

Optoelectronic Properties of Poly(2,5-dithienylpyrrole)s with Fluorophore Groups

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In this study two new, fluorophore anchored 2,5-dithienylpyrrole derivatives (SNS-Carb, SNS-Flo) were successfully synthesized via click chemistry. Both monomers were subjected to electrochemical polymerization and the corresponding polymers (PSNS-Carb and PSNS-Flo) were thoroughly characterized for their electrochromic properties. PSNS-Carb displayed yellow to blue coloration in 1.31 s with a coloration efficiency of 120 cm² C⁻¹ whereas PSNS-Flo revealed longer switching time (2.67 s) and lower coloration efficiency (78 cm² C⁻¹). Coexistence of 3,4-ethylenedioxythiophene (EDOT) with SNS-Carb or SNS-Flo in polymerization media resulted in the formation of novel copolymer films (P1 and P2, respectively) having entirely diverged multichromic, superior optoelectronic properties. P1 revealed a switching time of 1.33 s, with a coloration efficiency of 164 cm² C⁻¹, whereas P2 exhibited a slower response time (1.87 s) with a lower coloration efficiency (155 cm² C⁻¹), as in the case of their respective homopolymers. In general, P1 was shown to reveal higher ΔE values which indicate it's more noticeable and vivid color changing nature compared to P2. When the optoelectronic properties of homopolymers were compared with that of their respective copolymers, there was an explicit enhancement of the color pallet, switching time, optical contrast and coloration efficiency. (© 2015 The Electrochemical Society. [DOI: 10.1149/2.0311512]es] All rights reserved.

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Electrochromism, which refers to the reversible color change of a material upon electrochemical stimulus, have been the center of interest due to its promising commercial use in smart mirrors and windows, displays, active optical filters etc. Since the first discovery,¹ synthesis of new electrochromic materials and optimization of their optoelectronic properties have developed into an active interdisciplinary research area. Electrochromic materials could be basically subdivided as metal oxides,^{2,3} molecular dyes⁴ and conducting polymers.^{5,6} Although all the conducting polymers are potentially electrochromic, most of them are not of practical utility, since the commercial applications mandate some limitations on properties such as the color tone, switching time, optical contrast, coloration efficiency and stability. Therefore, there is an ongoing research on assessment of the factors affecting the optoelectronic properties of conducting polymers. Up to date, significant progress has been achieved by critical control of polymer chain structure through substitution of the repeating unit and utilization of terarylene monomers, which combine two heteroaromatic building blocks with a central aromatic unit.

Among conducting polymers, polypyrrole (PPy) and polythiophene (PTh) derivatives are by far the most extensively studied polymers due to their suitable oxidation potential, tolerable environmental stability and well developed synthetic chemistry. Lately, tailoring of the main chain of conducting polymers through association of thiophene and pyrrole units has been considered to be a rational, powerful approach⁷ for achieving electrochromic materials with distinct electronic and optical properties. Among these polymers, poly(2,5dithienylpyrrole) (PSNS) derivatives, which were generally synthesized by electrochemical or chemical polymerization of a thiophenepyrrole-thiophene trimeric unit, were examined in detail. Studies indicated that PSNS derivatives show low oxidation potential, relatively high electrochemical stability, and chromatic variation upon substitution through the central pyrrole unit.⁸⁻¹³ Hence, derivatization of basic PSNS structure with various groups has been considered as an exciting approach to manipulate the properties of these polymers. In this context, recently our group proposed utilization of Huisgen 1,3dipolar cycloaddition click reaction as an effective route for effortless synthesis of new monomers with substituents such as ferrocene,¹⁴ pyrene,¹⁵ and 1,8-naphthalimide.¹⁶ As a part of a broad survey, this study focuses on synthesis and electrochemical polymerization of two new SNS monomers (SNS-Flo, SNS-Carb) which are appended with fluorophore groups such as fluorene and carbazole, respectively. Moreover, fine tuning of optoelectronic properties of SNS-Flo and SNS-Carb based polymers was accomplished via copolymerization with 3,4-ethylenedioxythiophene (EDOT), where an impressive set

of multichromic polymers with enhanced electrochromic properties was realized. The characterization and investigation of optoelectronic properties of all polymers were elucidated via cyclic voltammetry (CV), FTIR, spectroelectrochemistry, kinetic and colorimetry studies.

