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Influence of the introduction of phenylene units into the polymer backbone on bandgap of conjugated poly(heteroarylene methines)

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Abstract

A series of conjugated poly(heteroarylene methines) containing alternating aromatic and quinoid phenylene–thiophene moieties in the main chain have been synthesized. These polymers are soluble in common organic solvents, such as chloroform, THF. The optical and electrochemical properties of the conjugated poly(heteroarylene methines), such as band gap, redox potentials, ionization potential, and electron affinity, were found to be significantly modified by the size of lateral groups on phenylene units and the number of phenylene units on the phenylene–thiophene moieties. With the increase of the size of lateral groups on phenylene units, the polymers show much bigger conjugated length. And the introduction of two phenylene units between two thiophene units lowers much more band gap than that of one phenylene unit.

Keywords: Conjugated polymers; Bandgap; Poly(heteroarylene methines)

1. Introduction

Conjugated polymers have attracted much attention due to their interesting electronic and optical properties [1–3]. As a kind of organic semiconductors, their photoelectric properties are mainly determined by the extent of their π-electron delocalizations. So it is important to design some energy band structure to realize proper photoelectric properties [4,5].

Especially, how to gain small band gap polymers has recently become the focus of attention due to their unique properties, such as intrinsic good conductivity without doping, good nonlinear optical and photoelectric properties and amphivalent electrochemical character [6–8]. Otherwise, they could be blended into conjugated polymers to expand the spectral region of bulk heterojunction solar cells [9], and applied in the organic light-emitting diodes [7]. At present, two approaches have been applied to reduce the band gap of conjugated polymers. One involves the introduction of quinoid character into the aromatic conjugated polymer backbone [10–13]. Another is the alternation of strong donor and acceptor moieties [14].

Here we reported our work on conjugated poly(heteroarylene methines). By modifying conjugated poly[(α-bithiophene)methines], we synthesized a series of conjugated polymers containing alternating aromatic and quinoid phenylene–thiophene moieties in the main chain, and characterized by optical and electrochemical measurements.

2. Experimental

1,4-Dibromobenzene, biphenyl, 1,4-dimethylbenzene, 3-bromothiophene, bromine, iodine granule, benzaldehyde and 3-bromobenzaldehyde were purchased from domestic chemical company and used without further purification. 2,3-Dicyano-5,6-dichloro-1,4-benzoquinone (DDQ) was recrystallized from ethanol. 1,4-Dioctoxylbenzeneand bis-(triphenylphosphino) dichloronickel(II) ($NiCl_2(PPh_3)_2$) were prepared according to the literature [15]. All of the solvents were analytic reagents (AR) and purified by standard distillation methods. All of the following reactions were carried out under argon atmosphere.

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2.1. Synthesis of monomers

2.1.1. 2,5-Dibromo-1,4-dimethylbenzene(1b) [16]

To a mixture of (55.21 g, 0.52 mol) of 1,4-dimethylbenzene and (0.23 g, 0.88 mmol) of iodine in 52 mL of dichloromethane and 15 mL of glacial acetic acid, (30 mL, 0.52 mol) of bromine was added dropwise under exclusion of light at room temperature. After stirring overnight the reaction mixture is poured into an aqueous solution of 20 wt% KOH and 10 wt% sodium thiosulfate. Stirring is continued until the color disappeared. The aqueous solution was extracted with dichloromethane three times. The organic layer was washed with water twice, dried with anhydrous magnesium sulfate, filtered and the solvent is removed by evaporation. The crude product was purified by recrystallization from ethanol to afford a white solid. Yield is 68%, mp 72–73 °C. FT-IR (KBr pellet, cm^{-1}): 2981.9, 2950.3, 2917.7, 2847.6, 1743.3, 1473.3, 441.3, 1377.6, 1342.7, 1260.6, 1185.6, 1054.6, 985.4, 877.8, 751.3. Anal. Calcd for $C_8H_8Br_2O_2$: C, 32.44; H, 2.72. Found: C, 32.59; H, 2.53.

2.1.2. 2,5-Dibromo-1,4-dioctoxylbenzene(1c)

The synthetic procedure was similar to 2,5-dibromo-1,4-dimethylbenzene. The product is a white solid. Yield: 97%, mp 64–66 °C. FT-IR (KBr pellet, cm^{-1}): 2918.1, 2848.3, 1674.5, 1494.7, 1462.6, 1395.0, 1362.0, 1269.7, 1212.6, 1126.3, 1065.9, 1031.0, 998.7, 848.4, 808.5. Anal. Calcd for $C_{22}H_{36}Br_2O_2$: C, 53.65; H, 7.36. Found: C, 53.39; H, 7.54.

