

Synthesis of new ferrocenyldithiophosphate derivatives: electrochemical, electrochromic, and optical properties

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ABSTRACT

In this study, three ferrocenyl dithiophosphate derivatives were synthesized and characterized by elemental analyses, IR, and NMR (^1H -, ^{31}P -) spectroscopy. Electroactivities of synthesized molecules were determined by cyclic voltammetry experiments. It was shown that all molecules were electroactive and only one of them that contained conjugated structure could be polymerized by electrochemical experiments. Characterization of electro-synthesized metallopolymer was realized and electrochromic and spectroelectrochemical properties were investigated. The onset energy for the π - π^* transition (electronic band gap), HOMO, and LUMO energy levels were calculated as 2.31, -4.44, and 2.13 eV, respectively. Switching time and optical contrast values of metallopolymer were found as 1.5 s and 41% at 435 nm, respectively, whereas these values were found as 2.5 s and 40%, respectively, at 700 nm.

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1. Introduction


Lawesson's reagent and ferrocenyl Lawesson's reagent have been utilized for the synthesis of amido and O-dithiophosphonates due to nucleophilic ring opening reaction with alcohols and amines in last decades.[1] Dithiophosphonate derivatives have played a significant role in agricultural, medicinal, and technological areas.[2] For instance, Zn(II)-dialkyldithiophosphates have been utilized as anti-wear additive in engine oil.[3] Many dithiophosphonates and their complexes were prepared previously and some of them have been synthesized in our laboratory.[4,5] However, studies of dithiophosphonates functionalized conducting polymers have been limited. A wide variety of 'metallopolymer' or 'metal-containing polymers' which have been defined containing metal atoms in the repeating monomer either as part of the backbone, or in side chains, has become easily acceptable in the last decade. The most valuable properties of the metallopolymer have been found in nanolithography, sensors, solar cells, memory and light-emitting devices (LED), catalysis, and controlled release.[6–10] Recent studies have pointed out that conductive polymer is used as metallopolymer. Conductive polymers have useful properties which are coloration efficiency, multiple colors with the same material,[11] fast switching ability,[12] and fine-tuning of

the bandgap (and the color) through chemical structure modification.[13]

In addition, conductive polymers have widely been used as LED,[14] photovoltaics, field-effect transistors,[15] biosensors [16], and coating material for detecting cancer cells.[17,18] Over the past few years, introducing the transition metal atoms into the conjugated polymer structures have attracted an increasing interest.[19] The conducting metallopolymer in the development of the ultimate application has a great potential.[20] Novel ferrocenyldithiophosphonate functional conducting polymers were synthesized and characterized by our research group in recent studies. The synthesis and the characterization of the first electroactive O-ferrocenyl dithiophosphonate conductive polymer was reported.[21] Biosensor applications investigated that ferrocene group on the polymer chain was used as a redox mediator.[22,23]

In this study, firstly conjugated amido ferrocenyldithiophosphonate compound, namely 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)amido ferrocenyldithiophosphonate (**2**) was synthesized via reaction of $[(\text{FcPS}_2)_2]$ and 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)aniline (**1**). After that, O-diacetyl-D-glucose-ferrocenyldithiophosphonate (**3**) was synthesized via reaction of $[(\text{FcPS}_2)_2]$ and diacetone-D-glucose. Finally, compound (**3**) was reacted with I_2 and disulfanediyl bis(O-diacetyl-D-glucose ferrocenyldithiophosphonate) (**4**) was

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synthesized. The compounds have been characterized by elemental analyses, IR, NMR (^1H -, ^{31}P -) spectroscopy. Electrochemical properties of the novel ferrocenyldithiophosphonates were investigated.

2. Experimental

2.1. Materials and instruments

Solvents were distilled before use by standard methods. Ferrocene, phosphorus pentasulfide, dichloromethane (DCM), tetrahydrofuran, aluminum chloride, and thiophene were purchased from Merck. Acetonitrile, toluene, succinyl chloride, hydrochloric acid, sodium bicarbonate, magnesium sulfate, ethanol, p-phenylen diamine, propionic acid, and tetrabutylammonium hexafluorophosphate (TBAFP) were purchased from Sigma-Aldrich.

There is a three-electrode cell which includes an ITO-coated glass slide as the working electrode, silver wire as the pseudo-reference electrode, platinum foil as the counter electrode. The ITO glass slide electrode was carefully cleaned using a detergent solution, distilled water and ethanol, respectively, in an ultrasonic bath between each run.

