Reactive & Functional Polymers 71 (2011) 579–587

Contents lists available at ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

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

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ARTICLE INFO

Article history:
Received 30 July 2010
Received in revised form 27 January 2011
Accepted 27 February 2011
Available online 5 March 2011

Keywords:
Quinoxaline
Electrochemical polymerization
Fluorescent polymer
Electrochromics
Ion sensitivity

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 ($Ep^{1/2} = 1.05$ 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 (2.7×10^3 M^{-1}) and (5.0×10^3 M^{-1}) for monomer and polymer solutions, respectively.

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]. Algı 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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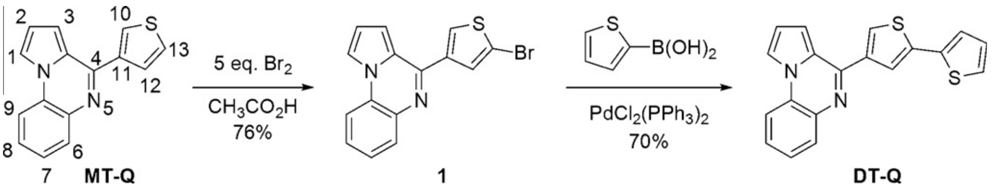
doi:10.1016/j.reactfunctpolym.2011.02.008



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]. Karastatiris et al. investigated the photophysical and emissive properties of poly(p-phenylene) derivatives containing quinoxaline moieties and reported that these materials exhibits 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 (TBAPF$_6$) 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 cm^2) 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 CDCl$_3$, 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.

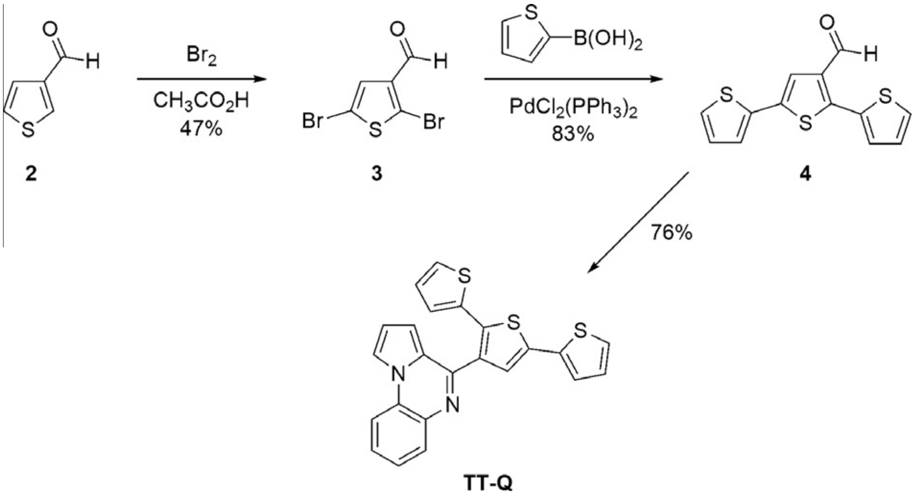
2.1. Synthesis of monomers, *MT-Q*, *DT-Q* and *TT-Q*

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]. ^{1}H NMR (400 MHz, CDCl$_3$): 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). ^{13}C NMR (100 MHz, CDCl$_3$): 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**).

added dropwise a solution of bromine (320 mg, 0.103 ml, 2 mmol) at room temperature. The mixture was warmed and stirred at 60 °C. When reaction was over, the mixture was poured into cold water and extracted with ethyl acetate. Organic phase was washed two times with Na_2SO_3, and then dried with $MgSO_4$. After the filtration, the solvent was removed on a rotary evaporator and the residue was purified by flash chromatography over silica gel eluting with hexane/ethyl acetate (9:1, v/v) to give a solid identified as 4-(5-bromothiophen-3-yl)pyrrolo[1,2-a]quinoxaline (**1**) (100 mg, 76%). ^1H NMR (400 MHz, $CDCl_3$): δ 9.27 (m, 1H, H-10), 8.05 (m, 1H, H-9), 8.00 (dd, $J = 2.9$ Hz, $J = 1.2$ Hz, 1H, H-1), 7.73 (dd, $J = 5.0$ Hz, $J = 1.2$ Hz, 1H, H-6), 7.48 (m, 3H, H-7, H-8 and H-12), 7.09 (d, $J = 4.3$ Hz, 1H, H-3), 6.89 (d, $J = 4.3$ Hz, 1H, H-2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 139.0, 137.0, 130.1, 128.4, 128.2, 127.4, 127.0, 126.5, 126.3, 126.1, 119.5, 115.4, 109.5, 99.9.

