PAPER

NJC
www.rsc.org/njc

Electrochromic conjugated *N*-salicylidene-aniline (anil) functionalized pyrrole and 2,5-dithienylpyrrole-based polymers†

Barry C. Thompson,[a] Khalil A. Abboud,[a] John R. Reynolds,*[a] Keitaro Nakatani[b] and Pierre Audebert*[b]

[a] *Department of Chemistry, Center for Macromolecular Science and Engineering, University of Florida, Gainesville, FL 32611, USA*
[b] *Laboratoire de Photophysique et Photochimie Supramoléculaires et Macromoléculaires, (CNRS UMR 8531), Ecole Normale Supérieure de Cachan, 61 Av. du Pt Wilson, 94235 Cachan, France*

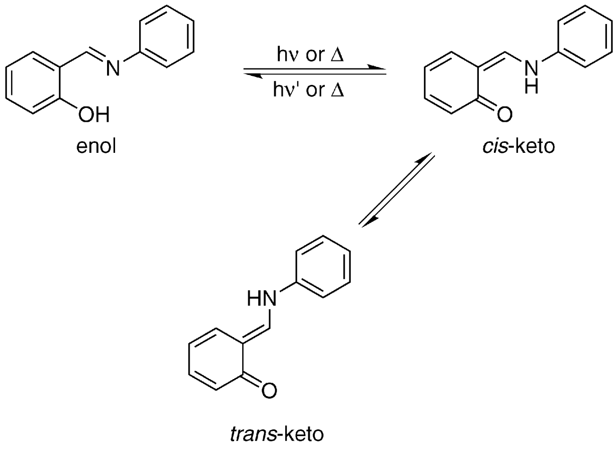
Received (in Montpellier, France) 1st April 2005, Accepted 31st May 2005
First published as an Advance Article on the web 8th July 2005

Here we describe the first report of a family of fully conjugated monomers bearing salicylidene-aniline (anil) photochromes as pendant functional groups. These monomers are either *N*-functionalized pyrroles or 2,5-dithienylpyrroles. While the pyrrole monomers are not found to electropolymerize, the 2,5-dithienylpyrrole monomers electropolymerize to yield electroactive films, with well-behaved electrochemical properties. Additionally, the polymer films are found to be electrochromic, changing from yellow in the neutral form, to a light green intermediate state at low levels of oxidation, and finally to a dark gray-blue upon oxidation. A photochromic response associated with the light induced tautomerization of the anil functionality is observed in powder form for two of the monomers, although no photochromic response is observed for the polymers in thin film form. Some NLO properties of the monomers are reported as well.

Introduction

A great deal of attention has been focused on conjugated polymers due to the broad range of applications for which they are potentially useful.[1] Photovoltaic devices,[2] LED's,[3] field effect transistors,[4] electrochromic devices,[5] and various types of sensors[6] based on conjugated polymers are under investigation by numerous researchers around the world. As such, the search for new functional and responsive conjugated polymers continues to be a subject of interest. Specifically, optically responsive conjugated polymers exhibiting electrochromism,[7] photochromism,[8] or NLO properties are especially sought after for use in such applications as display technology or data storage. A polymer that possesses a combination of several of these properties is an especially attractive target.

While all conjugated polymers are potentially electrochromic in thin film form, in order to achieve a photochromic effect, the incorporation of a photochromic moiety is required. Azobenzenes[9–11] and diarylethenes[12,13] are representative classes of photochromes that have been successfully incorporated into conjugated polymers. In designing a photochromic conjugated polymer, several approaches can be taken. In the simplest approach the photochrome can be attached as a pendant group to the polymer backbone through a nonconjugated linkage.[9] In a second approach, a fully conjugated polymer is synthesized in which the conjugation of the photochrome is continuous with that of the backbone by either incorporating the photochrome directly into the backbone[10,13] or using a fully conjugated pendant group.[11] Such fully conjugated polymers are especially interesting because of the possibility for a cooperative interaction between the polymer and the photochrome due to the continuous electronic conjugation. Following this motivation, electroactive polypyrroles and poly(2,5-dithienylpyrroles) bearing fully conjugated pendant azobenzene groups have recently been reported by one of us (Audebert *et al.*)[11] For all the cases examined, little effort has been made to fully characterize such polymers for both their electrochromic and photochromic response. In most cases, utilization of azobenzene or diarylethene photochromes has led to a limited photochromic response, especially in the solid state.



Scheme 1

---

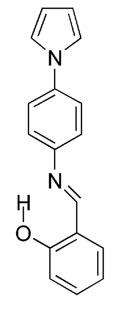
† Electronic supplementary information (ESI) available: Crystal structure information. See http://dx.doi.org/10.1039/b504577k

DOI: 10.1039/b504577k

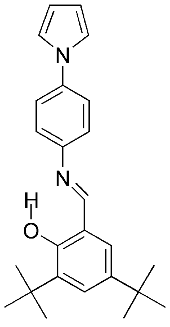
Another interesting class of photochrome that is somewhat less well known is the salicylidene-anilines (anils). For this class of photochrome, the mechanism for photochromism is based on a tautomerization reaction as shown in Scheme 1.[14] Here the enol form is colorless, but upon irradiation with UV light the colored keto form is produced.[15] This photoprocess is known to take place in the crystalline state, solid state, and in solution,[16] and the mechanism has been studied in great detail.[17] A close examination of the tautomerization reaction in the crystalline state allows one to understand the constraints and consequences of photoisomerization. It is known that most anils possess two distinct crystalline forms, α and β, which show mutually exclusive photochromism or thermochromism, respectively. In the α crystal (photochromic), a relatively open crystal structure results from a nonplanar molecular structure in which the salicylaldimino portion of the molecule is planar, while the aniline ring lies 40–50° out of plane. With photochromic anils, it is the stabilized *trans*-keto form that is the primary photoproduct and it is the more open crystal structure that allows the geometric isomerization necessary to convert from *cis*-keto to *trans*-keto after excited state proton transfer. However in the β crystal (thermochromic), the entire molecule is planar and the molecules pack tightly in a face-to-face manner.[17] For thermochromic anils it is the planar *cis*-keto form that is the result of temperature induced excited state proton transfer.