Silver wire was used as pseudo-reference electrode after being calibrated by adding ferrocene which has a stable reversible redox properties. Oxidation/reduction behaviors of the new ferrocenyldithiophosphonate derivatives (compounds **1–4**) were investigated by cyclic voltammetry (CV). All (CV) measurements were carried out in an inert atmosphere using a potentiostat/galvanostat device (Iviumstat, The Netherlands). Electrochemistry of ferrocenyldithiophosphonate derivatives were performed potentiodynamically in 0.1 M TBAFP/DCM electrolyte/solvent system.

For spectroelectrochemistry studies, we used Agilent 8453 UV-vis instrument. Spectroelectrochemical analyses of the polymers were performed to comprehend the band structure of the polymer. To perform the spectroelectrochemical experiments of **P(2)**, polymer film was electrochemically polymerized onto the ITO-coated glass and the spectral changes were recorded by the UV-vis spectrophotometer in 0.1 M TBAFP/DCM system.

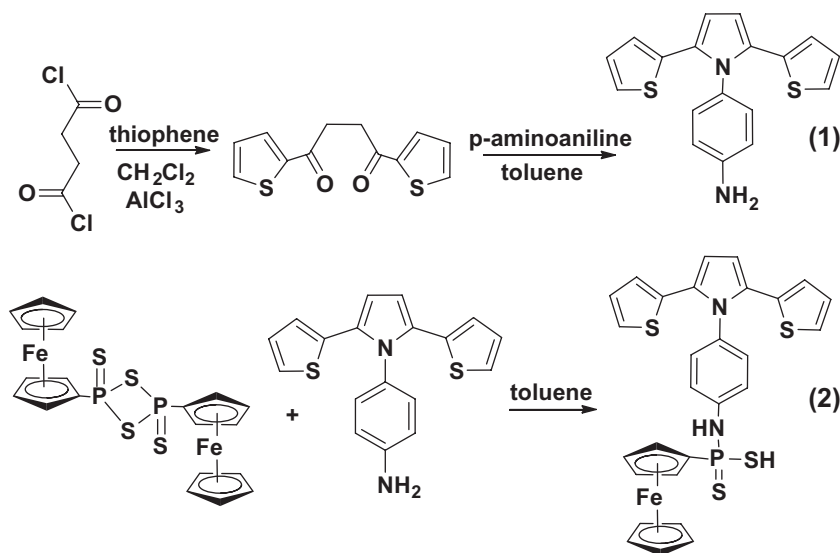
Elemental analyses were performed by Vario MICRO CHNS and melting points were done by electrothermal apparatus. NMR spectra were measured with a Bruker AVANCE DRX 400 NMR spectrometer. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrophotometer ($4000\text{--}400\text{ cm}^{-1}$).

2.2. Synthesis of (2) 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)amido ferrocenyldithiophosphonate

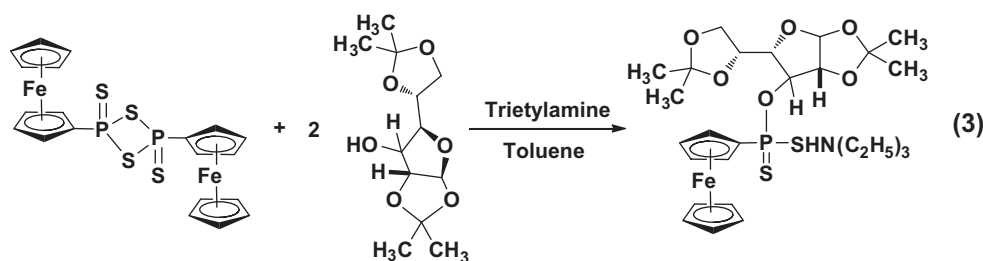
The monomers **1** and **2** were synthesized according to the known procedure (Scheme 1). The reaction of $[(\text{FcPS}_2)_2]$ and compound **1** gave rise to amido $[\text{FcP}(\text{S})(\text{SH})(\text{NHR}^1)]$ $\text{R}^1 = 4\text{-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)aniline}$. The obtained data are similar to the previously reported in the literature.[23]

2.3. Synthesis of O-diacetyl-D-glucose-ferrocenyldithiophosphonate (3)

The reaction of 2,4-bis(ferrocenyl)-1,3,2,4-dithiadiphosphatane-2,4-disulfide $[\text{FcP}(\mu\text{-S})_2]$ (0.25 g, 0.45 mmol) with diacetone-D-glucose (0.23 g, 0.90 mmol) in toluene (10 mL) gave rise to O-ferrocenyldithiophosphonic acid. The mixture was refluxed for 45–60 min. The obtained brown solution was cooled to 0–5 °C, filtered, and then



Scheme 1. Synthesis of 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)aniline (**1**) and 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)amido ferrocenyldithiophosphonate (**2**).



