

# Synthesis of New Thienylene Pyrrole Monomers and Their Electropolymerizations

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In this study, four new 2,5-dithienylpyrroles (SNS) 1-(3-fluoro-phenyl)-2,5-di(thiophen-2-yl)-1H-pyrrole (*m*-FPTP), 1-(3-chloro-phenyl)-2,5-di(thiophen-2-yl)-1H-pyrrole (*m*-BrPTP) and 1-(4-bromo-phenyl)-2,5-di(thiophen-2-yl)-1H-pyrrole (*p*-BrPTP) containing meta and para substituted benzene ring at the nitrogen atom were synthesized via Paal-Knorr condensation of 1,4-di(2-thienyl)-1,4-butanedione with corresponding halo-substituted anilines. The monomers were polymerized via potential cycling in LiClO<sub>4</sub>-acetonitrile (ACN) electrolytic solution. The replacement effect of halogen atoms as a substituent from para- to meta-positions and different halogen units (F, Cl, Br) at only meta-/para-positions in the structure on the electrochemical and optical properties of synthesized monomers/polymers were investigated. Computational investigations (M06/TZVP) were also performed on the monomer structures to support the electrochemical behavior of the structures. Furthermore, the synthesized polymer films exhibited reversible redox behavior accompanied with a reversible electrochromic behavior. It was also observed that the optical contrast value ( $\Delta T\%$ ) for polymers was significantly improved when compared with their analogs in the literature.

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Functional conjugated polymers (CPs) still are of great interest due to their large number of applications such as solar cells, light emitting diodes, optical displays and sensors.<sup>1–3</sup> They have been also widely employed as electrochromic materials in electrochromic devices due to their advantages over inorganic oxides. These advantages, such as multicolor, high contrast ratio and fast switching capability, can be tuned via structural tailoring of the starting materials. Thus, significant effort has been devoted to design and synthesize new polymeric electrochromics based on CPs. Among them, due to their stability and higher conductivities polypyrroles and polythiophenes and their derivatives attracted great attention.<sup>4</sup> Conjugated polymers containing both heterocyclic units along the polymer backbone would be interesting and Otero et al synthesized a hybrid monomer consisting of thiophene and pyrrole units, namely, dithienylpyrrole (SNS) for the first time and reported its electrochemical polymerization.<sup>5,6</sup> SNS has the advantage of tunable properties, via structural modification of the pyrrole unit through N-substitution,<sup>7-10</sup> including solubility and electrochromic properties. Soluble conjugated polymers bearing N-alkyl substituted SNS units were reported by Ferraris et al.<sup>11-14</sup> Toppare et al<sup>15–18</sup> and Cihaner et al<sup>19–21</sup> also reported synthesis and polymerization of a number of N-substituted SNS derivatives. We have also investigated the electrochemical polymerization and optoelectronic properties of phthalonitrile, phthalocyanine and luminol substituted SNS derivatives.<sup>22–25</sup> Yet, halo substituted phenyl rings on SNS were not studied extensively with respect to halogen effect on the electrochemical behavior of the compounds.

Herein, we report the synthesis and electrochemical polymerization of four new SNS derivative bearing halo substituted phenyl rings. The effect of halogen atoms (F, Cl, Br), at only meta-/para-positions of the benzene ring, on the electrochemical and optical properties of the monomers and their corresponding polymers were investigated. Furthermore, to support the experimentally obtained oxidation potentials of monomers, theoretical calculations (M06/TZVP) were also performed.

### Experimental

Materials and measurements.— All chemicals were purchased from Aldrich and Merck and used without any further purifica-

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tion. Prior to electrochemical polymerization, redox behavior of the monomers (5 mM) was investigated using CV in ACN solution containing 0.1 M LiClO<sub>4</sub> on platinum electrode, for comparison reason. The monomers were successfully electropolymerized via potentiodynamic method using three-electrode system containing a platinum disc (0.02 cm<sup>2</sup>) and a platinum wire as working and counter electrodes in the same electrolytic medium, respectively, as well as Ag/AgCl electrode (in 3 M NaCl (aq) solution) as a reference electrode. For electro-optical studies, indium-tin oxide (ITO, Delta Tech. 8–12  $\Omega$ , 0.7 cm  $\times$  5 cm) electrodes were coated by the polymer films. The coated electrodes were dipped into a UV cuvette with 1.0 cm path length containing 0.1 M tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) in ACN together with Pt wire and Ag wire as counter and pseudo-reference electrodes, respectively. The pseudo reference electrode was calibrated externally using 5 mM solution of ferrocene/ferrocenium couple in the same electrolytic solution. Prior to spectroelectrochemical measurements, the polymer films were switched between their neutral and doped state several times in order to equilibrate redox behavior in monomer-free electrolytic solution.