2.1.3. 4-((5-Thiophen-2-yl)thiophen-3-yl)pyrrolo[1,2-a]quinoxaline (DT-Q)

To a solution of 4-(5-bromothiophen-3-yl)pyrrolo[1,2-a]quinoxaline (**1**) (100 mg, 0.3 mmol), 2-thienylboronic acid (46 mg, 0.36 mmol) and $KHCO_3$ (42 mg, 0.42 mmol) in a round-bottomed flask in 4:1 DMF/H_2O (4 ml) was added $PdCl_2(PPh_3)_2$ (21 mg, 0.03 mmol). The solution was stirred for 5 min at room temperature and then heated to 100 °C until TLC revealed complete conversion of the starting material. The mixture was concentrated under reduced pressure and the resulting crude product was purified by flash chromatography over silica gel eluting with hexane/ethyl acetate (9:1, v/v) to give a solid assigned as 4-((5-thiophen-2-yl)thiophen-3-yl)pyrrolo[1,2-a]quinoxaline (**DT-Q**) (71 mg, 70%). Synthetic route for the **DT-Q** synthesis is given in Scheme 1. ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (dd, $J = 2.9$ Hz, $J = 1.2$ Hz, 1H, H-1), 8.03 (dd, $J = 8.1$ Hz, $J = 1.4$ Hz, 1H, H-9), 7.83 (dd, $J = 5.0$ Hz, $J = 1.2$ Hz, 1H, thiophenès H), 7.58 (dd, $J = 5.1$ Hz, $J = 1.2$ Hz, 1H, thiophenès H), 7.51 (m, 2H, H-6 and H-7), 7.41 (td, $J = 7.7$ Hz, $J = 1.3$ Hz, 1H, H-8), 7.25 (m, 4H, H-3 and thiophenès H), 6.94 (d, $J = 4.1$ Hz, 1H, H-2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 140.0, 137.4, 134.8, 130.3, 129.7, 129.2, 128.3, 128.2, 128.1, 127.7, 127.2, 126.7, 126.1, 125.4, 124.4, 118.9, 116.1, 108.2.

2.1.4. Synthesis of trithiophene-quinoxaline monomer (TT-Q)

2.1.4.1. 2,5-dibromothiophene-3-carbaldehyde (3). This compound was prepared from 3-thiophenecarboxaldehyde (**2**) according to

