

Synthesis and Characterization of Poly (N-Hexyl-2, 7-di(2-(4-hexylthiophene)carbazole)

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Abstract: One conjugated polymer consisting of carbazole and 3-hexylthiophene moiety, poly (N-Hexyl-2,7-di(2-(4-hexylthiophene)carbazole) (PNDC), has been synthesized by ferric chloride oxidative polymerization. The monomer N-Hexyl-2,7-di(2-(4-hexylthiophene)carbazole was synthesized and characterized by IR, ¹H-NMR, ¹³C-NMR and MS. UV-vis absorption spectrum, fluorescence spectrum, photoluminescence spectrum and electrochemical properties of the polymer were investigated. Polymer PNDC shows maximum peak appearing at 394 nm in UV-vis absorption spectrum, strongest fluorescence-emission at 482 nm in fluorescence spectrum and maximum emission peak at 492 nm in photoluminescence spectrum. The band-gap (E_g), HOMO energy (E_{HOMO}), and LUMO energy (E_{LUMO}) of the polymer were obtained as 2.58, -5.32, and -2.74 eV, respectively.

Key words: polycarbazole; polythiophene; ferric chloride

1 Introduction

Polymer based bulk heterojunction solar cells (PSCs), which are fabricated by solution processing including spin coating, printing and screenprinting have attracted much attention due to the advantages in the field of green energy production techniques. In these devices, large contact area between the donor and acceptor such as (6, 6)-phenyl C61-butyric acid methyl ester leads to efficient exciton dissociation and high power conversion efficiency(PCE)^[1, 2]. Meanwhile, polythiophene derivatives are mostly used as donor materials^[3]. Along with the synthesis and application of new structure polythiophenes, the power conversion efficiency of polymer solar cells has improved greatly up to 9.2%^[4], recently. Poly(2,7-carbazole) derivatives exhibit some unique advantages such as high hole mobility, low HOMO energy level^[5], and therefore can be widely used as hole-transporting materials as well as wide band-gap energy transfer donors^[6, 7]. A map about

the relationship of PCE and LUMO energy level (E_{LUMO}) & band-gap (E_g) of the bulk heterojunction polymer solar cells, figured by M.C.Scharber, demonstrates that the good matching of LUMO energy level and band-gap is important for obtaining highly efficient PSCs^[8]. Hence, designing and synthesizing novel conjugated polymers as donors and investigating the E_g , E_{HOMO} and E_{LUMO} of the polymers are of vital importance for screening materials (as the DONOR) with high power conversion efficiency.

Carbazole-based polymeric materials have been studied for more than 20 years for their unique electrical, electrochemical and optical properties^[9]. Poly (2, 7-carbazole) derivatives, due to their extended effective conjugation length, have attracted an increasing amount of attention in the research community^[10,11]. In this paper, we report the designing and synthesis of a monomer with incorporation of 3-hexyl-thiophene units to the 2- and 7- positions of N-hexyl-carbazole, and one novel polymer obtained by ferric chloride oxidative polymerization, together with studies of its optical and electrochemical properties.

2 Experimental

2.1 Materials and instruments

4,4'-dibromobiphenyl and tetrakis (triphenylphosphine)palladium(0) were purchased from

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Aladdin. Chloroform was distilled from calcium hydride under nitrogen before use. THF was dried by sodium. Column chromatography was carried out on silica gel (Energy Chemical, 200-300 mesh). All other solvents and chemicals used in this work were analytical grade and purchased from commercial sources and used without further purification.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer using CDCl_3 as solvent in all cases. FT-IR analyses were performed on a Nicolet 380 spectrometer. UV-vis spectra and Fluorescence spectra of the polymers were measured by HITACHI U-3310 spectrophotometer and HITACHI F-4500 fluorescence spectrophotometer, respectively. PL experiments were performed on a FL3-212-TCSPC fluorescence spectrophotometer. And the melting points were determined on a RY-1 melting point apparatus and temperatures were uncorrected. Cyclic voltammetry (CV) measurements were conducted on an electrochemistry workstation (LK-2005A, Tianjin) with the polymer film on platinum (Pt) plate as the working electrode, Pt wire as counter electrode, and Ag/AgCl electrode as a reference electrode with a scan rate of 50 mV/s. Tetrabutylammonium perchlorate (TBAP, 0.1 mol/L) and chloroform were used as supporting electrolyte and solvent, respectively. The measurements were calibrated using ferrocene as standard.