Scheme 2. Synthesis of O-diacetyl-D-glucose-ferrocenyldithiophosphonate.

treated with excess triethyl amine. The solution was kept in the freezer. A yellow product was collected, filtrated, washed with *n*-hexane, and then dried in air (Scheme 2). Yield: 0.37 g, 65%, m.p.: 146–147 °C. Anal. calcd for $C_{28}H_{44}PFeS_2NO_6$: C, 52.41; H, 6.91; N, 2.18; S, 9.99%. Found: C, 52.23; H, 7.24; N, 1.93; S, 9.61%. **IR**(cm^{-1}): 656.63($\nu_{asym} PS_2$) ve 587.42($\nu_{sym} PS_2$) cm^{-1} . **1H -NMR**($CDCl_3$): $\delta = 10.06$ (s, H, NH-) 5.83–5.82(d, H, –O–CH–O), 4.95–4.90(dd, H, O–CH– $^3J_{H-H} = 3.17$ Hz, $^3J_{P,H} = 14, 52$ Hz), 4.80–4.79(d, H, O–CH– $^3J_{H-H} = 3.17$ Hz), 4.58–4.56(d, 2H, O–CH₂ $^3J_{H-H} = 7.83$ Hz), 4.37–4.35(t, H, –CH–CH– $^3J_{H-H} = 2.73$ Hz), 4.25(s, 2H, –C₅H₄), 4.22(s, 5H, –(C₅H₅)), 4.19 (s, 2H, –C₅H₄), 4.01–3.97(d, H, CH–O– $^3J_{H-H} = 1.81$ Hz), 3.94–3.90(q, H, CH–O– $^3J_{H-H} = 7.00$ Hz, $^3J_{H-H} = 8.44$ Hz), 3.29–3.24(q, 6H, –N–CH₂X₃– $^3J_{H-H} = 7.24$ Hz), 1.40(s, 3H, CH₃), 1.38–1.35(t, 9H, (CH₃)₃– $^3J_{H-H} = 7.26$ Hz), 1.32(s, 3H, CH₃), 1.24(s, 3H, CH₃), 1.18(s, 3H, CH₃), **^{31}P -NMR**($CDCl_3$): $\delta = 110.602$. MS: m/z : 641.08[M]⁺, 539.421 [M–HN(C₂H₅)₃]. IR (Figure S3), 1H -NMR (Figure S4), ^{31}P -NMR (Figure S5), MS (Figure S6) graphics show in the Supplemental text.

2.4. Synthesis of disulfanediy bis(O-diacetyl-D-glucose ferrocenyldithiophosphonate (4))

Triethylammonium-diacetyl-D-glucose ferrocenyldithiophosphonate **3** (0.12 g, 0.187 mmol) was reacted with I_2 (0.014 g, 0.093 mmol) in THF (20 mL) and compound **4** was synthesized as shown in Scheme 3. The solution was stirred under mild condition for 2 h. A yellow precipitate obtained from solution, filtered, and then dried in air. Yield: 0.125 g, 62 %, m.p.: 197 °C. Anal. calcd for $C_{44}H_{56}Fe_2P_2S_4O_{12}$: C, 48.98; H, 5.23; S, 11.88 %. Found: C, 48.93; H, 5.105; N, 11.92 %. **IR**(cm^{-1}): 623.36($\nu_{asym} PS_2$) ve 587.42($\nu_{sym} PS_2$) cm^{-1} . **1H -NMR**($CDCl_3$): $\delta = 5.99$ –5.98 (d, 2H, (–O–CH–O)₂), 4.61 (d, 2H, (O–CH–)₂ $^3J_{H-H} = 2.37$ Hz, $^3J_{P,H} = 14, 13$ Hz), 4.58–4.57 (d, 4H, (O–CH₂)₂ $^3J_{H-H} = 3.60$ Hz), 4.44–4.43 (t, 2H, (O–CH–)₂, $^3J_{H-H} = 2.27$ Hz), 4.42 (s, 2H, (O–CH)₂), 4.37–4.35 (d, 4H, (–C₅H₄)₂ $^1J_{H-H} = 9.15$ Hz), 4.33 (s, 10H, –(C₅H₅)₂), 4.32–4.22 (s, 4H, (–C₅H₄)₂), 3.83–3.80 (q, 2H, (CH–O–)₂– $^3J_{H-H} = 6.12$ Hz, $^3J_{H-H} = 11.73$ Hz), 2.80(s, 12H, (–CH₃)₄), 1.50(s, 6H, (–CH₃)₂), 1.32(s, 6H, (–CH₃)₂), **^{31}P -NMR**($CDCl_3$): $\delta = 96.005$

MS: m/z : 1079.479 [M]⁺. IR (Figure S7), 1H -NMR (Figure S8), ^{31}P -NMR (Figure S9), MS (Figure S10) graphics show in the Supplemental text.