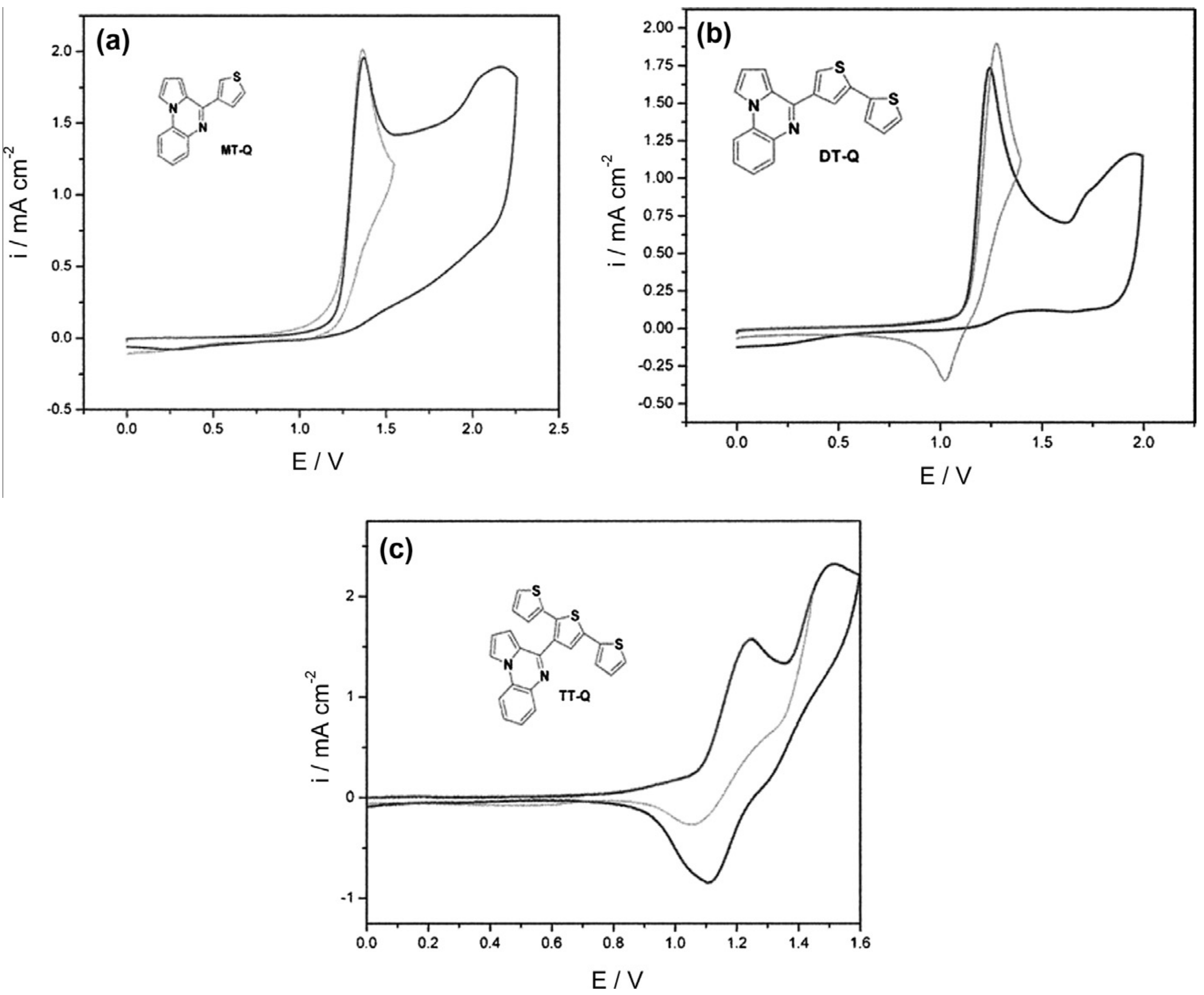


Fig. 1. Cyclic voltammogram comparison of oxidation potentials of **(a) MT.Q**, **(b) DT-Q** and **(c) TT-Q** on a Pt disc electrode at 100 mV s^{-1} in 0.1 M TBAPF$_6$/acetonitrile (dashed curve: peak clipping after the first oxidation potentials of **MT.Q**, **DT-Q** and **TT-Q**).

a literature procedure (350 mg, 47%) [35]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 7.34 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 183.2, 139.3, 128.7, 124.2, 113.4.

2.1.4.2. [2,2′;5′,2″]-Terthiophene-3′-carbaldehyde (4). To a solution of the 2,5-dibromothiophene-3-carbaldehyde (**3**) (100 mg, 0.37 mmol), 2-thienylboronic acid (46 mg, 0.36 mmol) and $KHCO_3$ (51.8 mg, 0.52 mmol) in a round-bottomed flask in 4:1 DMF/H_2O (2 ml) was added $PdCl_2(PPh_3)_2$ (26 mg, 0.037 mmol). The solution was stirred for 5 min at room temperature and then heated to 100 °C until TLC revealed complete conversion of the starting material. The mixture was concentrated under reduced pressure and the resulting crude product was purified by flash chromatography over silica gel eluting with hexane/ethyl acetate (19:1, v/v) to give a solid identified as [2,2′;5′,2″]-terthiophene-3′-carbaldehyde (**4**) (86 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.1 (s, 1H), 7.56

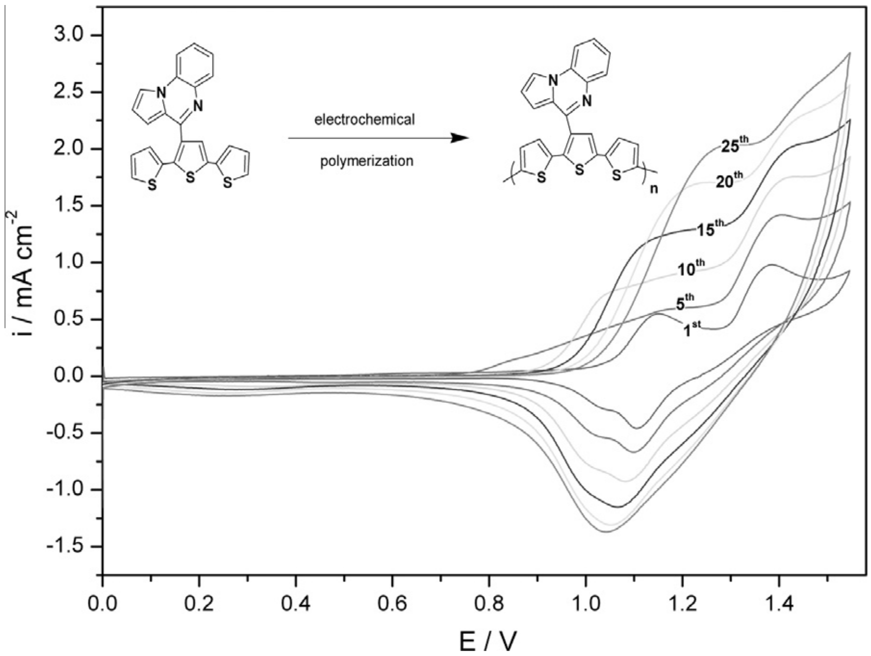


Fig. 2. Repeated potential scan electropolymerization of 2 mM **TT-Q** on a Pt disc electrode at 100 mV s^{-1} in 0.1 M $TBAPF_6$/DCM.

