

State of the art neutral tint multichromophoric polymers for high contrast see-through electrochromic devices

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We here report two new multichromophoric electrochromic polymers featuring a conjugated EDOT/ProDOT copolymer backbone (PXDOT) and a reversible Weitz-type redox active small molecule electrochrome (WTE) tethered to the conjugated chain. The careful design of the WTEs provides a highly reversible redox behaviour with a colourless \leftrightarrow red switching that complements the colourless \leftrightarrow blue switching of the conjugated backbone. Subtractive colour mixing successfully provides high performing solution processable polymeric layers with colourless \leftrightarrow neutral tint switchable limiting states for application in see-through electrochromic devices. Design, synthesis, comprehensive chemical and spectroelectrochemical characterization as well as the preparation of a proof-of-concept device is discussed.

1 Introduction

Organic electrochromic materials (OEMs) [1–5] offer a low power input and low cost solution for applications like smart windows,[6] electrochromic sunglasses,[7] electrochromic paper[8] and displays.[9] Depending on the specific application, suitable OEMs should offer a wide color palette, high electrochromic contrast, fast switching, low cost and high stability (chemical, photochemical, thermal, resistance to repeated on/off cycling). Devices assembled in appropriate conditions can comply with stability requirements.[10, 11] Relevant see-through applications for transmissive electrochromic devices (ECDs), like sunglasses and automotive, additionally require that the transmitted light experiences negligible colour distortion in both devices limiting states. During the past ten years the Donor-Acceptor (D-A) polymers concept promised to address this very challenging topic and looked as the most likely strategy to achieve a neutral tint to colourless switching see-through ECDs.[4, 12–16] Indeed, the preparation of copolymers constituted by alternating electron rich and electron poor groups leads to electrochromic films having grey low transmittance states. Regrettably, such polymers maintain a non-negligible absorption even in their corresponding greyish or greenish bleached states ($T \simeq 65\%$, $L^* 86$, $a^* -3$, $b^* -5$, $S_{ab} 7$)[12, 17], leading to both slight color distortion and sizeable light attenuation. The residual absorption is due to the tailing of the oxidized form absorption band

in the visible region. Prominent D-A polymers developers very recently explicitly commented on this issue and steered toward a new strategy based on an extended colour palette of different all-donor copolymers exploiting steric effect of substituents.[18, 19] Single constituents of this electrochromic polymers (ECPs) palette show remarkably good performances with bleached states transmittances in the 65-85% range over the visible region. This ECPs palette enabled the optimization of polymeric blends with matched redox active potentials that can produce, through colour mixing, a tunable neutral tint in the coloured state. Some of these blends show superior properties when compared to those of previous D-A polymers allowing a brown coloured state with a more transmissive bleached one ($T \simeq 70\%$, $L^* 89$, $S_{ab} 5$).[20] Despite the seminal relevance of these encouraging results, performance optimization of a single electrochromic polymer thin film switched in a liquid electrolyte solution does not straightforwardly leads to a performing ECD suitable for application.

Full electrochromic devices, in fact, are not functional without electrode substrates, electrolyte and a charge balancing counterelectrode (*i.e.*: another transmissive electroactive material). While transparent conductive substrates and electrolyte are an unavoidable burden that reduce practical achievable transmittance of the final device to 85-90%, both the electroactive materials play a crucial role in determining optical contrast performance and hue of the limiting states.[21] In this respect, highly transmissive bleached states of both primary and secondary electroactive materials ($T > 90\%$), represent a mandatory requirement for see-through devices in order to avoid drastic reduction of overall contrast and bleached state transmissivity; the latter being lower than the product of those of the

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two separate layers.[22] The most established concept makes use of a secondary electrochromic material at the counterelectrode that switches complementary to the primary one leading to simultaneous bleaching and colouring of the two within the device. Although the major part of the electrochromic contrast usually results from the primary electrochrome, a proper choice of the secondary complementary material can be exploited to further tune final hue to the desired values.[23, 24] A slightly different strategy was demonstrated by Reynolds *et al.* exploiting a secondary electroactive polymer based counterelectrode that is supposed to act as a charge storage layer without showing electrochromic behaviour or at least a negligible colour variation. They firstly explored a TEMPO-based non-conjugated radical polymer which benefits from the high transmissivity in both states but shows strong limitations due to lack of long term cycling stability and slow electrode kinetics that hamper the overall device performance.[25] A conjugated electrochromic anodically colouring polymer, namely a poly-(N-alkyl-3,4-propylenedioxy-pyrrole), was later developed by the same group in order to circumvent these limitations.[26] Polymeric thin films of this material exhibit good electroactivity, moderate cyclability and ease of processing combined with a low colouration efficiency over the whole visible region. The combination of this soluble anodically colouring polymer with the aforementioned D-A grey polymers gave a dual-polymer see-through ECD having a neutral purplish tint in its coloured state ($L^* 25$, $a^* 7$, $b^* -16$, $S_{ab} 57$) and blueish bleached state ($L^* 71$, $a^* -5$, $b^* -9$, $S_{ab} 14$).[17] Later on, a similar device using the optimized all-donor polymer blend lead to far better results with a neutral brown coloured state ($L^* 45$, $a^* 18$, $b^* 10$, $S_{ab} 42$) and colourless bleached state ($L^* 75$, $a^* 2$, $b^* 2$, $S_{ab} 4$).[20] Despite these impressive advancements and their invaluable on-demand switching feature, optical performance of neutral tint see-through ECDs does not compare to that of existing benchmark technologies (*i.e.* bleached photochromic lenses for eyewear require $T > 80\%$, $L^* 95$, $S_{ab} 1$) and new strategies have to be explored to fulfill market requirements.

