

Electrochemical polymerization of a new alkoxy-bridged dithieno (3,2-B:2',3'-D) pyrrole derivative

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Abstract: A novel alkoxy-bridged dithieno (3, 2-B:2',3'-D) pyrrole (DTP) derivative was synthesized and its corresponding polymer poly(1,2-bis(2-(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl)ethoxy)ethane) (P(DTP-alkoxy-DTP)) was successfully obtained electrochemically. The effects of alkoxy bridge in the structure on the electrochemical and spectroelectrochemical properties of the polymer were also investigated in detail. The results showed that the polymer film exhibits multielectrochromic behavior and a low band gap of 1.82 eV.

Key words: Conjugated polymers, dithieno (3, 2-B:2',3'-D) pyrrole, electrochromism, electrochemistry, optical properties

1. Introduction

Intrinsically conducting polymers (ICPs) are smart materials that can be integrated into organic electronics (organic light emitting diodes,¹ organic thin film transistors,² photovoltaic cells,^{3,4} electrochromic devices,^{5,6} in the fields of energy storage,^{7,8}) by modifying their chemical structure and optimizing electrochemical and optical properties of the materials. It is a fact that the share of influence over the optical and electrochemical properties for the polymer chain backbone is considerably higher than the nature of the substituted functional units of the polymer.⁹ Most conjugated monomers polymerizing, which are easy to be substituted with different functional groups, are based on thiophene, pyrrole, and aniline. Under these circumstances, most researchers try to synthesize new combinations or molecules functionalized. Dithieno [3,2-b:2',3'-d]pyrrole (DTP) is one such example since its chemical structure welcomes new functional groups with its strong electron donating ability.^{10–22} This precursor material promises a fused ring system and good planar structure in order to obtain a polymer with long chain after electropolymerization.^{23,24} To date, there have been many molecules of DTP moieties and their corresponding polymers, which have some application areas, such as optoelectronic devices, energy storage applications, biosensors, and electrochromic display applications.^{25–31} Among them, the number of electrochromic DTP polymers is still small and for that reason they attract more attention at first sight because of their redox active behavior, low band gap, and excellent electrochromic properties. Functionaliza-

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tion DTP polymer derivatives were also divided into three groups depending on the N-functionalized groups: first (N-alkyl or aryl), second (N-acetal), and new generation (N-alkyl-NH₂) DTP derivatives.^{10,24,31–35} The conjugated polymers of DTP monomers functionalized with ether units have also been synthesized for potentially promising electrode materials used in electrochemical energy storage (EES).³⁶ However, there has been no systematic study on the effect of an ether bridged substituted group between two DTP structures on optical and electrochemical properties. Thus, in the present study, we synthesized successfully a new monomer that bridges 2, 5-dithienylpyrrole (DTP) with an alkyl ether linkage. In this new chemical structure, DTP units will contribute with a long extended conjugation as well as electrochromic property and alkoxy ether bridge expected to provide store charge and easy redox capability and further study on these properties is in progress.

2. Results and discussion

2.1. Electropolymerization of 1,2-bis(2-(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl)ethoxy)ethane (DTP-alkoxy-DTP)

First 10 mM monomer was dissolved in 0.1 M TBAPF₆/ACN solution in order to polymerize the monomer. A CV technique was used and the monomer was oxidized at about 1.0 V versus a Ag wire pseudo-reference electrode at a scan rate of 100 mV s⁻¹ (Figure 1). Electrochemically conducting polymer, namely, poly(1,2-bis(2-(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl)ethoxy)ethane) (P(DTP-alkoxy-DTP)), was coated on an ITO working electrode after repetitive cycles (25 cycles) because a current density intensity occurred in each successive cycle.