Experimental

General.— The chemicals used for the synthesis of the monomers were purchased from Aldrich or Merck Chemicals as reagent grade. Lithium perchlorate was used in electroanalytical grade. Acetonitrile (ACN) was distilled over calcium hydride and it was kept on 4 Å molecular sieves. 1 1-(2-azido-ethyl)-2,5-dithiophen-2-yl-1H-pyrrole (SNS-N₃) was synthesized according to literature.¹⁷

Equipments.— NMR spectra were recorded with a Bruker Avance Spectrometer at 300 MHz for ¹H NMR and at 75 MHz for ¹³C NMR, with Bruker Spectrospin Avance DPX-400 spectrometer at 400 MHz for ¹H NMR and at 100 MHz for ¹³C NMR, with Varian Inova 500 Spectrometer at 500 MHz for ¹H NMR and at 250 MHz for ¹³C NMR. The FTIR spectra were recorded on a Brucker Tensor 27 spectrometer. Mass spectra (MS) were obtained on a Finnigan MAT 95 spectrometer. Varian Cary Eclipse was used for fluorescence spectroscopy studies. Electrochemical synthesis and cyclic voltammetry studies were performed on Ivium stat potentiostat/ galvanostat under argon atmosphere. A platinum wire was used as the counter electrode and Ag/Ag⁺ electrode was used as the reference electrode. Thermo Evolution Array UV-Visible spectrophotometer was utilized for spectroelectrochemistry and kinetic studies. 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. Provided L*,a*,b* data were calculated through conversion of Y,x,y values of each color and the standard illuminant (with a blank, bare ITO proper electrolyte) to tristimulus values. ΔE^* , which defines the difference between two colored states, were calculated according to the following formula $\Delta E_{ab}^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}.$

Synthesis of alkyne functionalized fluorophores.— The mixture of carbazole (4.175 g, 25 mmol) and metallic sodium (0.575 g, 25 mmol) in dioxane (20 ml) was refluxed under inert atmosphere until metallic sodium was completely dissolved. Later, propargyl bromide (3.38 ml, 39 mmol) was added into the mixture. The solution was cooled to room temperature and stirred for 18 h. Finally, water was added and the mixture was extracted with CH_2CI_2 . The organic phase was dried with NaSO₄ and filtered. The solvent was removed under vacuum and the residue was purified by column chromatography

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(10:1 Hexane/Ethyl acetate) to yield 9-(prop-2-yn-1-yl)-9H-carbazole (%76). Alkyne functionalized fluorene (2-ethynyl-9,9-dimethyl-9H-fluorene) was synthesized according to the literature¹⁸ with a yield of 75%. For 9-(prop-2-yn-1-yl)-9H-carbazole: ¹H NMR (500 MHz, CDCl₃): δ 8.12 (d, J = 7.8 Hz, 2H), 7.49–7.54 (m, 4H), 7.28–7.31 (m, 2H), 5.04 (dd, J = 1.0, 2.4 Hz, 2H), 2.26 (t, J = 2.4 Hz, 1H). APT NMR (125 MHz, CDCl₃): δ 139.81 (C_{quat}), 125.86 (CH), 123.24 (C_{quat}), 120.41 (CH), 119.55 (CH), 108.69 (CH), 77.83 (C_{quat}), 72.20 (CH*, alkyne), 32.23 (CH₂). For 2-ethynyl-9,9-dimethyl-9H-fluorene: ¹H NMR (500 MHz, CDCl₃): δ 7.72–7.71 (m, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.48–7.50 (m, 1H), 7.43–7.45 (m, 1H), 7.32–7.36 (m, 2H), 3.13 (s, 1H), 1.48 (s, 6H). APT NMR (125 MHz, CDCl₃): δ 153.85 (C_{quat}), 153.47 (C_{quat}), 139.88 (C_{quat}), 138.30 (C_{quat}), 131.18 (CH), 127.76 (CH), 127.06 (CH), 126.41 (CH), 122.60 (CH), 120.39 (C_{quat}), 120.31 (CH), 119.82 (CH), 84.43 (C_{quat}), 77.00 (CH*, alkyne), 46.79 (C_{quat}), 26.92 (CH₃).

Synthesis of SNS-Carb and SNS-Flo. - 0.5 mmol SNS-N₃, 0.5 mmol alkyne functionalized fluorophore were dissolved in THF (5 ml) and then water (5 ml), 1 M CuSO₄.5H₂O (0.1 ml), 1 M sodium ascorbate (0.17 ml) were added into the reaction media, consecutively. The mixture was stirred at room temperature for 3 h. Later, THF was evaporated and the reaction mixture was extracted with CH₂CI₂/H₂O. Finally, the residue was subjected to column chromatography (3:1 DCM/Hexane for SNS-Flo, and 5:1 DCM/Hexane for SNS-Carb) to yield SNS-Flo (0.19 g, 77%) and SNS-Carb (0.20 g, 80%). For SNS-Carb: ¹H NMR (400 MHz, Chloroform-d) δ 8.06 (d, J = 7.7 Hz, 2H), 7.46 - 7.36 (m, 5H), 7.22 (dd, J = 7.8, 1.4 Hz, 2H), 7.09 (d, J = 6.3 Hz, 2H), 6.50 (d, J = 4.6 Hz, 2H), 6.12 (s, 1H), 5.80 (s, 2H), 5.47 (s, 2H), 4.41 (t, J = 6.0 Hz, 2H), 4.09 (t, J = 6.0 Hz, 2H). MS $C_{29}H_{23}N_5S_2$ (m/z): calculated 505.66, found 505. For SNS-Flo: ¹H NMR (300 MHz, Chloroform-d) δ 7.95 - 7.86 (m, 1H), 7.79 -7.71 (m, 2H), 7.58 (dd, J = 7.9, 1.5 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.37 - 7.32 (m, 3H), 7.07 (dd, J = 5.2, 3.6 Hz, 2H), 6.98 - 6.92 (m, 3H), 6.41 (s, 2H), 4.71 (t, J = 6.1 Hz, 2H), 4.42 (t, J = 6.1Hz, 2H), 1.54 (d, J = 3.4 Hz, 6H). ¹³C NMR (75 MHz, CDCl3) δ 154.30, 153.90, 148.54, 139.26, 138.77, 133.57, 129.45, 128.89, 127.71, 127.40, 127.03, 126.71, 126.18, 124.76, 122.65, 120.27, 120.15, 120.05, 119.92, 111.97, 49.54, 46.99, 44.88, 27.17.

