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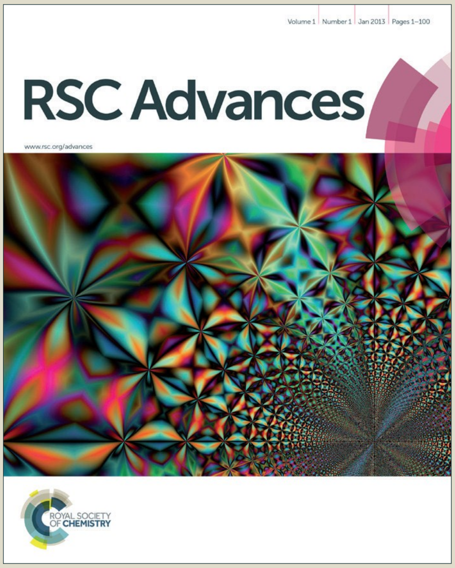

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Synthesis and characterization of triphenylamine-based polymers and their application towards solid-state electrochromic cells

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Four novel triphenylamine-based polymers, **PJK1**, **PJK2**, **PJK3** and **PJK4** were successfully synthesized and fully characterized by ^{1}H NMR, UV-VIS spectroscopy, cyclic voltammetry (CV), GPC and spectroelectrochemistry. These polymers are easily soluble in many common organic solvents, which make them appropriate for film deposition via spray-coating. We made fabricated electrochromic cells comprising ITO-coated glass/polymer/gel electrolyte/ITO-coated glass and patterned the color change by applying direct current with different voltages. We report herein color changes, from the neutral to oxidized form as follows: for **PJK1**, orange to dark green; for **PJK2**, light yellow to reddish brown; for **PJK3**, light blue to grey; and for **PJK4**, green to bluish green. The majority of the copolymers exhibited very good thermal stabilities, as evidenced by less than a 5% weight loss in temperatures exceeding 400 °C. To further characterize, we simulated the electrochemical and optical properties, which are good agreement with the experimental data.

1. Introduction

Electrochromism is generally known as a reversible optical change in a material induced by an external voltage; many organic and inorganic compounds exhibit electrochromism throughout the electromagnetic spectrum.[1] The idea of an electrochromic display was first suggested in 1961.[2] This property led to the expansion of many technological applications such as smart windows,[3] automatic anti-glazing mirrors,[4] chameleon materials,[5] and electrochromic displays.[6,7] In recent years, WO3[4] and viologen-based[8] electrochromic devices were commercialized. In the series of electrochromic compounds, conjugated polymers can display high coloration over a wide color range at low operating voltage with fast switching capabilities, high optical contrasts, rapid response times and the ability to modify their structure to create multicolor electrochromes.[9] Conjugated electrochromic polymers, such as poly(thiophene) (PTh), poly(aniline) (PANI) and poly(pyrrole) (PPy), have been extensively studied.[10] Previously, many electrochromic organic polymers were obtained by electropolymerization or oxidative polymerization,[11,12] but chemical polymerization has more advantages than these polymerization methods. Because in electropolymerization or oxidative polymerization methods we always get the problems, such as the lack of film uniformity over large surface, low material recovery, inability to form large amounts of processable polymer and irregular linkages within the polymer backbone.[13,14]

Triphenylamine (TPA) derivatives, which are electron-donating in nature, show excellent electrochemical stability, optoelectronic and electrochromic behavior.[15-18] The characteristic structural feature of triphenylamine is the nitrogen center, which also serves as its electroactive site. The nitrogen atom is connected to three electron-rich phenyl groups in a propeller-like geometry.[19] Electron-rich triphenylamine derivatives are easily oxidized to form stable polarons, an oxidation process that is always associated with a clear change in coloration of the molecule. Additionally, different thiophene-based derivatives have gained much attention during the past years, owing to the variation of the optical and electronic properties by simple structural modifications.[20,21] Fluorene is a biphenyl structure with rigid plane and huge π-conjugated molecule, whose derivatives have been widely used in organic electro-luminescence materials, photochromic materials two-photon absorbing materials, because of their very high photoluminescence, thermal stability, electroluminescence quantum efficiency, good solubility.[22-24]

Here in this research we designed a series of conjugated polymers as EC cells, wherein, triphenylamine (TPA) and thiophene or fluorene were chosen to build the backbone of our target molecule with the principle of different color properties and these copolymers are highly conjugated and giving a small band gap should therefore be more conducting nature. We reported the synthesis and full characterization of four triphenylamine-based polymers: **PJK1**, **PJK2**, **PJK3** and

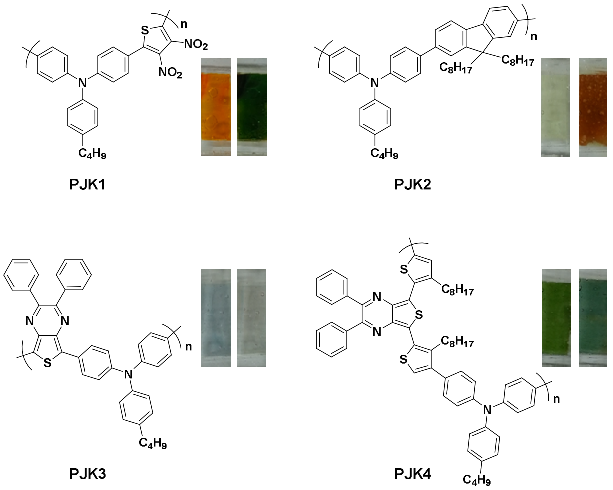

Fig. 1 Polymer structures and color transitions.

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Electronic Supplementary Information (ESI) available: detailed ^{1}H-NMR, ^{13}C-NMR, HRMS and IR data available. See DOI: 10.1039/x0xx00000x

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PJK4. The resulting copolymers were readily soluble in most industrial solvents such as chloroform, dichloromethane, DMF, and tetrahydrofuran. To evaluate the electrochemical properties, all-solid-state electrochemical cells were prepared by spray-coating chloroform solutions of the copolymers onto ITO-coated glass and used a polymer gel as the electrolyte. Neutral-to-oxidized color changes for the copolymers all differed, exhibiting transitions from orange to dark green, light yellow to reddish brown, light blue to grey, and green to bluish green (Figure 1).

2. Experimental Section

2.1. Materials and Characterization

All solvents and reagents (analytical and spectroscopic grades) were commercially obtained and used as received unless otherwise noted. Fourier 300, 7.05 Tesla, 300 MHz, an AVANCE III 600 spectrometer (Akishima, Japan) was operated at 600 MHz and 150 MHz for ^{1}H and ^{13}C NMR spectroscopy, respectively. $CDCl_3$ was used as the solvent, and Alice 4.0 software was used for analysis. The chemical shifts (δ values) are reported in ppm downfield from an internal standard (Me4Si). Mass spectra were recorded on a 4000 Q TRAP mass spectrometer. HRMS spectra were obtained using a micrOTOF-QII mass spectrometer. FT-IR spectra were recorded on an ALPHA-P spectrometer. UV-visible absorption spectra were recorded using an Agilent 8453 spectrophotometer. The electrochemical measurements, i.e., cyclic voltammetry (CV) experiments, were conducted using a Versa STAT 3 instrument using polymer films sprayed on platinum button, the electrolyte used was 0.1 M $TBABF_4$ in propylene carbonate, Ag/Ag+ electrode as the reference electrode and platinum wire as the counter electrode.

