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**Abstract:** Two novel 2,2'-biimidazole-thiophene structures, 5,5'-bis(2,2'-bithiophene-5-yl)-1,1'-dimethyl-2,2'-biimidazole and 5,5'-bis(3,4-ethylenedioxythiophene-2-yl)-1,1'-dimethyl-2,2'-biimidazole, have been synthesized and electrochemically polymerized. These materials underwent facile oxidation on Pt and ITO surfaces in CH<sub>2</sub>Cl<sub>2</sub>/Bu<sub>4</sub>NPF<sub>6</sub> to yield conjugated, electroactive polymer films. The films were characterized with cyclic voltammetry, electronic absorption spectroscopy, and atomic force microscopy.

Key words: imidazole, conjugated polymer, electropolymerization.

**Résumé :** On a effectué la synthèse de deux nouvelles structures de 2,2'-biimidazole-thiophène, le 5,5-bis(2,2'-bithiophén-5-yl)-1,1'-diméthyl-2,2'-biimidazole et le 5,5'-bis(3,4-éthylènedioxythiophén-2-yl)-1,1'-diméthyl-2,2'-biimidazole, et on a réalisé leur polymérisation par voie électrochimique. En solution dans un mélange de  $CH_2Cl_2/Bu_4NPF_6$ , sur des surfaces de Pt et d'ITO, ces produits donnent facilement lieu à des réactions d'oxydation qui conduisent à la formation de films de polymères conjugués électroactifs. On a caractérisé ces films par voltampérométrie cyclique, spectroscopie d'absorption électronique et par microscopie des forces atomiques.

Mots-clés : imidazole, polymère conjugué, électropolymérisation.

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# Introduction

Although published reports of electroactive heterocyclic polymers appeared as early as 1876,<sup>1</sup> these structures became more interesting to materials scientists around the time the first reports of highly conductive conjugated polymers emerged.<sup>2–4</sup> Since this event, homopolymers consisting of pyridine (1), pyrrole (2), thiophene (3), and other heterocvclic structures (Chart 1) have abounded and have found applications in electronics, corrosion inhibition, sensing, actuators, and energy technology, to name just a few of the more popular areas.<sup>5</sup> Several of these heterocycles may be polymerized electrochemically (e.g., aniline, pyrrole, and thiophene).<sup>6-9</sup> Electrochemical polymerization offers several advantages over chemical polymerization routes.<sup>10</sup> This collection of techniques comprises methods which allow controlled oxidation and (or) reduction of redox-active species at an electrode-solution interface, and thus the methods enable a degree of control over polymerization rate and provide a means of producing polymer films of a desired thickness (and perhaps, quality). Often, the most important advantage provided by electrochemical polymerization, however, is that problems which accompany low polymer solubilities

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729

(i.e., difficulties in polymer processing) can be circumvented. For structures which are unable to be polymerized via electrochemical methods (e.g., pyridine), it is usually possible to achieve this goal through the incorporation of polymerizable substituents. The most popular substituent in this application appears to be thiophene and its derivatives. Thienyl substituents have been used in the polymerization of a wide variety of heterocyclic compounds and in many cases, metal complexes.<sup>11–15</sup>

Imidazole (4) (Chart 1) has been the topic of relatively few investigations concerning conjugated polymers. This may seem surprising at first, since imidazole possesses pyrrole-like and pyridine-like nitrogens, which should make it an attractive candidate for chemical studies of this sort. The imine centers on imidazole enable derivatives like 2,2'-biimidazole (5a) (Chart 1) and others to be utilized as ligands in metal complexes.<sup>16,17</sup> Such assemblies have been shown to display pH-dependent properties and are thus intriguing in sensory applications.<sup>18,19</sup> Benzimidazole polymers and metallopolymers have also been reported to exhibit pH-responsive electrochemistry, which influences electronic communication between metal centers in these materials.<sup>20</sup>

There appear to be two reasons why imidazoles are not as widely studied as other heterocycles. Importantly, protecting groups are required when chemistry is to be carried out at any of the carbon centers on the ring, which adds to preparation time and cost.<sup>21</sup> Furthermore, when bicyclic **5a** is considered, low solubilities in most common organic solvents, due to strong self-association (hydrogen bonding and  $\pi$ -stacking), is a real problem.<sup>22</sup> Here, the use of protecting groups (e.g., benzyl, trimethylsilylethoxymethyl substituents) has been shown to greatly enhance solubility.<sup>23,24</sup>

Chart 1.



