

Green colouring electrochromic devices of water-soluble polythiophene

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The authors report on the electrochromic (EC) behaviour of the environmentally friendly water-soluble polythiophene sodium poly (2-(3-thienyl) ethoxy-4-butylsulfonate) (PTEBS) solid-state devices. Films are fabricated on indium tin oxide substrates and are composed of bilayers of PTEBS and poly (allylamine hydrochloride) using the ionic self-assembled multilayer approach. The self-assembled films showed high stability and demonstrated EC switching from orange to green with a contrast of 61% and colouration efficiency of $-238 \text{ cm}^2/\text{C}$ in $0.1 \text{ M NaClO}_4 \text{ (aq)}$ at 735 nm . 80-bilayer solid-state devices have an optical contrast of 38% at 735 nm , and 1-cm^2 active area devices show fast $t_{90\%}$ switching times of 125 ms for coloration and 225 ms for decoloration with applied voltage of 2 V for long-term switching of more than 50,000 cycles.

1. Introduction

The highly controllable electronic and optical properties of organic polymers have generated major research efforts in the areas of solar cells, light emitting diodes and electrochromics, among others. The major thrust towards the development of EC polymers has been their low cost as well as their potential for continuous colour tunability, fast switching speeds and long lifetimes, which makes them suitable for flexible flat-panel displays, electronic paper and 'smart windows'.^{1,2} Electrochromic polymers change colour as a result of oxidation or reduction caused by an applied voltage. Challenges remain to develop polymer-based devices that have the required optical contrast at appropriate wavelengths, fast switching times and manufacturability for use in commercial applications.

Polythiophene and its derivatives have been some of the most promising organic conducting polymers for commercial EC applications due to their ability to switch rapidly between redox states, high contrast, easy processability, and their ability to combine with other EC materials to allow a multi-chromic effect. The first synthesis of water-soluble conducting polymers was reported in 1987,³ but other than a few exceptions such as commercially available poly (3,4-ethylenedioxythiophene:poly(styrenesulfonate) and work by Reynolds *et al.*^{4,5} there has not been a lot of work done in fabricating solid-state EC devices with water-soluble polythiophene derivatives. Water solubility is a significant advantage so that organic solvents need not be used in the device manufacturing process. In addition to the easy processability of

the water-soluble conducting polymer sodium poly [2-(3-thienyl) ethoxy-4-butylsulfonate] (PTEBS), the ionic self-assembled multilayer (ISAM) fabrication approach provides nanoscale control of thickness, fast switching speed and ease in manufacturability.

The commercially available polythiophene PTEBS has been investigated for applications in photovoltaics,^{6,7} and its optical properties have been previously studied as well,⁸ but there is no prior report on the EC properties of this water-soluble polythiophene. In this manuscript, the authors present a detailed study of the EC properties of PTEBS, which changes colour from orange to green on oxidation. A similar colour change from orange to green has also been reported by Reynolds *et al.* for a different polythiophene derivative, but that polymer was not water-soluble, the devices showed low contrast between the two redox states, and no switching speed data were reported.⁹

While the colour change in PTEBS is not from completely transparent or light in colour to green, this is the first water-soluble polythiophene derivative to show a green colouration effect. A few demonstrations of green colour change in conducting polymers have been reported recently and special mention should be made of Sonmez *et al.* for the development of a class of polymers that fits the desirable three primary colours (red, green and blue (RGB)) necessary for the use of EC materials in displays.^{10–12} Along the same line, Toppare *et al.* have shown a colour change from transmissive light blue to green, but the optical contrast

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observed was relatively low (< 35%) in the visible region and the switching speed was not as high (>0.75 s) as reported for some other conducting polymers.^{13–15} Along with showing the ability of a polymer to be able to switch to green colour, high optical contrast and fast switching are important properties that should be addressed in EC polymers in detail. The main focus in this manuscript is the demonstration of high optical contrast (>61%) and fast switching (125 ms) in a solid-state conducting polymer device.

