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A Highly Conjugated p- and n-Type Polythiophenoazomethine: Synthesis, Spectroscopic, and Electrochemical Investigation

Marie Bourgeaux and W. G. Skene*

Department of Chemistry, Pavillon JA Bombardier,
University of Montreal, CP 6128, succ. Centre-ville,
Montreal, Quebec, Canada H3C 3J7

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Conjugated polymers are of great interest because of their optical, emitting, and conducting properties[1] that are ideal for electronic applications, including light-emitting diodes, molecular wires, flexible displays, and/or low-power consumption products. Because of these potential applications, great effort has focused on the synthesis of these and other new compounds with enhanced properties.[2] Current synthetic methods are however challenging and require anhydrous and oxygen-free conditions for Suzuki[3] or Wittig[4] coupling methods. These protocols are further complicated with difficult purifications, and the resulting polymers are sporadically contaminated with trace metals or other byproducts, resulting in poor batch-to-batch reproducibility. Electropolymerization additionally suffers from low to moderate yields and offers little control over the molecular weight. Furthermore, the regioselectivity of the resulting polymer cannot be regulated electrochemically,[5] which affects the degree of conjugation and limits the range of properties of the resulting polymer, making it unsuitable for functional devices. Therefore, simple, high-yielding synthetic protocols for the preparation of conjugated thiophene polymer with desired properties are quite rare.

Given the isoelectronic character of azomethines (−N═CH−) to its carbon analogues,[6] polymers synthesized using this connection would be suitable alternatives to conventional conjugated polymers. This is in part due to the mild reaction conditions required for their synthesis, leading to high yields and purity via the selective condensation between an amine and an aldehyde. Additionally, the resulting polymers are easily purified while the robust azomethine bond exhibits a high stability toward hydrolysis and reduction.[7−10] Polyazomethine derivatives are further advantageous because they can be both p- and n-doped, owing to their reversible oxidation[11] and reduction,[9,12] respectively. The end result is a polymer with mutual hole and electron charge carrier properties. This aspect is highly sought after for reducing the number of layers required for functional devices and is not readily achievable with current conjugated materials because of the incompatibility of the HOMO and LUMO energy levels with currently used electrodes.[13] In spite of this desired property, the majority of conjugated polymers exhibit uniquely either p- or n-type doping, and there are only a few examples of polymers that are capable of both reversible oxidation and reduction.[14] Since thiophenes have gained a wide importance because of their spectroscopic and electrochemical properties, azomethines derived from them would therefore possess ideal properties and be suitable for functional materials.[7,12,15]

Unfortunately, polyazomethine research has lagged behind its carbon homologues because of the limited number of known stable diaminoaryl monomers. These often undergo undesired decomposition while the resulting azomethine derived polymers do not have suitable properties for functional applications, and they suffer from problematic irreversible oxidation.[12,16] Only recently have these robust bonds been used to prepare azomethines consisting uniquely of thiophenes. Namely, we were the first to prepare oligothiophenoazomethines by selective reagent addition using a stable diaminothiophene (**1**).[11,17,18] The potential advantages of azomethine-based materials concomitant with our previous success with such compounds have prompted us to develop an unprecedented polyazomethine comprised entirely of thiophenes.[10] The present report describes the preparation and the preliminary photophysical and electrochemical characterization of this polymer consisting uniquely of thiophene repeating units. The spectroscopic and electrochemical properties are of particular interest given the limited number of such studies involving azomethines and their thiophene derivatives. The stable diaminothiophene (**1**) is an ideal monomer for the synthesis of novel conjugated polyazomethines consisting uniquely of thiophene units.[19] In addition to possessing a low oxidation potential, **1** is highly stable and it can be easily prepared by a modified Gewald reaction.[19,20] The other required monomer (**2**) was obtained by a Kumada reaction followed by standard formylation starting from 3,4-dibromothiophene.[21] The novel polyazomethine (**3**) was obtained by simply heating stoichiometric amounts of these two monomers under reduced pressure in the presence of a catalytic amount of trifluoroacetic acid in the absence of solvent. This leads to a blue polymer that does not require purification or postpolymerization treatment, unlike with conventional polythiophenes. The resulting polymer is highly soluble in standard volatile organic solvents, such as THF and toluene. This is in stark contrast to homoaryl azomethines that are soluble only in high boiling solvents such as DMAC, DMF, and DMSO, precluding their use as thin films since they cannot be spin-cast using volatile solvents. Furthermore, accurate molecular weight determination of previous polyazomethines is not possible owing to their limited solubility in commonly used solvents for GPC analyses. The increased solubility of **3** relative to its homoaryl analogues is in part due to the C10 alkyl chains of **2**. Molecular weight analysis of **3** using relative GPC with polystyrene standards was therefore possible owing to its high solubility in THF with $M_w = 15\,000$ g/mol and PDI = 1.3 being measured. The molecular weight of **3** is comparable to conventional polythiophenes that are obtained by coupling methods requiring elaborate postpolymerization purification and exhibit only limited solubility. Interestingly, the polydispersity of the synthesized polymer is considerably narrower than other polyazomethines whose values range between 1.9 and 3.3.[12]

