

Supplementary Information

Coloration efficiency of PEDOT-PB and PEDOT-PANI devices

For the PEDOT-PB device, at low potentials of -0.5 V, $\eta_{\max}$ is observed at the fag end of the visible spectrum, at 741 nm (170 cm² C⁻¹) owing to the strong absorption of PEDOT in the $800 - 900$ nm wavelength range, characteristic of the bipolaronic states, seen at this negative potential and also at -0.75 V (Fig. 5d in the manuscript). Although unlike the PEDOT-PANI device (Fig. 5c of the manuscript), wherein the individual chromic contributions of both the electrodes could be identified, here the contribution of PB is not easily fathomable. Only at -0.5 V, the broad peak in the $750 - 1000$ nm range (wherein coloring efficiency does not vary much with wavelength) hints at the contribution of the absorption due to the intervalence charge transfer between Fe^{3+} and Fe^{4+} states of this inorganic complex, which is typically observed in the $750 - 800$ nm wavelength range. For the PEDOT-PB device, coloration efficiency minima ($\eta \rightarrow 0$) are observed in the $730 - 745$ nm range under $E = -1.0, -1.5, -1.75$ and -2.0 V and at 800 and 1050 nm for $E = -1.25$ and -0.75 V. At the lowest applied voltage of -0.5 V, no such CE minimum was observed within the spectral range under consideration. Except for this potential, under all other conditioning potentials, coloration efficiency proceeds to increase beyond the minima to values greater than 100 cm² C⁻¹ ($\lambda = 1100$ nm), thus indicating that the PEDOT-PB device is quite effective in modulating radiation in the NIR region as well.

In the PEDOT-PANI device (Fig. 5c of the manuscript) although the $\eta_{\max}$ at longer wavelengths was observed in the $580 - 590$ nm range under all dc conditionings, but the first $\eta_{\max}$ at 455 nm was confined only to $E = -0.5, -0.75$ and -1.0 V. For all $E >$

−0.5 V, coloration efficiency minima ($\eta \rightarrow 0$) was observed in the 755 – 765 nm range, where as at $E = -0.5$ V the position of $\eta_{\min}$ redshifted to 872 nm. As in case of the PEDOT-PB device, in the PANI-PEDOT device too, coloration efficiency enhanced monotonically after the minima to about $100 \text{ cm}^2 \text{ C}^{-1}$ ($\lambda = 1100 \text{ nm}$) for almost all dc conditionings.

Optical and electrical response at 632.8 nm for PEDOT-PB and PEDOT-PANI devices

The coloring and bleaching times were calculated for PEDOT-PANI and PEDOT-PB devices for a decrease in transmission from 50 to 0 % and an increase in transmission from 0 to 50 %. These were deduced to be 2.0 and 2.5 s respectively for the PEDOT-PANI device and 1.0 and 2.5 s for the PEDOT-PB device (Fig. 1). When both the devices were colored and bleached under ± 2 V (Fig. 2), the PEDOT-PB device colors very deeply, to such an extent, that in the bleaching cycle, it is unable to acquire the fully transparent state (Fig. 2a). In the PEDOT-PANI device, the reverse occurs, the device is highly transparent in the bleached state, but it fails to attain the dark state in the coloration cycle (Fig. 2b). Higher applied potential causes degradation of the devices and this is reflected in the response shown here, the overall modulation is shifted to the lower half of the transmittance versus time plot in the PEDOT-PB device and it gets localized to the upper half of the plot in case of the PEDOT-PANI device. Under this bias, PEDOT-PANI shows 92 % of the modulation shown by the PEDOT-PB device, the modulation of the PEDOT-PB device continues to be larger than that of the PEDOT-PANI device, even at this potential. Coloration time is 15.6 s for a 90 % transmittance

increase for the PEDOT-PANI device and bleaching occurs in 7.8 s for a similar drop in transmittance. Under this conditioning, bleaching is faster than coloring as leakage current is higher during bleaching (0.26 mA) as compared to 0.05 mA during coloration (Fig. 2b'). Considering that under ± 2 V, the devices will not necessarily mimic the response shown at ± 1 V, for permanent ion-trapping and irreversible side reactions occur and these affect the overall response, it is unreasonable to draw inferences on the basis of the experimental observations. Color and bleach times are 2.6 and 10.5 s respectively for the PEDOT-PB device. In this device, however, the leakage currents are comparable in both coloring and bleaching cycles, about 0.65 mA (Fig. 2a'), which validates that detrimental processes do influence color-bleach characteristics and are responsible for the anomalous response observed at these potentials. The cycling life of the PEDOT-PB device was measured under ± 1 V for the PEDOT:PB device (Fig. 3). For a 50 % T change, the response times for the same device were as follows: $t_c, t_b = 1.0$ s (early cycles, Fig. 3a), after 1200 cycles, $t_c = 4.0$ s and $t_b = 2.0$ s (Fig. 3b) and after 2500 cycles, t_c was 2.1 s and t_b was 1.7 s (Fig. 3c).

