d, J = 15.6 Hz, 2H), 7.31(d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.60 (dd, J = 8.8, 1.6 Hz, 2H), 7.71 (d, J = 16 Hz, 2H), 7.78(d, J = 8.8 Hz, 2H), 8.25 (s, 4H). ^{13}C NMR(100MHz, $CDCl_3$) δ 157.9, 156.3, 140.9, 139.8, 137.5, 130.1, 127.1, 126.0, 123.3, 122.3, 122.0, 121.0, 116.7, 114.6, 113.6, 110.0, 109.2, 105.2, 45.5, 31.5, 30.8, 29.3 28.9, 26.9, 22.5, 13.9. Anal. Calcd for $C_{60}H_{68}Br_2N_4O$: C: 70.52, H: 6.66, N: 5.48; Found: C: 70.46, H: 6.59, N: 5.43



Scheme 1. Synthesis of monomers

2-{2, 6-bis [2-(5-bromo-4-dodecylthiophen-2-yl) vinyl] pyran-4-ylidene}-malononitrile (**M4**)

Dark red solid yield: 82 %. m.p.: 110-112°C ^{1}H NMR (400 MHz, $CDCl_3$): 0.88 (t, J = 6.0 Hz, 6H), 1.26-2.59 (m, 44H), 6.39 (dd, J = 15.8, 8.8 Hz, 2H), 6.61 (s, 2H), 7.03 (d, J = 8.8 Hz, 2H), 7.41(dd, J = 15.8, 5.2 Hz, 2H). ^{13}C NMR(100MHz, $CDCl_3$) δ 157.5, 155.1, 143.9, 141.2, 139.4, 136.4, 131.6, 129.9, 128.7, 117.1, 115.1, 113.6, 107.0, 60.1, 31.9, 29.5, 27.9, 22.7, 14.1. Anal. Calcd for $C_{44}H_{58}Br_2N_2OS_2$: C: 61.83, H: 6.79, N: 3.28; Found: C: 61.78, H: 6.73, N: 3.22

Synthesis of the target polymers

General procedure: To a mixture of 9,9-dihexylflurorene-2,7-bis (trimethylene boronates) (1.0 mmol) (**7**), dibromo-substituted intermediates **M1**, **M2**, **M3** or **M4** (1.0 mmol), and catalyst amount of $Pd(PPh_3)_4$ was added 5 mL toluene and 5 mL aqueous 2M potassium carbonate. The reactant was stirred at reflux under nitrogen for about 48 h. After the mixture was cooled down, it was poured into a mixture of 200 mL methanol and deionized water (10:1), then a fibrous solid was obtained by filtration. The solid was washed with methanol and water several times following by washing with acetone for 24 h in a soxhlet appratus.

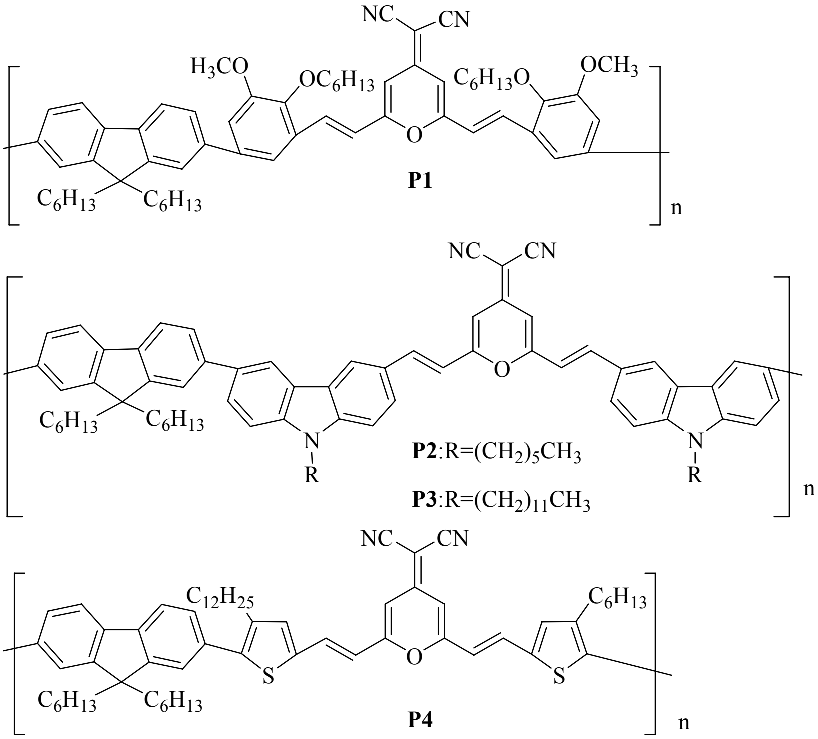
P1 was obtained as dark red powder with yield of 70% after drying under vacuum. ^{1}H NMR (400 MHz, $CDCl_3$): 0.76-2.06 (m, 48H) 3.87-3.93 (m, 6H, O-CH_3), 4.01-4.02 (m, 4H O-CH_2), 6.69-8.01 (m, 16H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 155.9, 153.4, 151.8, 147.3, 140.3, 139.5, 137.9, 133.9, 132.1, 129.2, 126.1, 121.2, 120.2, 117.6, 115.2, 113.5, 107.4, 74.4, 56.2, 55.5, 40.4, 31.6, 31.5, 30.3, 29.6, 25.8, 23.8, 22.6, 14.0 . IR (KBr, pellet) 2209.6[w ,υ (CN)] Anal. Calcd for $(C_{63}H_{77}N_2O_5)_n$: C: 80.34, H: 8.18, N: 2.98; Found: C: 80.01, H: 7.95, N: 2.88