2. Experiment and results

The ISAM film fabrication technique used here can be easily scaled up for manufacturing and can provide robust films because of the strong multiple ionic bonding mechanism. ISAM films are formed by a layer-by-layer (LbL) deposition technique that provides highly precise, nanometre-scale films on the electrode surface.¹⁶ ISAM films have been used for a variety of applications¹⁷; for example, in non-linear optics,^{18,19} permselective gas membranes,²⁰ antireflection coatings²¹ and photovoltaics.²² Compared with other techniques such as Langmuir–Blodgett, the ISAM technique can be easily tailored to incorporate a diverse array of substrate shapes and materials and shows more flexibility in choosing thin-film overlay materials for EC devices. Hammond and colleagues have fabricated EC devices from the water-soluble polythiophene complex poly (3,4-ethylenedioxythiophene:poly(styrenesulfonate) (PEDOT:PSS).²³ Lukkari *et al.*²⁴ demonstrated the successful deposition of self-assembled polyelectrolyte multilayers from water-soluble polythiophene derivatives other than PEDOT. Several other groups^{25,26} have also used the ISAM approach to form multilayers and studied the self-doping and ion-exchange properties of polythiophene derivatives.

The ISAM technique involves dipping a charged substrate alternately in a positively charged aqueous polymeric solution and negatively charged polymeric solution. The authors have used glass slides coated with indium tin oxide (ITO) as their substrate, poly (allylamine hydrochloride) (PAH) as the cationic polymer at a concentration of 10 mM and pH 3–5 and PTEBS (obtained from American Dye Source, Quebec, Canada) as the anionic polymer (see Figure 1(a) for PTEBS structure). A few drops of NaOH were added to ensure complete dissolution of PTEBS. The pH used for the PTEBS aqueous solution (1 mM concentration) is 3.0 as it forms a darkly coloured solution in acidic conditions and provides highly uniform orange-red films on deposition.

The authors have also fabricated PTEBS ISAM films at high pH (>7), but the films formed are thinner as compared to films at pH 3. The polycation PAH has increased charge density at lower pH while the reverse happens for the polyanion PTEBS. For the pH values used here, PAH with an increase in charge density tends to deposit highly interpenetrated layers in which the polymer chains adopt a somewhat flattened conformation that results in thinner films. While in the case of PTEBS, the lower charge density causes the polymer chains to adopt a more ‘loopy’ conformation resulting

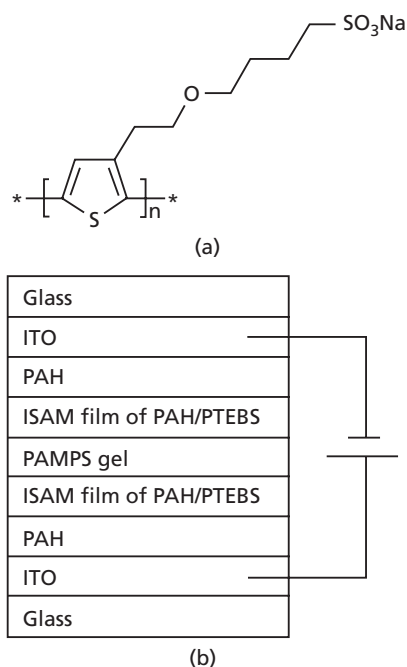


Figure 1. (a) Structure of the PTEBS polymer. (b) Symmetric solid-state device structure employing two similar PAH/PTEBS ISAM films

in thicker films as compared to films obtained at high pH levels. Adjustment of the thickness by varying the pH levels of the two solutions (polycation and polyanion) in the ISAM film fabrication technique is a very well-established phenomenon and has been explained in detail by Rubner *et al.*^{27,28} Therefore, to maximise the amount of PTEBS deposited (and the EC contrast), the authors preferred to use pH 3. The weak polyelectrolyte PAH is not EC and is only used to provide an alternating surface charge for film formation. The pH of the PAH solution was kept at 3–5 because the films formed at low pH for polycationic solution are thinner,²⁶ and this decreased thickness of the inactive material likely aids in achieving fast switching speed with solid-state devices.