In this study we evaluate two new tailor designed electrochromic multichromophoric polymers (MCPs) as a viable alternative to the D-A concept and All-Donor polymer blends to cope with the aforementioned requirements. Typical MCPs feature a conjugated polymer backbone (*i.e.* PEDOT), side chain functionalized with small molecule electrochromic derivatives acting as contrast enhancers and color tuning additives.[27] The best performing MCP so far reported, a naphthalenediimide containing cross-linked PEDOT, features a transmittance level above 80% all over the visible region in the bleached state ($L^* 93$, $a^* -3$, $b^* 1$, $S_{ab} 4$), along with a grey coloured state ($L^* 58$, $a^* -4$, $b^* -9$, $S_{ab} 16$).[28] Cycling stability in the excess of 1000 cycles was also demonstrated. It should be noted, however, that such polymers possess a three-stage electrochemistry, with the highly valued grey state as the intermediate one. Most

common electrochromic devices have a two electrodes configuration, offering no fine control over the absolute redox potential at the respective electrodes. As such, two-stage electrochromic materials are generally preferred. We here show how the application of specifically designed small molecules pertaining to the class of Weitz electrochromes to MCPs can overcome this limitation.[29] The resulting side chain EDOT/ProDOT copolymers are able to reversibly switch between a brown and a colourless state, showing superior optical performances combining state-of-the-art contrast with a dark neutral hue ($S_{ab} 24$) and a colourless high lightness ($L^* 94$, $S_{ab} 2$) limiting states. We show that such polymers can be used as the working electrode of solution processed electrochromic devices using Prussian blue (PB) as the counter electrode.[30] Both polymers and corresponding devices are stable to extensive cycling, delivering – to the best of our knowledge – state of the art performance in the field of neutral tint electrochromic polymers. Easy synthesis and scale up provide further added value to our approach.

2 Results and Discussion

2.1 Design principles

In a recent publication on building up from seminal contributions from the groups of Bäuerle and Lee, some of us proposed the so-called multichromophoric polymer approach as a viable alternative to produce high performing colourless transmissive to absorptive neutral hue switchable ECMs.[31–34] Basically this requires the formation of a composite polymeric material by incorporation (through side-chain functionalization) of a second, non-interacting, electrochrome inside the structure of a known conjugated electrochromic polymer (*i.e.* PEDOT) thus obtaining an easy way to tune the colour of the limiting states. Under the additional requirement that both the polymer and the discrete molecular electrochrome possess a colourless state in the same potential range, a colourless to coloured transition could in principle be observed.[27] On the basis of these previous observations we concluded that the target electrochrome should possess at least the following characteristics:

- highly reversible redox process without intermediate states;
- blue shifted absorption in the oxidized state with minimal tailing in the visible region;
- reduced state with absorption in the 450-500 nm range.

In light of these considerations we developed the structures, pertaining to the class of Weitz-type electrochromes (WTE), shown in scheme 1.[29] Both molecules, the design of which is reminiscent of a bis-acridinium derivative we previously published,[35] feature a single two-electron redox process and

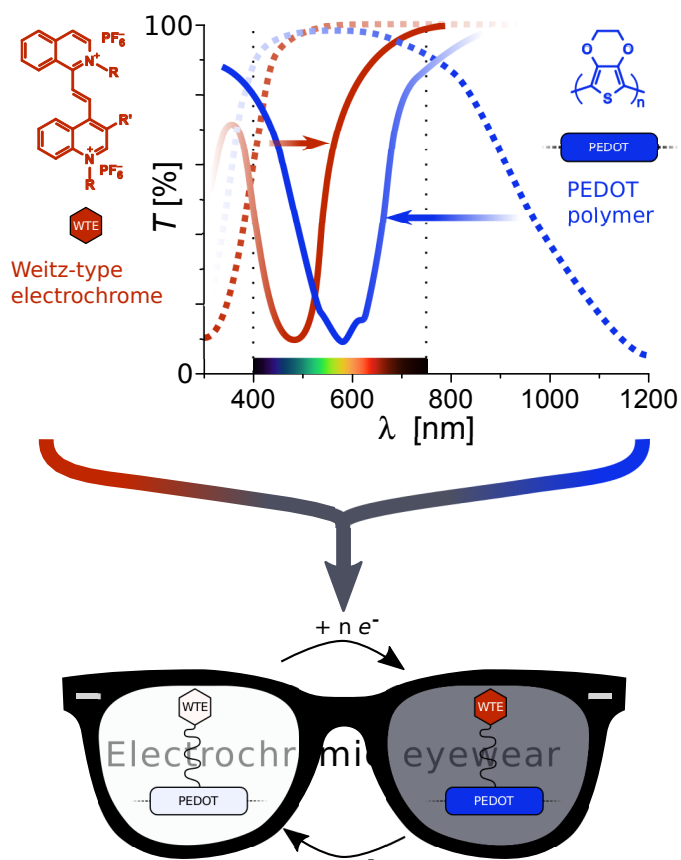


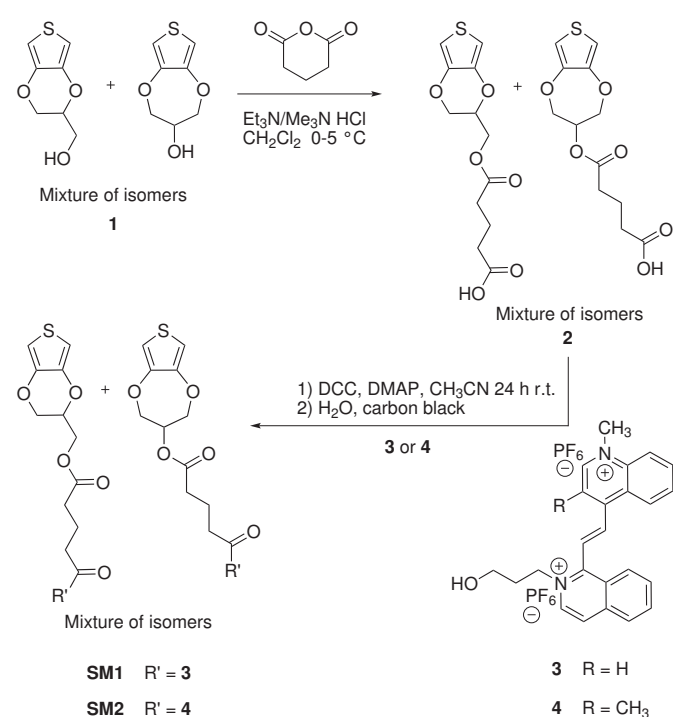
Figure 1 Design principle of the new colourless transmissive to absorptive neutral hue switchable MCPs. Transmission spectra of oxidized forms (dotted lines) of the conjugated backbone and WTE along with those of their corresponding reduced forms (solid lines) are depicted

were designed to achieve UV absorption in the oxidized state and a yellow-orange tint (complementary to the absorption band of undoped EDOT/ProDOT copolymer) in the reduced state as schematically depicted in figure 1.

