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Steric and Electronic Effects in Methyl-Substituted 2,2′-Bipyrroles and Poly(2,2′-Bipyrrole)s: Part I. Synthesis and Characterization of Monomers and Polymers

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The effects of *N*- and *C*-methyl substitution on electrical and spectral properties of pyrrole, 2,2′-bipyrrole, and the corresponding polymers were investigated. The whole series of monomethyl and *N*- or C_β-dimethyl-substituted 2,2′-bipyrroles was synthesized, and the electrochemical and spectral properties of all the compounds were investigated under identical testing conditions. The corresponding polymers were prepared by electrochemical anodic oxidation under comparable experimental conditions and their spectroscopic and conductivity properties evaluated for comparison. The higher degree of efficiency in transmission of electronic effects associated with methyl substitution at C_β with respect to substitution at N was clearly demonstrated. The influence of the symmetry of the starting monomer (C_{2v} or C_s) on the electrical properties of the resulting polymers is discussed.

Introduction

Many chemical, physical, and electronic properties of conducting polyheterocycles can be tuned by introduction of suitable substituents on the monomer. Chemical and electrochemical polymerization of β-alkyl-substituted thiophenes[1] and bithiophenes[2] give materials showing greater solubility in organic solvents and higher conductivity than unsubstituted polythiophene. The presence of methyl groups in polypyrroles produces different results depending whether substitution involves the nitrogen atom or the β-carbon atom of the pyrrole unit.

N-Alkylation generally affords scarcely conductive materials: for example, the measured conductivity of electrochemically produced poly(*N*-methylpyrrole) was found to be 10^{-3} S cm^{-1},[3,4] i.e. ~5 orders of magnitude lower than the value obtained for polypyrrole. This fact was tentatively attributed to a high torsional angle induced by the N-substituent between adjacent pyrrole rings and, in accordance with this hypothesis, the interannular torsion in all-α-tetra(*N*-methylpyrrole) was found to be about 50° in the solid state.[5] However, structural characterization of poly(*N*-methylpyrrole)[4] showed the presence of chemical defects, mainly carbonyl groups, which might contribute to reduce the electroconductivity of the material. These oxidative defects would be due to the high voltage required for *N*-methylpyrrole anodic electropolymerization. In fact, *N*,*N*′-bridged 2,2′-bipyrroles gave polymers with good conductivity, despite double N-substitution,[6] since their polymerization potential is less positive. The same effect was observed in electrochemically prepared polyfuran starting from terfuran.[7]

3-Alkyl substitution of pyrrole is so highly synthetically demanding that only a few reports have been

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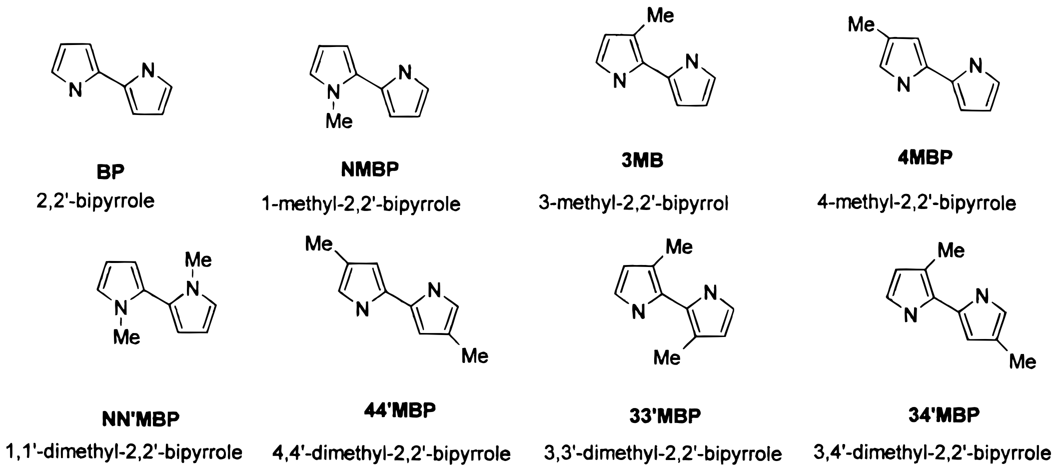
Scheme 1



published[8−13] on poly(3-alkylpyrrole)s. These materials were found to be much more conductive (2−10 S cm^{-1}) than the corresponding N-substituted polymers, and even more (270 S cm^{-1})[10] than polypyrrole itself (100 S cm^{-1}),[14] when prepared under specially selected, optimized conditions (e.g., propylene carbonate as solvent and hexafluophosphate as counterion). Furthermore, poly(3-alkylpyrrole)s, unlike poly(3-alkylthiophene)s, have not been satisfactorily investigated from a structural point of view since they show a very high degree of sensitivity to the air in the neutral state.

The problem of poly(*N*-methylpyrrole) was recently addressed by Rhode et al.,[15] who reported the synthesis and the spectral and electrical characterization of some oligo(*N*-methylpyrrole)s. These authors proposed that steric factors alone could not be responsible for the modest conductivity displayed by the polymers, given the higher conductivity (2 × 10^{-1} S cm^{-1})[16] shown by the more sterically hindered poly(3,4-dimethylpyrrole). They, however, did not suggest fully convincing explanations for the drastic drop in conductivity of poly(*N*-methylpyrrole), and simply evoked “other important effects, like the tertiary structure, dipole and hydrogen bonding interactions”.

To investigate the different effects of nitrogen and C_β-methyl substition on the electrical properties of polypyrroles, we synthesized and electrochemically polymerized 2,2′-bipyrrole and all its possible monomethyl and *N*- or C_β-dimethyl-substituted derivatives (Scheme 1). The use of 2,2′-bipyrrole instead of pyrrole as a polymerogenic basis allowed us to obtain defect-free materials, since the working potentials for bipyrroles are definitely less positive than those necessary for methyl-substituted pyrroles polymerization.

We also considered it extremely important to perform calculations on the evolution of the electronic properties of some of our monomers as a function of *N*- and *C*-methyl-substitution to explain the experimental data. The results of this theoretical investigation are reported in Part II, the following paper in this issue.

Results and Discussion

Synthesis of the Monomers. Examination of literature showed that some of the bipyrroles necessary for developing the project were already known, namely: 1-methyl-2,2′-bipyrrole (**NMBP**),[17] 1,1′-dimethyl-2,2′-bipyrrole (**NN′MBP**),[18] 3- and 4-methyl-2,2′-bipyrrole (**3MBP** and **4MBP**),[19] 4,4′-dimethyl-2,2′-bipyrrole (**44′MBP**),[20] and 2,2′-bipyrrole (**BP**).[21] The crucial monomer 3,3′-dimethyl-2,2′-bipyrrole (**33′MBP**) and the 3,4′-dimethyl-2,2′-bipyrrole (**34′MBP**) were hitherto unknown. In designing a satisfactory synthetic approach to these two compounds, we reconsidered also those currently available for all the other monomers.

The simplest approach to 2,2′-bipyrrole (**BP**) was found to be the Vilsmeier reaction between pyrrole and the 2-pyrrolidinone-phosphorus oxychloride adduct, followed by dehydrogenation of the 2-[2-(1-pyrrolinyl)]-pyrrole intermediate promoted by palladium on charcoal in refluxing mesitylene solution. Such a simple sequence made 2,2′-bipyrrole the logical starting material for the synthesis of **NMBP**, **NN′MBP**, **4MBP**, and **44′MBP**, as shown in Scheme 2.

