Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

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Solution processible neutral state colorless electrochromic devices: Effect of the layer thickness on the electrochromic performance

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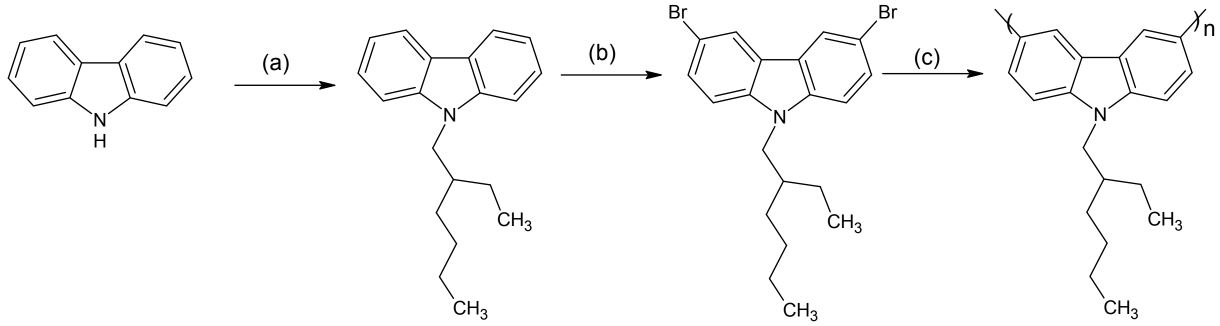
General Information:

All of the reagents were of commercial grade and used without any further purification. Synthetic route to poly(N-(2-ethylhexyl)carbazol-3,6-diyl) (PCbz) is given in the Scheme-S1.



a) KOH, Toluene, 18-Crown-6, 2-ethylhexyl bromide, 18h, 110^{o}C; b) Dichloromethane, NBS, 18h, r.t.; c) Ni(COD)$_2$, 1,5-cyclooctadiene, 2,2'-bipyridyl, *THF, 18h, 60 ^{o}C*

Scheme-S1. Synthetic route to poly(N-(2-ethylhexyl)carbazol-3,6-diyl)

First, 9-(2-ethylhexyl)-9H-carbazole was prepared by alkylation of carbazole in toluene solution using *2-ethyhexylbromide* in the presence of KOH and 18-Crown-6[1]. Then, this compound was brominated with NBS in dichloromethane at room temperature. Finally poly(N-(2-ethylhexyl)carbazol-3,6-diyl) (PCbz) was prepared by using the zero valent nickel reagent, bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)$_2$), in the presence of 1,5-cyclooctadiene (COD) and molar equivalent of (Bpy) at 60 °C[2] ^{1}. H NMR (Bruker Avance DPX-400) spectra were recorded at 25 °C in deuterated chloroform (CHCl$_3$-d) and TMS as internal standard. Gel permeation chromatography (GPC) was performed in THF relative to polystyrene standards (Scientific Polymer Products) on a system equipped with a three-column set (Polymer Laboratories 300 x 7.5 mm; 5 µm; pore sizes, 10–5, 10–4, and 10–3 Å) and a refractive-index detector (Agillent 1260) at room temperature with a flow rate of 1 mL min^{-1}. Electrochemical measurements were carried out using a Biologic SP-50 electrochemical workstation. The electrochemical cell consists of a Ag wire as reference electrode (RE), a Pt wire as counter electrode (CE) and platinum as a working electrode (WE) immersed in 0.1 M TBAPF$_6$ as the supporting electrolyte.

All measurements were carried out under argon atmosphere. UV-Vis absorption spectra were measured using an Analytic Jena Speedcord S-600 diode-array spectrophotometer. The optical band gap (*E_g*) of was calculated from their absorption edges[3].

Synthesis of PCbz. COD (4,125g, 15 mmol), Ni(COD) (4.954g, 18 mmol) and 2,2'-bipiridyl (2.811g, 18 mmol) were added to 100 mL of anhydrous THF under argon atmosphere. The solution was heated to 60 °C for 30 min, and then 3,6-dibromo-9-(2-ethylhexyl)-9H-carbazole monomer (6.558g, 15 mmol) solution in 20 mL of THF was slowly added to the reaction mixture. The reaction was continued for 18h at 90 °C. Finally, the reaction mixture was cooled and THF was removed by the rotary evaporator under reduced pressure. The residue was dissolved in 10 mL of chloroform and undissolved particles were removed by the filtration through a membrane filter (0.45 µm) to obtain transparent solution. The polymer solution poured into 300 mL of cold methanol and the white precipitate was filtered and dried to give the desired PCbz polymer (4.8 g). GPC: Mn 5.4 kDa, PDI 2.74.

^{1}H-NMR ($CHCl_3$ -d): δ ppm, 8.52 (s, 2H, Ha), 7.45 (m, 2H, Hb), 7.87 (d, 2H, Hc), 7.87 (d, 2H, -NCH_2-), 2.10-1.39 (m, 9H, CH aliphatic), 0.89 (t, 3H, -CH_3).

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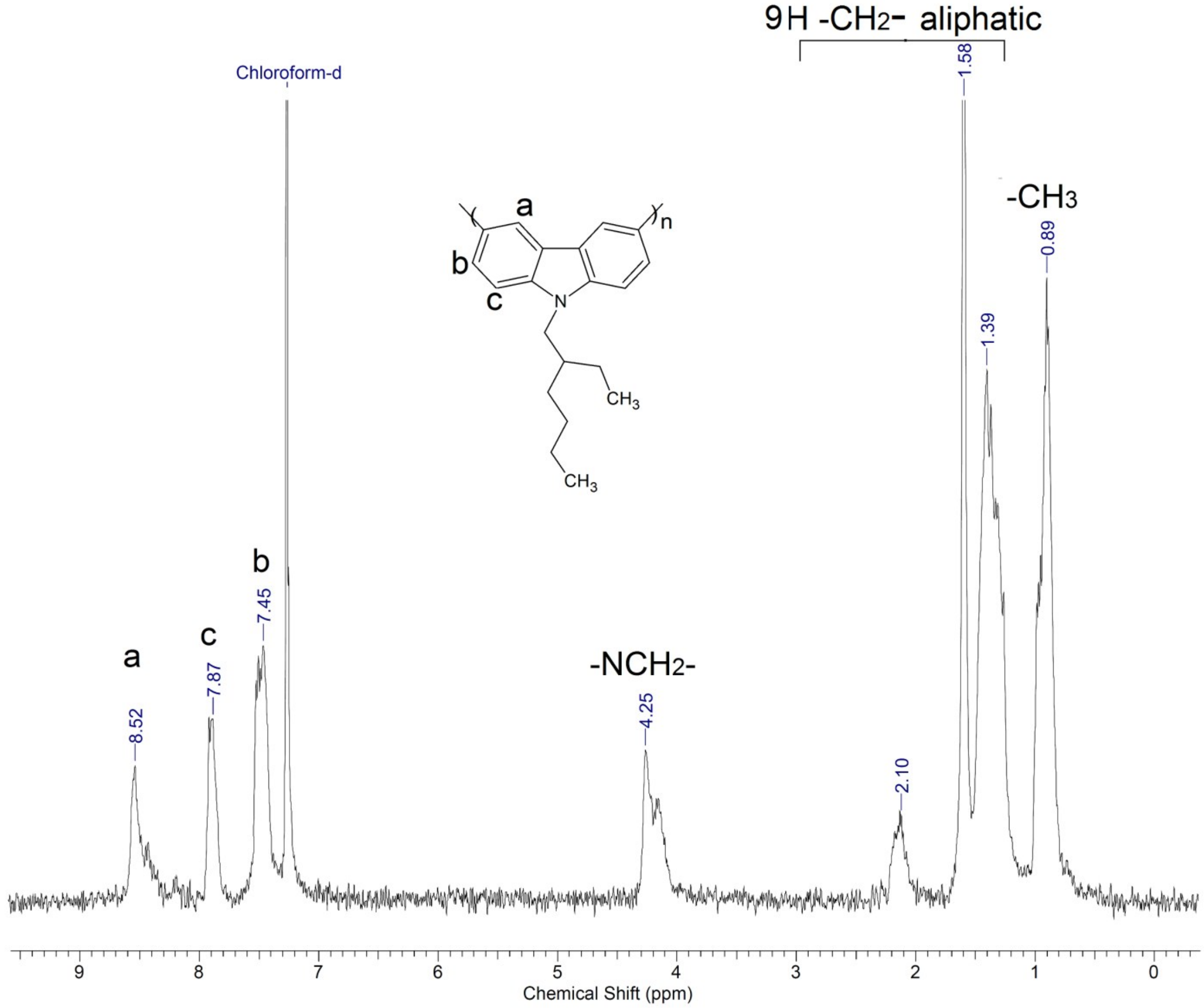