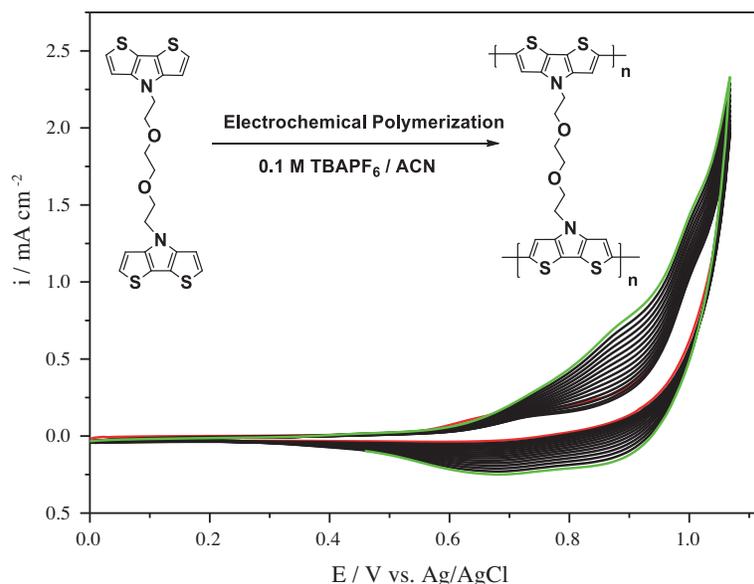


Figure 1. Electrochemical polymerization of DTP monomer in 0.1 M TBAPF₆/ACN solution on an ITO electrode.

2.2. Electrochemical characterization of poly (1,2-bis(2-(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl)ethoxy)ethane ((P(DTP-alkoxy-DTP)))

After electropolymerization on the ITO electrode, polymer film, P(DTP-alkoxy-DTP), was electrochemically characterized via a CV technique in monomer-free medium at different scan rates with increments of 20 mV s⁻¹ from 20 mV s⁻¹ to 200 mV s⁻¹. The polymer showed one reversible oxidation peak at about 0.95 V and

one reversible one at 0.85 V and one irreversible cathodic peak 0.72 V when the polymer was scanned at 200 mV s^{-1} . The second irreversible peak did not start to occur up to a scan rate of 120 mV s^{-1} . Charge trapping was observed at higher scan rates and a new cathodic peak emerged. The CV results are depicted in Figure 2a and the current density values depending on scan rates are drawn again in Figure 2b and a linear line is seen. The second peak was found to be reversible from CV studies. For that reason Figure 2b was drawn with respect to reversible peak values. A linear increase in the peak currents as a function of the scan rates confirmed well-adhered electroactive polymer films on the electrode surface as well as a nondiffusional redox process.

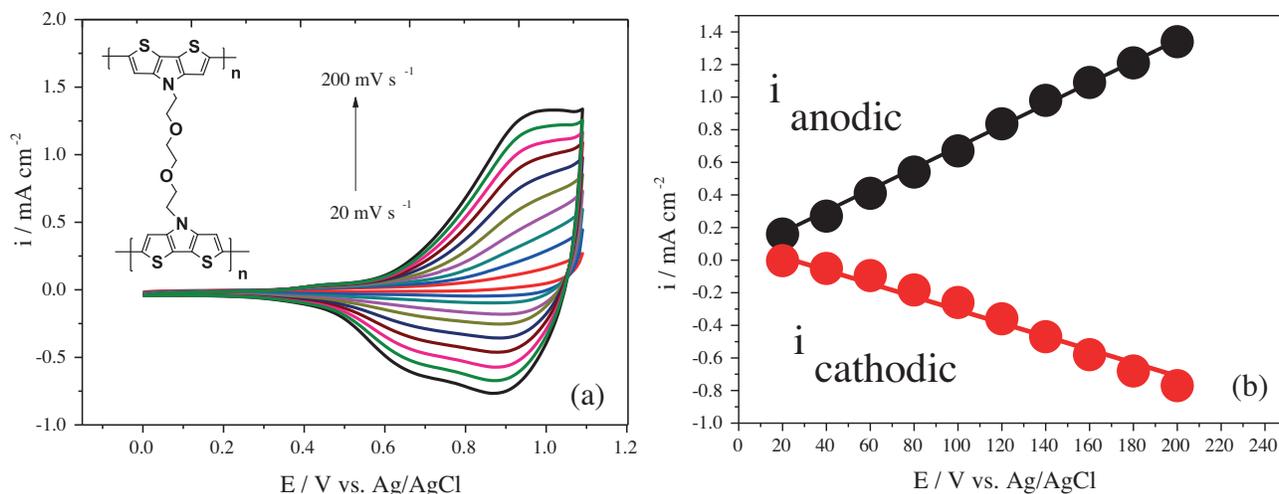


Figure 2. (a) p-Type doping behavior of P(DTP-alkoxy-DTP) film (b) relationship of anodic (i_{anodic}) and cathodic current ($i_{cathodic}$) peaks relationship of anodic (i_{anodic}) and cathodic current ($i_{cathodic}$) peaks at various scan rates in 0.1 M TBAPF₆/ACN.

