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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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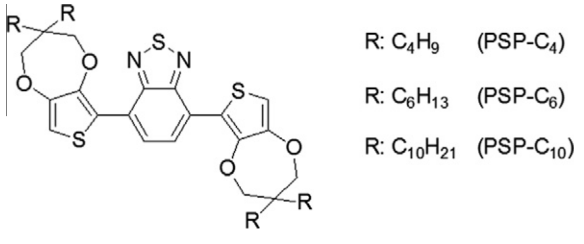
On the other hand, much of the focus has been on the design and synthesis of p-type (hole transporting) organic π-conjugated materials, probably due to the fact that it is relatively easier to design electron-rich conjugated polymers (p-type) rather than electron-poor ones (n-type). Besides, n-type (electron 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 $E^{\mathrm{ox}}_{p,1/2} = 0.39$ V potential during anodic scan (p-doping) but also show a reversible redox couple with a half wave potential of $E^{\mathrm{red}}_{p,1/2} = -1.34$ 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

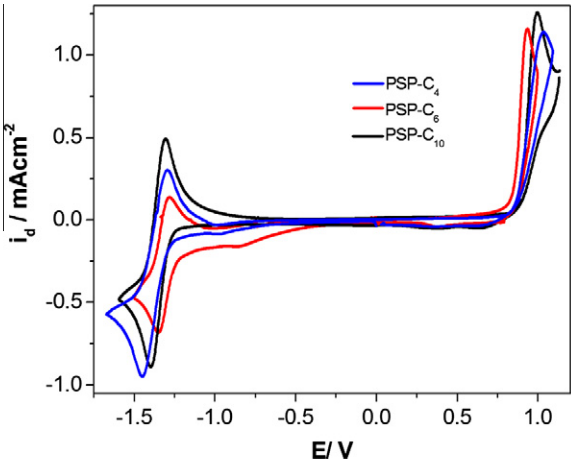
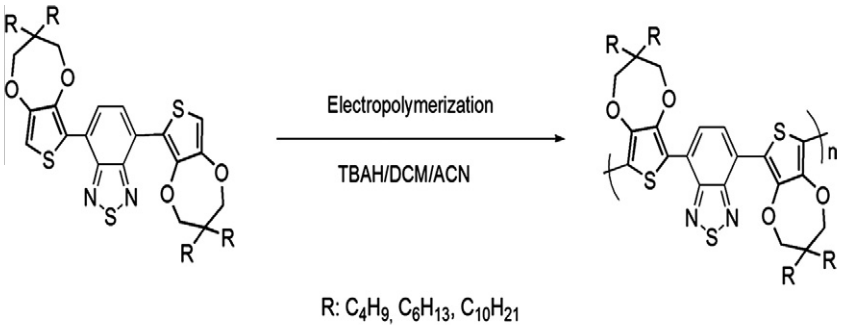


Fig. 1. Cyclic voltammograms of 2.05×10^{-3} M of PSP-C_4, 3.0×10^{-3} M of PSP-C_6 and 1.5×10^{-3} M of PSP-C_{10} in 0.1 M TBAH/ACN electrolyte solution at a scan rate of 100 mV/s vs. Ag/AgCl.



Scheme 2. Electrochemical polymerization of PSP-C_n.

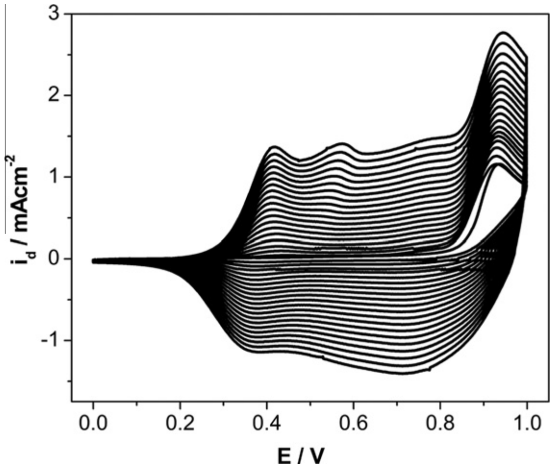


Fig. 2. Electropolymerization of 3.0×10^{-3} M PSP-C_6 in 0.1 M TBAH–DCM/ACN (5:95-v/v) at a scan rate of 100 mV/s by potential scanning to give PPSP-C_6.