P2: dark powder yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$): 0.745-2.131 (m, 48H), 4.22-4.38 (m, 4H N-CH_2), 6.48-8.46 (m, 24H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 156.1, 151.4, 143.2, 141.5, 140.1, 139.8, 139.1, 138.2, 135.3, 129.8, 128.2, 126.0, 125.5, 123.4, 123.0, 122.1, 121.5 121.0, 118.9, 115.2, 112.1, 110.4, 109.3, 106.1, 55.5, 43.4, 40.9, 40.7, 39.7, 31.6, 29.8, 29.1 26.9, 23.9, 22.5, 14.1. IR (KBr, pellet) 2200.6[w ,υ(CN)] Anal. Calcd for $(C_{73}H_{76}N_4O)_n$: C: 85.55, H: 7.42, N: 5.47; Found: C: 85.15, H: 7.22, N: 5.12

P3: dark powder yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$): 0.75-2.11 (m, 72H), 4.21-4.39 (m, 4H N-CH_2), 6.67-8.49 (m, 24H, Ar-H). ^{13}C NMR(100 MHz, $CDCl_3$) δ 158.5, 155.7, 151.8, 142.2, 141.8, 140.4, 139.5, 139.0, 138.4, 134.6, 129.8, 129.0, 126.0, 125.3 124.3, 123.7, 123.2, 122.4, 121.5, 121.0, 118.9, 115.7, 112.6, 110.7, 109.7, 106.1, 55.4, 43.5, 40.6, 31.9, 31.5, 30.4, 29.6, 29.5, 29.1, 28.9, 27.3, 23.8, 22.6, 20.9, 14.1. IR (KBr, pellet) 2204.2 [w ,υ(CN)] Anal. Calcd for $(C_{85}H_{100}N_4O)_n$: C: 85.57, H: 8.39, N: 4.70; Found: C: 85.03, H: 8.03, N: 4.55

P4: dark powder yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$): 0.69-2.65 (m, 76H), 6.44-7.50 (m, 14H, Ar-H). ^{13}C NMR(100 MHz, $CDCl_3$) δ 158.0, 151.5, 140.6, 137.9, 133.7, 130.7, 128.6, 128.2, 127.9, 123.5, 120.9, 118.9, 116.7, 115.4, 114.3, 110.3, 106.7, 62.0, 55.4, 55.2, 55.1, 40.6, 40.4, 31.9, 31.6, 30.9, 29.5, 27.9, 25.9, 23.8, 22.7, 14.1. IR (KBr, pellet) 2207.9[w ,υ(CN)] Anal. Calcd for $(C_{69}H_{90}N_2OS_2)_n$: C: 80.70, H: 8.77, N: 2.73; Found: C: 79.95, H: 8.25, N: 2.35

$$\mathbf{7} + \mathbf{M1 - M4} \xrightarrow[K_2CO_3/\text{Toluene}]{Pd(PPh_3)_4}$$



