Copolymers of 3-arylthieno[3,2-b]thiophenes bearing different substituents: Synthesis, electronic, optical, sensor and memory properties

DOI:
10.1016/j.eurpolymj.2022.111167

Document Version
Accepted author manuscript

Link to publication record in Manchester Research Explorer

Citation for published version (APA):

Published in:
European Polymer Journal

Citing this paper
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Abstract

Thienothiophene (TT) is one of the most impressive organic cores, and has gained significant attention in the organic polymeric materials in recent years. Possessing cyano (CN), carboxylic acid (COOH) and dimethylamine (N(CH₃)₂) substituted thieno[3,4-b]thiophene (TT), π-extended conjugated three novel polymers (P1-P3) with 3-hexylthiophene were successfully synthesized by the Suzuki coupling. All the polymers were found to be well soluble owing to the side chains. Their optical and electrochemical properties were investigated by experimental and computational studies. Moreover, the photophysical characterization of the novel polymers demonstrated a significant mega Stokes shift, reaching 138 nm with a bathochromic shift, and a changing electronic band gap between 1.91 and 2.33 eV as well as good thermal stability of degradation temperature around 320 °C. Also, their F⁻ anion-recognition abilities have been investigated with selectivity of different fluoride concentration for UV and emission titration spectra. Memristive switching properties were examined by using synthesized polymers as an active layer in memory devices. The highest ON/OFF ratio of the memory devices were recorded to be 10⁶ with good stability, which makes them suitable for electronic applications.

Introduction

Conjugated polymers have received increasing attention for use in various optical and electronic applications, such as organic light emitting diodes (OLEDs) [1,2], organic solar cells (OSCs) [3,4], luminescent sensors [5,6], electrochromic devices [7], capacitors [8], organic field-effect transistors (OFETs) [9,10], light-receiving transistors [11] and biological imagery [12]. Many π-conjugated aromatic units, such as benzene, thiophene, pyridine, fluorene and
carbazole, have been introduced in the conjugated polymer backbone [13,14]. Amongst them, thiophene exhibits outstanding properties, due to its high π-electron density, band gap tunability, more reactivity and stability. Extension of the π system increases the conjugated length of the molecule, leading to a decreased band gap and often increased charge carrier mobility [15,16]. Thienothiophenes (TTs) are the simplest fused and π-extended structures of the thiophene family. Especially, thieno[3,2-b]thiophene, is the most stable and highly conjugated isomer of TTs. Due to their electron rich, flat, rigid, and good electron delocalized skeleton, thieno[3,2-b]thiophene (TT) has been widely adopted as significant and interesting building block of various conjugated polymers in organic materials [17-33].

Among the conjugated polymers that have been used in OSCs, OFETs and memory devices, electron-donor and electron-acceptor moieties in the polymer backbones have played significant roles [34-36]. Donor-acceptor (DA) architecture could regulate electronic transition, intramolecular interactions, pull-push effect and bandgap which are required for high-performance devices [37,38]. In addition to main donor-acceptor units utilized in polymers, obtaining conjugated polymers with various functional electron rich or deficient groups is widely studied to generate D-A effect [39,41]. The functional substituents on the polymer strongly affect its electronic and optical properties, for instance the HOMO-LUMO level, oxidation and reduction potentials, absorption and emission maxima, intramolecular charge transfer (ICT) character and band gap of the polymer [35,36]. In this work, we report design and synthesis of three new copolymers (P1-P3) based on thieno[3,2-b]thiophenes, carrying different functional groups of cyano (CN), carboxylic acid (COOH) and dimethylamine (N(CH$_3$)$_2$) groups. To increase the solubility and mobility of the polymer’s backbone, diverse substituted TT units were polymerized by extending with 3-hexylthiophene. Effects of the functional groups (CN, COOH and N(CH$_3$)$_2$) on the polymers were compared and examined by optical, electronic, thermal, sensor study and memory applications as well as time-dependent DFT calculations for both monomers and dimers.

**Experimental**

**Materials**

3-Bromothiophene (97%, Across), 2-bromo-4′-cyanoacetophenone (97%, Across), 2-bromo-4′-nitroacetophenone (95%, Sigma-Aldrich), polyphosphoric acid (PPA, 115% H$_3$PO$_4$ basis, Sigma-Aldrich), n-butyllithium (2.5 M in hexanes, Sigma-Aldrich), sodium sulfate (Merck), tetrakis(triphenylphosphine)palladium (0) (Pd(PPh$_3$)$_4$), (99%, Sigma-Aldrich) were used as
received. Diethyl ether and THF were dried over metallic sodium. Dimethylformamide (HPLC grade) was stored over activated molecular sieves (4 Å). Dichloromethane (Aldrich) was used as received. 1-8, 10 and 11 were synthesized following our previous report [25-33].

