DOI: 10.1002/chem.201101397

Conjugated 4-Methoxybipyrrole Thiophene Azomethines: Synthesis, Opto-Electronic Properties, and Crystallographic Characterization

Tshitundu Tshibaka,[b] Sophie Bishop,[a] Ivan Ulliel Roche,[a, c] Stéphane Dufresne,[a] William D. Lubell,*[b] and William G. Skene*[a]

Abstract: In the search of functional materials with improved electrochromic properties, thiophenes and asymmetric bipyrroles have been conjugated with azomethine units. 4-Methoxy-2,2′-bipyrroles **3**–**6** were first synthesized by a general route from 4-hydroxyproline and converted subsequently to dialdehydes **8**–**15**, which underwent condensations with different aminothiophenes to provide azomethine conjugates **14**–**18** and **20**–**22**. The crystallization and X-ray analysis of **20** showed the heterocycles and azomethine bonds were all co-planar with the heterocycles adopting an anti-parallel arrangement. These configurations result in extended conjugation and enhanced opto-electronic properties of the azomethines. Oxidation potential (E_{pa}) was tailored by modification of the substitution pattern of the terminal thiophenes and central pyrroles of the azomethines. The combined low E_{pa} and extended azomethine degree of conjugation resulted in stark color transitions occurring between their neutral and oxidized states. Reversible color formation was induced both electrochemically and by doping/de-doping with trifluoroacetic acid/triethylamine.

Keywords: azomethines · electrochemistry · heterocycles · UV/Vis spectroscopy · unsymmetric bipyrroles

Introduction

Plastic electronics including light emitting devices (OLED), photovoltaic devices (OPVD), and organic field effect transistors (OFET),[1–6] all have made extensive application of thiophene-based materials. Thiophenes offer low oxidation potentials (E_{pa}) and reversible oxidation.[7] Conjugated systems containing thiophenes have been employed in electrochromic devices, because they may display sharp color changes within the visible spectrum upon electrochemical oxidation.[8]

Complementing thiophenes, pyrroles have been employed as components of conducting polymers, such as polypyrrole, which is used in sensors, due to their simple polymerization, stability, and good electrical conductivity.[9–11] Contingent on the structure of the pyrrole monomer,[12,13] conductivity and ease of synthesis may be altered. For example, poly(3,4-dimethoxypyrrole) has higher conductivity and is easier to synthesize than its unsubstituted and alkyl-substituted counterparts.[14,15] In this light, bipyrroles represent interesting starting points for constructing conducting polymers; however, to the best of our knowledge, only symmetric bipyrroles[9,16] have been studied, likely due to a dearth of methods for preparing unsymmetrical bipyrroles.[17–20]

Functional materials with multiple color states and a large palette of colors are required to meet the requirements for new electrochromic devices. Enhanced properties for improved color transitions have arrived from incorporating unsaturated linkages into conjugated materials, which may exhibit extended degrees of conjugation through coplanar aryl units.[8,21–26] For example, vinyl links have shown promise for preparing new functional materials; however, their synthesis by Gilch and Horner–Emmons protocols, often requires rigorous reaction conditions (i. e., anhydrous solvent and inert atmosphere), lacks atom economy and necessitates tedious product purification.[21,22] On the other hand, azomethines (−N=CH−) are isoelectronic to their vinyl counterparts,[27] however, their synthesis is relatively straightforward and efficient, involving condensation of amine and aldehyde components to produce the conjugate and water, facilitating purification.[28–30]

In spite of their practical synthesis, conjugated materials incorporating azomethines and heterocycles have not been pursued, likely because homoaryl azomethine counterparts exhibited properties incompatible for devices, such as poor electrochromic behavior and high E_{pa}.[31–35] Seeking new materials for electrochromic applications, we have studied het-

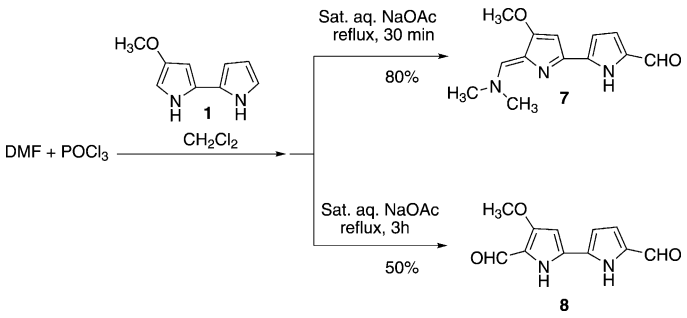
[a] S. Bishop, I. U. Roche, S. Dufresne, W. G. Skene
Laboratoire de caractérisation photophysique
des matériaux conjugués
Département de Chimie, Université de Montréal
CP 6128, succ. Centre-ville, Montréal
Québec, H3C 3J7 (Canada)

[b] T. Tshibaka, W. D. Lubell
Département de Chimie, Université de Montréal
CP 6128, succ. Centre-ville, Montréal
Québec, H3C 3J7 (Canada)

[c] I. U. Roche
Current Address: École Nationale Supérieure
de Chimie et Physique de Bordeaux (ENSCPB)
16 avenue Pey Berland, 33600 Pessac (France)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201101397.

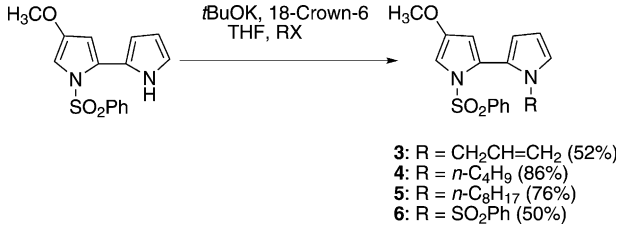
erocycle-azomethine conjugates exhibiting stark color transitions between neutral and oxidized forms at low E_{pa}. In particular, thiophenes and asymmetric bipyrroles have been conjugated with azomethine units. The synthesis of these novel conjugated systems is now reported as well as their characterization by X-ray crystallography and their electrochemical, spectroelectrochemical, and spectrochemical properties. Offering promise for use in functional electrochromic materials, these heterocycle–azomethine conjugates exhibit dramatic visible color changes upon electrochemical and chemical oxidization.



Scheme 2. Vilsmeier–Haack formylation of methoxybipyrrole **1**.

Results and Discussion

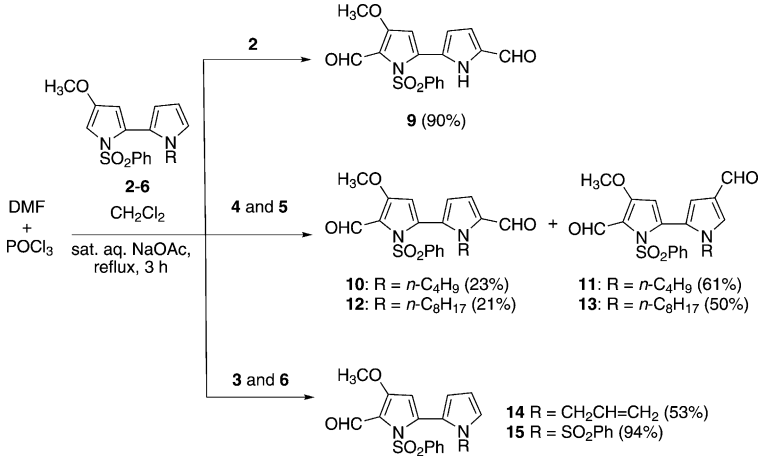
Synthesis: 4-Methoxy-2,2′-bipyrrole **1** and its sulfonamide **2**, were both prepared from hydroxyproline as described.[19,20] To explore the influence of a 1′-nitrogen substituent on the opto-electronic properties of bipyrrole analogs, the anion of the pyrrole nitrogen of **2** was generated with potassium *tert*-butoxide and [18]crown-6 ether in THF and respectively, alkylated in reactions with a set of alkyl iodides (allyl iodide, butyl iodide, octyl iodide) and sulfonylated with benzenesulfonyl chloride.[18,19] 4-Methoxy-1-phenylsufonyl-1′-allyl-2,2′-bipyrrole (**3**), its 1′-butyl and 1′-octyl counterparts **4** and **5** and 4-methoxy-1,1′-biphenylsufonyl-2,2′-bipyrrole (**6**) were isolated respectively after chromatography on silica gel in 52%, 86%, 76%, and 50% yields, respectively (Scheme 1).



Scheme 1. *N*′-Modification of bipyrrole **2**.

A series of mono- and bis-formyl analogs was then prepared by treating bipyrroles **1**–**6** under Vilsmeier–Haack formylation conditions[6] (Schemes 2 and 3). The Vilsmeier reagent was preformed in the neat by treating dimethylformamide with phosphoryl chloride and then added slowly to the respective bipyrrole in dichloromethane at −15 °C. The reaction mixture was then let warm to room temperature with stirring overnight. In the reaction of the parent 4-methoxy-2,2′-bipyrrole **1**, the workup with aqueous sodium acetate at reflux afforded enamine **7** in 80% yield (Scheme 2). On the other hand, bipyrrole dialdehyde **8** was isolated in 50% yield without need of further purification by extending the hydrolysis protocol and treating the reaction mixture with an aqueous solution of sodium acetate at reflux for 2 h. The same reaction and workup conditions used to prepare **8** were applied on sulfonamides **2**–**6** (Scheme 3).