Symmetric solid-state devices are fabricated in a similar fashion as explained in one of the recent papers of the authors²⁹ and also by Mercerreyes *et al.*³⁰ Briefly, two ITO slides coated with PTEBS/PAH bilayers were sandwiched together with a few drops of the transparent conducting gel poly (2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) (15 wt% in H₂O) placed in between. The PAMPS component of the device is not EC and does not contribute anything other than a medium for the charge transfer. In the final step, the solid-state devices are fabricated by pressure-laminating the ISAM-coated ITO electrodes with binder clips for 20 m, and then sealing the ends with epoxy so that the PAMPS does not evaporate or degrade from overexposure to air. The device structure is shown in Figure 1(b). The area of the EC device is controlled by appropriately etching our ITO substrates to create stripes or pixels of desired size.

The transmission spectrum of a 40-bilayer PAH/ PTEBS film on ITO immersed in 0.1 M NaClO₄ electrolyte solution as a function of voltage from 0 to 1.2 V is presented in Figure 2. The associated photographs show the colour change between orange-red and green with applied voltage from 0 to 1.2 V. The maximum change in transmission between 0 and 1.2 V is 61% at 735 nm. On stepwise oxidation, the absorption at 410 nm due to the π - π^* transition is decreased and the polymer absorbs at a longer wavelength of 735 nm due to polaronic transitions.

The PTEBS absorption spectrum shows a well-defined isobestic point at 550 nm. The energy band-gap of the PAH/PTEBS ISAM films as determined from the absorption onset (630 nm) is 1.95 eV, smaller than 2.2 eV obtained from solution-cast films of PTEBS by McLesky *et al.*⁶

The transmission spectrum (measured with a Filmetrics UV-Vis spectrometer) obtained from a solid-state device fabricated by sandwiching together two 40-bilayer PAH/PTEBS films (denoted as (PAH/PTEBS)₈₀) is shown in Figure 3. Fabrication and transmission spectra measurements of symmetrical solid-state devices made from a conducting EC polymer (PEDOT) have been shown previously by Mecerreyes *et al.*²⁷ In this case this symmetrical configuration utilises two similar PAH/PTEBS ISAM films as electroactive layers on each of the two ITO-coated substrates.

As a potential of 2 V is applied between the two PETBS layers, the device changes colour from orange to green. The change in

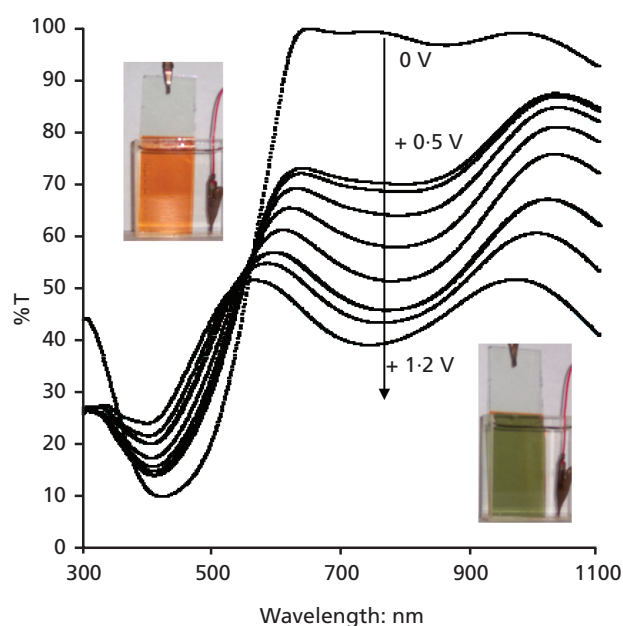


Figure 2. UV-Vis spectra of a PAH/PTEBS 40-bilayer film in 0.1 M NaClO₄ (aq) at 0 V and increasing voltage from 0.5 to +1.2 V, in 0.1 V steps. Inset: photographs show the film changing colour from orange-red (0 V) to dark green (1.2 V)

