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ARTICLE

Black to transmissive electrochromic switching polymer films via solution co-processing

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A pair of solution processable electrochromic polymers poly(2,3-bis(3,4-bis(dodecyloxy)phenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline) (P1) and poly(3,4-di(2-ethylhexyloxy)thiophene-co-3,4-dibutoxythiophene) (P2) were designed and synthesised through chemical oxidative polymerization and copolymerization approach. According to colour mixing theory, the two polymers with complementary colours (green for P1 and purple-red for P2) were utilised to create black-to-transmissive switching films via co-processing from solution containing them in appropriate mass ratio. The films exhibit deep black colour, moderate optical contrast and robust stability. This method and the films with favourable electrochromic performances could be employed for the realization of potential large area electrochromic device applications.

1. Introduction

Defined as a reversible optical absorbance/transmittance change in response to an externally applied potential, electrochromism has been developed over several decades.¹ Compared with inorganic counterparts, electrochromic (EC) polymers were paid more attention attributing to their numerous advantages such as relatively facile synthetic access, vivid colours, fast response time, environmental stability and solution processability.^{1, 2} In recent years, there is a rapid expansion of the demands for large area electrochromic device applications including smart windows,^{3, 4} mirrors^{5, 6} and displays.^{7, 8} Toward this end, solution-processable electrochromic polymers which can be dissolved in conventional organic solvents and spray-coated on large area substrates are exploited.⁹⁻¹³

The polymer materials that have uniform broadband absorbance across the whole visible spectrum are especially desirable for photovoltaic^{14, 15} and electrochromic applications. Although many different coloured-to-transmissive solution-processable polymeric electrochromes containing three primary colours (RGB), orange, and magenta have been investigated,¹⁶⁻¹⁸ it remains a challenge to obtain polymeric black-to-transmissive switching materials. This is due to the complexity in induction of a polymer absorption spectrum which covers evenly over the entire visible spectrum (400-800 nm) in the fully reduced state, while effectively bleaching out

in the same region in the fully oxidised state. Up to now, three strategies have been used for achieving this goal. The first approach is individual polymer or copolymer absorbing across visible spectrum. The first example is chemical copolymer of an increasingly substituted donor-acceptor system from Reynolds group.¹⁹ Subsequently, they ameliorated the synthetic method to access black-to-transmissive polymer via a random Stille polymerization.²⁰ All polymers exhibit excellent black-to-transmissive switching with high optical contrast ($\Delta T\%$), yet the synthetic process is rather complex. The second means is the blends or multilayers of several polymer electrochromes with complementary spectral absorption.^{21, 22} A blend of polymers with magenta and cyan colours in the neutral state was produced with the goal of generating dark colour, but the resulting colour has obvious purple-blue element. Besides the two strategies aforementioned, there is a third way towards black-to-transmissive switching, which was implemented in a pseudo three-electrode electrochromic device (P3-ECD).²³ It utilised two cathodically colouring EC polymers with deep purple and deep green colours correspondingly as two independently controlled working electrode materials. The fabrication of P3-ECD is complicated and it could be inconvenient for real applications albeit the accessibility of a full palette of colours.

In this work, we strive for solution-processable polymeric black-to-transmissive switching materials with the expectations of obtaining deep black colour through a relatively brief approach. Our group has been devoting ourselves to the research of EC materials. Recently, we have some investigations on solution-processable EC polymers.²⁴⁻²⁸ For example, we designed and synthesised a series of red-to-transmissive polymers with high optical contrast and good stability.²⁷ In addition, colour mixing theory claims that if two colour stimuli are mixed, the resulting colour will lie

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Journal Name

somewhere along a straight line connecting two points on the chromaticity diagram.²⁹ Herein, we utilised the colour mixing means owing to its simplicity and flexibility³⁰ and selected the green and purple-red colours as the complementary colours on the basis of our previous work. Specifically, we synthesised two new polymers poly(2,3-bis(3,4-bis(dodecyloxy)phenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline) (P1) and poly(3,4-di(2-ethylhexyloxy)thiophene-co-3,4-dibutoxythiophene) (P2). They exhibit green and purple-red respectively and both have decent solubility in conventional organic solvents. Then, the black-to-transmissive switching mixture films were produced via co-processing of mixture solution containing P1 and P2 in appropriate mass ratio.

