Electronic Supplementary Information (ESI)
for

First truly all-solid state organic electrochromic device based on polymeric ionic liquid

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1. Materials

Poly(ethylene glycol) dimethacrylate (PEGDM, M_n = 750 g/mol, Aldrich), 4-methoxyphenol (99%, Acros), phosphorus pentoxide (98%, Alfa Aesar), ethanol (HPLC grade, Carlo Erba), N,N-dimethylformamide (DMF, anhydrous 99,8%, Acros), 2-[2-(chloroethoxy)-ethoxy]ethanol (98+%, TCI Europe), lithium chloride (99+%, Acros) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, 99+%, Solvionic) were used without further purification. Metacryloyl chloride (Fluka, 98%) was distilled over linseed oil, while N-methylimidazole (99%, Acros) was distilled under inert gas over CaH_2. Dichloromethane, acetonitrile, ethyl acetate and diethyl ether were distilled over P_2O_5. 2,2'-Azobisisobutyronitrile (AIBN, 98%, Acros) was recrystallized from methanol. 3,4-Ethylenedioxythiophene (EDOT, Bayer) was distilled under vacuum. ITO-coated glass slides (14×50 mm, sheet resistance 30 $\Omega\cdot cm^{-2}$) were purchased from Solems S.A. and treated prior to use by sonication in acetonitrile.

2. Characterization

NMR spectra were obtained on Bruker AMX-400 spectrometer at 25°C in the indicated deuterated solvent and are listed in ppm. The signal corresponding to the residual protons of the deuterated solvent was used as an internal standard (^1H, ^{13}C relative to tetramethylsilane) and $CHCl_2F$ was used as an internal standard for ^{19}F NMR. A Nicolet Magna-750 Fourier IR-spectrometer was used to record IR spectra at a resolution of 2 cm^{-1} and with the scan number equal to 128 (KBr pellets).

Intrinsic viscosity [η] of bis(trifluoromethylsulfonyl)imide polymeric ionic liquid (PIL) was measured in an Ubbelohde type capillary viscometer at 25.0°C using 0.5M $Li(CF_3SO_2)_2N$ solution in DMF. The molecular weights (M_n, M_w) and polydispersity index (M_w/M_n) of the same PIL transformed to the water soluble chloride form were determined at 30°C on a LC-20AD gel permeation chromatograph (GPC, Shimadzu Corporation, Japan) equipped with a Tosoh TSK-GEL G6000 PW_{XL}-CP column and a refractive index detector. 0.5M $NaNO_3$ aq. solution was used as an eluent with a flow rate of 0.5 mL/min. The calibration was performed with pullulan standards (Shodex P-82).

The study of ionic liquid like monomer by differential scanning calorimetry was performed on a Q100 isothermal differential calorimeter (TA Instruments, USA) at a heating rate of 2.0°C/min in the range of -90 ÷ +100°C. Glass transition temperature (T_g) of PIL was determined by thermomechanical analysis (TMA) using Q400 (TA Instruments, USA) thermomechanical analyzer at a heating rate of 5°C/min and a constant load of 0.08 MPa. Thermogravimetric analysis (TGA) was performed in air on a Q50 model (TA Instruments, USA) applying a heating rate of 5°C/min.

Dielectric spectroscopy studies of PIL were run on a Novocontrol Broadband Dielectric Spectrometer equipped with an Alpha analyzer and a Quatro temperature controller (Novocontrol GmbH, Germany). Thin polymer films (0.15-0.20 mm) were cast directly on the gold-coated brass electrodes from acetonitrile solutions, dried at 80°C/1 mm Hg in a vacuum oven for 4 h, whereupon two electrodes were pressed together and put into the measuring cell. The experiments were carried out at 25°C in the10^{-1}-10^{7} Hz frequency range in air. Conductivities were duplicated by complex impedance analysis using impedance analyzer VSP (Bio-Logic Science Instruments, France). PIL was pressed into a thin film (0.2 mm) between stainless steel electrodes and was put in a cell with pressure contact. The runs were performed in inert atmosphere, varying the frequency from 10^{-2} to10^{8} Hz at 25°C.