Treatment of 1-phenylsulfonyl methoxybipyrrole **2** under the formylation and workup conditions used to prepare **8** provided 4-methoxy-1-benzenesulfonyl-5,5′-bisformyl-2,2′-bipyrrole **9** in 70% yield. Similarly, bis-formylation was observed with 1′-alkyl (butyl and octyl) bipyrroles **4** and **5**; however, mixtures of 5,5′- and 5,4′-regioisomers were obtained, with a preference for the latter (1:3 ratio). The 5,5′- and 5,4′-regioisomers were separable by chromatography such that 5,4′-substituted bipyrroles **11** and **13** were isolated in 61% and 50% yields, respectively, along with their 5,5′-counterparts **10** and **12** in 23% and 21% yields. 5,4′-Bis-formyl-2,2′-bipyrroles **11** and **13** were, however, unstable and observed by thin layer chromatography to degrade after a few hours at ambient atmosphere. Finally, selective monoformylation of the 5-position of the 1-phenylsulfonyl methoxypyrrole ring was observed when the same formylation and workup conditions were applied on 1-phenylsulfonyl 1′-

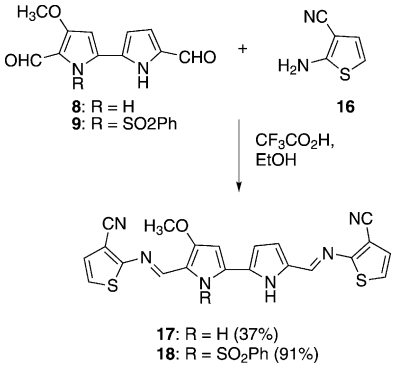


Scheme 3. Vilsmeier–Haack formylations of 1-phenylsulfonyl methoxybipyrroles **2**–**6**.

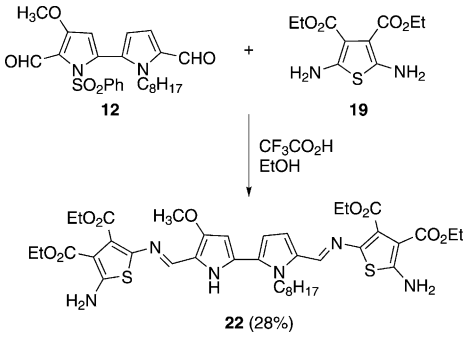
allylbipyrrole (**3**) and bis-sulfonamide **6** to respectively provide 5-formyl bipyrroles **14** and **15** in 50% and 94% yields, respectively (Scheme 3).

The position of bipyrrole formylation was determined by COSY and NOESY spectroscopy (see the Supporting Information). For example, in the NOESY spectrum of 5,5′-dialdehyde **9**, through space transfers of magnetization were observed, respectively, between the pyrrole 3-position proton (6.31 ppm) and the methoxy group singlet (3.9 ppm), between the 5-position aldehyde proton (10.17 ppm) and both the methoxy group singlet and the sulphonamide aromatic protons (7.37 ppm), and between the pyrrole 4′-position proton (6.99 ppm) and the 5′-position aldehyde proton (9.62 ppm). In the COSY spectrum of **9**, a through-bond coupling was observed between the pyrrole protons at the 3′- and 4′-positions (6.53 and 6.99 ppm). Similarly, in the NOESY spectrum of 5,5′-dialdehyde **10**, transfer of magnetization was respectively observed between the 5-position aldehyde proton (10.28 ppm) with the sulphonamide aromatic protons (7.5 ppm) and methoxy singlet (3.89 ppm), as well as between the 5′-position aldehyde proton (9.67 ppm) and both the pyrrole 4′-proton (6.99 ppm) and the butyl chain methylene proton signals (4.33 ppm). On the other hand, in the COSY spectrum of 5,4′-dialdehyde **11**, a through-bond coupling was observed between the 5-position aldehyde proton (10.27 ppm) and the pyrrole 3-position proton (6.18 ppm). In the NOESY spectrum of **11**, through-space transfer of magnetization was observed between the 4′-position aldehyde proton (9.79 ppm) and both the 3- and 5-position pyrrole protons (6.98 and 6.55 ppm). The COSY and NOESY spectra of *N*′-octyl bipyrroles **12** and **13** exhibited similar couplings and through-space transfer of magnetization as seen in spectra of **10** and **11**, respectively. For aldehyde **15**, the COSY spectrum exhibited coupling between the 3′-, 4′-, and 5′-pyrrole protons (6.22, 6.39, and 7.60 ppm) establishing the absence of a formyl group on the pyrrole B-ring. In addition, coupling was observed between the 5-position adehyde proton (10.22 ppm) with the pyrrole 3-position proton (5.93 ppm). The NOESY spectrum of **15** supported the assignment exhibiting through-space transfer of magnetization between the methoxy singlet (3.81 ppm) and pyrrole 3-position proton (5.93 ppm). For aldehyde **14**, the assignment of the aldehyde to the 5-position was based on its chemical shift (10.24 ppm), which in the case of dialdehydes **9**–**13**, appeared always further downfield relative to that of aldehydes on the pyrrole B-ring.

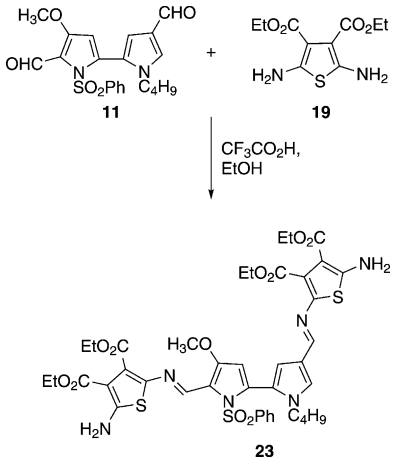
Asymmetric azomethine comonomers were next pursued by linking the 4-methoxy-2,2′-bipyrrole cores by way of imine bridges to two different amino thiophenes (Schemes 4–6). For these syntheses, 2-amino-3-cyanothiophene **16** and 2,5-diaminothiophene-3,4-dicarboxylic acid diethyl ester **19** were selected because of their previous application in condensations to form comonomers[28,37,38] and prepared as previously described.[39,40] The electron-withdrawing groups at the 3- and 4-positions of **16** and **19** deactivate the electron-rich amines at the 2- and 5-positions, conferring greater stability. Amine **16** and diamine **19** have the respective utility to end-cap the conjugated system and to allow for additional condensations to make longer comonomers.



Scheme 4. Condensations of methoxybipyrroles **8** and **9** with amino thiophene **16**.



Scheme 5. Condensation of methoxybipyrroles **12** with amino thiophene **19**.



Scheme 6. Condensation of methoxybipyrroles **11** with amino thiophene **19.**

The imine bridges were effectively assembled by dehydration of the respective bis-formyl bipyrrole and aminothiophene in ethanol containing catalytic trifluoroacetic acid (TFA) at reflux. Initially, the amino cyanothiophene **16** was employed in condensations under these conditions with the parent methoxybipyrrole **8** and its 1-phenylsulfonyl counterpart **9** to afford respectively the conjugated azomethine tet-

racycles **17** and **18**. In the case of the parent **8**, azomethine comonomer **17** was obtained after isolation by chromatography on silica gel in 37% yield. On the other hand, the reaction between 1-phenylsulfonyl methoxybipyrrole **9** and **16** did not provide product on heating at reflux with TFA in EtOH. At room temperature, however, the condensation of **9** and **16** went smoothly to yield azomethine tetracycle **17** in 91% yield after purification by chromatography on silica gel. Although the azomethine link appeared robust during the synthesis and analysis of the conjugated systems, certain products showed the appearance of new signals in their NMR spectra after storage over time, which may be due to various modes of decomposition.

Diaminothiophene **19** was subsequently reacted respectively with methoxybipyrrole **8** in ethanol containing catalytic TFA at reflux to provide conjugated azomethine tetracycle **20** in 65% yield after chromatography on silica gel. Attempts to perform the same condensation using the *N*-phenylsulfonyl analog **9** provided a condensation product in 28% yield after chromatography. Although the ion corresponding to azomethine tetracycle **21** was observed in the mass spectrometric analysis, inspection of the proton NMR spectrum demonstrated loss of the phenylsulfonyl group to provide **20**. Analysis of samples on silica plate suggested that the phenylsulfonyl group was likely removed from **21** during purification on silica gel.