In-situ spectroelectrochemical studies were performed with Hewlett–Packard 8453A diode array spectrometer. Electroanalytical measurements were performed with a Gamry PCI4/300 potentiostatgalvanostat.

*Theoretical calculations.*— All calculations were performed with Gaussian 09 A2.<sup>26</sup> The geometry optimizations were performed at the level of M06/TZVP as implemented in the program. To make sure that the optimized geometry in a minimum, we performed frequency calculations which did not result any imaginary frequency. The natural bond order (NBO) analyses were performed at the level of MP2/TZVP. Solvation energies were calculated at the level of CPCM //M06/TZVP.

1-(3-halo(Fluoro/Chloro/Bromo)-phenyl)-2,5-Synthesis of *di(thiophen-2-yl)-1H-pyrrole* 1-(4-bromo-phenyl)-2,5and di(thiophen-2-yl)-1H-pyrrole.— Paal-Knorr condensation of 1,4-di(2-thienyl)-1,4-butanedione with corresponding halogen substituted anilines was used in order to synthesize the monomers; 1-(3-fluoro-phenyl)-2,5-di(thiophen-2-yl)-1H-pyrrole (*m*-FPTP). 1-(3-chloro-phenyl)-2,5-di(thiophen-2-yl)-1H-pyrrole (m-CIPTP),1-(3-bromo-phenyl)-2,5-di(thiophen-2-yl)-1H-pyrrole (*m*-BrPTP) and 1-(4-bromo-phenyl)-2,5-di(thiophen-2-yl)-1H-pyrrole (*p*-BrPTP). A round-bottomed flask equipped with an argon inlet and magnetic stirrer was charged with 1,4-di(2-thienyl)-1,4-butanedione (1 eq.),

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X: halogen atom

Scheme 1. Synthetic route for the monomers.

aniline (1 eq), p-toluenesulfonic acid (PTSA) (5%) and toluene. The mixture was stirred and refluxed for 24 h under argon until the reactants were finished. Evaporation of the toluene, followed by flash column chromatography (SiO<sub>2</sub> column) afforded the desired compounds. The synthetic route of the monomer is shown in Scheme 1.

(*m*-**FPTP**); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 6.45 (s, 2H), 6.48 (dd, J = 4.0, 5.0 Hz, 2H), 6.77–6.80 (m, 2H), 6.92–6.95 (m, 1H), 6.98–7.02 (m, 2H), 7.06–7.1 (m, 2H), 7.29 -7.31 (m, 1H), <sup>13</sup>C NMR (100 MHz, CDCl3): 134.5, 130.2, 130.0, 127.1, 126.0, 124.4, 124.7, 117.6, 117.4, 116.3, 116.1, 110.3. Yield = 70.7%.

(*m*-CIPTP); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 6.45 (s, 2H), 6.48 (dd, J = 4.0, 5.0 Hz, 2H), 6.73–6.76 (m, 2H), 6.99–7.04 (m, 2H), 7.10–7.14 (m, 1H), 7.23 -7.26 (m, 2H), 7.33–7.36 (m, 1H)  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>): 132.2, 132.0, 127.8, 127.6, 126.8, 125.9, 124.5, 122.2, 121.9, 117.3, 116.2, 107.8. Yield = 57.1%.

(*m*-BrPTP); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 6.45 (s, 2H), 6.48 (dd, J = 4.0, 5.0 Hz, 2H), 6.73–6.78 (m, 2H), 6.98–7.02 (m, 2H), 7.14–7.19 (m, 2H), 7.39–7.42 (m, 1H), 7.49–7.52 (m, 1H),  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>): 139.5, 134.2, 132.8, 131.9, 129.9, 129.8, 128.5, 126.7, 124.4, 124.1, 122.1, 109.8. Yield = 74.6%.

