Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for

Neutral Color Tuning of Polymer Electrochromic Devices Using an Organic Dye

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Experimental

Materials

The small molecule organic yellow dye (YG) was a sample received from Lanxess, Inc. (Macrolex Yellow G, C.I. Solvent Yellow 114 CAS # 17772-51-9); its molecular weight is 289.28 g/mol. 3,4-ethylenedioxythiophene (EDOT) was purchased from Heraeus Clevios GmbH and was distilled under vacuum prior to use. Lithium trifluoromethane sulfonate (LiTRIF), propylene carbonate (PC), poly (ethylene glycol) methyl ether acrylate (M_n = 480 g/mol) (PEG-MA) and dimethoxyphenylacetophenone (DMPAP) were purchased from Sigma-Aldrich and used as received. Indium Tin Oxide (ITO) coated glasses (sheet resistance 8-12 Ohm/sq) were purchased from Delta Technologies and cleaned by acetone, isopropanol and methanol prior to use. ITO coated polyethylene terephthalate (PET) substrates were purchased from Bayview Optics and were cleaned by acetone prior to use. Copper tape was purchased from Newark and UV-sealant glue was purchased from Norland Optics.

Gel polymer electrolyte

1 g of LiTRIF, 3 g of PC, 7 g of PEG-MA and 17.5 mg of DMPAP were added together and sonicated for 10 minutes until fully dissolved. Monomer liquid gel electrolyte was prepared by dissolving a 2.5 wt% ratio of EDOT monomers into the gel electrolyte.

Molar absorptivity of small organic yellow dye

Molar absorptivity of YG was determined by monitoring the absorbance at 442 nm as a function of YG concentration in PC, solvent for the gel electrolyte. Results are shown below in **Fig. S1**. The molar absorptivity is determined to be 27,231 $M^{-1} \cdot cm^{-1}$ under this wavelength.

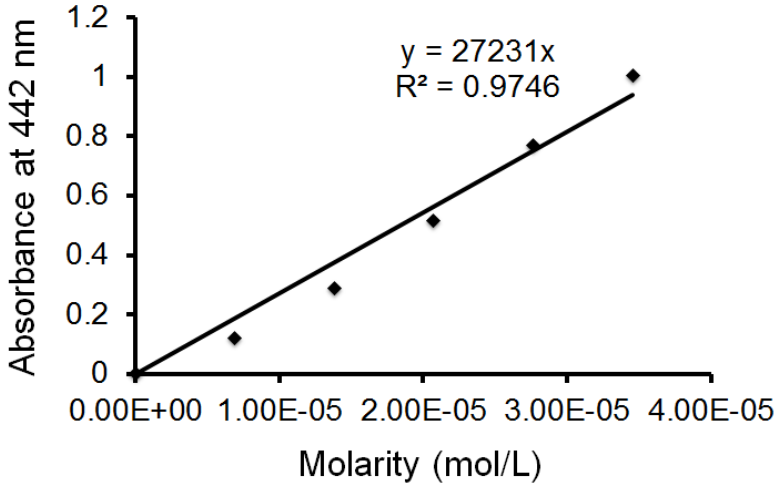

Fig. S1. Absorbance of YG at 442 nm as a function of YG molarity.

To prepare the YG-incorporated gel electrolyte, a YG stock solution was first prepared by dissolving 5 mg of YG into 5 g of PC. 205 mg of YG stock solution was then added into 10 g of the monomer gel electrolyte mentioned above. Number of moles of YG loaded was calculated to be 7.08×10^{-6} mol. Volume of the gel electrolyte was determined to be 8.5 mL. Thickness of gel layer was 0.8 mm.

Therefore, the concentration of the YG = $\frac{number\ of\ moles\ of\ YG}{Volume}$ = 8.34×10^{-5} M.

According to the Beer-Lambert law, the absorbance of YG at 442 nm wavelength inside an assembled device = ε × b× c = 0.182.

For further confirmation, absorbance at 442 nm of EDOT device (Abs = 0.467) shown in **Fig. 1** was subtracted from that of EDOT + YG device (Abs = 0.279), giving the background corrected absorbance of YG. This absorbance is calculated to be 0.188, which agrees well with the calculated value.

Electrochromic device assembly

For small area device fabrication, ITO coated PET (2 cm × 5 cm) was used as both working electrode and counter electrodes. The perimeter of one ITO/PET piece was covered with a rubber gasket (0.8 mm) to form the device active area (1.5 × 4.5 cm^2). The liquid monomer gel electrolyte (or YG-incorporated gel electrolyte) was then drop cast onto this active area and another ITO/PET piece was placed atop. The device was placed inside an UV crosslinker (UVP CL-1000, 5.8 mW/cm^2) to cure the gel electrolyte under 365 nm UV light for 20 min and sealed with UV curable glue. Under a constant potential of +3 V, the device was activated for 30 seconds time to achieve its optimal performance.

For large area device fabrication, a preassembled device frame sealed with epoxy adhesive was first built using 7.6 cm × 20 cm ITO coated glass for both substrates. The YG-incorporated gel electrolyte was then injected into the device frame and followed by UV curing and an activation process as stated above.