2.2 Synthesis of the monomer and the polymer

The synthetic routes of the monomer and the

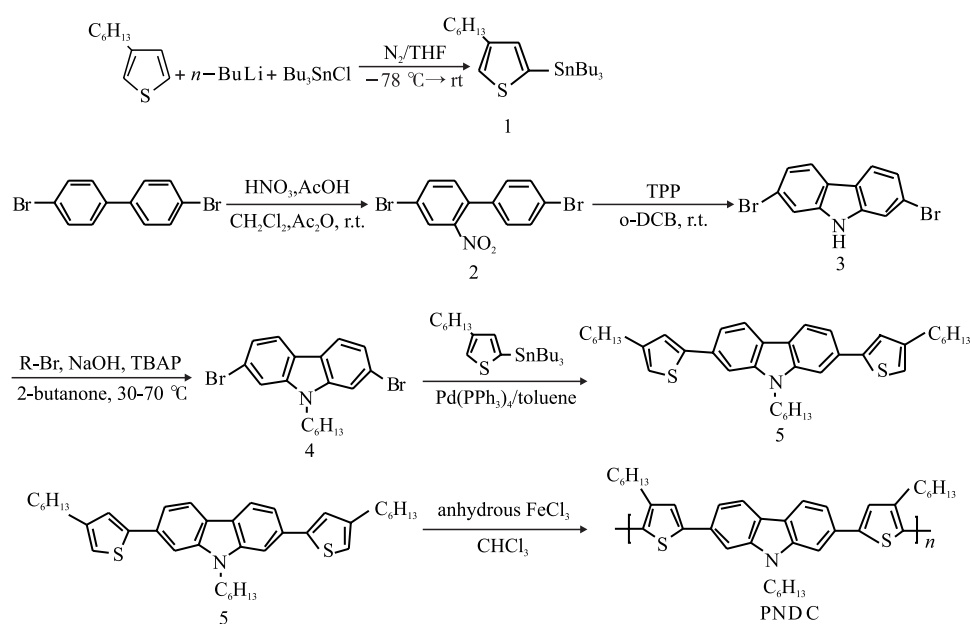
polymer are shown in Scheme 1, and the detailed synthetic processes are as follows.

2.2.1 4-hexyl-2-(tributyltin)thiophene (1)

5.4 mL 3-hexyl-thiophene (5.04 g, 30 mmol) and 40 mL of anhydrous THF were added into a flask under nitrogen atmosphere. The solution was cooled to $-78\text{ }^\circ\text{C}$ by a liquid nitrogen-acetone bath, and 16 mL of n-butyllithium (35 mmol, 2.2 M in n-hexane) was added dropwise. After the solution was stirred at $-78\text{ }^\circ\text{C}$ for 1 h, 10 mL tributyltin chloride (11.4 g, 36 mmol) was added slowly. The cooling bath was removed, and the reactant was stirred at ambient temperature for 24 h. Then, the reactant was poured into saturated sodium bicarbonate solution and extracted by dichloromethane 3 times. The organic layer was washed by water two times, and then dried by anhydrous MgSO_4 . After the solvent was removed under vacuum, 13.5 g colourless liquid was obtained stand-by.

2.2.2 4,4'-dibromo-2-nitro-biphenyl (2)

A total of 15 g (0.048 mol) 4,4'-dibromobiphenyl was dissolved in the mixed liquor consisting of 45 mL dichloromethane, 15 mL chloroform and 150 mL acetic anhydride in a 500 mL four-neck round flask under the magnetic stirrer. The solution was cooled down to $0\text{--}4\text{ }^\circ\text{C}$ with ice-water bath, to which 37.5 mL (0.83 mol) concentrated nitric acid and 22.5 mL (0.38 mol) glacial acetic acid mixed liquor were added to the vigorously stirred solution dropwise and maintained for 5 h, the solution turned from colorless to yellow gradually. The mixture was neutralized