2.1.3. 4,4′-Dibromo-p-biphenyl(1d)

The synthetic procedure was similar to 2,5-dibromo-1,4-dimethylbenzene. The product is a yellow solid. Yield: 97%, mp 73–75 °C. FT-IR (KBr pellet, cm^{-1}): 3062.4, 3030.0, 1905.6, 1585.4, 1475.4, 1448.3, 1392.4, 1340.0, 1079.7, 1001.7, 830.4, 810.6, 757.7, 737.7, 737.2, 688.8. Anal. Calcd for $C_{12}H_8Br_2$: C, 47.17; H, 2.58. Found: C, 47.32; H, 2.46.

2.1.4. 1,4-Di-2-thienylbenzene(2a) [17]

(24.45 g, 0.15 mol) of 2-bromothiophene in 34 mL of THF was slowly added to a cold solution of (3.60 g, 0.15 mol) of magnesium in 100 mL of THF at 0 °C. The reaction mixture was heated to reflux for 1.5 h and cooled to room temperature. And then the Grignard reagent was formed. The Grignard reagent was added to a solution of (14.15 g, 0.06 mol) of 1,4-dibromobenzene in 70 mL of THF with a catalytic amount of $NiCl_2(PPh_3)_2$. The reaction mixture was heated to reflux for 24 h. Then the reaction mixture was cooled, terminated with 2 M HCl aqueous solution, extracted with dichloromethane three times. The combined organic layer was washed with water and dried with anhydrous magnesium sulfate. After the solvent was removed by rotary evaporation, the residue was purified by silica-gel column chromatography using petroleum ether as the eluent. The product is a white crystal. Yield is 60%, mp 128–131 °C. Anal. Calcd for $C_{14}H_{10}S_2$: C, 69.38; H, 4.16. Found: C, 69.50; H, 4.21.

2.1.5. 1,4-Di-2-thienyl-2,5-dimethylbenzene(2b)

The synthetic procedure was similar to 1,4-di-2-thienylbenzene, except that the refluxing time was 48 h. Yield is 52%, mp 84–85 °C. Anal. Calcd for $C_{16}H_{14}S_2$: C, 71.07; H, 5.22. Found: C, 71.23; H, 5.19.

2.1.6. 1,4-Di-2-thienyl-2,5-dioctoxylbenzene(2c)

The synthetic procedure was similar to 1,4-di-2-thienylbenzene, except that the refluxing time was 48 h. Yield is 43%, mp 63–65 °C. Anal. Calcd for $C_{30}H_{42}S_2O_2$: C, 72.24; H, 8.49. Found: C, 70.95; H, 8.35.

2.1.7. 4,4′-Di-2-thienyl-p-biphenyl(2d)

The synthetic procedure was similar to 1,4-di-2-thienylbenzene, except that the refluxing time was 48 h. Yield is 46%, mp 78–79 °C. Anal. Calcd for $C_{20}H_{14}S_2$: C, 75.43; H, 4.43. Found: C, 74.14; H, 4.57.