All activated devices were switched between ±2 V (pulse width = 2 s) for five cycles to switch the electrochromic polymer between its oxidized and neutral states before optical characterization.

Electrochemistry

Electrochemical conversions and spectroelectrochemistry were carried out with a CHI 700 potentiostat.

Optical Characterization

Optical properties of assembled devices were measured with a Varian Cary 5000 UV-Vis-NIR spectrophotometer and corresponding built-in Color software. Colorimetric data were collected using a 10 degree standard observer angle in measurement range of 360-860 nm at 1 nm intervals based on a D65 standard illuminant.

Switching Speed

In situ PEDOT devices and *in situ* PEDOT + YG devices were switched between −2 V and +2 V and percentage transmittance (%T) value at 555 nm, where human eye has the highest sensitivity, was recorded as a function of time during redox switch process (**Fig. S2**). Switching speeds of the devices here were defined as the time required to achieve 95% of a full color change under the wavelength. Results are summarized in **Table S1**.

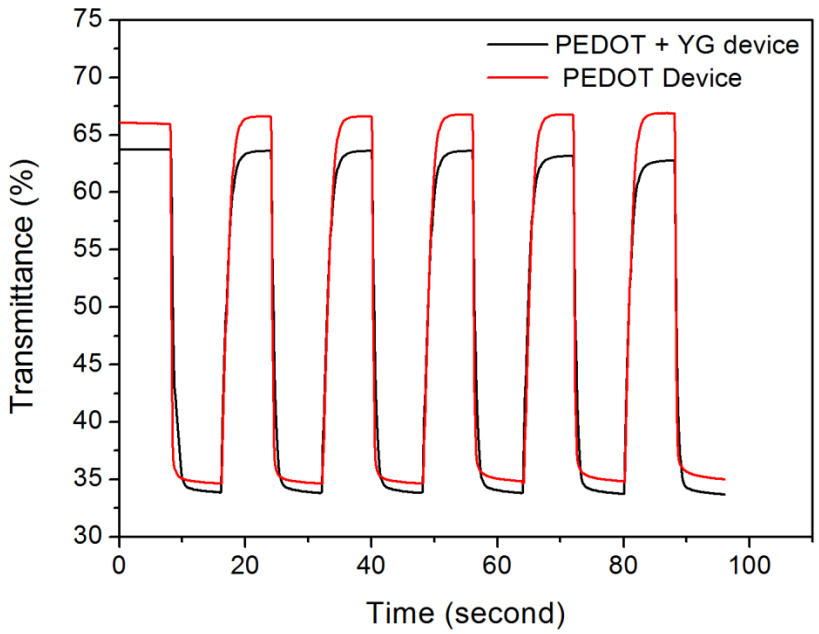

Fig. S2. Percent transmittance change at 555 nm for *in situ* PEDOT device and *in situ* PEDOT + YG device during constant potential stepping between -2 V to +2 V at an 8 s pulse width 320 time exhibiting 89 % charge retention.

Table 2. Redox switching speeds for *in situ* PEDOT device and *in situ* PEDOT + YG device

Device	Color state photopic transmittance	Bleach state photopic transmittance	Coloring Time (s)	Bleaching Time (s)
PEDOT	34.5%	66.5%	1	2.5
PEDOT + YG	33.5%	63.5%	1.5	2.7

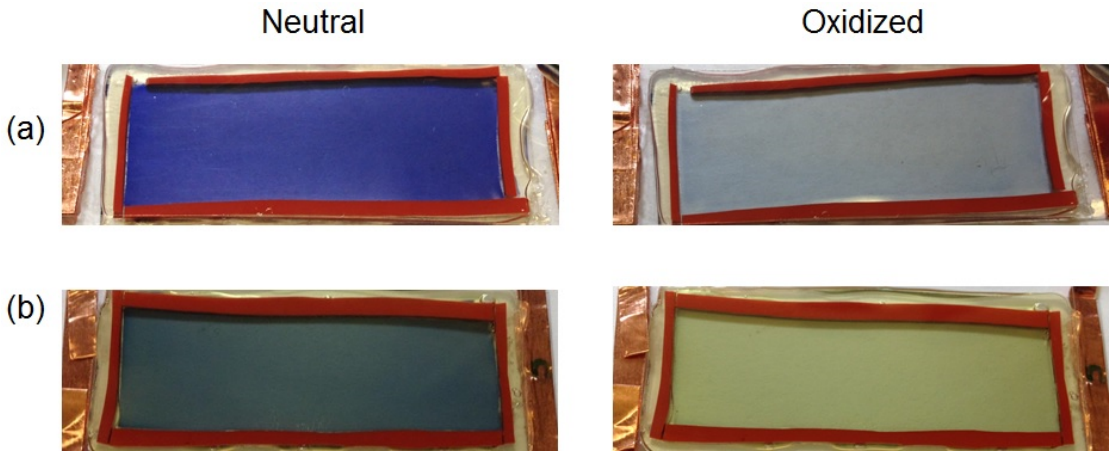

Fig. S3. Images of Neutral and Oxidized states for small area (1.5 × 4.5 cm^2) devices: (a) *in situ* PEDOT device and (b) *in situ* PEDOT + YG device