Even though azomethine formation is understood to be reversible, no undesired decomposition products were observed under conditions that otherwise would hydrolyze the product. No decomposition was also observed under prolonged ambient humid conditions and acid conditions. The azomethine stability is also evidenced by the lack of reaction with common reducing reagents such as $NaBH_3CN$ and $NaBH_4$.[10] Furthermore, the thiophenoazomethine has a high degree of resistance to oxidative decomposition unlike its carbon analogues.[22] The stability of **3** is also apparent through their resistance to photodecomposition

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* Corresponding author. E-mail: w.skene@umontreal.ca.

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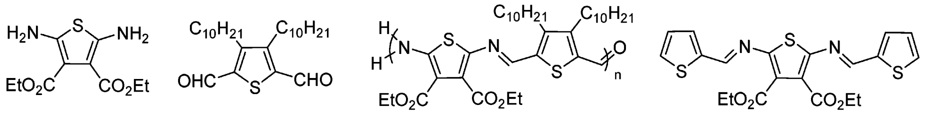
Chart 1. Monomers, the Resulting Polythiophenoazomethine, and Its Oligomeric Analogue



1 **2** **3** **4**

and photoisomerization with intense irradiation at 300 and 355 nm. The stability of the polymer is further evidence by TGA measurements that showed only two apparent decomposition temperatures. A decomposition occurred at 100 °C ascribed to the dehydration of the polymer while a second transition observed above 300 °C is the actual decomposition temperature. Given the observed high decomposition temperature, the polymer has appropriate thermal properties suitable for industrial processing and for possible use in functioning devices.[13]

Cyclic voltammetry of **3** in solution showed a quasi-reversible one-electron oxidation peak at 0.54 V (Figure 1). The oxidation peak is shifted by 1.03 V to lower potentials relative to **4**[11] owing to its relative high degree of conjugation. The reversible-like oxidation formation is in contrast to previous examples of azomethines that undergo irreversible oxidation regardless of the experimental conditions. Since earlier azomethine electrochemical studies involved only homologous aryl units, they not only exhibited irreversible oxidation,[23,24] but they also exhibited extremely high oxidation potentials. These undesired properties limit the usefulness of other azomethines as functional materials.[7,9,23,25,26] In addition to an oxidation process indicating its p-doping-type behavior, **3** also undergoes a reduction that is observed at relatively low potentials. The electrochemical reduction of azomethines can occur by two successive reversible one-electron steps in the absence of an added proton donor.[25] In the presence of proton donors or hydroscopic solvents, the electrochemical reduction is irreversible, yielding the same products as those obtained by standard chemical reductants such as $NaBH_4$. The observed cathodic process at −0.69 V is ascribed to the reduction of the thiophene moiety owing to the absence of azomethine reduction with standard reducing agents. The latter corroborates the robustness of the azomethine bond while the electrochemical reduction proves the n-doping-type character of the polyazomethine. This is in contrast to conventional thiophenes that do not exhibit a reduction within the standard working potentials of functioning devices. This notwithstanding, **3** sustained repeated oxidation and reduction without any significant change in the voltammogram, providing further evidence for its electrochemical stability.