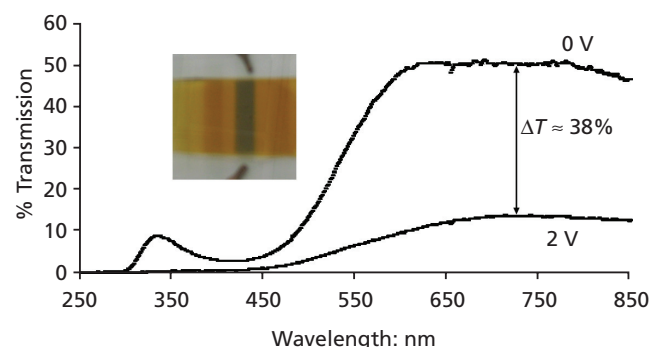


Figure 3. Transmission spectra at 0 and 2 V of a symmetric solid-state device fabricated by sandwiching two patterned ITO electrodes each coated with 40 bilayers of PAH/PTEBS. Inset: photograph of solid-state device with a stripe design changing colour from orange-red to dark green

colour occurs because of the oxidation of only one of the PTEBS layers, while the other PTEBS layer remains reduced and does not contribute to the colour change. The device goes back to the original orange colour once the potential is switched back to 0 V, showing no degradation or memory effect. In such a symmetrical device, the colour change is identical for either polarity of the applied voltage. An important point to note here is that there is no reduction partner for switching. Thus, when the voltage is removed, the device returns to its initial colour state rather than remaining in the switched state. This is in contrast to conventional EC devices. This also results in fast switching of the symmetrical solid-state devices as compared to asymmetrical solid-state devices in which both cathodically and anodically colouring material is required for device switching. There is a contrast of >38% in the broad range of 600–735 nm on application of 2.0 V, consistent with the data in salt solution. As a comparison to other reports of solid-state devices formed with ISAMs, the optical contrast reported by Hammond *et al.*³¹ for dual type EC devices (PANI and PEDOT) at 640–680 nm (colour change from blue-green to pale yellow) is 30%. Lee *et al.*³² have reported spin-coated polymer films in solid-state devices that have optical contrasts up to 40% at 494 nm. The EC response described here provides the flexibility of using the same material for the two primary colours of red and green. In addition to these two primary colours, blue can be easily obtained from PEDOT, which is a well-known EC material that changes from pale blue to dark blue on reduction at low voltages. In their previous work, the authors have demonstrated the ability of PEDOT to switch in the millisecond range while still maintaining high contrast.²⁹ Using the PEDOT and PTEBS polythiophenes, it would be possible to obtain all three primary colours (RGB) from two water-soluble polymers while keeping high colouration efficiency (CE) and fast switching speed.

The response time of the EC switching of the solid-state devices is measured by monitoring the transmittance of a He-Ne laser

(633 nm) with a photodiode as a square-wave voltage (-0.4 – 1.6 V) is applied to the EC device. In Figure 4(a), the authors show the EC film response as well as the applied square-wave voltage signal for a solid-state (PAH/PTEBS)₈₀ device. The contrast associated

with the switching experiments is approximately 20% at 633 nm. Figures 4(b) and 4(c) show the EC time response of colouration and decoloration of the (PTEBS/PAH)₈₀ device. A device with an active area of 1 cm^2 shows $t_{90}\%$ (time to achieve 90% of full EC response) of 125 ms for colouration and 225 ms for decoloration.

Devices with smaller active areas are expected to have faster switching speeds. This solid-state device has been switched more than 50,000 times and no significant (not more than $\pm 10\%$) degradation in the film quality, contrast or switching speed delay was observed.