Figure S1. *^{1}H-NMR spectrum of PCbz*

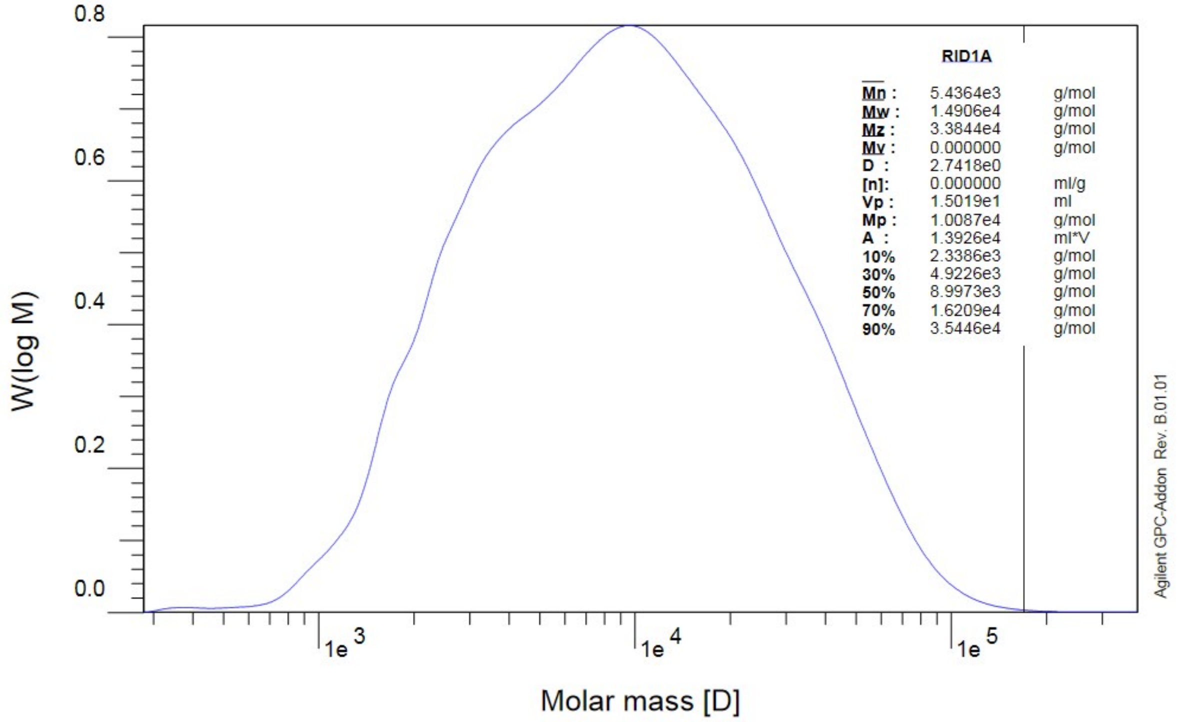

Figure S2. *GPC curve of PBbz*

Optical and Electrochemical properties of the PCbz

The UV-Vis absorption spectrum of **PCbz** is recorded in dichloromethane solution. The electronic absorption spectrum of **PCbz** exhibits a strong absorption band with a maxima at 361 nm attributed to π-π* transition of the conjugated PCbz main chain. In addition, the polymer only absorbs the UV light and onset of the band is observed at 412 nm corresponding to a band gap 3.01 eV. Due to no absorption in the visible regime, the polymer has good transparency and no color in the neutral state (Fig. S3).

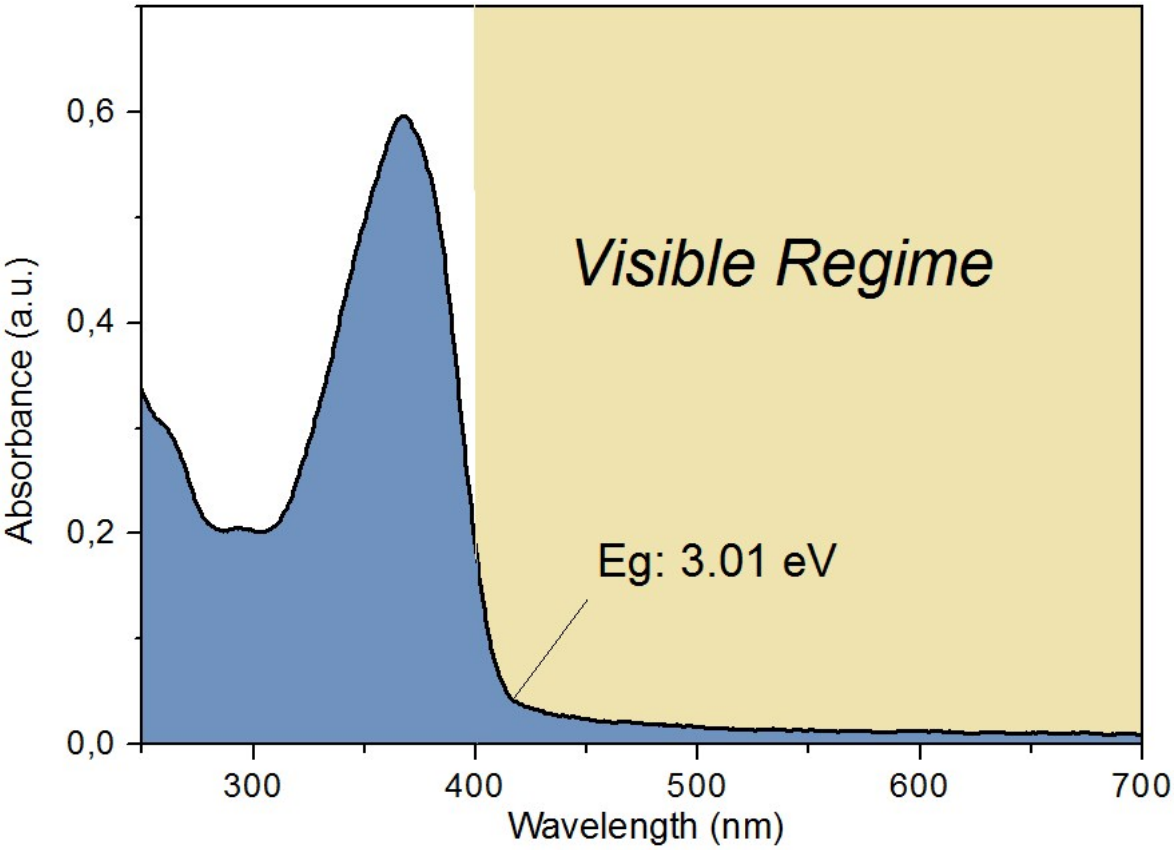

Figure S3. UV-Vis absorption spectrum of PCbz in DCM solution.