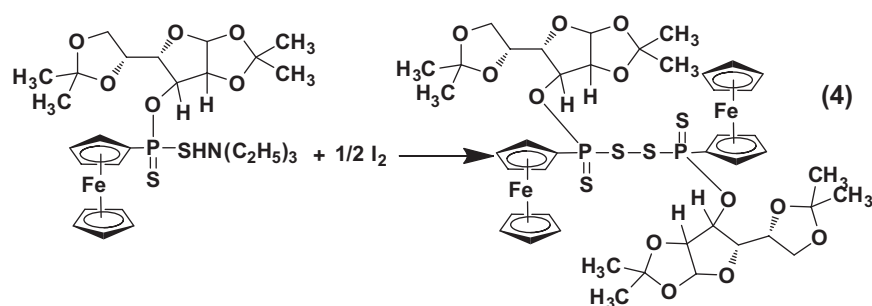
3. Result and discussion

3.1. Characterizations

Amido- and O-ferrocenyldithiophosphonates have been synthesized from the reaction of ferrocenyl Lawesson's reagent with 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)aniline or diacetone-D-glucose (Schemes 1 and 2). The reaction of ferrocenyl Lawesson's reagent and 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)aniline in toluene gave rise to amido ferrocenyldithiophosphonate. To obtain triethyl ammonium salt of O-ferrocenyl dithiophosphonate, the ferrocenyl Lawesson's reagent was reacted with diacetone-D-glucose and a crude O-ferrocenyldithiophosphonic acid was formed and then was treated with excess triethyl amine. When compound **2** isolated a green air-stable solid, the other were orange.

The IR spectra of electrochemically synthesized compound **2** showed the characteristic peaks of the monomer. C–H stretching band of thiophene at 763 cm^{-1} disappeared completely. The new band was also observed due to poly-conjugation at around 1634.76 cm^{-1} . IR spectrum of P(**2**) showed an intense peak at 1082.31 cm^{-1} resulting from the dopant ions. The IR spectra of compound **2–4** showed characteristic bands attributed to $\nu P-O$ (1014–1019 cm^{-1}), $\nu_{asym} PS_2$ (623–658 cm^{-1}), and $\nu_{sym} PS_2$ (539–587 cm^{-1}). The P–N stretching vibration of the compound **2** was observed at 1100 cm^{-1} . [23]

The 1H NMR spectra of compound **2–4** exhibited ferrocenyl protons at the range 4.22–4.19 ppm for C₅H₄ and 4.22–4.32 ppm for C₅H₅ group. [25] A broad singlet peak at 10.06 ppm for compound **3** was observed and can be assigned to NH proton of triethylammonium. The ^{31}P NMR spectra confirmed the formation of all compounds. In the ^{31}P NMR spectra of compounds **3** and **4**, one signal appeared at 110.60 and 96.00 ppm, respectively. In the ESI mass spectra of compounds **3** and **4**, molecular ion peaks were observed at m/z 641.08 and 1079.48, respectively. In



Scheme 3. Synthesis of disulfanediy bis(O-diacetyl-D-glucose ferrocenylthiophosphonate).

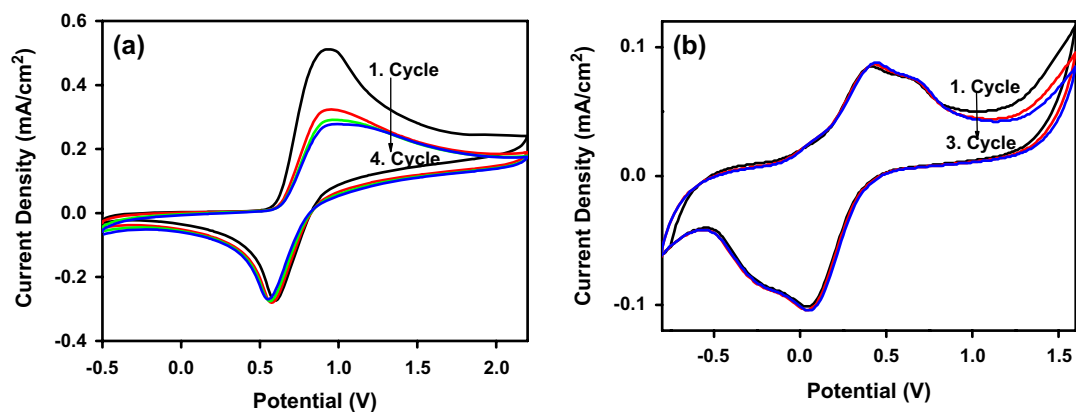


Figure 1. CV Graphs of (a) 3 (b) 4 in 0.1 M TBAFP/DCM electrolyte/solvent couple with 250 mV/s scan rate.