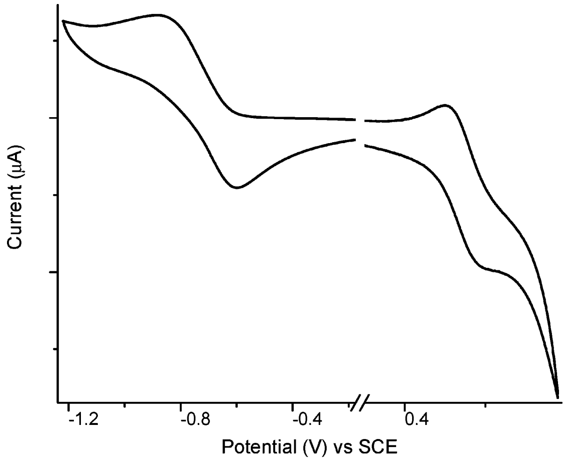


Figure 1. Cyclic voltammogram of **3** recorded in deaerated THF solution of 0.1 M of $TBAPF_6$ at a scan rate of 0.10 V/s.

Table 1. Spectroscopic Properties of 3 Measured in THF and 4 Measured in Dichloromethane

compd	λ_{abs}[a] (nm)	λ_{fl}[b] (nm)	Φ_{fl} (10^{-2})	ΔE (eV)[c]	E_g (eV)[d]
3	663 (721)[e]	791	<0.01	1.6	1.5 (1.3)
4	440 (524)[e]	534 (618)[e]	0.3	2.6 (2.2)[e]	2.3 (2.0)[e]

[a] Absorption. [b] Fluorescence. [c] Absolute HOMO−LUMO energy level difference. [d] Spectroscopic band gap. [e] Values in parentheses correspond to measured values with doping with methanesulfonic acid.

Table 2. Electrochemical Data of Thiophenoazomethines

compd	E_{pa}[a] (V)	E_{pc}[a] (V)	HOMO (eV)	LUMO (eV)	E_g (eV)[b]
3	0.55 (0.54)[d]	−0.74 (−0.69)[d]	−4.8	−3.8	1.0
4	1.51 (1.44)[d]		−5.3	−3.0[c]	

[a] Oxidation and reduction potentials, respectively. [b] Electrochemical band gap calculated according to known means from the electrochemical oxidation and reduction onsets.[27] [c] LUMO energy level calculated from the spectroscopic band gap according to LUMO = HOMO $-E_g$. [d] Values in parentheses refer to E^o determined from the electrochemical square wave.

The HOMO and LUMO energy levels of the polymer can be determined from the ionization potential (IP) and electron affinities (EA). These values are calculated from the oxidation and reduction potentials measured by cyclic voltammetry (Table 2) according to well-established equations.[27] These energy levels are required to evaluate the suitability of **3** for working devices such as light-emitting devices and were found to be −4.8 and −3.8 eV respectively for the HOMO and the LUMO. The calculated values are comparable to the work function of commonly used electrodes in the fabrication of emitting devices and further lead to a band gap of 1.0 eV. This is considerably lower than conventional polythiophenes and other polyazomethines. Even though the calculated HOMO level is compatible with the standard ITO anode, the low oxidation potential results in a LUMO level that is well below conventional polymers, making it comparable with common cathodes such as calcium (−2.9 eV) and magnesium (−3.7 eV).[28] The energy compatibility implies a low work function for the injection of electrons from the cathode to the LUMO of **3**. Significant enhancement can therefore be expected for the electron injection process from standard cathodes to **3** such that the polyazomethine can be alternatively used as an electron injection layer, thereby overcoming the barrier height for the electron-transfer process.[28,29] This is expected to lead to simpler device construction concomitant with increased device efficiency.

During the synthesis of **3**, a series of color changes from orange to red and finally to blue occurred. The observed bathochromic absorption shifts are indicative of the increased degree of conjugation occurring with polymerization. The visible color formation corresponds to lowering of the $\pi-\pi^*$ electronic transitions concomitant with the energy levels undergoing a pronounced stabilization from the heteroconjugated bond. Prior to undertaking the spectroscopic analyses, triethylamine was added to the sample to ensure the observed intense blue color was from the neutral polymer and not from its doped state. The observed increase degree of conjugation is consistent with a