Electrochemical synthesis.— PSNS-Carb and PSNS-Flo films were synthesized by the electrochemical polymerization of their respective SNS monomers (0.01 M) in 0.1 M LiCIO₄/ACN on ITO electrodes. In either case the electrochemical polymerization was achieved through potentiodynamic cycling between 0.0 V to 1.0 V with a scan rate of 100 mV/s. P1 was synthesized in a mixture of SNS-Carb (0.01 M) and EDOT (0.005 M) in 0.1 M LiCIO₄/ACN media via potentiodynamic cycling between 0.0 V to 1.0 V with a scan rate of 100 mV/s. Similar procedure was applied for the synthesis of P2 where the electrolysis media contained SNS-Flo (0.01 M) and EDOT(0.005 M).

Results and Discussion

Synthesis.— First (9,9-dimethyl-9H-fluoren-2-yl)ethynyl) trimethylsilane (1) was synthesized through Sonogashira crosscoupling reaction of 2-bromo-9,9-dimethyl-9H-fluorene with trimethylsilyl acetylene in the presence of $PdCl_2(PPh_3)_2$ and CuI and NEt₃. Later, (1) was treated with KOH to afford 2-ethynyl-9,9dimethyl-9H-fluorene in 75% yield. 9-(prop-2-yn-1-yl)-9H-carbazole (2), on the other hand, was synthesized through one pot reaction of carbazole with propargyl bromide in the presence of metallic sodium. Chemical structure of the products were verified by FTIR, ¹H NMR and ¹³C NMR analyses, where alkylenation reactions were followed by presence of the typical acetylenic stretching around 2120 cm⁻¹ in FTIR spectra and by the signals around 2.26–3.13 ppm in ¹H NMR spectra of (1) and (2). The final products (SNS-Carb and SNS-Flo) were readily prepared by click reaction of alkyne functionalized fluorophores (Scheme 1) with SNS- N_3 with yields higher than 75%. ¹H NMR spectra of both monomers displayed resonance signals of 2,5-dithienylpyrrole unit at around 7.3–6.4 ppm. In addition, ¹H NMR spectra of both SNS-Carb and SNS-Flo revealed typical resonance characteristic of their respective fluorophore groups around 8.06-7.36 ppm and 7.91-7.35 ppm, respectively. The chemical structure of the monomers was further supported via ¹³C NMR, FTIR and MS studies.

The UV–visible absorption spectra and photoluminescence (PL) emission spectra for the alkyne functionalized fluorophores, SNS-N₃, SNS-Flo and SNS-Carb were recorded in ACN (Figure 1). SNS-N₃ revealed a single, broad π to π^* absorption centered around 310 nm and its maximum emission wavelength was about 415 nm. The fluorophores, on the other hand, revealed multiple absorption peaks, which correspond to S₀ to S₁* transitions to different vibrational levels. As seen in Figure 1c and Figure 1f, the absorption spectra of both SNS-Carb and SNS-Flo are a linear combination of the spectra of their corresponding fluorophore and SNS-N₃. PL spectra of both monomers



Figure 1. Absorption and emission spectra of a) alkyne functionalized carbazole, b) SNS-N₃, c) SNS-Carb, d) alkyne functionalized fluorene, e) SNS-N₃ and f) SNS-Flo in ACN (excitation 310 nm).

are dominated by the intense broad signal at 415 nm, which is in accordance with the emission spectrum of $SNS-N_3$.