(*p*-BrPTP); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 6.44 (s, 2H), 6.47 (dd, J = 4.0, 5.0 Hz, 2H), 6.75–6.78 (m, 2H), 7.00–7.02 (m, 2H), 7.06–7.10 (m, 2H), 7.40–7.45 (m, 2H), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 137.5, 134.6, 132.4, 131.5, 129.9, 127.1, 124.8, 124.4, 122.9, 110.3. Yield = 66.5%.

#### **Results and Discussion**

Synthesis of monomers and theoretical calculations.— In the present study, four new SNS derivative bearing halo substituted phenyl rings were synthesized via Paal-Knorr condensation of 1,4-di(2-thienyl)-1,4-butanedione with corresponding halogen substituted anilines. The monomers were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

Table I.	The dihedral	angles for	the compounds.	The angles are
defined a	according to Fi	igure <mark>1</mark> .		

Compound	$<\!\!S_1C_1C_2N$	<SC <sub>4</sub> C <sub>3</sub> N	$< C_6 C_5 N C_2$
<b>PTP</b> $(C_s)$	-30.88	30.88	-89.56
m-FPTP (C <sub>s</sub> )	-34.22	34.22	-85.86
m-ClPTP (C <sub>s</sub> )	-33.47	33.46	-87.34
m-BrPTP (C <sub>s</sub> )	-36.60	36.64	-84.16
p-BrPTP (C <sub>s</sub> )	-32.08	33.60	-88.41
<b>PTP</b> $(C_2)$	38.84	38.96	-108.70
m-FPTP (C <sub>2</sub> )	38.65	38.75	-107.46
<i>m</i> -ClPTP (C <sub>2</sub> )	37.77	37.87	-108.81
<i>m</i> -BrPTP (C <sub>2</sub> )	40.194	38.29	-108.59
p-BrPTP (C <sub>2</sub> )	39.80	39.72	-110.20
PTP <sup>+</sup>	0.00	0.00	89.99
<i>m</i> -FPTP <sup>+</sup>	-0.30	0.30	-90.57
<i>m</i> -ClPTP <sup>+</sup>	-0.07	0.08	-90.02
<i>m</i> -BrPTP <sup>+</sup>	-1.29	1.33	-88.47
<i>n</i> -BrPTP <sup>+</sup>	-0.19	0.04	-89.96

To elucidate the substituent effects computational investigations were performed on the monomer structures utilizing M06/TZVP level of theory. Geometry optimization of the compounds revealed that the heterocyclic moieties are not planar. The angles are tabulated in Table I and the structure of 1-(phenyl)-2,5-di(thiophen-2-yl)-1Hpyrrole (PTP) showing dihedral angles is depicted in Figure 1. There are two possibilities of global minima for the compounds, either the sulfur atoms in thiophene units could point to the same direction, Cs, or they can point in different directions, i.e. one up the other down, C2. For unsubstituted molecule, PTP, *m*-FPTP and *m*-ClPTP the C2 symmetric compounds are more stable than the Cs ones. For the meta-bromo and para-bromo substituted compounds, the Cs conformers more stable than the C2 symmetric conformers. However, the energy differences are so low that the compounds can be found in both conformations in solution according to Boltzmann distribution. The substitution on the phenyl ring does not have an effect on the dihedral angles. However, the optimization for radical cations of each compound resulted in planar heterocyclic backbone. This shows that the positive charge is delocalized over the backbone (heterocyclic units). The phenyl ring in all cases are perpendicular to the heterocyclic backbone for the oxidized species. This indicates that the phenyl ring, substituted or unsubstituted, cannot contribute to the delocalization of charges through pi-overlap. Yet, it could stabilize or destabilize the backbone via inductive effects, which is predicted to be very small. NBO analysis for each compound showed that the charge distribution does not change significantly.