All electrochemical studies were performed using a VMP-PA potentiostat/galvanostat (Bio-Logic Science Instruments, France). Electrochemical characterizations of PEDOT thin films on ITO glass were carried out in 0.1M $Li(CF_3SO_2)_2N/CH_3CN$ by cyclic voltammetry in the range of -0.7 ÷ +1.0 V at 50 $mV \cdot s^{-1}$ (Fig. 1). Conventional three-electrode scheme consisted of ITO glass, silver wire and stainless steel lattice as working, reference and counter electrodes, respectively.

Optical characterization of the electrochromic devices (ECDs) was carried out using JASCO 570 UV-VIS-NIR spectrophotometer.

3. Ionic monomer synthesis

1-[2-(2-(2-hydroxyethoxy)ethoxy)ethyl]-3-methylimidazolium chloride

The solution of 2-[2-(chloroethoxy)-ethoxy]ethanol (23.7 g, 0.140 mol) in 60 mL of anhydrous methanol was added dropwise under inert atmosphere at 0-1 °C to the solution of freshly distilled N-methylimidazole (10.0 g, 0.122 mol) in 25 mL of methanol. The reaction mixture was stirred for 1 h at 0-1°C, 12 h at 20°C, 24 h at 40 °C and, finally, 30 h at 55°C. The solvent was removed under reduced pressure at 50 °C and the residual viscous oil was extracted with anhydrous diethyl ether (3×50 mL) under vigorous stirring. The product was dried at 50°C/1 mm Hg for 6 h (hereinafter with a special flask filled with P_2O_5 and introduced into the vacuum line). The resultant hydroxyl-functionalized ionic liquid was obtained as slightly yellow viscous oil. Yield: 24.5 g (80%); ^{1}H NMR (400 MHz, D_2O): δ = 8.94 (s, 1H, H2 (Im)), 7.69 (t, 1H, H4 (Im), J_{HH} = 1,6 Hz), 7.62 (t, 1H, H5 (Im), J_{HH} = 1,6 Hz), 4.53 (m, 2H, CH_2N), 4.03 (s, 3H,NCH_3), 4.01 (m, 2H, HO-$CH_2C\underline{H}_2$), 3.81-3.76 (br. m, 6H, HO-$C\underline{H}_2CH_2$-O-$C\underline{H}_2C\underline{H}_2$), 3.68 (m, 2H, $C\underline{H}_2CH_2N$); ^{13}C NMR (100 MHz, D_2O): δ = 136.5 (C2 (Im)), 123.6 (C4 (Im)), 122.8 (C5 (Im)), 71.9, 69.8, 69.5, 68.5, 60.5, 49.2, 36.0 ($\underline{C}H_3$-N); IR (KBr pellet): 3405 (br. vs, ν_{OH}), 2920 (m, $\nu_{C\text{-}H}$), 2874 (m, $\nu_{C\text{-}H}$), 2503 (w), 2331 (w), 2126 (w), 1645 (m), 1565 (s), 1554 (m), 1450 (m), 1420 (w), 1353 (m, δ_{OH}), 1298 (w), 1253 (m), 1203 (w), 1177 (vs), 1116 (vs, $\nu_{\text{-}C\text{-}O\text{-}C\text{-}}$), 1065 (vs), 933 (m), 927 (m), 832 (w), 769 (w), 643 (w), 615 (w) cm^{-1}.