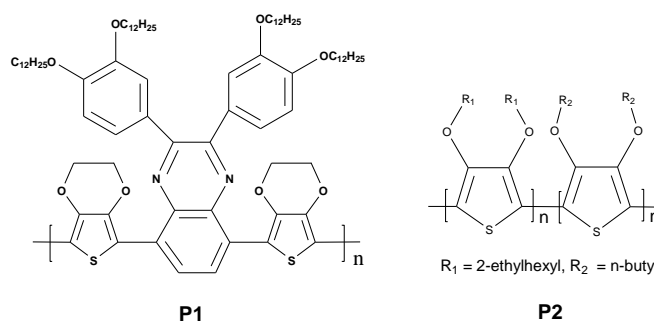
The electrochemical and spectroscopic characterizations of P1, P2 and mixture films were investigated. The full colourimetric and stability characterizations of mixture films were also studied in detail.

2. Experimental

2.1. Materials and Methods

All chemicals used in this work were purchased from Energy Chemical with analytical purity and were used as received without further purification unless otherwise noted. Lithium perchlorate (LiClO_4 , 99%, anhydrous) was purchased from Aladdin Industrial Inc. The indium tin oxide (ITO, $8 \Omega/\square$) glasses used were purchased from Wuhu Token Sciences Co., Ltd. The ITO glasses were cleaned through 15 minutes ultrasonic cleaning with deionized water and ethanol successively and then they were dried in oven at 120°C .

Nuclear magnetic resonance (NMR) spectra were collected on a 400 MHz Bruker Avance 400 spectrometer in deuteriochloroform (CDCl_3). Gel permeation chromatography (GPC) was performed on Agilent LC1200 liquid chromatography system using HPLC grade tetrahydrofuran (THF) as eluent at a flow rate of 1.0 ml/min. Injection was made at 1 g/L sample concentration using a 20 μl injection volume. Monodisperse polystyrene was used to generate the calibration curve. The surface morphologies of the polymer films were analysed using scanning electron microscope (SEM, Sirion200, FEI, Hillsboro, Oregon, USA). UV-vis-NIR spectra were recorded with a Jasco V670 spectrophotometer. The optical band gaps (E_g) of the polymers were calculated with the following equation: $E_g = 1240/\lambda_{\text{onset}}$ (eV). All of the electrochemical experiments were conducted using a CHI 650D electrochemical working station (Chenhua, Shanghai, China) in 0.1 M LiClO_4 /propylene carbonate (PC) electrolyte and under atmospheric conditions. A three-electrode cell was utilised with polymer films on ITO glasses (active area = $0.7 \times 3 \text{ cm}^2$) working electrode, a silver wire reference electrode (Ag/Ag^+ , referenced against ferrocene/ferrocium (Fc/Fc^+), 0.42 V) and a Pt wire counter electrode.^{19, 20, 22} Spectroelectrochemical properties of the films were worked out with an electrolytic cell, which was composed of a 1 cm UV cuvette, ITO glass as a working electrode, a Pt wire as a counter-electrode and a silver wire pseudoreference electrode. All optical measurements of



Scheme 1. Structures of P1 and P2.

polymer films were carried out with air as the background. Photographs of the polymer films were taken with a Canon (PowerShot SX20) digital camera. Colourimetric measurements were performed with a Jasco V670 spectrophotometer, and the colour coordinates were expressed in the CIE 1931Yxy colour space.

2.2. Synthesis

The monomers were synthesised according to the previous literatures.^{13, 27} Polymers P1 and P2 (scheme 1) were synthesised through a modified procedure.