Chemically polymerized 1,1'-diprotected-2,2'-biimidazoles have been detailed by Yamamoto et al.<sup>25,26</sup> In these studies, a range of biimidazoles that were 1,1'-difunctionalized with either alkyl (e.g., 5b) (Chart 1) or methoxymethyl (MOM) substituents were polymerized via chemical polycondensation reactions. In the case of poly(1,1'-dimethoxymethyl-2,2'-biimidazole), 90% deprotection of the MOM-protected biimidazole sites was possible, yielding a polymer with H-functionalized 2,2'-biimidazole units. Electropolymerizable models, such as 5,5'-bis(2,2'-bithiophene-5-yl)-1,1'dimethyl-2,2'-biimidazole (6) (Chart 1) and 5,5'-bis(3,4ethylenedioxythiophene-2-yl)-1,1'-dimethyl-2,2'-biimidazole (7) (Chart 1), would enable the synthesis of thiophene-imidazole copolymers through convenient electrochemical polymerization experiments. Structures possessing 1,1'-disubstituted biimidazole moieties would be interesting because they would be soluble in organic solvents and because the facile chemistry that yields 1,1'-disubstitution could be varied to

9

provide a means of tuning the electronic properties of such compounds and their polymers. Additionally, as noted earlier, it should be possible to tune their chemical behavior through judicious choice of solution pH. In fact, such a study has recently been reported for a related structure, 2,5-bis(2,2'-bithiophene-5-yl)-1-methylimidazole (8) (Chart 1), for which significant blue-shifts in the p-doping potentials of its polymerized form, poly-8, were observed upon the addition of trifuoroacetic acid to test solutions.<sup>27</sup>

10

A promising avenue of research for conjugated polymers containing 2,2'-biimidazole units would be heterogeneous catalysis, since these compounds would be capable of coordinating metal ions, and may thus be interesting for their potential as catalyst supports.<sup>28</sup> The ability to tune the electronic and chemical properties of such complexes would be of paramount importance in this application. Towards this end, we have synthesized the electropolymerizable 2,2'-biimidazole structures **6** and **7**.

# **Experimental section**

## Equipment

Cyclic voltammetry experiments were carried out with a PC-interfaced CH Instruments 750C bipotentiostat. Data acquisition was accomplished using CH Instruments software (version 6.24). Voltammetry experiments were conducted on platinum-button electrodes (CH Instruments, 1 mm diameter) in a three-compartment glass cell. Pt electrodes were cleaned prior to each experiment by polishing with an  $Al_2O_3$  dispersion (0.05 µm). Potentials are referenced to an Analytical Sensors, Inc. calomel electrode having a 4 mol L<sup>-1</sup> KCl internal solution. A platinum wire served as a counter electrode. A scan rate of 0.100 V s<sup>-1</sup> was used in each experiment, unless otherwise noted. Polymers obtained from electropolymerization experiments were washed with acetone and air-dried before subsequent experiments were carried out on them. Electrochemical solutions were purged for 10 min with nitrogen gas before experiments were carried out. A flow of nitrogen was maintained over the surface of each solution for the duration of these studies. All cyclic voltammetry experiments were carried out at 25 °C.

Electronic absorption spectrophotometry experiments were conducted with a JASCO J-815 instrument running in absorbance mode, employing baseline correction. Data acquisition was accomplished with Spectra Manager software (JASCO, version 1.54.03). The energies of  $\pi$ - $\pi$ \* transitions for the monomers in solution were determined from the onset of absorption by extrapolation of the low-energy side of these peaks and the baseline. Scans were conducted at a rate of 1 nm s<sup>-1</sup> with data collection at 2 nm intervals. Indium – tin oxide coated glass electrodes for experiments on polymer films were purchased from Delta Technologies ( $R_{\rm s} = 8-12 \ \Omega$ ).

Nuclear magnetic resonance (NMR) experiments were carried out on a Bruker Avance II 400 MHz instrument at room temperature. Chemical shifts are referenced to a TMS peak, which was assigned a value of 0 ppm. Elemental analyses were performed by Canadian Microanalytical Services Ltd., Delta, BC. Atomic force microscopy (AFM) was used to investigate polymer-film topology using a XE-120 Park Systems Inc. instrument in contact mode under ambient conditions. Melting points were carried out in air using an Electrothermal Mel-Temp capillary tube apparatus and are not corrected.

AM1 calculations were performed with Gaussian 03 and Gaussview 3.09 software.<sup>29,30</sup>

#### Materials

All chemicals employed in this study were of reagentgrade or better and were used as received unless otherwise noted. Syntheses of biimidazole monomers were carried out under an atmosphere of UHP-grade argon using standard Schlenk-line techniques. Acetonitrile (CH<sub>3</sub>CN) and *N*,*N*-dimethylformamide (DMF) were both anhydrous and purchased from Caledon Laboratories Ltd. These solvents were delivered from an MBraun solvent purification system onto type 4 Å molecular sieves and stored under argon before use. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, VWR) for cyclic voltammetry experiments was purified by distillation from P<sub>2</sub>O<sub>5</sub> and stored on type 4 Å molecular sieves prior to use. CH<sub>3</sub>CN for electrochemical experiments was stored on activated alumina under a blanket of argon until use. Tetraethylammonium perchlorate (Et<sub>4</sub>NClO<sub>4</sub>) was synthesized from perchloric acid and tetraethylammonium bromide, recrystallized three times from water, and dried in a vacuum oven at 110 °C. Tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) was synthesized from hexafluorophosphoric acid and tetrabutylammonium bromide, recrystallized three times from ethanol, and dried in a vacuum oven at 110 °C.