2.2 Synthesis of monomers

The synthesis of the small molecule electrochromic derivatives **3** and **4** is depicted in scheme 1 along with the synthetic pathway leading to their conversion to the corresponding polymeric derivatives **SM1** and **SM2**. The alcohol functionalized 3,4-alkylenedioxythiophene (XDOT) starting material was provided by COC - Centrum Organické Chemie s.r.o. as the mixture ProDOT and EDOT isomers **1** in a 1:4 ratio, unless differently specified. This particular isomers mixture, whose synthesis is detailed in the SI, correspond to a product originally developed by Stark GmbH.[36] Although we do not envisage any performance advantage in using the mixture over the pure

isomers, the beneficial impact on the economical and environmental aspects that results from avoiding the otherwise necessary energy and resource intensive derivatization steps, make it an obvious choice for our application driven approach.[37] The aforementioned mixture is converted, by esterification with glutaric anhydride, in the corresponding mixture **2**. [38, 39] The preparation of **3** and **4** follow a common strategy. An isoquinolinium salt carrying an alcohol functionality is obtained by alkylation of 1-methyl-isoquinoline with 3-bromopropanol, and subsequently condensed with the proper aldehyde in refluxing methanol with piperidine as a catalyst. Once optimized the following methylation step, performed with MeI in acetone under pressure in presence of 2 eq. of KPF_6 , proceed smoothly



Scheme 1

with high yields. The obtained alcohol functionalized violene systems were coupled with **2** through esterification to obtain the polymeric derivatives **SM1** and **SM2**. In this step, a Steglich esterification protocol was adopted.[40] This mild esterification method allowed to obtain the desired products in good yields and with an easy workup procedure as light brown powders. The synthetic approach proved to be easily upscalable thanks to high yields and lack of any (expensive and time consuming) chromatographic purification step allowing preparation of final product on multigram scale using common laboratory equipment.

2.3 Electrochemical characterization of monomers and polymers

A common feature of both developed monomers is the presence of a reversible redox process centred around ~ -0.7 V vs. Fc/Fc^+ . This feature can be easily observed in the cyclic voltammogram of intermediate **3**. The sharply peaked redox

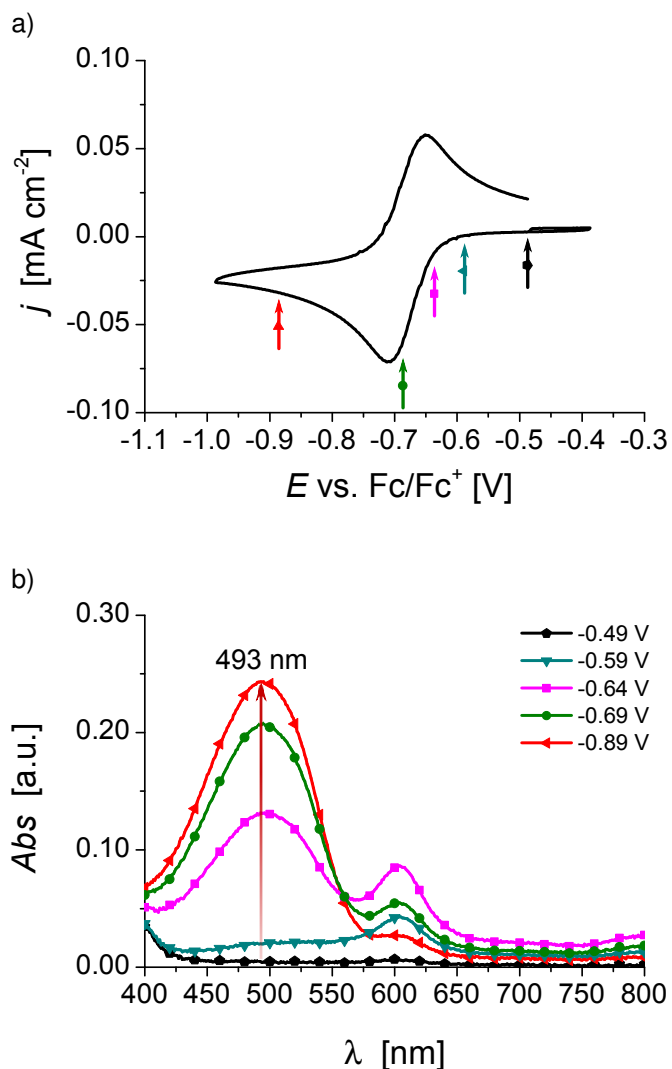


Figure 2 a) Cyclic voltammogram of a 1.9×10^{-4} M solution of **3** in the same electrolyte; WE: Au mesh; 50 mVs^{-1} . b) Spectroelectrogram of a 1.3×10^{-4} M solution of **3** in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{MeCN}$.