1-[2-(2-(2-(Methacryloyloxy)ethoxy)ethoxy)ethyl]-3-methylimidazolium chloride

Freshly distilled methacryloyl chloride (6.25 g, 0.059 mol) was dissolved in 10 mL of anhydrous acetonitrile, placed in a round bottom flask and cooled in an ice bath under inert atmosphere to 0-1°C. The solution of 1-[2-(2-(2-hydroxyethoxy)ethoxy)ethyl]-3-methylimidazolium chloride (10.0 g, 0.039 mol) in 20 mL of acetonitrile was slowly added dropwise to the cooled methacryloyl chloride solution with gentle stirring. The stirring was then continued at 0-1°C for 1.5 h, whereupon the ice bath was removed and the reaction mixture was allowed to warm up to room temperature. The reaction proceeded at 20°C for 5 h and finally at 40°C for 12 h. The obtained oil was thoroughly washed with diethyl ether (5x15 mL) in order to remove the excess of methacryloyl chloride. After evaporation of residual ether, the reaction mixture was redissolved in dichloromethane and twice precipitated in ethyl acetate. Catalytic amount of 4-methoxyphenol as an inhibitor was added and the product as light brown oil was dried at 25°C/14 mm Hg for 2 h and additionally at 25°C/1-2 mm for 2 h. Yield: 11.5 g (90%); ^{1}H NMR (400 MHz, D_2O): δ = 8.58 (s, 1H, H2 (Im)), 7.34 (m, 1H, H4 (Im)), 7.27 (m, 1H, H5 (Im)), 5.90 (s, 1H, $C\underline{H_2}$=C *Z*), 5.51 (m, 1H, $C\underline{H_2}$=C *E*), 4.20 (m, 2H, $C\underline{H_2}N$), 4.09 (m, 2H, CO-O-$C\underline{H_2}$), 3.72-3.69 (m, 2H+3H, CO-O-$CH_2C\underline{H_2}$+$NC\underline{H_3}$), 3.59 (m, 2H, CO-O-CH_2CH_2-O-$C\underline{H_2}$), 3.51-3.48 (br. m, 4H, $C\underline{H_2}$-O-$C\underline{H_2}CH_2$-N), 1.69 (s, 3H, $C\underline{H_3}$–C=); ^{13}C NMR (100 MHz, D_2O): δ = 169.2 ($\underline{C}$=O), 136.3 (C2 (Im)), 136.2 (CH_2=$\underline{C}(CH_3)$), 126.9 ($\underline{C}H_2$=$C(CH_3)$), 123.4 (C4 (Im)), 122.5 (C5 (Im)), 69.5, 68.4, 68.3, 64.1, 48.9, 35.8 ($\underline{C}H_3$-N), 17.4 (CH_2=$C(\underline{C}H_3)$); IR (KBr pellet): 3146 (m, $\nu_{C\text{-}H}$), 3093 (m, $\nu_{C\text{-}H}$), 2955 (s, $\nu_{C\text{-}H}$), 2918 (s, $\nu_{C\text{-}H}$), 2873 (s, $\nu_{C\text{-}H}$), 1716 (vs, ν_{CO}), 1634 (m, $\nu_{C=C}$), 1574 (s), 1454 (s), 1410 (w), 1388 (w), 1350 (w), 1319 (m), 1297 (s), 1252 (w), 1171 (vs), 1123 (vs, $\nu_{\text{-}C\text{-}O\text{-}C\text{-}}$), 1040 (m), 943 (m), 855 (w), 817 (m), 760 (w), 653 (m), 622 (m) cm^{-1}.

1-[2-(2-(2-(Methacryloyloxy)ethoxy)ethoxy)ethyl]-3-methylimidazolium bis(trifluorome-thylsulfonyl)imide