*Electrochemical characterization and polymerization of monomers.*— The electrochemical behavior of thienylenepyrole derivative (**SNS**) monomers bearing phenyl ring with halogen substituted units from meta- or para- position were investigated by CV in an electrolyte solution consisting of 0.1 M LiClO<sub>4</sub> dissolved in ACN solution for comparison reasons. For all the four monomers, an irreversible oxidation peaks observed during the first anodic scan at 0.80, 0.82 0.85 and 0.78 V for *m*-FPTP, *m*-CIPTP, *m*-BrPTP and *p*-BrPTP, respectively (See Fig SI.1). The first oxidation potential for the unsubstituted derivative, **PTP**, was reported as 0.45 V<sup>16</sup> in ACN. Comparison of this value with the halo-substituted derivatives, obtained in this work, indicates that presence of halo-substituents increases the oxidation potential by lowering the HOMO level of the molecule.

The slight differences in the oxidation potential of halo-substituted derivatives could be correlated to the free energies of the compounds both in gas phase and in the presence of a dielectric medium



Figure 1. Structure of PTP showing dihedral angles.

Table II. The relative energies for the reactions shown together with oxidation potential of monomers obtained from CV measurements.

Compound (symmetry) $\rightarrow$ Oxidized Form	$\Delta G$	$\Delta\Delta G  (solv)$	E/ V
<b>PTP</b> (C <sub>s</sub> ) $\rightarrow$ <b>PTP</b> <sup>+</sup>	143.915	113.268	0.45*
$m$ -FPTP (C <sub>s</sub> ) $\rightarrow m$ -FPTP <sup>+</sup>	145.578	113.542	0.80
$m$ -ClPTP (C <sub>s</sub> ) $\rightarrow m$ -ClPTP <sup>+</sup>	146.267	114.364	0.82
<i>m</i> - <b>BrPTP</b> ( $C_s$ ) $\rightarrow$ <i>m</i> - <b>BrPTP</b> <sup>+</sup>	146.134	114.420	0.85
<b>p-BrPTP</b> ( $C_s$ ) $\rightarrow$ <b>p-</b> <i>Br</i> <b>PTP</b> <sup>+</sup>	146.422	114.506	0.78
<b>PTP</b> (C <sub>2</sub> ) $\rightarrow$ <b>PTP</b> <sup>+</sup>	143.967	113.105	
<i>m</i> - <b>FPTP</b> (C <sub>2</sub> ) $\rightarrow$ <i>m</i> - <i>F</i> <b>PTP</b> <sup>+</sup>	146.375	114.168	
$m$ -ClPTP (C <sub>2</sub> ) $\rightarrow m$ -ClPTP <sup>+</sup>	146.428	114.358	
<i>m</i> -BrPTP (C <sub>2</sub> ) $\rightarrow$ <i>m</i> -BrPTP <sup>+</sup>	146.115	114.221	
<b>p-BrPTP</b> (C <sub>2</sub> ) $\rightarrow$ <b>p-BrPTP</b> <sup>+</sup>	145.987	113.870	

\*Data is taken from reference 16 in the medium of 0.1 M NaClO<sub>4</sub>:LiClO<sub>4</sub> in the ratio of 1:1 /ACN, electrolyte/solvent couple at a scan rate of  $500 \text{ mVs}^{-1}$ .

( $\varepsilon = 37.5$  for ACN) as tabulated in Table II. First oxidation potentials of the monomers were also included to the same table. Since the reactions are identical, that is all reactions are oxidation reactions, we could compare the results shown in Table II. The ease of oxidation for compounds in Cs conformation is PTP>*m*-FPTP>*m*-ClPTP>*m*-BrPTP>*p*-BrPTP, and in C2 conformation is PTP>*p*-BrPTP>*m*-FPTP>*m*-BrPTP>*m*-ClPTP. From the CV results, the ease of oxidation is PTP>*p*-BrPTP≅*m*-FPTP>*m*-ClPTP>*m*-BrPTP. The discrepancy between the experimental and theoretical values probably arises from presence of many minima on potential energy surfaces of the compounds. The comparison of the results reveals that the *m*-BrPTP and *p*-BrPTP are mostly in C2 conformer.

The oxidative electrochemical polymerization of the monomers were achieved by scanning in the potential ranges 0.0 V to +1.0 V in 0.1 M LiClO<sub>4</sub>/ACN, electrolyte/solvent couple utilizing CV. Repeated cycling of the monomers in this potential range resulted in the deposition of electroactive polymer on Pt disc electrode  $(0.02 \text{ cm}^2)$ . Figure 2 shows the evolution of the cyclic voltammograms of the monomers during repeated potential scans. The continuous increase in the amplitude of the cyclic voltammetric peaks (Figure 2a, 2b, 2c and 2d) indicates the formation of the polymer film on the electrode surface as a consequence of the electrochemical polymerization of SNS units. After the first cycle, observation of a new reversible redox couple with an increasing current intensity, after each successive cycle, proves the formation of electroactive polymer films.