Scheme 2. Synthesis of polymers

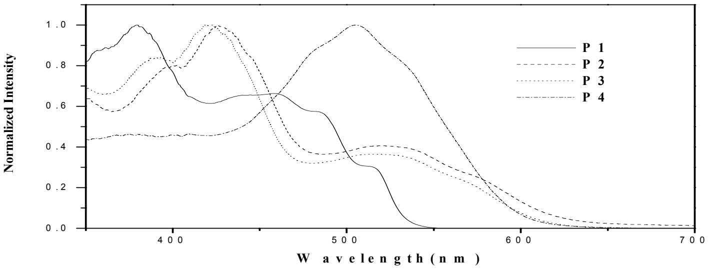


Fig.1. UV-*vis* absorption of **P1-P4** in 10^{-4}g/mL $CHCl_3$

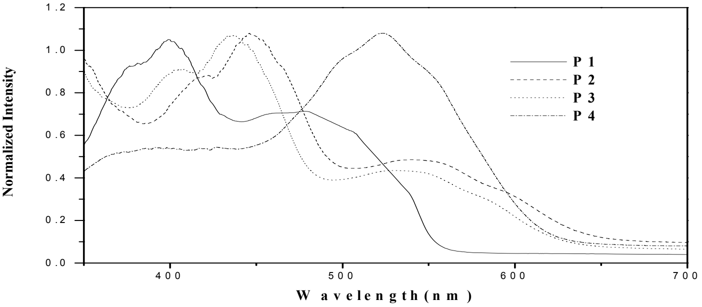


Fig.2. UV-*vis* absorption of **P1-P4** in thin film

Results and Discussion

Synthesis and Characterization: The general synthetic routes toward the monomers and polymers are outlined in scheme 1 and scheme 2. Monoaldehyde intermediates **3a**, **3b** and **6** were obtained from **2a**, **2b** and **5** by Vilsmeier-Haack reaction with an excess of $POCl_3$ and DMF, respectively. Compound **5** was prepared from monomer **4** and NBS in DMF [5]. The monomers **M1**-**M4** were prepared through Knoevenagel condensation between 2-(2, 6-dimethylpyran-4-ylidine) malononitrile and the corresponding bromoarylaldehydes in yields of over 75% [23-26]. The monomer **7** was prepared using 2, 7-dibromofluorene following the already published procedures [23]. Copolymers **P1**-**P4** were obtained through palladium-catalyzed Suzuki coupling reaction in yields of over 70%. All of these polymers are readily soluble in common solvents, such as CH_2Cl_2, $CHCl_3$ and THF, this may be assigned to the *n*-hexyl substituents in the 9-position of fluorene and *n*-alkyl side-chains linked to the PM unit. Their molecular weights were determined by gel permeation chromatography (GPC) using polystyrene as standard, the results indicated that they have weight-average molecular weights (M_w) of 9200~14000 with polydispersity indices (M_w/M_n) of 1.6 ~2.0, respectively.

Table 1. Properties of the copolymers **P1**-**P4**

	M_w[a]	M_n[a]	M_w/M_n	λ_{max} sol[b] (nm)	λ_{max} film[b] (nm)	Eg^{opt} (eV)
P1	9200	5400	1.7	379, 460	399, 477	2.1
P2	12600	6100	2.0	427, 523	445, 545	1.82
P3	14700	7500	1.95	420, 520	434, 532	1.89
P4	10400	6300	1.6	507, 404	523, 402	1.88

[a]GPC (THF), polystyrene standards. [b]Absorption spectra were recorded in the 10^{-4}g/ml $CHCl_3$ solution and in solid states on quarts

UV-visible absorption: the optical absorption spectra of the polymers were measured in the dilute chloroform solution ($1x10^{-4}$g/mL) as well as in solid thin film (show in figure 1 and figure 2) , the spectroscopic data of the polymers are summarized in table 1. In solution, **P1**, **P2** and **P3** all have two distinct absorption regions: one located in 379-427 nm and another located in 460-523 nm. The former peak can be assigned to the π-π* transition of the fluorene unites. The latter absorption region may be assigned to the π-π* transition of the sum of the delocalized structure resulted from the alternating donor-acceptor structure in the copolymer. However, **P4** show different absorption with its maximum absorption peak located in 507 nm with an additional peak at 404 nm. The difference shape and the red-shifted maximum peak may be caused by the different structure with extended lengths of π-conjugation.