Electrochemistry of SNS derivatives.-Electrochemical polymerization mechanism^{7,19} of 2,5-dithienylpyrrole derivatives was postulated by considering the formation of radical-cation of the trimeric unit (thiophene-pyrrole-thiophene), coupling of radical-cations and deprotonation of the dimer. Continuous chain growth is achieved by the further oxidation of the dimer which affords oligomers and so on. Figures 2a and 2b depict the redox behavior of the monomers, which were recorded in 0.1 M LiCIO₄/ACN media via cyclic voltammetry. As expected, due to their trimeric nature both monomers oxidized at lower potentials than pristine pyrrole (1.1 V) and thiophene (1.8 V). Comparison of the oxidation potentials of SNS-Carb ($E_{ox}^{m} = 0.93$ V) and SNS-Flo ($E^{m}_{ox} = 0.91$ V) with SNS-N₃ ($E^{m}_{ox} = 0.87$ V) reveals the limited influence of the substituents on monomer oxidation, which could be ascribed to the minor deviations from coplanarity of the trimeric molecule due to steric restrictions generated by the bulky fluorophore groups.²⁰

Upon repetitive cycling, formation of a new, lower potential reversible redox couple ($E_{P1/2} = 0.60$ V, $E_{P1/2} = 0.59$ V, respectively) was observed for both SNS-Carb and SNS-Flo, with a simultaneous increase in the current intensities after each cycling. Such observation indicated the enlargement of the surface area of the working electrode due to grafting of a conducting polymer on the electrode. Despite coloration of polymerization medium, which presumably indicated the leakage of oligomers, the thickness of the PSNS-Carb film gradually enhanced with the increase in number of scans. However, in case of potentiodynamic cycling of SNS-Flo, leakage of oligomers from the electrode surface was more severe and the linear correlation between the film thickness and number of scans was valid up to a lower extent. The lower film forming ability of PSNS-Flo could be related with higher solubility of its oligomers which might stem from the alkyl substitution of the fluorene unit.

In order to elucidate the redox behaviors, the polymers were subjected to linear sweep voltammetry in the monomer-free electrolyte solution (Figures 2c, 2d). Both polymer films exhibited a reversible redox couple (for PSNS-Carb Ep,a = 0.78 V and Ep,c = 0.51 V,



Figure 2. Cyclic voltammogram of a) SNS-Carb, b) SNS-Flo at 100 mV/s and c) PSNS-Carb, d) PSNS-Flo at various scan rates in 0.1 M LiCIO₄/ACN, plot of anodic and cathodic peak current density vs. scan rate for e) PSNS-Carb, f) PSNS-Flo.

for PSNS-Flo Ep,a = 0.82 V and Ep,c = 0.49 V). Intensity of the redox couple revealed a linear proportionality with the scan rate. This confirms the formation of an electro-active, surface confined material with non-diffusional redox process.²¹

Electrochromic properties of PSNS-Carb and PSNS-Flo.—Electrochromic response of a conducting polymer is based on reversible creation and destruction of charge carriers (polarons and bipolarons), which are signified by the evolution of new, lower energy absorption bands. Spectroelectrochemistry, which allows probing of the spectral variations as a function of electrochemical stimuli, is an eminent technique for elucidating optoelectronic properties of conducting polymers. Figure 3a represents the spectroelectrochemistry study of PSNS-Carb in monomer free electrolyte media, where a series of spectra were recorded while sequentially stepping the applied potential.

At -0.2 V (neutral state) PSNS-Carb revealed well-defined, multiple absorptions (π - π^* transition) at 330 nm and 345 nm with a shoulder at 370 nm. On the other hand, PSNS-N₃ (the PSNS derivative without fluorophore groups) showed a broad, featureless absorption band at 345 nm at neutral state with a band gap of 2.49 eV.¹⁷ The polymer displayed yellow to blue coloration upon doping. Band gap of PSNS-Carb was calculated through the lower energy edge of its absorption spectrum as 2.5 eV. Upon electrochemical oxidation of PSNS-Carb, intensity of π - π^* transition decreased, whereas new absorption bands located around 615 nm and 950 nm emerged simultaneously. At this state PSNS-Carb appeared as blue. Figure 3b represents the spectroelectrochemistry studies of PSNS-Flo. In neutral state the polymer had absorption bands (π - π^* transition) at 323 and 375 nm (shoulder) with a bandgap of 2.59 eV. Upon oxidation, the intensity of π - π^*



Figure 3. Spectroelectrochemistry of a) PSNS-Carb and b) PSNS-Flo films on an ITO coated glass slide in 0.1 M LiCIO₄/ACN.

transition declined slightly while charge carrier bands located around 620 and 940 nm evolved. The polymer appeared in light yellow and blue in neutral and oxidized states, respectively. However, it was not possible to fully oxidize either polymer.

Although absorption spectrum of an electrochromic film (in visible region) provides an objective measure for color absorption, it offers little insight on how it is perceived by human eye. Since color appearance depends on the light source, the sample size, the observer and the surrounding colors, the field of colorimetry has been developed for description of color in an objective manner.²² Hence, we have utilized in-situ colorimetric analysis for quantitative examination of PSNS derivatives at various states as reflected in Table I.