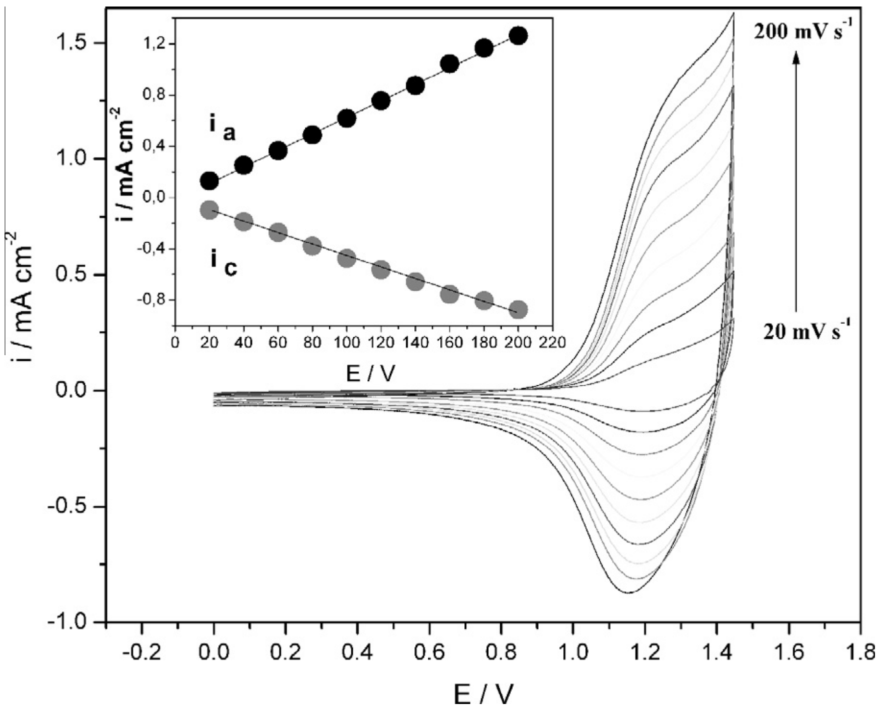


Fig. 3. Scan rate dependence of **P(TT-Q)** film (25 mC/cm^2) on a Pt disc electrode in 0.1 M $TBAPF_6$/DCM at different scan rates between 20 mV/s and 200 mV/s. (Inset: Relationship of anodic (I_a) and cathodic (I_c) current peaks as a function of scan rate).

(s, 1H), 7.49 (dd, $J = 5.1$ Hz, $J = 1.1$ Hz, 1H), 7.30 (m, 2H), 7.21 (dd, $J = 3.62$ Hz, $J = 1.1$ Hz, 1H), 7.15 (dd, $J = 5.2$ Hz, $J = 3.7$ Hz, 1H), 7.04 (dd, $J = 5.1$ Hz, $J = 3.7$ Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 185.2, 146.1, 137.8, 136.9, 135.7, 132.2129.4, 128.9, 128.5, 128.2, 125.9, 125.1, 122.5.

2.1.4.3. 4-((2,5-Dithiophen-2-yl)thiophen-3-yl)pyrrolo[1,2-a]quinoxaline (TT-Q). This compound was synthesized from [2,2′;5′,2″]-terthiophene-3′-carbaldehyde (**4**) according to known literature procedure [23]. Synthetic route for the **TT-Q** synthesis is given in Scheme 2. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (dd, $J = 7.8$ Hz, $J = 1.2$ Hz, 1H, H-9), 7.96 (m, 1H, H-1), 7.90 (d, $J = 8.0$ Hz, 1H, H-6), 7.55 (m, 2H, H-7 and H-8), 7.50 (s, 1H, thiophenès H), 7.29 (m, 3H, thiophenès H), 7.14 (d, $J = 5.2$ Hz, 1H, thiophenès H), 7.08 (m, 1H, H-3), 6.90 (dd, $J = 5.1$ Hz, $J = 3.8$ Hz, 1H, thiophenès H), 6.82 (m, 1H, H-2), 6.76 (m, 1H, thiophenès H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 150.3, 136.6, 135.9, 135.7, 135.2, 135.0, 134.9, 130.2, 128.3, 127.9, 127.8, 127.5, 127.1, 126.8, 126.33, 126.3, 125.8, 125.4, 125.0, 114.6, 114.1, 113.8, 108.7.

3. Results and discussion

3.1. Electrochemical polymerization of *TT-Q*

First of all, the redox behaviors of three different thiophene derivatives (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**)) were investigated by CV in 0.1 M $TBAPF_6$ dissolved in acetonitrile and the results are depicted in Fig. 1. The voltammogram of **TT-Q** exhibited one reversible oxidation peak at about 1.10 V and another irreversible peak at 1.30 V vs Ag/AgCl during the first anodic scan. Due to high electron affinity, the reversible peak most probably corresponds to the loss of electron from quinoxaline moiety. On the other hand, the irreversible peak at 1.30 V was assigned to oxidation of terthienyl system. A close inspection of Fig. 1a–c, clearly indicates that the irreversible peak shifts to more positive potentials with decreasing number of thiophene groups in the monomer. These results were in well agreement with