To investigate the electrochemical properties of **PCbz** on the ITO/glass surface, cyclic voltammetry technique is used (Fig S4). The electrochemical cell contains a Ag wire as reference electrode (RE), a Pt wire as counter electrode (CE) and ITO/glass as a working electrode (WE) immersed in 0.1 M $LiClO_4$ as the supporting electrolyte. The poly-(3,6-carbazoles has a unique property owing to their chemical structure; upon first oxidation as a typical conjugated polymer, an electron is removed from the polycarbazole conjugated backbone, and a polaron occurs. Normally, these radicals are unstable and combine with another cation on the polymer backbone. However, in the poly-3,6-Carbazoles, the polarons are separated from one another and do not combine because that the conjugation breaks between two carbazole units. Further oxidation at higher potentials, removes the second electron and produces bipolarons. Due to this property of poly-3,6-carbazoles, stable two distinct oxidation states (neutral, radical cation, and dication) can be obtained.[4] Two reversible oxidation peaks attributed to polaronic and bipolaronic species of the conjugated PCbz sturucture is observed at $E_{m,a}^{ox1}$ = 0.81 V and $E_{m,c}^{red1}$ = 0.67 V; $E_{m,1/2}^{ox/red1}$ = 0.74V and $E_{m,a}^{ox2}$ = 1.43 V and $E_{m,c}^{red2}$ = 1.32 V; $E_{m,1/2}^{ox/red2}$ = 1.20 V (vs. Ag wire) during the cathodic CV scan (Fig. S4).

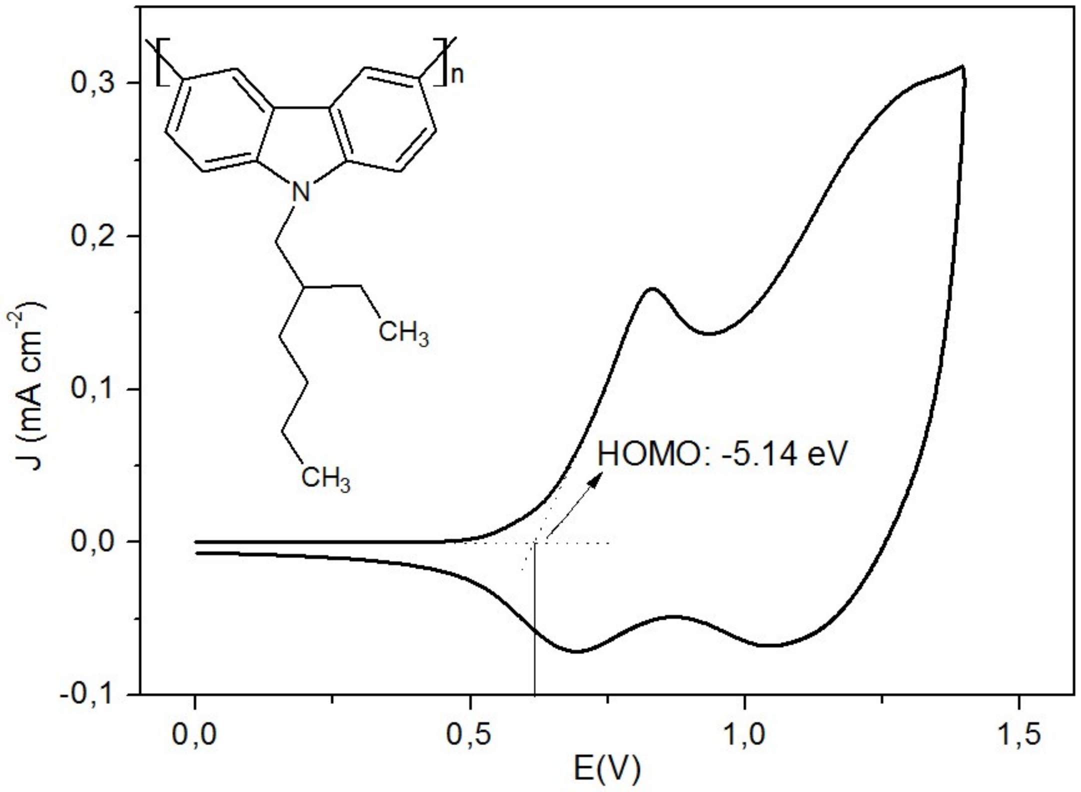

Figure S4. Cyclic voltammograms of **PCbz coated** on ITO/glass electrode in 0.1 M $LiClO_4$/ACN with a scan rate of 100 mVs^{-1} vs. Ag wire.

References

1. S. Koyuncu, I. Kaya, F. B. Koyuncu and E. Ozdemir, *Synthetic Met*, 2009, **159**, 1034-1042.
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3. G. Yu, Y. Yang, Y. Cao, Q. Pei, C. Zhang and A. J. Heeger, *Chem Phys Lett*, 1996, **259**, 465-468.
4. D. Witker and J. R. Reynolds, *Macromolecules*, 2005, **38**, 7636-7644.