In order to explore the switching characteristics of PSNS-Carb, a square wave potential step method coupled with simultaneous transmittance probing was performed. In this experiment, the initial potential was set at 0.0 V (according to spectroelectrochemistry study, neutral state) for 10 s, and it was stepped to 1.0 V (ultimate oxidation) for the same period of time. The percent transmittance change during this repetitive doping and de-doping process was simultaneous monitored at 900 nm and the switching time (t_{95}) , which is the response time required to attain 95% of total the transmittance difference, was calculated. Figure 4a represents the transmittance variations of PSNS-Carb in 0.1 M LiCIO₄/ACN. The polymer was found to reveal yellow to blue coloration in 1.31 s with an optical contrast of 27.78%. Similar to PSNS-Carb, PSNS-Flo was also subjected to kinetic studies while the potential was consecutively stepped from the neutral, light yellow state (0.0 V for 10 s), to blue state (1.0 V for 10 s). The switching time (t_{95}) of PSNS-Flo, was estimated as 2.67 s and the ultimate transmittance variation was recorded as 5.53%. Such a low optical contrast is valid with the spectroelectrochemistry studies, where PSNS-Flo revealed a lower extent of decline in the intensity of the π - π * transition upon oxidation compared to PSNS-Carb.

Another important, frequently used tool for evaluation of electrochromic materials is coloration efficiency (CE) measurements. As illustrated below, CE describes the relationship between the injected/ejected charge and change in optical density (Δ OD).²³ Materials which exhibit high optical contrast with a small amount of charge are known to have high CE. To elucidate the CE of PSNS derivatives the tandem chronoabsorptometry/chronocoulometry experiment was used at 95% of the maximum change of transmittance, where quantity of injected charge was attained through the integration of the current. Coloration efficiencies of PSNS-Carb and PSNS-Flo were estimated as 120 and 78 cm² C⁻¹, respectively.

$$CE(\lambda) = \Delta OD(\lambda) / (Q/A)$$
 [1]

Electrochemical copolymerization.—Tuning of electrochromic properties of conducting polymers is not only limited with the controlled polymerization of specifically designed monomers, but also it could be accomplished through techniques such as copolymerization and lamination. Electrochemical copolymerization, which amalgamates the advantages of the electrochemical techniques and copolymerization, is a robust, eminent technique for diversification of conducting polymers. Hence, this part of the work details the electrochemical and optoelectronic properties of SNS-Carb and SNS-Flo based copolymer films which were synthesized in the presence of EDOT (readily available, relatively cheap heteroaromatic compound).

Selection of a proper co-monomer with a suitable oxidation potential is the key for a successful electrochemical copolymerization, since its mechanism involves formation of radical cations of both components. Thus, overlapping of the oxidation potentials of the comonomers is mandatory for achieving true copolymers. The onset of oxidation potential of EDOT was recorded as 0.85 V in LiCIO₄/ACN. Since the oxidation potentials of both SNS-Carb and SNS-Flo were around 0.8 V, it is valid to assume formation of their radical cations in the same potential window with EDOT. Figures 5a, 5b represents the first anodic polarization curve of SNS-Carb and SNS-Flo in the presence of EDOT, where the typical redox behavior of both SNS derivatives and EDOT was observed. The well-defined redox peaks around 0.8 V and a steady increase in current density beyond 0.85 V for both SNS-Carb/EDOT and SNS-Flo/EDOT mixtures, signified the formation of radical cations of SNS derivatives and EDOT, respectively. Moreover, upon successive cycling between 0.0 V and 1.0 V, evolution of a lower potential, quasi-reversible redox couple showing a simultaneous increase in the current intensity after each cycling, was observed for both systems, which indicated the formation of a copolymer.

Figures 5c, 5d show the linear sweep voltammograms of P1 and P2 films in 0.1 M ACN/LiCIO₄ at different scan rates, where the abbreviations P1 and P2 refers to the copolymers which were synthesized in SNS-Carb/EDOT and SNS-Flo/EDOT mixtures, respectively. For both copolymers a proportional increase in the current intensity was observed with the increase in the scan rate. When the redox potentials of the copolymers ($E_{P,a} = 0.65 \text{ V}$ (P1), $E_{P,c} = 0.37 \text{ V}$ (P1) and $E_{P,a} = 0.65 \text{ V}$ (P2), $E_{P,c} = 0.32 \text{ V}$ (P2)) are compared with that of their respective homopolymers (Figures 2c, 2d), there is a clear cathodic shift. Taking into account the lower oxidation potential of pristine PEDOT,²⁴ cathodic shifting of redox potentials could be considered as an indirect indication for the reaction between the SNS and EDOT units, where the electron-rich EDOT unit could raise the HOMO of PSNS derivatives.