Thermogravimetric analyses (TGA) were performed on a Mettler Toledo instrument using a heating rate of 20 °C/min and nitrogen flow rate of 50 mL/min. Number-average (Mn) and weight-average (Mw) molecular weights were determined by gel permeation chromatography (GPC) using a Waters model 2690 instrument with THF (HPLC grade, Aldrich) as the eluting solvent. Spectroelectrochemical data of the polymers films were recorded by using an Instek model GPS-3303 instrument as a DC power source. Electrochromic polymer films were produced by spraying solutions of the polymers (5 mg/mL in chloroform) onto Indium tin oxide (ITO)-coated glass slides (square : surface resistivity : 8-12 Ω/sq, 25 mm × 25 mm × 1.1 mm, Sigma-Aldrich). The polymers were spray-coated onto the active surface of an ITO plate using a mask.

2.2. Synthesis of Monomer

2.2.1. 4-butyl-N,N-diphenylaniline (1): Bromobenzene (26.69 g, 170 mmol), 4-butylaniline (8.344 g, 56 mmol) and sodium *tert*-butoxide (19.23 g, 200 mmol) were added to a solution of bis[2-(diphenylphosphino) phenyl]ether (DPEPhos) (0.914 g, 1.7 mmol) and bis(dibenzylideneaceton)palladium ($Pd(dba)_2$) (0.789 g, 1.3 mmol) in toluene (160 mL) under an inert atmosphere. The resulting solution was stirred at 90 °C for 24 h. The reaction mixture was allowed to cool to room temperature, at which point 500 mL water was added, and the mixture was extracted with ethyl acetate (2×250 mL). The combined organic layers were dried over sodium sulfate, concentrated, and purified by silica gel column chromatography (10% ethyl acetate in hexane) to yield 14.02 g (83%) of the product as a yellow and viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17-7.08 (m, 4H), 7.01-6.83 (m, 10H), 2.48 (t, J = 7.7 Hz, 2H), 1.57-1.44 (m, 2H), 1.35-1.21 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.1, 145.3, 137.7, 129.2, 129.1, 124.7, 123.7, 122.1, 35.0, 33.6, 22.4, 13.9 ppm; IR ν_{max} in cm^{-1}(in $CHCl_3$): 2930, 1589, 1508, 1491, 1276, 1075, 903, 833, 723, 649, 621; ESI-MS: 302 $[M+H]^+$.

2.2.2. 2,3-diphenylthieno[3,4-b]pyrazine (7): Compound 6 (0.45 g, 3.95 mmol) was added to benzil (0.91 g, 4.34 mmol) in ethanol (85 mL) and refluxed overnight. The solution was evaporated and purified by column chromatography (10% ethyl acetate in hexane) to afford a yellow solid (0.81 g, 71%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.05 (s, 2H), 7.46-7.29 (m, 10H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ 153.4, 141.6, 139.1, 129.6, 128.8, 128.1, 117.5 ppm; IR ν_{max} in cm^{-1}(KBr): 3084, 3054, 1597, 1576, 1231, 1074, 839, 816, 723; ESI-MS: 289 $[M+H]^+$.

2.2.3. 5,7-dibromo-2,3-diphenylthieno[3,4-b]pyrazine (8): NBS (0.97 g, 5.4 mmol) was added to compound 7 (0.75 g, 2.6 mmol) in a mixture of chloroform/trifluoroacetic acid (16 mL; 1:1 v/v), and the mixture was stirred overnight in the dark. The mixture was extracted with ethyl acetate and dried over sodium sulfate, evaporated, and purified by column chromatography (50% dichloromethane in hexane) to afford a greenish-yellow solid (0.86 g, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46-7.27(m, 10H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.7, 139.3, 138.2, 129.8, 129.3, 128.1, 104.9 ppm; IR ν_{max} in cm^{-1}(KBr): 3051, 1596,1523, 1253, 1025, 811, 763, 739; HR-MS (ESI-MS) m/z calcd. For $C_{18}H_{11}Br_2N_2S$ $[M+H]^+$: 446.8984, found 446.8989.

2.2.4. 3,3''-dioctyl-[2,2':5',2''-terthiophene]-3',4'-diamine (13): Compound 12 (3.03 g, 5.4 mmol) was stirred in a mixture of HCl/ethanol (24 mL/35 mL) and cooled in an ice bath. Tin(II) chloride dihydrate (40 g, 177 mmol) was added in small portions to maintain the temperature at 25 °C. After the reaction was stirred overnight, the pH was adjusted to 10 with 4 M KOH, and the solution was extracted with ethyl acetate. The organic layer was dried with sodium sulfate and purified by column chromatography (70% ethyl acetate in hexane) to afford the desired compound as a brown oil (1.96 g, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29 (d, J =5.3 Hz, 2H), 6.99 (d, J =5.1 Hz, 2H), 3.35 (s, 4H), 2.62 (t, J =7.7 Hz, 4H), 1.65-1.52 (m, 4H), 1.37-1.15 (m, 20H), 0.87 (t, J =6.5, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ 142.33, 134.57, 129.28, 127.88, 125.29, 109.01, 31.88, 30.81, 29.45, 29.39, 29.25, 28.94, 22.65, 14.08 ppm; IR ν_{max} in cm^{-1}(in $CHCl_3$): 3413, 3325, 2922, 2852, 1613, 1572, 1496, 1451, 904, 829, 725, 648; ESI-MS: 503 $[M+H]^+$.

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2.2.5. 5,7-bis(3-octylthiophen-2-yl)-2,3-diphenylthieno[3,4-b]pyrazine (14): Compound 13 (1.85 g, 3.7 mmol) was added to a solution of benzil (0.85 g, 4.0 mmol) in ethanol (65 mL) and refluxed overnight. The solution was concentrated by evaporation and purified by column chromatography (10% ethyl acetate in hexane) to afford the desired compound as a purple solid (2.32 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55-7.42 (m, 4H), 7.41-7.29 (m, 8H), 7.03 (d, *J* =5.1 Hz, 2H), 2.97 (t, *J* =7.7 Hz, 4H), 1.81-1.68 (m, 4H), 1.43-1.14 (m, 20H), 0.86 (t, *J* =6.5 Hz, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.3, 141.0, 139.1, 137.7, 134.8, 130.0, 129.5, 128.8, 127.9, 126.8, 125.3, 31.9, 30.4, 30.3, 29.7, 29.5, 29.3, 22.7, 14.1 ppm; IR ν_{max} in cm^{-1}(KBr): 3083, 3060, 2951,1577, 1511, 1246, 1209, 713, 694, 640; ESI-MS: 678 $[M+H]^+$.

