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Spray Processable Green to Highly Transmissive Electrochromics via Chemically Polymerizable Donor–Acceptor Heterocyclic Pentamers**

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The concept of valence and conduction band broadening based on alternating electron rich and poor moieties in conjugated polymers was introduced in 1993 by Havinga et al.[1] With the ability to obtain energy gaps as narrow as 0.5 eV, a new dimension was added to the notion of band gap engineering and the ''donor-acceptor'' theory on a macromolecular level was born. In spite of the considerable impact of this discovery for device applications such as field-effect transistors,[2–4] light emitting diodes[5] and photovoltaics,[6–9] only recently has the use of donor-acceptor based conducting polymers attracted the attention of research groups with an interest in electrochromic polymers (ECPs).[10–14] On the other hand, the last two decades have seen a particular stress placed on incorporating ECPs as fast and reversible color changing materials in devices such as windows, mirrors and displays.[15] While a number of neutral state red and blue conjugated polymers were synthesized and their properties investigated,[16–18] attempts in making saturated green polymers, chemically or electrochemically synthesized, have met limited success[15] due to the complex nature of the required absorption spectrum that must contain at least two bands in the neutral state of the material.

In 2004, Wudl et al. reported on completing the additive primary color space: red, green and blue (RGB), with the first promising neutral green conjugated ECP, a donor-acceptor based material which exhibited a high degree of stability upon electrochemical switching.[19] Even though a soluble version of the neutral green polymer was achieved,[20] the persistent brown hue of its oxidized state remained an obstacle that could not be overcome.[15,20]

In recent work[13] from Toppare et al. published during the preparation of this manuscript, the donor-acceptor 4,7-di(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole (BEDOT-BTD), the synthesis and electrochemical properties having previously been reported,[21–23] was electropolymerized

and its subsequent polymer (PBEDOT-BTD) was re-investigated as a possible candidate for electrochromic applications. The insoluble polymer film was revealed to be a neutral state green material switching rapidly and reversibly to a transmissive light blue oxidized state,[13] an experimental result strongly supporting the utility of the donor-acceptor theory in the design of neutral green ECPs.

Herein, we report our approach for engineering soluble and processable neutral state green conjugated polymers of tunable hues which possess highly transmissive oxidized states, fast switching times, redox switching stability and excellent optical contrasts both in the visible and in the near infra-red (NIR) (Fig. 1). The synthesized green polyheterocyclics exhibit a repeat unit designed for two-band absorption in the visible whose molecular structure can be synthetically adjusted in order to tailor the energy gap and control the green hue of the polymer, a desirable property for applications in displays. Complete characterization in terms of structural and physical properties, as well as practical integration of ECPs into devices, requires solution-processability, which is not attained with the commonly insoluble electropolymerized materials. Here, the reported materials can easily be processed into electrochromic devices using convenient deposition methods such as spin coating and spray casting.

To achieve a neutral state green polymer, it is necessary to have a material that absorbs both red and blue light. Fine tuning of the energy gap, along with introduction of an adequate set of absorption bands in the visible spectrum, can be obtained by controlling the structure of the repeat unit that composes the conjugated material. Based on the theoretical work of Salzner et al. in addressing the relevance of the Donor–Acceptor approach for designing organic metals,[24,25] systems involving two distinct energy transitions are rationalized by considering the presence of low-lying unoccupied and localized energy levels within the band gap of the conjugated system in its ground-state. These localized energy levels are easily accessed from the valence band and should have little electron density on the donor substituents thus forming a discrete energy ''band'' (whose contribution would stem from the most electron poor heterocycle) lying beneath the conduction band in the orbital correlation diagram of the conjugated polymer.[25] The consequences of these assumptions on the optical spectrum of the undoped material described are two-fold: 1) low energy transitions from the valence band to the low lying unoccupied and localized energy levels result in a long wavelength absorption band 2) higher

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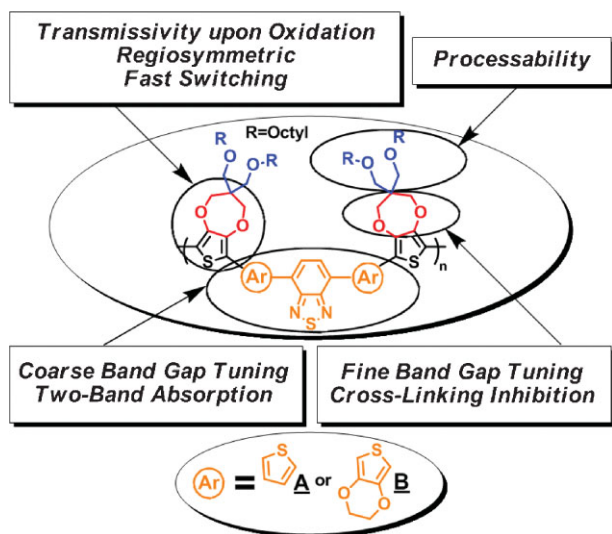E-mail: reynolds@chem.ufl.edu