2.3. Chemical and morphological analysis of poly(1,2-bis(2-(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl)ethoxy)ethane (P(DTP-alkoxy-DTP))

The growth of polymer film was also proved by FTIR spectroscopy (Figure SI.1). While most of the functional group peaks were the same, the peak at 692 cm^{-1} of the monomer completely disappeared, which indicates the formation of linear polymer chains via $\alpha-\alpha'$ linkages after polymerization, and a new peak of dopant at 835 cm^{-1} appeared, which indicates the presence of dopant anions PF₆.^{37–40} A rough surface was seen in the AFM image of the polymer film (Figure 3). The surface of the polymer film is very rough with globular morphology (peak to peak (Rt) = $5.84 \mu\text{m}$ RMS = $0.57 \mu\text{m}$). This kind of morphology is very important especially for easily movement of counterions into and out of the polymer film during doping or dedoping processes.

2.4. Spectroelectrochemical behavior of poly(1,2-bis(2-(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl)ethoxy)ethane (P(DTP-alkoxy-DTP))

For spectroelectrochemical characterization of P(DTP-alkoxy-DTP), the polymer film was scanned in the monomer-free medium via CV method. At the same time, UV-vis results were recorded, as seen in Figure 4. The polymer film gives a λ_{max} ($\pi-\pi^*$ transition) at about 450 nm in the neutral state. Upon oxidation (up to 0.8 V), this band decreases and a new band, which is called polaron charge, arises at about 710 nm. In the oxidation state, the intensity of this band remains approximately constant and a new band (bipolaron charge

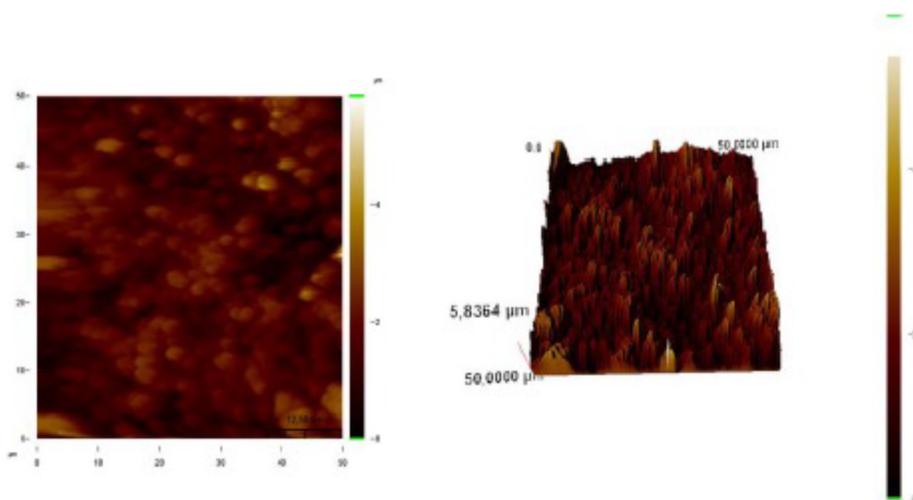


Figure 3. 2D and 3D AFM images of P(DTP-alkoxy-DTP) polymer.

transfer) at 900 nm begins to increase. The band gap of polymer was calculated as 1.82 eV from the onset of the low energy band.