wave ($E_{1/2} -0.68$ V vs. Fc/Fc^+) along with the low peak separation testifies the presence of a two-electron transfer process, a common feature of this class of Weitz-type electrochromes (Fig. 2a).[29] As clearly visible from figure 2b, showing the *in*

situ spectroelectrogram of a solution of the compound in a thin layer cell, a broad absorption band centred at 493 nm emerges as a result of the reduction process. A weak band at 603 nm is also present at intermediate potentials (-0.64 V vs. Fc/Fc^+) but is bleached at more reductive potentials. It is interesting to note that absorbance ratio at peak wavelength between the two limiting states is extremely high (> 50 vs. $\simeq 4$ for PEDOT films[41]) and represent a first indication, along with the involved spectral region, of the suitability of this material for our purpose. Once functionalized with EDOT/ProDOT moieties through esterification, derivatives **3** and **4** give the corresponding polymeric monomers **SM1** and **SM2**. The latter can be electrochemically polymerized (see experimental section and Supporting information for the details) according to a general approach originally proposed by Lee and further developed by Segura and Bäuerle.[31–34] A cyclic voltammogram of a solution of **SM1** in nitrobenzene (Fig. 3a) shows the distinct features of the electropolymerization process. An oxidative process at 1.13 V (vs. Fc/Fc^+) is present on the first cycle, followed by the onset of the oxidative polymerization at 1.44 V. Polymer growth is confirmed by the steadily increase of anodic and cathodic currents in the 0-1.44 V range upon cycling. The cyclic voltammogram of the obtained polymeric film in a monomer-free solution (Fig. 3b) clearly shows the doping/dedoping process of the PXDOT chain in the region above -0.48 V along with the presence of a redox wave centred at -0.704 V with a peak separation of 31 mV. A comparison with the corresponding process depicted in figure 2a reveals a minimal deviation in the half-wave potential with substantial broadening of both the cathodic and anodic waves as an expected consequence of inhomogeneities in the polymeric matrix and hindered diffusion of counterions. A pulsed deposition technique, proved to give the best results for both **SM1** and **SM2** electrochemical polymerization both in terms of film homogeneity and cycling stability (see SI for more details).[42]

2.4 Chemical polymerization

In order to attain easy scalability of the polymer deposition process to large area devices or even roll-to-toll (R2R) machinery we attempted an *in situ* oxidative chemical deposition of **MCP1** and **MCP2** using our experience with a similar multichromophoric derivative as a starting point.[20] This procedure involves the preparation of a solution of the monomer of choice and a chemical oxidant, namely an iron (III) salt, in organic solvents that can be directly used to coat the substrate. Polymer formation is observed upon solvent evaporation and mild thermal curing of the coated substrates that induces the oxidative polymerization process. Residual spent oxidant can be easily removed washing the insoluble polymeric films with lower alcohols according to an established protocol. Complete Fe removal is confirmed by the absence of $\text{Fe}^{2+}/\text{Fe}^{3+}$

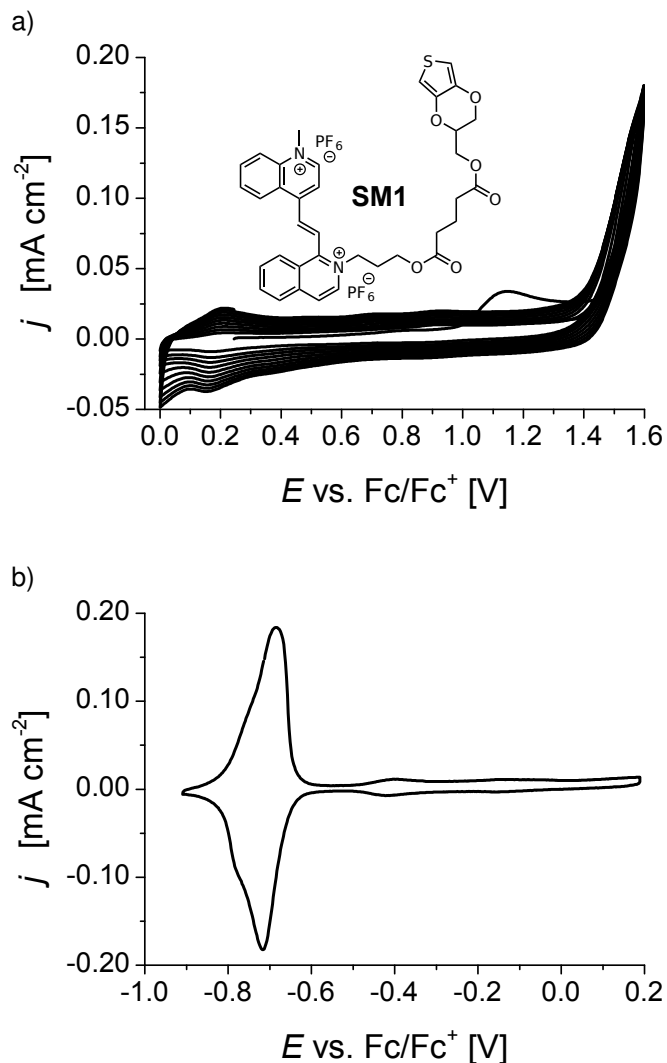


Figure 3 a) Cyclic voltammogram of a 10^{-3} M solution of **SM1** in 0.1 M Bu₄NPF₆/PhNO₂. WE: FTO/glass; 100 mV s⁻¹; 10 cycles. b) Cyclic voltammogram of a **MCP1** layer on FTO/glass in 0.1 M Bu₄NPF₆/MeCN monomer-free solution; scan rate 25 mV s⁻¹. Polymer was prepared by cyclic voltammetry 0-1.6 V vs. Fc/Fc⁺, 10 cycles.

redox peak on the CV traces and further supported by previous SEM/EDX analysis demonstrating the complete removal of such impurities from PEDOT films prepared under analogous conditions.[43] Further addition of additives and/or adhesion promoters can be applied to fine tune the final properties. Such approach was further extended, eventually leading to large area samples having comparable, if not better, stability than the electrochemically polymerized ones (see Figures S1-S5 of the Supporting Information for repeated cyclic voltammograms as well as charge capacity retention upon cycling for both polymers).