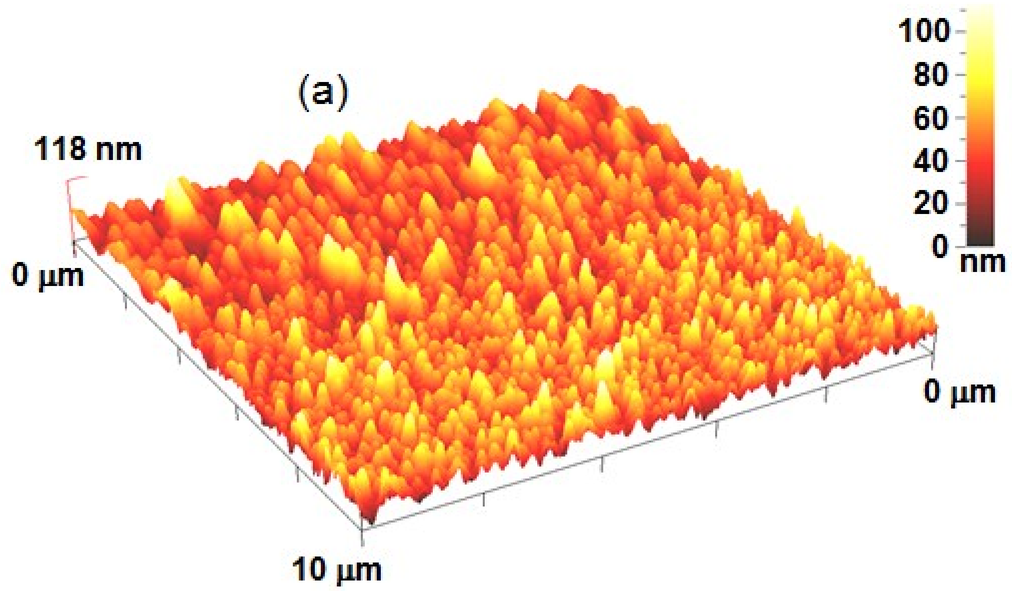

Figure S5. AFM images of layers of ECDs; 120 nm tick PEDOT:PSS

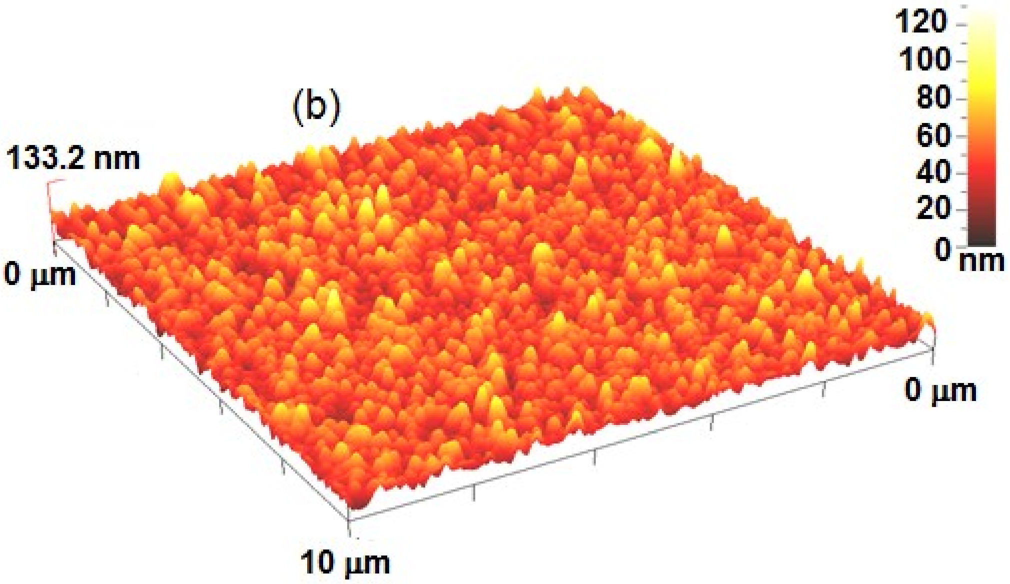

Figure S6. AFM images of layers of ECDs; 170 nm tick PEDOT:PSS

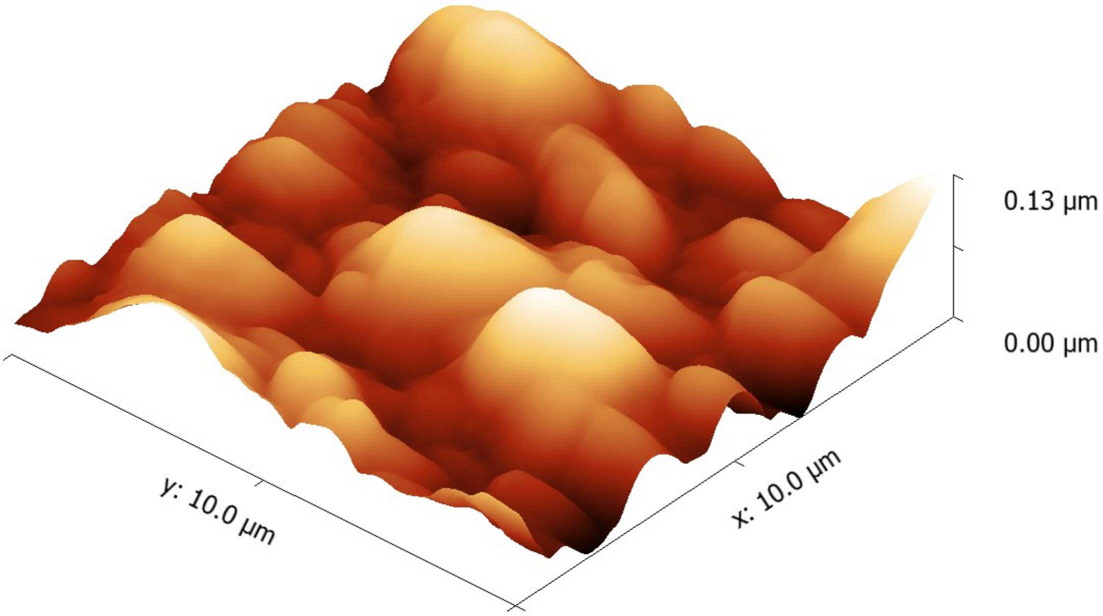

Figure S7. AFM images of layers of ECDs; 180 nm tick PCbz

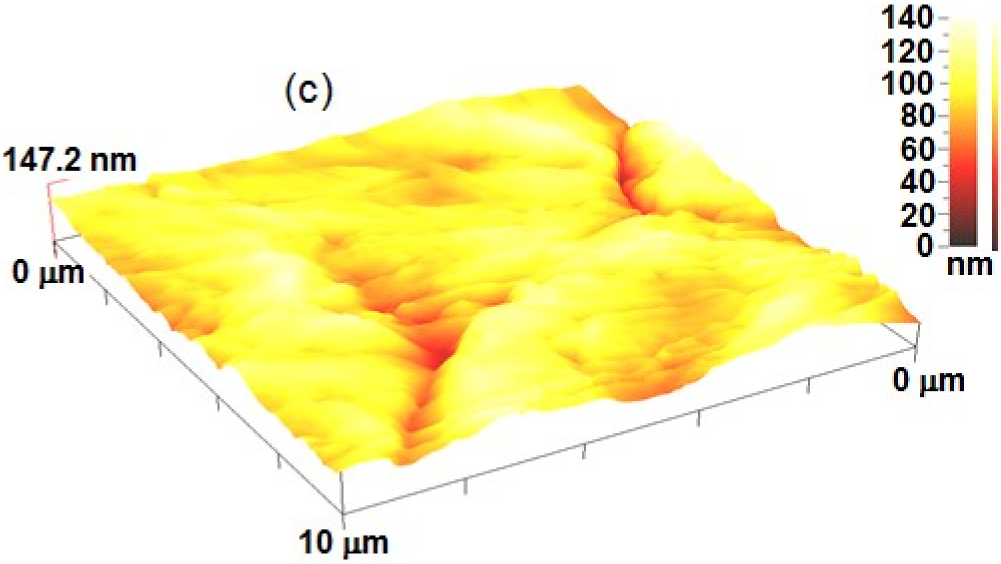

Figure S8. AFM images of layers of ECDs; 220 nm tick PCbz

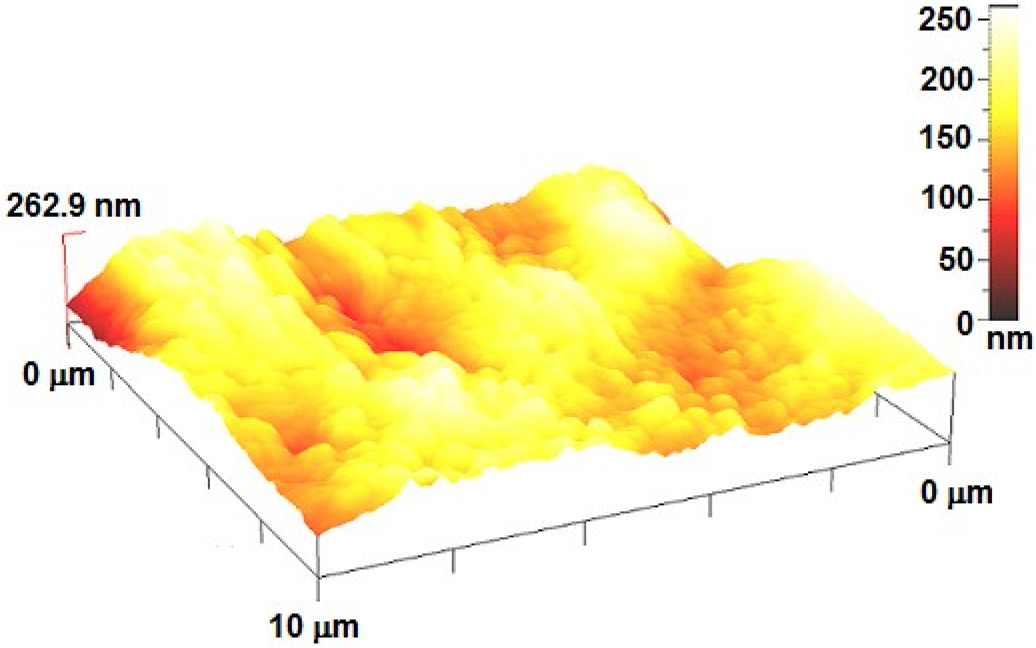