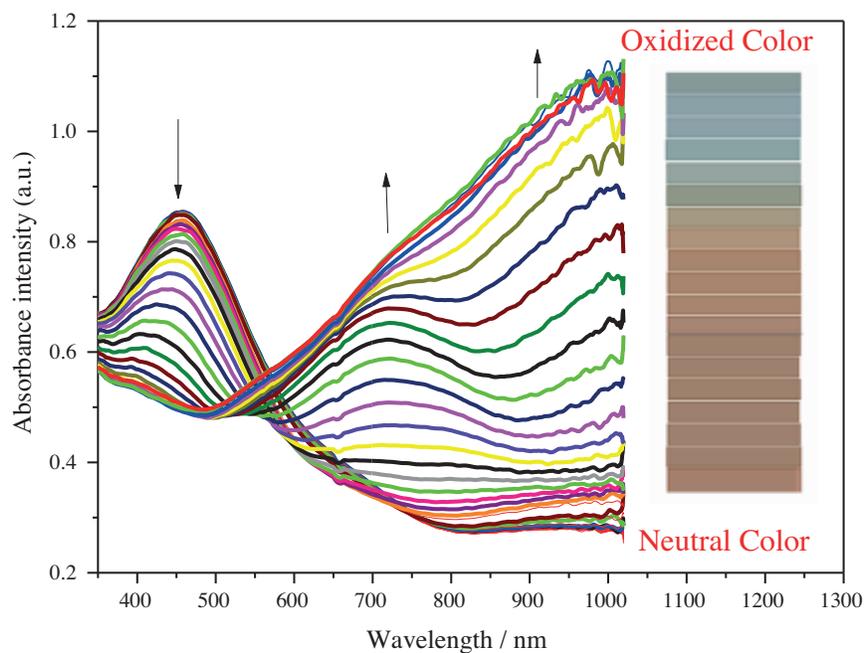


Figure 4. Electronic absorption spectra of P(DTP-alkoxy-DTP) on ITO in 0.1 M TBAPF₆/ACN.

Switching time, optical color contrast, and description of colors at different redox states for polymers are key parameters in order to characterize an electrochromic polymer. The switching times of polymer film are 1.2 s (at 450 nm), 0.7 s (at 710 nm), and 1.0 s (at 900 nm). Because of the charge trapping in the polymer matrix in the P(DTP-alkoxy-DTP) unit, the switching time of the material responds later than that of the P(DTP-alkyl-DTP) as shown in the Table. The optical contrasts values of polymer film are found to be 30% (at 450 nm), 23% (at 710 nm), and 40% (at 900 nm) (Figure 5). These values are lower than that of the

P(DTP-alkyl-DTP) (Table), which may be related to the response of the longer polymer chain of the polymer film. Colorimetry measurements are experiments in order to describe a polymer film color map universally. The results are gathered in the Table. The color transitions for polymer can also be seen in the inset of Figure 4. The polymer film had a red color at neutral state, gray and brown colors at intermediate state, and blue color at oxidized states. As seen in the Table, the colors were in line with the color order transitions of polymer film. The optical electrochemical and spectroelectrochemical data are summarized in the Table and the results were compared with those of alkyl bridged DTP polymer film (poly(DTP-alkyl-DTP)). From the results, the alkoxy bridged polymer film had greater oxidation potential value than poly(DTP-alkyl-DTP) polymer film. Although the monomer (DTP-alkoxy-DTP) has lower oxidation potential than that of the monomer with alkyl substituent (DTP-alkyl-DTP), their polymers have different oxidation onset potentials values, which may be related to the length of the polymer chain, as seen in the Table. While the band gaps of the polymer had about the same value (1.80 eV), HOMO and LUMO levels of the polymers changed depending on the chemical structure.

