

Synthesis of a novel fluorescent and ion sensitive monomer bearing quinoxaline moieties and its electropolymerization

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ABSTRACT

A novel terthienyl based fluorescent polymer bearing pendant quinoxaline moieties directly attached to the 3-positions of the central thiophene ring was synthesized by electrochemical polymerization of 4-((2,5-dithiophen-2-yl)thiophen-3-yl)pyrrolo[1,2-a]quinoxaline (**TT-Q**). The corresponding polymer was characterized by cyclic voltammetry, FT-IR and UV-vis spectroscopy. The polymer exhibits a reversible redox behavior ($E_p^{1/2} = 1.05$ V) accompanied with a reversible electrochromic behavior; yellowish orange in the neutral state and green in the oxidized state. Band gap of polymer was found ($E_g = 1.94$ eV). Moreover, the sensitivity of both the monomer and its polymer towards metal cations was investigated by monitoring the change in the fluorescence intensity. Among various common ions, both the monomer and its polymer were found to be selective towards Fe^{3+} ions by quenching the fluorescence efficiency with a Stern–Volmer constant (K_{sv}) of ($2.7 \times 10^3 M^{-1}$) and ($5.0 \times 10^3 M^{-1}$) for monomer and polymer solutions, respectively.

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1. Introduction

Quinoxalines are interesting functional materials due to their fluorescence properties with high quantum yields. The interest on these materials lies not only on the fact that they can be utilized as fluorescence probes in some chemosensors [1] but also their potential use in high technology applications including light emitting devices and solar cells [2–5]. Some quinoxaline derivatives are able to coordinate to various anionic species [6,7], and therefore they can be used as metal ion chelators [8–10]. In some cases, these applications might require the integration of quinoxaline moieties into a polymer matrix. Therefore, it might be interesting to incorporate the quinoxaline moiety as a pendant group to a conjugated polymer chain. Among conjugated polymers, polythiophenes are widely used because of their environmental stability and good electrical and optical properties [11]. Furthermore, the relative easiness of their functionalization makes polythiophenes attractive in the field of molecular tailoring for the desired properties [12]. Although there exists a large number of reports related to the electrochemical or chemical polymerization of various substituted thiophene derivatives, thiophene oligomers are also employed to avoid overoxidation of polythiophene [13,14]. The use of thiophene oligomers, in the form of dimeric and trimeric precursors, which has been developed by Reynolds and coworkers

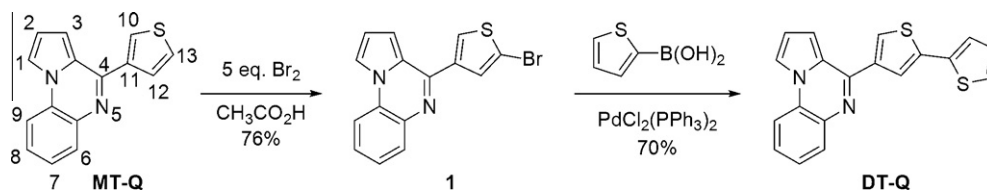
[15,16], brings the advantage of tuning the optoelectronic properties of the polymer. When the trimeric precursor contains donor and acceptor substituents in an alternating manner, the photovoltaic and electrochromic properties are greatly affected [17].

Conjugated polymers with alternating donor–acceptor repeating units have been widely studied to tailor the photovoltaic and electrochromic properties of the polymers [18–21]. Combining a strong donor with a strong acceptor not only lowers the band gap, but also increases the possible redox states for the conjugated polymer. Thus, the resulting hybrid material will exhibit multiple redox states in a small potential range. In 2004, Sonmez and his coworkers were able to synthesize neutral state green polymer via electrochemical polymerization of a precursor monomer obtained by combining electron rich and electron poor units [22]. Algi and Cihaner investigated the effect of donor and acceptor units on the intrinsic properties of polymer by using Se or S containing acceptor unit together with a thiophene or thiophene based donor unit [23].

Quinoxalines, due to presence of two unsaturated nitrogen atoms, have high electron affinities and are strong acceptor groups. This property together with their thermal stability makes quinoxalines as an attractive candidate for the synthesis of low band gap polymers [5,24]. Due to their high electron affinities, they are also promising electron transport materials in multilayer organic light emitting devices [26,27] and several copolymers containing quinoxalines either in the main chain or as pendant groups on the main chain has been reported [25–31]. Quinoxaline containing polymers prepared via condensation reaction were first used as heat and

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Scheme 1. Synthetic route of 4-((5-thiophen-2-yl)thiophen-3-yl)pyrrolo[1,2-a]quinoxaline (**DT-Q**).

chemical resistant materials and applied later in polymer light emitting devices [32,33]. Karastatis et al. investigated the photo-physical and emissive properties of poly(*p*-phenylene) derivatives containing quinoxaline moieties and reported that these materials exhibit greenish-yellow electroluminescence [6]. Thermal and optical properties of 2,7-carbazole and quinoxaline based alternating copolymers were investigated by Morin and Leclerc [31] and the low band gap of quinoxaline containing copolymer was attributed to the strong intramolecular interaction between donor and acceptor groups.

