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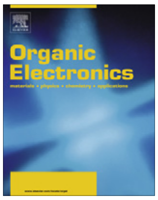

Donor–acceptor polymer electrochromes with cyan color: Effect of alkyl chain length on doping processes

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ABSTRACT

A new series of donor–acceptor–donor (D–A–D) type compounds consisting of dialkyl substituted 3,4-propylenedioxythiophene and benzothiadiazole units were synthesized and polymerized chemically and electrochemically to investigate the effect of alkyl chain length on the doping process of the conjugated polymers. It was found that the alkyl chain length plays a key role on both doping processes and the solubility of the polymer. It is also noteworthy that this new series of D–A–D electrochromes transmits or reflects the cyan color of the Cyan–Magenta–Yellow (CMY) color space in the neutral state which can be switched to transmissive grey when oxidized.

1. Introduction

The design and synthesis of novel organic materials, especially the conjugated polymers, are of considerable interest since they hold great promise for advanced technological applications in the fields of light emitting diodes [1,2], photovoltaics [3,4], and transistors [5,6]. In particular, they have been envisioned as one of the most useful electrochromes for high performance innovative devices [7,8], displays [9], smart windows [10,11], mirrors [12] and camouflage materials [13,14]. Organic polymer electrochromes (PECs) [15,16] can show high optical contrast ratio, high redox stability, long cycle life, multicolors with the same material, low response time and low operation voltage when compared to inorganic variants. Therefore, significant efforts have been devoted to design and synthesize novel solution-processable PECs [15,16] which exhibit many distinct and saturated colors of the visible spectrum including blue [17–19], green [19–21] and black [22–24] in the neutral state. Furthermore, it was shown that the neutral state colors of the PECs can easily be controlled through rational design of the backbone structures which mainly control the optical properties and allow spectral engineering [23,25]. In a recently published article by our group [19], the effect of donor (D) and acceptor (A) units on the structure–property relationships of PECs was investigated. Furthermore, various hues of blue and green pallets of the RGB color-space (red, green and blue constitute the primary additive colors) in the neutral state were achieved. However, it should be noted that the palette of colors that are available with PECs should be extended if the full color displays are desired where the PEC is an active colorant. On the contrary, it can be seen that organic PECs which reflect or transmit the colors of the primary substractive color space (cyan, magenta and yellow, CMY color space) [26,27] are inadequate in the literature.

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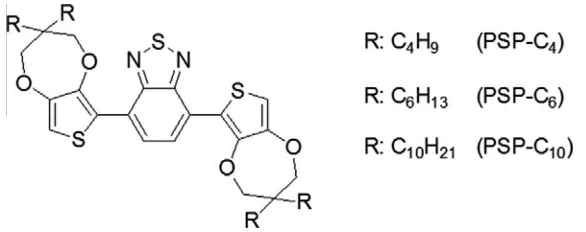
On the other hand, much of the focus has been on the design and synthesis of p-type (hole transporting) organic π-conjugated materials, probably due to the fact that it is relatively easier to design electron-rich conjugated polymers (p-type) rather than electron-poor ones (n-type). Besides, n-type (electron transporting) materials have some serious drawbacks such as instability in air and poor solubility. However, the systems exhibiting both n- and p-type doping would be fascinating in terms of extending the colors available with a single material [28].

Keeping all these in mind, our work to this end has revealed that the alkyl substituents on the D–A–D systems affect not only the solubility of the material but also the doping processes. This result is clear when PSP-C_{10} is considered (Scheme 1). It is found that the polymer obtained from PSP-C_{10}, that is PPSP-C_{10}, is an excellent processable high performance (high stability, high optical contrast, high coloration efficiency, and sub-second switching time) PEC candidate, which has a specific band gap to reflect the cyan color. However, PPSP-C_{10} does not show n-doping process. The fact that n-doping process is observed with similar systems without any alkyl chains, such as thiophene [29] and 3,4-ethylenedioxythiophene [30], has stimulated us to investigate the effect of the alkyl chain length of the D-units on the doping process (Scheme 1).

