Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary Information†

A Low Coloration Efficiency Dioxypyrrole Polymer as a Counter Electrode Material in Polymeric Electrochromic Window Devices

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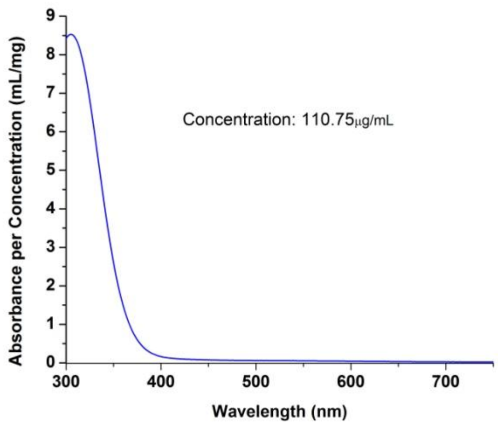

Figure S1. Solution absorbance for MCCP in toluene at a concentration of 110.75µg/mL, demonstrating a λ_{max} at 307nm. Solution absorbance of MCCP reported as normalized to the polymer concentration in solution.

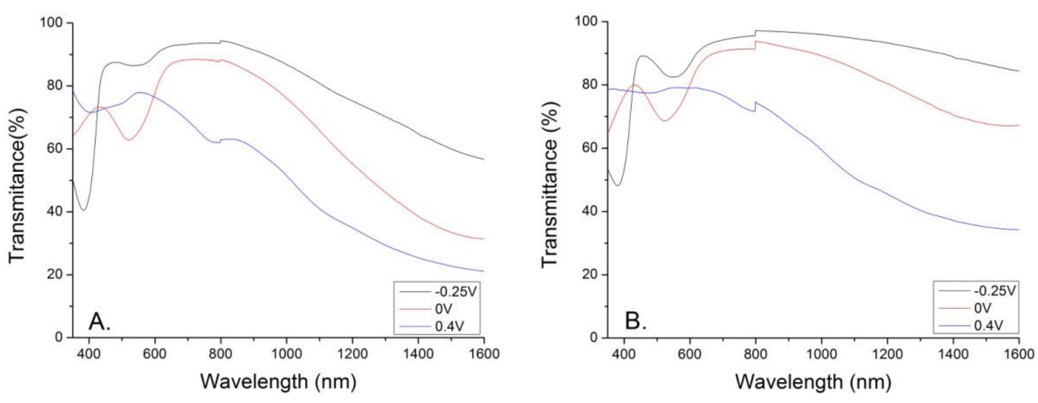

Figure S2. UV/Vis-NIR transmittance spectra for an MCCP film after switching in a cuvette with a platinum wire counter electrode and a Ag/Ag^+ reference electrode for A) 56,000 and B) 300,000 cycles between potentials of -0.25V and 0.4V. For acquisition of the spectra, the polymer film was switched at potentials of -0.25V, 0V, and 0.4V.

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The qualitative values used to calculate the integrated coloration efficiency (ICE) are shown in **Figure S3.** To calculate ICE, the integrated optical density (ΔIOD) was first obtained from the UV/VIS-NIR absorbance spectra of MCCP and ECP-Magenta films of 70 and 378 nm, as seen in **Figures S3A and S3C**, respectively. The green lines illustrate the ΔIOD, which is the absolute value of the difference between the integrated values of the oxidized (red) and reduced (black) curves for either spectrum, within the visible region, designated as 390 to 770nm. The ΔIOD values obtained for MCCP and ECP-Magenta were then divided by the charge accumulated during a 30s reduction of a film of MCCP and the charge accumulated during a 30s oxidation of a film of ECP-Magenta, illustrated in **Figures S3B and S3D**, respectively. Red squares show the corresponding charge value required to switch either film, calculated as the absolute value of the limits of the potential square-wave of the respective film.

