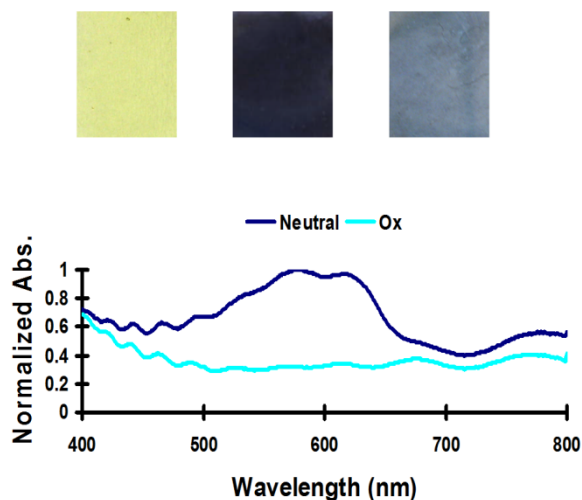


## SUPPORTING INFORMATION

### Device with ionic liquid electrolyte

Ionic liquid was used instead of propylene carbonate and lithium trifluoromethanesulfonate salt, poly(ethylene glycol) diacrylate, 2,2-dimethoxy-2-phenylacetophenone (DMPAP) and monomer remained the same in the electrolyte. Conversion and switching time are *ca.* 100 s and 3 s, respectively.



**Figure S.1** (Top from left) devices fabricated by using monomer gel made from ionic liquid BMIMPF<sub>6</sub> before conversion, in neutral state and oxidized state. (Bottom) Normalized UV-Vis spectrum of the devices in neutral (dark blue) and oxidized (light blue) states.

### Conversion yield inside the assemble ECD devices

According to Diaz's mechanism of the polymerization of conducting polymers, the amount of electrons transferred during the reaction is twice of that of the monomer

reacted. The charge consumed in the polymerization process is 0.125C, therefore, number of moles of electrons can be calculated:

$$\# \text{ of } e^- = 0.125C / (1.6e-19 * 6.02e23)$$

$$\# \text{ of monomers reacted} = \frac{1}{2} * \# \text{ of } e^-$$

$$\text{Conversion}\% = \# \text{ of monomers reacted} / 18\text{mg} * 100\% = 0.5\%$$

$$\text{Film thickness} = (\# \text{ of monomers reacted} * 142\text{g/mol} * 1\text{g/cm}^3) / (3.5\text{cm} * 4\text{cm}) = 65\text{nm}$$

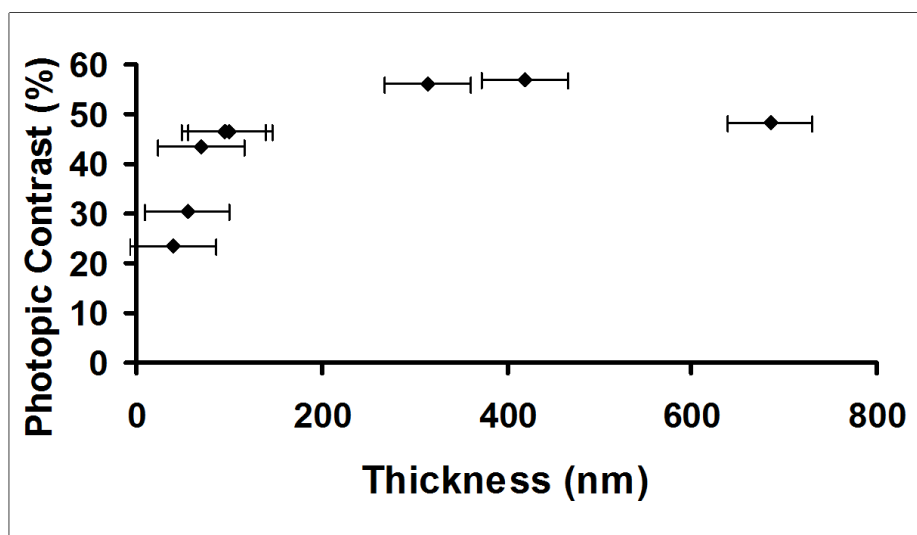
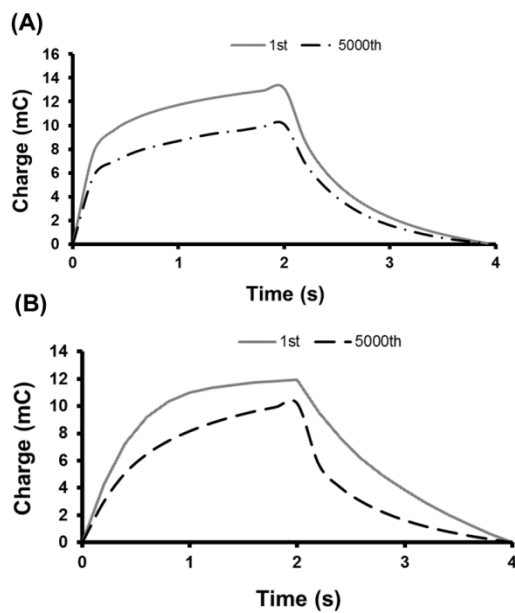


Figure S.2. Relation between photopic contrast and film thickness. <sup>1</sup>

Fig. S.2 showed the relation between photopic contrast and the thickness of PEDOT film, a device with photopic contrast of 45% was estimated to have an over 70nm thick film based on this plot. This further illustrated our hypothesis of the loosely packed chain inside the gel matrix compared to free standing films.

Stability of *in situ* devices and *ex situ* devices



**Figure S.3.** 1<sup>st</sup> and 5000<sup>th</sup> chronocoulometry switch cycles of (A) *ex situ* and (B) *in situ* device.

1. Invernale, M. A.; Seshadri, V.; Mamangun, D. M. D.; Ding, Y.; Filloramo, J.; Sotzing, G. A., *Chemistry of Materials* 2009, **21**, 3332-3336.