P1: The monomer 2,3-bis(3,4-bis(dodecyloxy)phenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (0.49 g, 0.38 mmol) was dissolved in dry chloroform (20 ml) under argon atmosphere. Iron(III) chloride (0.34 g, 2.09 mmol) was suspended in chloroform (20 ml) and added slowly to the monomer solution. The reaction mixture was stirred for 24 h and then added to methanol (500 ml). The precipitate was collected, dissolved in chloroform and hydrazine (20 ml) was added. The mixture was stirred for 6 h and then it was concentrated and precipitated into methanol (500 ml). The polymer was collected by filtration and purified via Soxhlet extraction for 12 h with methanol, 24 h with hexane and extracted for 6 h with chloroform. The chloroform fraction was concentrated by evaporation, collected as green solid, and dried under vacuum overnight (0.39 g, 79%). GPC (THF vs PS standards): Mw ca. 275 kDa, Mn ca. 153 kDa, PDI = 1.80; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 0.86 ($-\text{CH}_3$), 1.26 ($-\text{CH}_2$), 1.58–1.84 ($-\text{O}-\text{CH}_2-\text{CH}_2$), 3.86–4.02 ($-\text{O}-\text{CH}_2$), 4.31–4.45 ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$), 6.88 (pendant phenyl rings), 7.23 (pendant phenyl rings), 7.48 (pendant phenyl rings), 8.58 (quinoxaline).

P2: Iron(III) chloride (5.13 g, 31.68 mmol) was dissolved in ethyl acetate (110 ml) and stirred under ambient atmosphere. 3,4-di(2-ethylhexyloxy)thiophene (0.9 g, 2.64 mmol) and 3,4-dibutoxythiophene (0.6 g, 2.64 mmol) were dissolved together in ethyl acetate (40 ml) and added to the stirring solution of iron(III) chloride. The reaction mixture was stirred overnight at room temperature. Then the mixture was concentrated to ca. 40 ml and precipitated in methanol (500 ml). The polymer was collected by filtration and washed with methanol until the washings were clear, then it was dissolved in chloroform (150 ml), hydrazine monohydrate (5 ml) was added dropwise, and the solution was stirred for 4 h. The mixture was concentrated to ca. 40 ml and precipitated into methanol (400 ml). The

polymer was collected by filtration and purified via Soxhlet extraction for 12 h with methanol, 24 h with hexane and extracted for 6 h with chloroform. The chloroform fraction was concentrated by evaporation, collected as purple red solid, and dried under vacuum overnight (0.3 g, 20%). GPC (THF vs PS standards): Mw ca. 245 kDa, Mn ca. 65 kDa, PDI = 3.77; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) 0.86–0.97 ($-\text{CH}_3$), 1.27–1.50 ($-\text{CH}_2$), 1.85 ($-\text{O}-\text{CH}_2-\text{CH}_2$), 3.95–4.11 ($-\text{O}-\text{CH}_2$).

2.3. Preparation of films

The two polymers have decent solubility in conventional organic solvents for spray-casting, that is, they show maxima solubility of 8.6 mg/ml for P1 and 10.8 mg/ml for P2 in chloroform solution at room temperature, demonstrating excellent film-forming characteristics. Specifically, P1 and P2 were dissolved in chloroform with a concentration of 4 mg/ml. The mixture solution containing P1 and P2 in different mass ratios also maintains a concentration of 4 mg/ml. Thin films were spray-casted on ITO glasses from these solutions using a HD-130 airbrush at a air pressure of 15–20 psi until the desired absorption maximum (between 0.6 and 1.4 a.u.) were achieved for electrochemical and spectroelectrochemical analysis.

3. Results and discussion

The research mainly focuses on the production of black-to-transmissive polymer film and its electrochemical and electrochromic properties. In this work, all films were spray-casted on ITO glasses from their chloroform solutions until the desired absorption maximum (between 0.6 and 1.4 a.u.) was achieved. Furthermore, these spray-casted films were with the same absorbance maximum.

3.1. Solution and solid state optical absorption properties

As shown in Fig. 1, the green polymer P1 exhibits two absorption bands centred at the blue and red regions of visible spectrum in both solution and solid states. The maximum absorbance wavelengths (λ_{max}) of P1 are 415 and 732 nm in solution state and 436 and 748 nm in solid state respectively. The purple-red polymer P2 displays a single narrow absorption peak located in the green region ($\lambda_{\text{max}} = 502$ nm) of visible spectrum in solution. While in solid state, P2 possesses two distinct peaks at 536 and 571 nm, exhibiting the purple-red colour. This split from the interband $\pi-\pi^*$ transition is attributed to vibronic coupling.²¹ The bathochromic shift of the optical transitions relative to the solution spectra is expected due to a higher degree of order and coplanarity of the polymer chains in the solid state.