2.2.6. 5,7-bis(5-bromo-3-octylthiophen-2-yl)-2,3-diphenyl thieno[3,4-b]pyrazine (15): NBS (1.14 g, 6.4 mmol) was added to a solution of compound 14 (1.97 g, 2.9 mmol) in a mixture of chloroform/trifluoro acetic acid (14 mL; 1:1 v/v), and the mixture was stirred overnight in dark. The reaction mixture was extracted with ethyl acetate, dried over sodium sulfate and purified by column chromatography (50% dichloromethane in hexane) to afford the desired compound as a greenish, dark purple solid (2.39 g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, *J* =6.2 Hz, 4H), 7.39-7.30 (m, 6H), 6.98 (s, 2H), 2.91 (t, *J* =7.7 Hz, 4H), 1.78-1.66 (m, 4H), 1.45-1.18 (m, 20H), 0.87 (t, *J* =6.7 Hz, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.79, 141.14, 138.80, 137.65, 132.14, 130.07, 129.62, 129.06, 128.10, 124.24, 114.44, 31.87, 30.53, 30.06, 30.08, 29.73, 29.49, 29.29, 22.66, 14.08 ppm; IR ν_{max} in cm^{-1}(KBr): 3019, 1215, 905, 753, 726; HR-MS (ESI-MS) m/z calcd. For $C_{42}H_{46}Br_2N_2S_3Na$ $[M+Na]^+$: 857.1064, found 857.1037.

2.3. Copolymer synthesis

2.3.1. Poly(4-butyl-N-(4-(3,4-dinitrothiophen-2-yl)phenyl)-N-phenylaniline (PJK1): 4-butyl-N,N-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (0.2 g, 0.37 mmol), 2,5-dibromo-3,4-dinitrothiophene (0.12 g, 0.37 mmol), $Pd(0)(PPh_3)_4$ (0.02 g, 0.017 mmol), and aqueous 2 M K_2CO_3 (5 mL) were added to dry THF (15 mL). The mixture was vigorously stirred at 85-90 °C for 48-72 h. After the solution cooled to room temperature, the reaction mixture was poured into a cold mixture of methanol/deionized water (10:1 v/v). The solid polymer was collected by filtration and washed with methanol. The recovered polymer was then washed for 24 h in a Soxhlet apparatus using acetone to remove oligomers and catalyst residues. Finally, the polymer was redissolved in chloroform, precipitated from cold methanol and dried (112 mg, 61%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42-7.38 (m, 4H), 7.22-7.09 (m, 8H), 2.63 (t, *J* = 7.5, 2H), 1.66-1.60 (m, 2H), 1.43-1.35(m, 2H), 0.96(t, *J* = 7.24, 3H) ppm.

2.3.2. Poly(4-butyl-N-(4-(9,9-dioctyl-9H-fluoren-2-yl)phenyl)-N-phenylaniline (PJK2): The procedure used to synthesize **PJK1** was followed, using 4-butyl-N,N-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (0.2 g, 0.37 mmol), 2,7-dibromo-9,9-dioctyl-9H-fluorene (0.2 g, 0.37 mmol), $Pd(0)(PPh_3)_4$ (0.02 g, 0.017 mmol), THF (15 mL) and 2 M K_2CO_3 (5 mL). Yield (140 mg, 56%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76-7.72 (m, 2H), 7.60-7.54 (m, 8H), 7.24-7.19 (m, 4H), 7.15-7.11 (m, 4H), 2.64-2.59 (m, 2H), 2.60-1.92 (br, 4H), 1.66-1.60(m, 2H), 1.43-1.37 (m, 2H), 1.31-1.02 (m, 16H), 0.99-0.94(t, *J* = 7.34, 4H), 0.83-0.77(m, 9H) ppm.

2.3.3. Poly(4-butyl-N-(4-(2,3-diphenylthieno[3,4-b]pyrazin-5-yl)phenyl)-N-phenylaniline (PJK3): The procedure used to synthesize **PJK1** was followed, using 4-butyl-N,N-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (0.2 g, 0.37 mmol), 5,7-dibromo-2,3-diphenylthieno[3,4-b]pyrazine (0.17 g, 0.37 mmol), $Pd(0)(PPh_3)_4$ (0.02 g, 0.017 mmol), THF (15 mL) and 2 M K_2CO_3 (5 mL). Yield (108 mg, 51%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.23-8.17 (m, 4H), 7.55-7.50 (m, 4H), 7.36-7.27 (m, 6H), 7.25-7.21 (m, 2H), 7.18-7.07 (m, 6H), 2.64-2.57 (m, 2H), 1.67-1.60 (m, 2H), 1.43-1.37 (m, 2H), 0.99 (t, *J* = 7.53, 3H) ppm.

2.3.4. Poly(4-butyl-N-(4-(4-octyl-5-(7-(3-octylthiophen-2-yl)-2,3-diphenylthieno[3,4-b]pyrazin-5-yl)thiophen-3-yl)phenyl)-N-phenylaniline (PJK4): The procedure used to synthesize **PJK1** was followed, using 4-butyl-N,N-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (0.2 g, 0.37 mmol), 5,7-bis(5-bromo-3-octylthiophen-2-yl)-2,3-diphenylthieno[3,4-b]pyrazine (0.31 g, 0,37 mmol), $Pd(0)(PPh_3)_4$ (0.02 g, 0.017 mmol), THF (15 mL) and 2 M K_2CO_3 (5 mL). Yield (184 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63-7.53 (m, 8H), 7.37-7.29 (m. 6H), 7.21-7.09 (m, 10H), 3.03-2.97 (m, 4H), 2.64-2.58 (m, 2H), 1.84-1.16 (m, 28H), 0.99-0.79 (m, 9H) ppm.

3. Results and Discussion

3.1. Monomer Synthesis

The synthetic routes for all of the monomers are shown in Schemes 1-3. In Scheme 1, compound 1 was prepared by using the bis(dibenzylideneaceton)- palladium, ligand (bis-[2-(diphenylphosphino)phenyl]ether); compounds 2-6 were synthesized according to reported procedures.[25-30] Compound 7 was successfully prepared by condensation with benzil in ethanol. In IR spectrum disappearance of the N-H stretching band of the amino functionality at 3355 cm^{-1} was indicated successful arylation to compound 7. Compound 8 was synthesized in good yield using NBS in a mixture of TFA and chloroform at room temperature (Scheme 2). The bromination was confirmed by disappearance of the peak at δ 8.05 in the ^{1}H-NMR spectrum and characterization data for compound 8 fully matched with the reported data (Scheme 2).[31] Compund 9-12 prepared according to reported procedure.[32-38] To synthesize compound 15 (Scheme 3), we modified a reported route.[38] First, compound 12 was reduced using a mixture of HCl/ethanol and tin(II) chloride to compound 13. The previously reported yield for this reaction is 52%, which we were able to increase to 72% here. Subsequently, compound 13 was condensed with the benzil to give 14 in 92% yield, and