2.2. Synthesis of pre-polymers and polymers [18,19]

2.2.1. Poly[(1′,4′-di(α-thienyl)benzene-5,5″-diyl)benzylidene] (PDTBB)(3a)

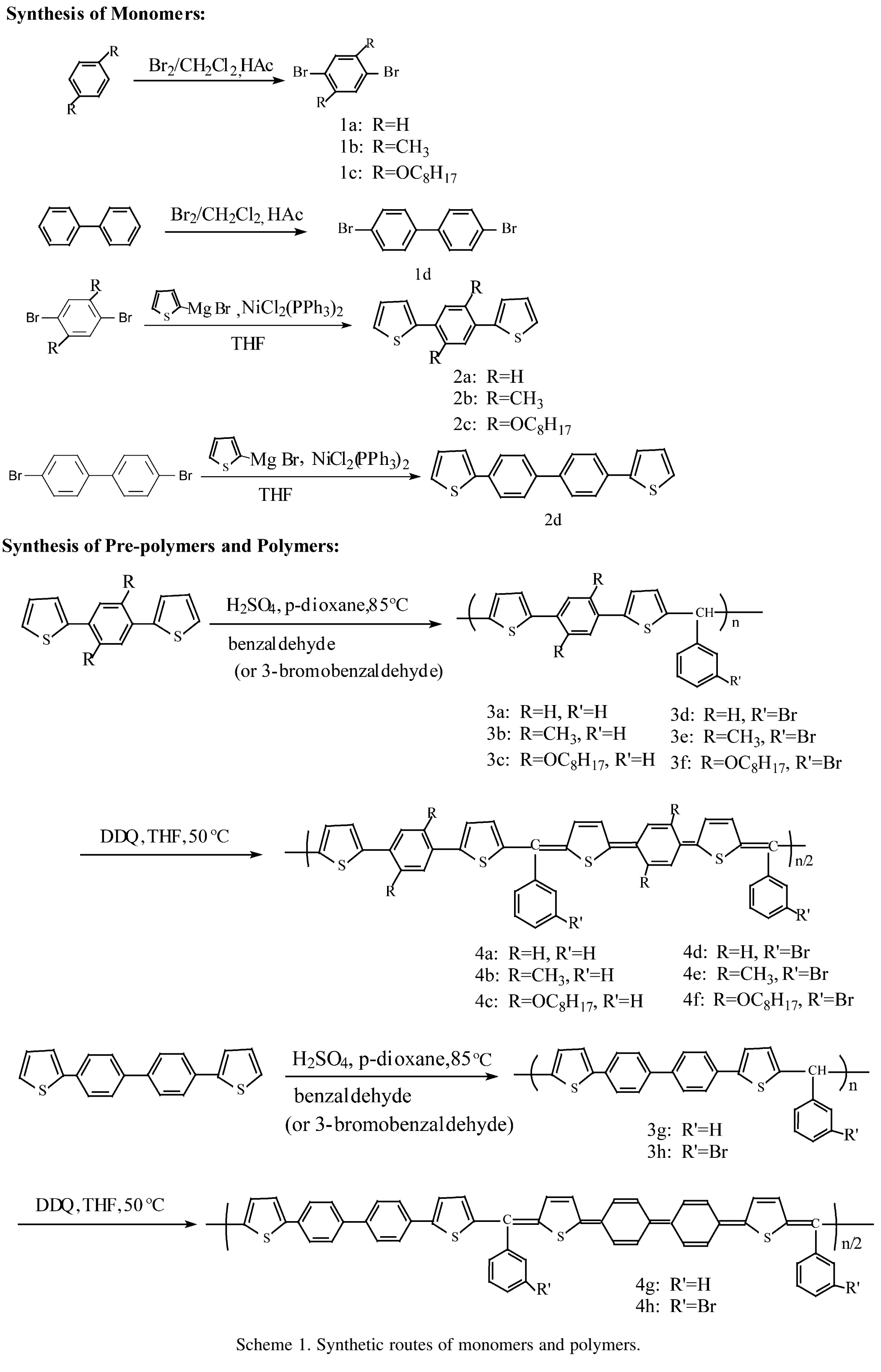
(0.908 g, 3.6 mmol) of 1,4-di(α-thienyl)benzene, (0.731 g, 5.4 mmol) of benzaldehyde and 8 mL of *p*-dioxane were added to a 25 mL round-bottom flask. The mixture were heat to 85 °C and 0.10 mL of 98% H_2SO_4 was added dropwise. Then, it reacted at same temperature for 24 h. The reaction mixture was poured into methanol. The precipitate was filtered, reprecipitated in THF/methanol twice and vacuum dried at 50 °C. The product is blue/black solid. FT-IR (KBr pellet, cm^{-1}): 3064.5, 1715.6, 1611.9, 1549.3, 1488.8, 1448.5, 1417.5, 1270.3, 1178.3, 1107.6, 1066.9, 1018.1, 961.0, 839.3, 798.0, 711.3, 689.3.

Poly[(1′,4′-di(α-thienyl)-2′,5′-dimethylbenzene-5,5″-diyl)benzylidene] (PDTDMBB)(3b), poly[(1′,4′-di(α-thienyl)-2′,5′-dioctoxylbenzene-5,5″-diyl)benzylidene] (PDTDOBB)(3c), poly(4′,4″-di(α-thienyl)-*p*-biphenyl-5,5‴-diyl)benzylidene] (PDTDBB)(3g), poly[(1′,4′-di(α-thienyl)benzene-5,5″-diyl)(*m*-bromo-benzylidene)] (PDTBB-Br)(3d), poly[(1′,4′-di(α-thienyl)-2′,5′-dimethylbenzene-5,5″-diyl)(*m*-bromobenzylidene)] (PDTDMBB-Br)(3e), poly[(1′,4′-di(α-thienyl)-2′,5′-dioctoxylbenzene-5,5″-diyl)(*m*-bromobenzylidene)] (PDTDOBB-Br)(3f), poly(4′,4″-di(α-thienyl)-*p*-biphenyl-5,5‴-diyl)(*m*-bromobenzylidene)] (PDTDBB-Br) (3h) were prepared by using the same procedure as PDTBB.