Instrumentation and characterization

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian model NMR spectrometer (500 and 126 MHz), chemical shifts of which were reported in ppm downfield from tetramethyl silane (TMS). UV-Vis absorption spectra were obtained using a HITACHI U-0080D spectrophotometer. Fluorescence spectra were recorded on a HITACHI F-4500 fluorescence spectrophotometer. Cyclic voltammetry (CV) measurements were performed using a PA4 polarographic analyzer (Laboratory Instruments, Prague, CZ) with a three-electrode cell. Platinum (Pt) wire electrodes were used as both working and counter electrodes. An Ag/AgCl electrode was used as a reference electrode. CV measurements were conducted in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in anhydrous acetonitrile under nitrogen atmosphere. Typical scan rate was 100 mV/s. Molecular weights and dispersities of the polymers were measured using gel permeation chromatography (GPC) employing an Agilent 1100 instrument, equipped with a differential refractometer using THF as an eluent at a flow rate of 0.3 ml min$^{-1}$ at 30 °C. Polystyrene was used as a standard.

Synthesis of 4-(2,5-dibromothieno[3,2-b]thiophen-3-yl)benzoic acid (9)

A mixture of 7 (200 mg, 0.5 mmol) and NaOH (2M, 30 mL) was refluxed in methanol (25 mL) for 2 hours. Reaction was quenched with 2 mL HCl. The mixture was then extracted with dichloromethane, washed with NaHCO$_3$ (10%) and water. The organic layer was dried over Na$_2$SO$_4$, filtered and the solvent was evaporated under reduced pressure to give the title compound 9. $^1$H NMR (500 MHz, DMSO-$_d_6$) $\delta$ 8.03 (d, $J = 8.3$ Hz, 2H), 7.84 (d, $J = 8.3$ Hz, 2H), 7.71 (d, $J = 3.3$ Hz, 1H).

Synthesis of 2,5-dibromo-3-hexylthiophene (13)

To a solution of 3-hexylthiophene 12 (200 mg, 1.2 mmol), dissolved in DMF (6 ml), was added NBS (465 mg, 2.6 mmol) at -10 °C in dark. After the reaction was stirred for 8 h at the same temperature, the mixture was poured into water (50 ml) and the precipitate was filtrated and purified by column chromatography eluting with a mixture of hexane:CH$_2$Cl$_2$ (3:1) to obtain the title compound 13. 1H NMR (500 MHz, CDCl$_3$) $\delta$ 7.13 (s, 1H), 2.71-2.68 (m, 2H), 1.73-1.65 (m, 2H), 1.41-1.30 (m, 6H), 0.93 (t, $J = 6.9$ Hz, 3H).
Synthesis of 4,4,5,5-tetramethyl-2-(thiophene-2-yl)-1,3,2-dioxaborolane (15)

To a solution of 13 (1.4 g, 4.3 mmol), dissolved in dry THF (50 mL) was added n-butyllithium (4 mL, 10 mmol, 2.5 M) at −78 °C, under nitrogen atmosphere and, then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 14 (2.6 mL). The mixture was stirred at room temperature under nitrogen atmosphere for overnight and the solvent was removed under reduced pressure. The crude product was dissolved in dichloromethane, washed with HCl solution (5 N), the organic layer was dried over Na₂SO₄, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography eluting with a mixture of hexane:CH₂Cl₂ (5:1) to give the title compound 15 (1.04 g, 60%). ¹H-NMR (500 MHz, DMSO-d₆) 8 7.66 (dd, J = 3.9Hz, J = 1.1 Hz, 1H), 7.64 (dd, J = 4.8 Hz, J = 1.1 Hz, 2H), 7.19 (dd, J = 4.8 Hz, J = 3.9 Hz, 2H), 1.35 (s, 27H), 0.8 (s, 6H)

Synthesis of P1

To a mixture of 5 (230 mg, 0.57 mmol) and 11 (240 mg, 0.57 mmol), dissolved in dry THF (30 ml), was added Pd(PPh₃)₄ (14 mg, 0.0125 mmol) and K₂CO₃ solution (4 ml, 2 M). The mixture was degassed for 45 min and stirred at 80 °C under nitrogen atmosphere for 48 h, after which the crude polymer was precipitated in methanol and filtered. It was purified by Soxhlet extraction with methanol, acetone, and chloroform. The solvent chloroform was evaporated under reduced pressure and the polymer was precipitated in methanol, filtered, and finally dried under reduced pressure to obtain red polymer P1 (73%, Mn = 7081, Mw = 9978, PDI = 1.40).