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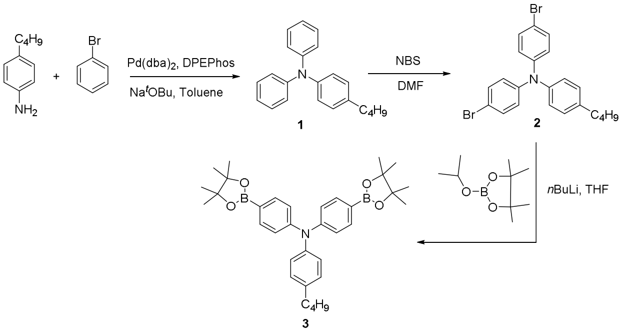
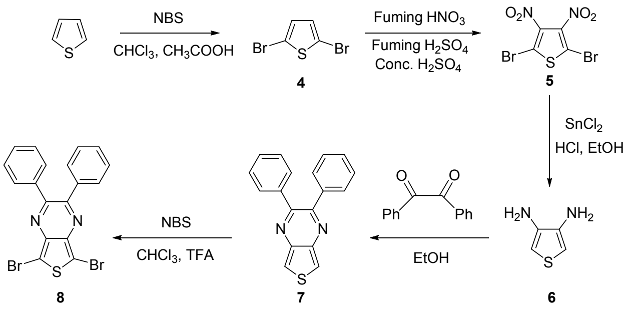
then brominated with NBS in TFA and chloroform to afford compound 15 in 98% yield. Using this method, we obtained a higher overall yield for these 3 steps compared with that obtained using the previous method. The structures of all the synthesized compounds were confirmed by ^{1}H-NMR, ^{13}C-NMR, IR and mass spectral analyses. Compound 16 was obtained from a commercial source.

3.2. Polymer Synthesis

Polymers **PJK1**, **PJK2**, **PJK3**, and **PJK4** were synthesized by the Suzuki coupling reaction of 4-butyl-N,N-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (3) with compounds 5, 8, 15 and 16, respectively. The reactions were performed in the presence of Pd(PPh$_3$)$_4$ and potassium carbonate in THF solution (Scheme 4).[39] The ^{1}H NMR spectrum of **PJK1** in CDCl$_3$ showed peaks indicative of the 12 protons assignable to the phenyl rings of triphenylamine at δ 7.30-7.36 ppm and 6.98-7.16 ppm, while signals of the Ar-CH$_2$ alkyl side chain of the phenyl units appeared at δ 2.56 ppm as a triplet, and the terminal -CH$_3$ appeared as a triplet at δ 0.89. Similarly, the ^{1}H NMR spectrum of **PJK2** in CDCl$_3$ exhibited peaks attributable to the 18 protons of the fluorene and phenyl groups in the aromatic region. The Ar-CH$_2$ alkyl side chain on the phenyl units appeared at *δ* 2.56 ppm as a triplet, while the -CH$_3$ protons appeared at *δ* 0.89 as a triplet. The ^{1}H NMR spectrum of **PJK3** in CDCl$_3$ revealed peaks in the aromatic region for the phenyl groups, and the peaks in the aliphatic region was also confirmed the structure. For the spectrum of **PJK4**, the two protons of the thiophene-CH$_2$ alkyl side chain appeared at *δ* 2.93 ppm as a broad signal, and protons attributable to the Ar-CH$_2$ alkyl side chain on the phenyl units appeared at δ 2.53 ppm as a triplet. Detailed ^{1}H-NMR data of the polymers can be found in the experimental section, while the ^{1}H NMR spectra can be found in the Supporting Information.



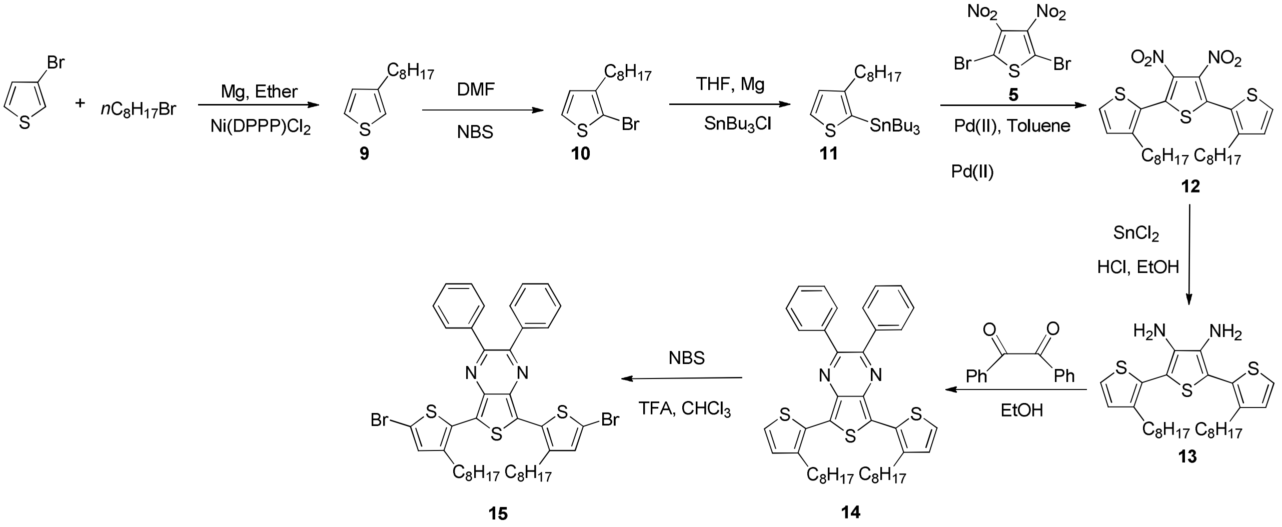
Scheme 1 Synthesis of 4-Butyltriphenylamine derivative.



Scheme 2 Synthesis of 5,7-dibromo-2,3-diphenylthieno[3,4-b]pyrazine.

3.3. GPC and TG analysis

The number-average molecular weight (Mn) and weight-average molecular weight (Mw) of the copolymers ranged from 2600 to 5400 and 4200 to 21,600, respectively, with polydispersity index ranging from 1.6 to 4.0. These data are summarized in Table 1. The thermal properties of all the copolymers were investigated by TGA under a nitrogen atmosphere and data are summarized in Table 1. Most copolymers exhibited very good thermal stabilities, losing less than 5% of their weight until well above 400 °C. The amount of



Scheme 3 Synthesis of 5,7-bis(5-bromo-3-octylthiophen-2-yl)-2,3-diphenylthieno[3,4-b]pyrazine.