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Figure 1. Engineering donor-acceptor heterocyclic polymers via polymerizable pentamers to yield conjugated and processable tunable hue neutral state green polymers which exhibit fast switching properties and highly transmissive oxidized states (full synthetic details relative to *pentamer A*, *pentamer B*, *polymer A* and *polymer B* are provided in the Supporting Information).

energy transitions from the valence band to the "true" conduction band are responsible for the presence of a distinct blue-shifted absorption band in the visible spectrum. In addition, for a polymeric material transmitting/reflecting green light, obtaining a highly transmissive state upon oxidation is an additional major difficulty due to the requirement for simultaneous and efficient bleaching of the two absorption bands that occurs in the blue and red portions of the visible region.

Figure 1 illustrates our approach for designing conjugated polymers with a two-band absorption in the visible so as to reflect and transmit the color green in the neutral state. At the same time, these polymers attain high transmissivity upon complete oxidation along with being solution-processable. Here, the acceptor 2,1,3-benzothiadiazole is symmetrically functionalized with different thiophenic donor substituents using repeated Stille couplings.[26–29] While the first substitution is expected to have the largest impact on the energy gap of the donor-acceptor system, a second substitution with a 3,4-propylenedioxythiophene (ProDOT) allows fine energy tuning and substantial control over the two-band absorption spectrum of the resulting oligomer (see Supporting Information). Polymerization of the heterocyclic pentamers gives a distinct optical (red) shift conveniently anticipated by results from various research groups.[30–33] In addition, as demonstrated earlier in our group,[34,35] alkoxy-derivatized ProDOT based polymers exhibit sub-second switching times, high EC contrast ratios, redox switching stability, transmissivity of the oxidized state, and a particular ease in synthesis that raises the synthon as a logical building unit in the design of heterocyclic precursors for colored to transparent switching ECPs. Regiosymmetric alkoxy-substituted ProDOTs also possess a low oxidation potential so that mild oxidizing agents can be

used for polymerizing the designed oligomers which limits the risks of cross-linking occuring during the polymerization and induces solution-processability to the subsequent polymers.

Polymers A and *B* (Fig. 1) were respectively achieved via chemical polymerization of the donor-acceptor based heterocyclic *pentamers A* and *B* making up the repeat unit of their subsequent polymeric analogues. Experimentally, it was found that symmetric addition of ProDOT on the donor-acceptor trimeric precursors (highlighted orange in Fig. 1) induces a bathochromic shift in the range 55–62 nm for the lower wavelength absorption band and 75–78 nm for the longer wavelength band (see Supporting Information). Polymerization adds a more significant red shift of about 80 nm for the lower wavelength transition, while ranging from 120 to 150 nm for the higher one (Fig. 2a). In solution, both polymers are green and show minor optical changes upon increase of the temperature between room temperature and 100 °C indicating neither significant disruption of effective conjugation[36,37] nor major aggregation of the backbones once solvated.[38,39] The key incorporation of regiosymmetric ProDOTs bearing two octyloxy solubilizing chains induces sufficient solubility (up to about 8 mg mL^{-1} in the case of *polymer A*) for solid thin film processing using common organic solvents. While *polymer A* shows good to excellent solubility at room temperature in toluene, chloroform and *ortho*-dichlorobenzene (ODCB), *polymer B* requires hot mixtures of toluene and chloroform (60 °C) or hot ODCB (80–100 °C) to be efficiently dissolved in solution.