While anils show photochromism in the crystalline form, in solution or in amorphous films the crystal packing and consequent effects cannot aid in the *cis–trans* isomerization process or in the stabilization of the *trans*-keto photoproduct. In amorphous films the free volume is critical in determining if the *cis–trans* isomerization can occur as well as the rate of the thermal back reaction. These geometrical constraints of anil photochromism appear to present an obstacle to the development of a photochromic conjugated polymer based on the amorphous nature of polymer films. Indeed limited work has been carried out to characterize the chromic response of anil compounds in amorphous polymer films. The first approach has been the inclusion of anils in the main chain of hydroxylated polyazomethine polymers.[18,19] In this case, the polymers are weakly thermochromic in thin film form, although no photochromic response is observed. The lack of photochromism is attributed to the large energy that would be required for the requisite *cis–trans* isomerization of the polymer backbone. Another approach that has been investigated is the incorporation of small molecule anil compounds into an amorphous polymer matrix.[20,21] In this case, a photochromic response is observed upon steady state irradiation of polymer films with UV light. The phenomenon is again closely related to the free volume in the polymer film and the freedom of molecular motion of the anil molecule in the amorphous matrix. A final approach has been the pendant functionalization of polymer backbones with anil moieties. Here, methyl methacrylate copolymers with anil molecules tethered to the backbone *via* alkyl chains of varying length were observed to display photochromism in thin film form, changing from clear to yellow upon UV-irradiation at room temperature.[22] As such it is apparent the anil photochromism is possible in amorphous polymer films when the anil functionality is pendant to the polymer backbone.

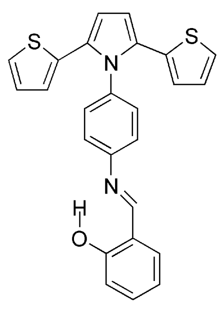
Analogous to previous work on *N*-azo pyrroles and 2,5-dithienylpyrroles,[11] here we present a new class of fully conjugated monomers (shown below), which contain a pendant photochromic anil functionality. Monomers **1** and **4** showed a photochromic response in powder form, changing from yellow to red. Monomers **3** and **4** were found to electropolymerize to yield electroactive films, which displayed an electrochromic response upon oxidation changing from yellow to gray-blue. To the best of our knowledge this is the first report of conjugated polymers containing anil photochromes.



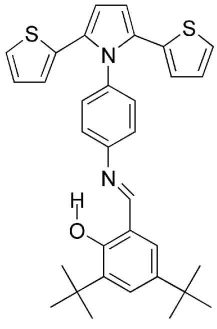
1



2



3



4

Experimental

Monomer syntheses

The pyrrole (**5**) and di(α-thienyl)pyrrole (**6**) compounds were prepared by a classical Paal–Knorr procedure using one equivalent of benzene diamine, and respectively one equivalent of dimethoxytetrahydrofuran, or 1,4-α-bisthienyl-1,4-dione using the same conditions as previously described.[11,23]

For 4-(1*H*-pyrrol-1-yl)benzenamine **5**: ^{1}H NMR (CDCl$_3$): 7.25, d (2H); 7.05, s (2H); 6.75, d (2H); 6.35, s (2H); 3.70, br (2H).

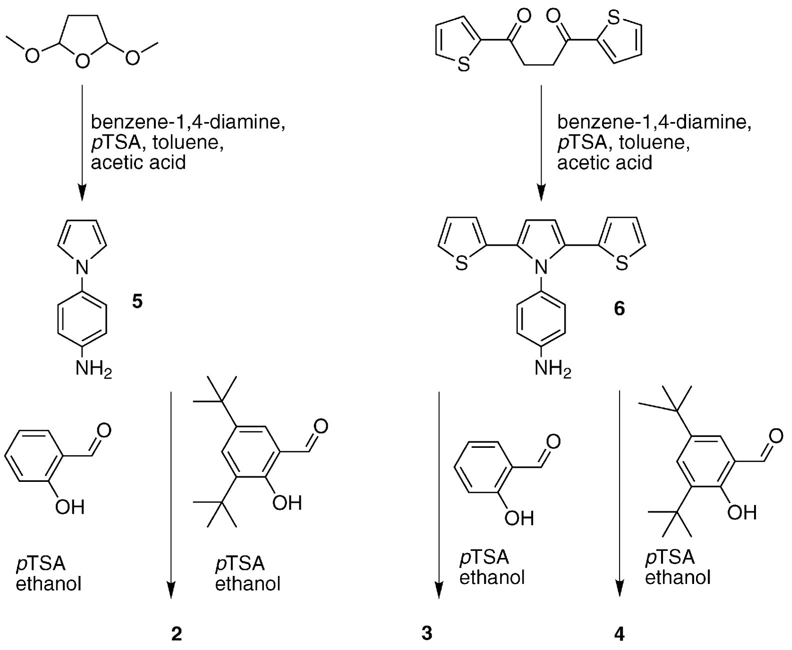
For 4-(2,5-di(2-thienyl)-1*H*-pyrrol-1-yl)benzenamine **6**:[23] ^{1}H NMR (CDCl$_3$): 7.10, m (4H); 6.87, m (2H); 6.75, m (2H); 6.65, m (2H); 6.55, m (2H); 3.87, br (2H).