Lithium bis(trifluorome-thylsulfonyl)imide (9.04 g, 0.031 mol) was dissolved in 10 mL of distilled water and added dropwise to the solution of 1-[2-(2-(2-(methacryloyloxy)ethoxy)ethoxy)ethyl]-3-methylimidazolium chloride (9.09 g, 0.029 mol) in 15 mL of H_2O at ambient temperature. The mixture was stirred 2 h at 25°C and the precipitation of oil was observed. The upper aqueous layer was decanted and the residual oil was redissolved in 90 mL of dichloromethane. The CH_2Cl_2 solution was washed with water (3 × 30 mL) and dried over anhydrous $MgSO_4$. The magnesium sulfate was filtered off and dichloromethane was stripped off under the reduced pressure at temperature ≤30^{o}C. The product was obtained as slightly brown transparent fluid oil, which was finally dried at 30^{o}C/1 mm Hg for 2 h. Yield: 13.7 g (85%); Found: C, 33.56%; H, 4.13%; N, 7.28%; F, 20.10%; Calc. for $C_{16}H_{23}F_6N_3O_8S_2$ (563.49): C, 34.10%; H, 4.11%; N, 7.46%; F, 20.23%; T_g = -67.2°C (DSC); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 1H, H2 (Im)), 7.37 (m, 1H, H4 (Im)), 7.23 (m, 1H, H5 (Im)), 5.97 (s, 1H, $C\underline{H}_2$=C *Z*), 5.48 (m, 1H, $C\underline{H}_2$=C *E*), 4.22 (m, 2H, $C\underline{H}_2N$), 4.16 (m, 2H, CO-O-$C\underline{H}_2$), 3.81 (m, 3H, $NC\underline{H}_3$), 3.71 (m, 2H, CO-O-$CH_2C\underline{H}_2$), 3.62 (m, 2H, CO-O-CH_2CH_2-O-$C\underline{H}_2$), 3.54-3.52 (br. m, 4H, $C\underline{H}_2$-O-$C\underline{H}_2CH_2$-N), 1.81 (s, 3H, $C\underline{H}_3$–C=); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0 ($\underline{C}$=O), 135.8 (C2 (Im)), 135.7 (CH_2=$\underline{C}(CH_3)$), 125.5 ($\underline{C}H_2$=$C(CH_3)$), 122.9 (C4 and C5 (Im)), 124.2-114.6 (q, $^1J_{CF}$ = 321 Hz), 69.8, 69.7, 68.6, 68.1, 63.3, 49.3, 35.7 ($\underline{C}H_3$-N), 17.7 (CH_2=$C(\underline{C}H_3)$); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = -79.3 (s, CF_3); IR (KBr pellet): 3158 (m, $\nu_{C\text{-}H}$), 3121 (m, $\nu_{C\text{-}H}$), 2960 (m, $\nu_{C\text{-}H}$), 2921 (m, $\nu_{C\text{-}H}$), 2879 (m, $\nu_{C\text{-}H}$), 1716 (vs, ν_{CO}), 1636 (m, $\nu_{C=C}$), 1573 (m), 1455 (m), 1354 (vs, ν_{asSO2}), 1299 (vs), 1195 (vs, ν_{CF}), 1138 (s, ν_{sSO2}), 1058 (vs, ν_{CF}), 945 (w), 852 (w), 789 (m), 741 (m), 653 (m), 618 (s), 571 (s), 513 (m) cm^{-1}.

4. Polymerization procedure

Radical polymerization of ionic monomer

1-[2-(2-(2-(Methacryloyloxy)ethoxy)ethoxy)ethyl]-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (2.00 g, 3.55 mmol), DMF (2.00 g) and AIBN (0.02 g, 1.0 wt.%) were gently mixed in a flask at ambient temperature. The solution was transferred into a glass ampoule. After triple freeze-thaw-pump cycles the ampoule was sealed under vacuum and heated to 60^{o}C for 6 h. The resulting transparent highly viscous polymer solution was slightly diluted with DMF and precipitated into dichloromethane. PIL was then thoroughly washed with dichloromethane and dried at 70^{o}C/1 mm Hg for 48 h. Yield: 1.20 g (60%); $[\eta]_{0.5M\ Li(CF3SO2)2N\ in\ DMF}$ = 0.46 dL·g^{-1} (25.0^{o}C); σ_{DC} = 1×10^{-5} S·cm^{-1} (25^{o}C); T_g = -17.5^{o}C; onset loss temperature T_d = 290^{o}C; IR (thin film): 3153 (m, $\nu_{C\text{-}H}$), 3109 (m, $\nu_{C\text{-}H}$), 2960 (m, $\nu_{C\text{-}H}$), 2878 (m, $\nu_{C\text{-}H}$), 1725 (s, ν_{CO}), 1574 (m), 1477 (w), 1353 (vs, ν_{asSO2}), 1324 (s), 1226 (s), 1198 (vs, ν_{CF}), 1140 (s, ν_{sSO2}), 1063 (s, ν_{CF}), 946 (w), 858 (w), 792 (m), 762 (w), 738 (m), 654 (m), 621 (s), 571 (s), 515 (m) cm^{-1}.

Polymer ion exchange

The solution of anhydrous lithium chloride (0.15 g, 3.56 mmol) in 15 mL of anhydrous DMF was added dropwise under inert atmosphere to the solution of PIL with bis(trifluoromethylsulfonyl)imide anion (1.00 g, 1.78 mmol) in 20 mL of anhydrous DMF. The precipitation of the respective chloride PIL was observed, whereupon it was collected by filtration, washed with DMF and purified by dialysis (Spectra/Por dialysis membrane, molecular weight cut off 6000÷8000) firstly in 0.5M aq. NaCl and decisively in deionized water. The final polymer solution was freeze-dried and chloride PIL was studied by GPC in 0.5M $NaNO_3$ aq. solution. $M_w = 3.8\times10^5$, $M_w/M_n = 4.4$.