## Synthesis of 2,2'-biimidazole, 5a

Ammonium hydroxide (300 mL, 18 mol L<sup>-1</sup>) was added dropwise over a 30 min period to an ice-cooled conical flask that contained a solution of 40% *w/w* glyoxal (170 mL). The opening between the funnel and flask was covered with a wax film to prevent leakage of NH<sub>3</sub>(g). The resulting, dark brown mixture was stirred overnight and then filtered. The residue was dissolved with 0.1 mol L<sup>-1</sup> HCl and heated to boiling. It was then treated with activated charcoal, filtered, and neutralized with a saturated K<sub>2</sub>CO<sub>3</sub>(aq) solution, precipitating a tan coloured solid. The product was collected by filtration and air-dried. <sup>1</sup>H NMR data were in agreement with those reported.<sup>23</sup> Yield: 21.22g (32%). Mp > 300 °C (Lit.<sup>31</sup> 307 °C). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 12.65 (s (br), 2H), 7.06 (s, 4H).

#### Synthesis of 1,1'-dimethyl- 2,2'-biimidazole, 5b

A method reported by Logemann and co-workers.<sup>32</sup> was followed: 2,2'-biimidazole (2.00 g, 1.49 mmol) was refluxed in a solution of 11.5 mL of 20% NaOH in 40 mL of ethanol. Dimethyl sulfate (8.66 g, 69 mmol) was added dropwise over a 30 min period. Refluxing was continued overnight. By the next day, the mixture had changed from a deep brown solution to an opaque, golden mixture. The reaction flask was cooled to room temperature and neutralized with aqueous NaHCO<sub>3</sub>. It was then filtered and extracted with CHCl<sub>3</sub> (3  $\times$  50 mL). The organic layer was washed with aqueous NaOH (2.4 g in 30 mL of H<sub>2</sub>O) and dried over MgSO<sub>4</sub>. It was then filtered and evaporated to dryness to yield an orange solid. This was recrystallized from heptane to yield pale-yellow needles. <sup>1</sup>H NMR signals were in agreement with those published for this structure.<sup>33</sup> Yield: 1.84g (76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.11 (s, 2H, J = 1.0 Hz), 6.95 (s, 2H, 1.0 Hz), 4.04 (s, 6H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 138.74, 127.88, 122.64, 35.37.

#### Synthesis of 5,5'-dibromo-1,1'-dimethyl-2,2'-biimidazole

*N*-Bromosuccinimide (0.764 g, 4.3 mmol) was added portionwise via a powder-addition funnel to a solution of 1,1'dimethyl-2,2'-biimidazole (0.349 g, 2.15 mmol) in CHCl<sub>3</sub> (25 mL). The solution immediately turned green before gradually becoming a brown–orange colour. The mixture was stirred overnight. The following day, the solution was washed with NaHCO<sub>3</sub>(aq) and then water. The organic solution was then dried over MgSO<sub>4</sub>, filtered, and evaporated to yield a beige solid, which was dried in vacuo. The product was recrystallized from heptane to yield pale yellow needles. <sup>1</sup>H NMR results were in agreement with the results reported by Yamamoto et al.<sup>26</sup> Yield: 0.524g (76%). Mp 155– 156 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.12 (s, 2H), 3.96 (s, 6H).

# Synthesis of 5,5'-bis(2,2'-bithiophene-5-yl)-1,1'-dimethyl-2,2'-biimidazole, 6

5,5'-Dibromo-1,1'-dimethyl-2,2'-biimidazole (0.678 g, 2.12 mmol) was stirred in a solution of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.149 g, 0.212 mmol) in anhydrous DMF (50 mL). 5-Tributyltin-2,2'-bithiophene (2.41 g, 5.29 mmol)<sup>34</sup> was added through a syringe, and the mixture was refluxed, causing a gradual colour change from pale yellow to dark brown. After removal of the solvent, the residue was washed with CH<sub>2</sub>Cl<sub>2</sub> using a Soxhlet extractor. The organic effluent was then washed with brine solution (25 mL), water (3  $\times$  25 mL), and dried over MgSO<sub>4</sub>. The solution was then filtered and treated with petroleum ether. Dropwise addition of the ether caused precipitation of a bright yellow solid, which was filtered and dried in vacuo. Yield: 0.675 g (65%). Mp 205–208 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.31 (s, 2H), 7.26 (d, 2H), 7.22 (d, J = 2.7 Hz, 2H), 7.20 (d, J = 3.7 Hz, 2H), 7.08 (d, J = 3.5 Hz, 2H), 7.05 (m, 2H), 4.10 (s, 6H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 140.0, 138.3, 136.7, 129.3, 128.6, 128.4, 128.0, 127.5, 124.9, 124.2, 124.1, 33.9. Elemental analysis: Calculated for C24H18N4S4: C 58.75%, H 3.70%, N 11.42%. Found: C 58.98%, H 3.93%, N 12.18%.