NMBP and **NN′MBP** were easily obtained by deprotonation of **BP** with 1 or 2 mol of sodium hydride, followed by alkylation with 1 or 2 mol of methyl iodide, respectively.

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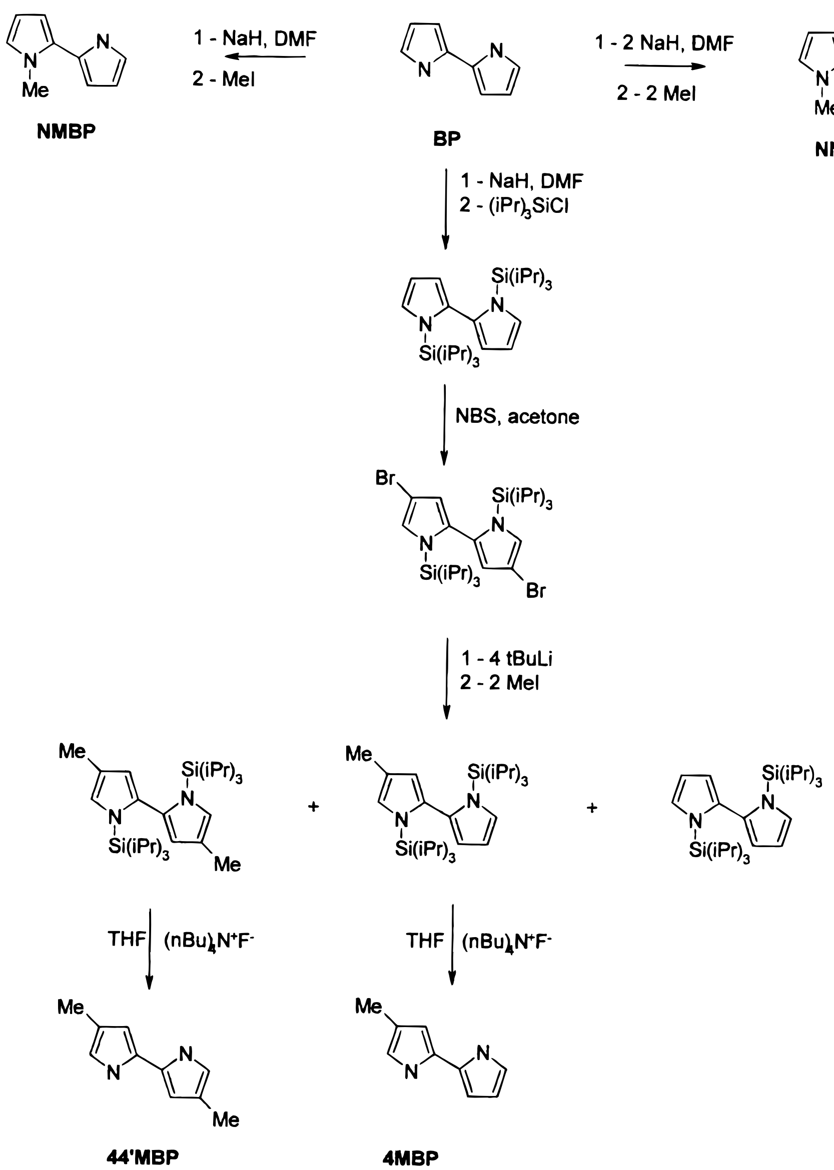
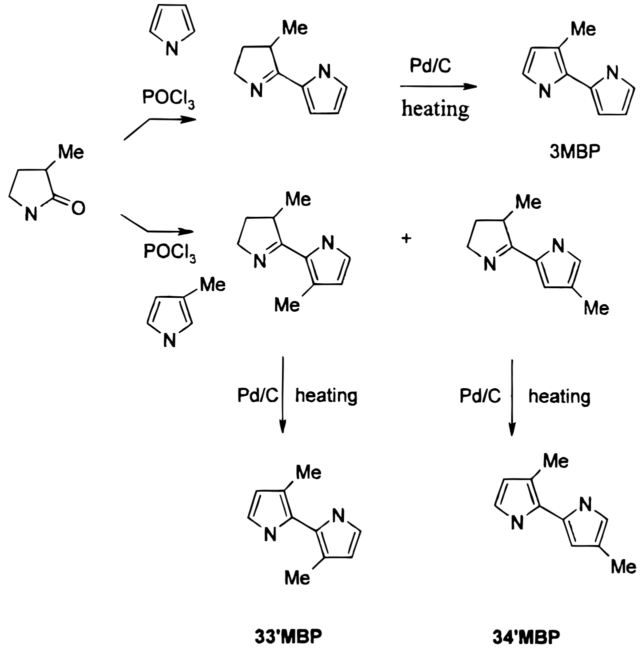
Scheme 2



The synthesis of **44′MBP** was achieved by double metalation, dialkylation, and desilylation of the 4,4′-dibromo-1,1′-di(triisopropyl)silyl-2,2′-bipyrrole, obtained by reaction of 1,1′-(triisopropyl)silyl-2,2′-bipyrrole with *N*-bromosuccinimide, taking advantage of the β-orienting effect of the bulky (triisopropyl)silyl group. The use of acetone as a solvent for the bromination reaction of protected bipyrrole is crucial to obtain the corresponding 4,4′-dibromoderivative in high yields. Synthesis of 1,1′-(triisopropyl)silyl-2,2′-bipyrrole was achieved by double deprotonation of **BP** with 2 equiv of sodium hydride and quenching of the dianion with 2 mol of triisopropylchlorosilane. The 1,1′-di(triisopropyl)silyl-4,4′-dibromo-2,2′-bipyrrole was treated with 4 equiv of *tert*-butyllithium and 2 mol of methyl iodide. A mixture of 1,1′-di(triisopropyl)silyl-4,4′-dimethyl-2,2′-bipyrrole (precursor of **44′MBP**), 1,1′-di(triisopropyl)silyl-4-methyl-2,2′-bipyrrole (precursor of **4MBP**), and 1,1′-di(triisopropyl)silyl-2,2′-bipyrrole was obtained. Desilylation of the crude mixture of these three products by reaction with tetrabutylammonium fluoride in tetrahydrofuran solution afforded **44′MBP**, **4MBP** and **BP**, which were obtained in a pure state by column chromatography.

The Vilsmeier reaction, described for the synthesis of 2,2′-bipyrrole, was successfully extended to the synthesis of **3MBP**, **33′MBP** and **34′MBP**, as shown in Scheme 3. The synthesis reported in the literature[19] for 3-methyl-2-[2-(1-pyrrolinyl)]pyrrole, precursor of **3MBP**, consists of a Vilsmeier condensation of 3-methylpyrrole and 2-pyrrolidinone in the presence of phosphorus oxychloride, giving the desired product and the 4-methyl-substituted isomer in a 1:1 ratio. The separation of these two constitutional isomers is described as very troublesome, requiring a 10 day procedure of continuous chromatographic separation on neutral alumina. We chose a more direct and streamlined synthetic scheme, involving pyrrole and 3-methyl-2-pyrrolidinone as starting materials. The latter is commercially available and its reactive position in the Vilsmeier reaction is univocally determined. **3MBP** was obtained in satisfactory yields according to this route. The Vilsmeier condensation involving 3-methylpyrrole and 3-methyl-2-pyrrolidinone gave a 1:1.2 mixture of 3-methyl-2-[2-(3-methyl-1-pyrrolinyl)]pyrrole and 3-methyl-5-[2-(3-methyl-1-pyrrolinyl)]pyrrole, which were dehydrogenated in a crude state with 10% palladium on charcoal in

Scheme 3



refluxing mesitylene solution. The two constitutional isomers, **33′MBP** and **34′MBP**, were then separated by column chromatography, using a CH_2Cl_2:hexane 7:3 mixture as an eluant.

