

The synthesis, optical and electrical properties
of novel polymers to increase the
electrochromic colour-changing service life of
poly(3-hexylthiophene).

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SUMMARY

Poly(3-alkylthiophene)s (P3ATs) are considered to be an important class of electrochromic materials because of their convenient processability and environmental stability. The adhesion of electrochromic polymer coatings on a conducting substrate is a significant factor affecting the durable colour-changing life of electrochromic devices. Traditional electrochromic coatings on transparent ITO glass electrodes often have poor cycling lifetimes, due to incompatibility between the polymers and the inorganic substrates. However, providing a bonding network between the active electrochromics and the ITO glass is an efficient method to increase the adhesion and hence to extend the service time successfully; the research described here involves Suzuki-Miyaura coupling of N-(3-methoxysilylpropyl)pyrrole (3TPP) onto poly(3-hexylthiophene) (P3HT), as a precursor to a sol-gel reaction. The Si-O-Metal network produced between the siloxane groups and metal oxide after the sol-gel reaction served to enhance the adhesion of the poly(3-hexylthiophene) onto ITO glass. With this stronger bonding, the colour-switching service time was found to be extended considerably by the observation of repeated electrochemical cycling tests. In addition, the optoelectrical and electrochemical properties of copolymers with various molar substitution ratios of 3TPP on P3HT were investigated by cyclic voltammetry and UV-visible spectroscopy. The π - π^* transition energy of P3HT increased with the degree of bromo-substitution, but diminished again after substituting with 3TPP. The hysteresis in electrochromic switching also became more noticeable with increased bromo-substitution on the P3HT, but it decreased when 3TPP was attached to the thiophene rings.

Keywords: Poly(3-hexylthiophene)s, P3HT, Suzuki coupling reaction, Sol-gel reaction, Electrochromic polymers

1. INTRODUCTION

Electrochromism is broadly defined as a reversible optical change in a material induced by an applied voltage or current, and many inorganic and organic species show electrochromism throughout the electromagnetic spectrum [1]. For good optical contrast between redox states, high chemical stability in the oxidatively doped state and ease of synthesis, electrochromic conjugated polymers have been investigated widely in the past two decades [2]. Poly(3-alkylthiophene)s (P3ATs) are considered to be promising materials for electrochromic applications because of their high solubility [3], convenient processability and environmental stability [4]. They have also been applied extensively in field-effect transistors [5, 6], optical and electronic sensors, light-emitting devices and non-linear optics [7]. However, their incompatibility with inorganic conductive substrates results in poor adhesion of organic polymers on indium-tin oxide (ITO) glass, which can lead to a short colour-changing lifetime when they are used as electrochromic materials [8]. New processes have been developed which could incorporate virtually any conventional vinyl polymer into an inorganic network via the sol-gel reaction [9, 10, 11]. Recently, substituting the 3- and 4- positions of the thiophene ring with other functional groups has attracted a great deal of attention, since the electrical and the optical properties of P3ATs can be modified by changing the electronic and steric interactions [12]. Unfortunately, some commonly-used methods of substitution have complicated synthetic procedures and the

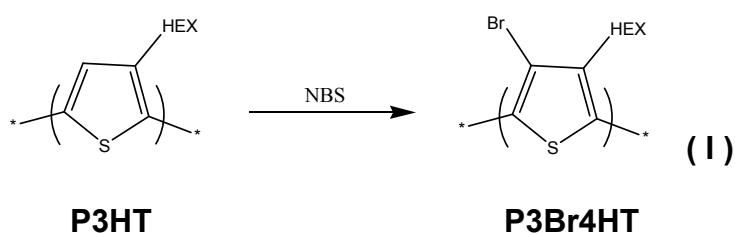
functional groups can inhibit the monomer polymerisation or cause irregular polymer structure if the normal oxidative polymerisation technique is used [13, 14]. A more convenient alternative approach to polymer modification uses the Suzuki-Miyaura reaction [15, 16], i.e. the palladium-catalysed coupling of aryl halides or pseudo-halides with an arylboronic acid. Possessing good thermal and chemical stability, organoboron reagents are sensitive electrophiles and good reactants for carbon-carbon bond formation [17], especially for coupling biphenyl groups; this method also avoids using heavy metals and polluting the environment.

In the present work, ring position 4 of poly(3-hexylthiophene) (P3HT) was substituted to form random copolymers with 10%, 30%, 50% and 100% bromination by electrophilic substitution (Scheme 1). A series of poly(3-hexylthiophene-co-3-bromo-4-hexylthiophene)s (P3Br4HT) was investigated to determine the quantitative limit of bromination which could maintain useful electrochemical properties. Next, the corresponding molar ratios of N-(3-trimethoxysilylpropyl)pyrrole (3TTP) were substituted for the bromo-group of P3Br4HT by Suzuki coupling catalysed by palladium acetate (Scheme 2). $^1\text{H-NMR}$ 400 Hz and FT-IR were used to confirm the successful bromo-substitution and combination between 3TTP and P3HT. GPC was used to observe the distribution of molecular weights for all the products. The siloxane groups of P3(TPP)4HT were acidified by 4-dodecylbenzenesulfonic acid (DBSA) and a Si-O-Metal network was constructed between ITO glass and the conjugated polymers via a sol-gel-like reaction (Scheme 3). Because the Si-O-Metal bonding in the sandwich structure was difficult to characterise by instruments directly, model experiments were carried out to form similar