Synthesis of P2

The polymer P2 was synthesized applying the same method used for P1. Red polymer P2 was obtained in 69% yield (Mn = 4831, Mw = 5210, PDI = 1.07).

Synthesis of P3

The polymer P3 was synthesized applying the same method used for P1. Red polymer P3 was obtained in 71% yield (Mn = 4153, Mw = 8066, PDI = 1.94).

Results and Discussion

Synthesis of Monomers

Syntheses of the monomers were conducted according to our previous reports (Scheme 1) [25-31]. 3-Bromothiophene 1 was lithiated with n-butyllithium at −78 °C, which was followed by addition of elemental sulfur and then the α-bromoketones 2 to yield the corresponding
monoketones 3 and 4, ring closure reactions of which in the presence of PPA in refluxing chlorobenzene gave 4-thieno[3,2-b]thiophen-3-ylbenzonitrile 5 and 3-(4-nitrophenyl)thieno[3,2-b]thiophene 6, respectively. They were brominated using NBS at -10 °C in DMF to produce the dibrominated thienothiophenes, 4-(2,5-dibromothieno[3,2-b]thiophen-3-yl)benzonitrile 7 and 3-(4-nitrophenyl)thieno[3,2-b]thiophene 8. Basic hydrolysis of 7 in the presence of NaOH in EtOH gave 4-(2,5-dibromothieno[3,2-b]thiophen-3-yl)benzoic acid 9. The nitro group of 8 was reduced to amine with Fe/HCl to yield the 4-(2,5-dibromothieno[3,2-b]thiophen-3-yl)aniline 10, which was noticed not to be stable enough for long-standing. It was then methylated with CH₃I in DMF to obtain 4-(2,5-dibromothieno[3,2-b]thiophen-3-yl)aniline 11, having dimethylaminophenyl group. Thus, electron deficient “CN” substituted 7 and “COOH” substituted 9, and electron donating “N(CH₃)₂” substituted 11 were obtained as dibrominated TT blocks ready for polymerization. For the other block of polymerization, 3-hexylthiophene 12 was dibrominated using NBS in DMF at -10 °C, to produce 2,5-dibromo-3-hexylthiophene 13. Then, 13 was lithiated with n-butyllithium at -78 °C in THF, which was followed by addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 14 to yield 2,2′-(3-hexylthiophene-2,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 15.
Synthesis of Polymers

The polymers P1, P2 and P3 were obtained by polymerizing the dibrominated TT 7, 9 and 11 with 15, respectively, applying Suzuki coupling reaction (Scheme 2). The polymers were purified by a Soxhlet extraction in methanol, acetone and then chloroform to remove oligomers and other small molecular parts.
Scheme 2. Synthetic routes of polymers

Molecular Weight Characterization of Polymers

Weight-average molecular weights (Mw), number-average molecular weights (Mn) and polydispersity index (PDI, Mw/Mn) were obtained from gel permeation chromatography (GPC) in THF solution using RI detection (Table 1). The GPC results showed that polymer P1 had higher molecular weight compare with the polymers P2 and P3.

Table 1 Molecular weights of Polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Mn</th>
<th>Mw</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>7081</td>
<td>9978</td>
<td>1.409</td>
</tr>
<tr>
<td>P2</td>
<td>4831</td>
<td>5210</td>
<td>1.078</td>
</tr>
<tr>
<td>P3</td>
<td>4153</td>
<td>8066</td>
<td>1.942</td>
</tr>
</tbody>
</table>

Photophysical Characterization of Polymers

Solution UV-Vis absorption spectra of P1–3 were recorded in THF (Figure 1, Table 2). As expected, the presence of electron donating or deficient substituents at the para position of the
phenyl moiety of the TT core had considerable effects on the optical properties of the corresponding polymers. P1-3 displayed $\pi-\pi^*$ absorptions at 437 (P1), 432 (P2), and 422 nm (P3). The strongest electron withdrawing effect of ‘CN’ group provided the longest absorption maximum for P1, while P2 had the shortest absorption with electron donating dimethylamine group. Compared to the CN group, COOH derived P2 has less electron-withdrawing effect and had an absorption band at 5 nm behind P1. The absorbance values indicated that electron deficient CN and COOH groups substituted polymers exhibit bathochromic shifts of $\pi-\pi^*$ transitions, compare to electron donating N(CH3)$_2$ substituted polymer, P3. From the spectra, the onset maximum values of 545, 539, and 527 nm are observed for P1-P3, respectively. Based on the onset values, the optical band gaps of the polymers were determined as 2.27, 2.30 and 2.35 eV for P1, P2 and P3, respectively.