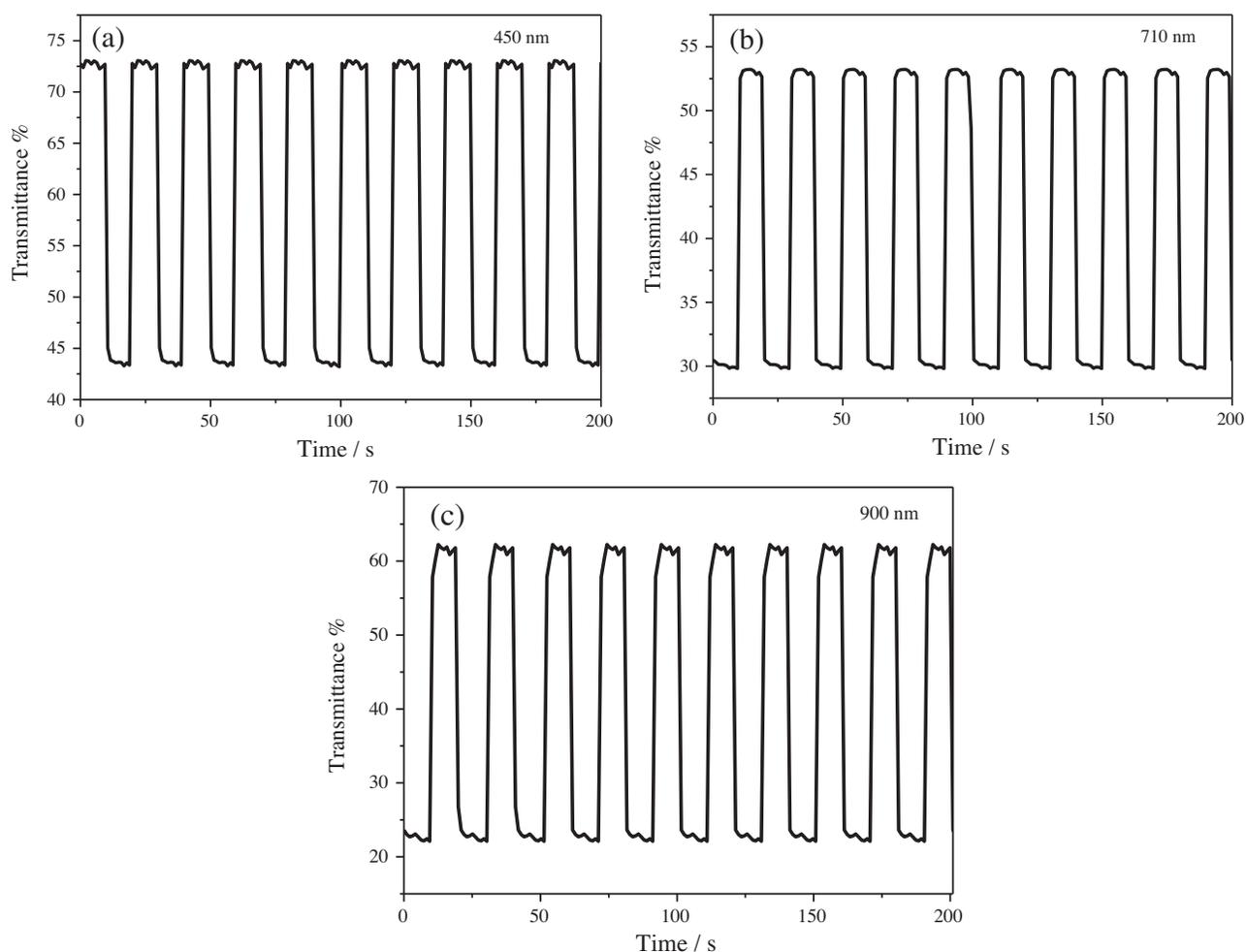


Figure 5. Chronoabsorptometry experiments for P(DTP-alkoxy-DTP) (25 cycled) at (a) 450 nm (b) 710 nm, and (c) 900 nm in 0.1 M TBAPF₆/ACN during the switching of the polymer film in 10 s between 0.0 V and 1.1 V vs Ag wire.

Table. Electrochemical and spectroelectrochemical data for alkyl and alkoxy bridged DTP polymers.