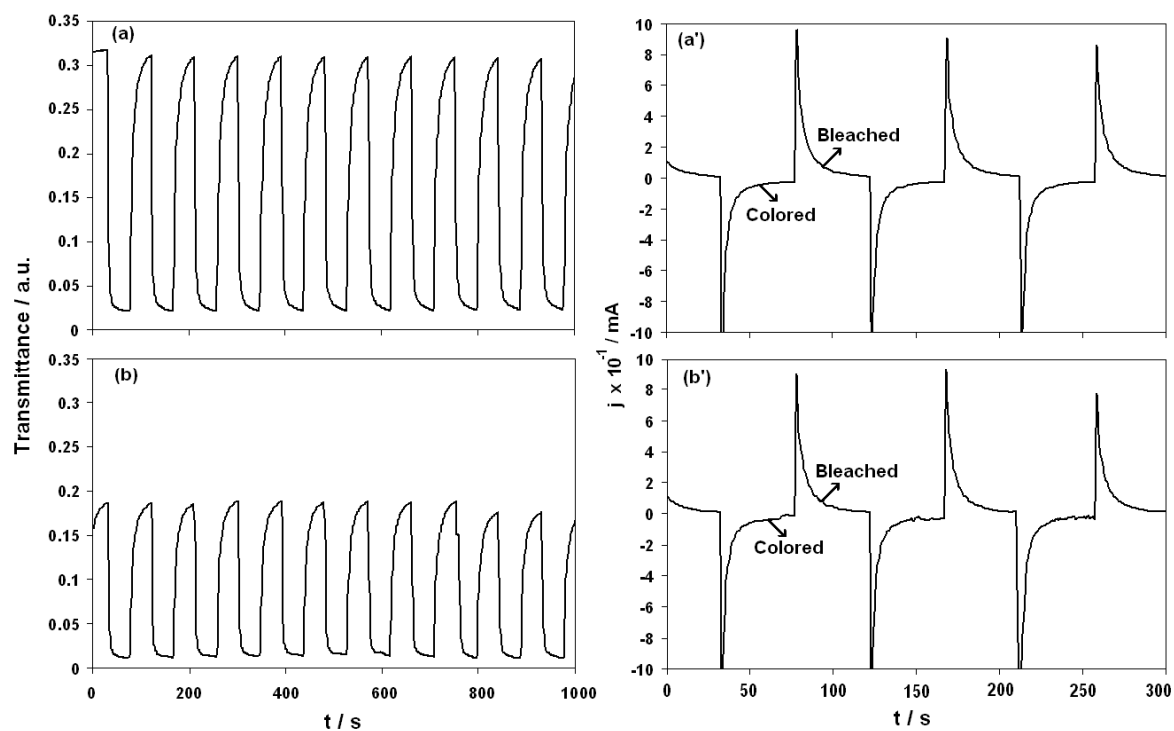


Fig. 1. Transmittance versus time and current versus time transients recorded when the devices were colored for 45 s and bleached for 45 s, on a repetitive basis at a photopic wavelength of 632.8 nm under ± 1 V for the (a,a'): PEDOT-PB device and (b,b'): PEDOT-PANI device.