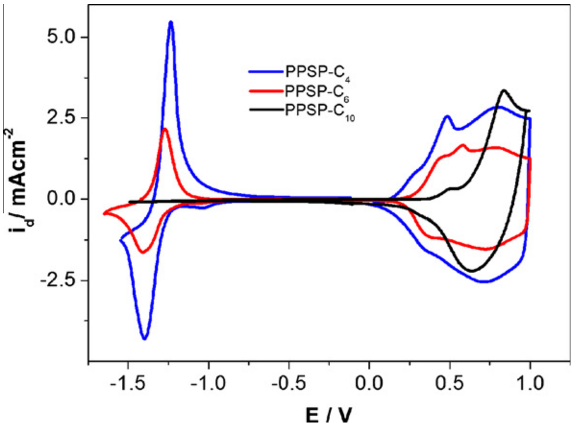


Fig. 3. Cyclic voltammograms of PPSP-C_4, PPSP-C_6 and PPSP-C_{10} in 0.1 M TBAH/ACN electrolyte solution at a scan rate of 100 mV/s vs. Ag/AgCl.

and supported by spectroelectrochemical studies as well as cyclic voltammetric measurements.

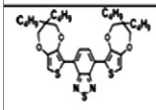
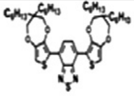
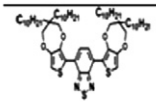
In view of device and high-performance display applications, the optical properties of the polymers should be manifested by using the changes in optical absorption spectra under various voltage pulses. Therefore, the optical properties of these novel systems were analyzed. All polymer films had similar optical properties bearing two absorption bands at about 410 nm and 670 nm (see Supporting information Fig. S13) reflecting or transmitting the greenish-blue and cyan colors in their neutral states (Table 1). To the best of our knowledge, these are one of the first PECs reflecting or transmitting the cyan color in the neutral state [26]. Also, the band gap values (E_g^{SPEL}) of the polymers calculated from the onset of π–π*-transition band at 670 nm were found to be around 1.50 eV (Table 1), which are in good agreement with the band gaps (E_g^{CV}) calculated from cyclic voltammogram data (Table 2).

During oxidation, π–π*-transition bands started to decrease and a concomitant increase was observed at 1000 nm due to the formation of charge carriers (Fig. 4). Upon further oxidation, the absorption band at 410 nm diminished completely and the absorption band at 670 nm reached a minimum level due to the leg of the absorption band of the charge carriers. During this process, all polymer films exhibited similar electrochromic behavior: switching from greenish-blue (PPSP-C_4) and cyan color (PPSP-C_6 and PPSP-C_{10}) in the neutral states to highly transmissive grey color when oxidized (Table 1).

In order to prove n-type doping of PPSP-C_4 and PPSP-C_6, the polymer films were scanned cathodically and the changes in optical spectra were monitored by in situ studies (Fig. 5). As in the case of p-type doping process, upon reduction, π–π*-transition bands started to decrease and the formation of charge carriers was observed beyond 800 nm, which explicitly indicated the ability of n-type doping of the polymers PPSP-C_4 and PPSP-C_6. During this process, the colors of the PPSP-C_4 and PPSP-C_6 films were turned from cyan to dark gray and cyan to brown, respectively.

Among the three polymer films, only PPSP-C_6 was both soluble and n-dopable. PPSP-C_{10}, on the other hand, was soluble but not n-dopable while PPSP-C_4 was insoluble but n-dopable. PPSP-C_6 was soluble in common organic solvents such as CH_2Cl_2 and $CHCl_3$, which clearly suggested that it could easily be processed over surfaces via spincoating, spraying, and printing techniques. Thanks to solubility of the polymer films, their doping processes were also performed chemically. For example, chemically obtained

Table 1
Electrochemical and optical data for PSP-C_n and their corresponding polymers.