The synthesis of the anil substituted monomers was realized using the following process: 1 mmol of the aminophenyl derivative **5** or **6**, and 1 mmol of salicylaldehyde, or 3,5-di-*tert*-butylsalicylaldehyde were dissolved in 30 ml of absolute ethanol, together with a few crystals of *p*-toluenesulfonic acid. After a time, depending upon the pair of reactants (from 5 minutes to two hours) the pure anils **1–4** crystallized, and were collected by suction on a glass frit (unoptimized yields 40–60%). The presence of more anil was acknowledged in the filtrate by TLC but was not recovered.

For **1**: ^{1}H NMR (CDCl$_3$): 13.20, br (1H); 8.72, s (1H); 7.46, m (6H); 7.16, m (2H); 7.03, m (2H); 6.42, m (2H). ^{13}C NMR (CDCl$_3$): 162.50, 161.34, 146.09, 139.72, 133.48, 132.52, 122.55, 121.45, 119.50, 119.38, 117.52, 110.94. HRMS: calc. 262.1106; found 262.1096. Mp 173–174 °C. $\lambda_{max} = 351$ nm $(\varepsilon = 1.6 \times 10^4\ \mathrm{L\ mol^{-1}\ cm^{-1}})$.

For **2**: ^{1}H NMR (CDCl$_3$): 13.65, br (1H); 8.71, s (1H); 7.45, m (3H); 7.39, m (2H); 7.28, m (1H); 7.14, m (2H); 6.41, m (2H); 1.38, s (18H). ^{13}C NMR (CDCl$_3$): 163.69, 158.47, 146.37, 140.92, 139.44, 137.27, 128.39, 127.06, 122.50, 121.46, 119.53, 118.50, 110.84, 35.34, 34.43, 31.70, 29.65. HRMS: calc. 374.2358, found 374.2351. Mp 181–182 °C. $\lambda_{max} = 336$ nm $(\varepsilon = 1.6 \times 10^4\ \mathrm{L\ mol^{-1}\ cm^{-1}})$.

For **3**: ^{1}H NMR (CDCl$_3$): 13.06, s (1H); 8.69, s (1H); 7.44, m (1H); 7.41, s (1H); 7.34, m (4H); 7.08, dd (2H); 7.05, m (1H); 6.97, m (1H); 6.85, m (2H); 6.60, dd (2H); 6.55, s (2H).



Scheme 2

^{13}C NMR (CDCl$_3$): 168.16, 164.04, 161.66, 145.60, 137.36, 135.17, 133.96, 132.92, 131.38, 130.55, 127.38, 124.95, 124.64, 122.26, 119.62, 117.76, 110.42. HRMS: calc. 426.0861, found 426.0857. Mp 208–210 °C. $\lambda_{\max}$ = 338 nm ($\varepsilon = 2.5 \times 10^4$ L mol^{-1} cm^{-1}).

For **4**: ^{1}H NMR (CDCl$_3$): 13.55, br (1H); 8.75, s (1H); 7.53, m (2H); 7.41, m (4H); 7.08, m (2H); 6.87, m (2H); 6.59, m (2H); 6.59, s (2H); 1.38, s (18H). ^{13}C NMR (CDCl$_3$): 164.98, 158.60, 149.49, 140.99, 137.35, 136.80, 135.05, 131.15, 130.39, 128.72, 127.25, 127.19, 124.64, 124.37, 122.10, 118.39, 110.18, 35.35, 34.43, 31.68, 29.64. HRMS: calc. 538.2113, found 538.2119. Mp 210–213 °C. $\lambda_{\max}$ = 328 nm ($\varepsilon = 2.6 \times 10^4$ L mol^{-1} cm^{-1}).

Electrochemistry and spectroscopy

All electrochemistry was performed using an EG&G PAR 273A potentiostat/galvanostat. A standard three-electrode electrochemical cell was employed with a silver wire pseudo-reference electrode (calibrated *vs.* ferrocene), a Pt button working electrode (A = 0.02 cm^2), and a Pt flag counter electrode. All measurements were performed in 0.1 M TBAP/acetonitrile unless otherwise noted.

UV–Vis–NIR spectra were recorded using a Cary 500 UV–Vis–NIR spectrophotometer. Colorimetry was performed with a Minolta CS100 colorimeter as has been previously described.[24] Polymer films for spectroelectrochemistry and colorimetry were deposited electrochemically in ITO coated glass slides (20 Ω sq^{-1}).

For NLO measurements,[25] powder (*ca.* 10 mg) of the four compounds was put between two glass plates. The incident beam was either the fundamental of a Nd/YAG nanosecond laser (10 ns, 10 Hz repetition rate) at 1064 nm or a 1907 nm beam obtained by Raman-shifting (through a 50 atm H$_2$ cell, 1 m long) the previous beam. The second harmonic (SH) intensity was measured by a photomultiplier and monitored on an oscilloscope. Photochromism of the powdered samples[26] was tested by irradiating the same samples as described above with a Hg lamp (400 W). The 365 nm ray was selected by an interference filter. The intensity was *ca.* 1 mW cm^{-2}.

The photochromism of polymer thin films was tested by irradiating the electrodeposited samples on ITO (in air or in electrolyte) with a 100 W Hg lamp. Light with a wavelength of 365 nm was selected by use of an interference filter.