## Synthesis of 5,5'-bis(3,4-ethylenedioxythiophene-2-yl)-1,1'dimethyl-2,2'-biimidazole, 7

5,5'-Dibromo-1,1'-dimethyl-2,2'-biimidazole (0.185g; 0.58 mmol) was dissolved in a solution of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.041 g, 0.058 mmol) in dry DMF (50 mL). 5-Tributyltin-3,4-ethylenedioxythiophene (0.623 g, 1.44 mmol)<sup>35</sup> was added through a syringe, and the resulting mixture was refluxed. The appearance of the mixture changed from a pale yellow to a deep brown overnight. Following removal of the solvent, the product was extracted from the residue with CH<sub>2</sub>Cl<sub>2</sub>, using a Soxhlet extractor. The resulting solution was dried over MgSO<sub>4</sub>, filtered, and concentrated on a rotary evaporator. The residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub> and precipitated by dropwise addition of petroleum ether. A pale, yellow product obtained, and was dried in vacuo. Yield: 0.241 g (94%). Mp 238–240 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.25 (s, 2H), 6.44 (s, 2H), 4.26 (s, 8H), 2.98 (s, 6H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 141.6, 139.6, 139.4, 129.1, 126.1, 104.5, 100.1, 68.8, 68.5, 33.6. Elemental analysis: Calculated for C<sub>20</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>: C 54.29%, H 4.10%, N 12.66%. Found: C 54.89%, H 4.25%, N 12.29%.

# **Results and discussion**

#### Synthesis

An early report concerning the synthesis of 2,2'-biimidazole involved bubbling ammonia gas into a solution of glyoxal to obtain the product as a light brown powder after purification.<sup>36</sup> Other preparations have emerged since this time<sup>37</sup>; however, we chose to use a modified version of the above route, since the reactants for this approach were readily available and because of the route's simplicity. We obtained better yields through a slow addition of NH<sub>4</sub>OH(aq) to a cooled, covered glyoxal solution. The product could be recrystallized from DMF to yield small, pale-yellow crystals; however, even without recrystallization, the product was pure enough to proceed with the next step. 1,1'-Dimethyl-2,2'-biimidazole was produced following a literature method.<sup>32</sup> On each occasion, the preparation was carried out in our hands, the reaction of dimethyl sulfate with deprotonated 2,2'-biimidazole yielded an acidic solution, unlike the mixture described by Logemann and co-workers.32 Neutralization was thus accomplished with a bicarbonate salt rather than HCl, as described. A Stille coupling reaction involving 5,5'-dibromo-1,1'-dimethyl-2,2'-biimidazole was used to at-2.2'-bithiophene and 3.4-ethylenedioxythiophene tach (EDOT) groups to the 2,2'-biimidazole moiety. Because of overlap with the solvent peak for 6 in CDCl<sub>3</sub>, a coupling constant for the signal at 7.26 ppm could not be determined. Both 6 and 7 were soluble in chloroform and dichloromethane, and insoluble in hexanes and petroleum ether, which permitted their precipitation from a mixed solvent system. The carbon content in the elemental analysis data for 7 is slightly high, a result of residual grease used in the preparation of this compound, which could not be removed after repeated washing with petroleum ether (Weak signals at 0.93) and 1.26 ppm could be seen in the <sup>1</sup>H NMR spectrum for this compound).

## Electrochemistry

Both 6 and 7 were able to be electrochemically polymerized using cyclic voltammetry from 1 mmol L<sup>-1</sup> monomer solutions in CH<sub>2</sub>Cl<sub>2</sub>/0.1 mol L<sup>-1</sup>Bu<sub>4</sub>NPF<sub>6</sub>. Cyclic voltammtery is often utilized in electrochemical polymerization experiments because it provides real-time "evidence" of electrochemical coupling. During potential cycling, electroactive polymer films deposited onto the electrode sufaces. With each potential cycle, as more electroactive polymer material is formed, a greater amount of charge is stored in the immobilized film. As a consequence of this, greater currents will be observed with each scan (Fig. 1). Films prepared by anodic electropolymerization are typically grown by recurrent cycling of the working electrode potential between a low limit (0 V vs. calomel electrode in this study), at which the monomer is not involved in an electron-transfer reaction, and a potential just above the monomer's peak oxidation potential. Poly-6 and poly-7 films were also able to be grown at constant applied potentials; however, no significant differences were observed in the cyclic voltammograms grown by potentiostatic polymerization versus potentiodynamic polymerization. Oxidation of 6 yielded a peak at ~0.90 V and a following wave centered at ~1.05 V. It was necessary to cycle the working electrode potential as high as 1.30 V to produce poly-6-coated modified electrodes having good coverage. Poly-6 films were grown by cycling the working electrode potential 10 times, and were obtained as dark yellow films on platinum and ITO-coated glass substrates. These films were dark green in the oxidized state. For 7, an oxidation peak is observed at  $\sim 0.84$  V on the first scan; this peak decayed on subsequent scans. Repetitive potential cycling between 0 V and 0.90 V suggested sustained polymerization of the monomer; however, visual inspection of the electrode surface following these experiments indicated that the surface coverage of the film was quite poor, even after 20 potential cycles. Scanning through a second oxidation peak at ~1.15 V permitted polymer-film deposition. Thus, poly-7 films were deposited by potential cycling within a 0 V to 1.20 V window. The films produced in this manner were dark green.