Herein, we wish to present our results concerning the design, synthesis and properties of a new series of D–A–D type compounds consisting of dialkyl substituted 3,4-propylenedioxythiophene and benzothiadiazole units. The effect of the alkyl chain length on the doping process of the conjugated polymers was investigated systematically. It was found that the alkyl chain length plays a key role on both the doping processes and the solubility of the polymer. More importantly, this series of D–A–D polymers allowed n- and p-dopable new PECs which transmit or reflect the cyan color of the CMY color space in the neutral state that can be switched to transmissive grey when oxidized. To the best of our knowledge, these are one of the first PECs reflecting or transmitting the cyan color in their neutral state.

2. Results and discussion

Three compounds with different alkyl chains (PSP-C_n, $n = 4, 6, 10$) were designed to investigate the effect of alkyl chain length on the doping process of the systems systematically (Scheme 1). These compounds were synthesized by Stille coupling reaction [31] and initial characterization of PSP-C_n compounds was based on ^{1}H, ^{13}C NMR and FTIR, which was in good aggreement with the structures (see Supporting information Figs. S1–S9).



Scheme 1. Chemical structures of the compounds based on D–A–D approach.

First of all, the electrochemical behaviours of the systems were investigated by cyclic voltammetry in order to investigate the effect of alkyl chain lengths on the redox behaviour. As shown in Fig. 1, the compounds exhibited one irreversible oxidation peak about at 1.0 V arising from the D-unit with a reversible reduction peak at about −1.35 V due to benzothiadiazole unit. Furthermore, no appreciable shift in the peak potentials values was observed.

Next, electrochemical polymerization of the systems was carried out in a mixture of DCM and ACN solution containing 0.1 M TBAH as a supporting electrolyte (Scheme 2). During the dynamic potential scanning, a new reversible redox couple appeared, which was a characteristic signature of a conducting polymer film formation on the electrode surface (Scheme 2 and Fig. 2, as a representative example, and also see Supporting information Figs. S10 and S11). Also, as expected from the formation of a conducting polymer film, after each successive scan, the current values of the redox couple were intensified, confirming the increasing polymer film thickness.

In order to represent the ability of n- and p-type doping of the polymer films, they were scanned both anodically and cathodically in a monomer-free electrolyte solution of 0.1 M TBAH/ACN. As reported previously [19], PPSP-C_{10} did not exhibit n-type doping process, but as shown in Fig. 3, the n-type doping capability can be imparted to the polymer films by decreasing alkyl chain length from decyl to hexyl and butyl. For example, PPSP-C_6 not only exhibited a reversible redox couple with a half wave $E^{\mathrm{ox}}_{p,1/2} = 0.39\,\mathrm{V}$ potential during anodic scan (p-doping) but also show a reversible redox couple with a half wave potential of $E^{\mathrm{red}}_{p,1/2} = -1.34\,\mathrm{V}$ during cathodic scan (n-doping). Also, a linear increase in the peak currents as a function of the scan rates confirmed a well-adhered electroactive polymer film on the electrode surface as well as non-diffusional redox process (see Supporting information Fig. S12). n-Type doping process was also confirmed

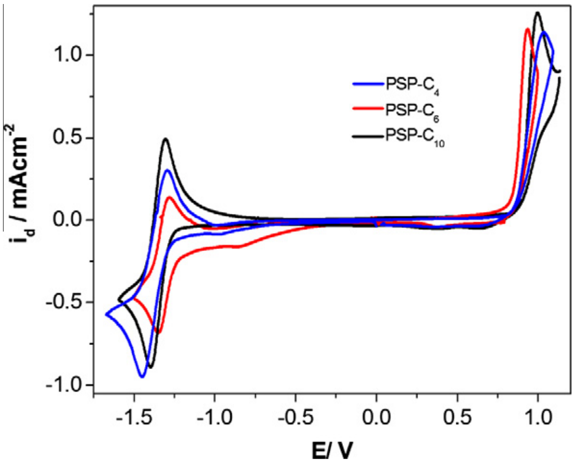


Fig. 1. Cyclic voltammograms of 2.05×10^{-3} M of PSP-C_4, 3.0×10^{-3} M of PSP-C_6 and 1.5×10^{-3} M of PSP-C_{10} in 0.1 M TBAH/ACN electrolyte solution at a scan rate of 100 mV/s vs. Ag/AgCl.