For cyclic voltammetry measurements, a PAH/PTEBS ISAM film is deposited on an ITO substrate ($8\text{--}12\text{ }\Omega/\text{cm}^2$) and acts as a working electrode while platinum and AgCl/Ag were used as the counter and reference electrode, respectively. A computer-controlled potentiostat/galvanostat (EG & G Princeton Applied Research 263A) was used for electrochemical studies of PTEBS. The measurements were carried out at scan rates ranging from 50 mV/s to 225 mV/s in 0.1 M NaClO_4 electrolyte solution. The electrochemical behaviour of PAH/PTEBS ISAM films is very similar to that observed for alkyl-sulfonated polythiophene³³ and PTEBS spin-cast films²⁴ reported earlier. On the reverse scan, a reduction peak of the oxidised film occurs at 0.5 V or lower and can be seen from the cyclic voltammetry curve in Figure 5(a). The linear increase of current density with the square root of scan rate (Figure 5(b)) for a 40-bilayer film confirms that the redox process is diffusion-controlled rather than surface controlled. Diffusion-controlled processes often result in slower switching speeds of the device, and also can result in increases in the contrast as the whole film changes colour, rather than just the outer surface of the film.²¹ It has been observed that in thick PEI/PEDOT: PSS ISAM films (>20 bilayers), salt ions have difficulty accessing all the bilayers.³⁴ Manipulation of pH (3.5 for PAH and 3 for PTEBS) gives us an ISAM film morphology that has a thicker PTEBS layer as compared to PAH. This helps in achieving higher contrast by accessing a large number of PTEBS sites in an ISAM film, while keeping the availability of inactive PAH sites just enough to build up the layers. This has resulted, in this case, in no significant loss of switching speed. In fact, manipulation of pH and polyelectrolyte solution concentrations provides a film morphology that shows a diffusion-controlled redox process but still a fast switching speed.

Colouration efficiency (CE) is a useful method in the study of electrochromism and has been used for the comparison of different EC materials.^{1,35} The CE, η (cm^2/C), is the ratio of the change in optical density to the injected/ejected charge per unit area (Q_d) and can be calculated using the equation $\eta = \Delta\text{OD}/Q_d$.^{36–39} The change in the optical density at any particular wavelength (λ_{max}) is calculated according to the equation, $\Delta\text{OD} = \log(T_{\text{bleach}}/T_{\text{coloured}})$, where T_{bleach} and T_{coloured} are the transmittance value of the bleached and coloured state, respectively, of the polymer. The colour change for a film in the electrolyte solution