Herein, we present our results concerning the synthesis and characterization of new fluorescent materials; 4-(thiophen-3-yl)pyrrolo[1,2-a]quinoxaline (**MT-Q**), 4-((5-thiophen-2-yl)thiophen-3-yl)pyrrolo[1,2-a]quinoxaline (**DT-Q**) and 4-((2,5-dithiophen-2-yl)thiophen-3-yl)pyrrolo[1,2-a]quinoxaline (**TT-Q**) (Scheme 1). Among them, the polymerization of **TT-Q** was feasible by electrochemical means to give poly(4-((2,5-dithiophen-2-yl)thiophen-3-yl)pyrrolo[1,2-a]quinoxaline, **P(TT-Q)**). Furthermore, the fluorescence properties of both the monomer and its polymer were investigated in dimethylformamide (DMF). The effect of various metal cations on the fluorescence intensity was also determined.

2. Experimental

All chemicals were purchased from Aldrich Chemical and used as received. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) dissolved in dichloromethane (DCM) was used as electrolyte solution. Cyclic voltammetry (CV) was performed in a three-electrode cell equipped with a platinum (0.02 cm²) working electrode, a platinum wire counter electrode and Ag/AgCl in 3 M NaCl(aq) solution as a reference electrode. Repetitive cycling or constant potential electrolysis was used to obtain the polymer films. For electro-optical studies, platinum and silver (calibrated externally using 5 mM solution of ferrocene/ferrocenium couple) wires were used as counter and reference electrodes, respectively.

An indium-tin oxide (ITO, Delta Tech. 8–12 Ω, 0.7 cm × 5 cm) coated by the polymer film was used as the working electrode. Prior to spectroelectrochemical investigations, the polymer films were switched between neutral and doped states several times in order to equilibrate its redox behavior in monomer-free electrolytic solution. Electroanalytical measurements were performed using a Gamry PCI4/300 potentiostat–galvanostat. The electro-optical spectra were monitored on a Hewlett–Packard8453A diode array spectrometer. FT-IR spectra were recorded on Nicolet 510 FT-IR with an attenuated total reflectance (ATR). NMR spectra were recorded on a Bruker NMR Spectrometer (DPX-400) in CDCl₃, and fluorescence measurements were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer. The quenching experiments were performed by successive additions of metal ions (each 2–10 mM) to the solution of **TT-Q** (1.0 × 10^{−5} M) and **P(TT-Q)** in DMF at room temperature, and the fluorescence spectra were measured after excitation at 350 and 500 nm, respectively. Photographs of the monomer and polymer solutions films were taken by using a Canon digital camera.

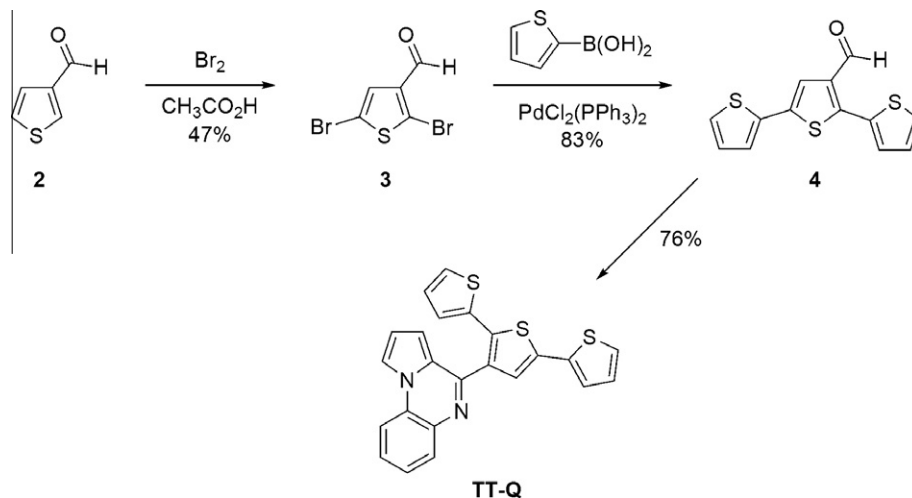
2.1. Synthesis of monomers, **MT-Q**, **DT-Q** and **TT-Q**

2.1.1. 4-(Thiophen-3-yl)pyrrolo[1,2-a]quinoxaline (**MT-Q**)

This compound was synthesized from 1-(2-aminophenyl)pyrrole and thiophene-3-carboxaldehyde according to known procedure [34]. ¹H NMR (400 MHz, CDCl₃): δ 8.08 (dd, *J* = 2.9 Hz, *J* = 1.0 Hz, 1H, H-1), 8.02 (dd, *J* = 7.8 Hz, *J* = 1.4 Hz, 1H, H-9), 7.98 (s, 1H, H10), 7.85 (m, 2H, H-6 and H-12), 7.50 (m, 3H, H-7, H-8 and H-13), 7.12 (dd, *J* = 4.0 Hz, *J* = 1.0 Hz, 1H, H-3), 6.91 (dd, *J* = 3.9 Hz, *J* = 2.8 Hz, 1H, H-2). ¹³C NMR (100 MHz, CDCl₃): δ 149.4, 140.3, 136.2, 130.2, 128.2, 127.6, 127.3, 126.7, 126.1, 129.5, 129.4, 114.8, 114.2, 113.8, 108.3.

2.1.2. 4-(5-Bromothiophen-3-yl)pyrrolo[1,2-a]quinoxaline (**1**)

To a solution of 4-(thiophen-3-yl)pyrrolo[1,2-a]quinoxaline (**MT-Q**) (100 mg, 0.4 mmol) in 10 ml of glacial acetic acid was



Scheme 2. Synthetic route of 4-((2,5-dithiophen-2-yl)thiophen-3-yl)pyrrolo[1,2-a]quinoxaline (**TT-Q**).

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