Scheme 1 Synthetic routes for the monomer and the polymer

using aqueous sodium hydroxide, extracted with dichloromethane and then dried with anhydrous Mg_2SO_4 . The solvent was evaporated under reduced pressure and the crude product was purified by the silica gel column chromatography using petroleum ether and dichloromethane (petroleum ether/dichloromethane=3:1) as the eluant. The product was obtained as yellow powder with a melting point of 125-127 °C. Yield: 11.2 g (65.3%). FT-IR (KBr, cm^{-1}): 3 089, 2 924, 2 856, 1 547, 1 522, 1 462, 1 347, 1 067, 999, 871, 811, 511, 470. 1H -NMR (400 MHz, DMSO- d_6): δ 8.297-8.293(d, 1H), 8.010-7.985(m, 1H), 7.687-7.666(d, 2H), 7.534-7.514(d, 1H), 7.329-7.308(d, 2H). ^{13}C -NMR (400 MZ, DMSO- d_6): δ 149.583, 136.279, 135.718, 133.945, 133.553, 132.248, 130.409, 127.280, 122.644, 121.740.

2.2.3 2,7-dibromo-9H-carbazole (3)

4,4'-dibromo-2-nitrobiphenyl (2.25 g, 6.3 mmol) and triphenylphosphine (4.95 g, 18.9 mmol) in *o*-dichlorobenzene (125 mL) were refluxed at 170 °C under nitrogen. After refluxing for 9 h, the reaction mixture was evaporated under reduced pressure, and then the dark brown precipitate was collected. The crude product was purified by the silica gel column chromatography using petroleum ether and dichloromethane (petroleum ether/dichloromethane=3:1) as the eluants. Then afforded a light yellow flaky solid with a melting point of 227-230 °C. Yield: 1.76 g (86%). FT-IR (KBr, cm^{-1}): 3 420, 2 921, 2 852, 1 648, 1 461, 1 328, 1 071, 980, 815, 701, 463. 1H -NMR (400 MHz, $CDCl_3$): 8.059(s, 1H), 7.914-7.893 (d, 2H), 7.603-7.599 (d, 2H), 7.397-7.372 (d, 2H). ^{13}C -NMR (400 MHz, $CDCl_3$): 140.286, 123.329, 121.804, 121.468, 119.754, 113.832.

2.2.4 N-Hexyl-2,7-dibromocarbazole (4)

2,7-dibromo-9H-carbazole (1.625 g, 5 mmol), 1-bromohexane (0.99 g, 6 mmol), sodium hydroxide (0.40 g, 10 mmol) and tetrabutylammonium perchlorate (0.085 g, 0.25 mmol) were dissolved in 2-butanone (30 mL) and refluxed at 70 °C. After refluxing for 12 h, the solution was cooled to room temperature. The mixture was neutralized using hydrochloric acid, extracted with dichloromethane and the organic layer was collected and then washed with water, and finally dried with anhydrous Mg_2SO_4 . The solvent was evaporated under reduced pressure and the crude product was purified by the silica gel column chromatography using petroleum ether and dichloromethane (petroleum ether/dichloromethane=3:1) as the eluants. The product was

obtained as light yellow solid with a melting point of 82-83 °C. Yield: 1.8 g (88%). FT-IR (KBr, cm^{-1}): 2 924, 2 855, 1 869, 1 586, 1 452, 1 423, 1 319, 1 229, 1 127, 996, 922, 792, 591, 465. 1H -NMR (400 MHz, $CDCl_3$): 7.928-7.907 (d, 2H), 7.556-7.553 (d, 2H), 7.375-7.351 (d, 2H), 4.240-4.202 (t, 3H), 1.897-1.824 (m, 2H), 1.361-1.336 (m, 6H), 0.924-0.890 (t, 3H). ^{13}C -NMR (400 MHz, $CDCl_3$): 141.403, 122.541, 121.462, 121.315, 119.697, 112.020, 43.385, 31.485, 28.759, 26.844, 22.517, 13.946.