Figure S9. AFM images of layers of ECDs; 325 nm tick PCbz

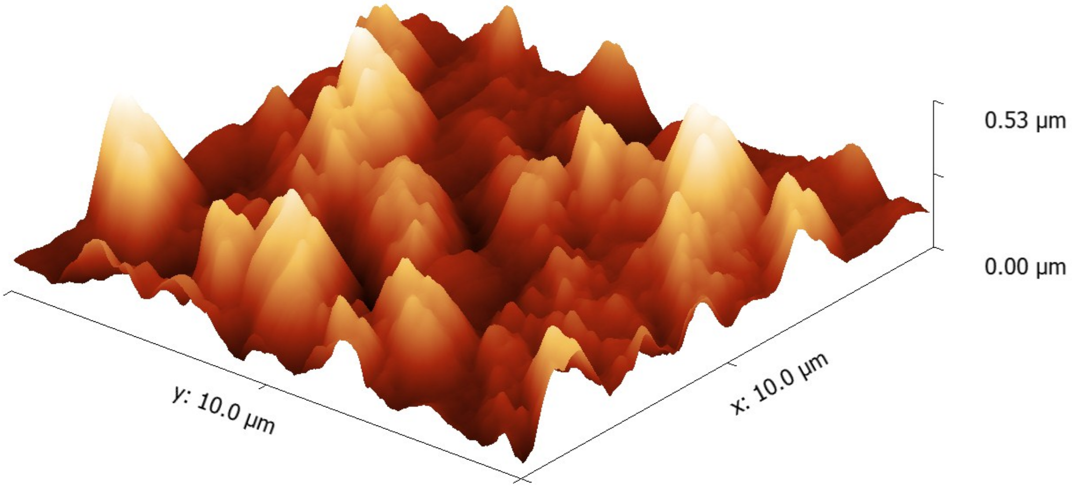

Figure S10. AFM images of layers of ECDs; 440 nm tick PCbz

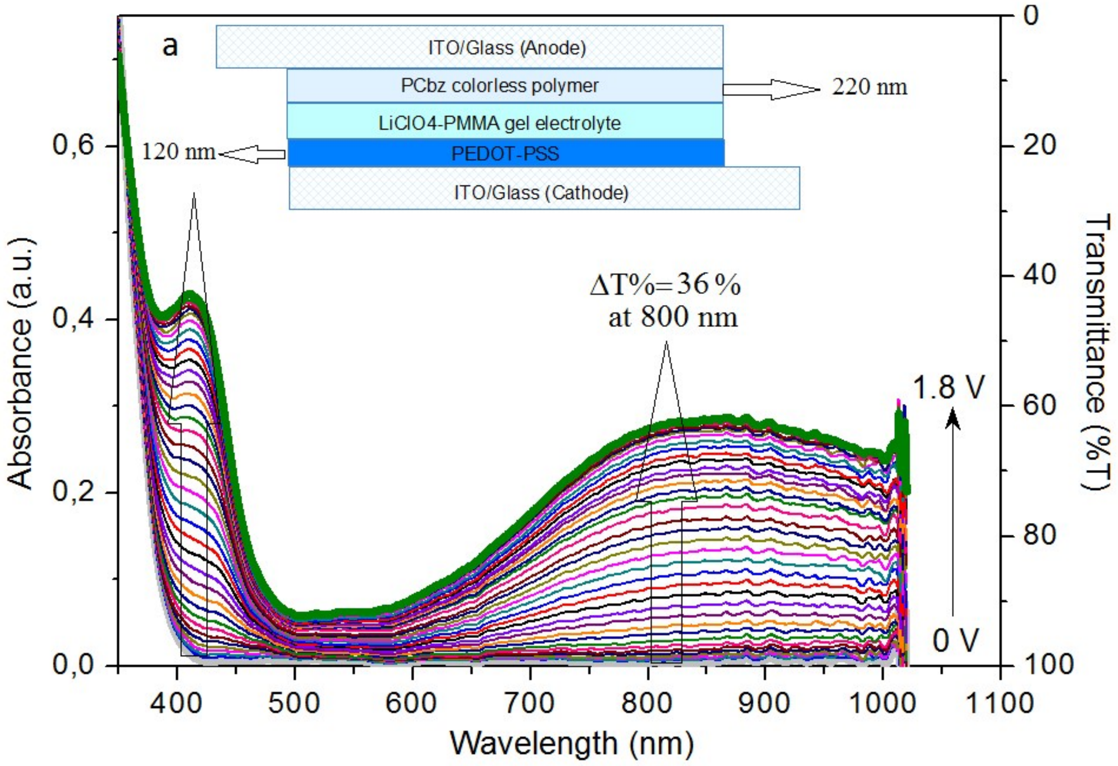

Figure S11. Spectro-electrochemical measurements of **PCbz/ PEDOT:PSS** device (ECD-2).

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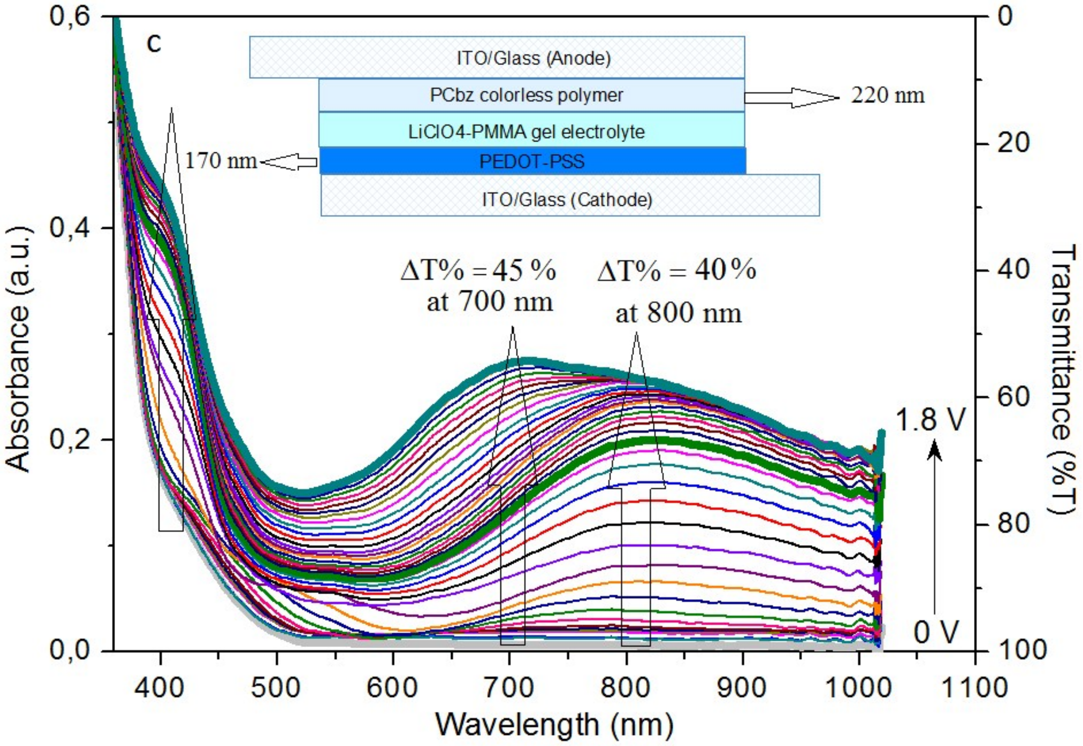

Figure S12. Spectro-electrochemical measurements of **PCbz/ PEDOT:PSS** device (ECD-2).