While 1-methylpyrrole (**NMP**) is commercially available, 3-methylpyrrole (**3MP**) was synthesized according to the procedure reported in the literature.[22]

Spectroscopic Characterization of the Monomers. The identity of all the substrates was ascertained on the basis of analytical and spectroscopic data (see Experimental Section).

As is commonly done, the electronic and steric effects of the methyl substituents on the intramolecular π conjugation were investigated by means of electronic absorption spectroscopy. Even though we are aware that UV data contain, in principle, information on both ground and excited states, we believe that in a homogeneous series of compounds, variations in the maximum absorption wavelength should parallel changes in π conjugation extent. UV data are reported in Table 1, where **BP** was used as reference standard.

The presence of one methyl group adjacent to the interannular carbon−carbon bond, connected either to the carbon (**3MBP**) or to the nitrogen atom (**NMBP**), produces a modest bathochromic shift of the maximum absorption wavelength. This indicates that loss in conjugation, produced by steric hindrance due to the presence of one methyl group, is negligible and unrelated to the methyl group position.

The presence of one methyl group in position 4, which cannot influence the interannular torsional angle, produces only a small red shift in the UV spectrum of **4MBP**, due to the electron-releasing properties of the methyl group. The presence of two methyl groups in positions 4 and 4′ (**44′MBP**) produces, as expected, a further shift of the conjugation band toward higher wavelengths.

Analysis of the UV spectra of dimethyl derivatives **NN′MBP** and **33′MBP** clearly shows that the presence of two methyl groups adjacent to the interannular bond, either at the nitrogen or at 3 and 3′ carbon atoms, produces a substantial loss in conjugation, which is definitely greater than that observed in the monomethyl-substituted derivatives.

In **34′MBP** the electron-donating effect of the "outer" methyl group seems to be compensated by the loss of π conjugation due to the presence of the "inner" substituent.

Electrochemical Characterization and Electrodeposition of *C*-Methyl-Substituted Bipyrroles and Characterization of the Resulting Polymers. As previously reported,[23,24] when acetonitrile was used as a solvent, the anodic coupling of 2,2′-bipyrrole was found to be strongly dependent on solvent water content and on the type of supporting electrolyte anion. Different results were obtained in the presence either of perchlorate or of tosylate anions.[25] The same dependence was also observed during anodic oxidation of the *C*-methyl-substituted 2,2′-bipyrroles investigated herein.

The *C*-methyl-substituted monomers were oxidized in a one-electron irreversible peak in acetonitrile in the presence of 0.1 M tetrabutylammonium perchlorate (TBAP). No reversible process was obtained up to 1000 V s^{-1}, thus indicating a fast coupling rate. Despite this observation, potential cycling did not easily produce polymers. In most cases repetitive potential cycling showed the appearance of multiple redox signals, probably due to the formation of soluble oligomers. A very low amount of polymer was deposited, as indicated by the calculated value of the charge yield (ratio between reversible charge, measured in monomer-free solution, and deposition charge) which was found to be only 1−2% vs the expected 25−40% value. This drawback, which was previously attributed to the protonation of intermediate oligomers, was overcome by the use of water as a proton scavenger.[25] The 1% addition of water caused the appearance of a new additional oxidation process, attributable to nonprotonated oligomers. Potential cycling above the potential of this new process allowed easy polymer deposition. Charge yield increased up to a 10−15% value.

When tetrabutylammonium tosylate (TBA-Tos) was used as a supporting electrolyte, in dry acetonitrile solution, the oxidation peak of all *C*-methyl-substituted bipyrroles shifted to less positive values (peak potentials, E_{pa}^{mon}, are given in Table 1) and corresponded to a two-electron oxidation process. Under these conditions the polymerization rate increased[25] and the polymer easily deposited on the anode (charge yield = 20−50%). TBA-Tos was then chosen as the standard supporting electrolyte for all the anodic oxidation experiments on *C*-methyl-substituted bipyrroles in the present study.

The values of E_{pa}^{mon} were in agreement with the electronic and steric effects of methyl groups on π conjugation, evaluated by means of UV spectroscopy.

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Table 1. $E_{pa}{}^{mon}$ (Oxidation Peak Potential of the Monomers[a,b]), $\lambda_{max}{}^{mon}$ (Maximum UV Absorption Wavelength of the Monomers (Ethanol)), $E°_{pol}$ (Redox Potential of the Polymers[c,d]), $\lambda_{max}{}^{neutralpol}$ (Maximum UV Absorption Wavelength of the Neutral Polymers[a,b]), and σ (Maximum In-Situ Conductivity of the Doped Polymers[c–e])

monomer	$E_{pa}{}^{mon}$ (V)^{a,b}	$\lambda_{max}{}^{mon}$ (nm)	polymer	$E°_{pol}$ (V)^{c,d}	$\lambda_{max}{}^{neutral\ pol\ a,b}$ (nm)	σ (S/cm)^{e}
			Reference Compounds			
P	$0.84^a/0.87^b$	208	poly(P)	$-0.60^c/-0.20^d$	$400^{a,b}$	$100^{c,d}$
3MP	0.67^a	210	poly(3MP)	-0.63^c	350, 420^{sh}	0.1^c
NMP	0.8^b	210	poly(NMP)	0.10^d		0.01^d
BP	$0.03^a/0.17^b$	278	poly(BP)	$-0.70^c/-0.45^d$	$400^{a,b}$	$70^c/20^d$
			C-Methyl-Substituted Compounds			
3MBP	0.03^a	270	poly(3MBP)	-0.78^c	365^{sh}, 450, 480^{sh}	6^c
4MBP	-0.05^a	280	poly(4MBP)	-0.70^c	360, 340^{sh}	3^c
33′MBP	0.08^a	257	poly(33′MBP)	-0.55^c	345	0.3^c
44′MBP	-0.07^a	284	poly(44′MBP)	-0.55^c	345	0.3^c
34′MBP	-0.07^a	276	poly(34′MBP)	-0.66^c	350, 420^{sh}	2^c
			N-Methyl-Substituted Compounds			
NMBP	0.2^b	270	poly(NMBP)	-0.20^d	370	0.8^d
NN′MBP	0.3^b	250	poly(NN′MBP)	0.0^d	295	0.3^d

[a] Supporting electrolyte: TBA-Tos. [b] Supporting electrolyte: TBA-ClO$_4$. [c] Counteranion: Tos$^-$. [d] Counteranion: ClO$_4{}^-$. [e] Measured at ~0.3 V positive vs $E°_{pol}$.

The effects of C- and N-substitution on oxidation potential of the various monomers were once again evaluated by comparison with the data found for **BP**.