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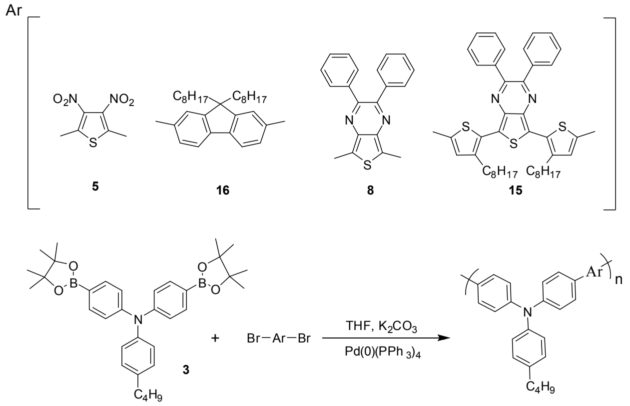

Scheme 4 Synthesis of copolymers.

carbonized residue (char yield) of these polymers in nitrogen atmosphere was more than 61% at 600 °C.

3.4. Cyclic voltammetry studies

The cyclic voltammograms (CVs) of all the polymers can be found in Figure 2 and the results are summarized in Table 1. Cyclic voltammograms were obtained by casting films of polymers onto a platinum button, propylene carbonate using 0.1 M TBABF$_4$ as the supporting electrolyte, an Ag/Ag+ electrode as the reference electrode and a platinum wire as the counter electrode, at a scan rate of 50 mV/s. The oxidation voltages of **PJK1**-**PJK4** films were 0.83 V, 0.67 V, 0.36 V and 0.46 V respectively. All new polymers are stable upon oxidation with potential of oxidation ranging from 0.36 to 0.83 V vs SCE. Here almost we observed that oxidation peaks has higher peak currents than reduction peaks and it shows these polymers better electron donors than acceptors.[41]

Cycling stability upon oxidation of all polymers has been conducted (see the Supporting Information). A thin film of polymer was placed on a platinum button and cyclic voltammetry was done at speed rate of 50mV/s. The cyclic voltammograms of **PJK1** between -0.5 and +1.5 V vs Ag/Ag+ shows a slight shift of the anodic peak (0.02 V) and a reduction of the current density of 40% after 500 cycles. For **PJK2**, the cyclic voltammograms at same conditions shows a shift of the anodic peak (+0.02 V) and a decrease in the current density after 500 cycles. For **PJK3** current decreased around 30%. Finally **PJK4** shows a shift of the anodic peak (+0.02 V) and a decrease of 30% in the current density. The minor shift of the anodic peak and the reduction of the current densities upon cycling can be attributed to an alteration in the film morphology or activation of new electro active site from freshly cast polymer film upon the repetitive insertion and extraction of counter ion through the oxidation process.[38]

Table 1 GPC, TGA and CV oxidation potential data of Polymer Derivatives.

Polymer	M$_n$	M$_w$	PDI	T$_{dec}$ in °C	E_{ox} vs SCE
PJK1	5400	12400	2.3	288	0.83
PJK2	4700	15000	3.1	467	0.67
PJK3	2600	4200	1.6	502	0.36
PJK4	5300	21600	4.0	460	0.46

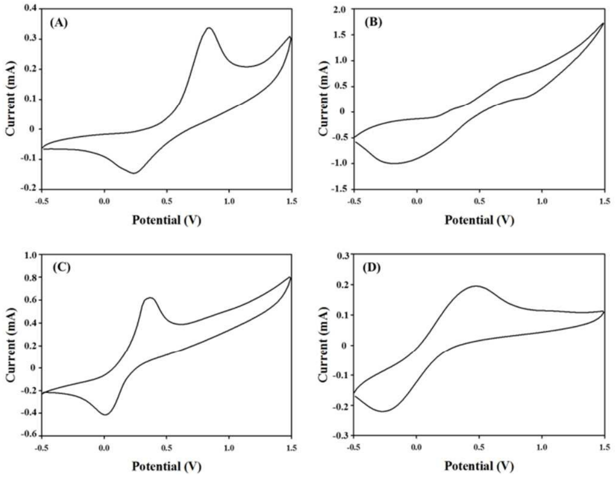

Fig. 2 Cyclic voltammograms of (A) **PJK1**; (B) **PJK2**; (C) **PJK3**; (D) **PJK4** on platinum button with propylene carbonate in 0.1 M tetrabutylammonium tetrafluoro borate. Scan rate: 50 mV s^{-1} at 18°C.

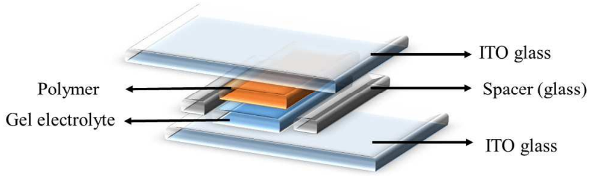

Fig. 3 Schematic cross-section of electrochromic cells

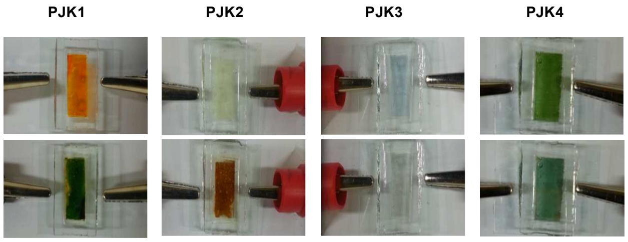

Fig. 4 Polymers with before and after applied potentials.

3.5. Spectroelectrochemical studies

Spectroelectrochemical measurements were performed on films of the polymers deposited onto ITO-coated glass substrates following the spray-coating technique reported by Reynolds et al.,[40] which facilitated formation of uniform polymeric layers. The gel electrolyte was spread on the polymer-coated side of the electrode, another ITO glass was sandwiched under atmospheric conditions, and glass spacers were used to fix the cell. To prevent leakage, an epoxy resin was applied to seal the device (see Figure 3). The gel electrolyte prepared by using PMMA, LiClO$_4$ and propylene carbonate in dry acetonitrile.[39] This electrolyte allow ion transport and utilized to afford a single layer electrochromic cell (Figure 4). DC voltage was fixed between 0.0 and 2.8 V for