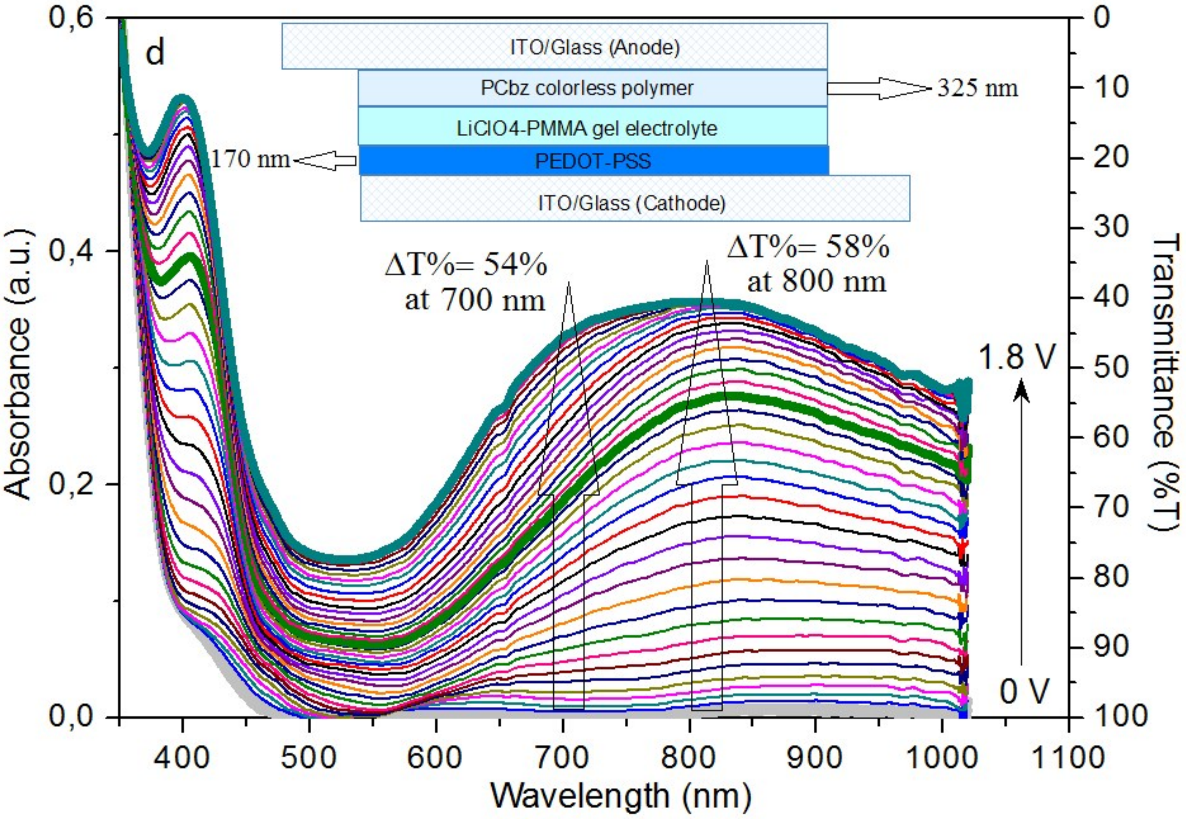

Figure S13. Spectro-electrochemical measurements of **PCbz/ PEDOT:PSS** device (ECD-4).

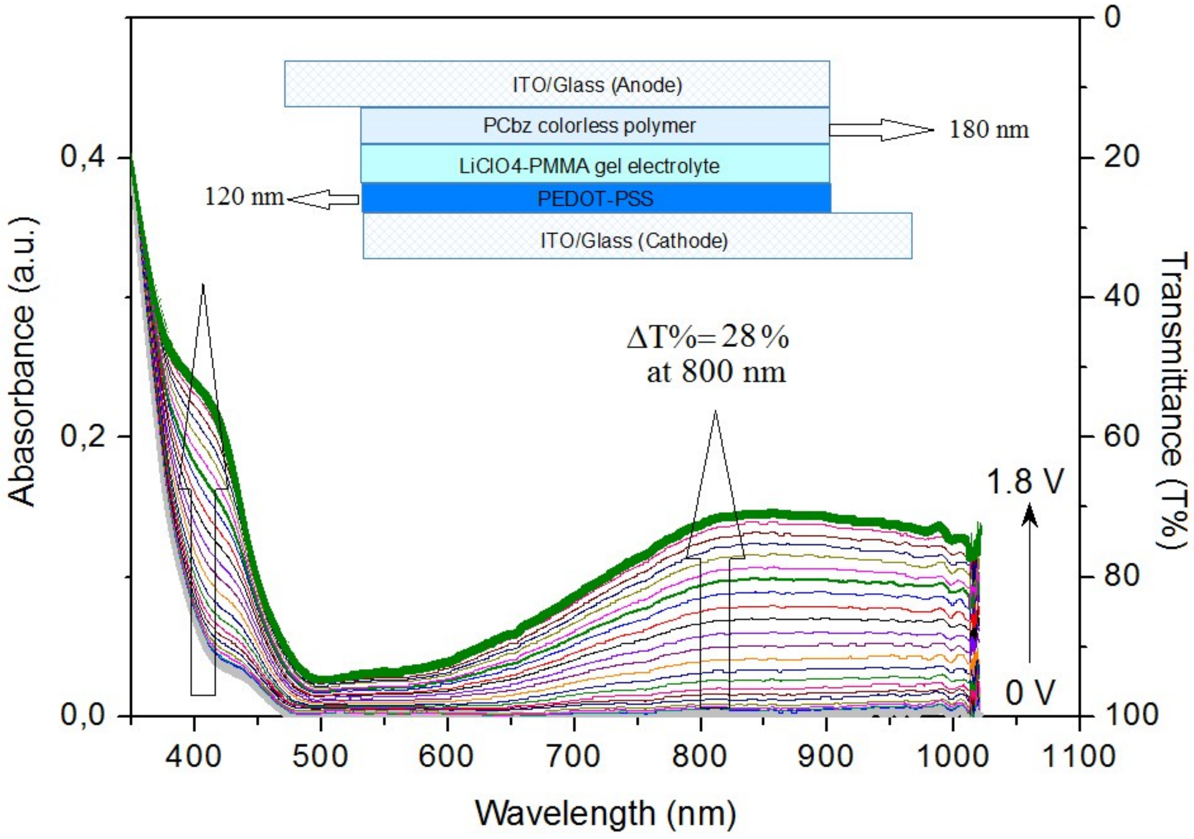

Figure S14. Spectro-electrochemical measurements of **PCbz/ PEDOT:PSS** device (ECD-5).

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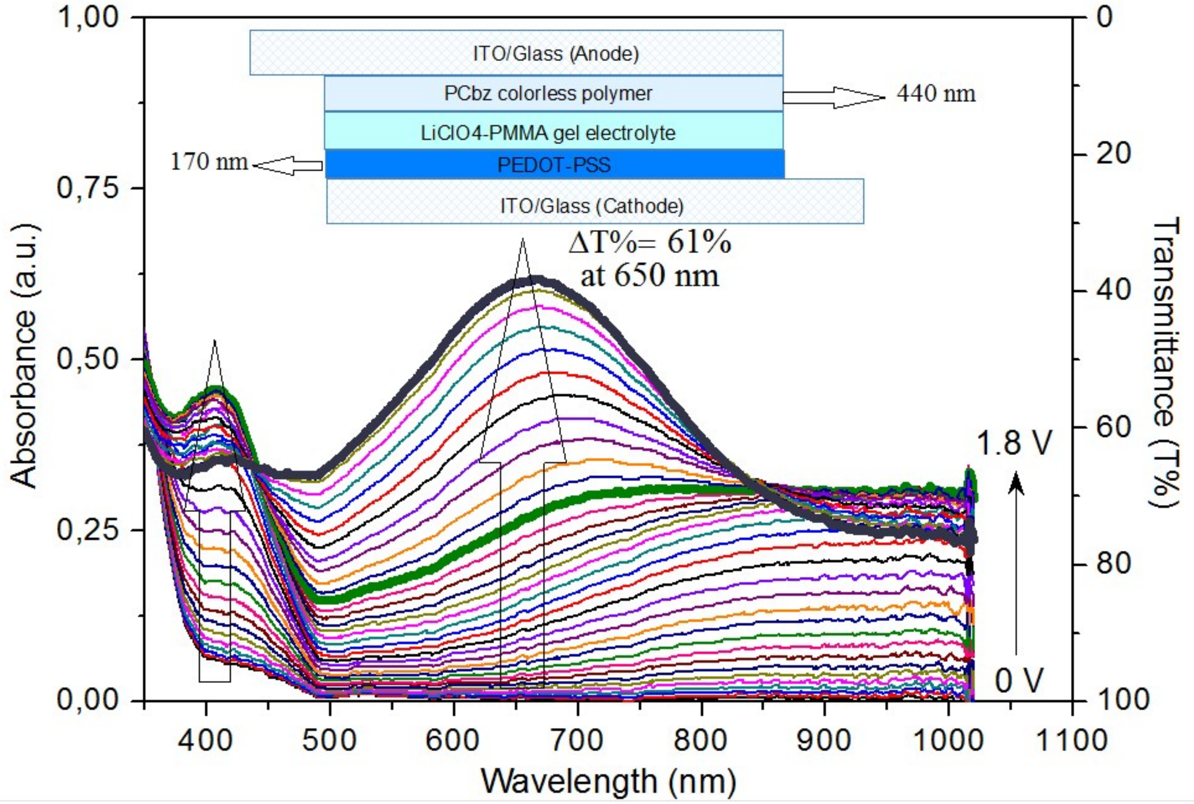

Figure S15. Spectro-electrochemical measurements of **PCbz/ PEDOT:PSS** device (ECD-6).