![Fig. 1. a) UV-Vis absorption and b) fluorescence spectra of the polymers in THF](image)

The emission measurements of P1, P2, and P3 were performed in THF (Figure 1, Table 2). The polymers displayed fluorescence maxima of 574 (P1), 570 (P2), and 540 nm (P3). A similar trend of emission bands with absorption, i.e. the longest and the shortest wavelength emissions with P1 (574nm) and P3 (540 nm) was observed. The Stokes shifts ranged from 118 (P3) to 138 (P2) nm. All the polymers displayed mega Stokes shifts (>100 nm), indicating a fast relaxation from the excited state to the ground state owing to intramolecular charge-transfer on the polymer backbones; strong electron flowing in the polymer’s backbone with a significant red shift and optically applicable feature [37-39].
Table 2 Optical data of the polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>UV$_{\text{max}}^a$ (nm)</th>
<th>UV$_{\text{onset}}$ (nm)</th>
<th>Fl$_{\text{max}}^a$ (nm)</th>
<th>Stokes Shift (nm)</th>
<th>E$_{\text{optic}}^b$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>437</td>
<td>534</td>
<td>574</td>
<td>137</td>
<td>2.30</td>
</tr>
<tr>
<td>P2</td>
<td>432</td>
<td>529</td>
<td>570</td>
<td>138</td>
<td>2.33</td>
</tr>
<tr>
<td>P3</td>
<td>422</td>
<td>527</td>
<td>540</td>
<td>118</td>
<td>2.35</td>
</tr>
</tbody>
</table>

$^a$Absorption and emission maxima in THF. $^b$E$_{\text{optic}}$ from the onset of absorption spectra

HOMO and LUMO energy levels of the polymers are very significant in order to gain more insight about their photophysical and electronic properties. Cyclic voltammetry (CV) measurements were conducted to examine the electrochemical properties of the polymers (Fig. S1, Table 3). P1 - 3 exhibited cycle with oxidation onset potentials (E$_{\text{onset(ox)}}$) at 0.95, 1.36, and 1.00 V, respectively. Moreover, E$_{\text{onset(red)}}$ were determined to be at -1.09, -0.97, and -0.91 V for P1 - 3, respectively. Based on the onset potentials, the HOMO and LUMO energies of P1 - 3 were predicted to be -5.35, -5.76, -5.40 eV and -3.31, -3.43, -3.49 eV, respectively, using equations of (HOMO = -(E$_{\text{onset(ox)}}$ + 4.40) (eV)) and (LUMO = -(E$_{\text{onset(red)}}$ + 4.40) (eV)). Electrochemical band gaps were calculated to be 2.04 (P1), 2.33 eV (P2), and 1.91 eV (P3) from E$_{\text{elec}}$ = E$_{\text{onset(ox)}}$ - E$_{\text{onset(red)}}$ = |LUMO-HOMO| equation. Higher band gap of P2 with lower HOMO level could be explained with the presence of carboxylic acid group, which is less electron withdrawing compared to the nitrile group. Better electron donating property of dimethylamine moiety provides P3 with a better conjugation and the lowest band gap among the three polymers.

Table 3 Electrochemical data of the polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>E$_{\text{onset(ox)}}$ (V)</th>
<th>E$_{\text{onset(red)}}$ (V)</th>
<th>HOMO $^a$ (eV)</th>
<th>LUMO $^b$ (eV)</th>
<th>E$_{\text{elec}}$ $^c$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0.95</td>
<td>-1.09</td>
<td>-5.35</td>
<td>-3.31</td>
<td>2.04</td>
</tr>
<tr>
<td>P2</td>
<td>1.36</td>
<td>-0.97</td>
<td>-5.76</td>
<td>-3.43</td>
<td>2.33</td>
</tr>
<tr>
<td>P3</td>
<td>1.00</td>
<td>-0.91</td>
<td>-5.40</td>
<td>-3.49</td>
<td>1.91</td>
</tr>
</tbody>
</table>

$^a$HOMO = -(E$_{\text{onset(ox)}}$ + 4.40) (eV). $^b$LUMO = -(E$_{\text{onset(red)}}$ + 4.40) (eV). $^c$E$_{\text{elec}}$ = E$_{\text{onset(ox)}}$ - E$_{\text{onset(red)}}$

