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COMMUNICATION

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

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Using polymeric ionic liquid and PEDOT as ion conducting separator and electrodes, respectively, the all-polymer-based organic electrochromic device (ECD) has been constructed. The advantages of such ECD are: fast switching time (3 s), high coloration efficiency (390 cm²·C⁻¹ at 620 nm), optical contrast up to ΔT = 22 % and possibility of working in vacuum.

Electrochromism involves electroactive materials that present a reversible change in optical properties when the material is electrochemically oxidized or reduced.¹ This phenomenon is interesting from both scientific and technological point of view. It was used for the development of storage devices, information displays, cathode ray tubes, actuators, electromagnetic shutter and mirrors.² More than decade ago truly all solid state ECDs based on inorganic materials were developed.³ Some of them were operated by H⁺ transport⁴ and some by Li⁺.⁵ However, their production required specific instrumentation (electron beam systems, plasma sources, etc.) and was quite expensive.³ In recent years the electronically conducting polymers (ECP) such as polythiophene, polyaniline, polypyrrole, etc. and their derivatives have been considered as one of the most promising materials for the creation of cheap and easier in manufacture “organic” ECDs.⁶ Among others, poly(3,4-ethylenedioxythiophene) (PEDOT) has attracted special attention due to the several reasons: it can be easily prepared by standard oxidative chemical or electrochemical polymerization; it has well defined polymer backbone structure with small amount of possible defects; it demonstrates higher electrochemical stability compared to other thiophene analogues and high conductivity (ca. 300 S/cm); it was found to be almost transparent or light blue in thin, oxidized (p-doped) films and dark blue in its undoped state.⁷ Till nowadays various organic ECDs based on PEDOT are described.^{1,8} Despite their good optical performances, the main drawback associated is the intricate multi-layer ECDs structure (up to 9 layers), that complicates the process of assembling, and the presence of

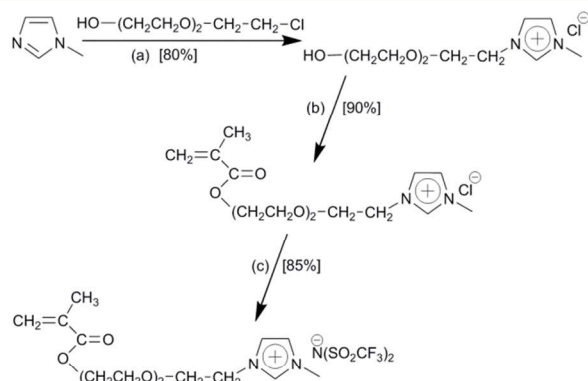
liquid containing electrolyte (salt solution in organic solvent or polymer gel electrolyte), that leads to the necessity of the device sealing and prevents development of ECD in wide glazing and display's applications. Therefore, the development of new non-volatile and highly ion conductive solid separator materials is necessary to improve the work ability and to increase the potential application of modern ECDs. One interesting strategy comprises the formation of “polymeric ionic liquids” (PILs), having ionic species covalently bonded with polymer backbone and combining all beneficial properties of ionic liquids with those of classical polyelectrolytes.⁹

The present work deals with the continuation of the development of the synthetic methods for well-defined PILs¹⁰ with high ionic conductivity and their first utilization in the construction of truly all-solid state thin-film organic ECDs having symmetrical structure: PEDOT/PIL/PEDOT.

Based on our previous studies on the investigation of the PIL's structure influence on ionic conductivity (σ_{DC})^{9h,11} and reaching the goal of further optimization of macromolecule's structure for the formulation of polyelectrolyte with higher σ_{DC} , we proposed synthesis of new well-defined polycation (Scheme 1). The synthetic procedure for ionic monomer (see ESI[†]) consists in quaternization of N-methyl imidazole by 2-[2-(chloroethoxy)-ethoxy]ethanol, further acylation of hydroxyl functionalized chloride ionic liquid with methacryloyl chloride and finally ion exchange with lithium bis(trifluoromethylsulfonyl)imide (TFSI). PIL was obtained by radical polymerization of the cited ionic monomer in DMF solution with 1.0 wt.% of AIBN at 60°C. It was found that PIL's intrinsic viscosity [η] is equal to 0.46 dL·g⁻¹ (0.5M Li(CF₃SO₂)₂N solution in DMF), while the exchange of the TFSI anion into chloride one allowed the estimation of $M_w = 3.8 \times 10^5$ and $M_w/M_n = 4.4$. The study of conductivity and thermal properties provided $\sigma_{DC} = 1 \times 10^{-5}$ S·cm⁻¹ (25°C), glass transition temperature $T_g = -17.5^\circ\text{C}$ and onset loss temperature $T_d = 290^\circ\text{C}$ (see ESI[†]).