Films of *polymer A* and *B* were spray-cast onto ITO-coated glass slides from room temperature solvents, and subsequently redox cycled until they reached a stable and reproducible switch prior to spectroelectrochemical analysis. As the potential applied to the film is increased from −0.3 V (versus Fc/Fc$^+$) for *polymer A*, −0.6 V for *polymer B*, simultaneous bleaching of both the low and high energy transitions is initiated (Fig. 2b and c). These values are consistent with the low onsets of oxidation of *polymers A* and *B* respectively estimated at −0.3 V and −0.55 V via differential-pulse voltammetry (see the Supporting Information). As the short and long wavelength absorption bands are depleted, new transitions progressively arise in the NIR indicating the formation of the charge carriers. Determined from the onset of their lowest energy π–π* transitions, *polymer A* exhibits a band gap at 1.47 eV and *polymer B* shows a more narrow value of 1.42 eV as expected considering that 3,4-ethylenedioxythiophene (EDOT) brings a higher energy HOMO than thiophene to the conjugated donor-acceptor system. When fully oxidized, both polymers show a high level of transparency to the human eye. Upon full oxidation the bipolaronic transition of *polymer B*, clearly more red-shifted in the NIR, tails less into the visible hence inducing a higher electrochromic contrast. From this data and taking the longer wavelength absorption maximum as a reference as it interacts with the near infrared tail of the fully doped polymer, a transmittance change up of about 32% for *polymer A* versus 53% for *polymer B* is calculated, indicative of the higher contrast observed for the latter polymer.
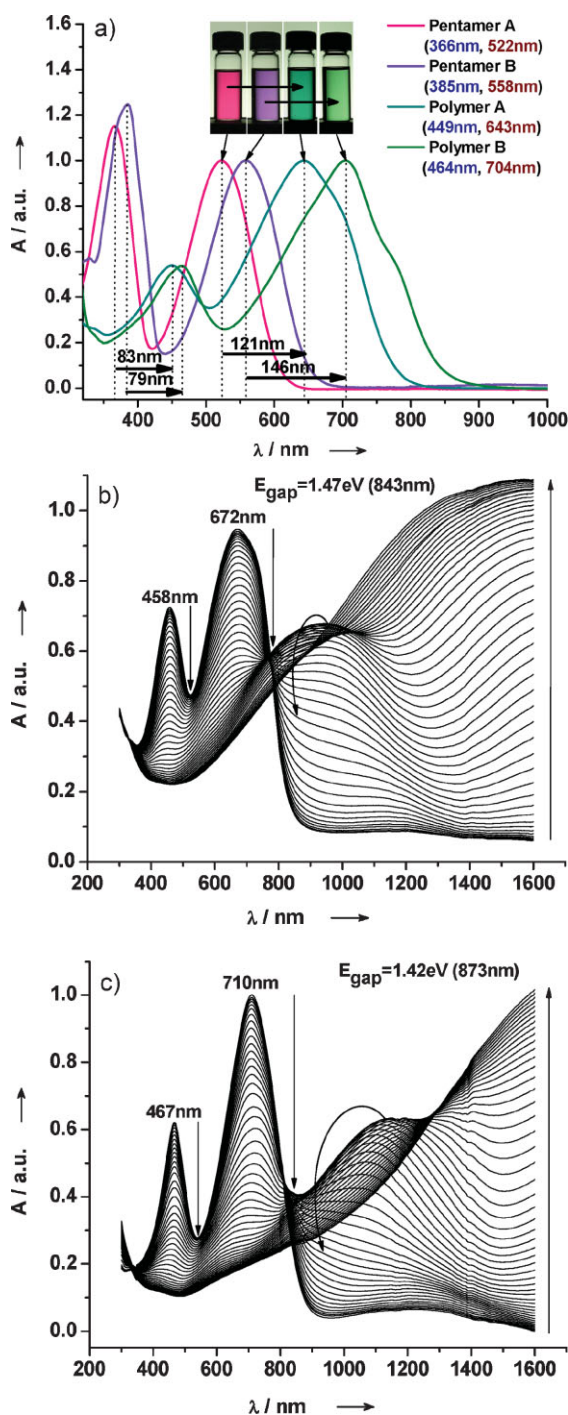
Figure 2. a) Solution optical absorbance of *Pentamer A*, *Pentamer B*, *Polymer A* and *Polymer B* in chloroform (Spectrum of each system is normalized at the longer wavelength absorption maximum). Legend specifies the values of the respective absorption maxima for both high (blue) and low energy (red) absorption bands. b) Spectroelectrochemistry of *polymer A* and c) *Polymer B* The films were spray-cast onto ITO-coated glass from solution (2 mg mL^{-1}) in toluene (*Polymer A*) or a hot mixture of toluene and chloroform (*Polymer B*). Electrochemical oxidation of the films was carried out in 0.1 M LiBF$_4$/ACN supporting electrolyte using a silver wire as a quasi-reference electrode (calibrated against Fc/Fc$^+$) and a platinum wire as the counter electrode. In both cases, the applied potential was increased in 25 mV steps: -0.4 V $\Rightarrow$ $+0.95$ V, *Polymer A*; -0.65 V $\Rightarrow$ $+0.65$ V, *Polymer B*.
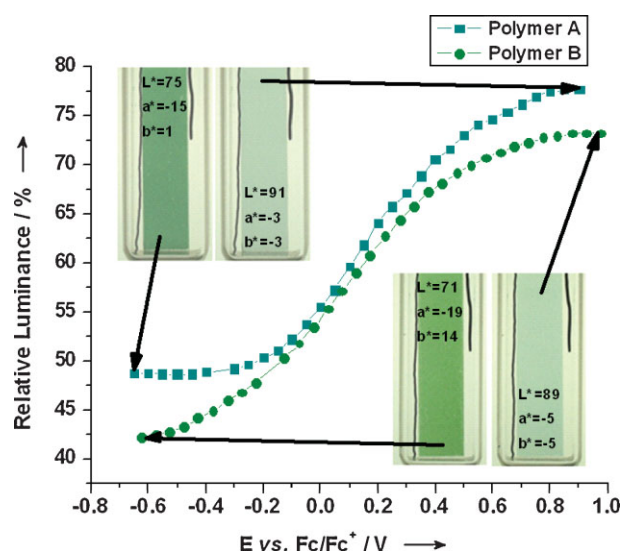