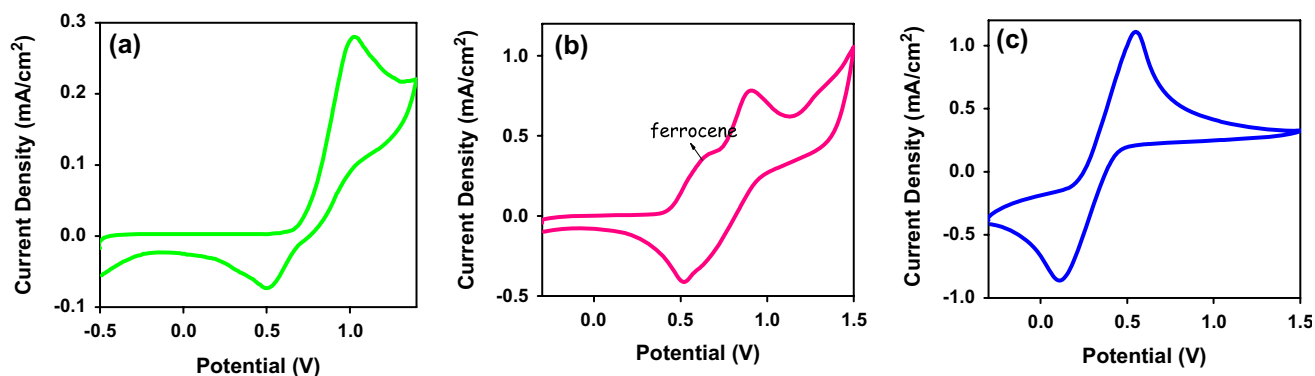


Figure 2. First cycle of the cyclic voltammogram graphs of (a) compound 1 (b) compound 2 (c) ferrocene in 0.1 M TBAFP/DCM electrolyte/solvent couple with 250 mV/s scan rate.

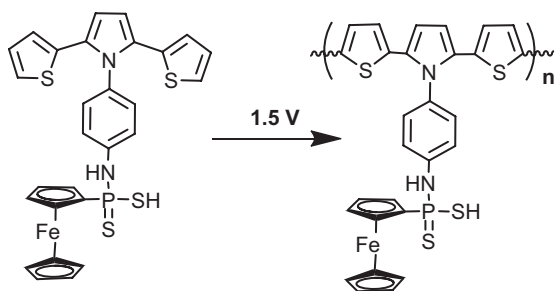
addition, mass spectra of the compounds **2** and **3** exhibited m/z values for identifiable certain fragments.

3.2. Electropolymerization

Polymerizations of new ferrocenyldithiophosphonate derivatives investigated in an electrolyte solution containing 0.1 M TBAFP/DCM electrolyte solvent couple with 250 mV/s scan rate by CV. CV graphics of compounds **3** (a) and **4** (b) are shown in Figure 1. According to these graphs, between potential ranges current increase was

not determined for subsequent cycles. For lack of polymerizable electroactive groups polymerization could not be achieved in these new ferrocenyldithiophosphonate derivatives.

The comparative CV graphs of compound **1**, **2**, and ferrocene in 0.1 M TBAFP/DCM electrolyte/solvent couple at 250 mV/s scan rate are shown in Figure 2. Electropolymerization of monomers were performed by CV. One oxidation peak at +1.0 V and one reduction peak at +0.51 V were observed in the first cycle of the cyclic voltammogram of compound **1**, shown in Figure 2(a).



Scheme 4. Electropolymerization of **2**.

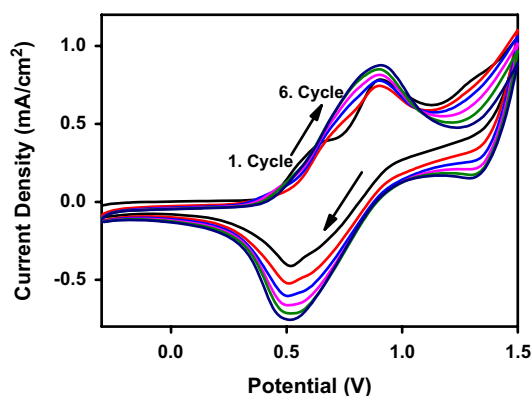


Figure 3. Cyclic voltammogram in 0.1 M TBAFP/DCM electrolyte/solvent couple with 250 mV/s scan rate for compound **2**.