Attempts were less successful to produce conjugated tetracycles from bipyrroles **10**–**13** possessing a 1′-alkyl substituent. No condensation product could be isolated from the reaction of 5,5′-bisformyl-1′-butylbipyrrole **10** and diaminothiophene **19** with TFA in ethanol at reflux. On the other hand, 5,5′-bisformyl-1′-octylbipyrrole **12** reacted with thiophene **19** and TFA in ethanol at room temperature to afford azomethine tetracycle **22** as a brown film in 28% yield (Scheme 5). Analysis of azomethine tetracycle **22** by proton NMR spectroscopy indicated that loss of the phenylsulfonamide had occurred in a similar way as described for **21** above. Temperature had an effect on the condensation of the 5,4′-bisformyl-1′-alkylbipyrroles **11** and **13**. From ethanol at reflux, no product was obtained in the condensation of thiophene **19** with 1′-*n*-octylbipyrrole **13**. On the contrary, the desired conjugated tetracycle **23** was isolated after chromatography on silica gel in 53% yield from condensation of 5,4′-bisformyl-1′-butylbipyrrole **11** with **19** using TFA in EtOH at room temperature. Conjugated tetracycle **23** proved, however, to be unstable and degraded as observed by thin layer chromatography, after sitting overnight under vacuum.

X-ray crystallography: Although only one isomer was detected by ^{1}H NMR spectroscopy of the azomethine analogs, assignment of *E* or *Z* configuration was not possible. Unequivocal assignment of the imine geometry was made possible by X-ray crystallography on a single crystal of tetracycle **20**, which crystallized from slow evaporation of acetone (Table 1). The crystal structure confirmed that **20** adopted the imine *E*-isomer. The methoxy group breaks the symmetry of tetracycle **20** and resulted in disordering within the crystal structure. The structure was solved without specific assignment of the position of the methoxy group; instead, the resolution was refined by placing its occupancy factor to 50%. The data nonetheless confirm the correct structure for **20** and illustrate a coplanar orientation of the heteroatoms in an anti-parallel arrangement (Figure 1), consistent with previous azomethine structures.[27,28,41]

Table 1. Details of crystal structure determination for **20**.

formula	$C_{31}H_{36}N_6O_9S_2$
M_r	699.19
crystal system	triclinic
space group	$P\bar{1}$
a [Å]	8.227 (10)
b [Å]	10.295 (10)
c [Å]	13.617 (18)
α [°]	73.85 (3)
β [°]	87.18 (5)
γ [°]	73.37 (3)
V [Å^3]	1061 (2)
Z	1
ρ_{calcd} [g cm^{-3}]	1.279
μ ($Cu_{K\alpha}$) [mm^{-1}]/abs. corr.	1.666/semi-empirical
F(000)	432
crystal size [mm^3]	0.10×0.07×0.04
T [K]	150(2)
reflections: collected/independent; R_{int}	13056/3938; 0.0322
M_w [g mol^{-1}]	816.93
crystal color and form	red plate
θ range [°]; completeness	3.38–71.11; 0.955
R_1(F); wR(F^2) [$I>2\sigma(I)$]	0.0492; 0.1474
R_1(F); wR(F^2) (all data)	0.0560; 0.1537
GOF(F^2)	1.050
max residual e$^-$ density	0.453 e$^-$ Å^{-3}

The terminal heterocycles of **20** were slightly twisted by 9.36° from the mean plane described by the central planar

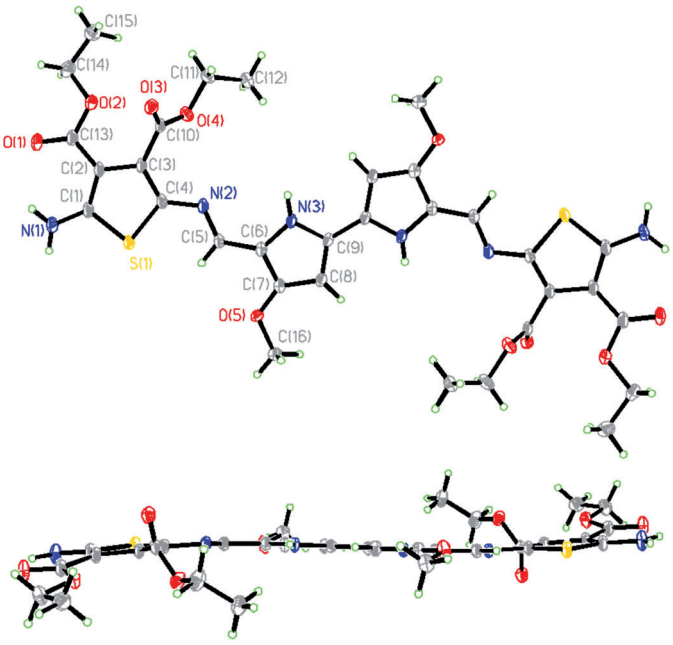


Figure 1. Structure of **20** (top) and seen along the *c* axis (bottom).

bipyrrole and the two azomethine bonds to which they are connected. The observed mean plane angles are in agreement with other heterocyclic azomethines and are in contrast to homoaryl azomethine structures, in which mean planes are highly twisted by 65°.[42] The C=N, N–aryl, and CH–aryl bond lengths for **20** were 1.299(3), 1.389(3), and 1.439(3) Å, respectively, on both sides. The observed coplanarity of the aryl groups and the azomethine bonds confirm the high degree of π-conjugation of the azomethine, as per the spectroscopic data.

Intermolecular interactions between the molecules in the solid state were apparent in the crystallographic data. For example, hydrogen bonds were observed between two terminal aminothiophenes and the carbonyl forming an acceptor-donor-acceptor motif, as seen in Figure 2. The distances for N1–H1A···O1^{i}, N1–H1B···O99^{iii}, and N3–H3A···O3^{ii} were 2.309, 2.015, and 2.194 Å, respectively. The angles of these hydrogen bridges were 136, 164, and 154°, respectively, which were consistent with hydrogen bonding. Every molecule was well-aligned in one direction within the 3D arrangement (Figure 3). No regular π-stacking was found, because hydrogen bonding shifted the direction of the π-stacking. Linear and coplanar configurations were adopted by the comonomers, because of the contributions of such interactions.

Electrochemistry: The electrochemical oxidation of the azomethines was investigated by cyclic voltammetry in anhydrous and deaeareted dichloromethane. The anodic behavior of tetracycles **20** and **22** was investigated at different scan speeds. The number of electrons involved in the anodic processes was assigned and the reversibility of the resulting intermediates was unequivocally determined. In contrast to analogous aminothiophene azomethines, which exhibited reversible radical cation formation,[28,29] the first oxidation of **20** and **22** was irreversible (Figure 4), most likely due to the unsubstituted pyrrole positions in the reactive radical cation, which may have underwent cross-coupling. The cathodic current associated with the second oxidation process was much smaller than its corresponding anodic current, which when taken together with the change in E_{pa} as a function of scan speed, confirmed that the second oxidation process was pseudo-reversible. The Randles–Sevcik relationship was used to determine the number of electrons participating in the anodic processes. The peak current at different scan rates, relative to ferrocene as internal reference, was em-

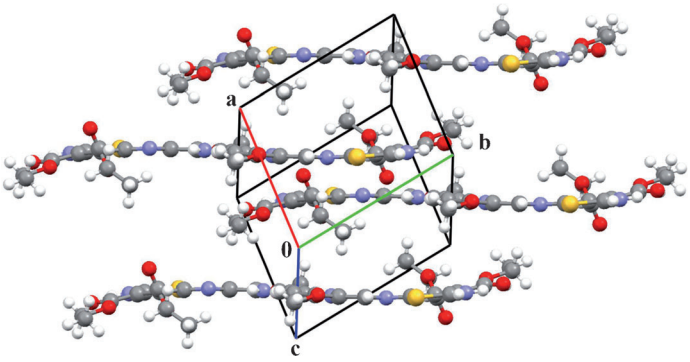


Figure 3. Structure of crystal matrix of **20** (solvent molecules omitted for clarity).

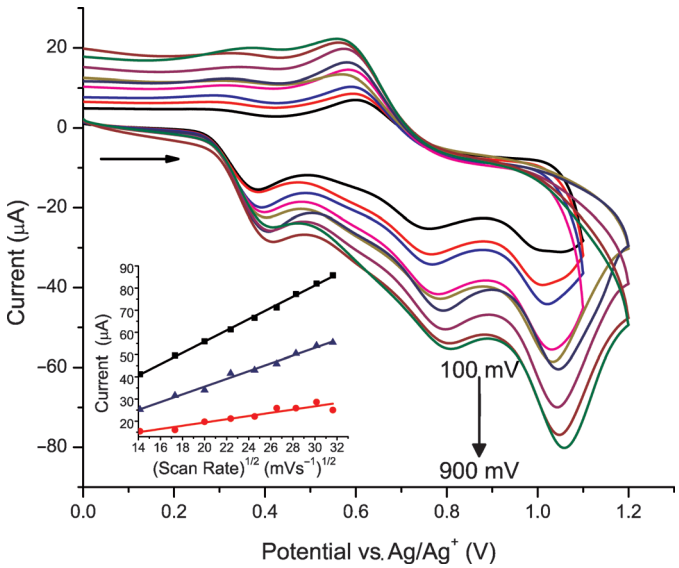


Figure 4. **20** measured at scan rates between 200 and 900 mV. Inset: Randles–Sevcik plot of the first (●) and second (▲) oxidation peaks of **20** relative to ferrocene (■) measured in dichloromethane.