Figure 3. Relative Luminance (%) as a function of applied potential for both spray-coated *Polymers A* and *B*. Pictures show the hues of green perceived and give an indication of the degree of transmissivity obtained upon complete oxidation. For color matching, *L*a*b** values (in the sense of the CIE 1976 *L*a*b** color model) of fully neutral and oxidized states are reported for the films.

The relative luminance change, estimating the brightness of the transmitted light as a percentage of the brightness of the light source, was measured as the doping level induced by electrochemical oxidation was progressively increased (Fig. 3). From their neutral green to fully oxidized transmissive state, the spray-cast polymers exhibit a relative luminance change of approximately 30%, a promising value considering that the light-adapted human eye is most sensitive to forest-green, a tone that almost equally stimulates two of the three kinds of cone cells in the eye and that is consequently likely to be perceived regardless of its intensity. It is worth noting that relative luminance can also be modulated and optimized as a function of deposited film thickness. The materials in their neutral state exhibit a saturated green, a fact supported by the very negative *a** values obtained, but they show different hues as characterized by the significantly different *b** values.[40] For instance, the large positive *b** value for polymer B translates the yellow tone of its green. *L** values (ranging from 0 to 100) such as those exhibited by *Polymer A* (*L** = 91) and *B* (*L** = 89) upon oxidation demonstrate their aptitude to nearly reach the "white point" (W) of color space. In the oxidized state, *a** and *b** drop down to orders as low as -3 (*polymer A*) and -5 (*polymer B*) yielding corresponding tints that can hardly be perceived by the human eye. The polymers complete their full switches in a potential window of less than 1.5 V, a parameter of significant interest for low-voltage device applications. The window necessary to achieve more than 90% of the optical change is considerably narrower: as low as 1.05 V for *Polymer A* and 1.15 V for *Polymer B*.