These peaks were attributed monomer oxidation and polymer reduction. In Figure 2(b), cyclic voltammogram of compound **2** shows two oxidation peaks at +0.65 and 0.9 V and consecutive reduction peaks at +0.7 and +0.52 V. Figure 2(c) shows an oxidation peak for cyclic voltammogram of ferrocene at 0.54 V and reduction peak at +0.1 V which is completely a different value when compared with compound **2**. When these three graphics are investigated, it is seen that compound **2** has specific ferrocene's oxidation peak at 0.65 V. This result indicates that there is chemical bond between ferrocene and the compound **1**.

The redox behaviors of compound **2** were investigated in an electrolyte solution containing 0.1 M TBAFP/DCM electrolyte solvent couple with 250 mV/s scan rate by CV. As shown in Scheme 4, P(**2**) was synthesized electrochemically, the potential was scanned between -0.5 and 1.5 V (Figure 3). Due to the increasing number of cycles, an increase in the intensity of current occurred. In this case, the increasing current leads to rise of total amount of electroactive polymer deposited on working electrode.

3.3. Peak current–scan rate dependence of P(**2**)

P(**2**) film was prepared with a constant potential, and the prepared film was investigated by CV at different scan rates in monomer-free electrolytic solution. The current

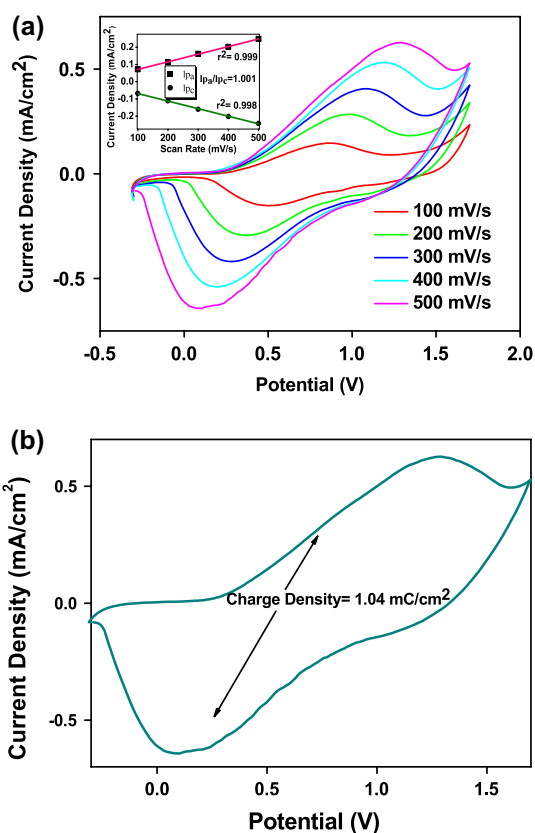


Figure 4. (a) CV of P(**2**) with different scan rates (b) Surface Coverage of Cyclic Voltammogram Graph of P(**2**) in 0.1 M TBAFP/DCM electrolyte/solvent couple.

density was directly proportional to the scan rate as shown in Figure 4(a). Anodic and cathodic peak currents show a linear dependence as a function of the scan rate as demonstrated in internal graphics. The linear dependence showed a strongly adsorbed electroactive thin film on electrode surface. This indicates that the electrochemical processes are not diffusion limited. Charge density (Q_d) is defined as total charge used for the polymers between neutral and oxidized states in monomer free. Q_d was calculated from cyclic voltammogram which is the obtained at 500 mV/s scan rate. The Q_d of the P(**2**) film is measured as 1.04 mC/cm^2 in Figure 4(b).

3.4. Spectroelectrochemistry of the P(**2**)

The polymer film was electrodeposited on ITO via potentiostatic electrochemical polymerization of P(**2**) in the presence of 0.1 M TBAFP/DCM electrolyte solvent couple at $+1.5$ V. P(**2**)-coated ITO was studied by UV–vis spectroscopy without monomer in the electrolytic system by switching between -0.2 and $+0.8$ V (Figure 5). The onset energy for the π – π^* transition (electronic band gap) was calculated as 2.31 eV. Also, redox colors of P(**2**) are yellow and blue.