Electropolymerization of 3,4-ethylenedioxythiophene (EDOT)

Electrochemical polymerization of EDOT was conducted in a one-compartment, three-electrode cell, containing 0.05M EDOT and 0.1M $Li(CF_3SO_2)_2N$ in anhydrous acetonitrile. A stainless steel lattice and silver wire were used as counter and reference electrodes, respectively. The working electrode was ITO glass of around 3.3 cm^2 area. All experiments were carried out under inert atmosphere at room temperature. After polymerization the ITO-coated glass substrates covered with PEDOT were removed from the electrolyte solution, rinsed with plenty of acetone and dried at 80°C/1 mm Hg for 2 h.

5. Device Assembly

For the manufacture of ECD the thin films (<0.5 μm) from 5 wt.% bis(trifluoromethylsulfonyl)imide PIL's solution in anhydrous CH_3CN were cast directly on the PEDOT electrodes deposited on ITO glasses (Fig. 2). After total removal of the solvent (80°C/1 mm Hg for 2 h) the two glasses were so clamped together that the films were contained between the glass and the following symmetrically layered ECD was obtained: ITO glass/PEDOT/PIL/PEDOT/ITO glass.

6. Coloration efficiency

The coloration efficiency $CE(\lambda)$ is related to the variation of the optical absorbance ΔAbs during a commutation step associated to a variation of charge[1].

$$CE(\lambda) = \Delta Abs \,/\, \mathrm{d}Q$$

As human eye is accurate only for 80-90% of optical variation, $CE(\lambda)$ is usually given in literature at 80 or 90% of ΔAbs. For organic ECDs the value of $CE(\lambda)$ sometimes is calculated at 95% of ΔAbs [2].

In our experiment, both dependences Abs = f(*time*) and Q = f(*time*) were combined in one figure (Fig. 4). ΔAbs was determined at 620 nm, while ΔQ was subsequently measured during the commutation step (at 90% of step commutation). Finally, $CE(\lambda)$ was calculated as

$$CE(\lambda) = \frac{\log\left(\frac{t_{90\%}}{t}\right) \cdot S}{\Delta Q}$$

, where S (cm^2) is the active surface area.

7. Figures

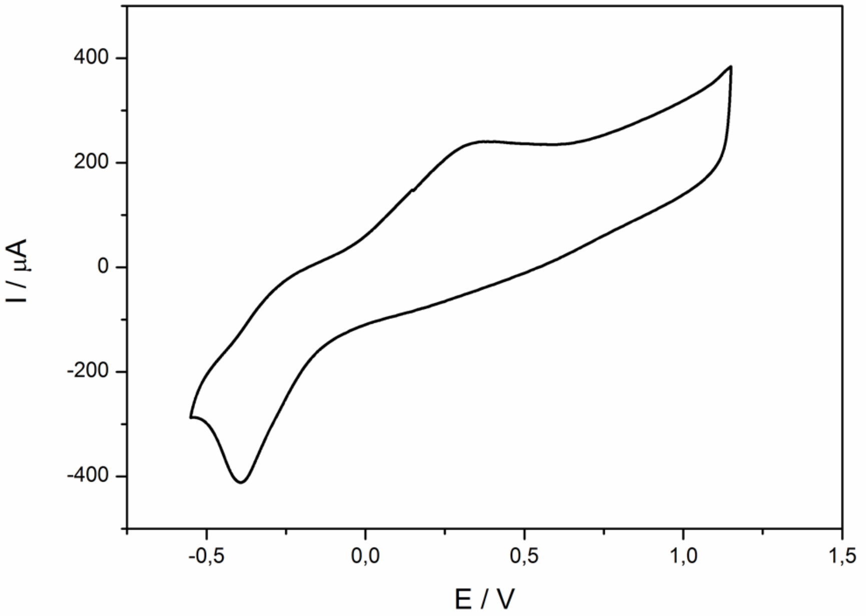

Fig. 1. Cyclic voltammogram at 25ºC of PEDOT electrode in 0.1M $Li(CF_3SO_2)_2N/CH_3CN$ using ITO glass, silver wire and stainless steel lattice as working, reference and counter electrodes, respectively; scan rate, 50 $mV{\cdot}s^{-1}$; the potential (V) was referenced to the ferrocene (Fc)/ferricinium (Fc^+) redox couple.