**Fig. 1.** Anodic polymerization of (*a*) **6** and (*b*) **7** from 1 mmol  $L^{-1}$  solutions of each monomer in CH<sub>2</sub>Cl<sub>2</sub>/0.1 mol  $L^{-1}$  Bu<sub>4</sub>NPF<sub>6</sub>.

While distinct oxidation processes were observable for both monomers **6** and **7**, it was found that reduction peaks for neither monomer were observed within the electrochemical window provided by the  $CH_2Cl_2/Bu_4NPF_6$  medium.

Immediately following their preparations, the polymer films were studied in monomer-free CH<sub>3</sub>CN/0.01 mol L<sup>-1</sup>  $Et_4NClO_4$  solutions (Fig. 2). The voltammograms shown in this figure illustrate the films' redox behavior after two complete cycles of the working electrode potential (0 V  $\rightarrow$  $\lambda \rightarrow 0$  V;  $\lambda = 1.20$  V for poly-6 and 1.00 V for poly-7). It was found that the appearance of the voltammograms did not change significantly in subsequent cycles. Oxidation of the polymers yields their p-doping, while reduction yields n-doped polymers. Poly-6 films were stable when p-doped; however, at potentials above 1.20 V, significant decreases in doping/undoping currents were observed, suggesting deactivation of the poly-6 conjugated backbone under these conditions. This outcome is likely due to attack of oxidized sites in the p-doped polymer by trace nucleophiles present in the solvent-electrolyte system. It is expected that such reactions would occur at electron-rich tetrathiophene segments of poly-6, rather than at dimethybiimidazole segments. Oxidation of thiophene at potentials that yield its polymerization is known to result in decreased conjugation lengths in

**Fig. 2.** P-doping and n-doping experiments for (*a*) poly-**6** and (*b*) poly-**7** in CH<sub>3</sub>CN/0.1 mol  $L^{-1}$  Et<sub>4</sub>NClO<sub>4</sub>.



the resulting polymers.<sup>38</sup> For poly-6, the p-doping and undoping peaks are centered around 1.05 V. Interestingly, a small reduction peak for poly-6 was found at ~ -1.65 V, which was not present in subsequent scans. This observation, as well as the magnitude of the peak (compared with the peak observed for p-doping) suggests that n-doped poly-6 is less stable than its p-doped form. Poly-7 films were stable at applied potentials of up to 1.00 V. The p-doping/ undoping peak for poly-7 is centered at ~0.88 V, a significantly lower potential than what was found for poly-6 films. Polymerized 3,4-ethylenedioxythiophene (PEDOT) films have been shown to undergo oxidation at low potentials to produce very stable p-doped materials.<sup>39</sup> The fused, electron-donating dioxyethylene component in EDOT facilitates oxidation in this structure and also enhances stereoregularity in polymers by preventing  $\alpha - \beta'$  coupling. A slight reduction wave for this polymer was evident at ~ -1.60 V, which was absent on following scans. Cyclic voltammograms collected at varying scan rates for these polymers indicate that the electrochemical reactions observed during p-doping/undoping cycles are surface-confined, and not due to reactions involving a solution species  $(i_p \text{ is proportional to the square})$ root of the scan rate). Figure 3 illustrates the scan-rate-dependence behavior of a poly-6 film.