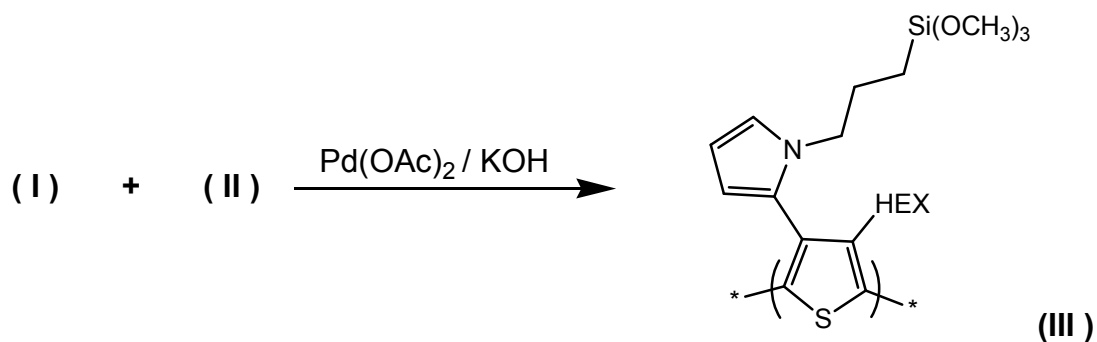
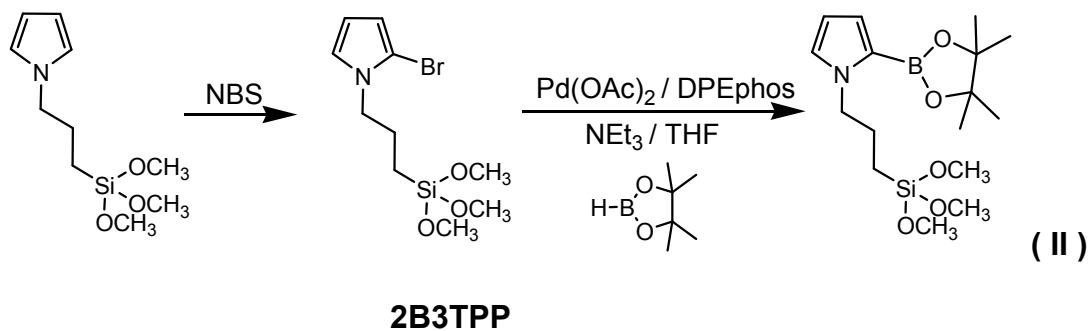
bonds by reaction with metal oxide powders, and then to characterise them by FT-IR spectroscopy.

The electrochemical properties of P3HT, P3(TPP)4HT 10% and 30% were investigated by cyclic voltammetry. The optoelectronic properties and repeated cycling performance were examined by UV-visible spectrometry, to indicate whether the colour-changing service life would be extended by the formation of an inorganic oxide network.

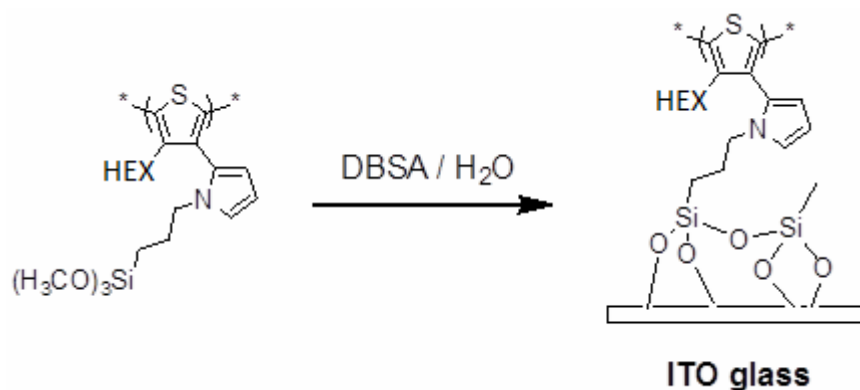
Scheme 1



Scheme 2



Scheme 3



2. EXPERIMENTAL

2.1 Chemicals and instrumentation

P3HT was synthesised from 3-hexylthiophene (Aldrich 99%) via oxidative polymerisation¹⁸ and 3TPP was obtained from ABCR GmbH & Co. KG. Pinacolborane (Aldrich 97%), (oxydi-1,2-phenylene)bis(diphenylphosphine) (DPEphos, Aldrich 98%), lithium perchlorate (Aldrich 95% A.C.S. reagent), 4-dodecylbenzenesulfonic acid (DBSA) (Fluka 90%), N-bromosuccinimide (NBS) (Fluka $\geq 95.0\%$), palladium (II) acetate (Aldrich 98%), trimethylamine (Fluka $\geq 98.0\%$ (GC)) and anhydrous chloroform (Aldrich 99%). Potassium hydroxide was obtained from Avocado ($\geq 85\%$), and all general solvents were from Thermo Fisher Scientific Inc.

Fourier-transform infrared (IR) spectra were measured using a Perkin-Elmer Spectrum One ATR, and nuclear magnetic resonance (NMR) spectra were run on a Bruker 400 MHz FT-NMR with ACD/NMR Processor Academic Edition Software. The UV-visible spectra were measured on a Varian Cary 100 spectrophotometer and the mass spectra on a Varian 1200L Quadrupole MS.

2.2 Synthetic procedures

2.2.1 The bromination of P3HT

P3HT (0.3g, 0.0018 mol) was dissolved in dry chloroform (10 mL) and stirred. NBS (0.3g, 0.002 mol) was added to the reaction flask and heated to ~80 °C. After becoming bright red, the solution was stirred overnight. The reaction was quenched by saturated aqueous sodium sulfite (20mL). The aqueous layer was separated, washed twice with chloroform (10mL) and the organic layers were re-combined. After drying with magnesium sulfate, the chloroform was removed by rotary evaporation. Yield 0.294g (99%). ¹H NMR (400 MHz CDCl₃): δ = 2.93, 2.73, 2.69, 1.58, 1.25, 0.84. FT-IR: 2954, 2900, 2855, 1728, 1463, 1377, 1172, 1099, 837, 724 cm⁻¹.

2.2.2 The synthesis of N-((3-trimethoxysilyl propyl)-2-bromopyrrole) (2B3TPP)

3TPP (0.41g, 0.0018 mol) and NBS (0.30g, 0.002 mol) were placed in a round bottom flask and stirred in THF (10 mL) in a dry ice bath for 8h. The work-up steps were similar to those for bromination of P3HT, but the washing solvent was diethyl ether (10mL) instead of chloroform. Yield 0.39g (1.3 mmol; 70%) ¹H-NMR (400 MHz CDCl₃): δ = 6.69-6.62 (m, 1H), 6.11-6.08 (m, 2H), 3.74-3.70 (m, 2H), 3.53-3.54 (m, 9H), 1.84-1.81 (m, 2H), 0.64-0.54 (m, 2H). ¹³C-NMR (400 MHz CDCl₃): 121.9, 111.7, 107.9, 107.6, 68.0, 50.6, 25.7, 6.1. FT-IR: 3411, 3017, 2944, 2842, 1701, 1640, 1215, 1088, 817, 668 cm⁻¹. M⁺ = 307 & 309 m/z, due to Br isotopes.

2.2.3 One-step boronation and Suzuki coupling reaction

N-((3-trimethoxysilylpropyl)-2-bromopyrrole) (2B3TPP) (0.0013 mol) was added to a stirred solution of N-triethylamine (0.53g, 0.0052 mol) and THF (10 mL). Palladium (II) acetate (5 mol%) and DPEphos (10 mol%) were added, along with pinacolborane (0.49g, 0.039 mol). The mixture was heated to 80 °C, and stirred for approximately 1 h. The appropriate amounts of P3Br4HT (Table 1) were added, along with potassium hydroxide (0.22g; 0.0052 mol) and palladium (II) acetate (5 mol%) and the mixture was stirred at 100 °C for 24 h. When the reaction was complete, the solution was poured into methanol (30 mL) to precipitate the product, and filtered. The compound was dried at 60°C under vacuum for 12 h.