X-Ray crystallography

X-Ray crystallography data were collected from a single crystal of **2** at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing MoKα radiation (λ = 0.710 73 Å). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the Direct Methods in SHELXTL6, and refined using full-matrix least squares. Crystal data: C$_{25}$H$_{30}$N$_2$O, M = 374.51, triclinic, a = 9.8773(6), b = 12.1540(7), c = 18.6430(11) Å, U = 2183.3(2) Å^3, α = 100.878(2)°, β = 93.328(2)°, γ = 94.944(2)°, T = 193 K, space group $P\bar{1}$, Z = 4, μ(MoKα) = 0.710 73 Å, 16332 reflections measured, 7625 unique (R_{int} = 0.0375). The final $wR(F^2)$ was 0.1413 (all data). The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. The asymmetric unit consists of two chemically equivalent but crystallographically independent molecules. One of the two had the methyl C atoms on C43 disordered and were refined in two parts with their occupation factors dependently refined. The bridging N4–C36 moiety is the same molecule is disordered along with the phenyl hydroxyl group. They were refined in two parts with their occupation factors dependently refined. A total of 581 parameters were refined in the final cycle of refinement using 16332 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 5.52% and 12.25%, respectively.‡

Results and discussion

Monomer syntheses and spectroscopic features of the monomers

The synthesis of monomers **1–4** was carried out in moderate (unoptimized) yields by Paal–Knorr condensation followed by condensation of the resulting amine with the appropriate salicylaldehyde as seen in Scheme 2. All four monomers are yellow solids and give brightly colored yellow solutions. The absorption spectra of the four monomers are shown in Fig. 1 at concentrations of 3×10^{-5} mol L^{-1}. Each monomer gives a

---

‡ CCDC reference number 268887. See http://dx.doi.org/10.1039/b504577k for crystallographic data in CIF or other electronic format.

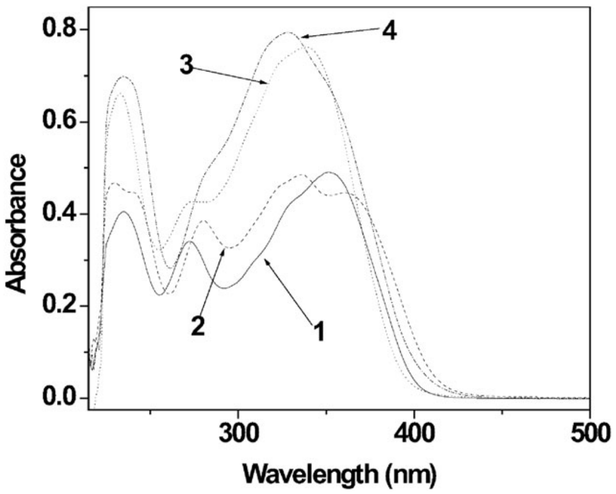


Fig. 1 Absorption spectra for compounds **1–4** in dichloromethane solution (conc. = 3×10^{-5} mol L^{-1} in each case).

complex absorption spectrum consisting of at least two peaks centered at 330–350 nm and 230–235 nm. The absorption bands centered at 330–350 nm and 230–235 nm can be assigned respectively to the π–π* and the n–π* transitions.[17] It can also be seen that the pyrrole derivatives show additional spectral structure and exhibit more well-defined peaks. Note that in the case of the pyrrole monomers (**1** and **2**) and the 2,5-dithienylpyrrole monomers (**3** and **4**), that the *tert*-butyl substituted derivative shows a red shift in the absorption onset relative to the unsubstituted monomer. This can be attributed to the inductive electron donation of the *tert*-butyl groups.

X-Ray crystallography

In order to fully understand the structures of the obtained monomers, various crystallization techniques were employed in order to achieve single crystals suitable for X-ray crystal structure determination. Single crystals of compound **2** were obtained by slow evaporation of ethanol and the structure is shown in Fig. 2. Compound **2** crystallizes to form a triclinic unit cell of space group $P\bar{1}$. In this crystalline form it can be seen that the molecule is not planar and that the incline angle between the planes of the pyrrole ring and the aniline phenyl ring is 32.6°, while the incline angle between the aniline phenyl ring and the salicyl phenyl ring is 33.1°. This nonplanar conformation gives rise to crystal packing that does not display a face-to-face structure, which is typical of α-type (photochromic) anil crystals. Additionally it is observed that the molecule is in the enol form with intramolecular hydrogen bonding between the phenolic OH (O1) and the imine nitrogen (N2) with bond lengths of 1.02 Å for the O–H bond and 1.63 Å for the N–H bond, indicating the stronger covalent nature of the O–H bond. No intermolecular hydrogen bonding was observed. Compounds **1**, **3**, and **4** were not found to give suitable crystals for X-ray analysis under a variety of conditions that were investigated. Multiple attempts at recrystallization led to crystals that were too small for proper analysis.

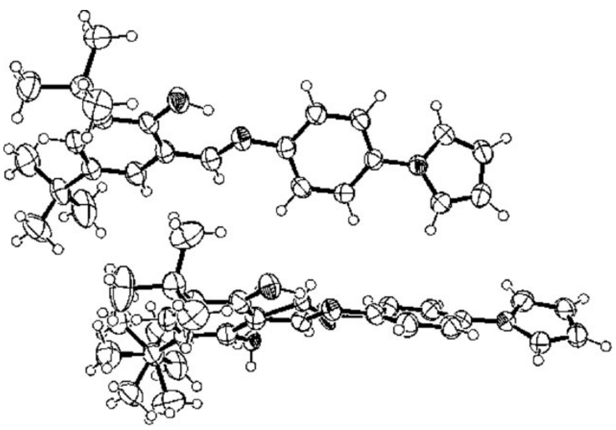


Fig. 2 Crystal packing in a single crystal of **2**.