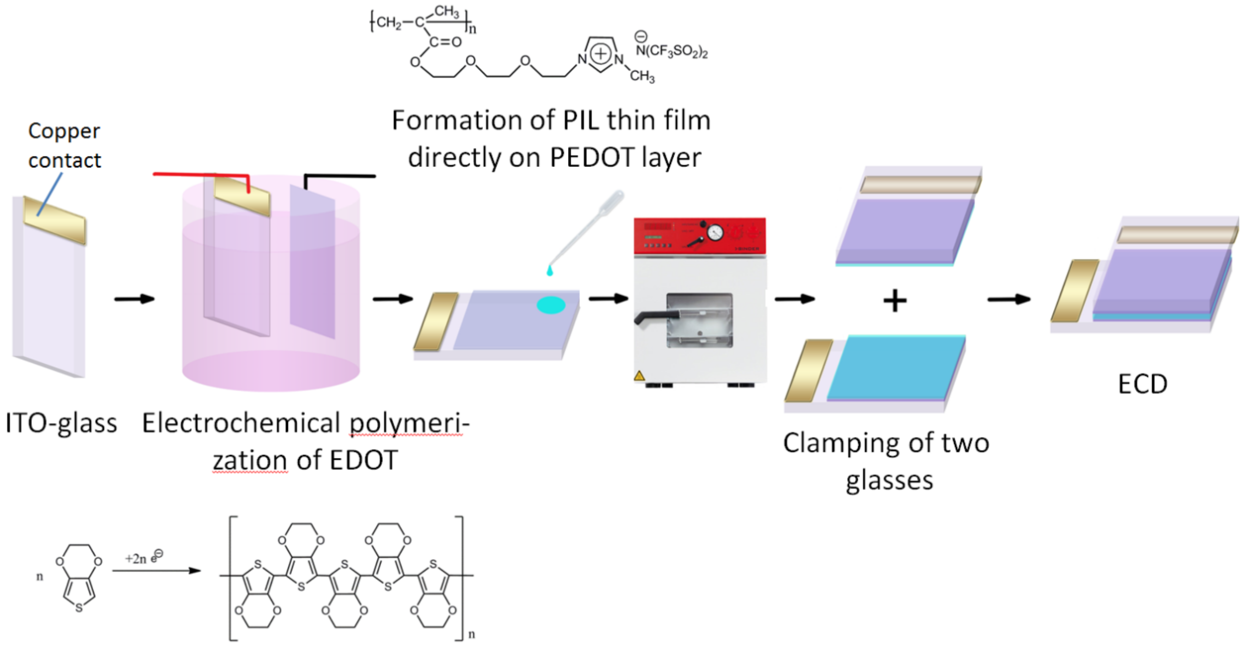

Fig. 2. Device assembly.