2.2.4 The formation of an inorganic linkage between ITO glass and P3(TPP)4HT via sol-gel-like reaction

Poly(3-(N-(3-trimethoxysilylpropyl)pyrrole-2yl)-4-hexylthiophene) (P3(TPP)4HT) (0.1g) and DBSA (0.1g) were dissolved in THF (5 mL) and stirred for 24 h. The mixture was poured into methanol (10 mL) to dissolve the excess acid, and the product was precipitated. The solid compound was collected on filter paper and dried in a vacuum oven at 60°C under reduced pressure for 2 h. The dry product was dissolved in chloroform (2 mL) and spin-coated onto ITO glass. After spraying water onto the surface, the ITO-coated glass was dried in an oven at 80°C for 48 h.

2.2.5 Model experiment to form bonds between oxide powders and siloxane groups via a sol-gel reaction

The inorganic network between ITO glass and P3(TPP)4HT was difficult to

detect by FT-IR because the background absorption was too strong and broad below 1000 cm^{-1} . Combining TEOS and TiO_2 nanoparticles by a sol-gel reaction was used as a convenient model experiment to observe indirectly the bonding between siloxane groups and ITO glass. TiO_2 5 nm powder (1.04g, 0.02 mol) was dispersed in water, together with TEOS (1.04g, 5 mmol) and 0.2M HCl solution (5mL), and stirred at 100°C for 24 h. The mixture was placed in an oven at 80°C under reduced pressure to remove the water until the grey compound had dried completely. Also, 40 μm indium tin oxide powder (In_2O_3 : $\text{SnO}_2 = 0.9 : 0.1$) (0.001 mol) from Sigma-Aldrich Ltd was reacted with TEOS (0.3 mmol) in 0.2N HCl solution (5mL). The mixture was stirred at 50°C for 1 week until it was completely dry, and was studied by IR spectroscopy.

2.3 Molecular weight analysis by Size Exclusion Chromatography (SEC or GPC)

A calibration plot was obtained using polystyrene standards with relative molecular masses of 1170, 3470, 5440, 12500, 27500, 51500, 125000 and 277000. The mobile phase was THF (HPLC grade) and the detector wavelength was 350 nm for all samples.

2.4 The electrochemical properties observed by cyclic voltammetry

0.01g polymer samples were dissolved in chloroform (2mL) and spin-coated (1300 rpm) onto ITO glass (30 mm \times 15 mm) electrodes to form the working electrode. The thickness of the coatings was estimated from the intensity of their $\pi\pi^*$ absorption. An (Ag/AgCl/1M KCl) reference electrode was used, together with a platinum counter electrode. The electrolyte was 0.1M $\text{LiClO}_4/\text{CH}_3\text{CN}$, i.e. lithium perchlorate (0.32g, 0.03mol) dissolved in anhydrous

acetonitrile (30 mL). The potential was scanned from -1000 mV to +2000 mV, at 100mV/s.

2.6 In-situ colour-switching analysis by UV-visible spectrophotometry, and switching time measurements

The working electrode was a rectangular piece of ITO glass (41mm X 9mm) spin-coated with polymer solutions (ca. 0.5 wt%) in chloroform, and then placed in an oven at 80°C for 24h. Ag/AgCl was again used as the reference electrode and platinum foil as a counter electrode. The electrodes were placed in a quartz cuvette with 0.1M LiClO₄/CH₃CN solution and connected to a potentiostat (Ministat Precision Potentiostat). The wavelength region was 350 to 900nm.

For the switching time experiments, the UV-vis spectroscopy mode was changed to kinetic scan (absorbance vs. time) and the wavelength was fixed on the polaron absorption peak (the value for P3HT was 827 nm, for P3(TPP)4HT 10% 729 nm and for P3(TPP)4HT 30% 775 nm). The data collection started when the potential was switched from 0.33 V to 1.08 V, and this was done repeatedly for five minutes. The switching time ($T_{1/2}$) was defined as that required to produce 50% of the final absorbance change, in accordance with common practice in the passive displays industry.

3. RESULTS AND DISCUSSION

3.1 ¹H-NMR spectroscopy

The peak due to protons on the thiophene rings was found at 6.96 ppm in the $^1\text{H-NMR}$ spectrum of P3HT (Figure 1 (a)). When position 3 was completely substituted by bromine, the peak at 6.96ppm vanished and other peaks due to the hexyl groups had less splitting, due to the absence of protons on the thiophene rings. In the spectrum of the target compound P3(TPP)4HT (Figure 1(b)), the peaks indicating protons on the thiophene rings were observed at lower field (between 5.9 ~ 8.1 ppm) because of the electron-withdrawing effect of the pyrrole rings. Hence successful coupling between thiophene and pyrrole via the Suzuki-Miyaura reaction was inferred from the proton NMR spectrum.

3.2 FT-IR spectroscopy

In the FT-IR spectrum of P3HT (Figure 2 (a)), the C-H bending and C=C stretching peaks of the thiophene ring were found at 1509, 1458 and 1377 cm^{-1} . After substituting with bromine to the extent of 10% at position 3 of P3HT (Figure 2 (b)), the peak at 1509 cm^{-1} disappeared and a very small new peak at 1728 cm^{-1} became visible, increasing proportionally with the degree of substitution. The reason for this peak shifting to the higher wavenumber was probably that the C=C bonds became less conjugated since bromine's steric crowding caused greater torsion between adjacent monomers. In the spectra of samples with various substitution percentages of 3TPP on P3HT (Figure 3), the peaks at 1589 and 1566 cm^{-1} respectively indicated "C=C and C=N stretching" modes from the pyrrole ring, and also a siloxane peak at 1071 cm^{-1} was observed for P3(TPP)4HT. These three peaks were reduced in intensity with decreasing proportions of 3TPP (30% to 10%). Once again, the spectral data indicated that the functionalisation of P3HT by 3TPP via the Suzuki coupling reaction was successful.

3.3 SEC (GPC) analysis

Upon increasing the degree of bromo-substitution, the number-average and weight-average relative molecular masses of P3HT, (initially 1773 and 4777 respectively) increased proportionally (Table 1). After combining the 3TPP 10%, 30% or 100 % with P3HT, the number-average RMM decreased again and the polydispersity was smaller compared with the P3HT. It appears that the indicated dispersity values were unreliable due to the fact that some parts of polymer may have been crosslinked. The SEC detector would clearly only respond to the soluble part rather than the entire product in that case.