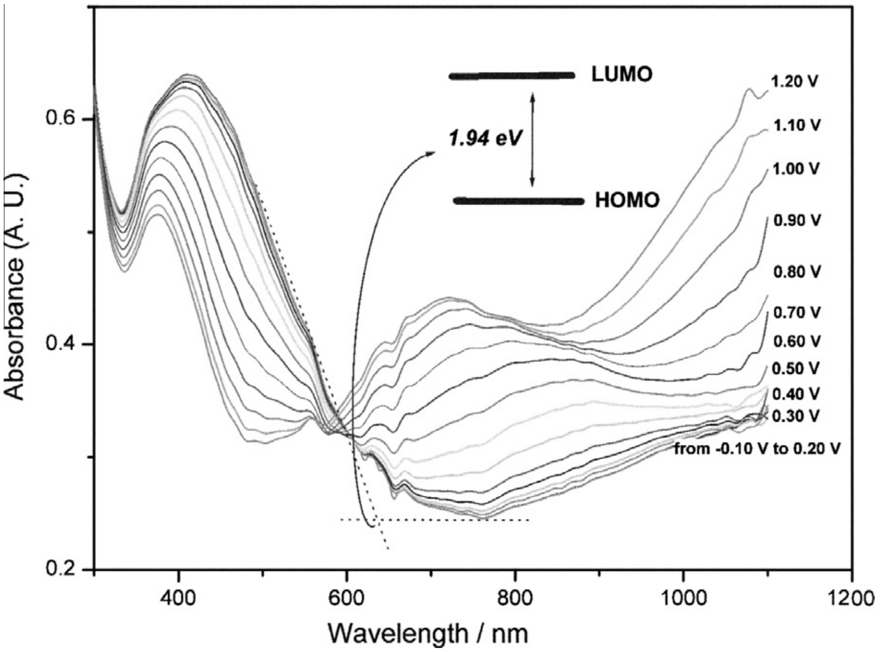


Fig. 4. Electronic absorption spectra of **P(TT-Q)** on ITO (25 mC/cm^2) in 0.1 M $TBAPF_6$/DCM solution during anodic oxidation of the polymer film.

Table 1
Voltammetric and spectroelectrochemical data for **P(TT-Q)** recorded in DCM containing 0.1 M $TBAPF_6$.

λ/nm at charge 25 mC/cm^2	$T_{bleached}$	$T_{colored}$	Δ%T	ΔOD	CE (cm^2/C)	Reduced state	Oxidized state
412	39.40	47.20	7.41	0.0784	114		
732	77.21	68.18	6.51	0.054	123		
1043	45.32	73.5	26.79	0.2017	426		

the electronic nature of each monomer: the oxidation potential was shifted to lower positive values with increasing π-conjugation [36].

Next, we focused on the electropolymerization of **MT-Q**, **DT-Q** and **TT-Q** monomers in dichloromethane (DCM) containing 0.1 M $TBAPF_6$ as supporting electrolyte via potential cycling. During repetitive anodic scans of **TT-Q** monomer, in the range of 0.00–1.55 V, a new reversible redox couple appeared at about 1.00 V. An increase in the current intensities of this new redox couple was also noted (Fig 2), indicating both the formation of an electroactive **P(TT-Q)** polymer film on the surface of the Pt disc working electrode and also an increase in the thickness of the polymer film. However, in the case of monomers **MT-Q** and **DT-Q**, no new redox couple with increasing intensity and no polymer film

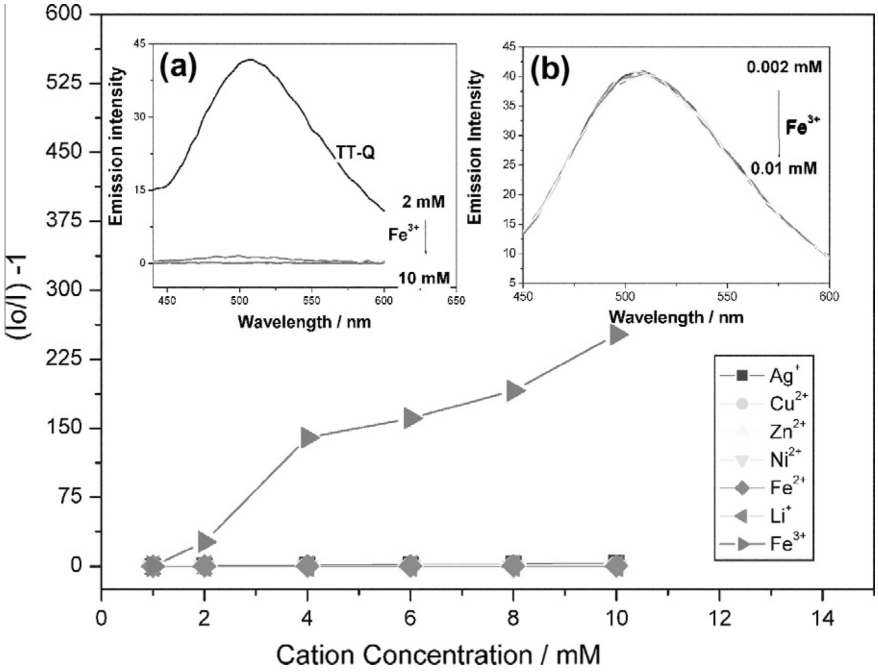


Fig. 5. The Stern–Volmer plots of **TT-Q** 1.0×10^{-5} M in the presence of various metal ions (each 2–10 mM). Metal ion solutions were prepared from $Fe(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $LiClO_4$, ferrocene and $AgNO_3$ in DMF. (Inset: The fluorescence emission spectra of **TT-Q** 1.0×10^{-5} M in DMF with successive addition of **(a)** 2–10 mM, **(b)** 2.0×10^{-3} to 10.0×10^{-3} mM Fe^{3+} ions. The excitation wavelength is 350 nm for **TT-Q.**