Electrochromic properties of P1 and P2.—Investigation of optoelectronic properties of a copolymer not only provides a powerful insight about its electrochromic properties but also offers a valid evidence for effective copolymerization through comparison of the spectral behaviors of the copolymer with that of parent homopolymers. Figure 6a represents spectroelectrochemical analysis of P1 in 0.1 M ACN/LiCIO₄. It can be seen that at -0.2 V (neutral state) P1 revealed two sets of absorption bands centered at 330–343 nm and 455 nm and appeared in ruby color. PSNS-Carb, on the other hand, appeared in yellow with a single set of absorption band with fine features (330–345 nm) at this state. Meanwhile, PEDOT exhibited a single, broad, featureless transition around 590 nm (Eg = 1.71 eV) and appeared in blue in neutral state. P1 had a bandgap of 1.80 eV which is significantly lower

| Material | | PSNS-Car | b | | P1 | | | PSNS-Flo | | | P2 | | |
|-------------------------------|-------|------------|-------|-------|------------|-------|------|----------|-------|-------|------------|-------|--|
| λ _{max} (nm) | | 330,345,37 | /0 | | 330,343,45 | 5 | | 323,375 | | | 323,490 | | |
| Eg (eV) | | 2.50 | | | 3.49, 1.80 | | | 2.59 | | | 3.56, 1.81 | | |
| to5 | | 1.31 | | | 1.33 | | | 2.67 | | | 1.87 | | |
| Optical Contrast $\Delta T\%$ | 27.78 | | | 34.75 | | | 5.53 | | | 31.26 | | | |
| $CE (cm^2/C)$ | | 120 | | | 164 | | | 78 | | | 155 | | |
| Colorimetry Data | Y | x | У | Y | x | У | Y | x | У | Y | x | у | |
| At -0.2 V | 793 | 0.371 | 0.399 | 597 | 0.426 | 0.405 | 1010 | 0.373 | 0.401 | 813 | 0.386 | 0.387 | |
| At 0.0 V | 841 | 0.375 | 0.402 | 631 | 0.426 | 0.410 | 999 | 0.374 | 0.402 | 866 | 0.387 | 0.389 | |
| At 0.1 V | 826 | 0.376 | 0.403 | 683 | 0.423 | 0.416 | 999 | 0.375 | 0.401 | 896 | 0.387 | 0.395 | |
| At 0.2 V | 854 | 0.377 | 0.404 | 727 | 0.413 | 0.422 | 1030 | 0.375 | 0.403 | 930 | 0.381 | 0.399 | |
| At 0.3 V | 868 | 0.378 | 0.405 | 785 | 0.398 | 0.423 | 1030 | 0.376 | 0.403 | 971 | 0.376 | 0.401 | |
| At 0.4 V | 835 | 0.376 | 0.403 | 714 | 0.378 | 0.417 | 1020 | 0.375 | 0.403 | 994 | 0.369 | 0.400 | |
| At 0.5 V | 737 | 0.364 | 0.394 | 688 | 0.360 | 0.400 | 1010 | 0.373 | 0.402 | 995 | 0.361 | 0.396 | |
| At 0.6 V | 606 | 0.348 | 0.378 | 598 | 0.344 | 0.381 | 931 | 0.363 | 0.394 | 937 | 0.350 | 0.382 | |
| At 0.7 V | 529 | 0.341 | 0.364 | 531 | 0.339 | 0.369 | 819 | 0.351 | 0.382 | 917 | 0.348 | 0.377 | |
| At 0.8 V | 478 | 0.345 | 0.360 | 508 | 0.342 | 0.365 | 703 | 0.350 | 0.373 | 891 | 0.350 | 0.375 | |
| At 0.9 V | 435 | 0.349 | 0.359 | 482 | 0.343 | 0.364 | 639 | 0.354 | 0.370 | 867 | 0.351 | 0.375 | |
| At 1.0 V | 370 | 0.352 | 0.361 | 415 | 0.345 | 0.366 | 574 | 0.359 | 0.371 | 848 | 0.352 | 0.376 | |
| At 1.1 V | 300 | 0.355 | 0.364 | 339 | 0.347 | 0.370 | 510 | 0.365 | 0.375 | 818 | 0.353 | 0.377 | |
| At 1.2 V | 254 | 0.360 | 0.366 | 298 | 0.350 | 0.371 | 457 | 0.374 | 0.378 | 785 | 0.354 | 0.377 | |

Table I. Electrochromic properties of PSNS-Carb, PSNS-Flo, P1 and P2.

than that of PSNS-Carb (2.50 eV). The lowering of the band gap and subsequent diversification of the color of the copolymer with respect to PSNS-Carb could be attributed to the increase in the content of the electron-rich heteroaromatic units (inclusion of EDOT units through copolymerization) within the backbone of P1, which could to raise

the HOMO of the polymer and lower the bandgap. When the applied potential increased, the two-band absorption of P1 (330–343 nm and 455 nm) in the visible region were simultaneously depleted with appearance of the polaronic charge transition bands around 800 nm. As the applied potential further increased, polaronic transitions merged



Figure 4. T% variations of a) PSNS-Carb and b) PSNS-Flo monitored at 900 nm, charge density variations of c) PSNS-Carb and d) PSNS-Flo during repetitive switching in 0.1 M LiCIO₄/ACN.

