3824 *Macromolecules* **1999,** *32,* 3824−3826

Thiophene-Linked Polyphenylquinoxaline: A New Electron Transport Conjugated Polymer for Electroluminescent Devices

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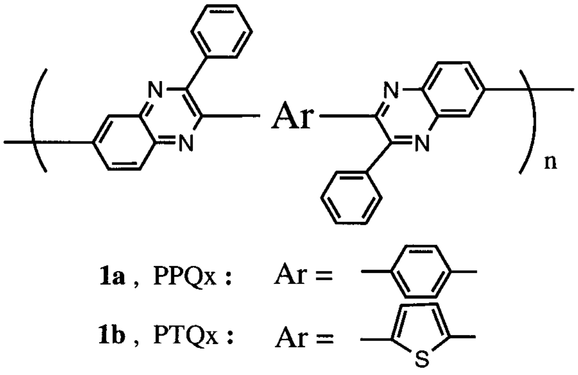
Received February 12, 1999
Revised Manuscript Received April 13, 1999

Electroluminescent semiconducting polymer devices are promising for display applications.[1] Because most current electroluminescent (EL) conjugated polymers inject and transport holes more efficiently than electrons,[1,2] synthesis of new and better electron transport (ET) polymers is needed to further improve device performance. n-Type conjugated polymers such as the polyquinolines,[3] polyquinoxalines,[4] polypyridine,[5] and polybenzobisazoles[6] have recently been demonstrated as ET layers in light-emitting diodes (LEDs). In this paper we report the synthesis of a new n-type, thiophene-linked, conjugated polyphenylquinoxaline (**1b**) and show that it is an excellent ET material for polymer LEDs. EL devices of the type ITO/poly(phenylenevinylene)/**1b**/Al were found to combine low turn-on voltage (3.6 V) and high brightness (710 cd/m^2 at 12 V) with good efficiency (0.4% photons/electron) under ambient air fabrication and operation. The preliminary results suggest that the new conjugated polyphenylquinoxaline is far superior as an electron transport material for EL devices compared to previously reported ET materials.[1−6]



1a , PPQx : Ar =

1b , PTQx : Ar =

We have previously shown that conjugated polyquinolines with diverse chain structures were good electron transport (n-type) materials whose highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels can be significantly varied.[7] The increased electron deficiency of the quinoxaline ring due to an additional imine nitrogen, compared to the quinoline ring, suggested that the LUMO levels of conjugated polyquinoxalines could be lower and perhaps improve electron transport properties. The well-known *p*-phenylene-linked polyphenylquinoxaline (**1a**, PPQx)[8] has already been reported to be an ET material for LEDs.[4] We synthesized and investigated the thiophene-linked derivative **1b**, poly[2,2′-(thiophene-2,5-diyl)-6,6′-bis(3-phenylquinoxaline)] (PTQx), to explore the feasible HOMO/LUMO level shifts due to its acceptor−donor-acceptor structure and their consequences for polymer/polymer heterojunction LED performance.

Monomer Synthesis. 2,5-Bis(phenylethynyl)thiophene (**2**) was synthesized according to the literature method.[9] Recrystallization from methanol afforded a yellow-brown product (90%), mp 84−86 °C (lit. 85 °C). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.18 (s, 2H), 7.41 (m, 6H), 7.58 (m,4H). 2,5-Bis(phenyloxoacetyl)thiophene (**3**): To a solution of **2** (2.84 g, 10 mmol) in 50 mL of dichloromethane was added 200 mg of Adogen 464 (Aldrich), 80 mL of water, 1.6 g of $NaHCO_3$, and 8 g of $KMnO_4$. After vigorous stirring at room temperature for 24 h, TLC indicated that the reaction was complete. Sodium bisulfite (14 g) and hydrochloric acid (6 mL) were slowly added to reduce excess oxidizing agents. After rotary evaporation of CH_2Cl_2, filtration, and recrystallization from ethanol, yellow needlelike crystals of **3** (65%) were obtained (mp 94−95 °C). MS (EI) 348 (calcd for $C_{20}H_{12}SO_4$), 348 (found). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (m, 4H), 7.70 (m, 2H), 7.83 (s, 2H), 8.10 (m, 4H). FT-IR (KBr, cm^{-1}): 1660, 1590, 1450, 1200, 1176, 790, 683, 652.