Taking these absorption characteristics of P1 and P2 into account, we speculate that the mixture of P1 and P2 in appropriate ratio will present dark colour, especially black colour, which absorbs homogeneously over a broad bandwidth of visible spectrum. As demonstrated by the solution and reduced state absorption curves in Fig 1, the mixture film B (B means the blend) with the mass ratio of 4:1 of P1 to P2 possesses the relatively even peaks spreading over visible spectrum, giving rise to black colour.

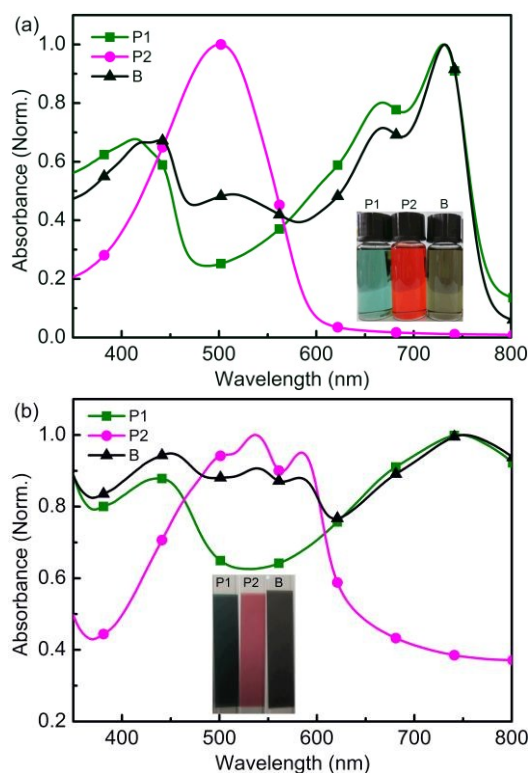


Fig. 1 Normalised solution and solid state (reduced state) optical absorbance of P1, P2 and mixture film B in dichloromethane and solid state respectively. The insets show the polymer solution and films colour.

To realise this goal, the optimal mass ratio is indispensable, assuring the broad entire visible spectrum absorption as homogeneous as possible. Hence we prepared mixture solutions and films with different mass ratio of P1 to P2 and finally obtained the black films with the mass ratio of 4:1 of P1 to P2, thus we chose the mixture film B for subsequent study.

3.2. Optimal absorbance maximum for black films

In order to scientifically research the properties of polymer films, the polymer films should be with the optimal film thickness and all films must be sprayed to the same absorbance maximum, allowing reliable comparison of their electrochromic performance.

In this work, we take optical density as representative of the thickness of thin polymer films. As we mainly focus on the black films, the optimal absorbance maximum for the mixture film B is of great concern.

As the general desired absorption maximum for spray-processable electrochromic polymers is between 0.6 and 1.4 (a.u.), we chose three different absorbance maximum, that is, 0.6, 0.8 and 1.0 (a.u.). When the mixture film B were endowed with different absorbance maximum, the transmittance in reduced state (T^{red}) and oxidised state (T^{oxi}) also with contrast ratio (ΔT) were presented in table 1.

Table 1 Transmittance of the mixture film B with different absorbance maximum.

absorption maximum (a.u.)	T^{reu} (%)	T^{oxi} (%)	ΔT (%)
0.6	24.5	46.6	22.1
0.8	17.8	43	25.2
1.0	10.3	34.1	23.8

The results indicate that the optimal absorbance maximum for mixture films B is 0.8 (a.u.). In fact, there is no obvious difference for the contrast ratio when absorbance maximum of films were located in interval of 0.6 and 1.4 as T^{reu} and T^{oxi} would synchronously change with the absorbance maximum.

In the following research, the absorbance maximum of all films was unified to 0.8 (a.u.).

3.3. Electrochemical properties

The cyclic voltammetry (CV) curves are shown in Fig. 2, which demonstrate well defined oxidation and reduction peaks. Table 2 summarises the electrochemical properties of P1, P2 and B.