2.2.2. Poly[(1′,4′-di(α-thienyl)benzene-5,5″-diyl)benzylidene-block-(1′,4′-di(α-thienyl)benzenequinodimethane-5,5″-dily)] (PDTBBQ)(4a)

The reaction mixture was (0.567 g, 1.7 mmol) of PDTBB, (0.288 g, 1.1 mmol) of DDQ and 25 mL of unhydrous THF. The reaction temperature was maintained at 50 °C for 10 h. A dark blue polymer was recovered in stirring methanol, dissolved in THF, recovered in methanol, extracted with hot methanol in a Soxhlet apparatus, and dried in a vacuum oven at 60 °C for 12 h. FT-IR (KBr pellet, cm^{-1}): 3067, 1609.4, 1548.3, 1488.3, 1448.7, 1411.1, 1298.2, 1224.8, 1119.0, 1066.4, 1017.0, 963.0, 840.2, 798.1, 712.1, 689.5.

Poly[(1′,4′-di(α-thienyl)-2′,5′-dimethylbenzene-5,5″-diyl)benzylidene-*block*-(1′,4′-di(α-thienyl)-2′,5′-dimethylbenzenequinodimethane-5,5″-dily)] (PDTDMBBQ)(4b),



Scheme 1. Synthetic routes of monomers and polymers.