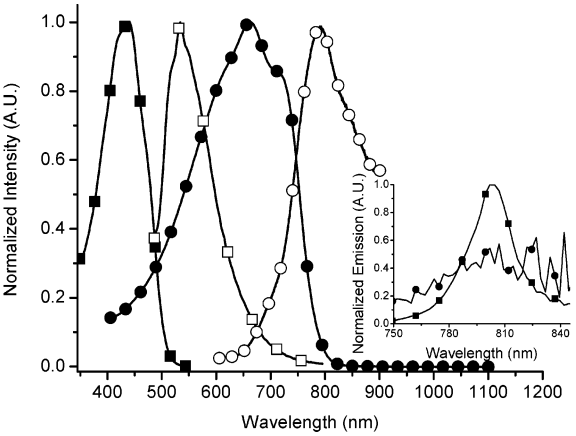


Figure 2. Normalized absorption (■) and emission (□) spectra of **4** in dichloromethane. Normalized absorption (●) spectra in toluene and normalized emission (○) spectra in THF of **3**. Inset: fluorescence of **3** recorded at 77 K (■) and at room temperature (●) in 2-methyltetrahydrofuran, magnified 40 times.

highly conjugated polymer, supported by the measured molecular weight (vide supra). The increased degree of conjugation results further in a stabilization of the HOMO and the LUMO levels observed by a 220 nm bathochromic shift for both the absorption and fluorescence of **3** relative to **4** (Figure 2 and Table 1). The net effect of the increased delocalization on the spectroscopic properties is a narrowing of the HOMO−LUMO energy gap to 1.6 eV, determined from the intercept of the absorption and emission normalized spectra (Figure 2), while the absorption onset leads to 1.5 eV. These values are 1.0 and 0.8 eV smaller than those for **4** and are consistent with the electrochemically derived values. Unlike its oligomeric analogue, **3** does not efficiently dissipate its excited-state energy by nonradiative internal conversion (IC). This is evident from the fluorescence measurements at 77 K, at which temperature a 4000-fold increase in the fluorescence was expected since all modes of excited deactivation involving bond rotation are suppressed at this low temperature. However, only a 40-fold fluorescence increase was observed for **3** at 77 K relative to room temperature, shown in the inset of Figure 2. Deactivation of the excited presumably occurs by intramolecular self-quenching.

The energy levels, and hence the band gap and the absorption properties, can be decreased further with acid doping to give semiconductor-like properties to the azomethines. Methanesulfonic acid is a suitable p-dopant that protonates the nitrogen azomethine, resulting in a localized charge on the heteroatom. Spectroscopically, the acid doping results in a 40 nm bathochromic shift in the absorption spectra both in solution and in thin films. The remarkable visible color change denotes an increased delocalization and an additional energy gap stabilization of ∼1.3 eV. Interestingly, the polymer can sustain reversible doping-dedoping with the successive addition of methanesulfonic acid and triethylamine without any apparent decomposition and serves to further illustrate the robustness of the azomethine bond toward hydrolysis.

Given the solubility of **3** in volatile solvents, thin films were easily prepared by spin-coating onto glass. The spectroscopic properties of the polymer in thin films are virtually identical to those measured in solution in 2-methyltetrahydrofuran and toluene with the exception of a 35 nm bathochromic shift in THF, resulting from solvent-induced polarity effects. Since large bathochromic shifts (>50 nm) are typical for thin films because of increased planarity induced by interchain stacking,[30] it can be concluded that the polymer inherently adopts a high degree of planarity in solution. This is consistent with our previous studies of oligothiophenoazomethine analogues such as **4** that were found to be planar and linear both in solution and in the solid state.[18,31]

In summary, we presented the first ever example of a highly conjugated polyazomethine consisting entirely of thiophene repeating units. The polymer is not only extremely stable, but it also does not suffer from the limitations of previous azomethines.[32] Furthermore, it has the added advantage of being isoelectronic to its carbon analogues,[6] making it a suitable replacement for conventional thiophene materials such as poly(thienylene vinylenes) for which there are only a limited number of examples owing to their difficult synthesis and instability.[33] Reversible-type oxidation occurring at moderately low potentials concomitant with an electrochemical reduction gives rise to a mutual p- and n-type dopable conjugated polymer. The inherently weak emission, low oxidation potential, and reversible-like radical cation formation combined with its thermal stability make this polymer suitable as a hole injection material in organic light-emitting diodes. The synthetically simple polymer can ultimately yield new materials suitable for functional devices with new operating properties while opening a new realm of stable thiophene-containing materials with desired properties, which are easily achievable unlike its carbon analogues.

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Supporting Information Available: Experimental details and synthetic procedures for **3** including GPC and TGA analyses; absorption and fluorescence spectra of **3** and its cyclic voltammogram. This material is available free of charge via the Internet at http://pubs.acs.org.

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