Monomers	$E^{ox}_{m,a}$ (V)	$E^{red}_{m,1/}$ (V)	$E^{ox}_{p,1/}$ (V)	$E^{red}_{p,1/2}$ (V)	$\lambda_{max,1}$ (nm)	$\lambda_{max,2}$ (nm)	E_g^{SPEL} (eV)	Colorimetric results	Neut.	Ox.	Colors of Polymers Neut.	Ox.
 PSP-C_4	1.03	-1.37	0.35	-1.29	409	674	1.51	L	50.81	73.25	🟩	⬜
								a	-26.92	-4.05		
								b	0.49	5.17		
 PSP-C_6	0.95	-1.32	0.40	-1.35	407	665	1.52	L	63.59	83.22	🟦	⬜
								a	-27.42	-3.55		
								b	-12.00	1.99		
 PSP-C_{10}*	1.01	-1.36	0.48	-	408	685	1.50	L	65.25	81.50	🟦	⬜
								a	-30.60	-3.64		
								b	-10.24	1.81		

[a] The color of PPSP-C_{10} was reported as greenish-blue in its neutral state in Ref. [19] due to the absence of L, a, b values. In the present study, all colors are reported with respect to L, a and b values.

Table 2
Electrochemically determined HOMO, LUMO and E_g values for PPSP-C_n.

Polymer	E_{ox} onset (V)	HOMO (eV)	LUMO (eV)	E_g^{CV} (V)
PPSP-C_4	0.22	5.02	3.58	1.44
PPSP-C_6	0.27	5.07	3.57	1.50
PPSP-C_{10}	0.33	5.13	3.65	1.48

polymer PPSP-C_6 was dissolved in DCM and by the addition of $SbCl_5$ as an oxidant to the polymer solution, the intensity of π–π^*-transition bands decreased and the formation of charge carriers was observed at around 1000 nm (Fig. 6). On the other hand, the polymer film was neutralized again by using hydrazinium hydroxide as reducing agent and this cycle between oxidation and reduction states can be repeated many times. During chemical doping, the color of polymer solution was changed from cyan to transparent gray as in the case of the electrochemical doping (Fig. 6, inset).

To be amenable for use in optical devices and displays, the percent transmittance ($\Delta\%T$, optical contrast), coloration efficiency (CE) and switching time (response time) of polymeric electrochromes between their redox states are key parameters in the technological applications. While the optical contrast of PPSP-C_6 was found to be 39% at

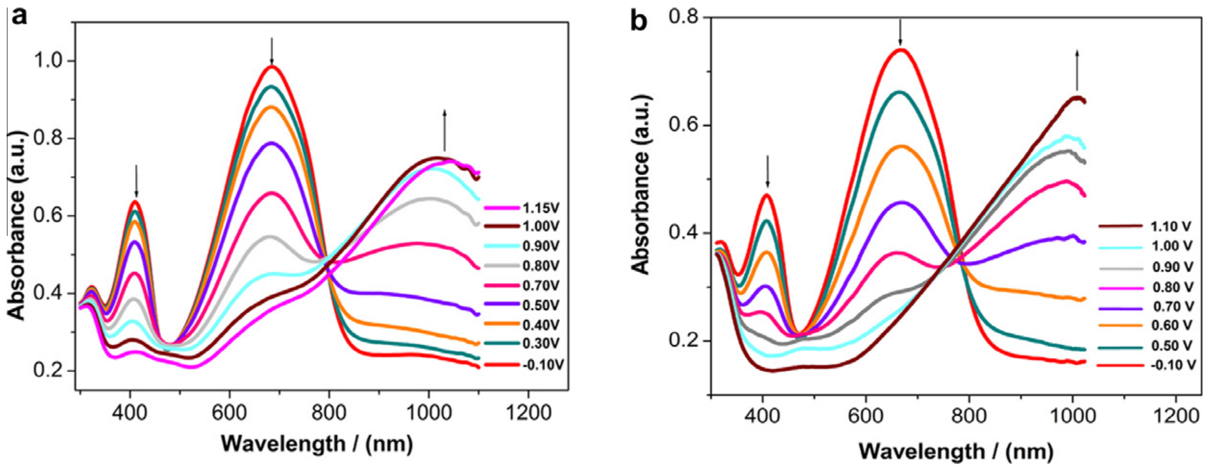


Fig. 4. Optical absorption spectra of (a) PPSP-C_4 and (b) PPSP-C_6 on ITO in 0.1 M TBAH/ACN at various applied potentials.