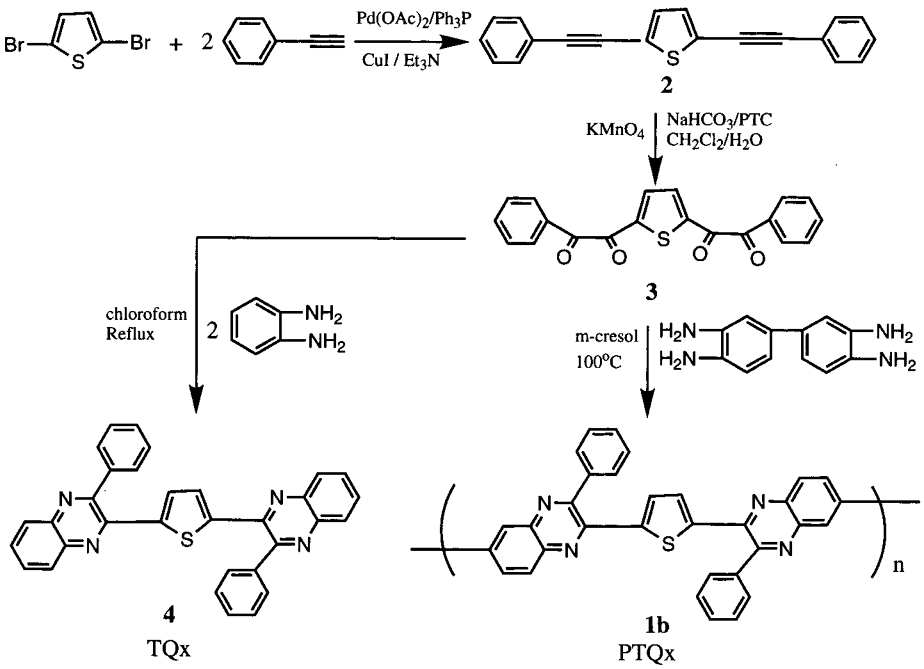
Oligoquinoxaline Synthesis. 2,2′-Bis(3-phenylquinoxaline)thiophene-2,5-diyl (**4**, TQx): A solution of monomer **3** (694 mg, 2 mmol) and 1,2-phenylenediamine (216 mg, 4 mmol) in 20 mL of chloroform was refluxed for 10 h. The crude product was recrystallized from ethanol to afford a yellow **4** (800 mg, 85%) (mp 312−314 °C). MS (EI) 492 (calcd for $C_{32}H_{20}N_4S$), 492 (found). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.53 (s, 2H), 7.55 (m, 6H), 7.68 (m, 4H), 7.83 (m, 4H), 8.20 (M, 4H). ^{1}H NMR (300 MHz, *d*-nitromethane/$GaCl_3$): δ 7.82, 7.90, 8.42, 8.50, 8.60.

Polymer Synthesis: PTQx (1b). Equimolar amounts of monomer **3** (694 mg, 2 mmol) and 3,3-diaminobenzidine (428 mg, 2 mmol) were dissolved in 8 mL of freshly distilled *m*-cresol in a glass reactor fitted with a mechanical stirrer, two gas inlets, and a sidearm. The reaction mixture was stirred under argon purge at 100 °C for 24 h during which progressive increase of the solution viscosity was observed. After cooling to room temperature the reaction mixture was poured into 100 mL of methanol, precipitating a red polymer product which was collected by suction filtration and continuously extracted with ethanol for 24 h. The product was vacuum-dried at 80 °C (95% yield): $[\eta] = 1.09$ dL/g in methanesulfonic acid (MSA) at 30 °C. ^{1}H NMR (300 MHz, *d*-nitromethane/$GaCl_3$): δ 7.80, 7.92, 8.65, 8.86, 9.10. FT-IR (KBr, cm^{-1}): 3030, 1620, 1530, 1480, 1345, 1185, 1020, 800, 700, 600.

Results. The new tetraketone **3** was synthesized and used to prepare oligomer **4** and thiophene-linked conjugated poly(phenylquinoxaline) **1b** (Scheme 1). ^{1}H NMR spectra of the oligomer in both $CDCl_3$ and *d*-nitromethane/$GaCl_3$ and that of the polymer PTQx in the latter solvent allowed the ready assignment of the proton resonances to the polymer structure. The onset of thermal decomposition under nitrogen in thermogravimetric analysis (TGA) was 580 °C. No phase transition was observed in differential scanning calorimetry (DSC) in repeated scans up to 300 °C, suggesting that the glass transition of the polymer is high.[4,8] PTQx was completely soluble in formic acid (red), *m*-cresol (red), MSA (blue), and nitromethane/$GaCl_3$, but

10.1021/ma9901994 CCC: $18.00

Scheme 1



it was only partially soluble in chloroform or tetrahydrofuran. A sample of PPQx (**1a**) synthesized[8] for comparison with PTQx had similar solubility characteristics except that it was also soluble in chloroform (yellow solution).