*Electrochemical behavior of polymer films.*— The electrochemical behavior of the polymer films obtained after 25 successive scans are also investigated in the monomer free electrolytic solution containing 0.1 M LiClO<sub>4</sub> in ACN. The polymer films coated on the working electrode were first rinsed with ACN in order to remove any oligomeric species and the electrolyte, and then were cycled between its neutral and oxidized states at various scan rates (Figure 3i), to elucidate the scan rate dependency of the anodic ( $I_{ac}$ ) and cathodic ( $I_{cc}$ ) peak currents (Figure 3(ii)). It is found that both anodic and cathodic peak currents increase linearly with increasing scan rate, indicating that the redox process is non-diffusional and the polymer film is well adhered to the working electrode surface.

Spectroelectrochemical properties of P(m-FPTP), P(m-ClPTP),P(m-BrPTP) and P(p-BrPTP).— The electro-optical properties of the polymer films, deposited on ITO working electrode via potential cycling, were investigated by monitoring the changes in the electronic absorption spectra under a voltage pulse in a monomer free electrolyte solution. The results are depicted in Figure 4. The electronic absorption spectra of neutral forms of the films exhibit absorption bands at around at around 406, 409, 417 and 407 nm



Figure 2. Repetitive cyclic voltammograms of (a) *m*-FPTP (b) *m*-CIPTP (c) *m*-BrPTP (d) *p*-BrPTP, recorded after each 5<sup>th</sup> cycle, in 0.1 M LiClO<sub>4</sub>/ACN at a scan rate of 100 mV s<sup>-1</sup> on Pt electrode.



Figure 3. CV of polymer films (a) P(*m*-FPTP) (b) P(*m*-ClPTP) (c) P(*m*-BrPTP) (d) P(*p*-BrPTP) in 0.1 M LiClO<sub>4</sub>/ACN at a scan rate of 100 mV s<sup>-1</sup> on Pt electrode on Pt electrode.

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Figure 4. Optical absorption spectra of (a) P(*m*-FPTP) (b) P(*m*-ClPTP) (c) P(*m*-BrPTP) (d) P(*p*-BrPTP) Polymer films on ITO electrode in 0.1 M LiClO<sub>4</sub> /ACN at a potential range between 0.0 V and 1.1 V vs. Ag-wire.

for P(m-FPTP), P(m-CIPTP), P(m-BrPTP) and P(p-BrPTP), respectively. These bands are due to  $\pi$ - $\pi$ \* transitions and they all lose intensity during oxidation which is accompanied by the appearance of new intensifying bands. For P(m-FPTP), as the valance-conduction band at 406 nm diminishes a new band starts to intensify at about 655 nm and shifts to 550 nm in the potential range of 0.0-0.70 V. Upon further oxidation, beyond 0.70 V, a new broad band around 836 nm also starts intensifying. Appearance of these new bands indicates the formation of charge carriers. In the case of P(m-CIPTP), P(m-BrPTP) and P(p-BrPTP) the new bands due to the formation of charge carriers appears at about 535, 514 and 576 nm, respectively. The changes in the electronic absorption spectra of P(m-FPTP), P(m-ClPTP), P(m-BrPTP) and P(p-BrPTP) films are also accompanied by a color change, from yellow in the neutral state to green in the fully oxidized state. There is no much difference between the colors of newly synthesized polymers, which means that the changing halogen atoms at meta-position have a little effect on the colors of corresponding polymers. On the other hand, while changing the position of bromine unit from para to meta-positions on the phenyl ring (P(p-BrPTP) to P(m-BrPTP)) doesn't lead to any color change, the replacement of fluorine atom from para (P(p-FPTP) to meta (P(m-FPTP)) positions caused a color change (blue for (P(p-FPTP)) to green for(P(m-FPTP)) at their fully oxidized states indicating a position effect on the electrochromic behavior of fluorine substituted polymer films.