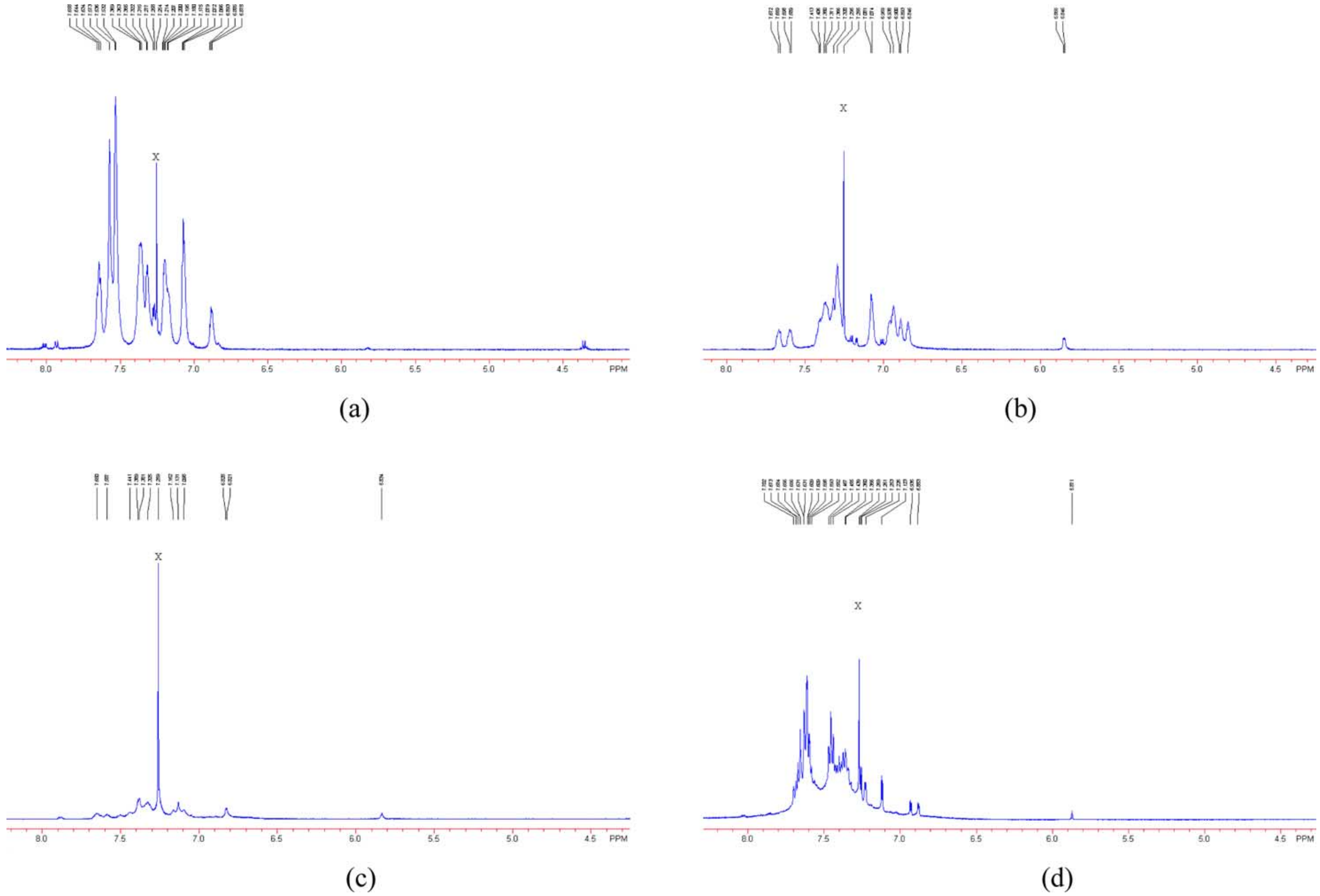


Fig. 1. ^{1}H NMR spectra of PDTBBQ (a), PDTDMBBQ (b), PDTDOBBQ (c), PDTDBBQ (d) in $CDCl_3$ (solvent peak at $\delta = 7.26$ ppm is marked 'X').

poly[(1′,4′-di(α-thienyl)-2′,5′-dioctoxylbenzene-5,5″-diyl)-benzylidene-*block*-(1′,4′-di(α-thienyl)-2′,5′-dimethylbenzenequinodimethane-5,5″-dily)] (PDTDOBBQ)(4c), poly[(4′,4″-di(α-thienyl)-*p*-biphenyl-5,5‴)benzylidene-*block*-(4′,4″-di(α-thienyl)-*p*-biphenyl quinodimethane-5,5″-dily)] (PDTDBBQ)(4g), poly[(1′,4′-di(α-thienyl)benzene-5,5″-diyl)(*m*-bromobenzylidene)-*block*-(1′,4′-di(α-thienyl)benzenequinodimethane-5,5″-dily)] (PDTBBQ-Br)(4d), poly[(1′,4′-di(α-thienyl)-2′,5′-dimethylbenzene-5,5″-diyl)(*m*-bromobenzylidene-*block*-(1′,4′-di(α-thienyl)-2′,5′-dimethyl benzenequinodimethane-5,5″-dily)) (PDTDMBBQ-Br)(4e), poly[(1′,4′-di(α-thienyl)-2′,5′-dioctoxylbenzene-5,5″-diyl)(*m*-bromobenzylidene)-*block*-(1′,4′-di(α-thienyl)-2′,5′-dimethylbenzenequinodimethane-5,5″-dily)] (PDTDOBBQ-Br)(4f), poly[(4′,4″-di(α-thienyl)-*p*-biphenyl-5,5‴)(*m*-bromobenzylidene-*block*-(4′,4″-di(α-thienyl)-*p*-biphenyl quinodimethane-5,5″-dily)) (PDTDBBQ-Br)(4h) were prepared by using the same procedure as PDTBBQ.

2.3. Measurements

FT-IR spectra were recorded on a Bruker Vector 22 IR spectrometer. ^{1}H NMR measurements were carried out on Advance DMX500, 500 MHz spectrometer (solvent: $CDCl_3$, internal standard: tetramethylsiliane). The elemental analyses were performed on ThermoFinnigan Instrument Flash EA1112. The molecular weights of polymers were obtained according to the elemental analyses. The UV–vis spectrum was recorded on a Varian Cary 100 Bio UV–vis spectrophotometer. Cyclic voltammetry was performed on a CHI440 Electrochemical Workstation. It was carried out in 0.1 M tetrabutylammonium perchlorate(TBAP)/dichloromethane, where the polymer concentration was 2–4 mg/mL, with platinum wires as both counter and working electrodes, and Ag/Ag^+ as a reference electrode. The ionization potential (IP) and electron affinity (EA) of the polymer solution were estimated using the following relations [20,21]: $[E_{on}]^{ox} = IP/e - 4.71$ and $[E_{on}]^{red} = EA/e - 4.71$, where e is the primary electron charge, the $[E_{on}]^{ox}$, $[E_{on}]^{red}$ are the onset potentials for the oxidation and reduction of polymers versus the reference electrode.