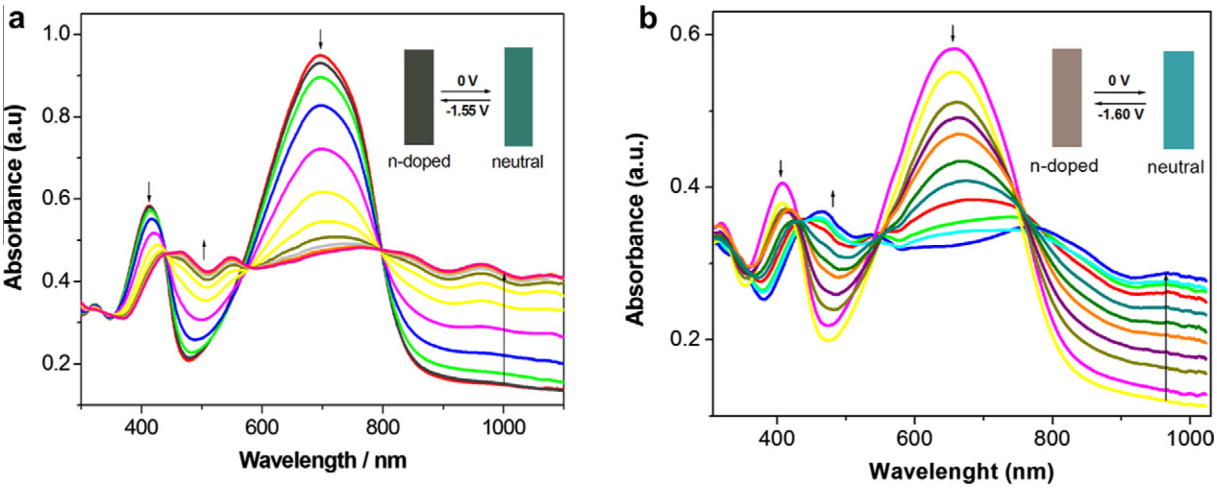


Fig. 5. Optical absorption spectra of (a) PPSP-C_4 (from 0 to −1.55 V) and (b) PPSP-C_6 (from 0 to −1.60 V) on ITO in 0.1 M TBAH/ACN at various applied potentials. Inset: Colors of (a) PPSP-C_4 and (b)PPSP-C_6 during cathodic scan.

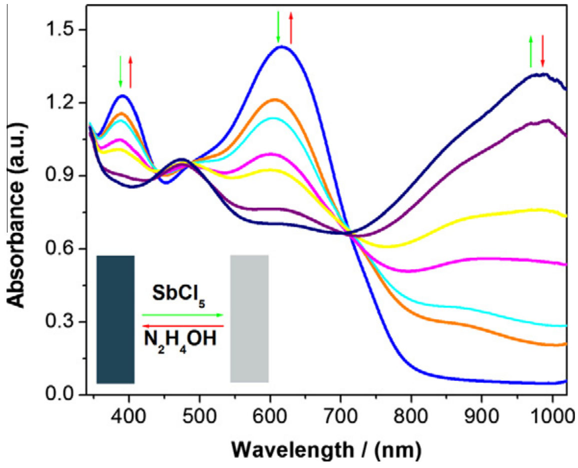


Fig. 6. Changes in optical absorption spectra of chemically obtained PPSP-C_6 in DCM solution after addition of 10 µL (for each spectrum) 5×10^{-4} M $SbCl_5$ and 10^{-2} M N_2H_5OH. Inset: Colors of PPSP-C_6 in DCM solution addition of $SbCl_5$ and N_2H_4OH.

Table 3
Optical and switching time data of PPSP-C_n. The given CE value is the best one at a corresponding wavelength.