Sensor Characterization of Polymers
Fluoride ion is generally used to investigate the binding and sensing properties of \(\pi\)-conjugated polymers [40-43]. Thus, the effect of electron withdrawing/donating groups on the polymer backbone for the photophysical properties, fluoride (F\(^-\)) anion sensor studies of the conjugated polymers with different substituents were conducted, applying absorption and emission titration experiments in THF (2.0\(\times\)10\(^{-5}\) M) using tetrabutylammonium fluoride (TBAF, 2.0\(\times\)10\(^{-5}\) M) as a fluoride anion source. Regarding CN and COOH substituted P1 and P2, they showed almost similar optical behavior with the addition TBAF in the absorption titration (Figure 2). However, depending on the electron withdrawing powers of the CN and COOH groups, P1 reached its maximum intensity at 0.7 eq. while P2 reached at 1.4 eq. The quicker response of P1 than P2 implies that fluorine anions attacked the CN carbon easier than removing H atom from COOH groups. Another difference between the CN and the COOH groups is that P1 displayed an increasing absorption while P2 had a decreasing behavior around 300-350 nm. A possible explanation could be that removal of carboxylic acid hydrogen generated a carboxylate anion leading to a decreasing absorption of P2. Between 400-500 nm, both P1 and P2 showed a similar slight decreasing intensity behavior. In addition, when the fluorine anion sensitivities of P1 and P2 polymers were examined up to 1.9 eq. from 0.8 and 1.5 eq., while no change was observed around between 400-500 nm, the wide peak of P1 between 275-350 nm became almost a single with a maximum at 328 nm (Fig. S2a). Regarding P2, continuation of the addition of fluoride anion from 1.5 to 1.9 eq. only a slight increase between 350-400 nm was observed. The rest of the peaks remained unchanged (Fig S2b). Unlike absorption behaviors of P1 and P2 during the titration, the N(CH\(_3\))\(_2\) substituted P3 gradually reached its maximum between 350-400 nm with the addition of TBAF up to 1.9 eq. Absorption behavior of P2 with carboxylic acid toward fluoride anion is understandable as its acid proton reacts with the anion. On the other hand, as the mechanism of the absorption spectra of the polymers P1 and P3 toward anion sensing was not that clear, computational studies were performed, which revealed that the closer absorption bands to the experimental results appeared with the attack of the anion to the nitrile carbon of P1 (Fig. S3) and the \(\alpha\)-carbon of TT of P3 (Fig. S4).
Fig. 2. UV-Vis titration spectra of the polymers a) P1, b) P2 and c) P3 in THF (2.0×10^{-5} M) upon the addition of fluoride anions (TBAF)

As in the absorption titration, in contrast to P3, P1 and P2 exhibited similar behavior in the emission fluoride sensor study (Fig. 3). The CN derived P1 suddenly reached its maximum fluorescence intensity with the addition of 0.9 eq. of TBAF. From 0.9 eq. to 1.9 eq., the emission decreased sharply, more than 5 times. Unlike P1, P2 reached its highest emission value by adding 1.6 eq TBAF. While P2 showed decreasing emission from 1.6 eq. to 1.9 eq. it had approximately 3 times more emission intensity at 1.6 eq. where it reached the maximum emission, compared to the initial state. As in the absorption fluorine titration, P1 with CN group responded faster than P2 with COOH group and showed fluorine sensing property with strong emission. On the other hand, P3 with dimethylamine group displayed a different fluorine emission titration, and made a gradual quenching with the addition of TBAF from 0.0 eq. to 1.9. eq.
**Fig. 3.** Fluorescence titration spectra of the polymers a) P1, b) P2 and c) P3 in THF (2.0 × 10^{-5} M) upon the addition of fluoride anions (TBAF). The excitation wavelength is absorption $\lambda_{\text{max}}$.

In both absorption and fluorescence titration, CN derived P1 responded to fluorine anion earlier than COOH derived P2 which revealed that P1 has stronger donor acceptor property, imposing a more effective pull-push interaction on the polymer backbone. When the same situation is evaluated for P3, N(CH$_3$)$_2$ derived P3 exhibited different fluoride sensor behaviors including gradually increased absorption and quenching emission compared to P1 and P2 in both absorption and fluorescence titration exhibiting its more electron donating properties and weaker pull-push effect.

**Memory Characterization of Polymers**

Memristor, a two-terminal passive device whose resistance can be modulated upon an electrical stimulation, have shown great promise in information storage, neuromorphic computing, and memory applications [44]. To date, a variety of organic [45], inorganic [46], and organic-inorganic hybrid [47] materials have been investigated in memory applications. As reported in the literature, resistive memory devices based on organic small molecules and polymers are capable of data storage by exhibiting high- and low-conductivity responses to an external
Organic and hybrid materials offer unique advantages over their inorganic counterparts, such as low cost, light weight, flexibility, and scalability [47,53,54].