Even though it is rather modest, the donor effect of the carbon-bonded methyl group, free from contribution related to steric interference, can be easily evaluated in the **BP**, **4MBP**, and **44′MBP** series, where we observed a progressive reduction in oxidative potential from 0.03 V for **BP** to −0.05 V for **4MBP** and to −0.07 V for **44′MBP.**

The effect on electrochemical oxidative potential of the methyl groups bound to carbon atoms adjacent to the interannular bond results from two competing mechanisms. The first is the electron-releasing capacity of the methyl group, which tends to reduce electrochemical oxidative potential value. The second is the induced distortion from planarity of the bipyrrole system, which tends to increase it. Once again, even though relatively modest, the effects can be evaluated without difficulty in the **BP**, **3MBP**, and **33′MBP** series. No variations were observed in $E_{pa}{}^{mon}$ on passing from the first to the second compound (0.03 V), in which there is perfect compensation between the electronic and steric effects. Loss in π conjugation prevails over electron donation with the second methyl group substitution and potential increases to 0.08 V in **33′MBP**.

34′MBP, which carries one inner and one outer methyl group, shows an electrochemical oxidative potential value of 0.07 V, identical to that exhibited by **44′MBP**. On the basis of these results, we can deduce that methyl group substitution produces a less marked shift in oxidative potential than in $\pi-\pi^*$ transition energy levels.

Cyclic voltammograms of the corresponding polymers, prepared in acetonitrile solution, in the presence of 0.1 M TBA-Tos, showed a neat process (Figure 1), quite similar to that of polypyrrole. The redox switching produced spectral (Figure 2) and conductivity (Figure 3) changes typical of pyrrole-based conducting polymers. The redox potentials of the polymers ($E°_{pol}$) are reported in Table 1, along with their electronic absorption maxima in the neutral state ($\lambda_{max}{}^{pol}$) and their conductivity (σ), as measured in situ.

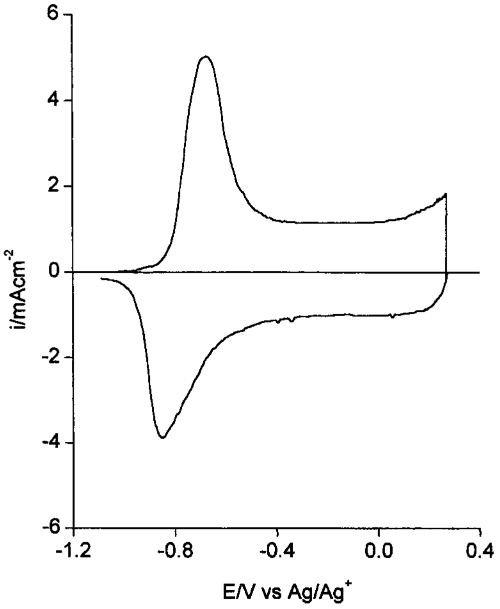

Figure 1. Cyclic voltammetry of poly(**3MBP**) in acetonitrile in the presence of 0.1 M TBATos. Scan rate: 0.1 V s^{-1}. Reversible charge: 19.5 mC cm^{-2}.

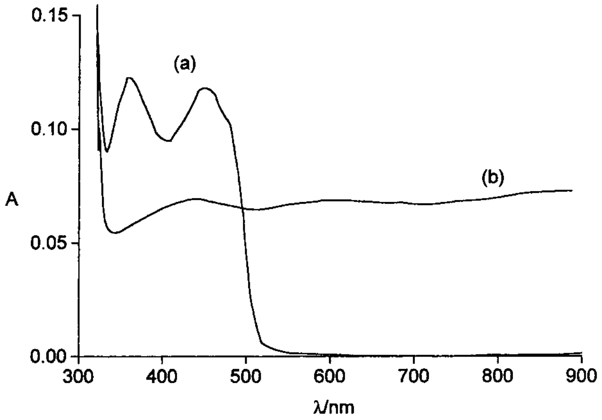

Figure 2. UV−vis spectrum of poly(**3MBP**): (a) neutral and (b) oxidized.

We compared electrochemical, optical and conduction properties of these materials with those of poly(2,2′-bipyrrole), poly(**BP**), as prepared by us under identical experimental conditions. Data relating polypyrrole, poly**P**, and poly(3-methyl)pyrrole, poly(**3MP**), are also

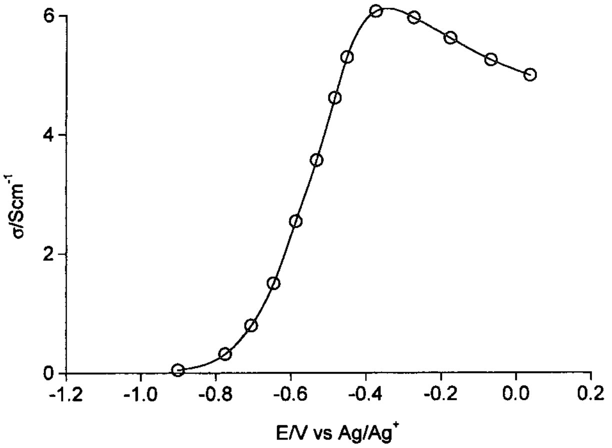

Figure 3. In-situ conductivity vs potential for poly(**3MBP**).

reported in Table 1.

Poly(C-dimethyl-substituted-bipyrrole)s were found to be characterized by less negative redox potential values (the only exception was poly(**3MBP**)), lower λ_{max}^{pol} (generally 50 nm lower) and lower conductivity than poly(**BP**) (from 1 to 2 orders of magnitude). However data regarding all of these parameters were, overall, quite close to those of the electrochemically prepared poly(**3MP**).

As expected, **33′MBP** and **44′MBP** gave the same polymer by anodic oxidation. This material shows all methyl groups facing each other. Since the positions involved in the polymerization process are homotopic in both of the monomers, which belong to the C_{2v} symmetry point group, there is not constitutional disorder in these materials.

The head-to-tail junction, with no facing methyl groups, is probably the preferred polymerization mode for the C_s symmetry **34′MBP**, since steric crowding is reduced with respect to head-to-head polymerization. A decrease in $E°_{pol}$ and enhancement of conductivity are expected. The polymer, poly(**34′MBP**), is structurally similar to poly(**3MP**), as shown by comparison of electrochemical and spectral data. Lower conductivity of the latter was attributed, as anticipated, to the presence of overoxidation defects, which are absent in the former, thanks to the lower oxidation potential of the starting monomer.

These data on poly(C-dimethyl-substituted bipyrrole)s are in line with those reported for poly(dialkyl-2,2′-bithiophene)s.[26] A lower degree of conjugation was observed in fact in poly-3,3′-dimethyl-2,2′-bithiophene, than in the poly-4,4′-dimethyl-substituted isomer.[26]

Comparison of the properties of poly(**BP**) with those shown by the polymers prepared from C-monomethyl- and C-dimethyl-substituted bipyrroles indicates that the higher the methyl group number, the higher the steric constraint and the lower the π conjugation.

The small differences in properties between poly(**3MBP**) and poly(**4MBP**), which, through a regioregular head-to-tail polymerization process would afford the same material, can be accounted for on the basis of the different situations produced by coupling. In poly(**4MBP**), occasional head-to-head junctions produce the facing of two methyl substituents on adjacent heterocyclic units. This sterically congested situation, which reduces π conjugation by hindering coplanarization of adjacent heterocyclic units and is responsible for the shift of $E°_{pol}$ to higher values and for the decrease of both λ_{max}^{pol} and conductivity (σ), cannot be produced in poly(**3MBP**). Poly(**3MBP**) shows maximum electronic absorption at 450 nm, i.e. at a higher wavelength value than that of poly(**BP**). Since the electronic effects of one methyl group on $\pi-\pi^*$ transition energy are negligible (the maximum absorption is shifted from the 278 nm of **BP** to the 280 nm of **4MBP**), this result was assumed to be evidence of a high degree of π conjugation in poly(**3MBP**).