Electrochemical behavior and electropolymerization

The electrochemical behavior of compounds **1–4** was investigated. Compounds **1** and **2** were not found to electropolymerize under a variety of conditions that were investigated. Peak monomer oxidation potentials were observed at 0.8–0.9 V *vs.* Fc/Fc^+ for both pyrrole derivatives, although in both cases peak currents were low and oxidations were broad and poorly defined. The lack of polymerization is not surprising, as *N*-substituted pyrroles are often difficult to polymerize, especially with a sterically demanding group,[27] such as a phenyl ring.[28]

Compound **3** was found to electropolymerize in a well-behaved manner upon repeated potential cycling (Fig. 3) in a solution that was 0.005 M in monomer with 0.1 M TBAP as supporting electrolyte in 50 : 50 acetonitrile–dichloromethane to yield an electroactive film (**P3**) on a Pt button electrode. The peak of monomer oxidation was found to occur at 0.46 V *vs.* Fc/Fc^+ and the resulting film was found to have an $E_{1/2}$ of 0.25 V *vs.* Fc/Fc^+, which is typical of 2,5-dithienylpyrrole polymers.[11,29] The peak current for the anodic and cathodic processes of the polymer were also found to scale linearly with scan rate as seen in Fig. 4 as is expected for an electrode-bound electroactive polymer film. Such a well-behaved electrochemical response is not a surprise, based on literature precedent for *N*-substituted thiophene–pyrrole–thiophene polymers.[30]

Monomer **4** was not found to polymerize under the conditions employed for **3**, however electropolymerization (E_{pm} = 0.49 V *vs.* Fc/Fc^+) was achieved upon repeated potential cycling in a solution that was 0.005 M in monomer and 0.1 M in TBAP with 50 : 50 acetonitrile–toluene as the electrolyte solution. As seen in Fig. 5, the growth for **P4** was much slower than that of **P3** as indicated by the much more limited current response of the growing polymer film. The film that resulted from deposition by cyclic voltammetry was of low quality and did not exhibit a well-defined electrochemical response. It can be proposed that the presence of the bulky, aliphatic *tert*-butyl groups on **P4** causes an enhanced solubility of the formed oligomers, resulting in a thin, low quality film. This is evidenced by a rapid darkening of the solution during electropolymerization. However, upon potentiostatic deposition

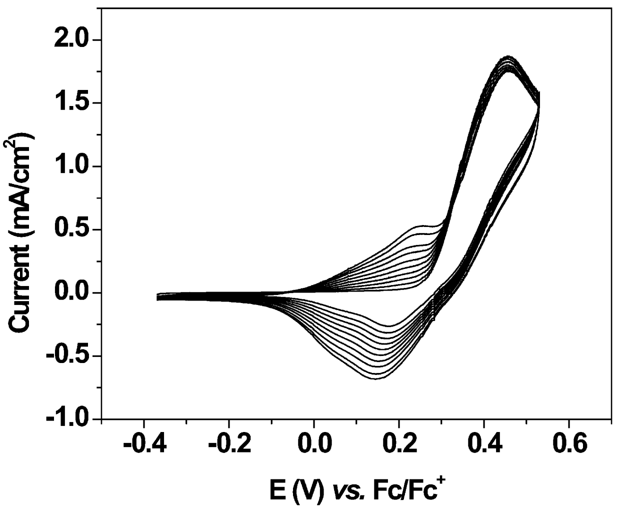


Fig. 3 Electrochemical deposition of **P3** on platinum in 50 : 50 acetonitrile–dichloromethane with 0.1 M TBAP at a scan rate of 50 mV s^{-1}.

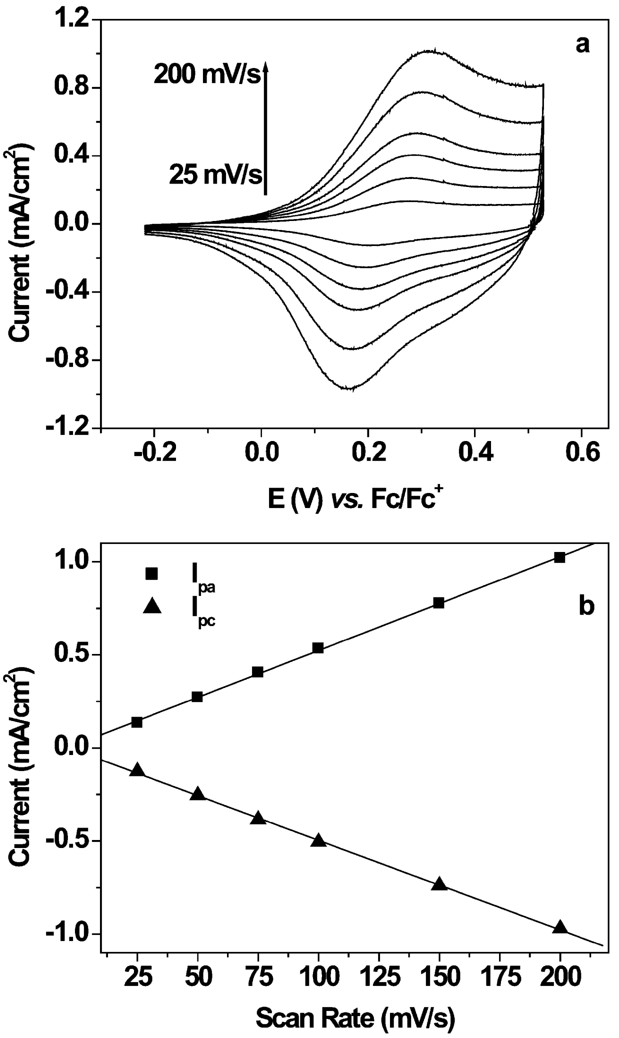


Fig. 4 (a) Cyclic voltammetry of **P3** at scan rates of 25, 50, 75, 100, 150, and 200 mV s^{-1} in monomer free 0.1 M TBAP–acetonitrile. (b) Plot of peak anodic current (I_{pa}) and peak cathodic current (I_{pc}) *vs.* scan rate for the data in Fig. 4a.

(+0.54 V *vs.* Fc/Fc^+) in the same electrolyte, a polymer film was deposited that showed an $E_{1/2}$ of 0.24 V *vs.* Fc/Fc^+. The scan rate dependence of this potentiostatically deposited film is shown in Fig. 6, which illustrates the nearly identical electrochemical behavior of **P3** and **P4**.