P1 and P2 exhibit $E_{1/2}$ of 0.02 V and 0.56 V respectively. These values fall in the same potential range for similar thiophene-based polymers. The difference is attributed to their structure. P1 is a donor-acceptor type polymer, with the character of low $E_{1/2}$ ¹³, however P2 is a copolymer of two acyclic thiophene-derived monomers, exhibiting relatively high oxidation potential.²⁷ As for the mixture film B, it exhibits two obvious oxidation potentials corresponding to P1 and P2. In the mixture film B, the green and purple-red polymer components work independently. The mixture film B is composed of P1 and P2 with the mass ratio of 4:1 of P1 to P2, as a consequence, the shape of its CV curve looks more like P1 simultaneously possessing the feature of P2. As the potential increased, the green polymer was firstly oxidised, and then the purple-red polymer started to be oxidised until 0.46 V. In the mixture film B, P1 and P2 incorporated each other and the onset potential and oxidation peaks shift a little, inducing to larger potential window. Moreover, the increase of both cathodic and anodic current density demonstrates that the interaction of P1 and P2 increases the electrochromic reaction activity in film B.

These CV investigations illustrate that the mixture film B could undergo complete electrochemical process, giving the result this film can be switched between coloured and bleached states.

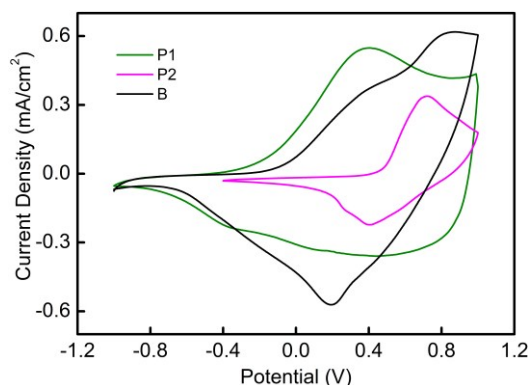


Fig. 2 Cyclic voltammetry of P1, P2 and mixture film B deposited on ITO glasses, with Pt wire counter-electrode and Ag wire pseudo reference electrode at a scan rate of 100 mV/s in 0.1 M LiClO₄/PC.

Table 2. Electrochemical properties of P1, P2 and B.

Polymer	$E_{\text{ox,onset}}$ (V)	$E_{\text{p,ox}}$ (V)	$E_{\text{p,red}}$ (V)	$E_{1/2}$ (V)
P1	-0.14	0.40	-0.36	0.02
P2	0.46	0.72	0.40	0.56
B	-0.11	0.42, 0.82	0.20	0.31, 0.51

3.4. Spectroelectrochemical properties

The colour changes and detailed optical properties can be obtained when different potentials are applied to polymer films. Generally, electrochemical doping induces the formation of radical cations (polarons) and further dication (bipolarons). These charge carriers possess longer optical absorption wavelength than the ones associated with the neutral polymer. When the neutral polymer's absorption is fully transferred from the visible region to the near-infrared (NIR) upon oxidation, it is cathodically colouring material with a highly transmissive doped state.

Fig. 3a-c show the spectral change occurring in the 350-1500 nm range upon electrochemical oxidation of P1, P2 and B, respectively. As the working potential increases, the absorbance in the visible region decreases, meanwhile transitions at the NIR region start to grow owing to the emergence of lower energy polaron and bipolaron charge carriers at the expense of the π -to- π^* transition. When fully oxidised, the polymer has strong absorption in the NIR that tails into the visible, giving the polymer oxidation state with a certain degree of residual colour (light yellow-green colour for P1 and B).