3. Results and discussion

As shown in Scheme 1, the polymers were prepared by the two-step synthetic routes, and the resulting polymers were obtained by dehydrogenation reaction of corresponding precursor polymers with DDQ in THF solution. Theoretically, 1 mol of a precursor polymer repeat unit requires 0.5 mol of DDQ to produce a completed dehydrogenated polymer unit. In experiment, we adopted 0.65 as the mole ratio of DDQ and precursor polymer repeat unit. The degree of dehydrogenation was determined from the integration peak of the methine hydrogen resonance in the ^{1}H NMR spectra [18]. Fig. 1 shows the ^{1}H NMR spectra of several polymers in $CDCl_3$. The characteristic methine hydrogen resonance at 5.7–5.9 ppm completely disappeared for PDTBBQ. But for PDTDMBBQ, PDTDOBBQ and PDTDBBQ, it still had little residue, which is due largely to the methine hydrogen of the polymer end groups that is still detectable by ^{1}H NMR in these low molecular weight polymers. So we could deduce that the precursor polymers almost have been successfully converted to the polymers by oxidative dehydrogenation. And ^{1}H NMR spectra of other polymers are the same as the above.

The molecular weights of polymers were calculated according to the elemental analyses. Table 1 shows the calculated molecular weights of some polymers. It was seen that such polymers were mostly oligomers, and the number of their average repeat units was not big.

Fig. 2 shows the optical absorption spectra of PDTBBQ, PDTDMBBQ, PDTDOBBQ and PDTDBBQ in THF. In the region of 250–1500 nm, these four polymers all have maximum absorptions among 300–400 nm, which could be assigned to the π–π* absorption bands of the aromatic heterocycle of polymer repeat units since they correspond to the same band in the precuror polymers. And the wavelength decreases from PDTDOBBQ (381 nm) to PDTBBQ (348 nm), PDTDBBQ (321 nm), PDTDMBBQ (314 nm). Except for PDTBBQ, other three polymers all have shoulder peaks in the visible region, which are assigned to the π–π* bandgap transition. And the relative absorption strength and wavelength decrease from PDTDOBBQ (588 nm) to PDTDBBQ (546 nm), PDTDMBBQ (516 nm). The corresponding absorption

Table 1
Molecular weights of several conjugated polymers calculated according to the element analysis

Polymers	Calculated molecular weights	Element analysis			
		Calcd		Found	
		C (%)	H (%)	C (%)	H (%)
PDTDOBBQ[a]	694.50	71.92	7.14	78.00	7.74
PDTDBBQ[a]	1114.70	76.47	4.36	75.05	4.31
PDTDOBBQ-Br[a]	1205.34	62.94	6.16	65.23	5.76
PDTDBBQ-Br[b]	936.17	63.56	3.57	63.71	3.43

[a] Calculated by the ratio of the contents of carbon and hydrogen.

[b] Calculated by the content of rest elements except carbon and hydrogen.

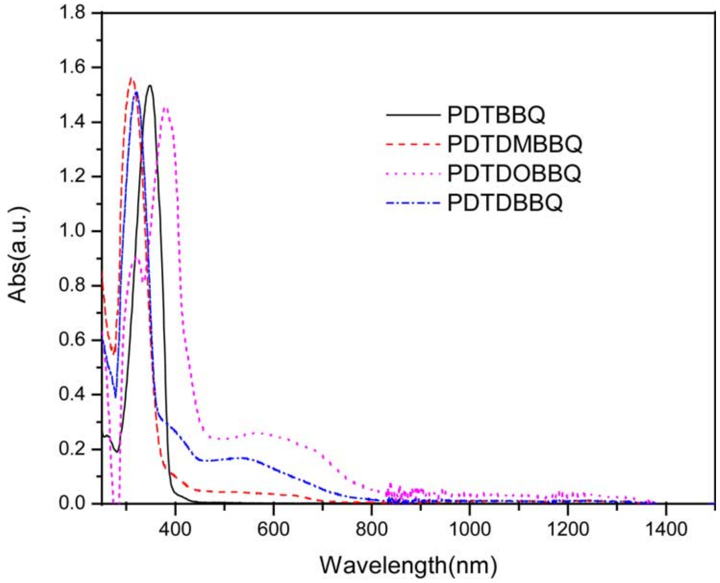


Fig. 2. Optical absorption spectra of PDTBBQ, PDTDMBBQ, PDTDOBBQ, PDTDBBQ in THF.