PEDOT electrodes as thin films (90 nm) on ITO glasses were obtained via electropolymerization of 3,4-ethylenedioxythiophene in

0.1M solution of $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ in anhydrous acetonitrile under inert atmosphere, using silver wire and stainless steel lattice as reference and counter electrodes, respectively. The electroactivity of PEDOT film was studied in 0.1M $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}/\text{CH}_3\text{CN}$ medium by cyclic voltammetry in the range of $-0.7 \div +1.0$ V at $50 \text{ mV}\cdot\text{s}^{-1}$ (Fig. 1, ESI[†]). The electrochemical behaviour of PEDOT suited well with literature data¹²: the observed anodic peak occurring at 0.33V corresponds to



Scheme 1. Synthetic route for the preparation of ILM. Reaction conditions: a) CH_3OH , $0 \rightarrow 55^\circ\text{C}$, 67 h; b) 1.5 methacryloyl chloride, CH_3CN , $0^\circ\text{C} \rightarrow \text{r.t.}$, 2.5 h; c) 1.1 $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, H_2O , r.t.

the oxidation of PEDOT, while cathodic peak at -0.39V stands for the reduction of PEDOT to a neutral state. The investigation of electrical conductivity of PEDOT film gives the value of $40 \text{ S}\cdot\text{cm}^{-1}$ (25°C).

For the manufacture of ECD the thin films ($<0.5 \mu\text{m}$) from PIL's solution in anhydrous CH_3CN were cast directly on the PEDOT electrodes deposited on ITO glasses. After total removal of the solvent two glasses were so clamped together that the following symmetrically layered ECD was obtained: ITO glass/PEDOT/PIL/PEDOT/ITO glass (Fig. 1) with the final thickness of PIL layer equal to $\sim 0.5 \mu\text{m}$ and an active surface area of 1.96 cm^2 .

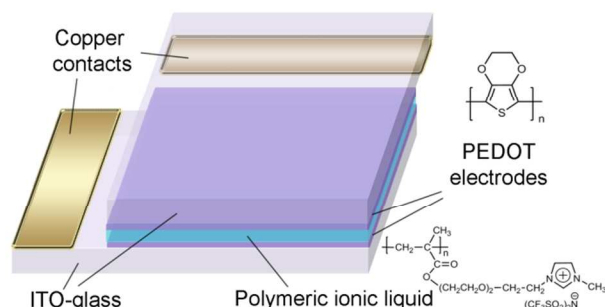


Fig. 1. Schematic representation of symmetrical PEDOT/PIL/PEDOT electrochromic device.

The UV-vis characterization of such ECD at various values of applied potential is presented in Fig. 2. The device is pale blue with low absorbance in the visible range at 0 V due to the partial p-doping/oxidation of both PEDOT layers by TFSI anions of PIL. Upon the application of 2.5 V, one PEDOT layer gets more transparent, while another undergoes undoping/reduction, the device becomes dark blue with a strong absorption band located at a λ_{max} of 620 nm (Fig. 2).

Simultaneously a modification in the transmittance is observed. At this, the increase in the applied potential led to the decrease in transmittance until the saturation at 2.5 V (Fig. 2). The maximum optical contrast ΔT (defined as the difference between $\%T_{0\text{V}} - \%T_{2.5\text{V}}$) at 620 nm was found to be 22%, that exceeds ΔT (15%) for known symmetrical ECDs based on PEDOT/polystyrenesulfonate electrodes and PEO/ LiCF_3SO_3 electrolyte,¹ although is less than for complicated ECDs with polypyrrole/dodecylsulfate//PEDOT/polystyrenesulfonate electrodes and poly(epichlorohydrin-co-ethylene oxide)/ LiClO_4 electrolyte (52%)^{8c} or for other PEDOT based ECDs with liquid electrolytes (33–45%).^{2b,2c,13} It is noteworthy that the same electro-optical answer is observed when the applied potentials are negative due to the symmetrical configuration of the device. The switching time defined as the time necessary to reach 90% of the maximum optical contrast at 620 nm was evaluated as 3 s both for coloring and bleaching (Fig. 3). Such value being in the range of switching times for ECDs having gel or liquid electrolytes ($1 \div 8 \text{ s}$)^{8a,14} and overrunning solid-state organic ECDs ($4 \div 60\text{s}$).^{1,2c,8c}