The intrinsic viscosity of PTQx (1.09 dL/g) was smaller than that of PPQx (1.43 dL/g) even though the thiophene-linked polymer had better film-forming properties. The reason for this difference is likely because the thiophene-linked polymer chain is more flexible compared to the 1,4-phenylene-linked PPQx. Early work on PPQx with an intrinsic viscosity of 2.62 dL/g also reported a $\bar{M}_w$ value of 350 000.[8a] Thus, the measured intrinsic viscosity of the present polymers reflects moderate molecular weights.

Oligoquinoxaline **4** solutions in $CHCl_3$ and formic acid had absorption maxima (λ_{max}) of 405 nm ($\log \epsilon = 4.69$) and 448 nm ($\log \epsilon = 4.75$), respectively. The corresponding emission maxima in the same solvents were 471 and 574 nm, respectively. Surprisingly, the solution absorption and emission spectra of PTQx were only moderately red-shifted from those of the oligomer. The absorption λ_{max} of PTQx in $CHCl_3$ and formic acid were 414 nm ($\log \epsilon = 4.64$) and 446 nm ($\log \epsilon = 4.80$), respectively. The emission maxima of PTQx in these two solvents were 522 and 603 nm, respectively. These spectral properties of PTQx and its oligomer **4** can be understood in terms of *intramolecular charge transfer* (ICT) between the electron-accepting phenylquinoxalines and electron-donating thiophene moiety within the polymer repeat unit.[7,10] The remarkable similarity of the absorption λ_{max} of oligoquinoxaline TQx and the conjugated polymer PTQx in formic acid arises from the dominant role of ICT when the quinoxaline rings are protonated and hence are stronger electron acceptor moieties.

The optical absorption and photoluminescence (PL) spectra of the PTQx thin film are shown in Figure 1. The $\pi-\pi^*$ absorption maximum at 434 nm (2.86 eV) in the thin film is red-shifted from that in chloroform solution (414 nm, 3.0 eV). A solid-state optical band gap (E_g^{opt}) of 2.41 eV was obtained from the optical absorption edge (Figure 1). The solid-state PL emission spectrum (430 nm excitation) shown in Figure 1 has a peak at 536 nm with a vibronic shoulder at 580 nm. The very poor fluorescence efficiency ($<10^{-2}$%) of the PTQx thin film and the moderate Stokes shift (0.55 eV) suggests excimer emission[11] as its origin although ICT may also contribute to the rather low PL quantum yield.

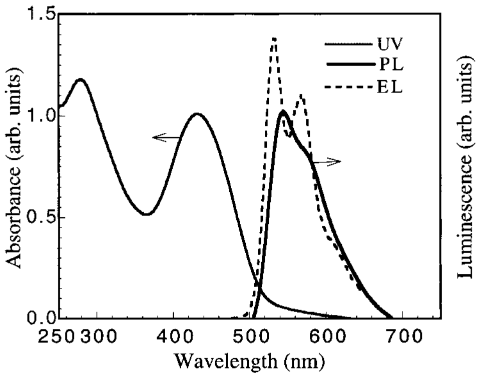


Figure 1. Optical absorption and PL spectra of PTQx thin film and electroluminescence spectrum of an ITO/PPV (35 nm)/PTQx (40 nm)/Al LED at a bias of 4 V.

Cyclic voltammetry of PTQx thin films revealed a reversible reduction and an irreversible oxidation waves. The formal potential $E^{0'}$ for the reduction was −1.60 V (versus SCE), and the onset reduction potential was −1.40 V. The oxidation had an onset potential of 1.14 V and a peak at 1.38 V. From these redox data we estimated an electrochemical band gap ($E_g^{el} = E_{onset}^{ox} - E_{onset}^{red}$) of 2.54 eV, an electron affinity ($EA = E_{onset}^{red} + 4.4$) of 3.0 eV, and an ionization potential ($IP = E_{onset}^{ox} + 4.4$) of 5.54 eV. We note that these EA and IP estimates are based on using the SCE energy level of −4.4 eV below the vacuum level;[7a] others[4] have used SCE energy levels as low as −4.8 eV, which would increase the EA value of PTQx to 3.4 eV. Even the conservative EA value of 3.0 eV is still quite large, which in conjunction with the reversible reduction suggests that PTQx is a good n-type conjugated polymer with potential for application