edges of the thin film spectrum and hence optical bandgaps are in the range of 657–1148 nm, decreasing from PDTDOBBQ (1148 nm, 1.08 eV) to PDTDBBQ (1017 nm, 1.22 eV), PDTDMBQ (788 nm, 1.57 eV), PDTBBQ (657 nm, 1.88 eV). It is seen that substituents of phenylene unit influence the optical absorption of polymers (Fig. 3). Although substituents have brought steric hindrance, effective conjugated length added with the increase of substituent chain length. And compared to PDTBBQ, the polymer, PDTDBBQ, has showed much more π-electron delocalization. Otherwise, for PDTBBQ-Br, PDTDMBBQ-Br, PDTDOBBQ-Br and PDTDBBQ-Br, their optical absorption spectra are similar to those above-mentioned (Fig. 4).

The electrochemical properties of the polymer solution were studied by cyclic voltammetry. The cyclic voltammograms (CVs) of these polymers are exemplified by the CV of PDTDOBBQ. Fig. 5 shows the CV of PDTDOBBQ solution in the potential range of +2.00 to −1.40 V. The peak potential (E_p) for electrochemical oxidation and reduction are not obvious. While the onset potentials (E_{on}) for electrochemical oxidation and reduction were observed at +0.54 and −0.62 V, respectively, which correspond to an ionization potential (IP) of 5.25 eV and an electron affinity (EA) of 4.09 eV. From the difference between IP and EA, the electrochemical band gap of PDTDOBBQ was calculated to be 1.16 eV. Relatively, it is higher than the optical band gap of the polymer. The electrochemical properties of other polymers are collected in Table 2. Deduced from sweep scope, the E_p values of the electrochemical oxidation of these polymers should exceed 1.50 V, but the E_p values of the electrochemical reduction of these polymers are about at 1.10 V. So such polymers have shown much more hole transport ability. And, it reveals that the electrochemical band gaps of these polymers have reduced with the increase of side length on the phenylene units, whose sequences are PDTDOBBQ < PDTDMBBQ < PDTBBQ, and PDTDOBBQ-Br < PDTDMBBQ-Br < PDTBBQ-Br. And the polymers with two phenylene units between two thiophene units have much lower band gap than those with one phenylene unit, such as PDTDBBQ < PDTBBQ, PDTDBBQ-Br < PDTBBQ-Br. The effects of substituents of phenylene units and numbers of phenylene units on the conjugated length are the same as those of optical absorption observations.

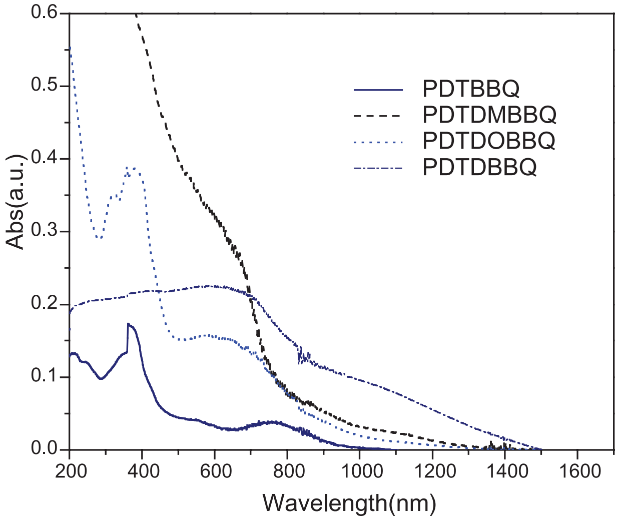


Fig. 3. Optical absorption spectra of thin film of PDTBBQ, PDTDMBBQ, PDTDOBBQ and PDTDBBQ on quartz glass substrate.