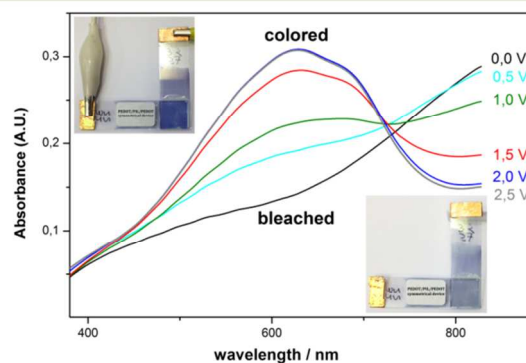


Fig. 2 UV-vis characterization of the electrochromic symmetrical PEDOT/PIL/PEDOT device under current applying.

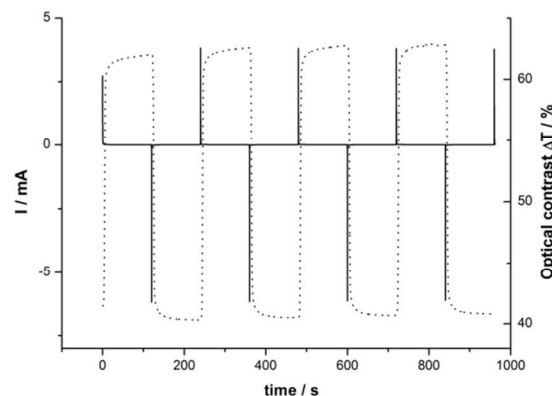


Fig. 3 Evolution of the current and the optical contrast at 620 nm upon application of potential steps (between 0 and 2.5 V during 1000 s) on symmetrical PEDOT/PIL/PEDOT electrochromic device.

The coloration efficiency $CE(\lambda)$ was defined as $\log(\Delta A_{\lambda_{\text{max}}})/Q$ where $\Delta A_{\lambda_{\text{max}}}$ is the variation of absorbance between the coloured and bleached states, while Q is the charge used to change the colouration (see ESI[†]). A $CE(\lambda)$ of $390 \text{ cm}^2\cdot\text{C}^{-1}$ was

obtained that is a very high value for the solid-state organic ECDs.^{1,8c}

The stability of electrochromic cell was studied by cyclic voltammetry along with spectrophotometry. After 1000 potentiodynamic cycles in the range between 0 and 2.5 V no significant decrease of electroactivity and optical contrast of the device was observed (ΔT varied between 21 and 22%).

Taking into account that our ECD is composed entirely of polymer films and contains no liquids, its work from an independent power source (AA battery) was tested in vacuum (Fig. 4). The vacuum commutation of ECD was successfully observed for long time (>3 days) making our approach interesting for spacecraft applications as well.

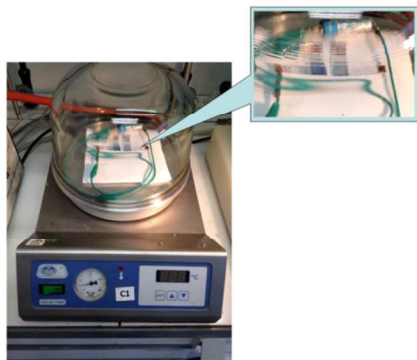


Fig. 4 Demonstration of the stable work of symmetrical PEDOT/PIL/PEDOT electrochromic device from ordinary AA battery in vacuum.

Conclusions

The new highly conductive, well-defined, high molar mass polymeric ionic liquid was synthesized and utilised for easy construction of novel truly all-polymeric symmetrical organic electrochromic device with PEDOT films acting as anode and cathode with electrochromic properties. The advantages of this technology is the fast switching times (3 s), high coloration efficiency ($390 \text{ cm}^2 \cdot \text{C}^{-1}$), high working stability (1000 cycles without change in optical contrast) and possibility of application in open air and in vacuum.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental procedures, NMR and IR spectra, elemental analysis and cyclic voltammograms]. See DOI: 10.1039/c000000x/

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