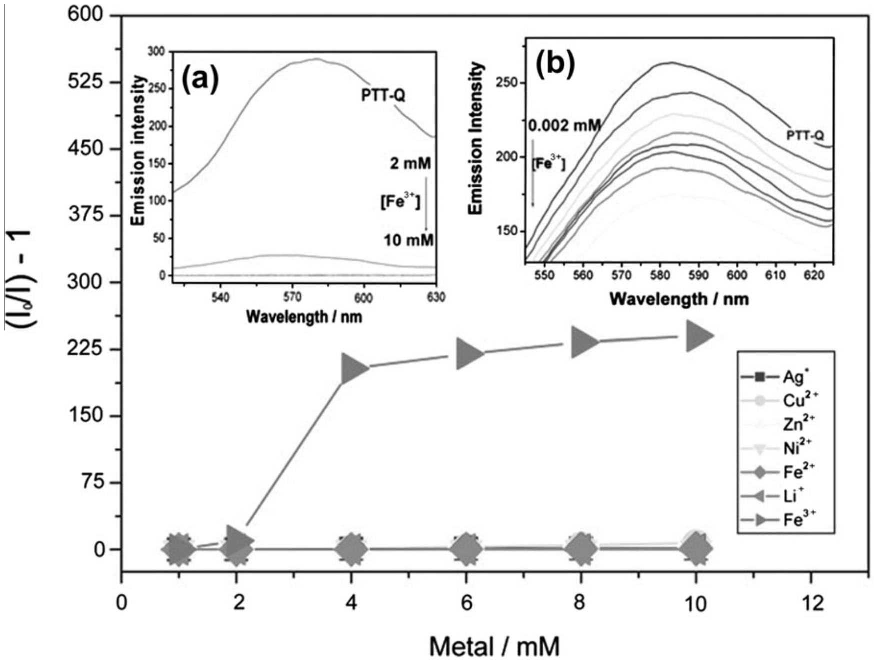


Fig. 6. The Stern–Volmer plots of **P(TT-Q)** in the presence of various metal ions (each 2–10 mM). Metal ion solutions were prepared from $Fe(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $LiClO_4$, ferrocene and $AgNO_3$ in DMF. (Inset: The fluorescence emission spectra of PTT-Q 1.0×10^{-5} M in DMF with successive addition of (a) 2–10 mM, (b) 2.0×10^{-3} to 10.0×10^{-3} mM Fe^{3+} ions. The excitation wavelength is 500 nm for **P(TT-Q)**.

formation were noted. Therefore, we focused our interest on the **TT-Q** monomer for the further investigations.

In order to elucidate the redox behavior of the polymer **P(TT-Q)**, the coated electrode was washed with DCM to remove the monomer and oligomeric species and then it was placed into monomer-free electrolyte solution. The polymer film exhibited a reversible redox couple ($E_{p,a}$ = 1.23 V and $E_{p,c}$ = 1.18 V) with a half peak potential of 1.05 V and the peak currents were linearly proportional to the scan rate indicating a non-diffusional redox process and a well-adhered electroactive polymer film (Fig. 3 and its inset). Formation of **P(TT-Q)** via potential cycling was also confirmed by recording the FT-IR spectra of both monomer and its polymer. It is noteworthy to mention that disappearance of 704 cm^{-1} and 3116 cm^{-1} peaks in the polymer spectrum indicates that polymerization proceeds via C-5 position of external thiophene units. Furthermore, presence of a new peak at about 835 cm^{-1} indicates the presence of dopant ion PF_6^-.

3.2. Electro-optical properties of *P(TT-Q)*

To reveal the electro-optical properties of the polymer film, optical changes were monitored while going from the neutral to the oxidized states. The **P(TT-Q)** film was coated on ITO via potential cycling and optical features of the film were elaborated in the monomer-free electrolyte solution by recording the changes in the absorption spectra under a variety of voltage pulses after neutralization at 0.0 V and results are shown in Fig. 4. As seen from Fig. 4, the neutral state polymer film has a well defined absorption band at 410 nm ascribed to the π–π^* transition and from the onset of lower energy end of this band, the band gap (E_g) was found to be 1.94 eV. Upon electrochemical oxidation, the **P(TT-Q)** film shows a simultaneous decrease in the absorbance at 410 nm, which is accompanied with a color change from yellowish orange to green. A new intensifying band at 700 nm was also noted, indicating the formation of charge carriers, with increasing applied potentials. Beyond 0.50 V another new band in the near IR region was also noted.