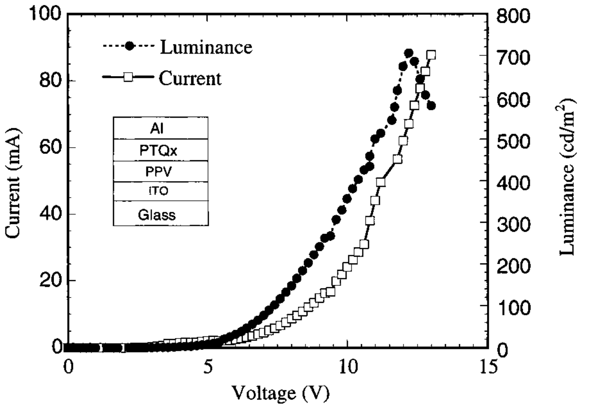


Figure 2. Current–voltage and luminance–voltage curves of an ITO/PPV (35 nm)/PTQx (40 nm)/Al LED. Inset shows the schematic device structure.

as an electron injection and transport layer in EL devices.

We fabricated polymer/polymer heterojunction LEDs of the form ITO/PPV (35 nm)/PTQx (40 nm)/Al to evaluate the potential of PTQx as an electron transport material for EL devices. The poly(*p*-phenylenevinylene) (PPV) thin film was spin-coated onto ITO-coated glass from a sulfonium precursor in methanol solution followed by standard procedures (thermal conversion at 250 °C for 1.5 h).[1] The PTQx thin film was spin-coated from its formic acid solution (1 wt %) onto the PPV layer and dried at 80 °C in a vacuum. The EL spectrum from the PPV/PTQx heterojunction device at a bias voltage of 4 V is also shown in Figure 1. The EL spectrum with vibronic peaks at 532 and 568 nm is identical to the PL spectrum of PPV, the EL spectrum of a single-layer ITO/PPV/Al device, and other reported PPV EL spectra.[1]

The current–voltage and luminance–voltage characteristics of the ITO/PPV(35 nm)/PTQx (40 nm)/Al LED are shown in Figure 2. The turn-on voltage of the device is 3.6 V, which is much less that the 7 V observed for the single-layer ITO/PPV/Al device. The substantially lowered turn-on and drive voltages of the PPV/PTQx diode (Figure 2) show that the new thiophene-linked conjugated poly(phenylquinoxaline) is a good electron-injecting and electron transport material for PPV-based EL devices.[1] The maximum luminance of the PPV/PTQx diode is 710 cd/m^2, at a current density of 400 mA/cm^2 and a drive voltage of 12 V, which is about 40 times as bright as the single-layer PPV diode. The corresponding maximum EL efficiency was 0.4% photons/electron, which is significantly enhanced compared to 0.01% for the single-layer PPV diode. Although comparative PPV/PPQx bilayer LEDs had a similar 3.6 V turn-on voltage, the maximum luminance achieved under similar conditions was only 80 cd/m^2, which means that PTQx is far superior as an electron transport material compared to existing poly(phenylquinoxaline)s.[4,8] In fact, the present PPV/PTQx LEDs are also significantly improved compared to previously reported devices of PPV/poly(phenylquinoxaline)s,[4] PPV/polypyridine,[5] and PPV/polyquinolines.[3]

Several factors may account for the observed good performance of PPV/PTQx diodes and particularly PTQx thin films as ET layers. The ready reversible electrochemical reduction of PTQx and its high electron affinity suggest efficient electron injection and transport to the PPV/PTQx interface. The HOMO/LUMO levels of PTQx (5.54/3.0 eV) relative to PPV (5.11/2.71 eV)[7a] ensure that there are energy barriers to electrons and holes at the interface where injection of electrons could control recombination. Absence of evidence of exciplex formation[11] or energy transfer at the heterojunction is also beneficial. Its high thermal stability, high intrinsic viscosity (molecular weight), and good amorphous film-forming properties are additional beneficial factors.

Summary. New thiophene-linked conjugated polyquinoxaline PTQx and oligoquinoxaline TQx have been synthesized and characterized. Comparison of their electronic absorption spectra revealed the dominant role of intramolecular charge transfer in their electronic structures and properties. PTQx has a reversible electrochemical reduction and high electron affinity and ionization potential which make it an attractive n-type conjugated polymer. Evaluation of PTQx as an electron transport material for PPV-based light-emitting devices showed that it was far superior to previous ET materials.

Acknowledgment. This work was supported by the Office of Naval Research and the National Science Foundation (CHE-9120001, CTS-9311741).

Supporting Information Available: UV–vis absorption spectra of TQx and ^{1}H NMR spectra of PTQx and TQx in various solvents, cyclic voltammogram of PTQx in acetonitrile, and current–voltage and luminance–voltage plots of ITO/PPV/PPQx/Al and ITO/PPV/Al devices. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA9901994