2.5 Electrochromism of MCP1 and MCP2 films

Both **MCP1** and **MCP2** polymers possess a very interesting multichromic behaviour. As an example, figure 4 shows the spectroelectrogram of an electrochemically deposited **MCP1** thin film cycled in a monomer-free solution. A broad absorp-

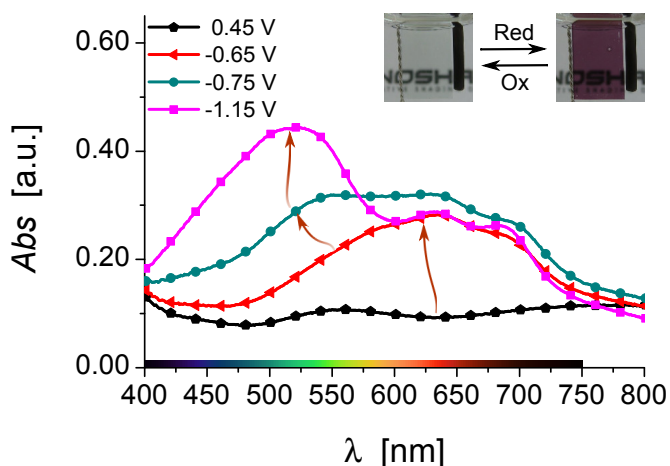


Figure 4 Spectroelectrogram of a **MCP1** layer in 0.1 M Bu₄NClO₄/MeCN monomer-free solution. Polymer was deposited by LSV on FTO/glass substrate.

tion band, centred at 632 nm, gradually appears on cathodic scanning at potentials below 0.3 V vs. Fc/Fc⁺. This absorption is attributed to the reduction of the PxDOT chains. During this process the film colour changes from colourless ($L^* 92, a^* 1, b^* -2, S_{ab} 2$) to blue ($L^* 82, a^* -5, b^* -13, S_{ab} 17$ @ -0.65 V vs. Fc/Fc⁺). On further cathodic scanning, another redox process takes place at potentials between -0.65 and -0.9 V. This process leads to the appearance of a new absorption band, centred at 519 nm, that changes the colour of the thin film to a purplish hue ($L^* 72, a^* 15, b^* -3, S_{ab} 20$). A thicker film of **MCP1** obtained by pulsed galvanostatic deposition better shows off the extremely high contrast values ($\Delta L^* 72$) achievable with this material (Figure S10). Chronoabsorptometric data (Figure S6) show fast switching between the two limiting states with 3.0/3.7 s and 3.3/1.9 s for the colouration/bleaching processes,

at 505 nm and 631 nm respectively, to attain 95% of the final ΔT . It is noteworthy that, upon application of the potential steps, both electrochromic processes of the PXDOT-backbone and of the side-chain electrochrome proceed with similar kinetics thus minimizing chameleon effect. As already mentioned in section 2.4, the possibility to straightforwardly coat uniform films of **MCP1** and **MCP2** using *in situ* chemical polymerization represent a key enabling feature for large area substrates and device manufacture. Figure 5a shows the transmittance spectrum of the limiting states of a **MCP2** chemically deposited film along with its cyclic voltammogram (Fig 5b).

With respect to **MCP1** the slight structural modification in **MCP2** provides a blue shift (ΔE 0.11 eV) of the reduced Weitz-type electrochrome absorption band from ~ 515 nm to 493 nm (see figure S7). This subtle substitution effect gives **MCP2** a unique low saturation brown hue ($L^* 58, a^* 13, b^* 6, S_{ab} 24$) in its reduced form combined with an high lightness completely colourless oxidized one ($L^* 94, a^* -1, b^* -2, S_{ab} 2$). Moreover, the stability to repeated cycling in a liquid electrolyte is also very high, being essentially comparable with that of PEDOT on plastic substrates.

2.6 Complementary PB/MCP2 proof-of-concept ECD

A 5×5 cm² sample of the polymeric film was employed for the preparation of the dual electrochromic device demonstrator shown in Figure 6. The device was obtained by lamination at 50 °C of a polymer membrane (courtesy of Hydro-Québec Research Institute, Montreal, Canada) containing bis(trifluoromethane)sulfonimide lithium salt (LiTFSi) as the electrolyte on top of the chemically deposited **MCP2** layer in its fully oxidized state. The latter was then laminated on top of a layer of electrochemically deposited, fully reduced, Prussian blue on PET-ITO film.[30] Figure 6a shows the contrast of such device between the coloured (right) and highly transmissive (left) state. Thanks to the contribution of the Prussian blue counter electrode absorbing in the 600-800 nm region, the lower wavelength absorption of the cathodically colouring polymeric material is perfectly balanced resulting in a dark coloured state with very low saturation ($L^* 34, a^* 3, b^* -10, S_{ab} 31$) and an high lightness colourless state ($L^* 83, a^* -3, b^* 0, S_{ab} 4$) with an extremely high contrast ($\Delta L^* 49$) (Fig. 6c). The latter value is even more prominent once considering that it include the optical properties from the substrates and the electrolyte membrane as measurements were made versus air. The device remained distinctly grey and colourless in the two limiting states even after 500 cycles (Figure S9). The only effect we observed was a progressive drift of oxidation and reduction potentials in the device CV traces, likely connected with a morphological evolution at the electrode/electrolyte interfaces (Figure S8).