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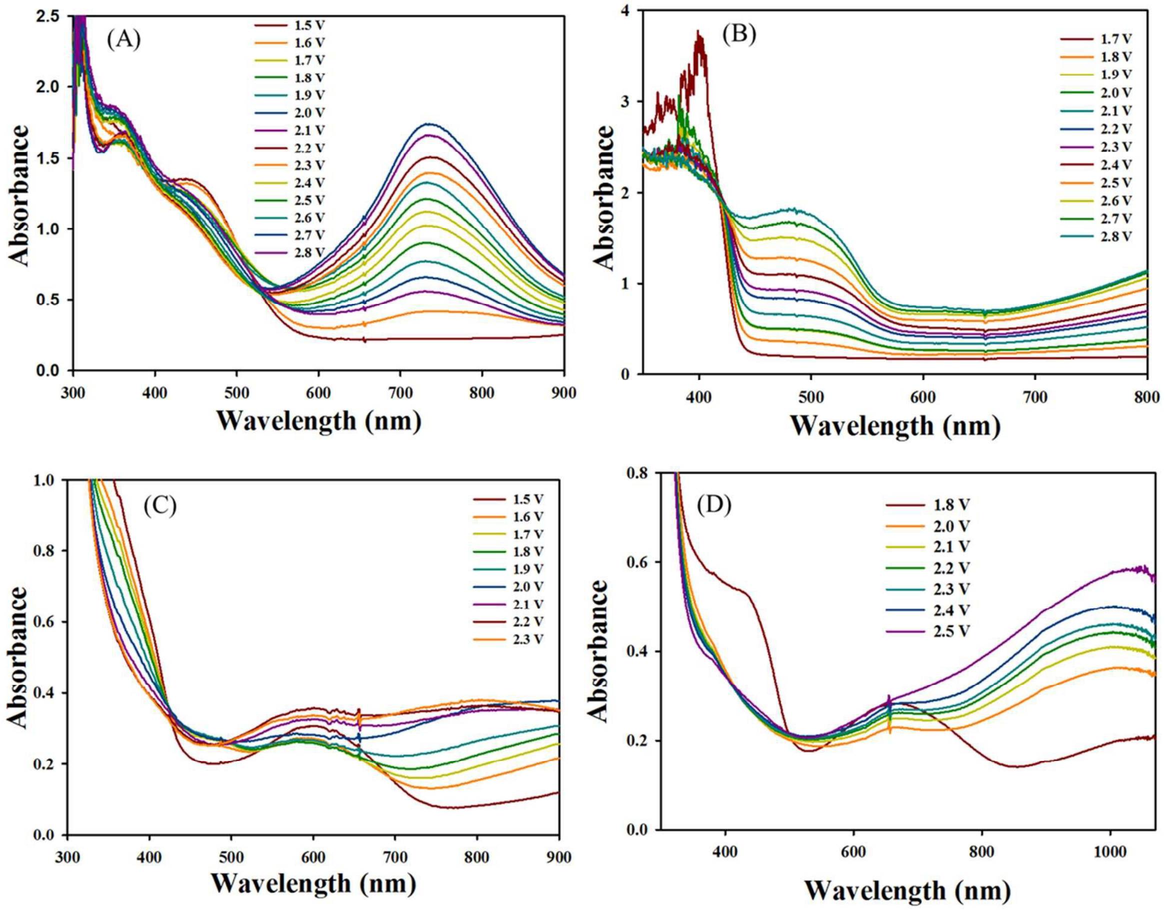

Fig. 5 Absorption spectra of **PJK1** (a), **PJK2** (b), **PJK3** (c) and **PJK4** (d) solid state EC using gel electrolyte (DC power supply).

PJK1. At 0.0 V, polymer **PJK1** is in a neutral state, and the color is orange. The change in absorption of the film of **PJK1** at various applied potentials is shown in Figure 5a. In the neutral form, at 0 V, **PJK1** exhibited a strong absorption at 438 nm. Upon application of the voltage, this absorption band decreased while a new absorption peak starting at 580 nm and extending to above 900 nm in the NIR region grew in, while the color changed to green. The new absorption band exhibited a higher extinction coefficient value at 2 V, and then decreased after that voltage. The color change of the fabricated electrochromic cell was uniformed across the film.

Figure 5b displays the spectroelectrochemical spectrum of **PJK2** at various DC voltages up to 2.8 V. When a voltage of 0.0 V was applied, the polymer was in the neutral state with a light yellow color. When the applied voltage was increased to a maximum of 2.8 V, the color changed from light yellow to reddish brown with a uniform color change across the entire film. For potentials up to 1.7 V, **PJK2** exhibited an absorption band at 399 nm; when the voltage was increased, this absorption band slowly diminished while a new absorption peak appeared between 430 and 580 nm, corresponding to a reddish brown color. **PJK3**, which was light blue in color, exhibited absorption maxima at 598 nm up to 1.5 V. By increasing the DC voltage, this absorption peak decreased, and a new absorption peak appeared in the region of 680 to 900 nm, resulting in a grey color (Figure 5c). Finally, **PJK4** exhibited a green color in its neutral state at 0.0 V, corresponding to an absorption maximum at 655 nm. Upon increasing the voltage, a new peak appeared starting at 700 nm and extending above 900 nm in the NIR region, resulting in a color change to bluish green (Figure 5d). Moreover, these polymers displayed high molar extinction coefficient values in solution state, which was confirmed to present a good coloration efficiency (see supporting information, Figure 49).[42]

3.6. Electrochromic switching

Electrochromic switching studies for the all polymers were done to monitor the % transmittance (T) as a function of time at their absorption maximum and to regulate the response time by stepping potential repeatedly between the neutral and oxidized states.[43] The active area of the polymer film on ITO-glass is around 1 cm^2 in TBABF$_4$, in propylene carbonate. Fig. 6 represents the %T and current density changes of **PJK1**, **PJK2**, **PJK3** and **PJK4** as a function of the time at their longer wavelength absorption maximum, 731 nm for **PJK1** with 0 to 2.5V potential, 480 nm for **PJK2**, 776 nm for **PJK3** and 1033 nm

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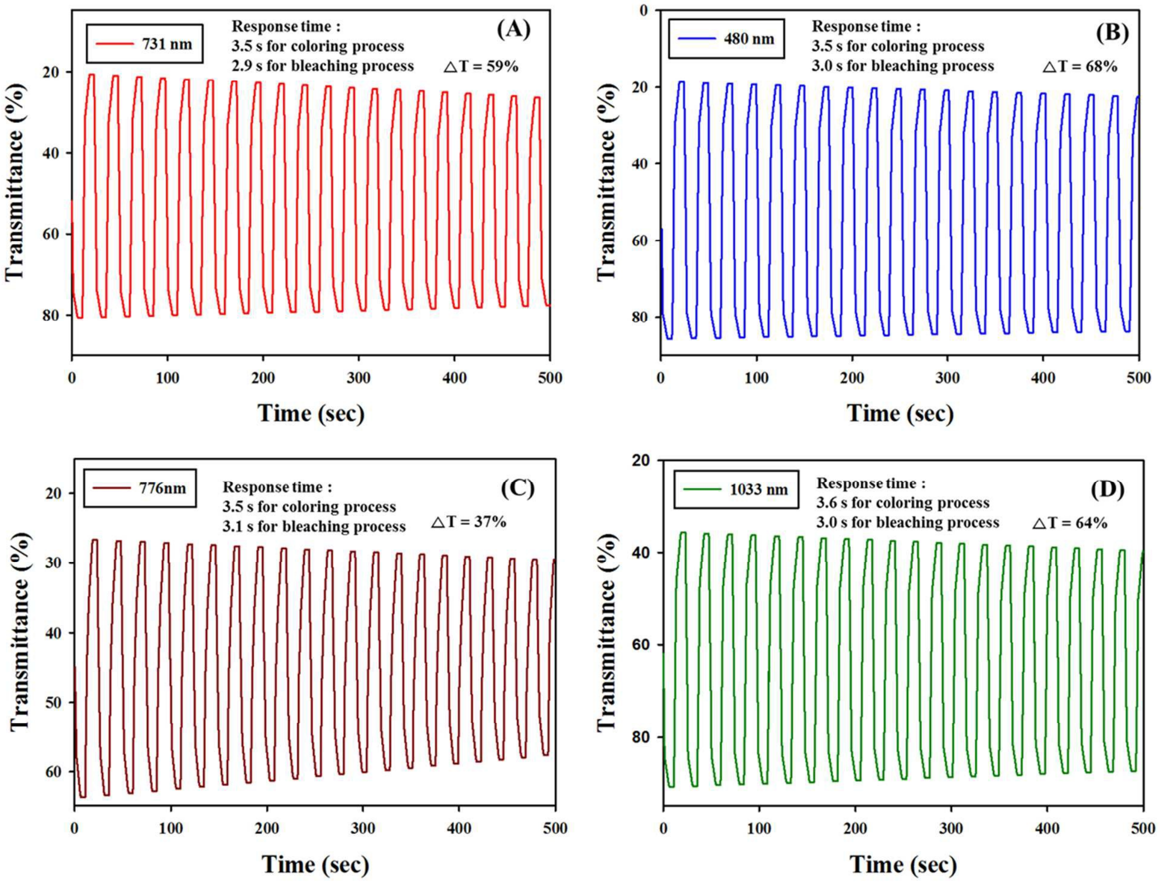