Polymer	λ_{max} (nm)	Contrast (%T)	CE (cm^2/C)	Switching time (s)
PPSP-C_4	684	33	235	0.7
PPSP-C_6	665	39	202	0.95
PPSP-C_{10}	690	51.4	538	1.4

665 nm with a response time of 0.95 s (95% of full optical switching), the optical contrast and response time were calculated as 33% and 0.7 s at 684 nm, respectively, for PPSP-C_4. Also, those of PPSP-C_{10} were found to be 51.4% and 1.4 s at 690 nm (see Table 3 and Supporting information Fig. S14). It is important to note that the polymer films exhibited higher CEs than PEDOT (183 cm^2/C) [32,33], one of the mostly used electrochromic materials for optical devices and displays. The calculated CE values are 235 cm^2/C for PPSP-C_4, 202 cm^2/C for PPSP-C_6 and 538 cm^2/C for PPSP-C_{10} (Table 3).

It is generally considered that in solar cells the polymer film used as an electron donor part must have at least 0.3–0.4 eV more higher LUMO level than that of PCBM used as an electron acceptor part in order to provide an efficient charge separation between these parts [34,35]. Also, the HOMO level of the low band gap polymer film (lower than 1.8 eV) must have a desired position with respect to the LUMO level of the acceptor since higher HOMO level will decrease the open circuit voltage and lower HOMO level will cause to reduce the power output [36]. Based on the foregoing findings, as shown in Fig. 7, all polymers have not only desired LUMO levels with respect to the acceptor but also lower band gaps in order to match of the solar spectrum. Among the polymer films, PPSP-C_{10} polymer film has the most suitable HOMO and LUMO levels as well as the low band gap with respect to the acceptor, which means that the polymer was a potential candidate for use in solar cells.

Stability and robustness under ambient conditions are important parameters for any material for use in technological applications. For this aim, the stability of the polymer films was studied under atmospheric pressure (without purging and sweeping the electrolyte solution with inert gas) between their redox states by using a square wave potential method. As shown in Fig. 8, the polymer films are very robust and 62% and 94% of the electroactivity remains for PPSP-C_4 and PPSP-C_6, respectively, after 2000 switchings. This value is 72% for PPSP-C_{10} [19].

In endeavors to reveal the doping–dedoping mechanism of the obtained polymers, ESR measurement was carried out. For this aim, PPSP-C_{10} was dissolved in DCM and then 10^{-8} M $SbCl_5$ solution in DCM was added drop wise. After addition of each drop, an ESR spectrum had been recorded. As it can be seen from Fig. 9, before addition of $SbCl_5$, that is the polymer was in its neutral state, no signal was observed. As $SbCl_5$ solution was added drop wise, a singlet with a *g* value very close to that of free electron

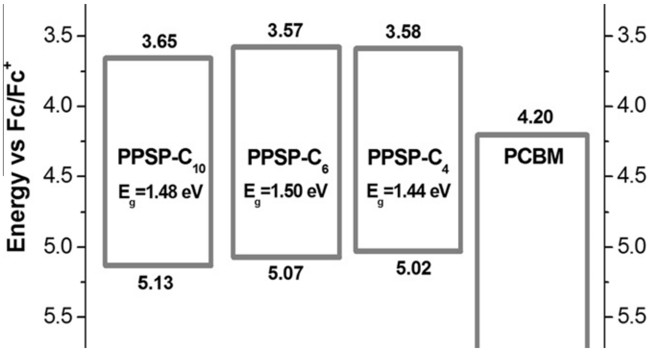


Fig. 7. Band gap diagram of PPSP-C_n polymers with respect to PCBM.