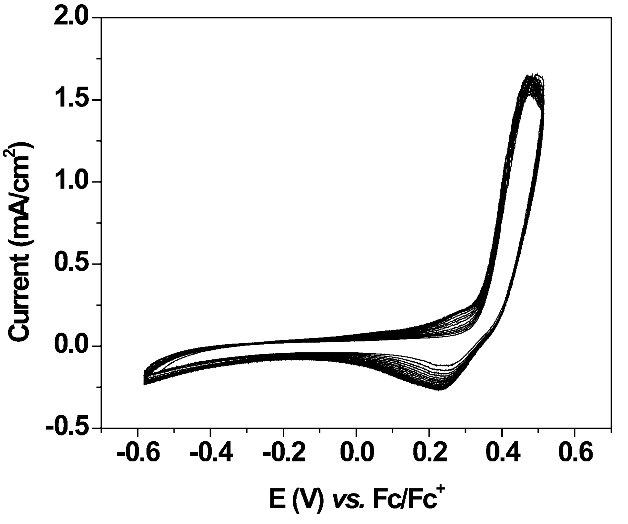


Fig. 5 Electrochemical deposition of **P4** on platinum in 50 : 50 acetonitrile–toluene with 0.1 M TBAP at a scan rate of 50 mV s^{-1}.

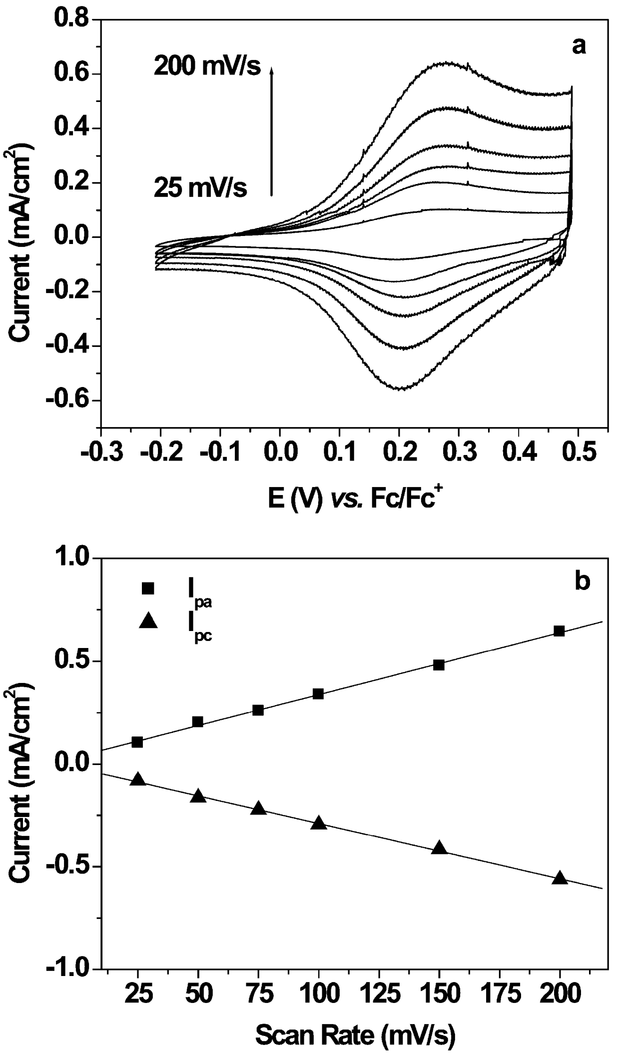


Fig. 6 (a) Cyclic voltammetry of **P4** at scan rates of 25, 50, 75, 100, 150, and 200 mV s^{-1} in monomer free 0.1 M TBAP–acetonitrile. (b) Plot of peak anodic current (I_{pa}) and peak cathodic current (I_{pc}) *vs.* scan rate for the data in Fig. 6a.

Spectroelectrochemistry and colorimetry

For spectroelectrochemistry, **P3** was deposited potentiostatically on ITO (in 0.1 TBAP/50 : 50 acetonitrile–dichloromethane) at +0.5 V *vs.* Fc/Fc^+ and Fig. 7a shows the spectroelectrochemical series for **P3**. From the neutral scan (−0.37 V *vs.* Fc/Fc^+) the band gap can be estimated as 2.2 eV from the onset of the π–π* transition ($\lambda_{max} = 430$ nm). In the neutral form the polymer film is yellow, which is similar to the reported color for thin films of poly(dithienyl-*N*-phenylpyrrole).[31] It can be seen that as the potential is increased from −0.37 V to +0.73 V there is a steady increase in the absorbance of the polymer film across the NIR, as is expected upon oxidatively induced charge carrier formation in a conjugated polymer. Concurrent with this increase in NIR absorption, the π–π* transition is bleached. The polymer film is thus observed to change from yellow in the neutral form to a light green color at low levels of oxidation (+0.1 V *vs.* Fc/Fc^+) and finally to a gray-blue at higher doping levels, which is consistent with the gray-brown reported for *N*-phenyl analogue reported in the literature.[31]

Potentiostatic deposition of **P4** on ITO (in 0.1 TBAP/50 : 50 acetonitrile–toluene) at 0.5 V *vs.* Fc/Fc^+ led to the formation of an electroactive film that also changed from yellow to gray-blue upon oxidation, yielding an essentially identical spectroelectrochemical series (Fig. 7b) and a visually identical color change. Note that for both polymers there is a broad absor-