Fig. 6 Electrochromic switching under an applied square voltage signal for (A) **PJK1** at 731 nm, (B) **PJK2** at 480 nm, (C) **PJK3** at 776 nm and (D) **PJK4** at 1033 nm respectively, as a function of time.

for **PJK4** with 0 to 2.3V potential by applying square-wave potential steps of 12 s (complete cycle time is 24 s) with 20 cycles. The optical contrast of the **PJK1** was found to be 59% at 731 nm with a switching time of 3.5 seconds for coloring process and 2.9 seconds for bleaching process.[44,45] **PJK2**, **PJK3** and **PJK4** exhibit electrochromic performance with contrast value (ΔT) 68%, 37%, 64% with switching time of 3.5s/3s, 3.5s/3.1s and 3.6s/3.0s respectively. From the data, it can be clearly found that **PJK1**, **PJK2** and **PJK4** were have the better stability and higher percent transmittance contrast than **PJK3** after regular switching for 500s (Figure 6). Mainly **PJK1** and **PJK4** have the good optical contrasts in the NIR region, which is a very important property for various NIR applications, such as camouflage devices and polymer based field-effect transistors.

3.7. Theoretical investigation

For this study, all the calculations were done for **PJK** polymer series using commercial package Gaussian 03.[46] As shown in Fig. 7, the optimized geometries of monomers at neutral and oxidation states were obtained using Hartree-Fock (HF) combined with 3-21G* bases set.[47] By using the semi-empirical quantum chemical method ZINDO including 25 lowest-energy electronic transitions, oscillator strength and absorption wavelength were generated.[48]

As shown in Table 2 and Fig 8, optical (absorbance wavelength and oscillator strength) and transition properties in the neutral and oxidation states were used for investigation to better understand the optical transition of **PJK** materials. For the neutral state of **PJK1**, HOMO→LUMO+2 transition mainly dominates S0→S7 transition with the absorption wavelength of 328 nm, which is contributed by charge transfer from the whole to the triarylamine part (Fig. 8). The transitions HOMO→LUMO, HOMO-2→LUMO and HOMO-1→LUMO+1 correspond to **PJK2**, **PJK3** and **PJK4** in the natural state mainly

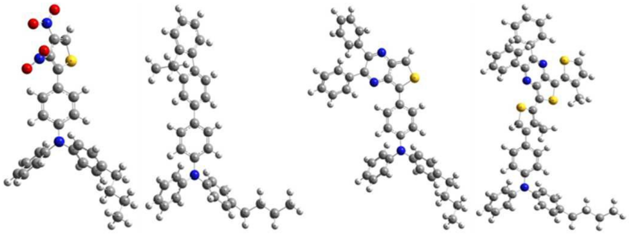

Fig. 7 Optimized geometries of monomers of conjugated polymers.

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Table 2 The calculated absorption wavelength (*λ*), oscillator strength (*f*) and the corresponding MO transitions of monomers in neutral and oxidation states. The electronic transitions corresponding to the first excited state and the largest oscillator strength are shown.

	Neutral state				**Oxidation state**			
	State[a]	*λ* (nm)	*f* (a.u.)	Transition character	State	*λ* (nm)	*f* (a.u.)	Transition character
PJK1	$S_0 \rightarrow S_1$	532	0.02	HOMO→LUMO+1 (11%)	$S_0 \rightarrow S_1$	818	0.84	HOMO→LUMO (91%)
	$S_0 \rightarrow S_7$	328	0.54	HOMO→LUMO+2 (49%)	$S_0 \rightarrow S_2$	614	0.37	HOMO-1→LUMO (79%)
PJK2	$S_0 \rightarrow S_1$	318	1.15	HOMO→LUMO (49%)	$S_0 \rightarrow S_1$	750	1.22	HOMO→LUMO (92%)
	$S_0 \rightarrow S_{19}$	222	1.02	HOMO-3→LUMO (27%)	$S_0 \rightarrow S_2$	528	0.97	HOMO-1→LUMO (89%)
PJK3	$S_0 \rightarrow S_1$	482	0.36	HOMO→LUMO (78%)	$S_0 \rightarrow S_1$	652	0.42	HOMO-1→LUMO (70%)
	$S_0 \rightarrow S_3$	340	0.74	HOMO-2→LUMO (26%)	$S_0 \rightarrow S_7$	429	0.44	HOMO-5→LUMO (41%)
PJK4	$S_0 \rightarrow S_1$	544	0.44	HOMO→LUMO (42%)	$S_0 \rightarrow S_1$	858	0.68	HOMO→LUMO (65%)
	$S_0 \rightarrow S_5$	397	0.81	HOMO-1→LUMO+1 (63%)	$S_0 \rightarrow S_3$	572	0.59	HOMO-2→LUMO (37%)