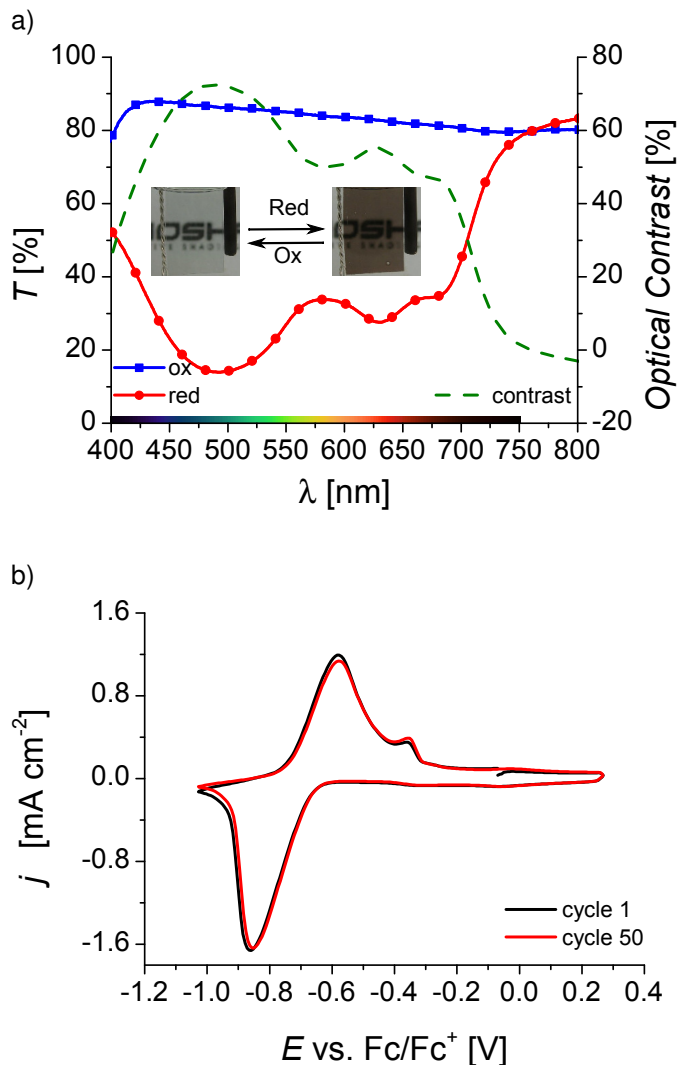


Figure 5 Electrochemical characterization of a chemically deposited **MCP2** film on FTO/glass: a) Transmittance spectra of the limiting states (left axis) and corresponding optical contrast (right axis). Film is switched in in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{MeCN}$ solution. b) Cyclic voltammogram of the film in the same electrolyte; scan rate 50 mV s^{-1} .

3 Conclusion

In conclusion, we designed, synthesized and polymerized two new Weitz type electrochromes bearing a polymerizable EDOT/ProDOT side chain residue (**SM1** and **SM2**). The corresponding MCPs obtained through *in situ* polymerization show state-of-the-art performances in terms of overall electrochromic contrast, transmissivity and colorlessness in the bleached state as well as electrochemical stability and reversibility. Thanks to these unique characteristics, a proof-of-concept complementary ECD was demonstrated showing state-of-the-art contrast (ΔL^* 49) along with an high lightness colourless state (L^* 83, S_{ab} 4). In view of these favourable characteristics such materials represent a new paradigm in the design of efficient, neutral tint, electrochromic materials for see-through applications. We further envisage that after careful device optimization, final performances could closely match those of benchmark technologies for eyewear applications. The relatively simple and scalable synthetic access to the monomers, as well as the scalability of the polymerization protocol contributes in making our materials an important step forward towards satisfactory switchable eyewear and other electrochromic shading devices.

4 Experimental Section

Chemicals: All chemicals and solvents were purchased from Sigma Aldrich, TCI Europe and Alfa Aesar. They were all used as received and not further purified. $\text{Fe}(\text{OTf})_3$ 40% oxidant solution in 1-butanol (Clevios CB-40) was purchased from Heraeus. Mixture of isomers **1** was prepared as reported in the literature procedure.[36]

Characterization: NMR spectra were recorded with a Bruker AMX 500 Avance operating at 500 MHz for ^1H and ^{13}C and with a Bruker AC 200 operating at 200 MHz for ^1H of compound **6**. Melting points were determined using an OPTIMELT MV160 apparatus and are uncorrected. Electrochemical measures were carried out using a PARSTAT 2273 potentiostat in a single chamber three electrodes electrochemical cell, in a glove box filled with Argon ($[\text{O}_2] \leq 1$ ppm). Glassy Carbon (GC) and gold discs were used as working electrodes. The counter and pseudoreference electrodes were a Pt flag and a Ag/AgCl wire, respectively. Both GC and gold pins were well polished with alumina 0.1 μm suspension, sonicated for 15 min in acetone and washed with 2-propanol before use. The Ag/AgCl pseudoreference electrode was calibrated before and after each measurement using a 1 mM ferrocene solution in the electrolyte; no more than 5 mV difference was observed between two successive calibrations.

Optical absorption spectroscopy was performed using a Jasco V570 spectrophotometer. Spectroelectrochemical measures of solutions were performed using a thin layer quartz cell with 0.5 or 1 mm optical path lengths (Als Co. Ltd; Japan), and using gold mesh, Pt wire and Ag/AgCl as working, counter and reference electrodes respectively.

Electrochemical polymerization of SM1 and SM2: Pulsed deposition technique gave the best results for both SM1 and SM2 electrochemical polymerization. The resting periods between the pulses permit to replenish the diffusion layer, reestablishing the bulk monomer concentration in front of the electrode. When using pulsed deposition, a subtraction of the charging current of the electrochemical double layer has to be performed in order to evaluate the Faradaic current. Depositions were performed directly on PET-ITO starting from a 5×10^{-3} M monomer solution