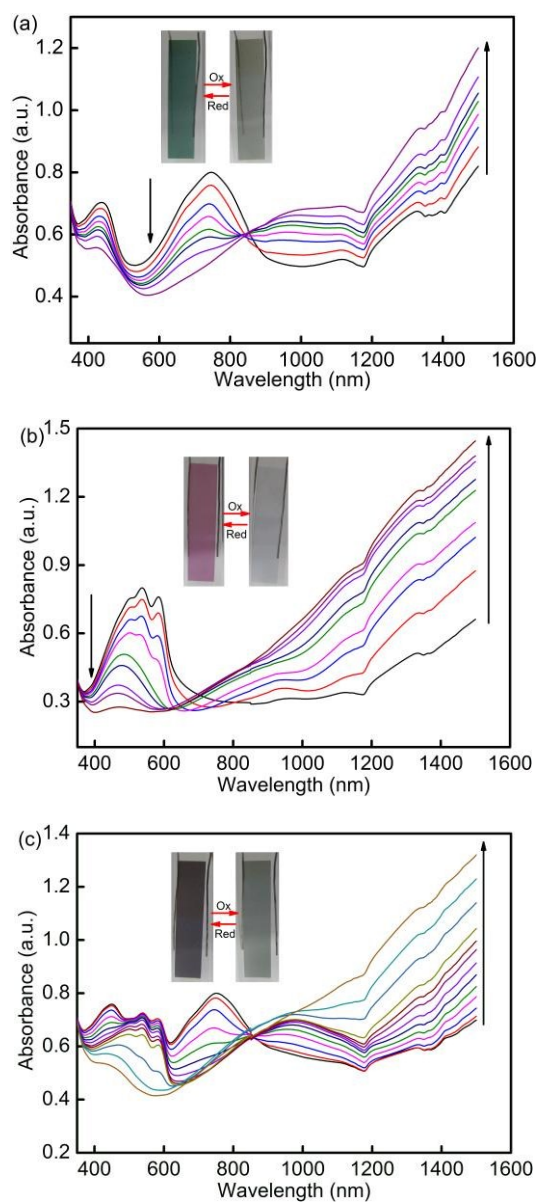


Fig. 3 Spectroelectrochemistry of (a) P1, (b) P2 and (c) mixture film B on ITO glasses, with Pt wire counter-electrode and Ag wire pseudo reference electrode in 0.1 M LiClO₄/PC. The arrows show the direction of increasing potential and the insets show colour of the polymer film in two states. The applied potential was, P1: -0.4, -0.1, 0.02, 0.06, 0.12, 0.16, 0.24 and 0.40 V; P2: -0.4, 0.49, 0.53, 0.55, 0.57, 0.59, 0.65, 0.69 and 0.81 V; B: -0.6, -0.1, 0.02, 0.10, 0.18, 0.26, 0.34, 0.42, 0.46, 0.50, 0.54, 0.58 and 0.72 V.

In neutral state, P1 films reveal two absorption bands, as expected from a donor-acceptor type polymer, centring at 436 and 748 nm. The two absorption bands are close to excellent absorption maxima needing to yield a saturated green colour in the reduced state. P1 has an absorption onset at 932 nm corresponding to an optical bandgap of 1.33 eV, which is a reasonable bandgap value, keeping in mind that polymers with donor-acceptor units in general exhibit bandgaps between 0.9 and 1.3 eV.¹³ The purple-red polymer P2 owns a λ_{max} of 540 nm with an absorption onset at 720 nm, resulting in an optical bandgap of 1.72 eV.

As shown in Fig. 3c, the absorption curves of mixture film B combine the characteristics of P1 and P2, resulting in a nearly homogeneous absorption over the visible spectrum in the reduced state. As a result, the mixture film B shows a deep black colour, demonstrating powerfully that we can obtain the dark especially black colour by mixing the complementary colour of green and purple-red in a proper ratio. However, the mixture film manifests some yellow-green colour in its oxidation state, attributing to the big amount of P1 component in film B, as P1 exhibits a non-transparent yellow-green colour in oxidation state. Furthermore, the hazy character of films and the absorbance of ITO glasses resulted in absorbance at wavelengths higher than 800 nm in their neutral state.