Since one of the important characteristics of an electrochromic material is its electrochemical/optical stability upon multiple switching in a short response time [37], these parameters for electrochemically synthesized **P(TT-Q)** film was investigated under a square wave input of 0.0–1.3 V in 10 s intervals by monitoring the visible transmittance at 412, 732 and 1043 nm and the results are tabulated in Table 1. It is found that the polymer film showed a reversible response between a potential range from 0.0 V (neutral) to +1.3 V (oxidized) with a response time of 1.50 s at 95% of the maximum transmittance and the optical contrast (Δ%T) was calculated as 7.41%, 9.51% and 26.79% at 412, 732 and 1043 nm, respectively. Coloration efficiency (CE) is a useful term for measuring the power efficiency of the electrochromic devices and can be calculated via optical density using the following equations at a given wavelength [38];

$$\text{CE}(\lambda) = \Delta\text{OD}(\lambda)/\text{Q}_\text{d} \text{ and } \Delta\text{OD}(\lambda) = \log[T_\text{OX}(\lambda)/T_\text{red}(\lambda)]$$

where Q_d is the injected/ejected charge during a redox process, T_ox and T_red are the transmittance in the oxidized and the neutral states, respectively.

On the basis of these equations**,** **P(TT-Q)** exhibited CE of 114 and 123 cm^2/C at 412 and 732 nm respectively. On the other hand, at 1043 nm, its CE was found to be relatively high (426 cm^2/C) at 95% of the full switch, which indicated that the **P(TT-Q)** might be a good candidate for electrochromic and optical device application.

3.3. Fluorescence study

Since the electrochemically obtained **P(TT-Q)** was found to be soluble in DMF its fluorescence property was investigated in this solvent. Although the monomer exhibits an emission at about 520 nm when excited at 350 nm, its polymer has a relatively intense emission at about 585 nm when excited at 500 nm, corresponding to orange color. These results indicate that the polymer is an orange emitter and may find applications in various fields, such as light emitting diode, organic lasers and electroluminescent materials. Binding affinities of **TT-Q** and **P(TT-Q)** towards various ions were evaluated by monitoring the change in the fluorescence

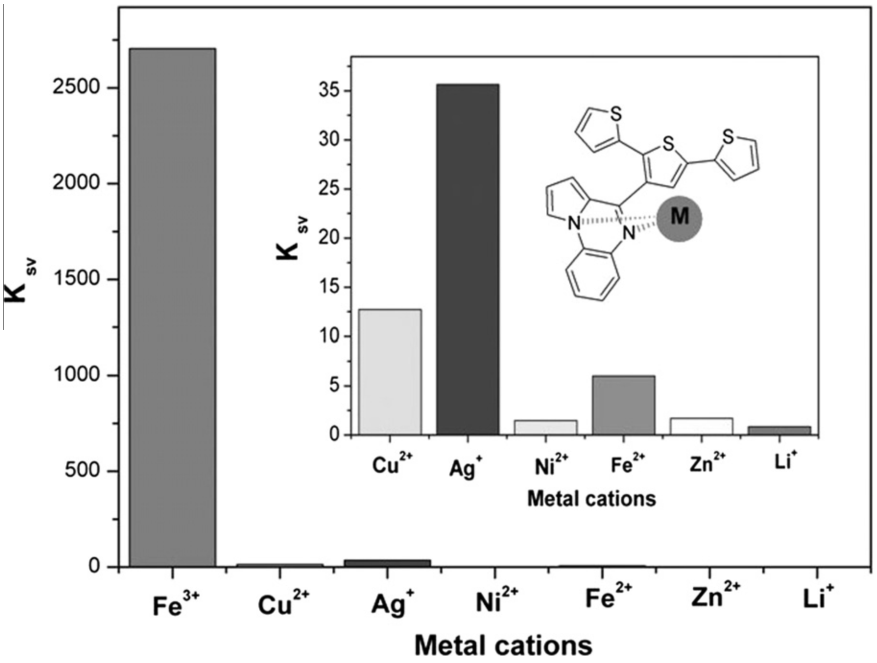


Fig. 7. K_{SV} values of **P(TT-Q)** in the presence of Fe^{3+}, Cu^{2+}, Ag^+, Ni^{2+}, Fe^{2+}, Zn^{2+}, Li^+ (each 2–10 mM in DMF). (Inset: K_{SV} values of **TT-Q** in the presence of Cu^{2+}, Ag^+, Ni^{2+}, Fe^{2+}, Zn^{2+}, Li^+ (each 2–10 mM in DMF)).