Table 1 presents a comparison of data for 6, 7, poly-6, and poly-7 films with the related systems, 5,5'-bis(2,2'-bithiophene-5-yl)-1,1'-dimethyl-2,2'-bipyridine (9) and 5,5'bis(2-thienyl)-2,2'-bithiazole (10) (Chart 1), from cyclic voltammetry and electronic absorption spectroscopy experiments.<sup>34,35,40</sup> Data in Table 2 present AM1 energies for the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in each of these same systems. The 2,2'-bipyridine-containing system, 9, displays the lowest HOMO energy in the series, while 7 possesses the highest LUMO energy. Since oxidation involves the HOMO, it should be expected that oxidation will be observed at a higher potential for poly-9 than for poly-6 and poly-7. Likewise, reduction of poly-9 should occur at higher (less negative) potentials as compared with poly-6 and poly-7. Experimentally, oxidation is found to occur at higher potentials for poly-9, and a distinct reduction process is observable for this polymer.<sup>34</sup> On the basis of the calculated energies, it should be easier to reduce poly-6 than poly-7; however, the above experiments demonstrate that both poly-6 and poly-7 are unstable when n-doped. The higher HOMO energy in 7 supports the notion of the greater electron-donating capacity of the EDOT groups in this compound, as compared with the bithiophene substituents of 6. Poly-10 incorporates bithiophene segments in its conductive backbone, unlike the tetrathiophene links present in poly-6, poly-7, and poly-9. Poly-10 would thus be expected to undergo p-doping at the highest potential, and this is confirmed by the data presented in Table 1.

#### **Electronic absorption spectrophotometry**

Polymer-coated ITO electrodes for electronic absorption studies could be grown as described above, through cyclic voltammetry experiments. However, more uniform films could be grown on ITO-coated glass electrodes by application of a constant potential, and so this approach was used to coat electrodes for electronic absorption studies. The best results were found for poly-6 films grown at 1.25 V and poly-7 films grown at 1.00 V.

**Table 1.** Comparison of electrochemical data (formal potential for oxidation,  $E^{\circ\prime}$ ) and spectroscopic data ( $\lambda_{max}$ ,  $\lambda_{onset}$ ) for poly-**6** and poly-**7** with related 2,2'-bipyridine and 2,2'-bithiazole systems. The data for poly-**9** were reported in MeCN/0.1 mol L<sup>-1</sup> Bu<sub>4</sub>NPF<sub>6</sub> vs. Ag wire (ferrocene internal reference) and poly-**10** data in MeCN/0.1 mol L<sup>-1</sup> Et<sub>4</sub>NClO<sub>4</sub> vs. SSCE. Polymer absorption data are presented for solid films deposited onto ITO-glass slides, while the monomer data are presented for CH<sub>2</sub>Cl<sub>2</sub> solutions.

| Compound | $E^{\circ\prime}$ | $\lambda_{max} \ (nm)$ | $\lambda_{onset} \ (nm)$ |
|----------|-------------------|------------------------|--------------------------|
| 6        | _                 | 364                    | 430                      |
| 7        | _                 | 316                    | 370                      |
| 9        | _                 | 400                    | 442                      |
| 10       | _                 | 404                    |                          |
| Poly-6   | 1.05              | 402                    | 532                      |
| Poly-7   | 0.88              | 326                    | 418                      |
| Poly-9   | 1.12              | _                      | _                        |
| Poly-10  | 1.24              |                        |                          |

Table 2. Semi-empirical AM1 HOMO and LUMO energies for 6, 7, 9, and 10.

| Compound | HOMO<br>(eV) | LUMO<br>(eV) |
|----------|--------------|--------------|
| 6        | -7.957       | -0.936       |
| 7        | -7.807       | -0.657       |
| 9        | -8.363       | -1.169       |
| 10       | -8.464       | -1.375       |

Data obtained in electronic absorption studies are summarized in Table 1. Absorption peaks  $(\lambda_{max})$  for 6 and 7 were found at 364 nm and 316 nm, respectively. For the polymer films, absorption peaks were broader, and redshifted (Fig. 4). The peak absorption for poly-6 was shifted by about 38 nm, and was considerably broader. Conversely,  $\lambda_{max}$  for poly-7 was found to be red-shifted by only 10 nm. These red shifts can be explained by an enhanced degree of conjugation in the longer polymer structures relative to what exists in the monomers. It is also acknowledged here that absorption data obtained for monomers will be influenced by solvents, and that absorption data for solid polymers will be influenced by counter-ions to a small degree. The broader polymer absorption profiles can be attributed to the polydispersity of poly-6 and poly-7, as well as non-uniform ( $\alpha - \alpha'$ ,  $\alpha$ - $\beta'$ ) links between thiophenes in poly-6 chains. The absorption peak observed for poly-7 was less broad than for poly-6, likely a consequence of the greater stereoregularity provided by the EDOT substituents of 7. HOMO-LUMO energy differences for 6 and 7 can be estimated using the low energy wavelength edge ( $\lambda_{onset}$  in Table 1) for  $\pi - \pi^*$  absorptions. These energies are 2.88 eV for 6 and 3.35 eV for 7. Optical bandgaps for the polymer films, estimated from  $\lambda_{onset}$  values, are found to be 2.33 eV for poly-6 and 2.97 eV for poly-7.