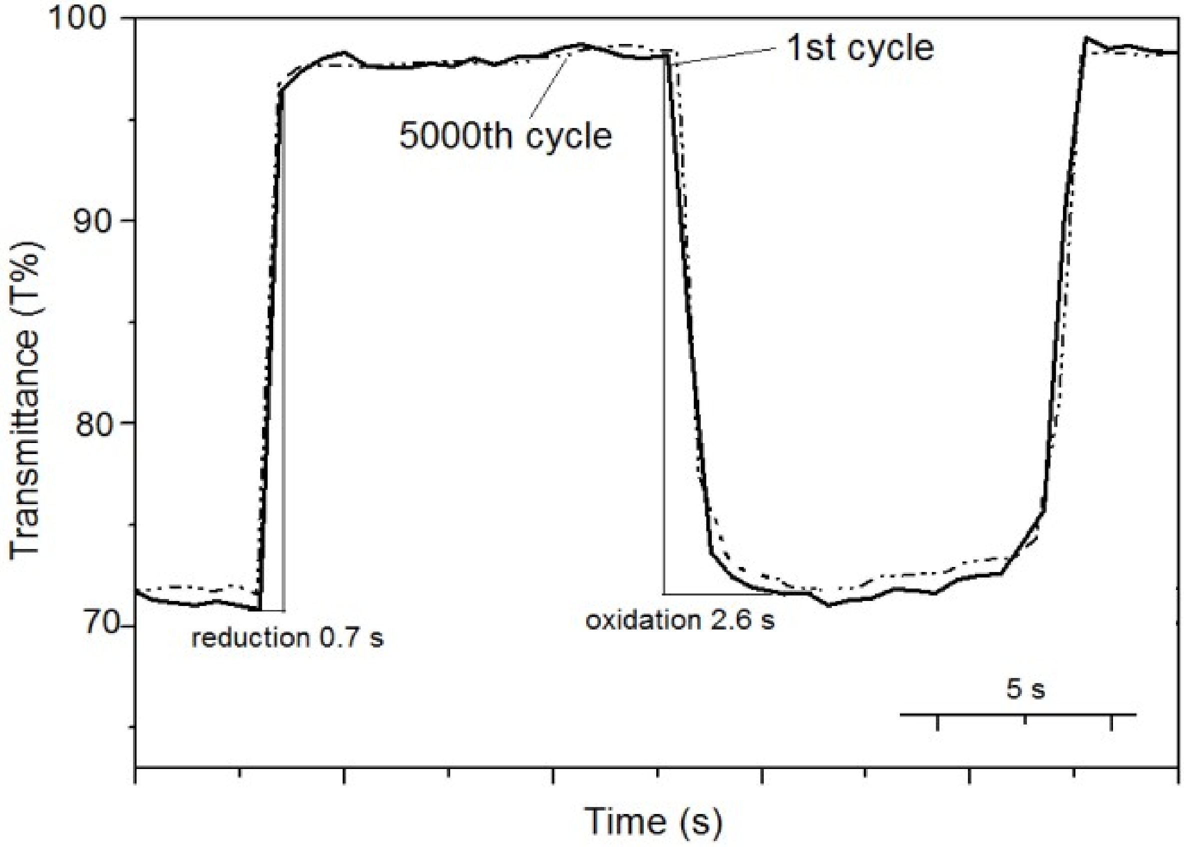

Figure S16. Electrochromic switching, optical absorbance monitored at 800 nm nm for PCbz/PEDOT:PSS based device (ECD-1) between -1.0 and 1.8 V

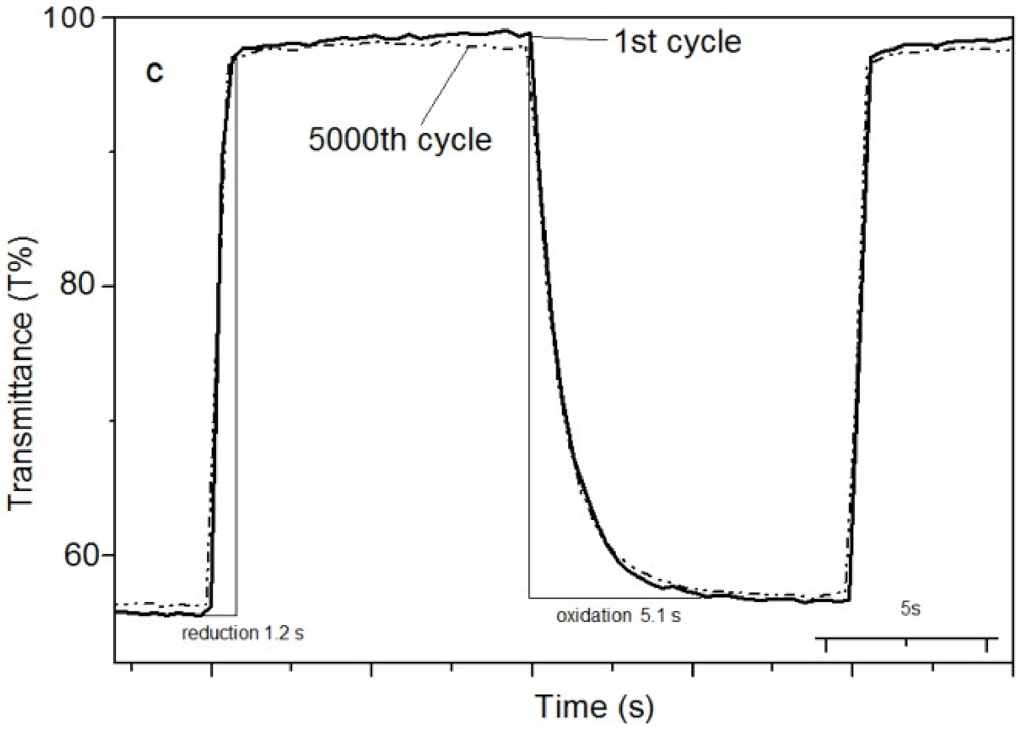

Figure S17. Electrochromic switching, optical absorbance monitored at 800 nm nm for PCbz/PEDOT:PSS based device (ECD-3) between -1.0 and 1.8 V