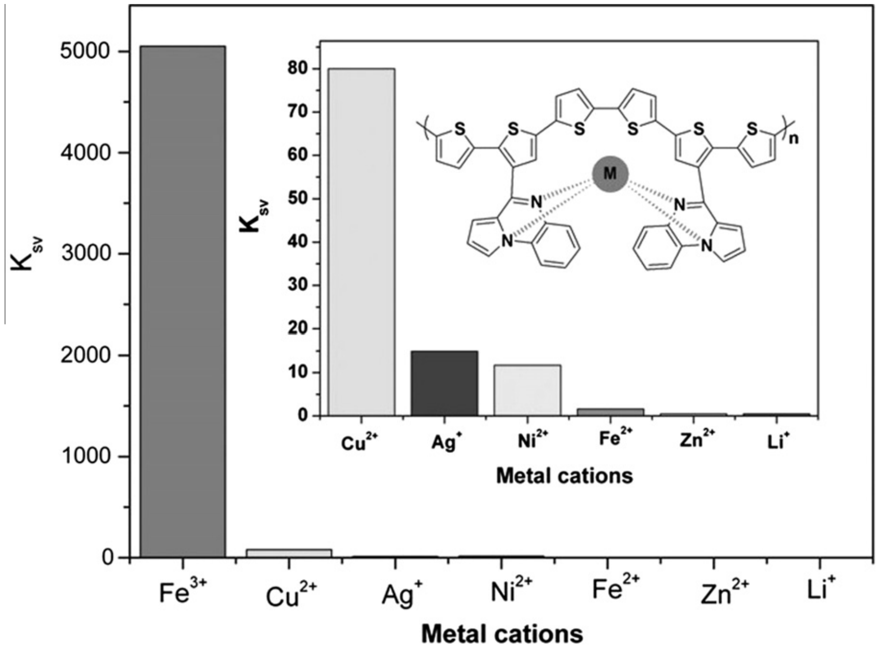


Fig. 8. K_{SV} values of **P(TT-Q)** in the presence of Fe^{3+}, Cu^{2+}, Ag^{+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Li^{+} (each 2–10 mM in DMF). (Inset: K_{SV} values of **P(TT-Q)** in the presence of Cu^{2+}, Ag^{+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Li^{+} (each 2–10 mM in DMF)).

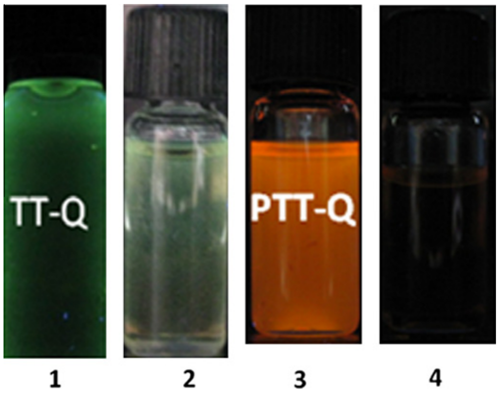


Fig. 9. Emission colors of (1) **TT.Q**, (2) **TT-Q** in the presence of Fe^{3+} ion (3), **P(TT-Q)**, (4) **P(TT-Q)** in the presence of Fe^{3+} ion in DMF under handheld UV lamp.

intensity upon successive addition of metal ions and the results are depicted in the form of Stern–Volmer plots in Figs. 5 and 6, respectively. Inset of Fig. 5 shows the emission spectra of **TT-Q** in DMF upon successive addition of Fe^{3+} ion with an excitation wavelength of 350 nm (Fig. 5). As seen from inset **a** of Fig. 5, the addition of the Fe^{3+} ion resulted in a gradual decrease in the intensity of the fluorescence maximum at 520 nm due to electron or energy transfer between metal ion and **TT-Q** fluorophore, and a maximum quenching efficiency of 95% was obtained. The fluorescence quenching response of **P(TT-Q)** emission upon adding Fe^{3+} ions was also determined and the results are depicted in the inset of Fig. 6.

As there is no quenching effect for lower concentration of ion Fe^{3+} to the monomer (Inset b of Fig. 5), polymer has more quenching effect (Inset b of Fig. 6).

The Stern–Volmer quenching constant, K_{SV}, was also determined and the results are depicted in Figs. 7 and 8 for monomer and polymer solutions, respectively [39]. It is noteworthy that the fluorescence of **TT-Q** and **PTT-Q** is not significantly influenced by the addition of Cu^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Li^{+} and Ag^{+} ions indicating that both the monomer and its corresponding polymer can be utilized for fluorometric detection of Fe^{3+}. This behavior can be clearly seen by naked eye under UV lamp. The emission color of **TT-Q** in DMF, for example, turned from green to colorless after the addition of Fe^{3+} ions. Also, the addition of this ion to the polymer solution causes a quenching in the intensity of the orange color emission of the polymer (Fig. 9).

4. Conclusion

In summary, three fluorescent monomers, **MT-Q**, **DT-Q** and **TT-Q**, based on thienyl systems bearing pendant quinoxaline moieties were synthesized. Among them, only electrochemical polymerization of **TT-Q** was feasible in DCM-TBAPF$_6$, solvent-electrolyte system, yielding a fluorescent polymer, **P(TT-Q)**. Studies on the electro-optical properties of the polymer film revealed that **P(TT-Q)** shows a reversible redox couple with a band gap of 1.94 eV and electrochromic response during p-doping with a relatively high coloration efficiency (426 cm^2/C at 1043 nm). Furthermore, fluorescence of both monomer, **TT-Q**, and its polymer were found to be highly sensitive towards Fe^{3+} ions which make them a promising sensor candidate for Fe^{3+} ion detection, besides the use of **P(TT-Q)** in electronic and optical applications.

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