In this work, volatile and/or non-volatile memristive switching properties of P1-P3 were evaluated for applications in electronic devices. Two-terminal organic resistive memristors with a stack configuration of Al/polymer/Au (Fig. 4 (a)) were fabricated. 100 nm of aluminum (Al) bottom electrode (BE) was thermally evaporated through a patterned shadow mask on a pre-cleaned corning glass substrate. A 0.5 wt % solution (filtered) of P1-P3 polymers in chloroform was subsequently spin-coated at 2000 rpm onto the Al electrodes and annealed at 80 °C for two hours under N2. Finally, to complete the vertical heterostructure, a 50 nm-thick gold (Au) top electrode (TE) is deposited by thermal evaporation through a matching shadow mask. Each fabricated substrate consisted of 40 identical resistive memristors.

**Fig. 4.** a) Schematic illustration of the fabricated organic resistive memory devices; a thin layer of spin-coated P1-P3 active layer is sandwiched between Al top electrode (TE) and Au bottom electrode (BE). b) The energy band diagram of the memory device showing work functions of BE and TE relative to the HOMO and LUMO of P1-P3. Blue arrows represent charge injection from Au electrode to the HOMO level of each corresponding polymers under an applied voltage bias.

The current-voltage (I–V) responses of memory devices were measured by sweeping a DC bias voltage to TE from 0 V to 3 V to -3 V to 3 V at 0.1 V/step, while BE was grounded. As depicted in Fig. 4 (b), following applying an external voltage, the conduction processes in all devices are
dominated by hole injection, since the energy barrier for hole injection is much lower than that for electron injection.

The pinched hysteretic loop of linear I−V characteristic (Fig. 5), which is a fingerprint of memristive devices, was observed for all devices (with P1-P3 polymers). The I−V graphs on semi-log scale (Fig. 6) of all three devices exhibit bipolar resistive switching behavior as their currents pass through 0 V [48-52, 55]. As the magnitude of positive voltage increases, so does the current through the active layer, and the device resistance is switched from the high resistance state (HRS, OFF state) to the low resistance state (LRS, ON state) at 3 V, known as a ‘SET’ process [56]. On the other hand, when the opposite voltage sweep is applied, a ‘RESET’ process occurs as the magnitude of the negative voltage increases and the resistance is switched from LRS to HRS in the negative voltage region (0 V to -3 V) [56].

Fig. 5. Hysteresis loops in the linear scale bipolar IV curves of resistive memory devices with a) P1, b) P2 and c) P3 polymers. Arrows indicate the sweep directions.
As seen in Fig. 6, all three devices show uniform and symmetric SET/RESET voltage. The IV characteristics are repeatable with good accuracy and no device degradation was observed. The abrupt or ‘firing’ increase in current/resistance around ±2.8V for P1-P3, as the sweeping voltage progresses, indicates the corresponding devices are digital or threshold switching (TS) memristors \[57,58\]. Abrupt digital switching is highly advantageous for memory applications, while for neuromorphic applications, gradual switching is more desirable \[55\]. The TS voltage for all devices is closely matching which could probably initiate from relative similarity in HOMO energy levels of P1-P3 \[59\].

**Fig. 6.** Semi-log current-voltage (I–V) switching characteristics of the resistive memory devices with a) P1, b) P2 and c) P3 polymers as the active layer. Arrows and the associated numbers indicate the sweep directions and steps respectively.

To further evaluate the impact of different electron rich and deficient functional groups in P1-P3 memory devices, various quantitative parameters were compared. All devices showed a sharp bipolar increase in current when a (positive or negative) voltage is applied. However, after the positive voltage sweeps return to zero, P1 and P2 devices with CN and COOH electron-withdrawing substituents respectively, remain in the low resistance states, while P3
devices with electron-donating N(CH$_3$)$_2$ substituent show no retention of ON state and quickly switches back to its original high resistance state after the voltage is swept to zero, presenting a volatile memory [60]. The semi-log I-V bistable switching characteristics confirm the P1 and P2 memristors are non-volatile, flash memory devices, as HRS and LRS can be sustained after the voltage bias is removed or reversed. The switching from OFF to ON state and vice versa by applying an appropriate voltage, referred to as the “writing” and “erasing” process in a memory device respectively, illustrates the memory effect in P1 and P2 devices as rewritable (i.e. flash memory) [48,51,52,55,61]. In particular, P1 memristor with a stronger electron-withdrawing group (CN) stays in LRS the longest in the subsequent sweep (longer retention time) and start to descend to HRS at 1V. Therefore, the pinched hysteretic loop for P1 memristor exhibits a sizeable hysteresis in forward and reverse sweeps, while P2 and P3 devices shows moderate and minimal hysteresis respectively. A notably large ON/OFF resistance ($R_{on}/R_{off}$) ratio of 10$^5$ is recorded for memory devices with P1 and 10$^4$ for P2 polymers, while this ratio is only 10$^2$ for P3 devices. The relatively large ON/OFF current ratio of P1 and P2 memory devices may provide a low misreading rate when used in a memory application [62].