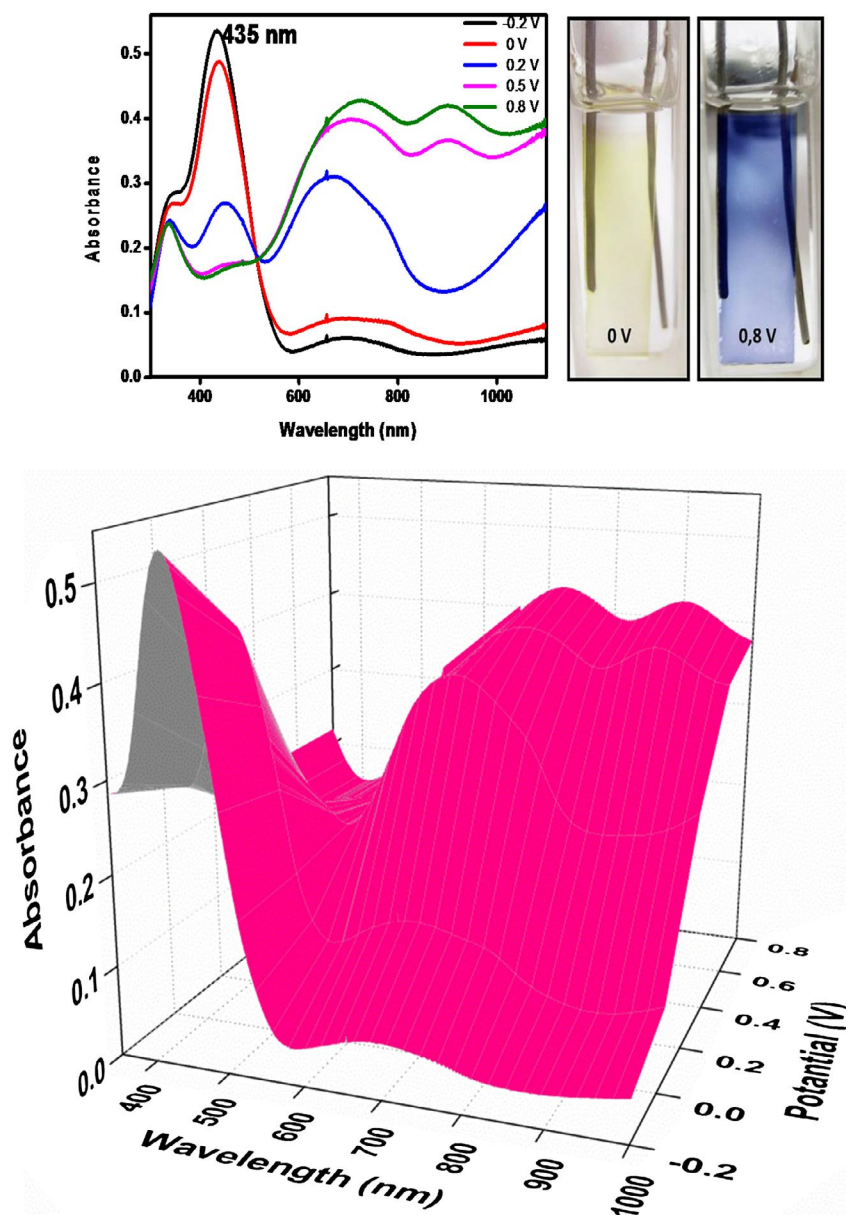


Figure 5. Optoelectrochemical spectrum of 2D and 3D graphs of P(2) film.

HOMO–LUMO energy levels of conducting polymers are very significant in their application areas.[26] While the oxidation process response to removal of the electron from the HOMO energy level, the reduction process response to electron addition to the LUMO energy level. The energy between the HOMO and LUMO levels of the polymer is defined as the electronic band gap (E_g). HOMO energy level was calculated -4.44 eV for P(2) using the onset of the corresponding oxidation potential. This polymer has only p-doping characteristics, hence LUMO energy levels were calculated using HOMO energy and optical band gap value and calculated as -2.13 eV.

The colors of the electrochromic materials were defined by the colorimetric measurements. Colorimetry measurements were performed with a Minolta CS-100

Table 1. HOMO and LUMO energy levels and the color coordinates of conducting polymer, P(2) in accordance with CIE standards.

Polymer P(2)	HOMO (eV)	LUMO ^a (eV)	λ_{\max} (nm)	E_g (eV)
	-4.44	-2.13	435	2.31
	Potential	Luminance (L)	Hue (a)	Saturation (b)
	0 V	89	-3	18
	0.8 V	51	2	-34

^aLUMO energy levels calculated using optical band-gap values and HOMO energy levels.

spectrophotometer. CIE system is a quantitative criterion to describe and compare colors.[27] Three features of color; hue (a), saturation (b), and luminance (L) are measured and given in Table 1.