2.2.5 N-Hexyl-2,7-di(2-(4-hexylthiophene)carbazole (5)

N-Hexyl-2, 7-dibromocarbazole (0.41 g, 1 mmol), 4-hexyl-2-(tributyltin)thiophene (1.14 g, 2.5 mmol) and Pd(PPh_3)₄ (0.02 g, 0.017 mmol) in toluene (25 mL) were refluxed under nitrogen. After refluxing for 15 h, the solution was cooled to room temperature and the organic layer was obtained by suction filtration, washed with water, and finally dried with anhydrous Mg_2SO_4 . The solvent was evaporated under reduced pressure and the crude product was purified by silica gel column chromatography using petroleum ether and dichloromethane (petroleum ether/dichloromethane=3:1) as the eluants. The product was obtained as faint yellow solid with a melting point of 81-82 °C. Yield: 0.37(63.5%). FT-IR (KBr, cm^{-1}): 2 920, 2 852, 1 647, 1 541, 1 462, 1 337, 1 059, 811,715,465. 1H -NMR (400 MHz, d_6 -DMSO): 8.128-8.107 (d,2H), 7.817 (s,2H), 7.523 (s,2H), 7.461-7.441 (dd,2H), 7.146 (s,2H), 4.512-4.477 (t,2H), 2.637-2.599 (t,4H), 1.832-1.800 (m,2H), 1.670-1.635 (m,4H), 1.385-1.276 (m,18H), 0.901-0.866 (t,6H), 0.842-0.806 (t,3H). ^{13}C -NMR (400 MHz, d_6 -DMSO): δ 144.580, 144.421, 141.635, 132.294, 125.398, 121.835, 121.272, 120.336, 117.526, 106.056, 31.559, 31.364, 30.523, 30.392, 28.890, 26.511, 22.529, 14.401, 14.280. MS: $C_{38}H_{49}NS_2$, $m/z=584.3 [M^+]$ (calcd 583.9).

2.2.6 Poly (N-Hexyl-2,7-di(2-(4-hexylthiophene) carbazole) (PNDC)

0.291g (0.5 mmol) N-Hexyl-2,7-di(2-(4-hexylthiophene)carbazole in 20 mL chloroform was added dropwise to a solution of 0.325 g (2 mmol) anhydrous ferric chloride and 10 mL anhydrous chloroform in an ice bath at 0-5 °C under nitrogen, then the mixture was stirred for 3 h in an ice bath. When the mixture was stirred for another 24 h at room temperature, dark grey-colored precipitate was obtained. The precipitate was filtered, washed with water thoroughly, and then dried in vacuum to generate a black solid as product. Yield: 0.28 g (94.7%).

3 Results and discussion

3.1 Optical properties

The UV-visible spectrum of polymer PNDC in DMF solution is shown in Fig.1. The corresponding data are summarized in Table1. The solution absorption spectrum of polymer PNDC shows profile with