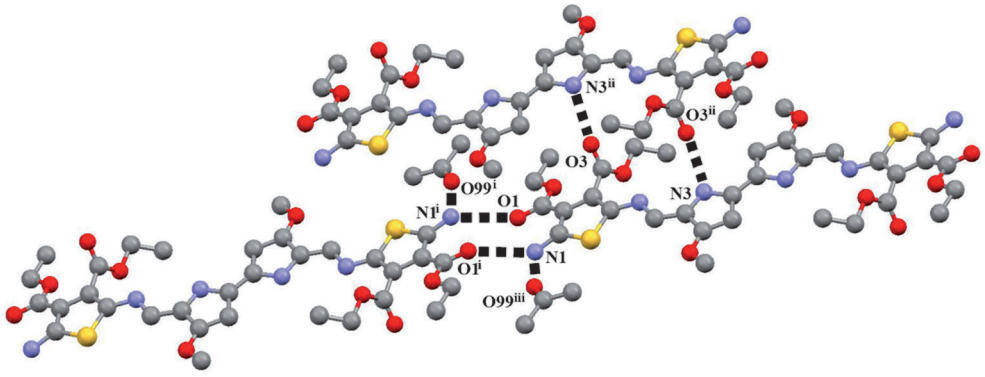


Figure 2. Structure of **20**. Symmetry codes: i) $-x$, $2-y$, $-z$; ii) $1-x$, $1-y$, $1-z$; iii) x, y, $1+z$; hydrogen bonds are indicated with dotted lines.

ployed to derive the number of electrons participating in the oxidation processes according to: $i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C v^{1/2}$, in which i_p is the peak current, n the number of electrons involved in the oxidation process, D the diffusion coefficient, A the electrode surface area, C the concentration, and v the scan rate. Ferrocene ($E_{pa} = 0.46$ vs. SCE in dichloromethane) was also used as an internal reference for determining the diffusion coefficient concomitant with other parameters of the Randles–Sevcik equation.[43] Azomethine **20** underwent two oxidation processes: one at about 0.4 and another at approximately 0.7 V. The oxidation of **20** was determined to proceed by a sequential one-electron process, by taking into account the different diffusion rates, which correlated with formation of the radical cation and dication (Figure 4).

The double oxidation was also observed for **22**. Conversely, both **17** and **18** underwent a single oxidation process. The oxidation potentials measured for the azomethines at similar scan speeds are summarized in Table 2. From the tabulated data, it is obvious that the first oxidation potentials of **20** and **22**, corresponding to the radical cation, are lower than for **17** and **18**. This is a result of the strong electron donating character of the terminal amine that decreases the oxidation potential. The second one-electron oxidation affording the dication of **17** and **18** is not visible, which is assumed to be a result of their higher E_{pa} relative to **20** and **22**, implying that dication oxidation occurs beyond the working solvent redox window. By tailoring the N-pyrrole and terminal-thiophene substitutions with varying electronic groups, we were thus able to adjust the potential at which the radical cation was formed. It should be noted that the exact heterocycle that is oxidized to form the radical cation and further oxidized leading to the dication cannot be determined. However, the semi-empirically calculated SOMO levels for **20** (see Figures 6 and 7 in the Supporting Information) show the radical cation and dication are not localized on a specific heterocycle; instead, they are evenly distributed across the tetracycle.

Table 2. Spectroscopic and electrochemical data of neutral and corresponding radical cations of unsymmetric bipyrrole azomethines.

Compound	λ_{abs} [nm]	R^+ [nm][a]	E_{pa} [V][b]	E_{pc} [V][b]	E_g [eV][c]
20	520	560 (605)	0.4; 0.8	−1.3	1.1
22	480	540 (610)	0.3; 0.7	−1.3	1.1
17	520	785	0.8	−1.1	1.4
18	480	540	1.1	−1.2	1.8

[a] Absorbance of radical cation. [b] Potentials vs. Ag/Ag^+, corrected using ferrocene (0.435 V) as an internal reference.[43] [c] Electrochemical energy-gap taken as the difference between the measured HOMO and LUMO values.

The HOMO and LUMO energy values can be determined from the redox onsets (E^{onset}) according to: HOMO = $-(E_{pa}^{onset}+4.4)$ and LUMO = $-(E_{pc}^{onset}+4.4)$ (Table 2). The energy-gap (E_g) calculated from the energy levels was approximately 1.5 eV and illustrated that the compounds were air stable and did not spontaneously oxidize or decompose under ambient conditions.

The spectroelectrochemistry of the azomethines was investigated for assessing the spectroscopic properties of the electrochemically induced radical cation intermediates. Upon applying potentials slightly greater than the first E_{pa}, both **20** and **22** underwent stark color changes (Figure 5 inset). The initial red color of neutral **20** ($\lambda_{max} = 520$ nm) bleaches concomitant with a new absorbance of the blue radical cation, visible at 560 nm. Similarly, the radical cation of **22** was also blue and bathochromically shifted 60 nm from the neutral absorbance; however, **22** had a strong shoulder absorbance at 610 nm. The clear isosbestic point seen for both **20** and **22** confirmed the interdependence of the neutral and oxidized states, demonstrating that oxidation of these azomethines gave rise to a single product, which was assigned to the radical cation based on the cyclic voltammetric measurements. The spectroelectrochemical data demonstrated that the azomethines undergo reversible stark visible color changes upon radical cation formation.

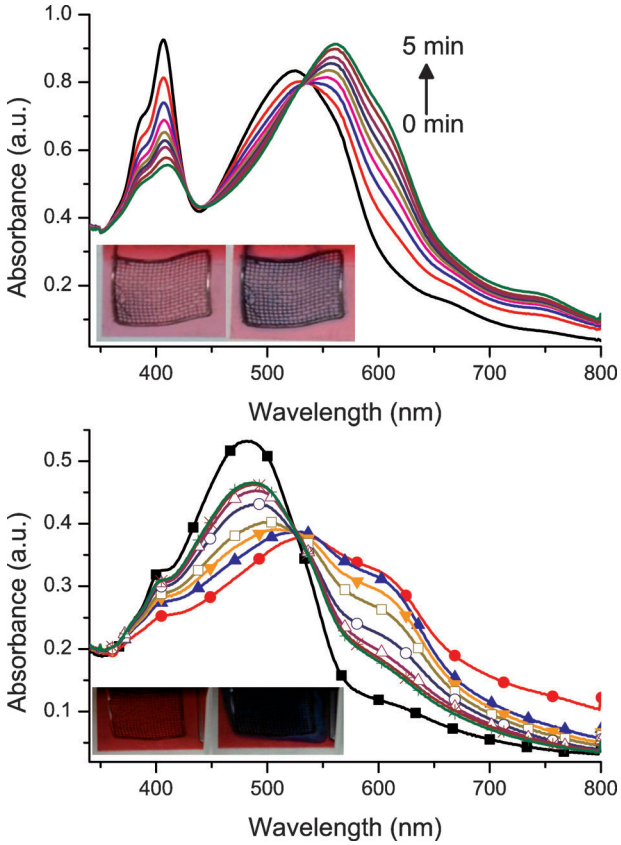


Figure 5. Absorbance spectra change of **20** upon applying an oxidation potential of 0.4 V for 0 to 5 min. Inset: Color change of **20** before (left) and after (right) electrochemical oxidation. Bottom: Absorbance spectra change of **22** upon applying an oxidation potential of 0.5 V for 0 (■) and 3 min (●) followed by applying a potential of −0.1 V for 0 (▲), 1 (▼), 4 min (□) followed by −0.25 V applied for 1 (○), 2 (△), 3 (*), and 5 (+). Inset: Color change of **22** before (left) and after (right) electrochemical oxidation.

The stability of the oxidized intermediate under the spectroelectrochemical conditions was examined by applying a negative potential to neutralize the anodically induced intermediate of **22** (Figure 5). The absorbance spectrum of the reduced intermediate was identical to that of the original neutral **22**; however, the intensity of the neutralized radical cation was somewhat lower than that of the original **22**, likely because of cross-coupling of the radical cation, as noted previously in the cyclic voltammetric studies. The clear isosbestic point and the persistent absorbance at 520 nm confirmed the lack of azomethine decomposition and illustrated the robustness of the azomethine-linked heterocyclic systems.

Chemical oxidation: Azomethines have been misperceived to be susceptible to decomposition.[44] On the contrary, azomethines **17**, **18**, **20**, and **22**, all exhibited spectroelectrochemical properties indicative of their stability during reversible oxidation. Chemical doping of **20** was next performed, because significant spectroscopic changes between the neutral and oxidized forms of this azomethine were observed when electrochemically oxidized. Chemical doping affords the means to investigate the stability of both the doped products and neutral azomethines via dissipation and/or irreversible color formation, because of diffusion controlled kinetics, in contrast to the spectroelectrochemical measurements. For example, the chemical doping of **20** with increasing amounts of TFA was contingent on the number of equivalents of added acid and the apparent color shift from 520 to 625 nm was observed as the neutral species converted to the radical cation and finally to the dication (Figure 6). Moreover, the doped intermediate could be neutralized with excess of triethylamine to restore the original color of neutral **20**. The robustness of azomethine **20** was illustrated by performing multiple doping/dedoping cycles without significant color variation.