4. Conclusion

In conclusion, we have successfully synthesized a series

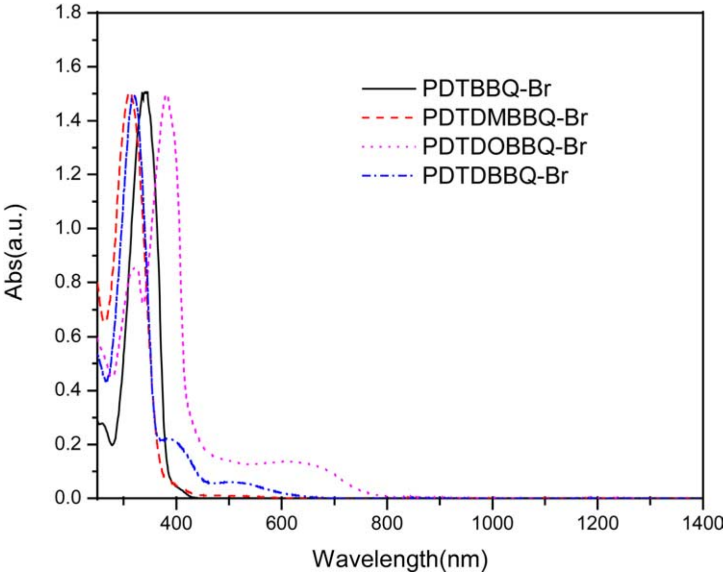


Fig. 4. Optical absorption spectra of PDTBBQ-Br, PDTDMBBQ-Br, PDTDOBBQ-Br and PDTDBBQ-Br in THF.

Table 2
Electrochemical properties of conjugated polymers

Polymers	Oxidation (vs Ag/Ag^+)			Reduction (vs Ag/Ag^+)			E_g (eV)
	E_{on} (V)	IP (eV)	E_p (V)	E_{on} (V)	EA (eV)	E_p (V)	
PDTBBQ	1.09	5.80	–	−0.81	3.90	−1.12	1.90
PDTDMBBQ	0.71	5.42	–	−0.80	3.91	−1.14	1.51
PDTDOBBQ	0.54	5.25	–	−0.62	4.09	−1.11	1.16
PDTDBBQ	0.68	5.39	–	−0.69	4.02	−1.15	1.37
PDTBBQ-Br	1.08	5.79	–	−0.93	3.78	−1.17	2.01
PDTDMBBQ-Br	0.84	5.55	–	−0.89	3.82	−1.11	1.73
PDTDOBBQ-Br	0.73	5.44	–	−0.68	4.03	−1.04	1.41
PDTDBBQ-Br	0.87	5.58	–	−0.78	3.93	−1.11	1.65

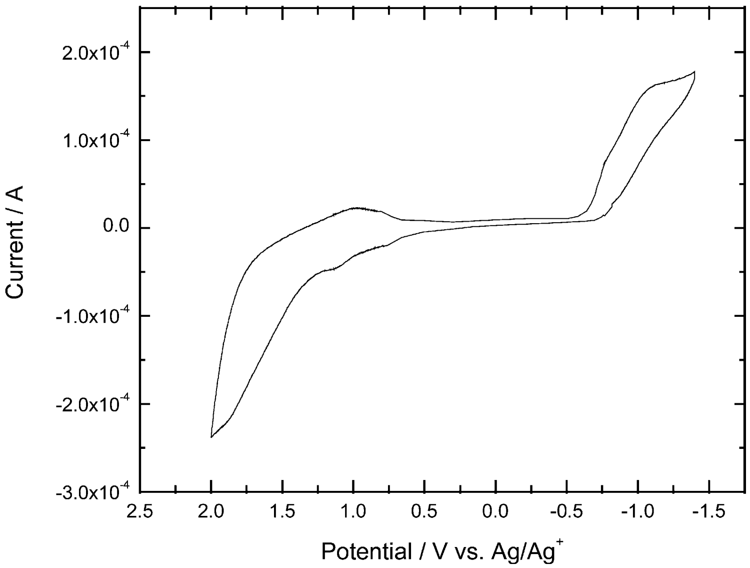


Fig. 5. Cyclic voltammogram of PDTDOBBQ at 100 mV s^{-1} in CH_2Cl_2+TBAP (0.1 M) from +2.00 to −1.40 V.

of conjugated poly(heteroarylene methines). These polymers are soluble in common organic solvents, such as chloroform, THF. By modifying conjugated backbone with the introduction of the rigid phenylene units between two thiophene units, we found that the optical and electrochemical properties of the conjugated poly(heteroarylene methines), were significantly modified by the size of side groups on phenylene units and the number of phenylene units on the phenylene–thiophene moieties. With the increase of substituent chain length on the phenylene units, the optical and electrochemical band gap of these polymers have gradually reduced, and the polymers shows much bigger conjugated length. And the polymers with two phenylene units between two thiophene units have much lower band gap than those with one phenylene unit. And for PDTDOBBQ, PDTDBBQ, PDTDOBBQ-Br, PDTDBBQ-Br, they could be seen as low band gap polymers.

Acknowledgements

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