A comparison of the absorption data shows that 9 displays a smaller optical bandgap than the other systems considered here. Since both 6 and 7 undergo oxidation at comparatively



Fig. 5. Atomic force microscopy images of top: poly-6; middle: poly-7; and bottom: a bare ITO-coated glass slide. Images are presented as 3-D surfaces (left) and 1<sup>st</sup> derivatives (right).



low, positive potentials, it would be expected that reduction of both of these monomers must require quite negative potentials, presumably a consequence of the greater electron-donating nature of the dimethylbiimidazole center. Indeed, we were unable to observe these processes in our experiments.

#### Atomic force microscopy

736

Atomic force microscopy (AFM) was used to investigate the topography of poly-6 and poly-7 films deposited onto ITO-coated glass electrodes (Fig. 5). These films appeared smooth to the naked eye. The 25  $\mu$ m  $\times$  25  $\mu$ m images of poly-6 show a fairly homogeneous polymer surface, with polymer particles of roughly 1  $\mu$ m diameter distributed on the electrode surfaces. Note that the vertical scale in this image is roughly one-tenth the *x*- and *y*-axis scales. The poly-7 surface looks smooth in most areas, but also shows regions where larger grains have deposited, of approximately 1  $\mu$ m diameter, on average.

## Conclusions

Two novel thiophene–imidazole structures have been synthesized, and their electrochemical and electronic properties were investigated. Polymer films of 5,5'-bis(2,2'-bithiophene-5-yl)-1,1'-dimethyl-2,2'-biimidazole and 5,5'-bis(3,4ethylenedioxythiophene-2-yl)-1,1'-dimethyl-2,2'-biimidazole were grown on platinum and indium-tin oxide-coated glass through electrochemical polymerization. The films deposited were fairly homogeneous, as indicated by AFM studies. The facile polymerization of these materials and the potential to vary the identity of the substituent on N<sub>1</sub> makes these materials promising candidates for further studies aimed at creating supports for tunable heteogeneous electrocatalysts.

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#### References

- (1) Goppelsroeder, F. Bull Soc. Ind. 1876, 82, 1392.
- (2) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. J.; Heeger, A. J. J. Chem. Soc, Chem. Commun. 1977, 59.
- (3) Chiang, C. K.; Fincher, C. R.; Park, Y. W.; Heeger, A. J. *Phys. Rev. Lett.* **1977**, *39* (17), 1098–1101. doi:10.1103/ PhysRevLett.39.1098.
- (4) Chiang, C. K.; Druy, M. A.; Gau, S. C.; Heeger, A. J.; Louis, E. J.; MacDiarmid, A. G.; Park, Y. W.; Shirakawa, H. J. Am. Chem. Soc. 1978, 100 (3), 1013–1015. doi:10. 1021/ja00471a081.
- (5) Skotheim, T. A.; Elsebaumer, R. L.; Reynolds, J. R., Eds.; In *Handbook of conducting polymers*, 2nd ed, revised and expanded; Marcel Dekker: New York. 1998.
- (6) Guiseppi-Elie, A.; Pradhan, S. R.; Wilson, A. M.; Allara, D. L.; Zhang, P.; Collins, R. W.; Kim, Y. T. *Chem. Mater.* **1993**, *5* (10), 1474–1480. doi:10.1021/cm00034a017.