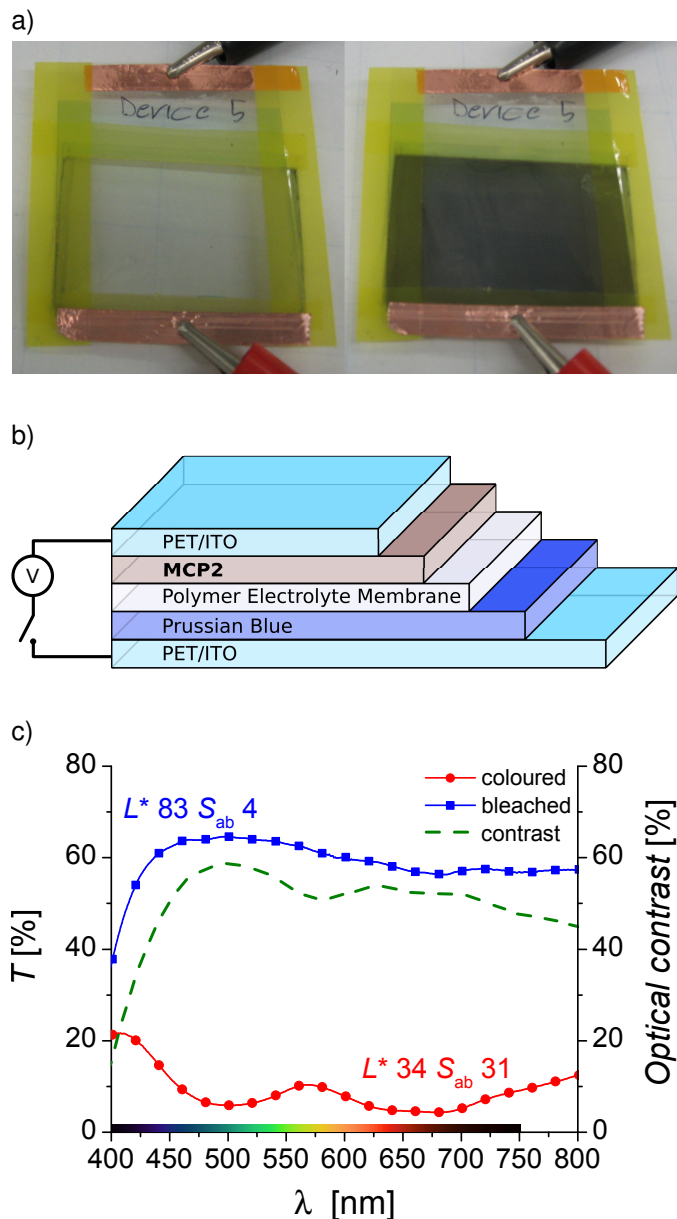


Figure 6 PET/ITO/MCP2/electrolyte/PB/ITO/PET proof-of-concept electrochromic device (ECD). a) ECD in its fully coloured and fully bleached states; b) Scheme of the ECD structure; c) Transmittance spectra of the limiting states (left axis) and corresponding optical contrast (right axis). Lightness (L^*) and saturation (S_{ab}) values are reported for both states.

in 0.1 M Bu₄NClO₄/MeCN. Pulse: 4 s @ 0.75 mA + 5 s @ 0 mA (resting time).

Chemical oxidative polymerization of SM1 and SM2: A solution of the monomer (SM1 or SM2) was prepared adding to 150 mg of the pure compound: propylene carbonate (90 mg), nitromethane (678 mg) and 1-methoxy-2-propanol (1044 mg) in the stated order. An oxidant solution (426 mg) of Fe(OTs)₃ (36%) and PEG-*ran*-PPG (9%) in 1-butanol (prepared from Clevios CB40) was added to the aforementioned one under stirring at room temperature. The mixture was heated at 70 °C in a water bath for 5 min, and then kept at room temperature for 4 h. The obtained green solution was microfiltered through a 0.45 μm PTFE filter and deposited by spin coating on clean substrates (deposition @ 0 rpm + 30 s @ 600 rpm + 10 s @ 1200 rpm). After 5 min at room temperature, the substrates were cured in an oven at 115 °C for 30 min. Once cooled, the polymerized layers were rinsed in EtOH for 2 min and blown dried with compressed air.

Colorimetric data: The colours of literature ECMs along with those developed by us were consistently reported using CIE L* a* b* colour coordinates. In this colour space L* represents the lightness (L* 0 yields black and L* 100 indicates white), while a* (green/magenta oriented coordinate) and b* (blue/yellow oriented coordinate) identify the hue. These values where quantified converting the recorded absorbance spectra using D50 standard illuminant spectral power distribution. In this colour space the perceived colour saturation is expressed by $S_{ab} = 100 * C_{ab} / \sqrt{C_{ab}^2 + L^{*2}}$, where $C_{ab} = \sqrt{a^{*2} + b^{*2}}$. Therefore S_{ab} 0 represents neutral hue (grey) while S_{ab} 100 is pure colour.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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References