Thin films of the copolymers were obtained by spin-coating from their chloroform solution. UV-vis absorption spectra of the polymers in the solid state are similar to those in solution, despite that they are a little red-shifted compared those in solution. The red shift indicates higher coplanarity of the polymers and enhanced intermolecular electronic interactions in the solid state [27].

The optical band gaps of **P1**, **P2**, **P3** and **P4**, determined from the onset of the spectra, are 2.1 eV, 1.82 eV, 1.89 eV and 1.88 eV. The band gaps of the **P2** and **P3** are similar to that of **P4** but lower than that of **P1**, possibly due to the presence of alkoxy-benzene which is less effective in lowering the band gap of the polymer than the electron-donating carbzole and thiophene units do. The strong electron-donating carbzole and thiophene segments in the polymers can raise the HOMO level and consequently reduce the band gap of the copolymer. The lower band gaps should help improve the absorption efficiency that match with the solar spectrum.

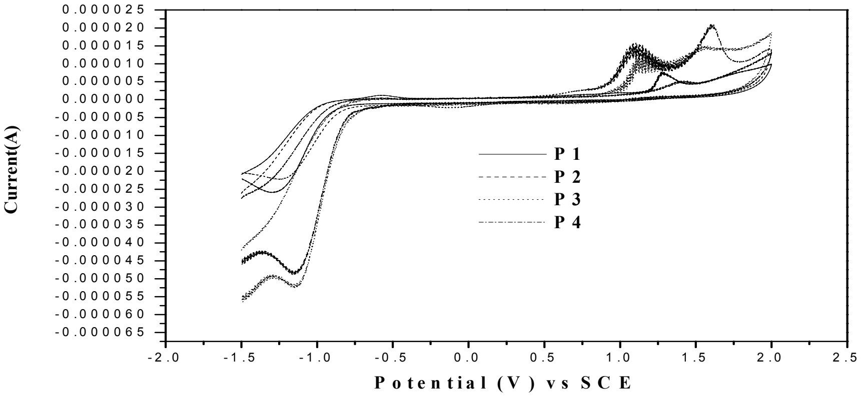


Fig.3. Cyclic voltamogram of **P1**-**P4** (in 0.1M *n*-Bu_4NClO_4 / CH_3CN with a scan rate of 100mV/s)

Table 2. Electrochemical properties and band gaps of polymers **P1-P4**

Copolymer	$E_{\text{onset, ox}}$ [a] (V vs SCE)	$E_{\text{onset, red}}$ [a] (V vs SCE)	HOMO(Ip [b]) (eV)	LUMO(Ea [c]) (eV)	Eg^{elec} [d] (eV)
P1	1.2	-0.85	-5.59	-3.54	2.05
P2	0.88	-0.84	-5.27	-3.55	1.72
P3	0.95	-0.86	-5.34	-3.53	1.81
P4	1.1	-0.75	-5.49	-3.64	1.85

[a] Oxidation and reduction onset potential measured by cyclic voltammogram (vs SCE).
[b] Ionization potential: I_p (HOMO) = -($E_{\text{onset, ox}}$ +4.39) (eV), [c] Electron affinity: E_a (LUMO) = -($E_{\text{onset, red}}$ +4.39) (eV). [d] Chemical band gaps obtained from electrochemical data: $E_g^{\text{elec}} = E_{\text{onset, ox}} - E_{\text{onset, red}}$

Electrochemical properties: Cyclic voltammetry (CV) was employed to investigate the electrochemical behaviors of the polymers, and estimate the HOMO and LUMO energy levels of the materials as well. The polymer films were obtained by dip-casted onto a Pt working electrode, the positively and negatively scans were performed at a scan rate of 100 mV/s in 0.1 M solution of tetra-*n*-butylammonium perchlorate (n-Bu_4NClO_4) in anhydrous acetonitrile. Fig. 3 shows the CV of **P1**-**P4** and Table 2 summarizes the electrochemical properties of **P1**-**P4**. In the anodic scan, the onsets of oxidation of **P1**-**P4** occur at 1.2 eV, 0.88 eV, 0.95 eV and 1.1 eV, respectively. The corresponding onsets of reduction appear at -0.85 eV, -0.84 eV, -0.86 eV and -0.75 eV, respectively. From the onset potentials of the oxidation and reduction process, the band gap of the polymers were estimated to be 2.05 eV, 1.72 eV, 1.81 eV and 1.85 eV for polymer **P1**, **P2**, **P3** and **P4**. The values of ionization potentials (I_p) and electron affinities (Ea) can be obtained from following empirical relationships [28, 29]. I_p(HOMO) = -($E_{\text{onset, ox}}$ + 4.39) eV, E_a(LUMO) = -($E_{\text{onset, red}}$ + 4.39) eV. Where $E_{\text{onset,.ox}}$