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Figure 5. Cyclic voltammogram of a) SNS-Carb/EDOT, b) SNS-Flo/EDOT at 100 mV/s and c) P1, d) P2 at various scan rates in 0.1 M LiCIO₄/ACN and plot of anodic and cathodic peak current density vs. scan rate for e) P1, f) P2.

into the broader bipolaronic transition, which entail in to the visible region. When fully oxidized, P1 film showed a dramatic absorption within NIR region. Such impressive set of spectral variations resulted in multichromic behavior where the polymer displayed vivid color changes from ruby (-0.2 V) to various tones of orange (0.1 V), yellow (0.3 V), green (0.4 V), blue (0.7 V) to gray (1.2 V) upon oxidation. To objectively elucidate the color of P1, colorimetric measurements were performed, and photographs were obtained at each potential. Figure 7a represents the x,y data (CIE 1931) of P1 at various potentials which are completely different from that of PSNS-Carb.

The divergence of color is objectively evaluated through ΔE_{ab}^* (color difference) which is the Euclidian distance between two points in CIE 1976 color space. Basically, a large color difference (large ΔE) indicates the greater difference between the two colored states. ΔE_{ab}^* equal to 2.3 refers to the "just noticeable difference" (JND) threshold, where the values less than 2.3 signifies that the difference between the two colors is perceptually indistinguishable. On the contrary, ΔE_{ab}^* values higher than 4 indicate that the two colors are noticeably different from one another. Table II reflects the L*a*b* data (CIE-1976) of P1 at different potentials and the calculated ΔE^* values between each states. As we could see the ΔE values for ruby to orange, orange to yellow, yellow to green, green to blue and ruby to blue transitions are almost always higher than 7, which are well above the JND, indicating the visually apparent, vivid color change of P1 upon amplification of applied potential.

To evaluate the speed at which the color change takes place a chronoabsorptometry/chronocoulometry study was performed on P1 under repeated cycling between 0.0 V and 1.0 V in square wave form at 900 nm. P1 displayed color variation in less than 1.33 s, which is close to PSNS-Carb. As seen in Figure 8a, P1 exhibited higher transmittance change (34.75%) and higher CE (164 cm² C⁻¹) compared to PSNS-Carb. The substantial improvement of CE upon copolymerization could be attributed to the inclusion of EDOT moieties within PSNS-Carb chain backbone, which lowers the oxidation potential and might provide higher accessibility to the doping sites.

To evaluate the electrochromic properties of P2, similar type of studies were conducted. Figure 6b represents the spectroelectrochemistry study of P2 in 0.1 M ACN/LiCIO₄ which was recorded during



Figure 6. Spectroelectrochemistry of a) P1 and b) P2 films on an ITO coated glass slide in 0.1 M LiCIO₄/ACN.

gradual amplification of applied potential from -0.2 V to 1.2 V. At neutral state P2 displayed two maxima at 323 nm and 490 nm and the polymer film appeared in boysenberry color. As the applied potential increased, evolution of polaronic charge carrier bands was clearly observed at around 800 nm with a concurrent decrease in higher energy bands. Beyond 0.5 V a very broad, overwhelming bipolaronic charge carrier band gradually intensified while the residual absorption at 325 nm remained as of PSNS-Flo. In accordance, the copolymer revealed multichromic behavior, displaying a wide range of colors from boysenberry to various tones of orange, yellow, green, blue and gray, which were objectively evaluated by the colorimetry studies (Table I). When the ΔE values for these color transitions were calculated, we could state that all the color transitions are noticeable by an average person, but not as obviously and vividly as P1. Figure 8b represents the % transmittance change (900 nm) of P2 upon repeated stepping of the polarization potential between 0.0 V and 1.0 V. P2 exhibited an optical contrast of 31.26%, which was determined through the transmittance difference between the two extreme redox states. The current and charge responses accompanying the transmittance (color) change were uniform. P2 had a switching time of 1.87 s and a CE of 155 cm² C⁻¹, which are significantly improved compared to that of PSNS-Flo.