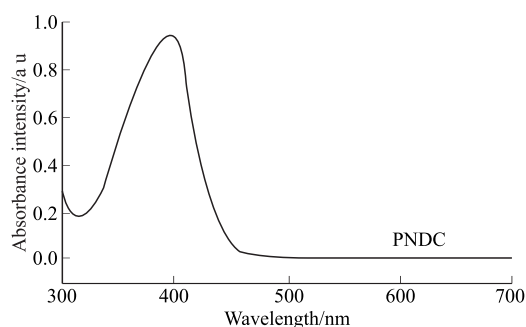


Fig.1 UV-vis spectrum of the polymer

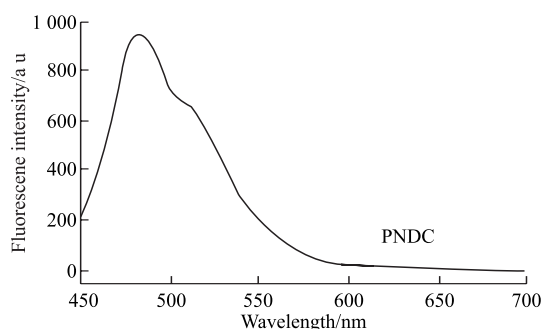


Fig.2 Fluorescent spectrum of the polymer

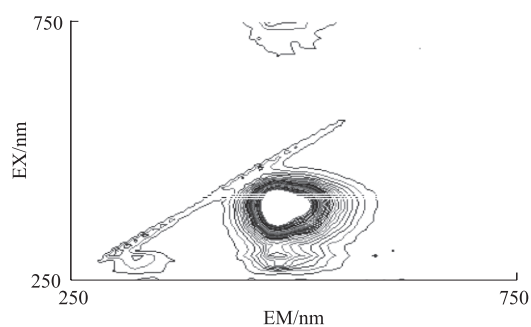


Fig.3 Fluorescent 3D scan of the polymer

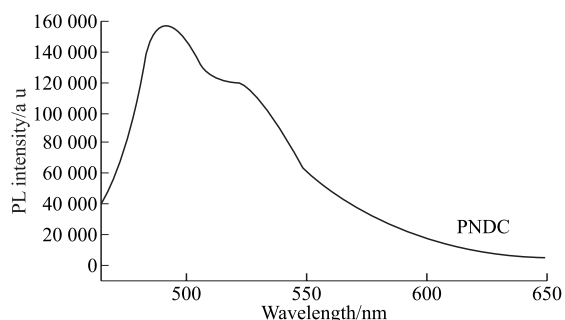


Fig.4 Photoluminescence spectrum of the polymer

maximum peak appearing at 394 nm with scanning wavelength from 300 to 700 nm. From the edge of the absorption spectrum ($\lambda_g=480$ nm) in Fig.1, the band-gap ($E_g=1240/\lambda_g$) of the polymer is estimated to be 2.58 eV.

The fluorescence spectrum of polymer PNDC was obtained with the same concentration in UV-vis spectrum (Fig.2). Fig.3 shows the fluorescent 3D scan of polymer PNDC with scanning range from 250-750 nm. When the excitation wavelength was fixed at 396 nm, polymer PNDC shows the strongest fluorescence-emission at 482 nm with respect to fluorescence response range of 430-570 nm. The results show that polymer PNDC exhibited good optical performance. Photoluminescence (PL) spectrum of polymer PNDC was taken under an excitation of 440 nm. Fig.4 shows the photoluminescence spectrum. The emission curve of polymer PNDC shows its emission maxima at 492 nm with photoluminescence response range between 450-620 nm, which was similar to its fluorescence performance in solution.

3.2 Electrochemical properties

The electrochemical property of polymer PNDC was investigated by cyclic voltammetry (CV) to determine the energy level of its HOMO and LUMO. The HOMO and LUMO energy levels (E_{HOMO} and E_{LUMO} , respectively) of the polymer were calculated by use of the following empirical formulas^[12], where E_{ox} and E_{re} are the onset oxidation and reduction potentials, respectively.

$$E_{\text{HOMO}} = -(E_{\text{ox}} + 4.40) \text{ eV},$$

$$E_{\text{LUMO}} = -(E_{\text{re}} + 4.40) \text{ eV},$$

$$E_g^{\text{opt}} = 1240/\lambda_{\text{edge}}^{\text{opt}} = E_{\text{LUMO}} - E_{\text{HOMO}}$$

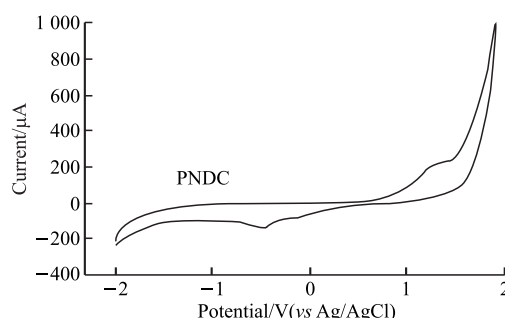


Fig.5 Cyclic voltammograms of the polymer

Fig.5 shows cyclic voltammogram of polymer PNDC and the derived E_{HOMO} , E_{LUMO} are summarized in Table 1. The estimated E_{LUMO} was -2.74 eV, meanwhile the E_{HOMO} value was found to be -5.32 eV, with a band-gap of 2.58 eV.

Table 1 Optical and electrochemical data of polymer PNDC

Polymer	UV-vis λ_{\max}/nm	Fluorescence λ_{\max}/nm	Photoluminescence		Cyclic voltammetry		
			λ_{\max}/nm	$\lambda_{\text{edge}}^{\text{opt}}/\text{nm}$	$E_{\text{HOMO}}/\text{eV}$	$E_{\text{LUMO}}/\text{eV}$	$E_{\text{g}}^{\text{opt}}/\text{eV}$
PNDC	394	482	492	480	-5.32	-2.74	2.58