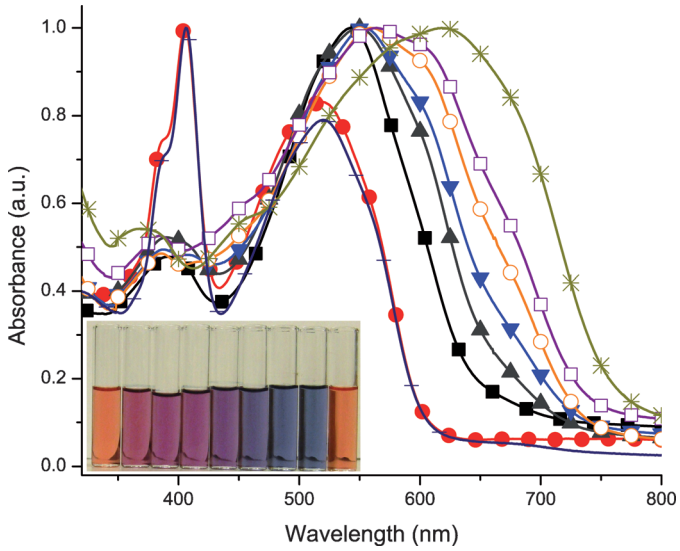


Figure 6. Compound **20** with added TFA 0 (●), 1 (■), 2 (▲), 5 (▼), 20 (○), 40 (□), 100 (*) equivalents followed by the addition of 100 equivalents of Et_3N (–). Inset: Change in color of **20** with the addition of increasing amounts of 0–100 equivalents trifluoroacetic acid (from left to right) followed by the addition of 100 equivalents of triethylamine (right).

Conclusion

Conjugated azomethines composed of thiophene and bipyrrole units were synthesized. They were oxidized at low potentials and switched reversibly between oxidized and neutral states giving rise to stark color transitions. The heterocyclic conjugated azomethines, such as **20** and **22** exhibited enhanced spectroscopic and electrochemical properties, which could be tuned by modification of pendant groups. In light of the stark color states exhibited by the bipyrrole–thiophene aozmethine analogues, resounding evidence was obtained to demonstrate that robust conjugated azomethines may be prepared for employment in functional materials for potential electrochromic applications.

Experimental Section

General protocols: Unless noted otherwise, all reactions were performed under argon atmosphere, using anhydrous conditions and flame-dried glassware. Anhydrous solvents (tetrahydrofuran, toluene and methylene chloride) were obtained by passage through solvent filtration systems (GlassContour, Irvine, CA). 4-Methoxy-2,2′-bipyrrole **1** and its sulfonamide **2**, both were prepared from hydroxyproline as previously described.[19,20] Chromatography was performed on silica gel (Silicycle; 230–400 mesh). Melting points are uncorrected. NMR spectra were recorded on Bruker AV 400 MHz and AV 300 MHz spectrometers. Chemical shifts are reported in ppm (δ units) downfield from internal tetramethylsilane ($(CH_3)_4Si$), or relative to peaks for residual solvent: $CHCl_3$, $(CH_3)_2CO$, and DMSO. Accurate mass measurements were performed by the Centre Régional de Spectrometrie de Masse de l'Université de Montréal on a LC-MSD-TOF instrument from Agilent technologies in positive electrospray mode. Either protonated molecular ions $[M+H]^+$ or sodium adducts $[M+Na]^+$ were used for empirical formula confirmation.

Absorption measurements were performed on a Cary-500 spectrometer and fluorescence studies were carried out on an Edinburgh Instruments FLS-920 fluorimeter after degassing the samples thoroughly with nitrogen for 20 min. Compounds were dissolved in anhydrous, degassed dichloromethane at 10^{-5} M.

Cyclic voltammetry measurements were performed on a Bio Analytical Systems EC Epsilon potentiostat. Compounds were dissolved in anhydrous, deaerated dichloromethane at 10^{-4} M along with sufficient NBu_4PF_6 as supporting electrolyte for satisfactory conductivity. A platinum button electrode was used as the working electrode. Platinum wire and silver wire electrodes were employed as auxiliary and reference electrodes, respectively.

Spectroelectrochemical measurements were performed by combining a Bio Analytical Systems EC Epsilon potentiostat with a Cary-500 spectrometer, using a thin optical path length cuvette (from NSG Precision Glass) with a platinum gauze wire as the working electrode, a platinum counter electrode, and saturated Ag/AgCl or silver wire Ag/Ag^+ reference electrode, applying a potential greater than the E_{pa} of the given compound. The spectroelectrochemical cell was provided by CH Instruments Japan (CHI140 A) with a spectroscopic height of 6.5 mm and an optical path length of 1 mm.

Representative method A for bipyrrole *N*-alkylation

4-Methoxy-1-phenylsufonyl-1′-allyl-2,2′-bipyrrole (3): A solution of 4-methoxy-1-benzenesulfonyl-2,2′-bipyrrole **2** (15 mg, 0.04 mmol, 1 equiv) in

THF (1 mL) was added dropwise to a 0 °C solution of potassium *tert*-butoxide (15 mg, 0.13 mmol, 3.2 equiv) and [18]crown-6 ether (2 mg, 0.008 mmol, 0.1 equiv) in THF (1 mL), stirred for 30 min, and treated with allyl iodide (11 μL, 1.2 mmol, 1.2 equiv). The ice bath was removed and the solution was allowed to warm to room temperature, with stirring overnight. The reaction mixture was partitioned between water (3 mL) and EtOAc (5 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 mL). The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum to a residue that was purified by column chromatography on silica gel (R_f=0.3; 50% EtOAc/hexanes). Evaporation of the collected fractions gave the allyl bipyrrole **3** as a green oil (9 mg, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.56–7.52 (m, 5H), 6.91 (d, J=2.1 Hz, 1H), 6.74 (t, J=2.4 Hz, 1H), 6.14 (t, J=3.6 Hz, 1H), 6.00 (d, J=2.1 Hz, 1H), 5.89–5.87 (m, 2H), 5.12 (d, J=1.5 Hz, 1H), 5.03 (d, J=1.5 Hz, 1H), 4.22 (m, 2H), 3.75 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=151.2, 139.1, 135.2, 134.4, 129.5 (2C), 128.2 (2C), 126.4, 123.0, 122.4, 118.1, 113.9, 111.9, 108.3, 103.9, 58.4, 50.5 ppm; HRMS: *m*/*z* calcd for $C_{18}H_{19}N_2O_3S$: 343.1110 $[M+H]^+$; found: 343.1121.

4-Methoxy-1-phenylsulfonyl-1′-butyl-2,2′-bipyrrole (**4**): This compound was obtained using Method A from 4-methoxy-1-benzenesulfonyl-2,2′-bipyrrole (**2**, 30 mg, 0.1 mmol) and 1-iodobutane (17 μL, 0.14 mmol) as a brown oil (31 mg, 86%), after chromatography. R_f=0.5 (20% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ: 7.56–7.41 (m, 5H), 6.93 (t, J=1.5 Hz, 1H), 6.77 (d, J=0.9 Hz, 1H), 6.12 (d, J=2.1 Hz, 1H), 6.02 (d, J=1.5 Hz, 1H), 5.81 (t, J=1.2 Hz, 1H), 3.77 (s, 3H), 3.69–3.65 (m, 2H), 1.58 (m, 2H), 1.21 (m, 2H), 0.88–0.84 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=151.2, 139.1, 134.3, 129.5 (2C), 128.3 (2C), 126.9, 122.8, 122.5, 113.5, 111.9, 107.8, 103.9, 58.5, 47.9, 33.9, 20.9, 14.4 ppm: HRMS: *m*/*z* calcd for $C_{19}H_{23}N_2O_3S$: 359.1423 $[M+H]^+$; found: 359.1425.

4-Methoxy-1-phenylsulfonyl-1′-octyl-2,2′-bipyrrole (**5**): This compound was obtained using Method A from 4-methoxy-1-benzenesulfonyl-2,2′-bipyrrole (**2**, 25 mg, 0.08 mmol) and 1-iodooctane (22 μL, 0.12 mmol) as a brown oil (26 mg, 76%), after chromatography. R_f=0.53 (20% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.55–7.41 (m, 5H), 6.93 (t, J=1.5 Hz, 1H), 6.77 (d, J=0.9 Hz, 1H), 6.12 (d, J=2.1 Hz, 1H), 6.01 (d, J=1.5 Hz, 1H), 5.82 (t, J=1.2 Hz, 1H), 3.77 (s, 3H), 3.66 (m, 2H), 1.58 (m, 2H), 1.23 (m, 10H), 0.90–0.88 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=151.2, 139.1, 134.4, 129.6 (2C), 128.3 (2C), 126.9, 122.8, 122.3, 113.4, 111.8, 107.7, 103.9, 58.3, 48.2, 32.5, 31.7, 29.9, 29.9, 27.5, 23.3, 14.9 ppm; HRMS: *m*/*z* calcd for $C_{23}H_{31}N_2O_3S$: 415.2050 $[M+H]^+$; found: 415.2051.