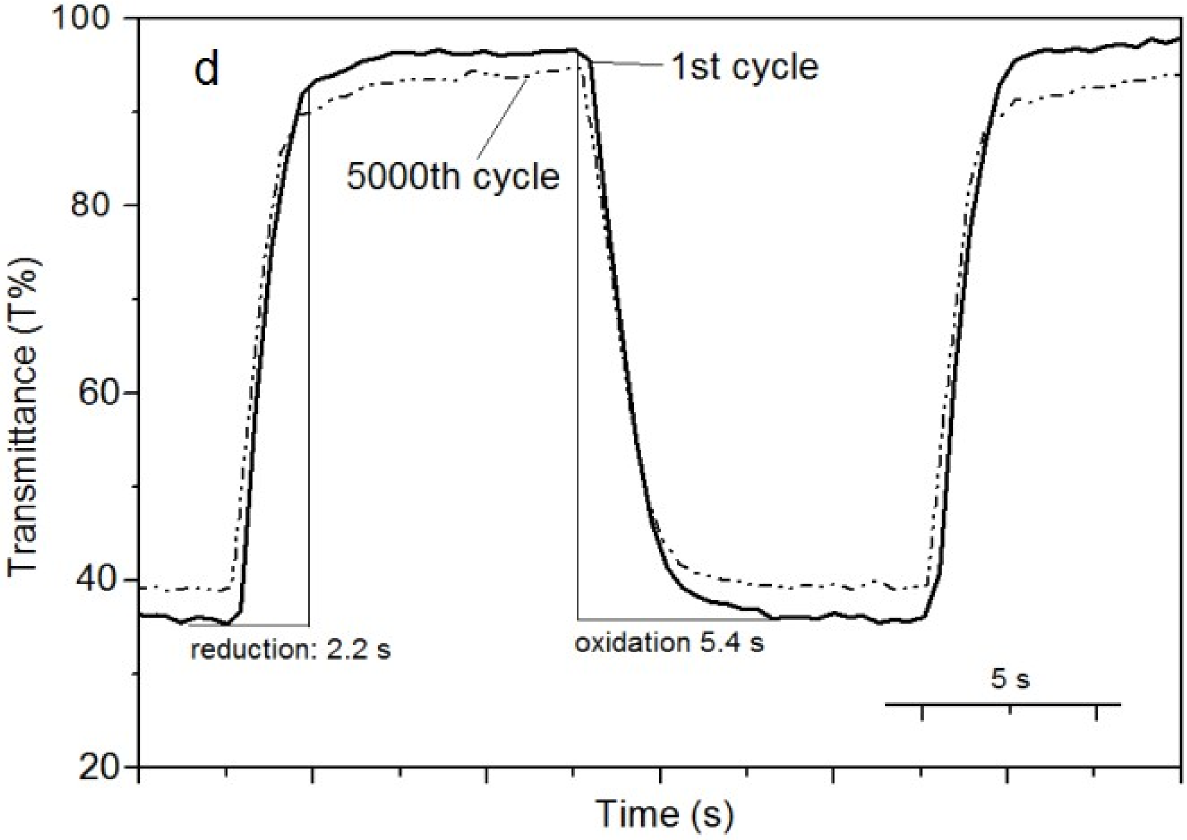

Figure S18. Electrochromic switching, optical absorbance monitored at 800 nm nm for PCbz/PEDOT:PSS based device (ECD-4) between -1.0 and 1.8 V

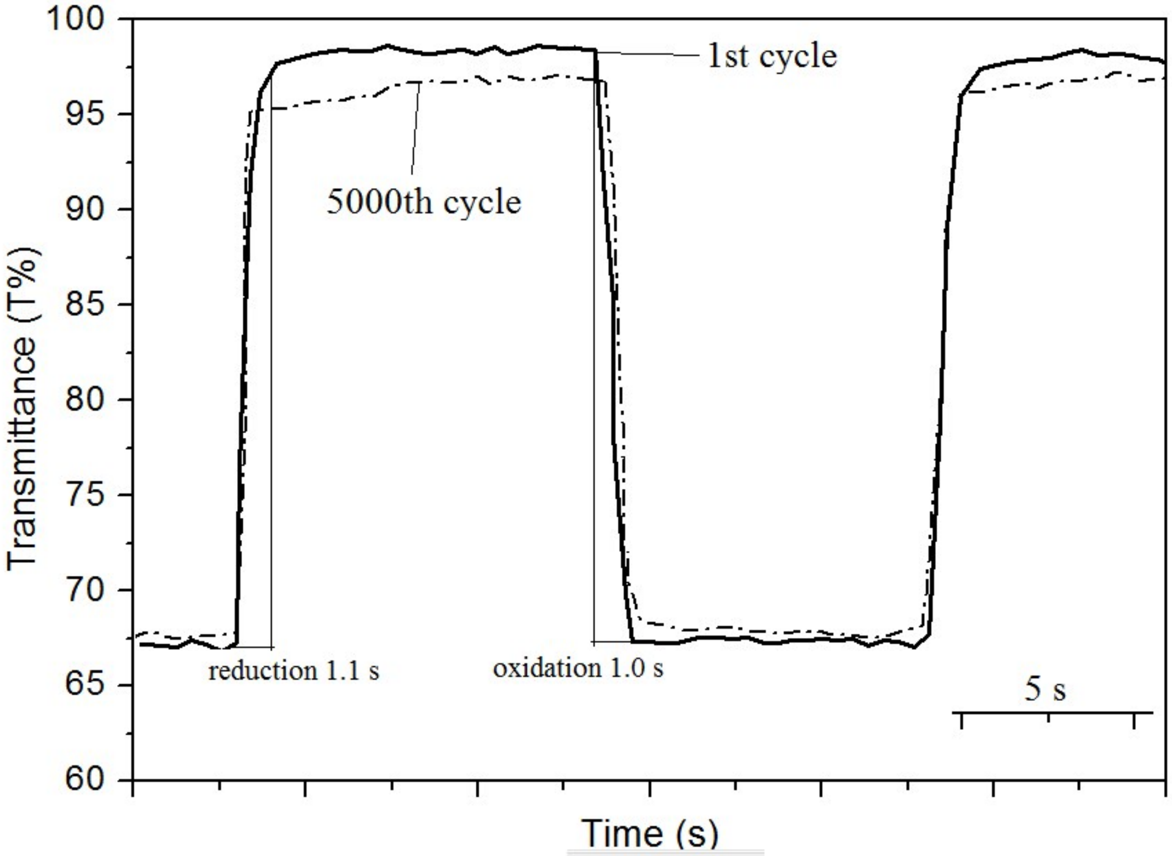

Figure S18. Electrochromic switching, optical absorbance monitored at 800 nm nm for PCbz/PEDOT:PSS based device (ECD-5) between -1.0 and 1.8 V

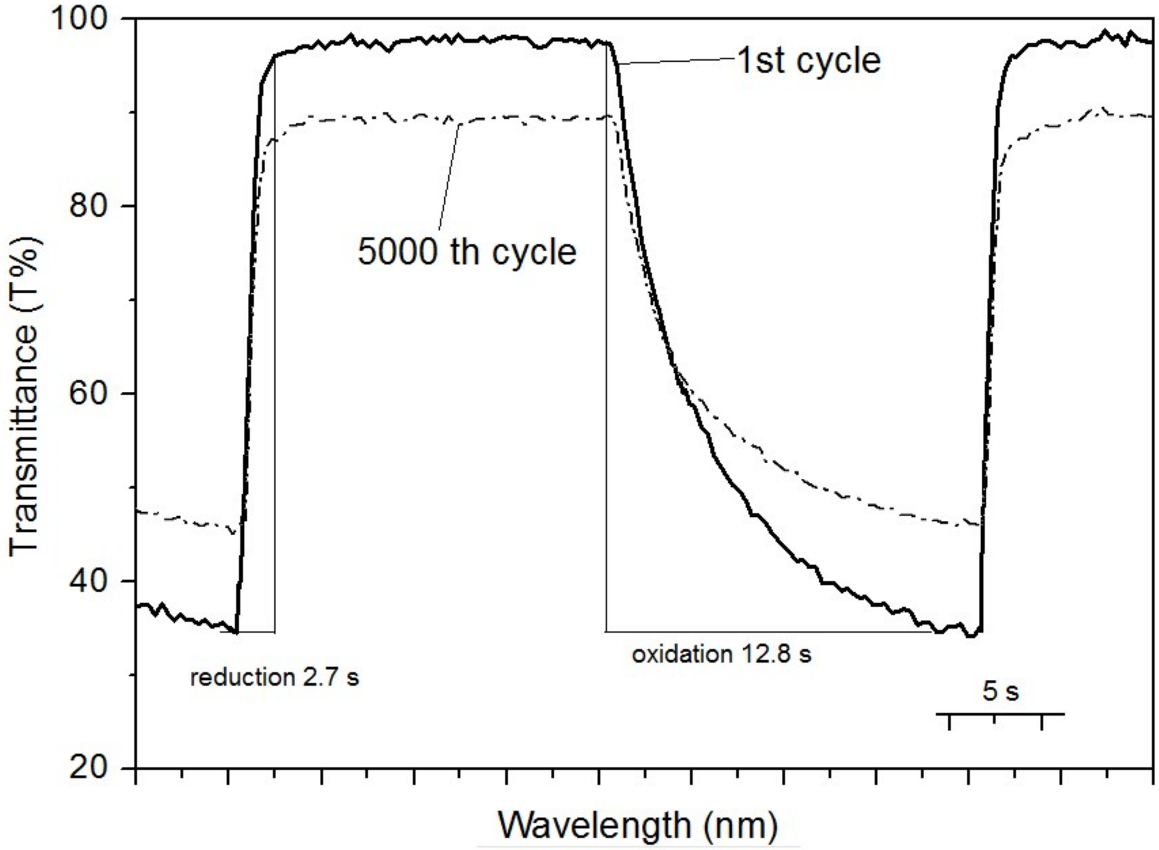

Figure S20. Electrochromic switching, optical absorbance monitored at 800 nm nm for PCbz/PEDOT:PSS based device (ECD-6) between -1.0 and 1.8 V