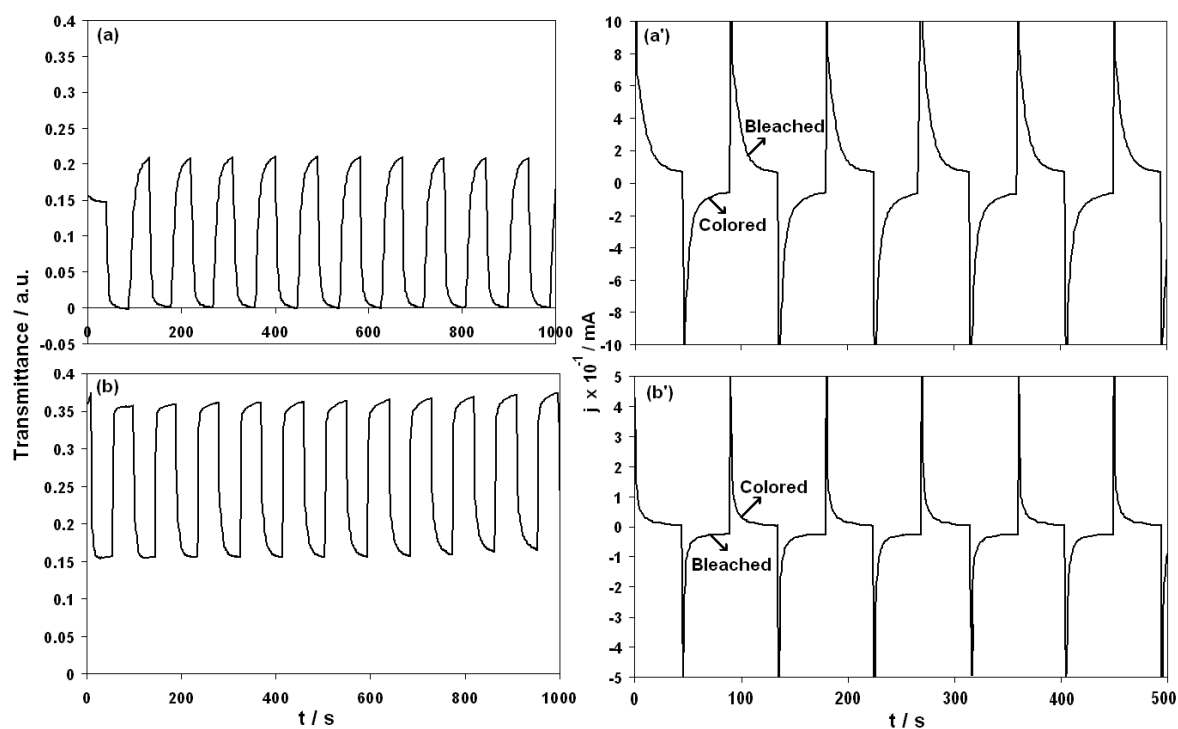


Fig 2. Transmittance versus time and current versus time transients recorded when the devices were colored for 45 s and bleached for 45 s, on a repetitive basis at a photopic wavelength of 632.8 nm under ± 2 V for the (a,a'): PEDOT-PB device and (b,b'): PEDOT-PANI device.

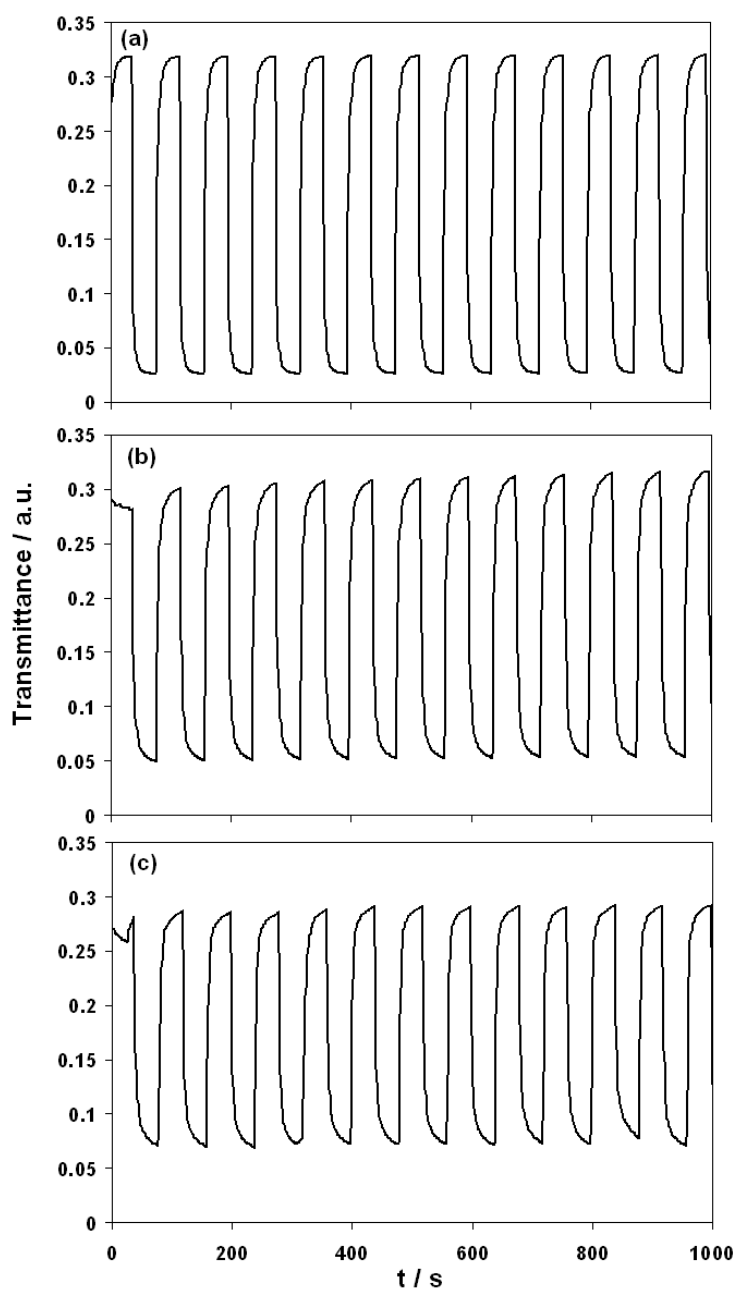


Fig. 3. Transmittance versus time transients recorded when a PEDOT-PB device was subjected to ± 1 V under a step time of 40 s, repeatedly at a photopic wavelength of 632.8 nm: (a) in the initial cycles, (b) after 1200 cycles and (c) after 2500 cycles of clear to dark and dark to clear.