The contrast ratios (%ΔT) were monitored as a function of time at the longer wavelength absorption maximum of each
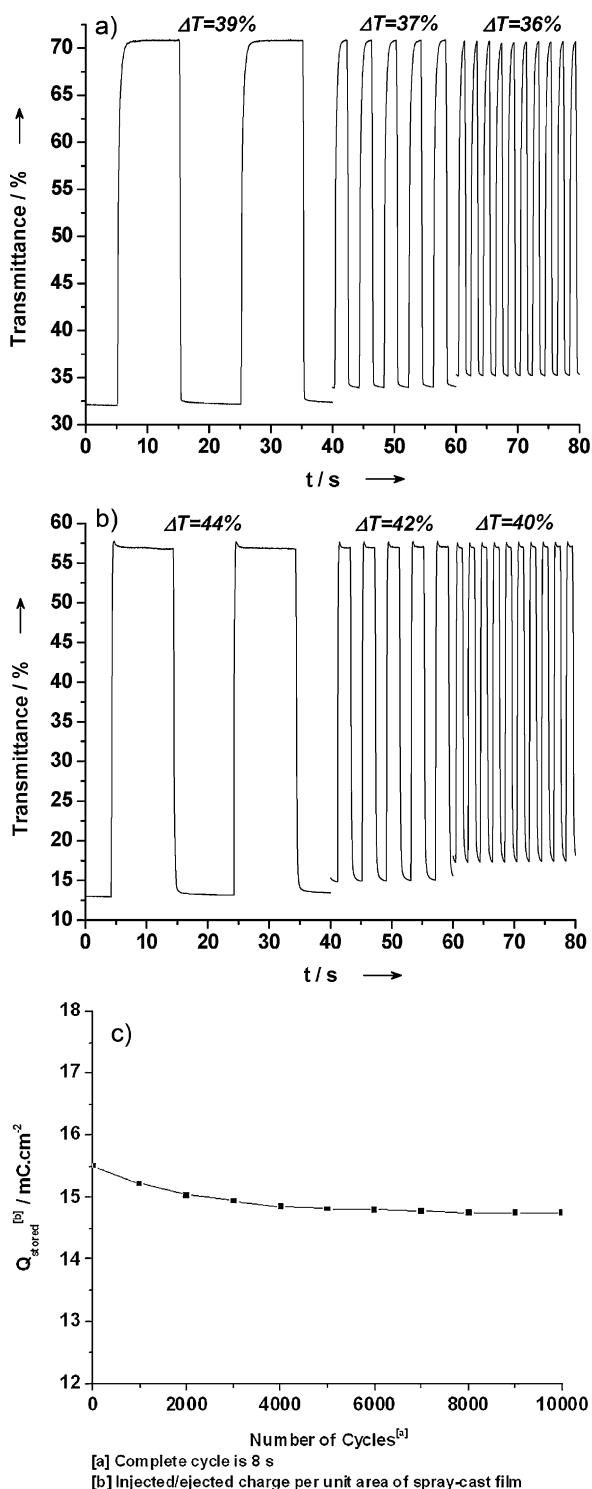
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material applying square-wave potential steps of 10 s, 2 s, and 1 s in order to characterize their respective response time (Fig. 4a and b). As predicted by the spectroelectrochemical study, the film of *polymer B* exhibits higher contrasts (44–40%) than *polymer A* (39–36%), although in either case a variation in electrochromic contrast of only 3 to 4% is observed as the switch time is increased from 10 to 1 second. Measured at the shorter wavelength absorption maximum of *polymer A* and *B*, %ΔT was estimated at 27% and 45%, respectively.

A new film of *polymer A* was spray-coated onto ITO and its stability upon square-wave potential stepping electrochromic switching was investigated in 0.1 M LiBF$_4$/propylene carbonate solution using a switch time of 2 s (see the Supporting Information). At the longer wavelength absorption maximum, a loss of electrochromic contrast of only 5.5% is estimated after 1000 cycles along with no significant change in coloration efficiency (CE) which indicates the proper relationship between charge stored (calculated from integration of the current) and contrast observed. This result is significant considering the nature of the substrate used, and the redox induced solubility of the polymer in the electrolyte, as there is little to prevent the chains from slowly migrating away from the working electrode to the platinum counter electrode during the experiment. In order to highlight the influence of the substrate on stability studies, long term switching was also investigated on a Pt button electrode (Fig. 4c). While the decay in charge stored per unit area of spray-coated film of *polymer A* is in the order of 5.5% onto ITO, a film drop-cast on Pt shows about 2% loss after 1000 cycles, about 3% after 2000 cycles and less than 5% after 10 000 cycles (nearly 24 hours) which reinforces the potential of this ECP for commercial applications.

In conclusion, two new symmetrical donor-acceptor heterocyclic pentamers were designed, synthesized and chemically polymerized affording organic soluble neutral state green conjugated polymers of different hues adequate for RGB realization. Optical and electrochemical investigation of the green conjugated polymers revealed highly transmissive oxidized states, excellent optical contrasts both in the visible and in the NIR, small potential windows of operation, fast switching times and long-term stability. Such remarkable properties combined with the convenient ability to process the finely engineered hybrids into solid thin films upon spin coating and spray casting leave the doors for dual ECP, photovoltaic and NIR device applications wide open.

Figure 4. a) Square-wave potential step absorptometry of spray-coated *Polymer A* (monitored at 672 nm, −0.5 V ⟶ + 1.05 V versus Fc/Fc$^+$) and b) *Polymer B* (Bottom, monitored at 710 nm, −0.7 V ⟶ + 1 V versus Fc/Fc$^+$) onto ITO in 0.1 M LiBF$_4$/ACN solution. Switch times: 10 s step for 40 s (2 cycles), then 2 s step for 20 s (5 cycles) and 1 s step for 20 s. (10 cycles). c) Square-wave potential stepping electrochromic switching of drop-cast *Polymer A* onto Pt in 0.1 M LiBF$_4$/propylene carbonate solution switching between −0.4 V and +0.85 V (versus Fc/Fc$^+$) with a switch time of 4 s.

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