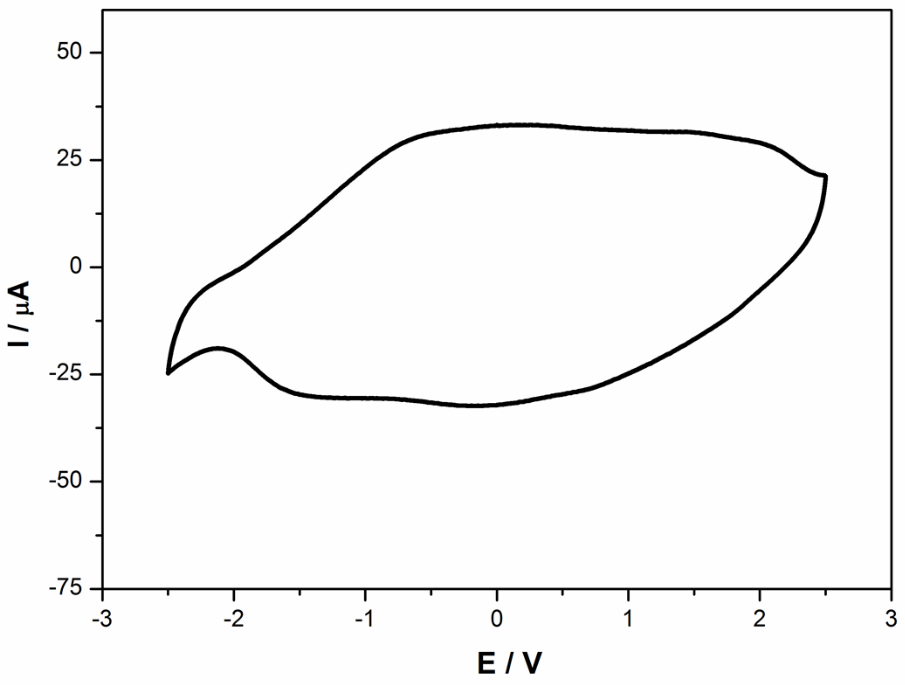

Fig. 3. Electrochemical characterization of symmetrical PEDOT/PIL/PEDOT electrochromic device by cyclic voltammetry at 60 mV·s^{-1}.

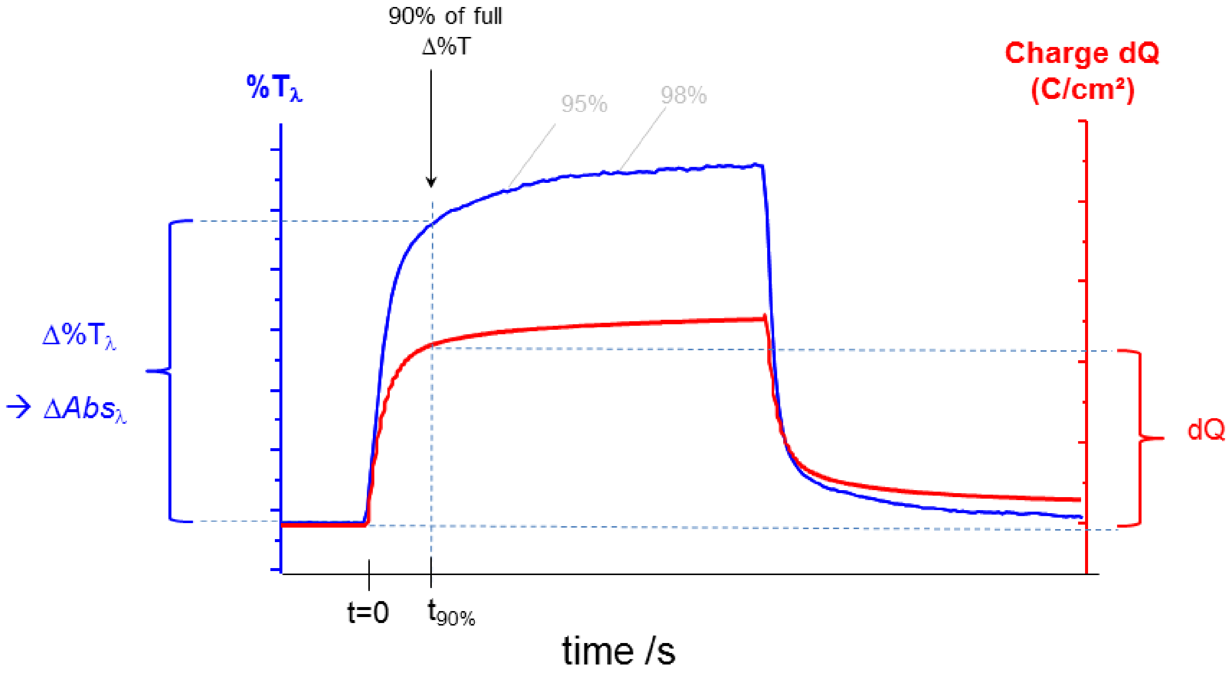

Fig. 4. Determination of the ECD's coloration efficiency.

8. References

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2. P. Shi, C.M. Amb, A.L. Dyer and J.R. Reynolds, *ACS Appl. Mat. Interfaces*, 2012, **4**, 6512-6521.