and $E_{onset.\ red}$ are the onset potentials for oxidation and reduction *vs* SCE. From this equation, the HOMO and the LUMO of the polymer were estimated to be -5.59 eV, -5.27 eV, -5.34 eV, and -5.49 eV and -3.54 eV, -3.55 eV, -3.53 eV and -3.64 eV for **P1**, **P2**, **P3** and **P4**.

Photoluminescence Properties: Nanoporous TiO_2 combined with conjugated polymer overlayer compromise a promising system for low cost photovoltaics [30]. According to the electrochemical properties that shown in Table 2, the copolymers can be blended with TiO_2 to yield thin films suitable for fabrication of photovoltaic devices. As depicted in Fig. 4, The HOMO and the LUMO levels of the copolymers **P1**-**P4** are higher than that of TiO_2, implying the energy band gaps of copolymers **P1**-**P4** are matching that of TiO_2.

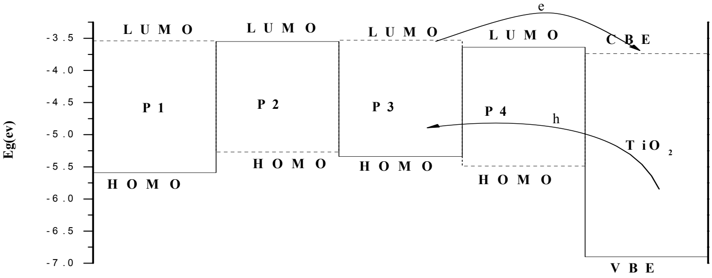


Fig.4. Energy band diagram of P1-P4 and TiO_2

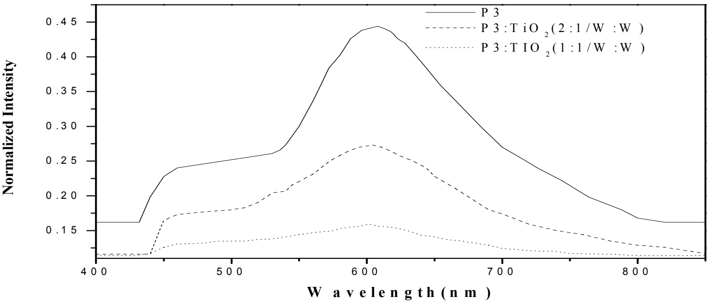


Fig.5. PL spectra of P3:TiO_2 bulk-heterojunctions with varying amounts of Ti $(OC_3H_7)_4$

For proving above argumentation, we present a study on solid-state thin film photoluminescence spectra of **P3** in the presence of TiO_2. The PL spectra of **P3** and TiO_2 bulk-heterojunctions films with varying amounts of TiO_2 were displayed in Fig.4. These films were prepared by spin-coating on quartz plates from the chloroform solutions of blends of various concentrations of **P3** / TiO_2 (1/0, 2/1, 1/1 w/w). The PL spectra of bulk-heterojunction thin film decreased with increasing amount of Ti $(OC_3H_7)_4$ compared to that of a pristine copolymer film, and would be significantly quenched in the 50% blend. The PL emissions of the polymer composite films were quenched 2-10 times than that of the pristine **P3** film. This may be assigned to the existence of strong photoinduced electronic interactions between **P3** and TiO_2; i.e., indicative of efficient exciton dissociation in the blend [31, 32].

Conclusions

Novel fluorene based copolymers containing donor-acceptor structures were prepared through Suzuki coupling polymerization. These polymers show satisfied film-forming properties. The electrochemical and photophysical properties were investigated, and the results show that they may be suitable candidates for solar cells due to their broad optical absorption, low band gaps and possibly high mobility. Further studies on the application as the photovoltaic materials are in progress.

Acknowledgment. This work was supported by the key foundation of education ministry of China. (No.105142)

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