3.4 Solubility tests

Of the three major polymers, P3HT had a high solubility in CHCl_3 (Table 1) but was only partially soluble in CH_2Cl_2 and THF; this is in agreement with previous studies [3,4]. However, after brominating the P3HT, its solubility was increased, probably due to expansion of the intermolecular space by the bulky groups. Due to the interaction between aromatic groups, P3Br4HT had a good solubility in toluene. When 3TPP was attached to the thiophene ring, the solubility of P3(TPP)4HT again increased remarkably. As a result of the interaction between the siloxane groups and polar solvents, the novel product was partially soluble in acetonitrile or methanol, but was still insoluble in water.

3.5 The interaction between TiO_2 and TEOS and metal oxide surfaces, observed by FT-IR

In the spectrum of TiO_2 (Figure 4 (a)), a very strong peak was observed below about 650 cm^{-1} , and after the sol-gel reaction with TEOS, a new peak

appeared at 1080 and 950 cm^{-1} . The peak at 1080 cm^{-1} was indicative of the siloxane groups, and if the siloxane group were acidified, Si-OH, the peak should be obtained at lower than 900 cm^{-1} . Thus, the peak at 950 cm^{-1} was attributed to a new Ti-O-Si bond after sol-gel reaction between TiO_2 and Si-OH (Figure 4 (b)). In fact, the same peak appeared at 980 cm^{-1} in the FT-IR spectrum of indium-tin oxide after a sol-gel reaction with TEOS (Figure 5 (a)). It was expected that the Metal-O-Si interaction would be detected in the region from 1000 to 900 cm^{-1} of the FT-IR spectrum.

3.6 Cyclic Voltammetry

The oxidation and reduction peaks of P3HT were observed respectively at 1700 mV and 620 mV (vs. Ag/AgCl) (Figure 6 P3HT). Upon 10 mol% substitution with bromine at position 3 (Figure 6 P3Br4HT 10%), the oxidation peak shifted to 1870 mV. In addition, new oxidation and reduction peaks were observed at 1250 mV and -1660 mV. As the proportion of substitution was increased, the redox peaks began shifting to a higher potential, suggesting that bromine atoms were removing electrons from the conjugated groups. The bulky bromine groups were also causing steric hindrance within the polymer chain, due to the rearrangement of the monomer units into the out of plane position, contributing to the hysteresis effect. Upon increasing the degree of substitution to 30 mol% (Figure 6 P3Br4HT 30%), the major oxidation peak increased to 2000 mV, which eventually resulted in the polymer chains becoming damaged by the strongly-oxidising conditions. From this, we can deduce that to avoid polymer chain breakage, a limit of 30 mol% substitution should be used.

After substituting P3HT with 3TPP to the extent of 10 mol%, the oxidation peak in the first cycle shifted to higher potential (over 2000 mV), and the potential difference between the reversible redox peaks increased considerably from 950 mV to 1040 mV (Figure 7 (b)). This phenomenon indicates that the bulky groups caused the monomer rings to twist out of planarity, so the hysteresis effect became greater. However, on increasing the proportion of 3TPP to 30 mol% (Figure 7 (c)), this hysteresis effect diminished, becoming even less than for P3HT (Figure 7 (a)), probably because strong adhesion within the inorganic network improved the electron transfer from the ITO glass to the polymer. The delay in observing a hysteresis effect until after many more cycles indicated that the electrochromic cycling lifetime was extended, and this inference was subsequently supported by spectroelectrochemical and switching time tests.

3.7 Spectroelectrochemistry in the visible region

The fundamental π to π^* absorption for P3HT was around 2.4 eV, but it shifted to higher energy and the intensity diminished gradually upon increasing the applied voltage (Figure 8 (a)). The polaron transition peak at 1.6 eV became more intense as the doping level was increased. When the P3HT was functionalised with 10% 3TPP, the π to π^* absorption shifted to higher energy by 0.2 eV and the polaron absorption by 0.15 eV (Figure 8 (b)). In addition, the driving voltage for colour changing increased from 1.08 V to 1.18 V. This was probably because the bulky substituent groups decreased the planarity of the conjugated polymer chains. However, the potential returned to a lower value after substituting by 30% 3TPP (Figure 8 (c)) and also the driving voltage decreased to a similar level to P3HT. This reverse trend suggested that more delocalised regions offered from pyrrole groups overcame the torsional effect,

or that the attractive interaction between pyrrole units led to a more planar conformation. Also, the Si-O-Metal inorganic network contributing better adhesion caused electrons to transfer more efficiently from the polymers to ITO glass.

3.8 Repetitive switching tests

An examination of repetitive switching performance was used to assess both the colour-changing durability and the electrochromic switching time from the doped to the dedoped state. In Figure 9 (a), the intensity range of the repeating curve for P3HT decayed slowly, but the P3(TPP)4HT 10% and 30% were still very stable during the running time (Figure 9 (b) and (c)). This improvement suggested that the Si-O-Metal network extended the service life of modified P3HT successfully due to the strong adhesion between the electrochromic polymer and the ITO glass electrode. The reproducible peak for the spectra of the P3(TPP)4HT 10% and 30% indicated that the colour variation still persisted after substituting 3TPP onto the P3HT. In addition, the average switching time ($T_{1/2}$) for P3(TPP)4HT 30% was prolonged slightly to around 0.025 s longer than P3HT (The $T_{1/2}$ of P3HT and P3(TPP)4HT were 0.318 and 0.576 s respectively) but for P3(TPP)4HT, the $T_{1/2}$ increased to 1.8 s. The delay of switching time when P3HT was combined with 3TPP resulted from the transfer of electrons between the conjugated polymer and the ITO being slowed by the Si-O-Metal network.

4. CONCLUSION

P3HT and 3TPP were coupled successfully by using the Suzuki-Miyaura reaction proved by ^1H -NMR and FT-IR spectrum. An inorganic Si-O-Metal network was created after a sol-gel-like coupling reaction between the novel compound P3(TPP)4HT and ITO glass. Due to the difficulty of detecting it directly, the Si-O-Metal bonding was detected indirectly by FT-IR spectrometry in a model experiment to forming bonds between TEOS and TiO_2 powder by a sol-gel reaction. To maintain the electrochromism, the maximum quantity of substituting 3TPP at position 3 of P3HT was 30 mol %. Cyclic voltammetry, spectroelectrochemistry and repetitive switching tests indicated that the modification was successful in extending the colour-changing service time of P3HT. The reason for this prolongation was probably that the Si-O-Metal network contributed to a stronger adhesion between the conjugated polymer and the ITO glass which caused the electron transfer to be more durable and efficient without being affected by the bulky substituent group.