[a] $\lambda_{\text{edge}}^{\text{opt}}$ was calculated from the intersection of the tangent on the low energetic edge of the absorption spectrum with the baseline; [b] The onset potentials (E_{ox}) were obtained from the intersection of the two tangents down at the rising current and the baseline changing current of the CV cures; [c] Band-gap ($E_{\text{g}}^{\text{opt}}$) was estimated from the onset wavelength of the optical absorption: $E_{\text{edge}}^{\text{opt}} = 1240/\lambda_{\text{g}}^{\text{opt}}$

4 Conclusions

We have synthesized one conjugated polymers bearing carbazole and 3-hexylthiophene in the main chain. The monomer N-Hexyl-2,7-di(2-(4-hexylthiophene)carbazole) was synthesized and characterized by IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$. UV-vis absorption spectrum, fluorescence spectrum, photoluminescence spectrum and electrochemical properties of the polymer (PNDC) have been investigated. Polymer PNDC shows maximum peak appearing at 394 nm in UV-vis absorption spectrum, strongest fluorescence-emission at 482 nm in fluorescence spectrum and maxima emission peak at 492 nm in photoluminescence spectrum. The band-gap (E_{g}), HOMO orbital energy (E_{HOMO}), and LUMO orbital energy (E_{LUMO}) of the polymer were obtained as 2.58, -5.32, and -2.74 eV, respectively. The results show that polymer PNDC exhibited good optical and electrochemical properties.

References

- [1] Li G, Shrotriya V, Yao Y, et al. Manipulating Regioregular poly(3-hexylthiophene): [6,6]-phenyl-C61-butyric Acid Methyl Ester Blends-route Towards High Efficiency Polymer Solar Cells[J]. *J. Mater. Chem.*, 2007, 17: 3 126-3 140
- [2] Guan Z L, Kim J B, Wang H, et al. Direct Determination of the Electronic Structure of the poly(3-hexylthiophene): Phenyl-[6,6]-C61 Butyric Acid Methyl Ester Blend[J]. *Org. Electron.*, 2010, 11(11): 1 779-1 785
- [3] Smith Z C, Pawle R H, Thomas S W, et al. Photoinduced Aggregation of Polythiophenes[J]. *ACS Macro Lett.*, 2012, 1 (7): 825-829
- [4] Service R F. Outlook Brightens for Plastic Solar Cells [J]. *Science*, 2011, 332 (6 027): 293
- [5] Zhao W, Cai W Z, Xu R X, et al. Novel Conjugated Alternating Copolymer Based on 2,7-carbazole and 2,1,3-benzoselenadiazole[J]. *Polymer*, 2010, 51: 3 196-3 202
- [6] Ohmori Y, Kajii H, Sawatani T, et al. Enhancement of Electroluminescence Utilizing Confined Energy Transfer for Red Light Emission[J]. *Thin Solid Films*, 2001, 393: 407-411
- [7] Lamansky S, Kwong R C, Nugent M, et al. Molecularly Doped Polymer Light Emitting Diodes Utilizing Phosphorescent Pt(II) and Ir(III) Dopants[J]. *Org. Electron*, 2001, 2(1): 53-62
- [8] Scharber M C, Mühlbacher D, Koppe M, et al. Design Rules for Donors in Bulk-Heterojunction Solar Cells-Towards 10% Energy-Conversion Efficiency[J]. *Adv.Mater.*, 2006, 18(6): 789-794
- [9] Grazulevicius JV, Strohriegel P, Pielichowski J, et al. Carbazole-containing Polymers: Synthesis, Properties and Applications[J]. *Prog. Polym. Sci.*, 2003, 28: 1 297-1 353
- [10] Tirapattur S, Belletêtea M, Drolet N, et al. Steady-state and Time-resolved Studies of 2,7-carbazole-based Conjugated Polymers in Solution and as Thin Films: Determination of Their Solid State Fluorescence Quantum Efficiencies[J]. *Chem. Phys. Lett.*, 2003, 5(370): 799-804
- [11] Yasutania Y, Honshoa Y, Saeki A, et al. Polycarbazoles: Relationship between Intra- and Intermolecular Charge Carrier Transports[J]. *Synth. Met.*, 2012, 17(162): 1 713-1 721
- [12] Wang E, Wang M, Wang L, et al. Donor Polymers Containing Benzothiadiazole and Four Thiophene Rings in Their Repeating Units with Improved Photovoltaic Performance[J]. *Macromolecules*, 2009, 42(13): 4 410-4 415