Journal of The Electrochemical Society, **163** (8) H679-H683 (2016)
0013-4651/2016/163(8)/H679/5/$33.00 © The Electrochemical Society

Transparent-Blue Colored Dual Type Electrochromic Device: Switchable Glass Application of Conducting Organic-Inorganic Hybrid Carbazole Polymer

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A new organic-inorganic hybrid monomer, O-2-(9H-carbazyl) ferrocenyldithiophosphonate (CzFc), was synthesized and characterized. Electropolymerization was realized with an applied potential of 1.5 V in boron trifluoride diethyl etherate (BFEE). Spectroelectrochemical and colorimetry studies have shown that P(CzFc) has transmissive colored in neutral state. For switchable glass applications, it has to be two electrochromic polymers have tranmissive states in different oxidation states. So we were constructed dual-type complementary colored polymer switchable glass derived from P(CzFc) as anodically coloring material and P(EDOT) as cathodically coloring material in sandwich configuration. Optoelectrochemical studies indicate that the reduced state of the switchable glass shows blue color for the oxidized state whereas it shows transmissive color for the reduced state. P(CzFc)/P(EDOT) device has good switching time, high optical contrasts and excellent redox stability.
 [DOI: 10.1149/2.0711608jes]

Manuscript submitted April 8, 2016; revised manuscript received May 9, 2016. Published May 31, 2016.

Organic–inorganic hybrid materials are promising systems for a variety of applications due to their extraordinary properties based on the combination of the different building blocks. Combine with inorganic components and the organic polymeric structure have shown promising applications in various fields of polymer chemistry. One important class of hybrid materials is that in which the organic fraction is composed by conducting polymers such as polythiohene (PTh), polypyrrole (PPy) and polyaniline (PANI), which have been intensively studied.[1–4] The purpose of the synthesis hybrid materials containing inorganic components in the conductive polymer scaffold is to obtain new materials with complementary behavior between polymer structure and inorganic part. Significant characteristics of the intended target material depend on the properties of the chosen part of the inorganic moiety. This approach can be very useful to obtain materials with predetermined properties[5–7]

Conjugated organic polymers have growing interest in the field of plastic electronics because of their fundamental structural characteristics such as low cost scalability, mechanical flexibility, structural control and processing.[8–10] In considering the most technological applications, polymeric semiconductors are expected to find widespread application in thin film transistors,[11,12] photovoltaic cells,[13,14] sensors,[15–17] fuel cells,[18,19] electrochromic devices (ECDs)[20–25] and light emitting diodes (OLEDs).[26,27] All of the possible applications, light-emitting and electrochromic devices require precise control of the colors displayed in terms of their hue, saturation, intensity, and their brightness. In electrochromic device (ECD) technologies, developing new methods that cause changes in the polymeric structure has been an important approach to color-tuning. These methods include planarity of the backbones, varying electron donor-acceptor groups of the building block, integration of fused heterocycles that reduce the polymer bond-length and copolymerization with different monomers. Alternatives have consisted in blending different electroactive components, or creating laminates and composites with other types of chromophores or insulating materials.[9,28] Combining fast response times, high contrast ratios, and narrow potential windows of application with the viewpoint for long-term electrical and optical stability, processable electrochromic polymers are now influence the development of both reflective and transmissive ECD applications.[29,30]

During the past decade, substantial synthetic attempt on CPs with higher contrasts, improved ambient stability and new colors have been consecutively developed. Accordingly, it has been described some considerable effective strategies in the construction of ECDs to improve the lifetime and performance substantially. In practice, various colored CP in different redox states can only be used in display devices owing to absence of its transmissive state. Although there are many studies in the literature on the display device, there are few studies on the construction of switchable glass making. For switchable glass applications, it has to be two electrochromic polymers have tranmissive states. Also these transmissive states have to be in different oxidation states of these electrochromic polymers.[31–34]

In this study, we synthesized organic-inorganic hybrid electroactive monomer that has a transmissive state in reduction of its polymer. As is known, P(EDOT) has a transmissive state when it is oxidized. We have made smart glass consisting of these two polymers for switchable glass application. Dual-type complementary colored polymer ECD on P(CzFc) and P(EDOT) were constructed in sandwich configuration. Spectroelectrochemical studies revealed that the oxidized state of the ECD shows blue color whereas it shows transmissive for the reduced state. Switching time and maximum contrast (Δ%T) of the ECD were measured as 1.0 s and 55% for 605 nm.

Experimental

Materials.—Dichloromethane (DCM) (Merck), 9*H*-carbazol-2-ol (Aldrich), toluene (Aldrich), nitromethane (Aldrich), methanol (Merck), acetonitrile (AN) (Merck), NaOH (Merck), $LiClO_4$ (Aldrich), propylene carbonate (PC) (Aldrich) and poly(methyl methacrylate) (PMMA) (Aldrich) were used without further purification. 3,4-ethylenedioxythiophene (EDOT) (Aldrich) was used as received. Borontrifluoride ethylether (BFEE) was purchased from Aldrich.

Equipments.—NMR spectrum of the monomer was recorded on a Bruker-Instrument-NMR Spectrometer (DPX-400) by using $CDCl_3$ as the solvent. An Ivium potentiostat/galvanostat interfaced with a personal computer was used in all electrochemical measurements. Agilent UV–vis spectrophotometer was used in order to perform the spectroelectrochemical studies of polymer and the characterization of the devices. Colorimetry measurements were recorded on a Minolta CS-100A Chroma Meter in a proper box having D-50 illumination. Measurements were performed with a 0/0 (normal/normal) viewing geometry as recommended by CIE. Three-electrode cell geometry was used in all electrochemical experiments. ITO (indium tin oxide) coated glass rectangular (0.9 cm × 2.7 cm) slide was used as the working electrode. Pt and Ag wires were used as the counter and reference electrodes respectively. All potential values are referred to Ag/Ag^+ reference electrode. In situ UV-vis spectroelectrochemical measurements were carried out in three-electrode quartz cell.

Synthesis of monomer (CzFc).—CzFc was synthesized by the reaction of 2,4-bis(ferrocenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide $[FcP(=S)(\mu\text{-}S)]_2$ with 9*H*-carbazol-2-ol in toluene

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