Polymer	Poly(DTP-alkyl-DTP)*	Poly(DTP-alkoxy-DTP)
E_{man}^{ox} (V)	1.10	1.00
E_p^{ox} (V)	0.65	0.95
HOMO (eV)	-5.20	-5.73
LUMO (eV)	-3.40	-3.91
E_g^{opt} (eV)	1.80	1.82
E_{max} (nm)	490/680/1040	450/710/900
Optical contrast (%)	45/24/56	30/22/40
Switching time (s)	0.8/0.5/0.8	1.2/0.7/1.0
Colors (L, a, b) (applied potential)	Red (46.6, 53.8, 36.9) (0.0 V)	Red (59.8, 11.6, 17.7) (0.0 V)
	Dark brown (50.2, 23.6, 34.8) (0.2 V)	Brown (63.5, 11.3, 19.7) (0.5 V)
	Light gray (53.5, -11.4, 13.6) (0.3 V)	Gray (66.9, -3.6, 8.7) (0.7 V)
	Blue (63.0, -29.7, -6.53) (0.5 V)	Blue (65.8, -4.4, -2.33) (1.1 V)

*Data were taken from ref 31. E_{man}^{ox} is oxidation potential of monomer. E_p^{ox} is oxidation potential of polymer. E_{max} (nm) is maximum wavelength.

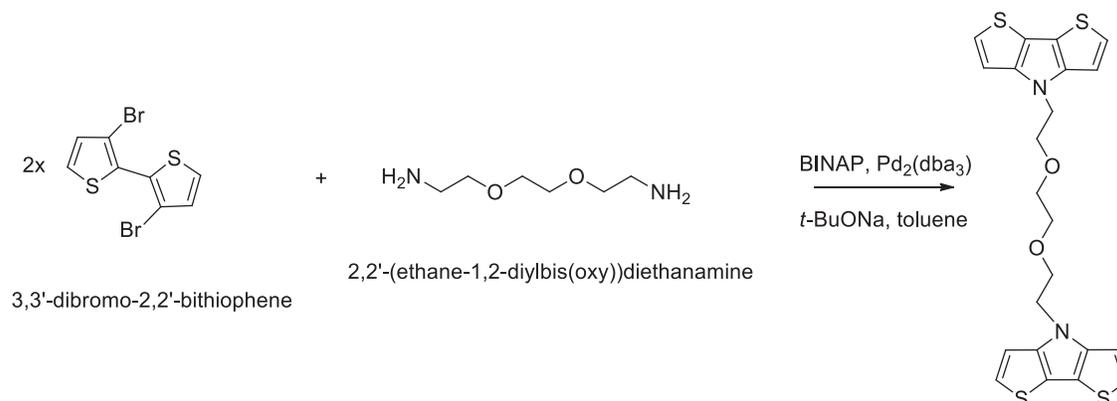
3. Experimental

The chemicals were purchased from Sigma-Aldrich and used without further purification; 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) was used as supporting electrolyte and acetonitrile (ACN) was used as solvent during polymerization and electrochemical characterization of corresponding polymer. A typical three-electrode system containing reference (Ag wire as a pseudo-reference electrode (calibrated externally using a solution of ferrocene/ferrocenium couple)), counter (Pt wire), and working (indium-tin oxide (ITO, Delta Tech. 8-12 Ω , 0.7 \times 5 cm²) electrodes was used for electrochemical deposition and characterization. Homopolymer film was successfully synthesized via cyclic voltammetry (CV) technique. The electrochemical and spectroelectrochemical properties of polymer film were analyzed in the monomer-free medium (0.1 M TBAPF₆/ACN). The obtained polymer film was switched several times between its neutral and oxidized states in order to get more reliable results from the experiments in the monomer-free medium. Electrochemical analysis was recorded via an Ivium Stat electrochemical analyzer. The electro-optical spectra were measured on a Specord S600 spectrometer and color space was given by the International Commission of Illumination with luminance (L), hue (a), and intensity (b). FTIR spectra were recorded on Bruker Equinox 55 with an attenuated total reflectance (ATR). An atomic force microscope (AFM) from Nanomagetics Instruments was used for investigating the

morphologies of the films under ambient laboratory conditions. NMR spectra were recorded on a Bruker NMR spectrometer (DPX-400).