The bandgap (Eg) values of polymer films deposited on ITO electrodes via potential cycling were also determined from the commencement of low energy end of  $\pi$ - $\pi$ \* transitions (i.e., 406, 409, 417 and 407 nm for **P**(*m*-**FPTP**), **P**(*m*-**CIPTP**), **P**(*m*-**BrPTP**) and **P**(*p*-**BrPTP**), respectively), utilizing spectroelectrochemical data as summarized in Table III. Eg values of meta substituted SNS derivatives were found as 2.25 eV. On the other hand, in the case of **P**(*p*-**BrPTP**) Eg value was found to be 2.10 eV. This bandgap lowering might be due to the slight increase in the HOMO level of polymer and is in accordance with the oxidation potential of the monomers ( $E^{\text{ox}}(P(\rho-BrPTP))$ ). This trend was same for the fluorine halogenated one (2.25 to 1.94 eV for **P**(*m*-**FPTP**) and **P**(*p*-**FPTP**),<sup>27</sup> respectively).

Due to its importance in electrochromic applications, switching times and optical contrast of the polymer films on ITO were also investigated under square wave input of 0.0–1.0 V in 10 s intervals by monitoring the visible transmittance and the kinetic responses of the film (Table II), the highest optical contrast ( $\Delta$ T%) values were found as 53.4 (at 550 nm), 14.5 (at 514 nm), 19.0 (at 409 nm) and 5 (at 576 nm) for **P(***m***-FPTP)**, **P(***m***-CIPTP)**, **P(***m***-BrPTP)** and **P(***p***-BrPTP)**, respectively.  $\Delta$ T% values for all polymer films are tabulated in Table III, for comparison reasons. Among the four new polymers and other derivatives **P(PTP)** and **P(***p***-FPTP)**,<sup>16,27</sup> **P(***m***-FPTP)** exhibits the highest value 53.4 (at 550 nm) indicating that **P(***m***-FPTP)** is a promising candidate for electrochromic device applications. Switching times were reported as 3.4, 1.2 s for **P(***m***-FPTP)**; 2.1, 0.9 s for

Table III.	Summary of optica	l properties of P(PTP)	, P( <i>m</i> -FPTP), P(	m-CIPTP), P(m-BrPTP),	P(p-BrPTP), P(p-FrPTP).
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Chemical Structure	λ <sub>max</sub> / nm	ΔT%	Switching time/s	Band Gap (eV)	Color	
					Neutral	Oxidized
	413	27.0	1.7			
s s	600	-	-	2.20	yellow	green
[16]	884	-	-			
N N	398	2.3	0.8	1.94	yellow	blue
S S	510	6.0	1.2			
F [27]	850	-	-			
	407	3.8	1.2			
s s	576	5.0	1.9	2.10	yellow	green
Br	935	-	-			
	406	19.5	3.4			
S S	550	53.4	1.2	2.25	yellow	green
F	836	-	-			
	417	12.0	2.1			
s s	514	14.5	0.9	2.25	yellow	green
Br	830	-	-			
	409	19.0	1.6	2.25	yellow green	
s s	535	14.5	0.9			green
CI	855	-	-			

**P**(*m*-**CIPTP**); 1.6, 0.9 s **P**(*m*-**BrPTP**) and 1.2, 1.9 s for **P**(*p*-**BrPTP**) at corresponding wavelengths, as indicated in Table III.

## Conclusions

In this study, four new SNS derivatives; **P(m-FPTP)**, **P(m-CIPTP)**, **P(m-BrPTP)** and **P(p-BrPTP)**, containing meta and para substituted benzene ring at the nitrogen atom were synthesized via Paal-Knorr condensation and their electrochemical behavior were investigated in terms of substituent effect. CV results revealed only slight variations in the oxidation potentials depending on the substituent position and these results were also confirmed by computational studies. The higher oxidation potentials for the monomers as compared to unsubstituted one (**PTP**) indicates a decrease in the HOMO level upon halogen substitution. The monomers were successfully polymerized via potential cycling and only minor substituent effect was observed on their optical properties and bandgap values. Among the polymers obtained in this work **P(m-FPTP)** was found to exhibit highest optical contrast value with relatively fast switching time making it a promising candidate for electrochromic device applications.

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