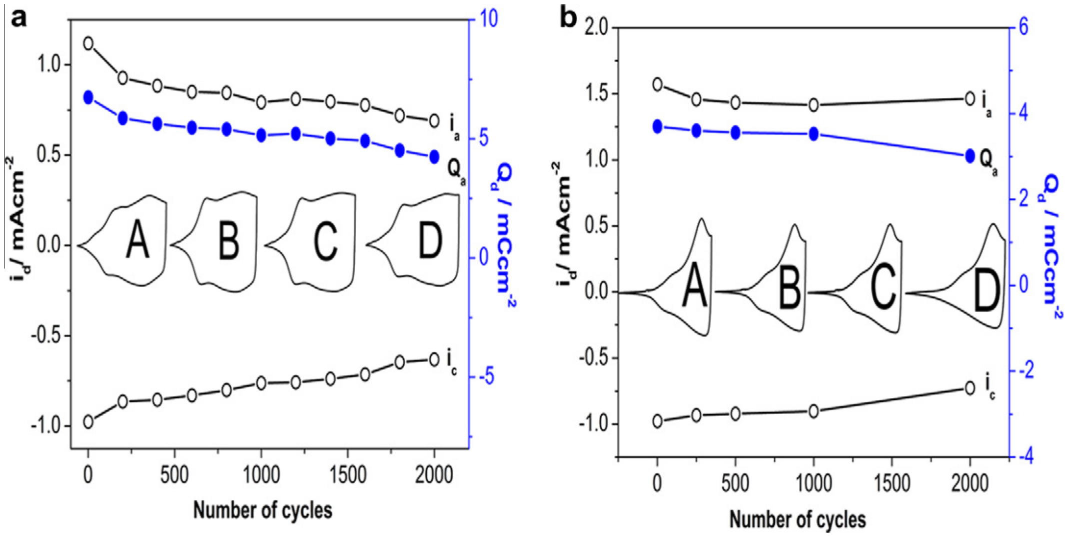


Fig. 8. Stability test for (a) PPSP-C_4 and (b) PPSP-C_6 films in 0.1 M TBAH/ACN by a square wave potential method between −0.3 and 0.6 V with 2 s intervals under ambient conditions and cyclic voltammograms of A: 1st; B: 500th; C: 1000th; D: 2000th cycles at a scan rate of 75 mV s^{-1}: Q_a: (Anodic charge stored), i_a: (anodic peak current), i_c: (cathodic peak current).

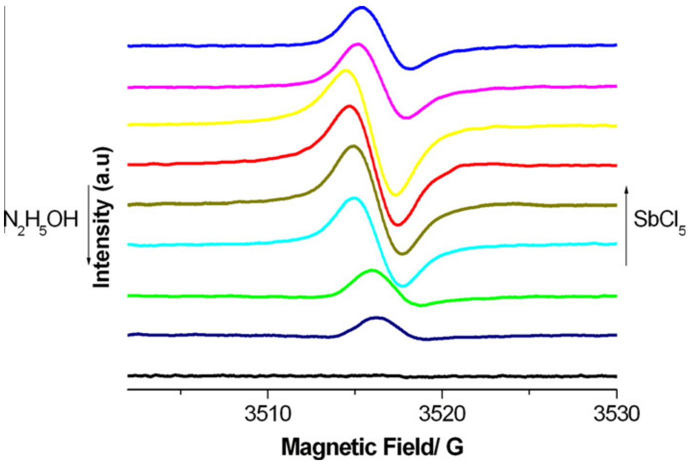


Fig. 9. ESR spectrum results of PPSP-C_{10} via addition of 10^{-8} M $SbCl_5$ and 10^{-5} M N_2H_5OH dissolved in DCM.

and linewidth $\Delta H_{pp} = 0.29$ mT value started to intensify proving the formation of the polaron charge carriers. The intensifying singlet became almost asymmetric during a point of the experiment indicating an increase in the conductivity of polymer via doping process [37]. Upon further addition of $SbCl_5$ solution causes a decrease in the intensity of the singlet signal, corresponding to the formation of bipolaron. This procedure can be reversed by drop wise addition of 10^{-5} M N_2H_5OH (Fig. 9).

The molecular weight of chemically obtained PPSP-C_6 polymer was analyzed by GPC measurements where polystyrene was used as standard and THF as solvent. The polymer had a number average molecular weight (M_n) of 10098, indicating a minimum average number of 13 repeating units including 39 heterocyclic units.

3. Conclusion

A series of dialkyl substituted ProDOT and benzothiadiazole units which were combined on D–A platform was synthesized and the effect of the alkyl chain lengths on n-doping process of the corresponding polymer films was demonstrated. It was shown that among the polymer films, dihexyl substituted PPSP-C_6 exhibited very impressive properties like processability, and ambipolar doping process (p- and n-type doping). Also, the polymer films reflected blue–green and cyan colors in their neutral states, respectively. Moreover, the change in color from cyan to highly transmissive state during oxidation makes these materials promising PEC candidates for electrochromic applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.orgel.2011.10.018.

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