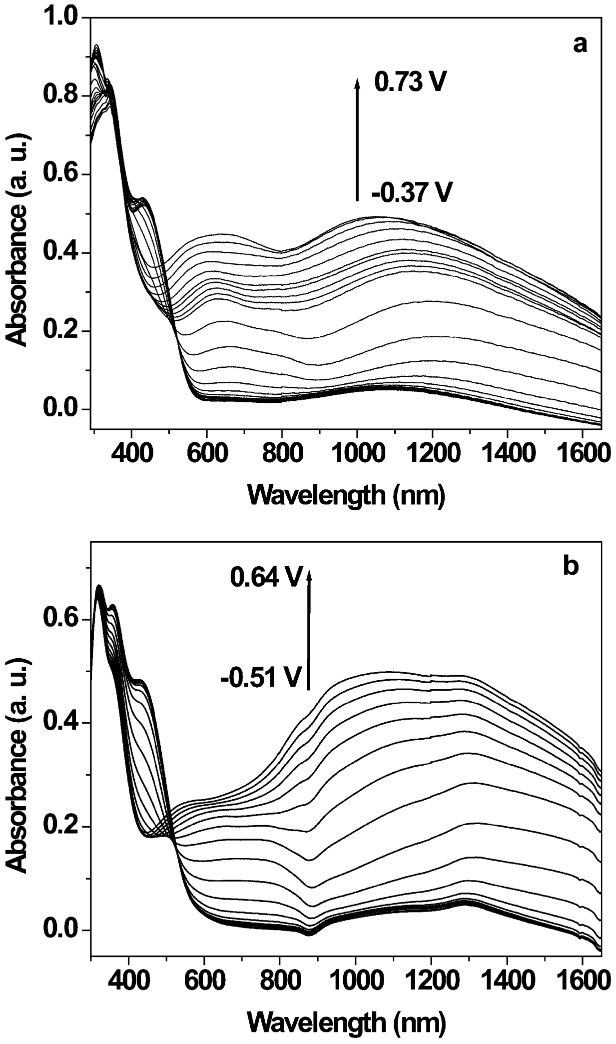


Fig. 7 (a) Spectroelectrochemical response for **P3** on ITO. Scans are taken at 50 mV increments from −0.37 to +0.73 V *vs.* Fc/Fc$^+$. (b) Spectroelectrochemical response for **P4** on ITO. Scans are taken at 50 mV increments from −0.51 to +0.64 V *vs.* Fc/Fc$^+$.

bance from 800–1200 nm in the neutral form. This absorbance is due to trapped charge carriers in the oxidatively deposited film that could not be removed even upon electrochemical or chemical (hydrazine) reduction.

Colorimetric analysis was also employed as means of further characterizing the electrochromic properties exhibited by these polymers. Table 1 summarizes the *Yxy* and relative luminance coordinates for the two polymers in their yellow neutral state, light green intermediate state, and in the gray-blue oxidized state. Fig. 8 shows the relative luminance (%*Y*) of the two polymer films as a function of potential, along with representative color swatches (derived from the *Yxy* data) for the three observed states. Here it can be seen that the yellow form of the polymers is transmissive while the gray blue form is more highly absorptive. Note that the film of **P3** is observed to be more transmissive across the range of applied potentials than **P4**. This can be attributed to **P3** being the thinner of the two films.

Table 1 Colorimetric coordinates for **P3** and **P4** in neutral, intermediate, and fully doped forms

	E/V	%*Y*	*x*	*y*
P3 Neutral (yellow)	−0.62	83	0.424	0.455
P3 Intermediate (green)	+0.13	65	0.378	0.427
P3 Oxidized (gray-blue)	+0.53	44	0.354	0.387
P4 Neutral (yellow)	−0.58	60	0.424	0.455
P4 Intermediate (green)	+0.07	55	0.356	0.396
P4 Oxidized (gray-blue)	+0.52	25	0.353	0.388

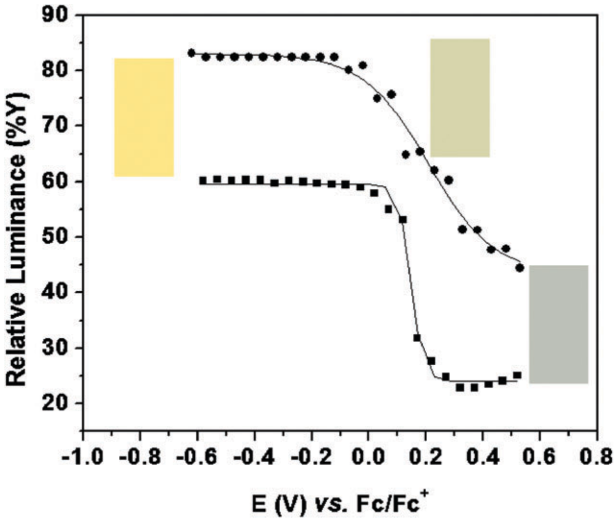


Fig. 8 A plot of relative luminance (%Y) *vs.* applied potential for **P3** (●) and **P4** (■) with color swatches to represent the color states.

Photochromism, thermochromism, and NLO properties

In addition to the electrochromism exhibited by the polymers, we find that molecular photochromism is exhibited by several of the monomers. The photochromic response of the monomers was investigated in solution and in crystalline powders. No photochromic response was observed for any of the monomers in dichloromethane solution upon irradiation with 365 nm light. This is not surprising as the photoproduct in solution is a transient species that is only observable by flash photolysis techniques.[32] In crystalline powder form, compounds **1** and **4** showed a photochromic response upon irradiation with 365 nm light, changing from yellow to red. Compounds **2** and **3** did not show any color change under the same conditions. It should be noted that in powder form, compound **1** is the only compound to exhibit second harmonic (SH) generation with an SH intensity of 0.3 times that of urea powder, indicating that the molecular packing in the crystal is non-centrosymmetric.

Encouraged by the molecular photochromism, initial photochromic studies were attempted on polymer films. For experiments on polymers, films were deposited potentiostatically on ITO as described above. To probe the photochromic response of the polymers, films were irradiated with 365 nm light in both the neutral and oxidized states as well as in air and electrolyte solution at room temperature. In all cases no visible color change was observed and no changes were found in the absorption spectra. To further investigate the chromic response of the polymer films, the thermochromic behavior was tested. Cooling polymer films in the neutral yellow form in liquid nitrogen yielded no change in film color. Additionally, polymer films were heated to 250 °C and again, no color change was observed. This lack of photochromic and thermochromic response is not totally surprising based on the number of complications associated with photoisomerization in an amorphous film.