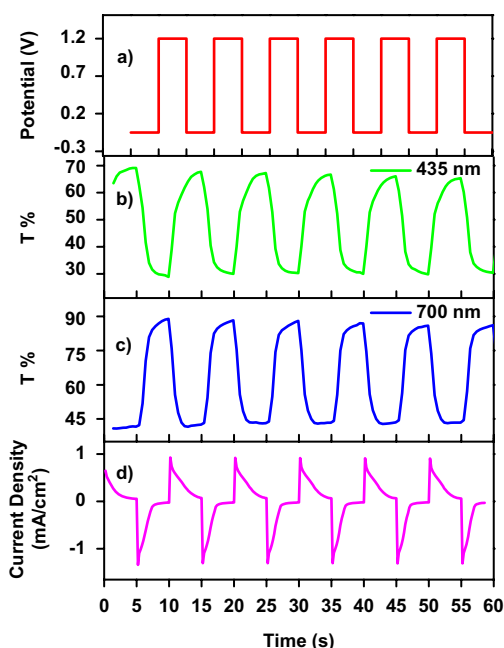


Figure 6. (a) Potential-time (b) absorbance-time at 435 nm (c) absorbance-time at 700 nm (d) current density – time graphs for P(2).

Table 2. Comparison of electrochemical properties of ferrocene containing conducting polymers in literature.

Material	λ_{\max} (nm)	E_g (eV)	Switching time (s)	Optical contrast (% ΔT)	Refs.
P(TP-Fc-co-Py)	332	2.12	2.0	12	[28]
P(ThFc)	390	2.14	–	–	[21]
Fc-PEDOT	580	–	0.6	20	[29]
P(Py4Fc)	365	2.61	–	–	[30]
P(2)	435	2.3	1.5	41	This work

Notes: P(TPFC-co-Py)/CH₃CN: Poli(O-1-(4-phenyl)-1H-pyrrole ferrocenyldithiophosphonate-co-pyrrol).

P(ThFc): Poli(O-2-(thiophen-3-yl)ethyl ferrocenyl dithiophosphonate).

Fc-PEDOT: the ferrocene grafted Poli(3,4-ethylenedioxythiophene).

P(Py4Fc): Poli(4-ferrocenyl-1-[4-(pyrrol-1-yl)butyl]-1H-1,2,3-triazole).

3.5. Electrochromic switching

Electrochromic switching experiments were done to analyze the ability of a polymer to switch increasingly and the ability to show remarkable color change. They are performed by spectroelectrochemistry which polymer switch between its neutral form and doped states with a change in transmittance at a fixed wavelength. During the experiment, maximum contrast values were found at 435 and 700 nm for P(2). At these wavelengths, a polymer which has reduction and oxidation potential between -0.5 and $+1.2$ V potential is given 5 s in solution without monomer. As seen in Figure 6, switching time and optical contrast values of P(2) were found as 1.5 s and 41% at 435 nm,

respectively, whereas these values were found as 2.5 s and 40%, respectively, at 700 nm.

Table 2 summarizes a comparison of electrochemical properties of ferrocenyldithiophosphonate containing conducting polymers in literature.

4. Conclusion

In this study, firstly 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl) aniline (**1**) was synthesized. Then 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)amido ferrocenyldithiophosphonate (**2**) synthesized was via reaction of $[(\text{FcPS}_2)]_2$ and compound **1**. $[(\text{FcPS}_2)]_2$ was reacted with diacetone-D-glucose to obtained O-diacetyl-D-glucose-ferrocenyldithiophosphonate (**3**). Finally, compound **3** was reacted with I_2 in THF and disulfanediyl bis(O-diacetyl-D-glucose ferrocenyldithiophosphonate (**4**) was synthesized. The compounds have been characterized by elemental analyses, IR, NMR (^1H -, ^{31}P -). Metallopolymers' electrochromic and spectroelectrochemical properties were investigated. And conducting metallopolymer **2** has onset energy for the π - π^* transition (electronic band gap) was 2.31 eV and switching time of 1.5 s and 41% optical contrast values at 435 nm, 2.5 s switching time, and 40% optical contrast values at 700 nm. Satisfactory results implied that the obtained metallopolymer can probably be further developed in various applications, such as electrochromic devices, optical displays, and other applications.

Supporting information

Supporting information may be found in the online version of this article.

Disclosure statement

No potential conflict of interest was reported by the authors.

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