- [1] P. M. Monk, R. J. Mortimer, D. R. Rosseinsky. *Electrochromism: fundamentals and applications*. John Wiley & Sons, **2008**.
- [2] G. Sonmez. *Chem. Commun.* **2005**, , 42 5251.
- [3] A. A. Argun, P.-H. Aubert, B. C. Thompson, I. Schwendeman, C. L. Gaupp, J. Hwang, N. J. Pinto, D. B. Tanner, A. G. MacDiarmid, J. R. Reynolds. *Chem. Mater.* **2004**, *16*, 23 4401.
- [4] G. Sonmez, C. K. F. Shen, Y. Rubin, F. Wudl. *Angew. Chem. Int. Ed.* **2004**, *43*, 12 1498.
- [5] A. Argun, A. Cirpan, J. Reynolds. *Adv. Mater.* **2003**, *15*, 16 1338.
- [6] Z. Xie, X. Jin, G. Chen, J. Xu, D. Chen, G. Shen. *Chem. Commun.* **2014**, *50*, 5 608.
- [7] C. Ma, M. Taya, C. Xu. *Polym. Eng. Sci.* **2008**, *48*, 11 2224.
- [8] P. M. Monk, F. Delage, S. M. C. Vieira. *Electrochim. Acta* **2001**, *46*, 13-14 2195.
- [9] D. Corr, U. Bach, D. Fay, M. Kinsella, C. McAtamney, F. O'Reilly, S. Rao, N. Stobie. *Solid State Ionics* **2003**, *165*, 14 315 , fifth International Meeting on Electrochromism.
- [10] J. Jensen, M. V. Madsen, F. C. Krebs. *J. Mater. Chem. C* **2013**, *1* 4826.
- [11] R. H. Bulloch, J. R. Reynolds. *J. Mater. Chem. C* **2016**, *4*, 3 603.
- [12] P. M. Beaujuge, S. Ellinger, J. R. Reynolds. *Nat. Mater.* **2008**, *7*, 10 795.
- [13] P. M. Beaujuge, C. M. Amb, J. R. Reynolds. *Acc. Chem. Res.* **2010**, *43*, 11 1396.
- [14] P. M. Beaujuge, J. R. Reynolds. *Chem. Rev.* **2010**, *110*, 1 268.
- [15] G. Gunbas, L. Toppare. *Chem. Commun.* **2012**, *48*, 8 1083.
- [16] S. Ozdemir, M. Sendur, G. Oktem, zdemir Doğan, L. Toppare. *J. Mater. Chem.* **2012**, *22*, 11 4687.
- [17] P. Shi, C. M. Amb, E. P. Knott, E. J. Thompson, D. Y. Liu, J. Mei, A. L. Dyer, J. R. Reynolds. *Adv. Mater.* **2010**, *22*, 44 4949.
- [18] J. A. Kerszulis, K. E. Johnson, M. Kuepfert, D. Khoshabo, A. L. Dyer, J. R. Reynolds. *J. Mater. Chem. C* **2015**, *3*, 13 3211.
- [19] A. L. Dyer, M. R. Craig, J. E. Babiarez, K. Kiyak, J. R. Reynolds. *Macromolecules* **2010**, *43*, 10 4460.
- [20] A. M. Österholm, D. E. Shen, J. A. Kerszulis, R. H. Bulloch, M. Kuepfert, A. L. Dyer, J. R. Reynolds. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3 1413.
- [21] J. Jensen, M. Hösel, A. L. Dyer, F. C. Krebs. *Adv. Funct. Mater.* **2015**, *25*, 14 2073.
- [22] J. Padilla, T. Otero. *Electrochem. Commun.* **2008**, *10*, 1 1.
- [23] S. A. Sapp, G. A. Sotzing, J. R. Reynolds. *Chem. Mater.* **1998**, *10*, 8 2101.
- [24] P. Chandrasekhar, B. J. Zay, C. Cai, Y. Chai, D. Lawrence. *J. Appl. Polym. Sci.* **2014**, *131*, 22.
- [25] S. V. Vasilyeva, E. Unur, R. M. Walczak, E. P. Donoghue, A. G. Rinzler, J. R. Reynolds. *ACS Appl. Mater. Interfaces* **2009**, *1*, 10 2288.
- [26] E. P. Knott, M. R. Craig, D. Y. Liu, J. E. Babiarez, A. L. Dyer, J. R. Reynolds. *J. Mater. Chem.* **2012**, *22*, 11 4953.
- [27] L. Beverina, G. A. Pagani, M. Sassi. *Chem. Commun.* **2014**, *50*, 41 5413.
- [28] M. Sassi, M. M. Salamone, R. Ruffo, C. M. Mari, G. A. Pagani, L. Beverina. *Adv. Mater.* **2012**, *24*, 15 2004.
- [29] K. Deuchert, S. Hnig. *Angew. Chem. Int. Ed.* **1978**, *17*, 12 875.
- [30] U. Posset, B. Herbig, G. Schottner, K. Zaghbi, J. Labreque, A. Guerfi, M. Perrier, R. Ruffo, M. Salamone, C. Mari, et al. Flexible transparent electrochromic devices and their production. WO2013041562A1, **2013**.

- [31] J. Arias-Pardilla, T. Otero, R. Blanco, J. Segura. *Electrochim. Acta* **2010**, *55*, 5 1535.
- [32] J. Y. Lim, H. C. Ko, H. Lee. *Synth. Met.* **2006**, *156*, 9-10 695.
- [33] J. L. Segura, R. Gómez, R. Blanco, E. Reinold, P. Bäuerle. *Chem. Mater.* **2006**, *18*, 12 2834.
- [34] H. Ko, S. Kim, H. Lee, B. Moon. *Adv. Funct. Mater.* **2005**, *15*, 6 905.
- [35] B. Bröker, R.-P. Blum, L. Beverina, O. T. Hofmann, M. Sassi, R. Ruffo, G. A. Pagani, G. Heimel, A. Vollmer, J. Frisch, J. P. Rabe, E. Zojer, N. Koch. *ChemPhysChem* **2009**, *10*, 17 2947.
- [36] O. Stéphan, P. Schottland, P.-Y. L. Gall, C. Chevrot, C. Mariet, M. Carrier. *Journal of Electroanalytical Chemistry* **1998**, *443*, 2 217.
- [37] B. Groenendaal. 3,4-alkylenedioxythiophene compounds and polymers thereof. EP1321483A1, **2003**.
- [38] S.-C. Luo, E. M. Ali, N. C. Tansil, H. hua Yu, S. Gao, E. A. B. Kantchev, J. Y. Ying. *Langmuir* **2008**, *24*, 15 8071.
- [39] E. M. Ali, E. A. B. Kantchev, H. hua Yu, J. Y. Ying. *Macromolecules* **2007**, *40*, 17 6025.
- [40] B. Neises, W. Steglich. *Angew. Chem. Int. Ed.* **1978**, *17*, 7 522.
- [41] J. Padilla, V. Seshadri, G. Sotzing, T. Otero. *Electrochem. Commun.* **2007**, *9*, 8 1931.
- [42] W. Schuhmann, C. Kranz, H. Wohlschlger, J. Strohmeier. *Biosensors and Bioelectronics* **1997**, *12*, 12 1157.
- [43] R. Ruffo, A. Celik-Cochet, U. Posset, C. M. Mari, G. Schottner. *Solar Energy Materials and Solar Cells* **2008**, *92*, 2 140.