Electrochemical Characterization and Electrodeposition of N-Substituted Bipyrroles and Characterization of the Polymers. The effects of methyl substition at nitrogen on oxidation potential can be evaluated in the **BP**, **NMBP**, and **NN′MBP** series, where behavior quite different from that found in the carbon-substituted series can be observed.

We have previously shown that tosylate, as anion in the supporting electrolyte, not only does not favor polymerization of N-substituted pyrroles, but also has detrimental effects on the process.[25] Thus, we used perchlorate in electrochemical oxidative polymerization of *N*-methyl-substituted bipyrroles. Furthermore, we found that water effectively favors anodic polymerization of *N*-methyl-substituted monomers and that the 1% (in volume) addition of water to the solvent doubles the oxidation current. To have electrochemical and spectral data of poly(*N*-methylpyrrole), poly(**NMP**), available as reference data, we performed electropolymerization of *N*-methylbipyrrole (**NMBP**), *N*,*N*′-dimethyl-2,2′-bipyrrole (**NN′MBP**), and of *N*-methylpyrrole (**NMP**) itself, under the same experimental conditions. **NMP** was oxidized in 1% aqueous acetonitrile solution, in the presence of 0.1 M TBAP, at $E_{pa} = 0.8$ V. At low monomer concentrations, anodic oxidation led to a scarcely electroactive material, as shown by the occurrence of electrode fowling. However, polymer deposition easily proceeded at 0.1 M (or higher) monomer concentration, at working potentials lower than 0.8 V (typically 0.65 V). The CV of the deposited material showed a neat process at $E° = 0.1$ V (Figure 4a) with a ~12% charge yield. EQCM measurements afforded a reversible charge value corresponding to ~0.25 anions per pyrrole ring. These data are in agreement with the charge yield value and indicates negligible loss of oligomers during deposition. The EQCM analysis showed the reversibility of the anion exchange, as already observed in other N-alkyl-substituted polypyrroles.[27]

Detailed evidence of the degradation processes affecting the polymerization of **NMP** was provided by UV and IR spectra of the neutral material. The UV spectrum of the neutral yellow polymer showed a much broader and tailed absorption band (Figure 5a), than those shown by other polypyrroles. The IR data clearly indicated the defective and oligomeric nature of the electrodeposited material. The spectrum was characterized by the antisymmetric stretching bands of aromatic and aliphatic hydrogens at 3100 and 2940 cm^{-1} respectively, and by

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[26] Krische, B.; Hellberg, J.; Lilja, C. *J. Chem. Soc. Chem. Commun.* **1987**, 1476.

[27] Schiavon, G.; Zotti, G.; Comisso, N.; Berlin, A.; Pagani, G. *J. Phys. Chem.* **1994**, *98*, 4861.

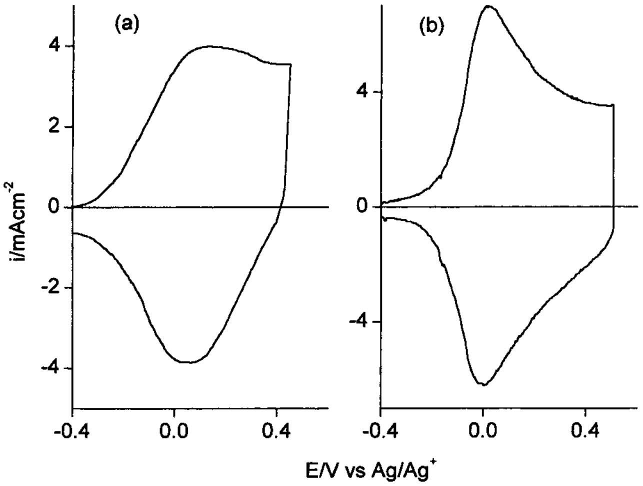

Figure 4. Cyclic voltammetry of (a) poly(**NMP**) and (b) poly(**NN′MBP**). Scan rate: 0.1 V s^{-1}. Reversible charge: (a) 17 and (b) 26 mC cm^{-2}.

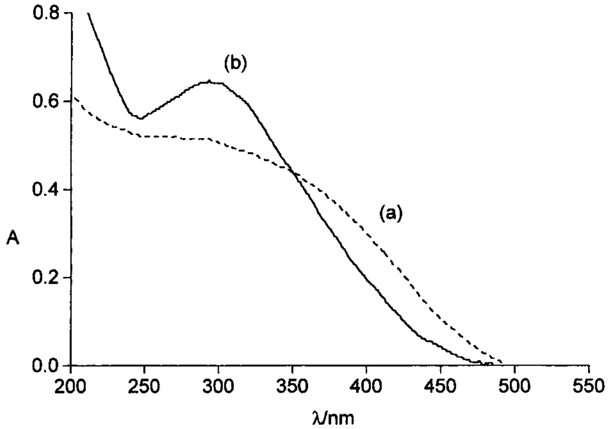

Figure 5. UV−vis spectra of (a) poly(**NMP**) and (b) poly(**NN′MBP**).

the ring deformation bands at 1440, 1360, and 1055 cm^{-1}. A strong band at 1610 cm^{-1}, due to oxidative defects,[28] could be considered as the most striking evidence of polymer overoxidation. Furthermore, the CH deformation band at 760 cm^{-1} was weak and accompanied by another band of comparable intensity at 715 cm^{-1}. Comparison of this spectrum with the IR spectrum of **NN′MBP** (vide infra) allowed us to assign this latter band to the CH out of plane bending of the terminal rings.

The conductivity of poly(**NMP**), measured in situ, was meager (10^{-2} S cm^{-1}), though 10 times higher than that found in ex-situ measurements.

The first N-substitution on **BP** raises the potential value from 0.03 V to the 0.2 V of **NMBP**, and the second one to the 0.3 V of **NN′MBP**.

Comparison of these data with those observed for **3MBP** (0.03 V) and for **3,3′MBP** (0.08 V), clearly demonstrates the different electronic effect exerted by methyl groups, depending on whether they are bonded to a nitrogen or to a carbon atom adjacent to the interannular bond. It is also interesting to note that this remarkable dependence of the electrochemical oxidative potential of the monomers on C- or N-substitution does not exist in the case of $\lambda_{max}{}^{mon}$. The **3MBP** e **NMBP** monomers display identical $\lambda_{max}{}^{mon}$ (270 nm) and very similar absorption maxima are found inside the **3,3′MBP-NN′MBP** couple (257−250 nm) as well. The difference in effect created by C- or N-substitution is also evident upon inspection of the UV spectral data and oxidative potential of **3MP** e **NMP**.

As for the materials resulting from N-substituted bipyrroles, **NN′MBP** was oxidized in a 1% aqueous acetonitrile solution, in the presence of 0.1 M TBAP, at $E_{pa} = 0.3$ V, i.e. at a potential value 0.5 V more negative than that of **NMP**. As a consequence of this easier oxidation process, it was possible to deposit an electroactive material even at a very low substrate concentration (10^{-3} M). The CV of poly(**NN′MBP**) showed a neat process with $E° = 0.0$ V (see Table 1 and Figure 4b), a value significantly shifted (0.1 V) toward less positive potentials than poly(**NMP**). Both the charge yield value (15%) and EQCM measurements revealed that the charge reversibly exchanged by the polymer corresponds to ∼0.33 anions per pyrrole ring, thus indicating that substantial loss of soluble oligomers occurred during deposition.