4-Methoxy-1,1′-biphenylsulfonyl-2,2′-bipyrrole (**6**): This compound was prepared using Method A from 4-methoxy-1-benzenesulfonyl-2,2′-bipyrrole (**2**, 25 mg, 0.08 mmol) and benzenesulfonyl chloride (49 μL, 0.23 mmol) as a white solid (18 mg, 50%) after chromatography. R_f=0.79 (50% EtOAc/hexanes); ^{1}H NMR (400 MHz, CDCl): δ=7.62 (m, 6H), 7.48 (m, 5H), 6.94 (d, J=2 Hz, 1H), 6.31 (t, J=1.2 Hz, 1H), 5.99 (d, J=1.6 Hz, 1H), 5.77 (s, 1H), 3.78 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=149.2, 138.4, 138.4, 133.5, 133.3, 128.7 (2C), 128.6 (2C), 127.1 (2C), 126.9 (2C), 123.9, 122.2, 121.6, 118.9, 11.4, 110.7, 103.4, 57.3 ppm; HRMS: *m*/*z* calcd for $C_{21}H_{19}N_2O_5S_2$: 443.0730 $[M+H]^+$; found: 443.0730.

Representative Method B

4-Methoxy-1-benzenesulfonyl-5,5′-bisformyl-2,2′-bipyrrole (9): Phosphoryl chloride (49 μL, 0.52 mmol, 4 equiv) was added to dimethylformamide (0.1 mL, 1.3 mmol, 10 equiv) at 5–10 °C and stirred for 30 min. A solution of 4-methoxy-1-benzenesulfonyl-2,2′-bipyrrole (**2**, 40 mg, 0.13 mmol, 1 equiv) in 1.6 mL of dichloromethane was cooled to −15 °C, and treated dropwise with the preformed solution of Vilsmeier reagent. The reaction mixture was stirred at −15 °C for 30 min, at 0 °C for 9 h, at room temperature overnight, treated with a saturated aqueous sodium acetate solution (3 mL) and heated to a reflux for 2 h. The layers were separated and the aqueous layer was extracted with EtOAc. The organic layers were combined, washed with brine, dried ($MgSO_4$), and concentrated to a residue that was purified by chromatography on silica (60% EtOAc in hexanes). Evaporation of the collected fractions yielded dialdehyde **9** as a green oil (43 mg) in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ=10.17 (m, 2H), 9.62 (s, 1H), 7.55 (m, 1H), 7.37 (m, 4H), 7.00 (dd, J=1.5, 2.5 Hz, 1H), 6.53(dd, J=1.5, 2.5 Hz, 1H), 6.32 (s, 1H), 3.88 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=180.7, 179.7, 159.1, 136.3, 134.7, 134.5, 134.3, 129.2, 128.2, 127.1, 121.1, 120.4, 115.2, 107.1, 59.0 ppm; HRMS: *m*/*z* calcd for $C_{17}H_{15}N_2O_5S$: 359.0696 $[M+H]^+$; found: 359.0708.

4-Methoxy-5,5′-bisformyl-2,2′-bipyrrole (**8**): This compound was prepared according to method B from bipyrrole **1** (40 mg, 0.24 mmol) without purification by chromatography. Dialdehyde **8** was obtained as a green oil (26 mg, 50%). R_f=0.54 (50% EtOAc/hexanes); ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ=9.56 (s, 1H), 9.53 (s, 1H), 7.07 (d, J=4 Hz, 1H), 6.93 (m, 2H), 6.85 (br, 1H), 6.65 (s, 1H), 3.91 ppm (s, 3H); HRMS: *m*/*z* calcd for $C_{11}H_{11}N_2O_3$: 219.0764 $[M+H]^+$; found: 219.0754.

4-Methoxy-1-phenylsulfonyl-1′-allyl-5-formyl-2,2′-bipyrrole (**14**): This compound was prepared according to method B from bipyrrole **3** (7 mg, 0.03 mmol) as a green oil (4 mg, 53%). R_f=0.3 (50% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.23 (s, 1H), 7.59–7.41 (m, 5H), 6.92 (s, 1H), 6.25 (t, J=3.2 Hz,1H), 6.17 (t, J=2 Hz, 1H), 6.08 (s, 1H), 5.89 (m, 1H), 5.16 (d, J=10.4 Hz, 1H), 5.08 (d, J=16.8 Hz, 1H), 4.56 (d, J=5.6 Hz, 2H), 3.87 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=181.5, 160.2, 137.4, 136.6, 135.1, 134.7, 129.7 (2C), 128.4 (2C), 125.7, 123.1, 121.1, 118.7, 114.8, 109.1, 107.9, 59.7, 51.6 ppm; HRMS: *m*/*z* calcd for $C_{19}H_{19}N_2O_4S$: 371.1060 $[M+H]^+$; found: 371.1070.

4-Methoxy-1-benzenesulfonyl-1′-butyl-5,5′-bisformyl-2,2′-bipyrrole (10) and 4-methoxy-1-benzenesulfonyl-1′-butyl-5,4′-bisformyl-2,2′-bipyrrole (11): These compounds were prepared according to method B from bipyrrole **4** (27 mg, 0.08 mmol) and separated during purification by column chromatography on silica gel. First to elute was 5,5′-dialdehyde **10** as a brown oil (7 mg, 23%): R_f=0.27 (40% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ=10.28 (s, 1H), 9.67 (s, 1H), 7.63 −7.43 (m, 5H), 6.98 (d, J=4.2 Hz, 1H), 6.22 (s, 1H), 6.18 (d, J=4.2 Hz, 1H), 4.33 (br, 2H), 3.90 (s, 3H), 1.58 (m, 2H), 1.18 (m, 2H), 0.83 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=181.4, 180.3, 159.6, 137.6, 135.7, 134.4, 133.3, 131.9, 130.0 (2C), 128.3 (2C), 124.1, 121.5, 114.6, 108.9, 59.7, 47.9, 34.2, 20.5, 14.6 ppm; HRMS: *m*/*z* calcd for $C_{21}H_{23}N_2O_5S$: 415.1322 $[M+H]^+$; found: 415.1329. Second to elute was 5,4′-dialdehyde **11** as a yellow oil (19 mg, 61%). R_f=0.17 (40% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ=10.2 (s, 1H), 9.8 (s, 1H), 7.62–7.43 (m, 6H), 6.54 (d, J=1.8 Hz, 1H), 6.18 (s, 1H), 4.08 (t, J=6.9 Hz, 2H), 3.88 (s, 3H), 1.68 (m, 2H), 1.28 (m, 2H), 0.90 ppm (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=185.8, 181.4, 159.9, 137.2, 135.7, 134.2, 132.2, 130.0 (2C), 128.3 (2C), 126.3, 126.08, 121.3, 112.6, 109.1, 59.5, 49.6, 33.3, 20.7, 14.3 ppm; HRMS: *m*/*z* calcd for $C_{21}H_{23}N_2O_5S$: 415.1322 $[M+H]^+$; found: 415.1330.

4-Methoxy-1-benzenesulfonyl-5,5′-bisformyl-1′-octyl-2,2′-bipyrrole (12) and 4-methoxy-1-benzenesulfonyl-5,4′-bisformyl-1′-octyl-2,2′-bipyrrole (13): These compounds were prepared according to method B from bipyrrole **5** (21 mg, 0.05 mmol) and separated during purification by column chromatography on silica gel. First to elute was 5,5′-dialdehyde **12** as a clear oil (5 mg, 21%): R_f=0.32 (40% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ=10.28 (s, 1H), 9.67 (s, 1H), 7.65–7.42 (m, 5H), 6.98 (d, J=3.9 Hz, 1H), 6.21 (s, 1H), 6.18 (d, J=3.8 Hz, 1H), 4.32 (br, 2H), 3.90 (s, 3H), 1.58 (m, 2H), 1.24 (m, 10H), 0.86 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=181.3, 180.6, 159.3, 137.7, 135.4, 134.3, 133.4, 132.0, 129.9 (2C), 128.4 (2C), 123.8, 121.5, 114.7, 109.0, 59.9, 48.1, 32.6, 31.9, 30.0, 29.9, 27.5, 23.4, 14.9 ppm; HRMS: *m*/*z* calcd for $C_{25}H_{31}N_2O_5S$: 471.1948 $[M+H]^+$; found: 471.1951. Second to elute was 5,4′-dialdehyde **13** as an orange oil (12 mg, 50%). R_f=0.22 (40% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ=10.11 (s, 1H), 9.78 (s, 1H), 7.83 (d, J=1.5 Hz, 1H), 7.75 (m, 1H), 7.61 (m, 4H), 6.61 (s, 1H), 6.55 (d, J=1.5 Hz, 1H), 4.12 (m, 2H), 3.88 (s, 3H), 0.83–1.71 ppm (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=185.7, 181.3, 159.7, 137.2, 135.6, 134.1, 132.4, 130.0 (2C), 128.2 (2C), 126.3, 126.2, 121.3, 112.5, 109.1, 59.7, 49.9, 32.5, 31.1, 29.9, 29.8, 27.3, 23.4, 14.9 ppm; HRMS: *m*/*z* calcd for $C_{25}H_{31}N_2O_5S$: 471.1948 $[M+H]^+$; found: 471.1950.