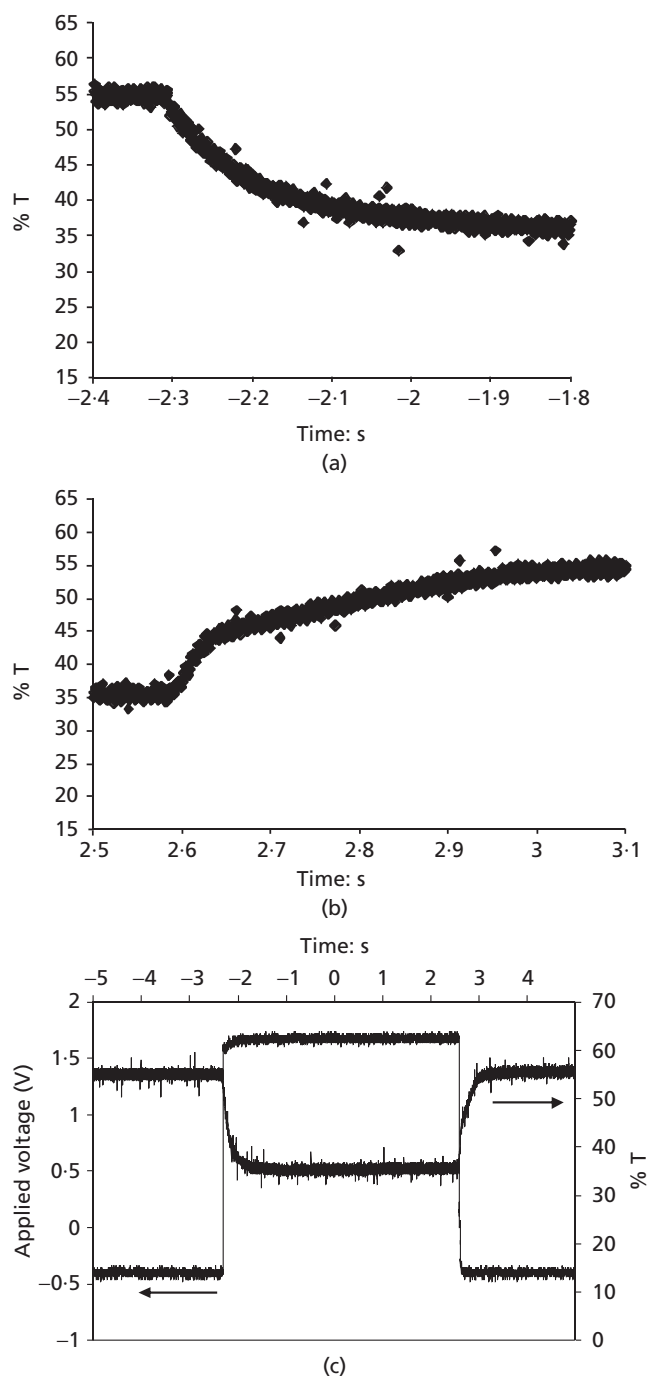


Figure 4. (a) Change in optical density of a symmetric (PAH/PTEBS)₈₀ solid-state device (1 cm^2) at 633 nm on application of a square-wave potential between -0.4 and $+1.6$ V. (b) Decoloration. (c) Coloration blow-ups of the switching curve in (a)

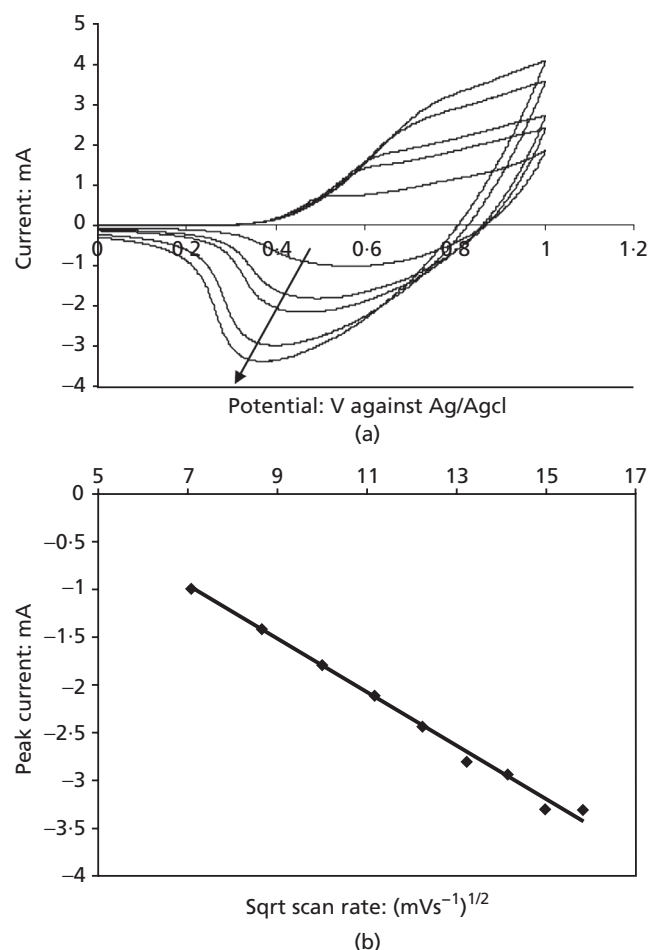


Figure 5. (a) Cyclic voltammograms of a 40-bilayer PAH/PTEBS ISAM film in 0.1 M NaClO₄ (aq) against AgCl/Ag at scan rates from 50 mV/s to 225 mV/s. (b) Linear variation in peak current density with the square root of scan rate