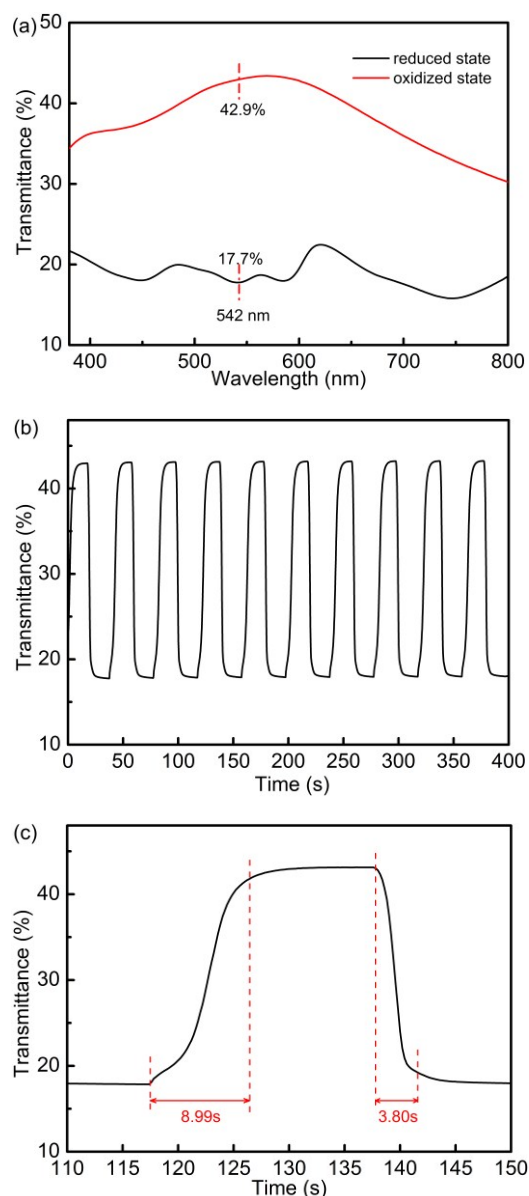


Fig. 4 (a) Transmittance of the mixture film B over the entire visible spectrum; (b) and (c) Square-wave potential step absorptometry of mixture film B (monitored at 542 nm). Measurements were performed in 0.1 M LiClO₄/PC of films on ITO glasses electrodes, with Pt wire counter-electrode and Ag wire pseudo reference electrode.

3.5. Transmittance, contrast and switching speed

The transmittance of the mixture film B in the two states over the entire visible spectrum was performed to explore its broadband absorbance character. Meanwhile, optical contrast ($\Delta T\%$), switching times of the mixture film B upon electrochromic switching between the reduced (-0.6 V) and oxidised (0.8 V) states were investigated at its λ_{\max} .

As presented in Fig 4a, the transmittance curve of mixture film B in the reduced state retains in a narrow range and exhibits approximate transmittance from 380 to 800 nm, indicating that film B possesses the relatively even absorbance spreading over the whole visible spectrum. Furthermore, the film B exhibits the max contrast ratio at the wavelength of 542 nm.

The $\Delta T\%$ of black film B was calculated to be 25.2% at 542 nm. The mixture film achieves 95% of $\Delta T\%$ in 8.99 s for bleaching and 3.80 s for colouring. From the switching curves of P1 and P2 (Fig S1 in electronic supplementary information), P1 reveals 3.54 s for bleaching and 6.91 s for colouring and P2 reveals 5.32 s for bleaching and 9.84 s for colouring. Compared to previous literatures, the switching speed of our polymer films is relatively slow and this may be attributed to the dense surface micrographs of films (Fig S2 in electronic supplementary information). We will proceed on this research and enhancing optical contrast and switching speed is also an important point in our future work.

3.6. Colourimetry

In order to scientifically quantify the colour of polymer films, colour change of polymer films during redox process as a function of applied potentials was monitored by colourimetry investigation. The applied potential was -0.6, -0.1, then increasing in 20 mV steps from 0.02 to 0.72 V for black films. Colour of material is represented quantitatively using three attributes "L*" (brightness), and two colour components "a*" (the axis extends from -a* (green) to +a* (red)) and "b*" (the axis extends from -b* (blue) to +b* (yellow)) as defined by Commission Internationale de l'Eclairage (CIE).

As indicated in Fig. 5a, the mixture film B has a deep black colour ($L^* = 41.26$, $a^* = 2.34$, $b^* = 2.93$) with little orange hue in neutral state. When increasing positive potentials are applied to polymer films, a^* value increases, along with the green polymer P1 in the mixture film bleaches. Then the purple-red polymer P2 begins to be oxidised and a^* and b^* values decrease. Ultimately, the film is fully oxidised, giving rise to a light yellow-green colour ($L^* = 57.72$, $a^* = -2.14$, $b^* = 7.53$) on account of the yellow-green colour of P1 in oxidation state.

In Fig. 5b, the colourimetrically determined relative luminance change was measured as a function of applied potentials. It estimates the brightness of the transmitted light as a percentage of the brightness of the light source. The luminance change ($\Delta Y\%$) value is 16.5%.