4-Methoxy-1,1′-diphenylsulfonyl-5-formyl-2,2′-bipyrrole (**15**): This compound was prepared according to method B from bipyrrole **6** (15 mg, 0.03 mmol). Purification by column chromatography on silica gel afforded **15** as a brown solid (15 mg, 94%). R_f=0.27 (50% EtOAc/hexanes); m. p. 156–158 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=10.22 (s, 1H), 7.75–

7.45 (m, 11H), 6.40 (t, $J=3.3$ Hz, 1H), 6.22 (m, 1H), 5.91 (d, $J=0.6$ Hz, 1H), 3.81 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=181.2$, 158.6, 139.4, 138.8, 135.1, 135.0, 131.9, 130.1 (2C), 129.9 (2C), 128.5 (2C),128.2 (2C), 126.3, 123.8, 121.1, 119.3, 112.2, 108.6, 59.5 ppm; HRMS: *m/z* calcd for $C_{22}H_{19}N_2O_6S_2$: 471.0679 $[M+H]^+$; found: 471.0690.

5′-(Dimethylamino)methylene-4-methoxy-1*H*,5′*H*-2,2′-bipyrrole-5-carbaldehyde (7): This compound was prepared according to method B from bipyrrole **1** (16 mg, 0.05 mmol). The hydrolysis with saturated aqueous sodium acetate solution was stopped after 30 min and **7** was isolated by extraction with ethyl acetate. The organic extracts were dried over $MgSO_4$, filtered, and evaporated to a green solid (20 mg, 80%): m. p. 205–208 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=9.82$ (s, 1H), 7.50 (s, 1H), 6.96 (d, $J=3.9$ Hz, 1H), 6.75 (d, $J=3.9$ Hz, 1H), 6.18 (s, 1H), 3.95 (s, 3H), 3.91 (s, 3H), 3.50 ppm (s, 3H); ^{13}C NMR (100 MHz, $(CDCl_3)$: $\delta=$ 180.9, 165.6, 143.9, 143.5, 137.0, 128.8, 117.8, 115.0, 110.9, 94.9, 59.6, 49.7, 44.3 ppm; HRMS: *m/z* calcd for $C_{13}H_{16}N_3O_2$: 246.1237 $[M+H]^+$; found: 246.1230.

Representative procedure C

Tetraethyl-5,5′-[(4-methoxy-1*H*,1′*H*-2,2′-bipyrrole-5,5′-diyl)bis(methanylydene)]bis(azanylylidene) bis(2-aminothiophene-3,4-dicarboxylate) (20): A solution of 2,5-diaminothiophene-3,4-dicarboxylic acid diethyl ester (**19**, 76 mg, 0.29 mmol, 2.2 equiv) in absolute ethanol (31 mL) was treated with 4-methoxy-5,5′-bisformyl-2,2′-bipyrrole (8, 29 mg, 0.13 mmol, 1 equiv) followed by a catalytic amount of trifluoroacetic acid, heated at reflux for 3 h, cooled, and evaporated to an orange film, which was purified by column chromatography on silica gel to afford conjugated tetracycle **20** as an orange film (60 mg, 65%). $R_f=0.44$ (60% EtOAc/hexanes); ^{1}H NMR (300 MHz, DMSO): $\delta=11.76$ (br, 1H), 11.35 (br, 1H), 7.82 (s, 1H), 7.81 (s, 2H), 7.66 (m, 3H), 6.75 (m, 2H), 6.53 (s, 1H), 4.30 (m, 4H), 4.16 (m, 4H), 3.84 (s, 3H), 1.19 ppm (m, 12H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$): $\delta=166.6$, 166.4, 164.8, 164.7, 160.9, 160.1, 155.9, 144.5, 140.2, 136.7 135.1, 132.1, 130.8, 129.7, 127.2, 124.8, 120.0, 120.0, 116.5, 111.9, 111.6, 101.5, 62.0, 61.9, 60.7, 60.6, 59.2, 32.0, 30.9, 15.5, 15.3 ppm; HRMS: *m/z* calcd for $C_{31}H_{35}N_6O_9S_2$: 699.1901 $[M+H]^+$; found: 699.1901.

2,2′-[(4-Methoxy-1-phenylsulfonyl-1*H*,1′*H*-2,2′-bipyrrole-5,5′-diyl)bis(methanylylidene)]bis(azanylylidedene) bis(thiophene-3-carbonitrile) (18): This compound was prepared by a modification of method C from 4-methoxy-1-benzenesulfonyl-5,5′-bisformyl-2,2′-bipyrrole (**9**, 10 mg, 0.03 mmol) and 2-amino-3-cyanothiophene (**17**, 8 mg, 0.40 mmol) by stirring for 30 min at room temperature. Purification by column chromatography on silica gel afforded conjugated tetracycle **18** as a brown solid (16 mg, 91%). $R_f=0.41$ (50% EtOAc/hexanes); ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta=12.43$ (br, 1H), 8.80 (s, 1H), 8.48 (s, 1H), 7.74 (m, 1H), 7.58 (m, 2H), 7.42 (m, 4H), 7.33 (m, 2H), 7.08 (s, 1H), 6.94 (s, 1H), 6.69 (s, 1H), 3,86 ppm (s, 3H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta=165.8$, 165.0, 158.8, 151.6, 150.9, 136.0, 135.5, 135.1, 134.1, 132.1, 129.7 (2), 129.0, 127.9, 126.7 (2), 121.6, 121.5, 117.4, 116.3, 115.3, 115.3, 109.5 (2), 102.4, 102.3, 59.3 ppm; HRMS: *m/z* calcd for $C_{27}H_{19}N_6O_3S_3$: 571.0675 $[M+H]^+$; found: 571.0679.

Tetraethyl-5,5′-[(4-methoxy-1-phenylsulfonyl-1*H*,1′*H*-2,2′-bipyrrole-5,5′-diyl)bis(methanylydene)]bis(azanylylidene) bis(2-aminothiophene-3,4-dicarboxylate) (21): This compound was prepared according to method C from 4-methoxy-1-benzenesulfonyl-5,5′-bisformyl-2,2′-bipyrrole (**9**, 12 mg, 0.03 mmol) and 2,5-diaminothiophene-3,4-dicarboxylic acid diethyl ester (**19**, 19 mg, 0.07 mmol). Purification by column chromatography on silica gel (50% EtOAc/hexane) afforded conjugated **22** as an orange film (8 mg, 28%) which displayed the same physical and spectral properties as **20**, which was observed to contain a trace of **21** by HRMS: *m/z* calcd for $C_{37}H_{39}N_6O_{11}S_3$: 839.1833 $[M+H]^+$; found: 839.1807).

2,2′-[(4-Methoxy-1*H*,1′*H*-2,2′-bipyrrole-5,5′-diyl)bis(methanylylidene)]-bis(azanylylidedene) bis(thiophene-3-carbonitrile) (17): This compound was prepared according to method C from 4-methoxy-5,5′-bisformyl-2,2′-bipyrrole (**8**, 40 mg, 0.18 mmol) and 2-amino-3-cyanothiophene (**17**, 50 mg, 0.40 mmol). Purification by column chromatography on silica gel afforded conjugated tetracycle **17** as an orange film (19 mg, 37%). $R_f=$ 0.7 (50% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=10.0$ (br, 1H), 9.57 (br, 1H), 8.24 (s, 1H), 8.21 (s,1H), 7.1 (d, $J=5.7$ Hz, 1H), 7.03 (d, $J=5.7$ Hz, 1H), 6.98 (d, $J=5.7$ Hz, 1H), 6.89 (s, 1H), 6.86 (m, 1H), 6.68 (d, $J=3.9$ Hz, 1H), 6.28 (s, 1H), 3.93 ppm (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$): $\delta=166.6$, 164.9, 158.0, 150.2, 144.9, 131.7, 131.4, 130.9, 127.7, 127.5, 122.2, 120.5, 118.8, 117.0, 115.4, 114.9, 111.8, 102.8, 100.8, 95.2, 58.0 ppm; HRMS: *m/z* calcd for $C_{21}H_{14}N_6OS_2$: 431.0743 $[M^+]$; found: 431.0747.