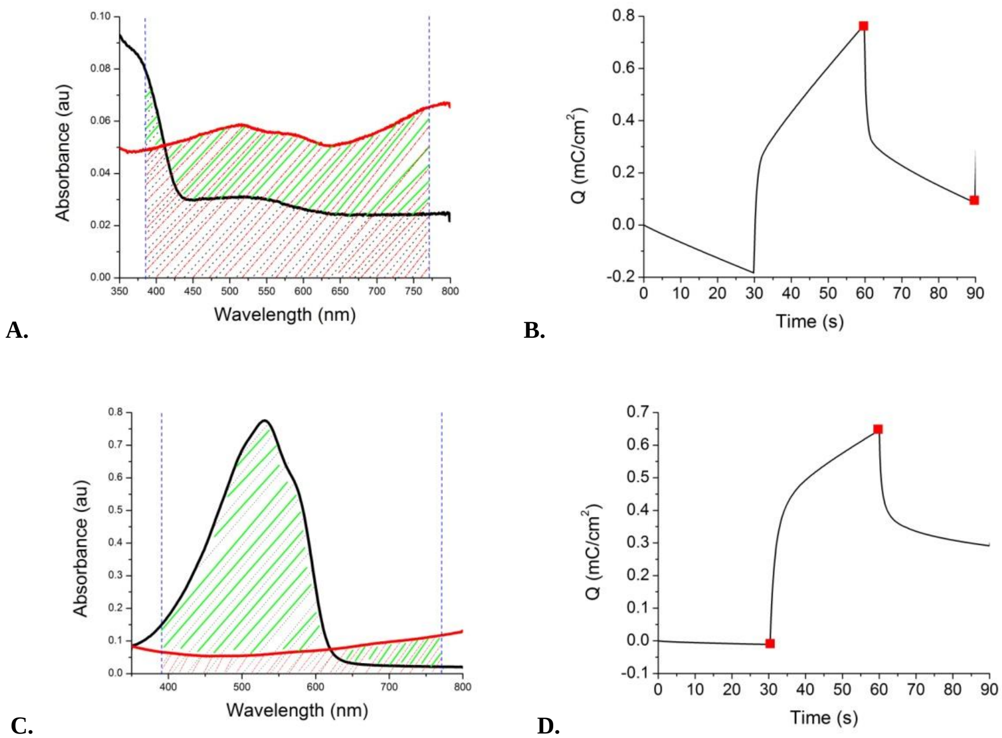

Figure S3. UV/VIS-NIR absorbance spectra for the extreme optical states of polymer films of A) MCCP and C) ECP-Magenta films for the region of 390nm to 770nm, illustrating the ΔIOD (green lines), and the charge accumulated during a 30 second switch of a film of either B) MCCP or D) ECP-Magenta. The films were switched in a cuvette with a platinum wire counter electrode and a Ag/Ag^+ reference electrode.

To probe for the optimum functional conditions of a device utilising MCCP and ECP-Magenta as the counter and working electrodes, respectively, we constructed several devices wherein the electrochromic charge for MCCP is varied while that for ECP-Magenta remained constant. The charge ratio (Q_{Ratio}) was calculated for each potential device according to the formula shown below, where Q is charge to switch of the respective polymer:

$$Q_{Ratio} = \frac{Q_{MCCP}}{Q_{ECP-M}}$$

Twelve devices were constructed and the device optical contrast (Δ%T) and luminance contrast (Δ %Y) were measured for each device. As a control, we additionally constructed a device wherein the counter electrode was comprised of an uncoated ITO electrode, with no MCCP. For each set of devices, overall device performance was analysed according to the following qualities: overall percent transmittance and percent luminance contrast for static measurements **(Table S1)**, and percent transmittance contrast as a function of switching speed **(Table S2)**. **Figure S4** illustrates the relationship between transmittance (black) and luminance (red) contrast with varying values of Q_{Ratio}, between 0.31, 0.57, 1.0, 1.3, and 1.65. The devices were assembled, by spray-casting the polymers onto ITO glass (25 x 75 x 0.7 mm, sheet resistance, R_s 8-12 Ω/sq) with the desired thickness obtained by monitoring the film absorbance at λ_{max} (350nm for the MCCP and 540nm for ECP-Magenta). The device exhibiting the greatest contrast (%T and %Y) was the device that had a Q_{Ratio} of 1. This is not unexpected as we would anticipate a balanced charge to switch between the working and counter electrode to result in the most efficient electrochromic response of the device.

The ECD with an Q_{Ratio} value of 1.0 exhibited a luminance of 29% in the colored state and 75% in the bleached state, with the greatest luminance contrast of 46%. Similarly, this device achieved 61% transmittance contrast, with 12% transmittance in the colored state and reaching 73% transmittance in the bleached state.

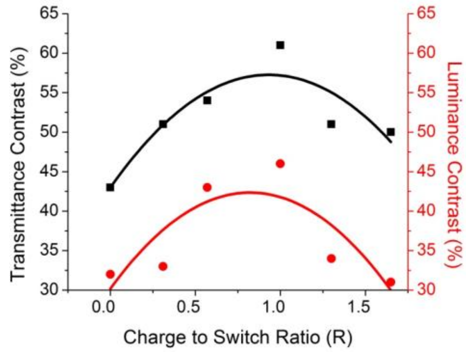

Figure S4. The relationship between charge to switch ratios, Q_R, for MCCP/ECP-Magenta ECDs and the transmittance and luminance contrasts of those devices, indicating the greatest contrasts for a device with a charge to switch ratio of one (Q_{Ratio} = 1).

Table S1. The overall percent transmittance and percent luminance contrast at 540 nm for static measurements of various ECP-Magenta/MCCP devices demonstrating a correlation between device performance and switch ratio, Q_R.

Q_R	Transmittance Contrast at 540 nm (%)	Luminance Contrast (%)
0	43	32
0.31	51	33
0.57	54	43
1.0	61	46
1.3	51	34
1.65	50	32

Table S2. The relationship between transmittance contrast and switch time for various ECP-Magenta/MCCP Devices demonstrating a correlation between device performance and switch ration, Q_R. The transmittance values were for a wavelength of 540 nm.

Switch Interval	Blank Set	Set 1 (Q_R = 0.31)	Set 2 (Q_R = 0.57)	Set 3 (Q_R = 1.0)	Set 4 (Q_R = 1.3)	Set 5 (Q_R = 1.65)
60s	39	39	56	59	54	49
30s	23	34	52	55	50	45
10s	15	19	46	49	43	40
5s	9	12	42	44	40	32
3s	7	8	39	40	38	28
1s	4	5	27	29	26	19