The major mechanism proposed responsible for the memristive behavior are the formation of an electric field-induced charge transfer (CT) state between electron-donating and electron-withdrawing moieties and conformational ordering of the polymer side chains/backbones [48,63,64]. Charge transfer most frequently occurs in polymers with electron donor-acceptor structure in which there is a partial transfer of electronic charge from the donor to the acceptor moiety following a voltage bias, which can result in a sharp increase in conductivity [48,49]. The presence of electron deficient CN and COOH functional groups in P1 and P2 polymers may results in formation of a relatively strong dipole moment which helps to maintain the conductive CT state and consequently a non-volatile memory device in obtained (Fig. 5 (a and b)). On the contrary, for P3 with an electron rich N(CH$_3$)$_2$ functional group, CT state is not stable and can dissociate after removal of the voltage bias when the dipole moment is week which results in a volatile memristive behavior (Fig. 5 (c)) [65,66]. As aforementioned, the stronger electron affinity of CN compared to COOH has led to higher ON/OFF current ($I_{on}/I_{off}$) and $R_{on}/R_{off}$ as well as longer retention time in memory devices with P1 than P2.
Fig. 7. Retention characteristics of P1-P3 resistive memory devices

Fig. 7 illustrates retention times and stress tests for P1-P3 memristors for at least $10^3$ s at room temperature. All devices showed reliable retention with no obvious degradation in the current in both the OFF- (HRS) and ON-states (LRS) under a constant stress of -1 V for more than $10^3$ s. This suggests that formed CT states had good stability. Moreover, the $I_{on}/I_{off}$ ratios of all devices kept steady throughout the measurement, with the highest ratio measured was $10^6$ for P1 devices, while P2 and P3 devices had $I_{on}/I_{off}$ of $10^4$ and $10^3$ respectively. One of the reasons for higher $I_{on}/I_{off}$ of P1 is the higher ON current and lower OFF current measured for the corresponding device, indicating better conductivity of P1 competed to P2 and P3. On the whole, the thiophene-based polymers reported in this work are suitable candidates for memory applications, as they offer tunable memory characteristics (volatile and non-volatile) at low voltages due to their different functional groups. Such polymer-based memory devices can pave the way towards low-cost, mechanically flexible, high endurance with relatively fast response data storage applications.
**Computational Study**

The structures of the present polymers were modelled by using density functional theory (DFT). The geometry optimizations were performed at B3LYP/6-31G(d,p) level of theory (Fig. 8). B3LYP functional was successively used to study organic molecules both in geometry optimization and their electronic spectra [67]. The geometries were found to be in good agreement with the experimentally determined XRD structures [68]. All computations were performed in the implicit THF medium (\(\varepsilon=7.4257\)) using conductor-like polarizable continuum solvent model (CPCM) [69] implemented in Gaussian’16 program package [70].

![Fig. 8. Optimized geometries (in THF) of a) P1 b) P2 c) P3 monomer molecules.](image)

Sulfur atoms prefer trans configuration to minimize the repulsions between them as expected. The dihedral angle between TT plane and the substituted phenyl ring for monomeric P1, P2 and P3 molecules was predicted as 47° and found to be the same in the case of dimeric molecules. The change in the electronic properties and spectra upon dimerization was also examined. The optimized geometries of the dimer molecules were shown in Fig. 9 at the same level of theory.
Fig. 9. Optimized geometries (in THF) of a) P1 b) P2 c) P3 dimer molecules.

Time-dependent DFT (TD-DFT) calculations were performed to calculate the excited state energies and the corresponding theoretical UV-Vis spectra. The optical band gap values were predicted from the $\lambda_{\text{onset}}$ values, which were calculated from the onset of the UV curves (Table 4). Theoretically predicted optical band gap values were found to be in agreement with the experimental values (Table 2).