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Table 1. The molecular weights, solubility and of π to π^* transition absorption for the (undoped) polymers.

Sample	NBS loading (mol %)	3TPP (mol%)	Average Molecular Weight			π to π^* absorption (nm)	Solubility Test		
			Mn	Mw	Polydispersity		CHCl ₃	THF	CH ₃ OH
P3HT	0	---	1773	4777	2.6941	442	++	+	-
P3Br4HT 10%	10	---	2031	5598	2.4326	402	++	++	-
P3Br4HT 30%	30	---	2543	6758	2.6570	390	++	++	-
P3Br4HT 50%	50	---	2817	8347	2.9630	386	++	++	-
P3Br4HT 100%	100	---	4150	12249	2.9513	350	++	++	-
P3(TPP)4HT 10%	---	10	2061	4502	2.1835	404	++	++	-
P3(TPP)4HT 30%	---	30	2067	4284	2.0718	427	++	++	-
P3(TPP)4HT 100%	---	100	2227	6758	3.0343	448	++	++	+

Figure 1. ^1H -NMR spectra of (a) P3HT, (b) P3Br4HT 100% and (c) P3(TPP)4HT 100%

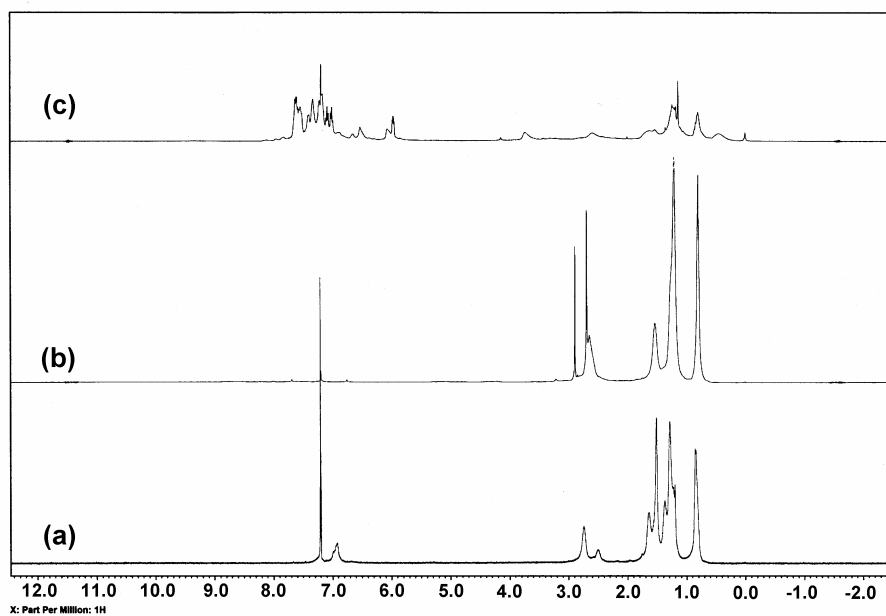


Figure 2. FT-IR spectra for the series of P3Br4HT substituted by bromine to the extent of: (a) 0% (b) 10% (c) 30% (d) 50% (e) 100%