3.1. Synthesis of 1,2-bis(2-(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl)ethoxy)ethane (DTP-alkoxy-DTP)

The synthesis of 1,2-bis(2-(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl)ethoxy)ethane is summarized in the Scheme. To 200 mg (0.62 mmol) of 3,3'-dibromo-2,2'-bithiophene (2) and 53 mg (0.31 mmol) of 2,2'-(ethane-1,2-diylbis(oxy))diethanamine were added 35 mg (0.05 mmol) of BINAP, 28 mg (0.030 mmol) of Pd₂(dba)₃ (3) and 140 mg (1.44 mmol) of t-BuONa consecutively and the solution dissolved in 5 mL of anhydrous toluene for 10 min. Nitrogen gas was passed through the oil bath in nitrogen atmosphere at 135 °C for 5 days. The progress of the reaction was followed by TLC, the reaction was stopped when the starting material had been exhausted, and the solvent was removed in a vacuum. The crude product was dissolved in 30 mL of EtOAc and washed with water (1 × 20 mL). The water phase was again washed with EtOAc (2 × 30 mL). The MgSO₄-dried organic phase solvent was removed in a vacuum. The solution of DTP-alkoxy-DTP in DCM had two absorption peaks at 235 nm and 312 nm.



Scheme. The synthesis route for 1,2-bis(2-(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl)ethoxy)ethane (DTP-alkoxy-DTP).

A brown solid was obtained. (Scheme). (Yield 5%). ¹H NMR (400 MHz, CDCl₃, δ): 7.18 (d, *J* = 2.8 Hz, 2H), 7.02 (d, *J* = 2.8 Hz, 2H), 4.22 (m, 8H), 4.11 (q, *J* = 1.6 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃, δ): 130.78, 129.45, 128.73, 127.47, 68.14, 68.12, 67.7.

4. Conclusion

A novel alkoxy bridged DTP monomer was successfully synthesized and its corresponding polymer were successfully synthesized via electrochemical methods and also characterized. Poly(DTP-alkoxy-DTP) showed a well-defined redox couple. The band gap of poly(DTP-alkoxy-DTP) was found to be 1.82 eV. The polymer exhibited multielectrochromic property. The electrochemical and spectroelectrochemical performance of the polymer film were also investigated in detail. The functional alkoxy unit between two DTP units led to some changes in optical and electrochemical properties, which makes the polymer favorable for use in electrochromic devices and displays. Work in this line is currently underway in our laboratories.

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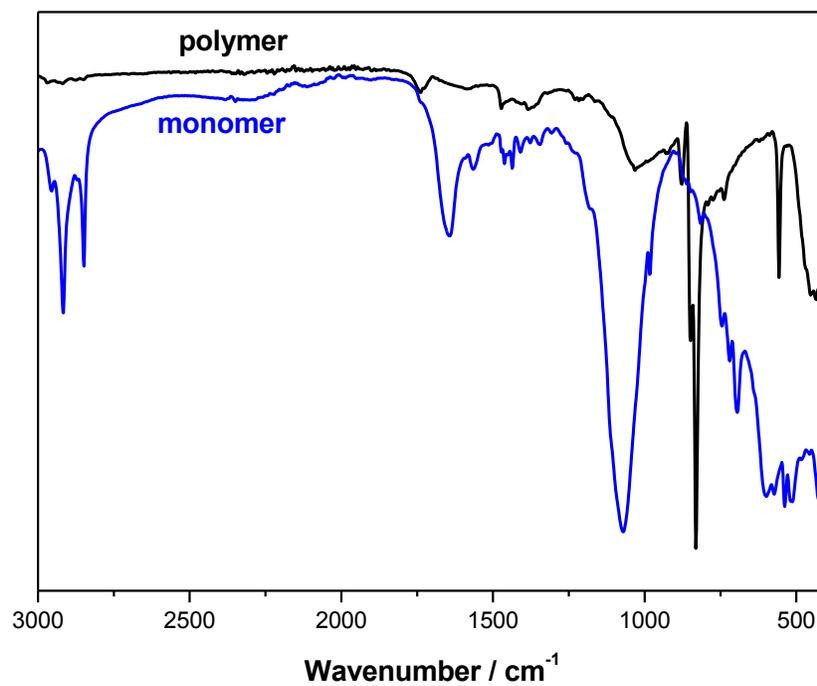


Figure SI.1. FTIR spectra of monomer and its corresponding polymer.