Conclusions and outlook

Here we have presented the synthesis of a novel series of pyrrole-based monomers bearing salicylidene-aniline photochromes. The 2,5-dithienylpyrrole monomers (**3** and **4**) were found to electropolymerize to give electroactive and electrochromic polymer thin films that were observed to change from yellow to green to gray-blue upon oxidative doping. The polymers were not observed to show a photochromic response despite the photochromism observed in monomer **4**. Based on the promising initial results presented here concerning polymer electrochromism and molecular photochromism, it is possible that additional studies on polymer films may yield a further chromic response. Application of methods to increase the degree of order within a polymer film could facilitate a photochromic response and could serve to aid in the realization of a dual photochromic–electrochromic polymeric material based on salicylidene-aniline photochromes.

Acknowledgements

We wish to thank the NSF International Grant (INT-0339735) and the CNRS for funding this project. KAA wishes to acknowledge the National Science Foundation and the University of Florida for funding of the purchase of the X-ray equipment.

References

1 *Handbook of Conducting Polymers*, ed. T. A. Skotheim, R. L. Elsenbaumer and J. R. Reynolds, 2nd edn, Marcel Dekker, New York, 1998.
2 C. J. Brabec, N. S. Sariciftci and J. C. Hummelen, *Adv. Funct. Mater.*, 2001, **11**, 15.
3 R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund and W. R. Salaneck, *Nature*, 1999, **397**, 121.
4 N. Stutzmann, R. H. Friend and H. Sirringhaus, *Science*, 2003, **299**, 1881.
5 A. A. Argun, A. Cirpan and J. R. Reynolds, *Adv. Mater.*, 2003, **15**, 1338.
6 D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537.
7 A. A. Argun, P.-H. Aubert, B. C. Thompson, I. Schwendeman, C. L. Gaupp, J. Hwang, N. J. Pinto, D. B. Tanner, A. G. MacDiarmid and J. R. Reynolds, *Chem. Mater.*, 2004, **23**, 4401.
8 M. J. Marsella, Z.-Q. Wang and R. H. Mitchell, *Org. Lett.*, 2000, **2**, 2979.
9 I. Levesque and M. Leclerc, *Macromolecules*, 1997, **30**, 4347.
10 A. Izumi and R. Nomura, *Macromolecules*, 2001, **34**, 4342.
11 P. Audebert, S. Sadki, F. Miomandre, P. Hapiot and K. Chane-Ching, *New. J. Chem.*, 2003, **27**, 798.
12 M. Irie, *Chem. Rev.*, 2000, **100**, 1685.
13 F. Stellacci, C. Bertarelli, F. Toscano, M. C. Gallazzi, G. Zotti and G. Zerbi, *Adv. Mat.*, 1999, **11**, 292.
14 H. Durr, Photochromic Nitrogen-Containing Compounds, in *CRC Handbook of Organic Photochemistry and Photobiology*, ed. W. M. Horspool, CRC Press, Boca Raton, 1995, p. 1129.
15 J. W. Lewis and C. Sandorfy, *Can. J. Org. Chem.*, 1982, **60**, 1738.
16 T. Rosenfeld, M. Ottolenghi and A. Y. Meyer, *Mol. Photochem.*, 1973, **5**, 39.
17 E. Hadjoudis, Tautomerism by Hydrogen Transfer in Anils, Aci-Nitro and Related Compounds, in *Photochromism: Molecules and Systems*, ed. H. Durr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990, p. 685.
18 J. L. Laverty and Z. G. Gardlund, *J. Polym. Sci. Polym. Lett.*, 1969, **7**, 161.
19 M. S. M. Rawat and J. L. Norula, *Eur. Polym. J.*, 1985, **21**, 659.
20 M. Yin, Y. Haramoto and M. Nanasawa, *Polym. J. (Tokyo)*, 1995, **27**, 136.
21 M. Yin, T. Kuwabara, Y. Haramoto and M. Nanasawa, *Macromol. Chem. Phys.*, 1996, **197**, 575.
22 M. Hirai, T. Yuzawa, Y. Haramoto and M. Nanasawa, *React. Funct. Polym.*, 2000, **45**, 175.
23 P. E. Just, K. I. Chane-Ching and P. C. Lacaze, *Tetrahedron*, 2002, **58**, 3467.
24 B. C. Thompson, P. Schottland, K. Zong and J. R. Reynolds, *Chem. Mater.*, 2000, **12**, 1563.
25 R. Loucif-Saïbi, K. Nakatani, J. A. Delaire, M. Dumont and Z. Sekkat, *Chem. Mater.*, 1993, **5**, 229.
26 S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798.
27 S. Sadki, P. Schottland, N. Brodie and G. Sabouraud, *Chem. Soc. Rev.*, 2000, **29**, 283.
28 J. R. Reynolds, P. A. Poropatic and R. L. Toyooka, *Macromolecules*, 1987, **20**, 958–961.
29 (*a*) D. L. Meeker, D. S. K. Mudigonda, J. M. Osborn, D. C. Loveday and J. P. Ferraris, *Macromolecules*, 1998, **31**, 2943–2946; (*b*) J. P. Ferraris and G. D. Skiles, *Polymer*, 1987, **28**, 179–182.
30 J. P. Ferraris and M. D. Newton, *Polymer*, 1992, **33**, 391–397.
31 D. S. K. Mudigonda, D. L. Meeker, D. C. Loveday, J. M. Osborn and J. P. Ferraris, *Polymer*, 1999, **40**, 3407–3412.
32 E. Hadjoudis and I. M. Mavridis, *Chem. Soc. Rev.*, 2004, **33**, 579–588.