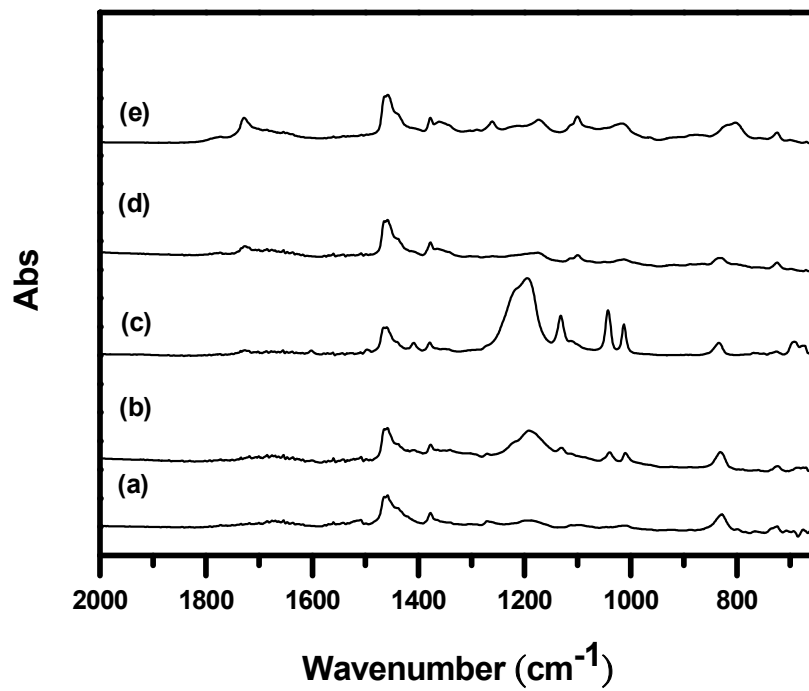


Figure 3. FT-IR spectra of P3(TPP)4HT (a) 10% (b) 30% (c) 100%

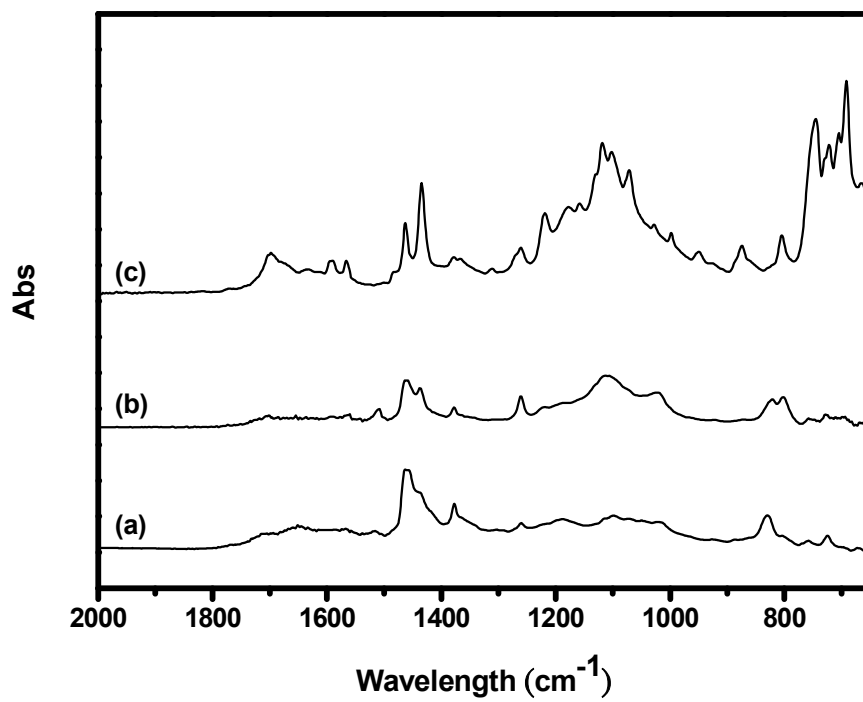


Figure 4. FT-IR spectra of (a) TiO₂ (b) TiOSi

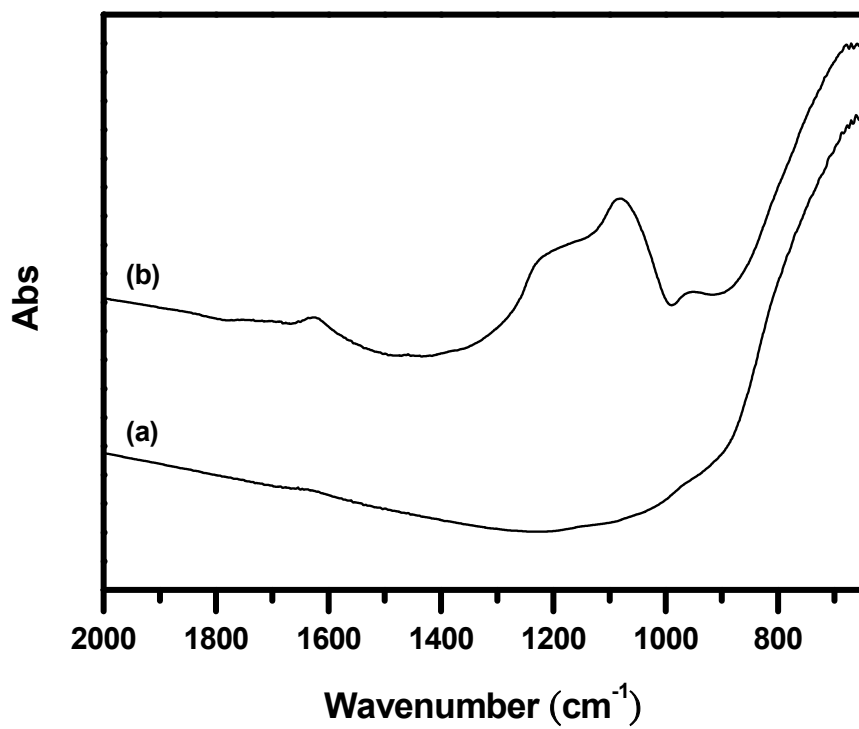


Figure 5. FT-IR spectra of (a) SiO-ITO (b) ITO

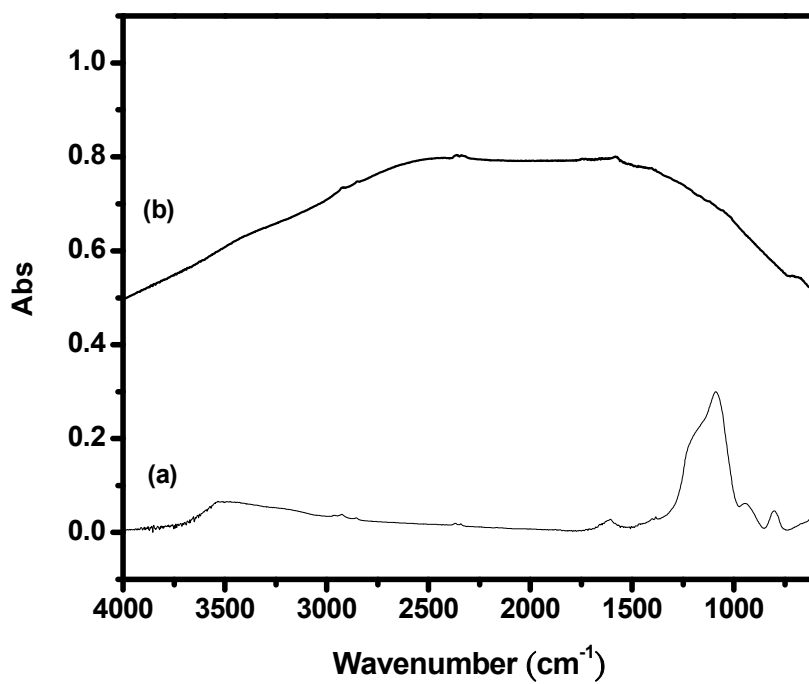


Figure 6. Cyclic voltammograms of P3HT, P3Br4HT 10% and P3Br4HT 30% (Scan rate 100 mV s⁻¹)