The fact that poly(**NN′MBP**) exchanges one electron per three pyrrole rings, while poly(**NMP**) can exchange one per four pyrrole rings, suggests greater availability of poly(**NN′MBP)** for charge release/acceptance and a higher degree of regularity vs poly(**NMP**).

The absorption spectrum of neutral, light yellow, poly(**NN′MBP**) was evenly broad and no tailing in the visible region was observed (Figure 5b). The maximum absorption wavelength (295 nm) matched the value (290 nm) extrapolated from UV spectra of oligomers for the infinite polymer.[16]

The IR spectrum of neutral poly(**NN′MBP**) showed great intensity enhancement of the CH deformation band (760 cm^{-1}) and of the corresponding CH stretching band (3100 cm^{-1}). The band at 1610 cm^{-1}, due to oxidative defects, was found to be very weak. The intensity ratio between the out of plane bending of terminal (715 cm^{-1}) and inner (760 cm^{-1}) ring CH allowed a polymerization degree estimate of ∼30−40 units.

The low *E*° value of poly(**NN′MBP**), its clean and bathochromically shifted UV absorption band, the features of its IR spectrum and the high EQCM anion exchange value clearly indicate the production of a defect-free polymer. As a consequence, the in situ conductivity (0.3 S cm^{-1}) (Figure 6) was found to be 30 times higher than that shown by poly(**NMP**).

The decrease in *N*-methyl group loading in the polymer on passing from poly(**NN′MBP**) to poly(**NMBP**) and then to poly(**BP**) led to spectral and conduction properties (see Table 1) typical of a definitely better-conjugated material.

Comparison of Spectroscopic and Electrochemical Data of *C*-Methyl- and *N*-Methyl-Substituted Pyrroles, Bipyrroles, and Poly(Bipyrroles). As for monomers, the anodic peak potentials of pyrroles (**3MP** vs **NMP**), monomethyl bipyrroles (**3MBP** vs **NMBP**) and dimethyl bipyrroles (**33′MBP** vs **NN′MBP**) show that C-substituted derivatives are electron-richer than the N-substituted ones. This observation suggests that the electron-donating properties of a methyl group are

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[28] Gustafsson, G.; Lundström, I.; Liedberg, B.; Wu, C. R.; Inganäs, O.; Wennerström, O. *Synth. Met.* **1989**, *31*, 163.

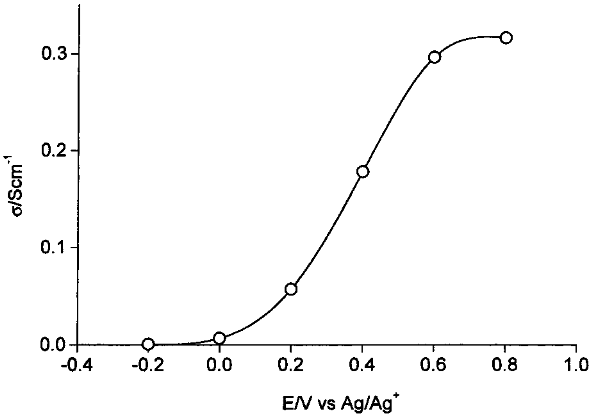

Figure 6. In-situ conductivity vs potential for poly(**NN′MBP**).

more effectively transmitted through carbon rather than through nitrogen. Interestingly enough, no substantial differences are however observed in the UV spectra of analogously C- and N-substituted derivatives.

In the case of polymers, electrical conductivity and π conjugation of poly(*C*-methyl-substituted-bipyrroles), evaluated by means of redox potentials and UV absorption maxima, progressively decrease as methyl group loading increases. The lowest values of conductivity are shown by the material obtained from **33′MBP** and **44′MBP**, where the methyl groups regularly face each other. The same trend is observed in the series of *N*-methyl-substituted polymers where, however, increased methyl group loading produces much more deleterious effects on the electrical and spectral properties than C-substitution.

Poly(**NN′MBP**) is characterized by a highly twisted main chain due to the presence of methyl groups facing each other at each interannular bond. As a matter of fact, this material shows an absorption maximum close to that of terpyrrole. Conductivity value is, however, identical to that shown by poly(**33′MBP**) [or poly(**44′MBP**)], which is much more electron rich (see E°_{pol}) and better conjugated (see $\lambda_{\text{max}}^{\text{neutral pol}}$). Thus, doping seems to increase intramolecular π conjugation in poly(**NN′MBP**), probably by forcing the twisted system to a higher degree of interannular coplanarity.

Poly(**3MBP**) and poly(**4MBP**) are more easily oxidized and more conductive than poly(**NMBP**) (see E°_{pol}), even though conjugation of these three polymers is fully comparable. Since constitutional disorder, related to head-to-head and head-to-tail junction mode, is possible in all these cases, even though with different statistical distribution, the higher electron-donating ability of the methyl group at carbon with respect to the methyl group bonded to nitrogen is once more quite evident.

We considered theoretical calculations as likely the most suited tool for explaining the differences in efficiency exhibited by C- and N-bound methyl groups in electronic effect transmission. The results of a theoretical work devoted to interpret this point are reported in Part II, the following article in this issue.

Conclusions

The results of this research (Parts I and II) have brought the long-debated question of the different effects on spectral and electrical properties of a polypyrrole chain produced by the presence of methyl groups either on the nitrogen atom or on the β carbons to a highly mature level of comprehension.

In this part, the whole series of pure *N*-methyl- and 3-methylpyrrole, monomethyl-substituted 2,2′-dipyrroles (three substrates) and dimethyl-substituted 2,2′-dipyrroles (four substrates), some of them hitherto unknown in the literature, were prepared. The electrochemical work was carried out under fine-tuned, comparable experimental conditions, to allow a reliable comparison of the results.

It was demonstrated that methyl C-substitution is more efficient than N-substitution in electron injection on the ring, as judged by electrochemical oxidative potentials along the series **P**, **NMP** and **3MP**. The increasing loss of planarity expected as a consequence of methyl-substitution in position adjacent to the interannular bond is likely to be the main responsible for the parallel increase in oxidation peak potential in the **BP**, **33′MBP**, and **NN′MBP** series. The higher oxidation peak potential for **NN′MBP** as compared to **33′MBP** suggests again a higher electronic transmission efficiency of C-3 substitution as opposed to N-substitution (see Part II).

This observation holds true also in the case of polymers where electrical conductivity decreases and λ_{max} progressively increases as methyl group loading raises. These effects are, however much more deleterious in the series of *N*-methyl-substituted polymers than in C-substituted materials.

C-Monosubstituted monomers, **3MBP** and **4MBP**, give materials which are more easily oxidized and more conductive than poly(**NMBP**), even though their π conjugation (λ_{max}) is comparable. The higher electron-donating ability of the C-bonded methyl group with respect to N-bonded methyl group is once more evident.

In the series of poly(disubstituted-dipyrrole)s, the presence of methyl groups facing each other at the interannular bond produces twisted chains, as inferred from $\lambda_{\text{max}}^{\text{neutral pol}}$. Torsion is, however, definitely much higher in poly(**NN′MBP**) than in poly(**33′MBP**) [or poly(**44′MBP**)]. Conductivity values of these materials are, instead, nearly identical even though the latter polymer is much more electron-rich and better conjugated than the former. It was believed[29] that the significantly smaller conductivity values achieved in the past for doped poly(*N*-methylpyrrole) as opposed to doped poly(3-alkylpyrrole) had to be due, at least in part, to the greater difficulty for the chains of the former to become coplanar: as a consequence, the intrachain mobility of the charge carriers in doped poly(*N*-methylpyrrole) would be lower and conductivity significantly smaller. Conversely, this work shows that the use of pure C_{2v} symmetry monomers, with homotopic coupling sites, and the adoption of fine-tuned experimental working conditions in the electrochemical anodic oxidation process, allowed us to obtain defect-free poly(**NN′MBP**) endowed with conductivity properties very similar to those shown by poly(**33′MBP**).