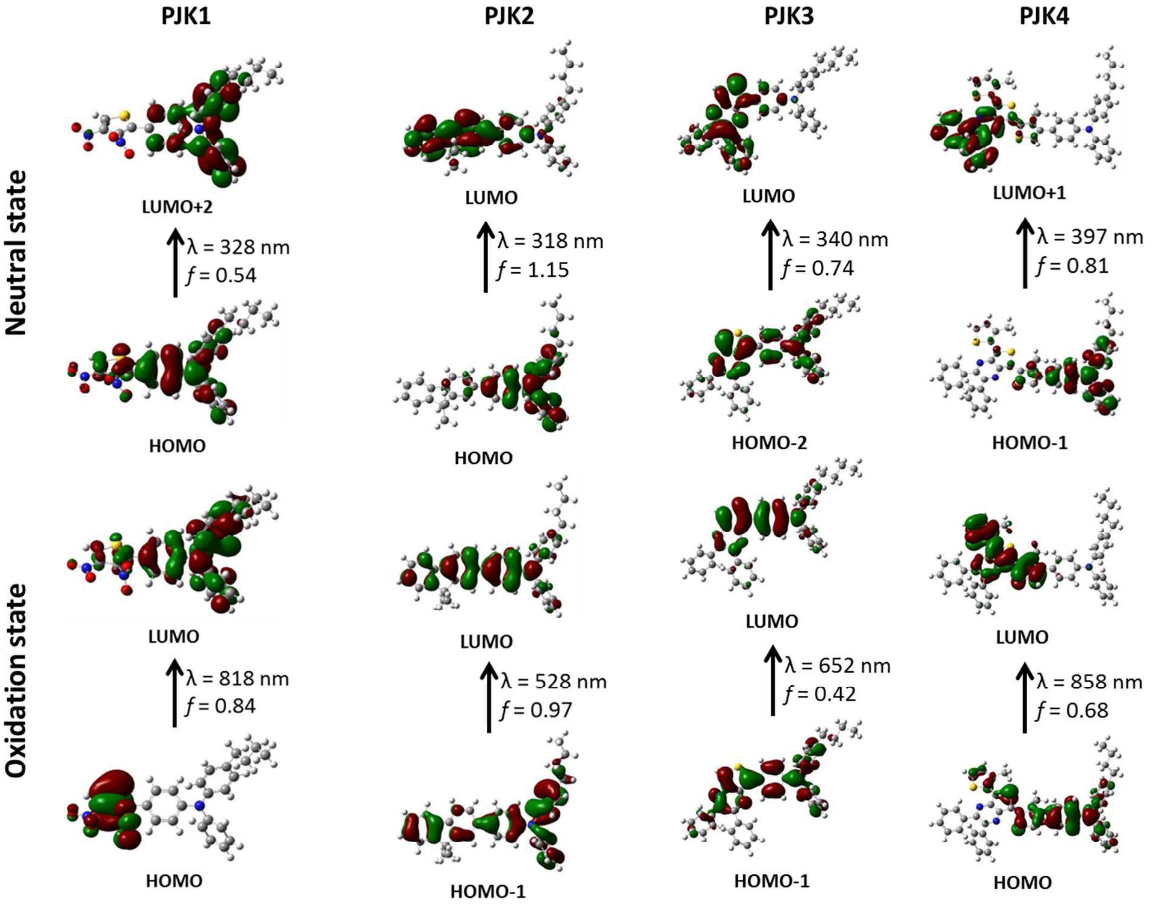

Fig. 8 Electronic transitions of **PJK1**, **PJK2**, **PJK 3** and **PJK4** in ground and excited states.

dominate S0→S1, S0→S3 and S0→S5 electronic transitions having large oscillator strength with absorption at 318, 340 and 397 nm respectively. Which are contributed by charge transfer from triarylamine to the rest of the molecule. For the oxidation state of **PJK1**, **PJK3** and **PJK4**, HOMO→LUMO, HOMO-1→LUMO and HOMO→LUMO transitions respectively, mainly controls S0→S1 transition with maximum absorption at 818, 652 and 858 nm, respectively. While, for **PJK2** in the oxidation state, HOMO-1→LUMO transition related to 528 nm mainly dominates S0→S2 transition. The absorption wavelengths for the conjugated polymers are close to the experimental values (Fig. 5). Upon oxidation, the changes in the conjugation length in conjugated polymers **PJK1**, **PJK2**, **PJK3** and **PJK4** in the film state can be explained from this theoretical study. Thus, the NIR electrochromic phenomena of reported conjugated polymers can be successfully proved by theoretical investigation.

4. Conclusions

We have prepared four soluble, electrochromic triphenylamine-based copolymer derivatives and reported their fabrication into electrochromic cells using ITO-glass. The electrochromic devices were shown to exhibit good color

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changes when modulated between their neutral and oxidized states and color changes for **PJK1**, the color changed from orange to dark green; for **PJK2**, from light yellow to reddish brown; for **PJK3**, from light blue to grey; and for **PJK4**, from green to bluish green. These polymers revealed well switching times, is an important candidate for electrochromic display applications. These polymer electrochromic cells may be useful for conductive textiles, whose interesting features could find applications in adaptive camouflage.

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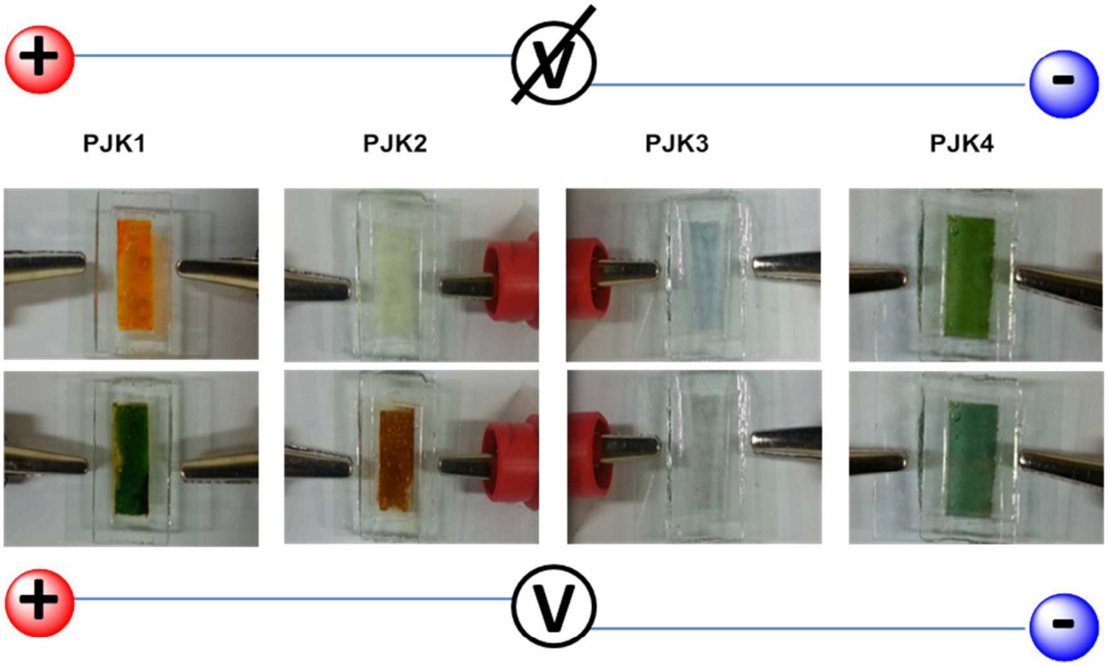
Graphical Abstract

A series of triphenyl amine based new molecules, coded PJK1, PJK2, PJK3 and PJK4 synthesized for electrochromic cells. Here we achieved color change for PJK1, orange to dark green; for PJK2, light yellow to reddish brown; for PJK3, light blue to grey; and for PJK4, green to bluish green.



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