of the transmittance state from orange-red to dark green at 735 nm gives an optical density change of 0.44 and the charge, $Q_d = 1.85 \text{ mC/cm}^2$ for the reduction step, is calculated as the area under the CV curve for the reduction peak, affording a maximum CE of $-238 \text{ cm}^2/\text{C}$. The active working area of the polymer film on the ITO electrode was 10 cm^2 . The CE value reported here for PTEBS is much higher than the inorganic^{31,40} and bipyridinium^{34,41} EC materials, and at par with most of the conducting polymers^{33,42} studied. Employment of EC materials for the fabrication of fast switching, stable displays, light modulators and so on would only be possible if they demonstrate high CE for long term; PTEBS satisfies these requirements well.

The original colour of the ISAM film formed from a PTEBS solution of pH 3 is orange-red that changes to bright green on oxidation. A fine-tuning of the colour (and the bandgap) of the PTEBS solution from red to orange is possible by varying the pH

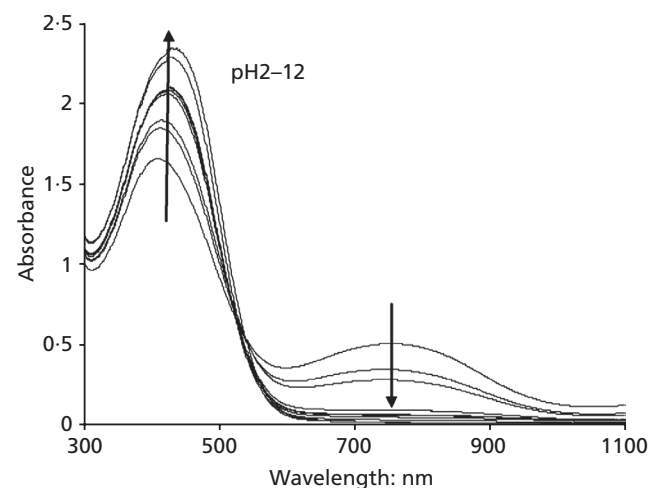


Figure 6. PTEBS (0.5 mM in water) solution absorbance change with varying pH from 2 to 12

from 2 to 11. Figure 6 shows the absorption spectra as a function of solution pH. The absorption curves for the same concentration solution (0.5 mM) in water at different pH show the change in the doping state of PTEBS. Acidic solutions are dark brown in colour while basic solutions are transparent orange-red in colour. The basic and acidic solutions were obtained by adding a few drops of 1M NaOH or HCl, respectively. The absorption peak at 430 nm of the de-doped sulfonated polythiophene corresponds to $\pi-\pi^*$ transition.

The doped polythiophene results in a decrease in absorption at 430 nm as well as a slight blue shift to 410 nm and the appearance of a new peak in near-infrared (IR) region at around 750 nm, which is in agreement with prior observations.^{6,9,43–44}

3. Conclusions

A water-soluble polythiophene solid-state EC device fabricated by LbL assembly has been demonstrated, and shows high contrast (38% for solid-state sandwich devices and 61% in electrolyte solution at 735 nm) and fast switching speed ($<200 \text{ ms}$ for 1-cm^2 active area). PTEBS, as a readily available commercial product, is an excellent candidate for EC displays, exhibiting long-term solid-state switching stability at low power requirements; and the LbL fabrication technique is easily adapted for manufacturing. The combination of PTEBS (dark green) with other polymeric EC materials such as PEDOT (dark blue) and poly 3-(methyl or hexyl) thiophene (red) can enable fine colour tuning of a wide range of colours. Additionally, the combination of the ISAM film fabrication technique allows us to deposit these polymers on a wide variety of substrates without the restriction of shape. Colorimetric and solid-state switching study of PTEBS in combination with other EC materials deposited in the ISAM film will be shown in the forthcoming papers of the authors.

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