- (7) Guiseppi-Elie, A.; Wilson, A. M.; Tour, J. M.; Brockmann, T. W.; Zhang, P.; Allara, D. L. *Langmuir* **1995**, *11* (5), 1768–1776. doi:10.1021/la00005a055.
- (8) Barbarella, G.; Bongini, A.; Zambianchi, M. Macromolecules 1994, 27 (11), 3039–3045. doi:10.1021/ma00089a022.
- (9) Zhang, W.; Plieth, W.; Koßmehl, G. *Electrochim. Acta* 1997, 42 (11), 1653–1661. doi:10.1016/S0013-4686(96)00301-5.
- (10) Roncali, J. J. Mater. Chem. 1999, 9 (9), 1875–1893. doi:10. 1039/a902747e.
- (11) Demeter, D.; Blanchard, P.; Allain, M.; Grosu, I.; Roncali, J. *J. Org. Chem.* **2007**, *40*, 4481.
- (12) Cebeci, F. Ç.; Sezer, E.; Sarac, A. S. *Electrochim. Acta* 2007, 52 (5), 2158–2165. doi:10.1016/j.electacta.2006.08. 033.
- (13) Albano, V. G.; Bandini, M.; Moorlag, C.; Piccinelli, F.; Pietrangelo, A.; Tommasi, S.; Umani-Ronchi, A.; Wolf, M. O. *Organnometallics* 2007, 26 (18), 4373–4375. doi:10.1021/om0702101.
- McQuade, D. T.; Pullen, A. E.; Swager, T. M. Chem. Rev. 2000, 100 (7), 2537–2574. doi:10.1021/cr9801014. PMID: 11749295.
- (15) Li, G.; Wang, T.; Schulz, A.; Bhosale, S.; Lauer, M.; Espindola, P.; Heinze, J.; Fuhrhop, J. H. *Chem. Commun. (Camb.)* 2004, (5): 552–553. doi:10.1039/b313415f. PMID:14973603.
- (16) Derossi, S.; Adams, H.; Ward, M. D. *Dalton Trans.* 2006,
  (1): 33–36. doi:10.1039/b614346f. PMID:17160171.
- (17) Majumdar, P.; Peng, S.-M.; Goswami, S. J. Chem. Soc., Dalton Trans. 1998, (10): 1569–1574. doi:10.1039/a801071d.
- (18) Haga, M.; Ali, M. M.; Arakawa, R. Angew. Chem., Int. Ed. Engl. 1996, 35 (1), 76–78. doi:10.1002/anie.199600761.
- (19) Carina, R. F.; Verzegnassi, L.; Williams, A. F.; Bernardinelli, G. *Chem. Commun. (Camb.)* **1998**, (24): 2681–2682. doi:10.1039/a807321j.
- (20) Cameron, C. G.; Pittman, T. J.; Pickup, P. G. J. Phys. Chem. B 2001, 105 (37), 8838–8844. doi:10.1021/jp0109325.
- (21) Chadwick, D.; Ngochindo, R. I. J. Chem. Soc., Perkin Trans. 1 1984, 481. doi:10.1039/p19840000481.
- (22) Cromer, D. T.; Ryan, R. R.; Storm, C. B. Acta Crystallogr. 1987, 43, 1435.
- (23) Sánchez-García, D.; Borrós, S.; Nonell, S.; Borrell, J. I.; Colominas, C.; Teixidó, J. *J. Heterocycl. Chem.* **2002**, *39* (4), 733–735. doi:10.1002/jhet.5570390418.
- (24) Matthews, D. P.; Whitten, J. P.; Mccarthy, J. R. J. Heterocycl. Chem. 1987, 24 (3), 689–692. doi:10.1002/jhet. 5570240328.
- (25) Yamamoto, T.; Uemura, T. J. Polym. Sci. Part Polym. Chem. 2002, 40 (15), 2686–2688. doi:10.1002/pola.10354.
- (26) Yamamoto, T.; Uemura, T.; Tanimoto, A.; Sasaki, S. *Macro-molecules* 2003, *36* (4), 1047–1053. doi:10.1021/ma0211232.
- (27) Toba, M.; Terashima, T.; Nakashima, T.; Kawai, T. Jpn. J. Appl. Phys. 2008, 47 (2), 1371–1373. doi:10.1143/JJAP.47. 1371.
- (28) Ochmanska, J.; Pickup, P. G. Can. J. Chem. 1991, 69 (4), 653–660. doi:10.1139/v91-099.
- (29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Po-

melli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT; 2004.

- (30) Dennington, R., II; Keith, T.; Millam, J.; Eppinnett, K.; Hovell, W. L.; Gilliland, R. *GaussView*, Version 3.09; Semichem, Inc.: Shawnee Mission, KS; 2003.
- (31) Matthews, D. P.; Whitten, J. P.; McCarthy, J. R. Synthesis 1986, 1986 (04), 336–337. doi:10.1055/s-1986-31607.
- (32) Melloni, P.; Dradi, E.; Logemann, W.; De Carneri, I.; Trane, F. J. Med. Chem. 1972, 15 (9), 926–930. doi:10.1021/ jm00279a012. PMID:4340569.

- (33) Casas, J. S.; Castiñeiras, A.; Parajó, Y.; Sánchez, A.; Sánchez-González, Á.; Sordo, J. *Polyhedron* **2005**, *24* (10), 1196–1202. doi:10.1016/j.poly.2005.04.008.
- (34) Zhu, S. S.; Swager, T. M. Adv. Mater. **1996**, 8 (6), 497–500. doi:10.1002/adma.19960080609.
- (35) Zhu, S. S.; Swager, T. M. J. Am. Chem. Soc. 1997, 119 (51), 12568–12577. doi:10.1021/ja972794w.
- (36) Kuhn, R.; Blau, W. Justus Liebigs Ann. Chem. 1957, 605 (1), 32–35. doi:10.1002/jlac.19576050106.
- (37) Matthews, D. P.; Whitten, J. P.; MacArthy, J. R. *Synthesis* **1986**, 337.
- (38) Krische, B.; Zagorska, M. Synth. Met. 1989, 28 (1-2), 263–268. doi:10.1016/0379-6779(89)90531-6.
- (39) Dietrich, M.; Heinze, J. J. Electroanal. Chem. 1994, 369 (1-2), 87–92. doi:10.1016/0022-0728(94)87085-3.
- (40) MacLean, B. J.; Pickup, P. G. J. Mater. Chem. 2001, 11 (5), 1357–1363. doi:10.1039/b009568k.