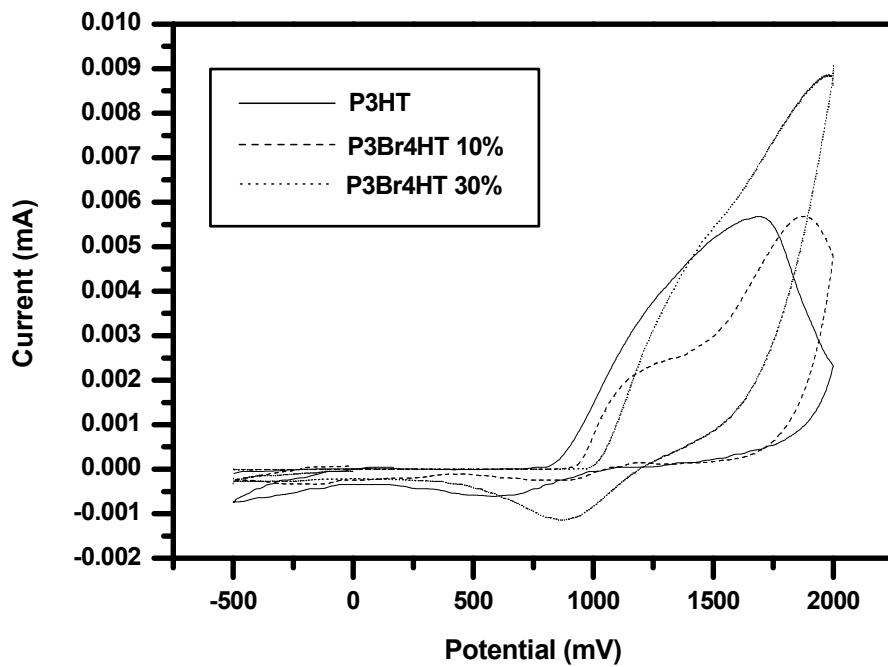
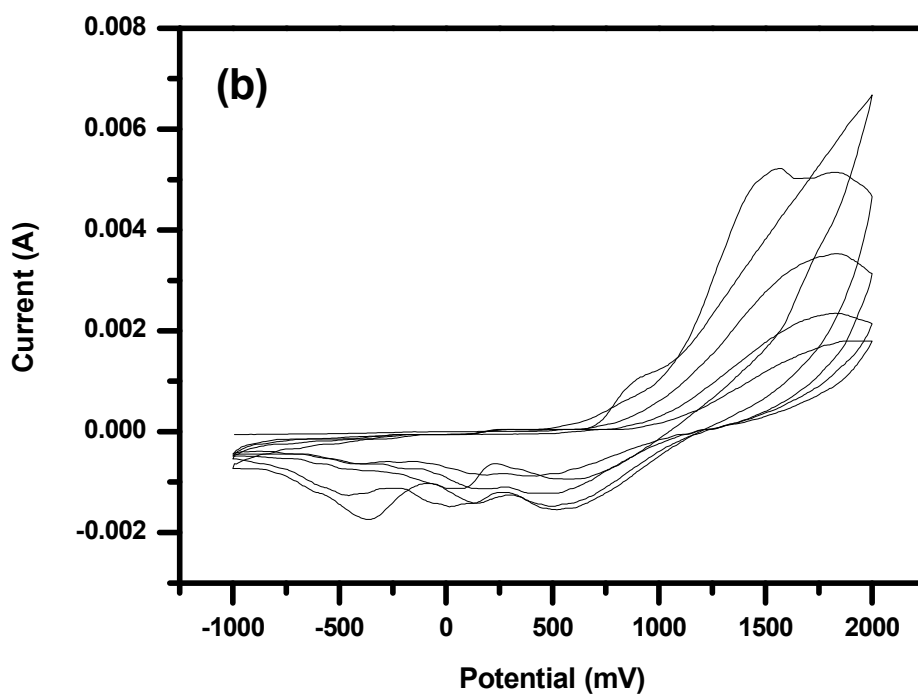
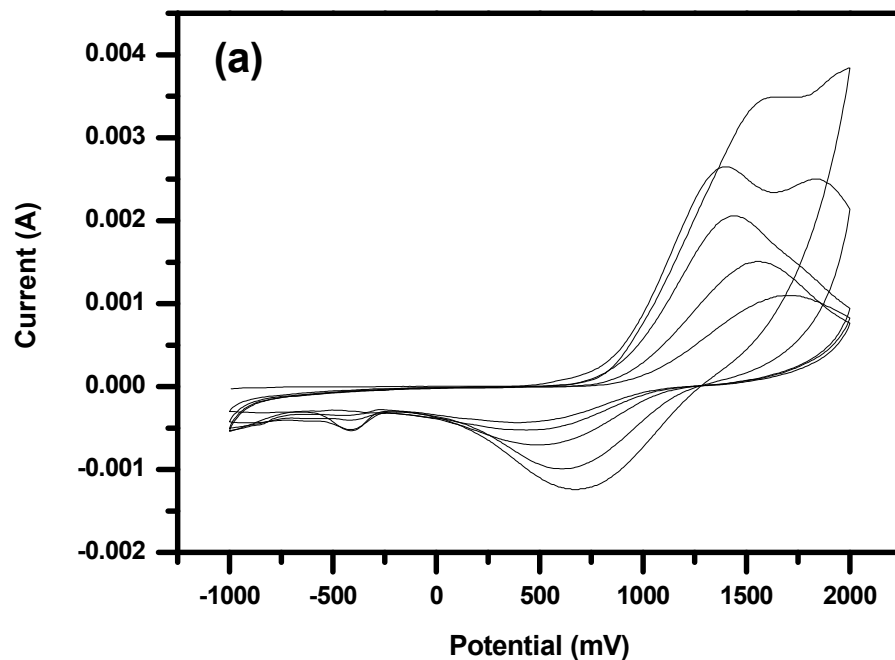


Figure 7. Cyclic voltammograms of (a) P3HT, (b) P3(TPP)4HT 10% and (c) P3(TPP)4HT 30% (Scan rate = 100 mV s⁻¹)