Table 4. The calculated energies of the frontier orbitals, HOMO-LUMO energy gap ($\Delta$), $\lambda_{\text{max}}$, $\lambda_{\text{onset}}$ and optical band gap values (in THF) for the studied molecules

<table>
<thead>
<tr>
<th></th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$\Delta$ (eV)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\lambda_{\text{onset}}$ (nm)</th>
<th>$E_{\text{optic}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 monomer</td>
<td>-5.66</td>
<td>-1.86</td>
<td>3.80</td>
<td>377</td>
<td>460</td>
<td>2.69</td>
</tr>
<tr>
<td>P2 monomer</td>
<td>-5.60</td>
<td>-1.80</td>
<td>3.80</td>
<td>377</td>
<td>455</td>
<td>2.72</td>
</tr>
<tr>
<td>P3 monomer</td>
<td>-5.02</td>
<td>-1.33</td>
<td>3.69</td>
<td>386</td>
<td>466</td>
<td>2.66</td>
</tr>
<tr>
<td>P1 dimer</td>
<td>-5.40</td>
<td>-2.09</td>
<td>3.31</td>
<td>441</td>
<td>550</td>
<td>2.25</td>
</tr>
<tr>
<td>P2 dimer</td>
<td>-5.23</td>
<td>-1.91</td>
<td>3.32</td>
<td>443</td>
<td>548</td>
<td>2.26</td>
</tr>
<tr>
<td>P3 dimer</td>
<td>-4.73</td>
<td>-1.46</td>
<td>3.27</td>
<td>458</td>
<td>565</td>
<td>2.20</td>
</tr>
</tbody>
</table>

Thermal Characterization of Polymers

Thermal stability is an important physical parameter to evaluate polymers for applications. Thermal properties were studied with thermal gravimetric analysis (TGA) up to 700 °C at a
heating rate of 10 °C min\(^{-1}\) under N\(_2\) protection. While the first decomposition temperatures (Td, corresponding to 5% weight loss) of P2 and P3 were measured to be at around 215 and 260 °C, respectively, P1 had a decomposition temperature of 320 °C (Fig. 10). Their second degradations with the percentage weight loss took place at 422 °C (15%), 388 °C (30%) and 363 °C (45%) for P1, P2 and P3, respectively. Although all the polymers displayed a similar thermal behavior, P1 had a better thermal stability compared with P2 and P3, indicating that CN substituted skeleton provided the polymer backbone with relatively higher thermal resistance compared to COOH and N(CH\(_3\))\(_2\) derived polymers.

![TGA graph](image)

**Fig. 10.** Thermal gravimetric analysis (TGA) of the polymers.

**Conclusions**

In this work, CN, COOH and N(CH\(_3\))\(_2\) derived conjugated building TT blocks were synthesized and polymerized with 3-hexylthiophene applying Suzuki coupling to obtain the conjugated copolymers, P1-3. Their photophysical and electrochemical properties were examined both experimentally and theoretically. All the polymers showed mega Stokes shift reaching up to 138 nm, suggesting a strong intramolecular charge transfer in the polymer backbones. Investigation of fluoride anion sensing properties demonstrated that change of the functional groups at the para positions of the phenyls of TT skeletons had remarkable changes on the properties of the polymers. In the absorption titration of the polymers with fluoride anion, CN substituted P1 reached the maximum absorption at 0.7 eq. of F\(^-\) anion rapidly, while COOH
functionalized P2 reached at 1.4 eq. On the other hand, N(CH₃)₂ derived P3 sensed by demonstrating a gradual increase up to 1.9 eq. of TBAF; unlike the other polymers. Electron flow mechanisms of the sensing properties were supported by a computational study. In addition to the photophysical properties of the polymers, memory device studies, retention times and stress tests were investigated. The memory devices of the polymers exhibited a high ON/OFF ratio reaching up to 10⁶, which indicated an excellent conductivity as suitable fast response data storage polymers. Moreover, all the polymers showed good retention without any degradation in both OFF- and ON-states under a constant stress of -1 V. The TT-based polymers, having varying functional groups, presented in this study, were found to be suitable active materials for the high-performance memory devices. The present study is expected to advance the ongoing investigations into optic and electronic applications, and the design of TT-based polymers with varying functional groups to produce outstanding high-performance memory devices having anion sensing properties, thermal stabilities and photophysical features.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

We thank Higher Education Council of Turkey (YOK) and TUBITAK grants to Recep Isci (PhD, 100/2000 YOK and 2211A BIDEP/TUBITAK), and Dilara Gunturkun (2210A BIDEP/TUBITAK), 118C365 numbered TUBITAK BIDEB 2232 Project and Unsped Global Lojistik, Turkey, for financial support.

**Data availability**

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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