Experimental Section

^{1}H NMR spectra ($CDCl_3$ as a solvent) were recorded on a Varian XL-300 spectrometer or on a Bruker VP-80 SY spec-

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(29) Brédas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 6555.

trometer. The electronic spectra of the monomers (EtOH unless otherwise stated) were recorded on a Perkin-Elmer Lambda 6 spectrophotometer.

1-Methyl-2,2′-bipyrrole (NMBP). An 80% oil dispersion of NaH (0.045 g, 1.5 mmol) was added in one portion to a solution of 2,2′-bipyrrole (0.200 g; 1.5 mmol) in DMF (15 mL), under a nitrogen atmosphere. After 20 min of stirring, methyl iodide (0.228 g, 1.6 mmol) was added dropwise; the reaction mixture was left at room temperature for 30 min, then poured into water, and extracted with methylene dichloride. The organic phase was dried over Na_2SO_4 and the solvent removed under reduced pressure. The residue was chromatographed on silica gel, using hexane as an eluant. The last eluted fractions gave the title compound as a viscous oil; bp 100 °C at 1 Torr (0.114 g, 52%). ^{1}H NMR (80 MHz): δ 8.1 (broad s, 1H), 6.8 (q, $J = 2.5$ Hz, 1H), 6.68 (t, $J = 3.0$ Hz 1H), 6.25 (m, 4H), 3.7 (s, 3H).[17]

1,1′-Dimethyl-2,2′-bipyrrole (NN′MBP). A solution of 2,2′-bipyrrole (1.50 g, 11.4 mmol) in DMF (10 mL) was dropped into a suspension of an 80% oil dispersion of NaH (0.703 g, 23.4 mmol) in DMF (15 mL), under a nitrogen atmosphere. After 20 min, methyl iodide (3.32 g, 23.4 mmol) was added dropwise; the mixture was stirred for further 30 min, poured into water, and extracted with diethyl ether. The organic phase was dried over Na_2SO_4 and the solvent removed under reduced pressure to give a residue, which was chromatographed on silica gel using a methylene dichloride/hexane 2:8 mixture as an eluant. The first eluted fractions gave the title compound as a viscous oil: bp 80 °C at 1 Torr (1.10 g, 62%). ^{1}H NMR (80 MHz) δ 6.68 (t, $J = 3.0$ Hz, 2H), 6.15 (m, 4H), 3.50 (s, 6H).[18]

2-[2-(3-Methyl-1-pyrrolinyl)]pyrrole. Phosphorus oxychloride (2.7 mL) was dropped under stirring into neat pyrrole (10 g, 0.15 mol) at 0−5 °C over a 40 min period. A solution of 3-methyl-2-pyrrolidinone (3.70 g, 0.037 mol) in dry chloroform (20 mL) was then added in 1 h. After the addition was complete, the reaction mixture was stirred for 1 h at room temperature, and then poured into a 0.3 M solution of sodium acetate in water, at 0 °C. The resulting mixture was made basic with a 4 M sodium hydroxide solution. The organic layer was separated, filtered on a cell cake, and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave a residue, which was crystallized from a 2-propanol/water 3:1 mixture, to give the title compound: mp 93−97 °C (2.7 g, 49%); ^{1}H NMR (80 MHz) δ 6.9 (dd, $J = 2.5$ and 3.0 Hz, 1H), 6.4 (dd, $J = 2.5$ and 3.0 Hz, 1H), 6.25 (m, 1H), 3.9 (m, 2H), 3.3 (m, 1H), 1.5−2.5 (m, 2H), 1.25 (d, 3H).

3-Methyl-2,2′-bipyrrole (3MBP). A suspension of 2-[2-(3-methyl-1-pyrrolinyl)]pyrrole (7.9 g, 0.053 mol) and of 5% palladium on activated charcoal (5.0 g) in mesitylene (50 mL) was refluxed for 3 h. The hot reaction mixture was filtered on a cell cake, and the filtrate was brought to dryness under reduced pressure. The residue was chromatographed on silica gel, using methylene dichloride as an eluant. The first eluted fractions gave **3MBP** (2.3 g, 30%) as a pure compound: mp 195 °C; ^{1}H NMR (80 MHz) δ 6.8 (m, 1H), 6.7 (t, $J = 3.0$ Hz, 1H), 6.2 (m, 2H), 6.05 (m, 2H), 2.22 (s, 3H).[19]

1,1′-Di(triisopropyl)silyl-2,2′-bipyrrole. A solution of 2,2′-bipyrrole (3.0 g, 0.023 mol) in DMF (30 mL) was added to a stirred suspension of an 80% oil dispersion of NaH (1.6 g, 0.053 mol) in dry DMF (30 mL), under a nitrogen atmosphere. After 30 min of stirring at room temperature, triisopropylchlorosilane (12.5 mL, 11,4 g, 0.059 mol) was added dropwise at 10 °C. After 3 h of stirring at room temperature, the reaction mixture was poured into water and extracted with methylene dichloride. The organic layer was dried over Na_2SO_4 and the solvent removed under reduced pressure. The residue was chromatographed on silica gel, using hexane as an eluant, and the first eluted fractions gave the title compound, as a colorless solid, which was purified by crystallization from 2-propanol: mp 76 °C (2.4 g, 23%); ^{1}H NMR (300 MHz) δ 6.85 (dd, $J = 1.3$ and 2.6 Hz, 2H), 6.25 (dd, $J = 1.3$ and 3.5 Hz, 2H), 6.15 (dd, $J = 1.3$ and 3.5 Hz, 2H), 1.2 (m, 6H), 0.9 (d, 36H); EI-MS *m/z* (relative intensity) 361.

Further elution with a methylene dichloride/hexane 1:1 mixture gave 1-triisopropylsilyl-2,2′-bipyrrole (0.655 g, 10%): ^{1}H NMR (300 MHz) δ 6.88 (t, $J = 2.6$ Hz, 1H), 6.72 (q, $J = 2.5$ Hz, 1H), 6.25 (m, 2H), 6.18 (t, $J = 3.0$ Hz, 2H), 1.1 (m, 3H), 1.0 (d, 18H).

4,4′-Dibromo-1,1′-di(triisopropyl)silyl-2,2′-bipyrrole. A solution of *N*-bromosuccinimide (0.44 g, 2.5 mmol) in acetone (10 mL) was dropped into a stirred solution of 1,1′-di(triisopropyl)silyl-2,2′-bipyrrole (0.50 g, 1.1 mmol) and hydroquinone (0.10 g) in acetone (10 mL), under nitrogen, at 0 °C. After 1 h of stirring, the solvent was removed under reduced pressure. The residue was chromatographed on silica gel, using hexane as an eluant. The first eluted fractions gave the title compound: mp 114 °C (0.460 g, 70%); ^{1}H NMR (300 MHz) δ 6.75 (d, 2H), 6.25 (d, $J = 1.3$ Hz, 2H), 1.0−1.4 (m, 6H), 1.0 (d, $J = 7.0$ Hz, 36H); EI-MS *m/z* (relative intensity) 600.