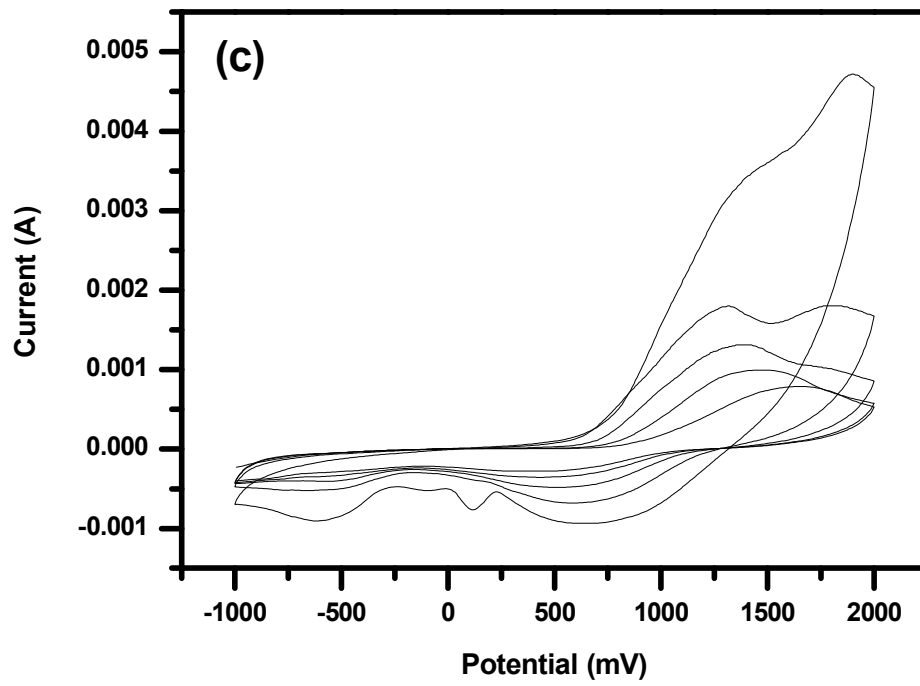
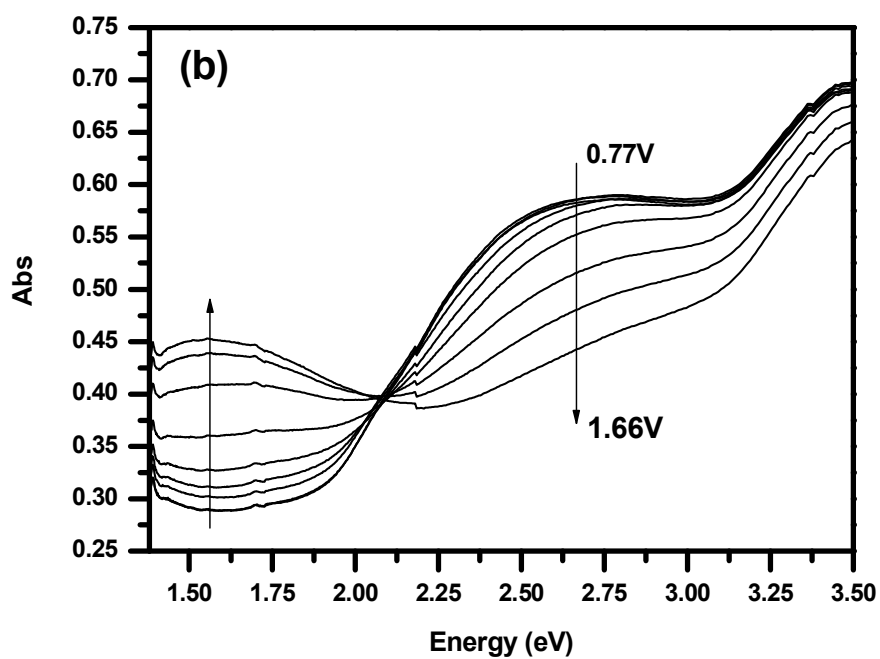
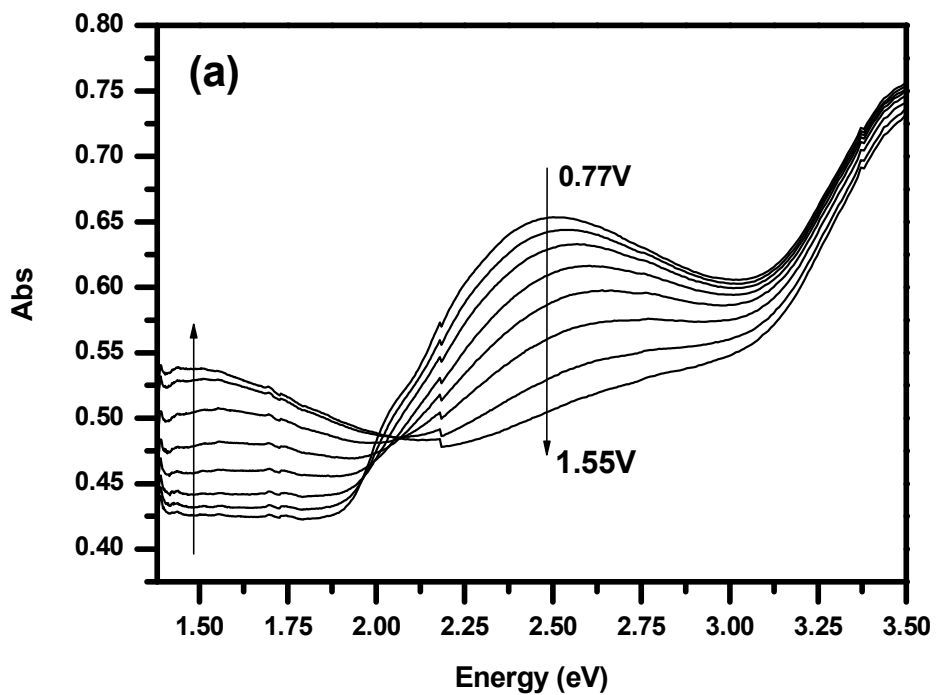


Figure 8. UV-visible spectra corresponding to electrode potentials of 0.77V, 0.89V, 0.97V, 1.08V, 1.18V, 1.30V, 1.44V, 1.55V and 1.66V for (a) P3HT, (b) P3(TPP)4HT 10% and (c) P3(TPP)4HT 30%



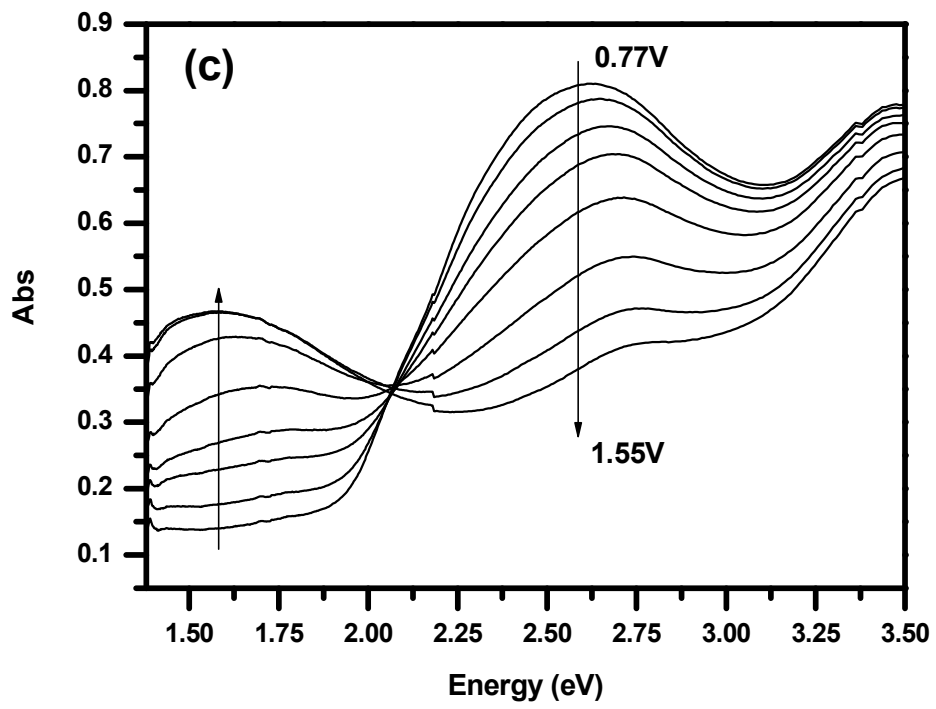


Figure 9. The electrochromic light absorption response of (a) P3HT, (b) P3(TPP)4HT 10% and (c) P3(TPP)4HT 30%, on switching the electrode potential from 0.33V to 1.08V vs. Ag/AgCl.