Tetraethyl-5,5′-[(4-methoxy-1-octyl-1*H*,1′*H*-2,2′-bipyrrole-5,5′-diyl)bis-(methanylydene)]bis(azanylylidene) bis(2-aminothiophene-3,4-dicarboxylate) (22): This compound was prepared by a modification of method C from bipyrrole **12** (3.6 mg, 0.008 mmol) and 2,5-diaminothiophene-3,4-dicarboxylic acid diethyl ester (**19**, 4.3 mg, 0.017 mmol) by stirring for 1 h at room temperature. Purification by column chromatography on silica gel afforded conjugated tetracycle **22** as an orange film (2 mg, 28%). $R_f=0.61$ (60% EtOAc/hexanes); ^{1}H NMR (700 MHz, $CDCl_3$): $\delta=8.92$ (br, 1H), 7.89 (s, 1H), 7.83 (s, 1H), 6.65 (d, $J=4.2$ Hz, 1H), 6.42 (s, 1H), 6.27 (s, 2H), 6.19 (s, 2H), 6.06 (s, 1H), 4,62 (m, 2H), 4.37 (m, 4H), 4.28 (m, 4H), 3.91 (s, 3H), 0.9–1.43 ppm (m, 27H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=166.0$, 165.7, 164.5, 164.5, 158.6, 158.1, 144.2, 139.9, 136.0, 132.5, 131.1, 128.9, 126.6, 126.6, 124.8, 120.4, 120.4, 116.5, 103.2, 103.1, 95.7, 95.7, 61.4, 61.3, 60.2, 60.1, 58.1, 46.6, 31.9, 31.1, 29.7, 29.4, 29.3, 26.4, 22.7, 14.4, 14.3, 14.2, 14.1 ppm; HRMS: *m/z* calcd for $C_{39}H_{50}N_6O_9S_2$: 811.3107 $[M+H]^+$; found: 811.3114.

Crystal structure determination: Diffraction data for **20** was collected on a Bruker FR591 diffractometer using graphite-monochromatized $Cu_{K\alpha}$ radiation with 1.54178 Å. The structures were solved by direct methods (SHELXS97). All non-hydrogen atoms were refined based on Fobs2 (SHELXS97), while hydrogen atoms were refined on calculated positions with fixed isotropic U, using riding model techniques. CCDC-831157 (**20**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

NSERC Canada is thanked for DG, SRG, and RTI grants, and CFI is thanked for equipment funding. W. G. S. also thanks both the Alexander von Humboldt Foundation and the RSC for a J. W. T. Jones Travelling Fellowship, allowing this manuscript to be completed. S. D. and I. U. R. acknowledge graduate scholarships from NSERC and the Direction des Relations Internationales of the Université de Montréal, respectively.

[1] P. M. Beaujuge, J. R. Reynolds, *Chem. Rev.* **2010**, *110*, 268–320.
[2] R. J. Mortimer, A. L. Dyer, J. R. Reynolds, *Displays* **2006**, *27*, 2–18.
[3] H. Ma, H.-L. Yip, F. Huang, A. K. Y. Jen, *Adv. Funct. Mater.* **2010**, *20*, 1371–1388.
[4] J.-L. Bredas, J. R. Durrant, *Acc. Chem. Res.* **2009**, *42*, 1689–1690.
[5] A. C. Grimsdale, K. Leok Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* **2009**, *109*, 897–1091.
[6] K. Lee, P. R. Nair, A. Scott, M. A. Alam, D. B. Janes, *J. Appl. Phys.* **2009**, *105*, 102046–102013.
[7] J. Roncali, *Acc. Chem. Res.* **2009**, *42*, 1719–1730.
[8] P. M. S. Monk, R. J. Mortimer, D. R. Rosseinsky, *Electrochromism and Electrochromic Devices*, Cambridge University Press, Cambridge, **2007**.
[9] G. Broncová, S. Anikin, U. Lange, P. Matejka, M. Krondak, V. Kral, V. M. Mirsky, *J. Solid State Electrochem.* **2010**, *14*, 1035–1044.
[10] K. Maksymiuk, *Electroanalysis* **2006**, *18*, 1537–1551.
[11] S. L. Hung, T. C. Wen, A. Gopalan, *Mater. Lett.* **2002**, *55*, 165–165.
[12] Y. Chen, C. T. Imrie, J. M. Cooper, A. Glidle, D. G. Morris, K. S. Ryder, *Polym. Int.* **1998**, *47*, 43–49.
[13] G. Zotti, S. Zecchin, G. Schiavon, B. Vercelli, *Chem. Mater.* **2003**, *15*, 4642–4650.
[14] F. Gassner, S. Graf, A. Merz, *Synth. Met.* **1997**, *87*, 75–79.
[15] G. Zotti, S. Zecchin, G. Schiavon, L. B. Groenendaal, *Chem. Mater.* **2000**, *12*, 2996–3005.
[16] A. Merz, S. Anikin, B. Lieser, J. Hienze, H. John, *Chem. Eur. J.* **2003**, *9*, 449–455.

[17] M. Yu, G. D. Pantos, J. L. Sessler, B. L. Pagenkopf, *Org. Lett.* **2004**, *6*, 1057–1059.
[18] B. Jolicoeur, W. D. Lubell, *Org. Lett.* **2006**, *8*, 6107–6110.
[19] B. Jolicoeur, W. D. Lubell, *Can. J. Chem.* **2008**, *86*, 213–218.
[20] T. Tshibaka, I. U. Roche, S. Dufresne, W. D. Lubell, W. G. Skene, *J. Org. Chem.* **2009**, *74*, 9497–9500.
[21] N. Yu, R. Zhu, B. Peng, W. Huang, W. Wei, *J. Appl. Polym. Sci.* **2008**, *108*, 2438–2445.
[22] J.-F. Morin, N. Drolet, Y. Tao, M. Leclerc, *Chem. Mater.* **2004**, *16*, 4619–4626.
[23] J. Roncali, P. Blanchard, P. Frère, *J. Mater. Chem.* **2005**, *15*, 1589–1610.
[24] C. Groves, O. G. Reid, D. S. Ginger, *Acc. Chem. Res.* **2010**, *43*, 612–620.
[25] G. Li, V. Shrotriya, Y. Yao, J. Huang, Y. Yang, *J. Mater. Chem.* **2007**, *17*, 3126–3140.
[26] J. Mei, N. C. Heston, S. V. Vasilyeva, J. R. Reynolds, *Macromolecules* **2009**, *42*, 1482–1487.
[27] C.-J. Yang, S. A. Jenekhe, *Chem. Mater.* **1991**, *3*, 878–887.
[28] S. Dufresne, A. Bolduc, W. G. Skene, *J. Mater. Chem.* **2010**, *20*, 4861–4866.
[29] A. Bolduc, S. Dufresne, W. G. Skene, *J. Mater. Chem.* **2010**, *20*, 4820–4826.
[30] S. Barik, W. G. Skene, *Polym. Chem.* **2011**, *2*, 1091–1097; S. Barik, W. G. Skene, *Macromolecules* **2010**, *43*, 10435–10441.
[31] K. Suematsu, K. Nakamura, J. Takeda, *Colloid Polym. Sci.* **1983**, *261*, 493–501.
[32] P. W. Morgan, S. L. Kwolek, T. C. Pletcher, *Macromolecules* **1987**, *20*, 729–739.
[33] S. Destri, M. Pasini, C. Pelizzi, W. Porzio, G. Predieri, C. Vignali, *Macromolecules* **1999**, *32*, 353–360.
[34] G. Zotti, A. Randi, S. Destri, W. Porzio, G. Schiavon, *Chem. Mater.* **2002**, *14*, 4550–4557.
[35] N. Kiriy, V. Bocharova, A. Kiriy, M. Stamm, F. C. Krebs, H.-J. Adler, *Chem. Mater.* **2004**, *16*, 4765–4771.
[36] C. Schmuck, V. Bickert, M. Merschsky, L. Geiger, D. Rupprecht, J. Dudaczek, P. Wich, T. Rehm, U. Machon, *Eur. J. Org. Chem.* **2008**, 324–329.
[37] S. Dufresne, W. G. Skene, *J. Org. Chem.* **2008**, *73*, 3859–3866.
[38] M. Bourgeaux, W. G. Skene, *J. Org. Chem.* **2007**, *72*, 8882–8892.
[39] V. K. Gewald, M. Kleinert, B. Thiele, M. Hentschel, *J. Prakt. Chem.* **1972**, *314*, 303–314.
[40] M. Bourgeaux, S. Vomscheid, W. G. Skene, *Synth. Commun.* **2007**, *37*, 3551–3558.
[41] S. Dufresne, T. Skalski, W. G. Skene, *Can. J. Chem.* **2011**, *89*, 173–180.
[42] W. G. Skene, S. Dufresne, *Org. Lett.* **2004**, *6*, 2949–2952.
[43] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877–910.
[44] S. B. Park, H. Kim, W. C. Zin, J. C. Jung, *Macromolecules* **1993**, *26*, 1627–1632; J. Du, J. Fan, X. Peng, P. Sun, J. Wang, H. Li, S. Sun, *Org. Lett.* **2010**, *12*, 476–479.

Received: May 6, 2011
Published online: August 31, 2011