Among many other factors, the critical role of film morphology on switching properties of the conducting polymers is generally acknowledged in literature. In a general perspective the polymer films having more open morphology are expected to provide smaller diffusion distance for the dopant ions and thereby they allow effective doping-dedoping with shorter switching times.^{25–28} Figure 9 represents the SEM images (under the same magnification) of P1, P2 and

Table II. CIE 1976 data and calculated ΔE values of PSNS-Carb, PSNS-Flo, P1 and P2 at various states.

| PSNS-Carb | P1 | PSNS-Flo | P2 |
|--------------------------------------|--------------------------------------|---|---|
| (V) Color L* a* b* ΔE_{ab}^* | (V) Color L* a* b* ΔE_{ab} * | (V) Color $L^* a^* b^* \Delta E_{ab}^*$ | (V) Color $L^* a^* b^* \Delta E_{ab}^*$ |
| -0.2 V Yellow 84 -3 13 | -0.2 V Ruby 78 15 27 | -0.2 V Light Yellow 90 -2 12 7 00 | -0.2 V Boysen-berry 85 8 9 |
| 0.6 V Green 76 -4 0 | 0.1 V Orange 82 11 32 | 0.6 V Green 87 -4 6 | 0.1 V Orange 88 6 13 |
| 0.7 V Blue 72 $-1 -6$ | 0.3 V Yellow 87 0 29 | 0.7 V Blue $82 - 4 - 1$ | 0.2 V Yellow 90 2 13 |
| 1.1 V Gray 56 3 -3 | 0.4 V Green 84 -6 21 | 1.1 V Gray 68 4 0 | 0.3 V Green 91 -1 13 |
| | 0.7 V Blue 74 -4 -5 | | $\begin{array}{cccc} 16.25 \\ 0.7 \text{ V} & \text{Blue} & 89 & -3 & -3 \end{array}$ |
| | 15.81 1.2 V Gray 59 0 -2 | | 1.2 V Gray 84 0 -2 |
| -0.2 V Yellow 84 -3 13 32.80 | -0.2 V Ruby 78 15 27 37.78 | -0.2 V Light Yellow 90 -2 12 25.77 | -0.2 V Boysen-berry 85 8 9 13.64 |
| 1.1 V Gray 56 3 -3 | 1.2 V Gray 59 0 -2 | 1.1 V Gray 68 4 0 | 1.2 V Gray 84 0 -2 |
| a) | 0.3V 0.2 V |]b) | 0.3 V |
| 0.42 - | 0.4 V 0.1 V | 0.40 - | 0.4 V 0.2 V |

0.0 V 0.5 \ 0.1 V 0.40 0.39 0.0 V -0 2 V 0.6 0.38 0.38 0.9 V P2 0.36 0.8 0.36 0.38 0.40 0.42 0.37 0.34 0.35 0.36 0.38 0.39 x х

Figure 7. x,y data of a) P1 and b) P2.

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Figure 8. T% variations of a) P1 and b) P2 monitored at 900 nm, current density variations of c) P1 and d) P2 and charge density of e) P1 and P2 during repetitive switching in 0.1 M LiCIO₄/ACN.



Figure 9. SEM micrographs of a) P1 (1000 X), b) P2 (1000 X) and c) PEDOT (1000 X).

PEDOT which were synthesized under identical conditions. As we could see P2 film showed a dense, uniform compact structure with a lower surface roughness, whereas PEDOT film revealed a porous, cauliflower type of morphology. P1, on the other hand, revealed globular morphology having less compact structure compared to P2, which is in accordance with calculated switching times of the respective copolymers.

Conclusions

In this study we have synthesized two new SNS monomers (SNS-Carb, SNS-Flo) which are appended with fluorophore groups such as fluorene and carbazole. Both monomers were subjected to electrochemical polymerization in 0.1 M LiCIO₄/ACN and optoelectronic properties of their corresponding polymers (PSNS-Carb, PSNS-Flo) were investigated by means of electrochemical and spectroscopic methods. PSNS-Carb displayed yellow to blue coloration in 1.31 s with a coloration efficiency of $120 \text{ cm}^2 \text{ C}^{-1}$. PSNS-Flo, on the other hand, revealed yellow to gray coloration in 2.67 s with a coloration efficiency of 78 cm² C⁻¹. In order to enhance the available color pallet, electrochemical copolymerization of SNS-Carb and SNS-Flo in the presence of 3,4-ethylenedioxythiophene were performed. The resultant copolymers (P1 and P2, respectively) displayed astonishing sets of colors which were thoroughly examined via colorimetry studies according to CIE standards. Moreover, for both copolymers the color difference between their states was evaluated through calculation of ΔE . In general P1 was shown to reveal higher ΔE values, which indicates it's more noticeable and vivid color changing nature compared to P2. P1 revealed a switching time of 1.33 s, with a coloration efficiency of 164 cm² C⁻¹, whereas P2 exhibited a slower response time (1.87 s) with a lower coloration efficiency $(155 \text{ cm}^2 \text{ C}^{-1})$, as in the case of PSNS-Flo. The explicit enhancement of the color pallet, switching time, optical contrast and coloration efficiency safely confirms formation of entirely new, superior polymers upon copolymerization, which are suitable for esthetically pleasing display applications.

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