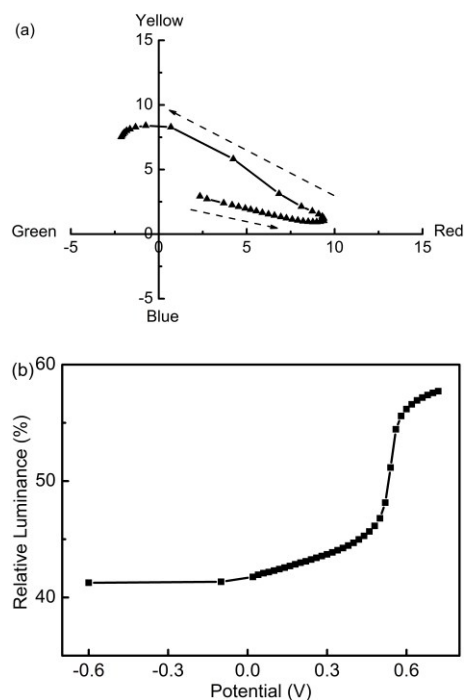


Fig. 5 (a) CIE1976 a^*b^* values of mixture film B. The arrow shows the direction of increasing potential. (b) Relative luminance as a function of increasing applied potential for mixture film B. Measurements were performed in 0.1 M LiClO_4/PC of films on ITO glasses electrodes, with Pt wire counter-electrode and Ag wire pseudo reference electrode.

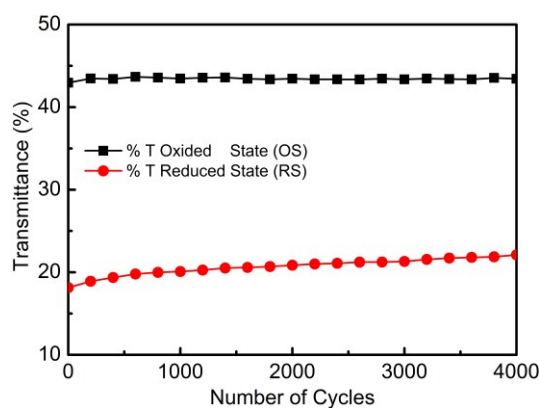


Fig. 6 Long-term switching of mixture film B (monitored at 542 nm, -0.6 V to 0.8 V, square-wave potential steps of 15 s, full cycle is 30 s). Measurements were performed in 0.1 M LiClO_4/PC of films on ITO glasses electrodes, with Pt wire counter-electrode and Ag wire pseudo reference electrode.

3.7. Stability

To reinforce the potential of this co-processing method of multiple spray-processable polymers for integration into commercial applications, its long-term switching was investigated. Fig. 6 demonstrates the performance of the mixture film B subjected to 4000 redox cycles.

As revealed in Fig. 6, the mixture film B shows only contrast loss of 3.5% (from 24.8% to 21.3%) over 4000 switching cycles. The result suggests that the black film possesses good stability.

4. Conclusions

In summary, we synthesised two new polymers with complementary colours in their reduction states and attained black-to-transmissive films via co-processing of mixture solution containing P1 and P2 in optimal mass ratio 4:1 of P1 to P2. The mixture films combine the characteristics of P1 and P2, resulting in a nearly homogeneous absorption over the visible spectrum in the reduced state. As a result, the mixture film shows a deep black colour. Moreover, P1 and P2 have decent solubility in conventional organic solvents, indicating that the mixture films can be prepared by co-spray-coating and co-ink-jet printing methods. The black films exhibit moderate optical contrast of 25.2% and robust stability retaining 86% of its original optical contrast after 4000 cycles, which meet the requirements for windows and displays applications.

Acknowledgements

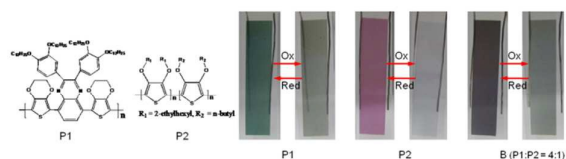
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Black to transmissive electrochromic switching polymer films via solution co-processing

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Two newly synthesized electrochromic polymers were utilized to prepare black films, which exhibited moderate optical contrast and robust stability.