4,4′-Dimethyl-2,2′-bipyrrole (44′MBP) and 4-Methyl-2,2′-bipyrrole (4MBP). A 1.5 M solution of *t*-BuLi in pentane (1.18 mL, 2.7 mmol) was added dropwise into a solution of 4,4′-dibromo-1,1′-di(triisopropyl)silyl-2,2′-bipyrrole (0.40 g, 0.67 mmol) in tetrahydrofuran (20 mL), at −50 °C, under a nitrogen atmosphere. Methyl iodide (0.190 g, 1.34 mmol) was added after 15 min, and the reaction was stirred at room temperature for 2 h. The reaction mixture was poured into water and extracted with diethyl ether. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure, to give a mixture (0.310 g) of 1,1′-di(triisopropyl)silyl-2,2′-bipyrrole, 4,4′-dimethyl-1,1′-di(triisopropyl)silyl-2,2′-bipyrrole, and 4-methyl-1,1′-di(triisopropyl)silyl-2,2′-bipyrrole, which was used without any further purification. This mixture was dissolved in tetrahydrofuran (15 mL), and tetrabutylammonium fluoride trihydrate (0.420 g, 1.6 mmol) was added. The reaction mixture was stirred at room temperature, for 1 h, then concentrated under reduced pressure, diluted with water, and extracted with diethyl ether. The organic phase was dried over Na_2SO_4 and the solvent removed under reduced pressure to give a residue, which was chromatographed on silica gel, using a methylene dichloride/hexane 1:1 mixture as an eluant. The first eluted fractions gave **44′MBP**: mp 156 °C (0.01 g, 0.062 mmol); ^{1}H NMR (80 MHz) δ 7.9 (broad s, 2H), 6.5 (m, 2H), 6.0 (m, 2H), 2.10 (s, 6H).[20] The intermediate fractions gave **4MBP**: mp 196 °C (0.038 g, 0.24 mmol);[19] ^{1}H NMR (80 MHz) δ 8.05 (broad s, 2H), 6.7 (dd, $J = 2.0$ and 3.0 Hz, 1H), 6.5 (m, 1H), 6.15−6.05 (m, 3H), 2.1 (s, 3H). The last eluted fractions gave **BP** (0.015 g, 0.11 mmol).[21]

3-Methyl-2-[2-(3-methyl-1-pyrrolinyl)]pyrrole and 4-Methyl-2-[2-(3-methyl-1-pyrrolinyl)]pyrrole. Phosphorus oxychloride (1.7 mL) was dropped under stirring into a solution of 3-methylpyrrole (1.6 g, 0.020 mol)[22] in dry chloroform (10 mL) at 0−5 °C, over a 40 min period. A solution of 3-methyl-2-pyrrolidinone (1.8 g, 0.018 mol) in dry chloroform (20 mL) was then added in 1 h. After the addition was complete, the reaction mixture was stirred at room temperature for 1 h, and then poured into a 0.3 M sodium acetate solution in water, at 0 °C. The mixture was made basic with a 1 M sodium hydroxide solution and extracted with methylene dichloride. The organic layer was separated, filtered on a cell cake, and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave a residue, which was chromatographed on silica gel, using an ethyl acetate/methanol 9:1 mixture as an eluant. The first eluted fractions gave a 1:1.2 mixture of the title compounds (0.900 g), which was used without any further purification. 3-Methyl-2-[2-(3-methyl-1-pyrrolinyl)]pyrrole: ^{1}H NMR (80 MHz) δ 6.85 (d, $J = 2.5$ Hz, 1H), 6.06 (d, $J = 2.5$ Hz, 1H), 5.9 (broad s, NH), 3.0−3.5 (m, 2H), 2.3 (s, 3H), 1.5−2 (m, 3H), 1.13 (d, $J = 7$ Hz, 3H). 4-Methyl-2-[2-(3-methyl-1-pyrrolinyl)]pyrrole: ^{1}H NMR (80 MHz) δ 6.65 (m, 1H), 6.4 (m, 1H), 5.9 (broad s, NH), 3.6−4.0 (m, 2H), 2.1 (s, 3H), 2.0−2.5 (m, 3H), 1.2 (d, $J = 7$ Hz, 3H).

3,3′-Dimethyl-2,2′-bipyrrole (33′MBP) and 3,4′-Dimethyl-2,2′-bipyrrole (34′MBP). A suspension of the crude mixture of 3-methyl-2-[2-(3-methyl-1-pyrrolinyl)]pyrrole and 4-methyl-2-[2-(3-methyl-1-pyrrolinyl)]pyrrole (0.900 g) and 1.0 g of 5% palladium charcoal in mesitylene (20 mL) was refluxed for 3 h. The hot reaction mixture was filtered on a cell cake, and the filtrate was brought to dryness under reduced pressure. The residue was chromatographed on silica gel, using a methylene dichloride/hexane 7:3 mixture as an eluant. The first eluted fractions gave **33′MBP** (0.050 g, 17%) as a pure compound: ^{1}H NMR (80 MHz) δ 7.95 (broad s, 2H), 6.72 (t, J = 2.5 Hz, 2H), 6.1 (t, J = 2.5 Hz, 2H), 2.16 (s, 6H); EI-MS m/z (relative intensity) 160. The subsequent fractions gave **34′MBP** (0.060 g, 21%): ^{1}H NMR (80 MHz) δ 8.0 (broad s, 2H), 6.5−6.7 (m, 2H), 6.05 (m, 2H), 2.25 (s, 3H), 2.1 (s, 3H); EI-MS m/z (relative intensity) 160.

Apparatus and Procedures for Anodic Oxidation Experiments. Acetonitrile was distilled twice over P_2O_5 and once over CaH_2. The supporting electrolytes tetrabutylammonium perchlorate (TBAP) and tetrabutylammonium tosylate (TBATos) were dried under vacuum at 70 °C. Anodic oxidation experiments were performed at 25 °C under nitrogen in a three electrode cells. The counter electrode was platinum; reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The working electrode for cyclic voltammetry was a platinum microdisk electrode (0.003 cm^2). For electronic spectroscopy 0.8 × 2.5 cm indium−tin−oxide (ITO) sheets (∼20 ohm/square resistance, from Balzers, Liechtenstein) or Au sputtered (15 nm thickness) quartz plates were used. A platinum sheet (15 cm^2) was used in reflection−absorption FTIR spectroscopy. Unless otherwise stated, 5×10^{-3} M monomer solutions in acetonitrile with the appropriate electrolyte were used. Polymer deposits for in-situ conductivity were obtained potentiostatically at 0.1 V beyond the oxidation peak potential. The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator.

The apparatus and procedures used in the in-situ conductivity experiments were previously described in details.[23] The relevant working electrode was a two-band platinum electrode (0.3 cm × 0.01 cm for each band) with interband spacing of 20 μm, typically polymer-coated with the passage of 20 mC, which assured the attainment of limiting resistance conditions. Poly(3-methylthiophene) (60 S/cm)[24] was used as conductivity standard. Though the in-situ conductivity determination does not provide absolute conductivity values, it is, however, very useful and meaningful for comparative purposes.

Electrochemical quartz crystal microbalance (EQCM) analyses were performed with a gold-coated AT-cut quartz electrode (0.35 cm^2), resonating at 6 MHz, onto which the polymers were deposited. The oscillator circuit was homemade, and a Hewlett-Packard model 5316B frequency counter was used. Data were collected by a microcomputer with a homemade analyzing software by which frequency changes $\Delta\nu$ were monitored as mass changes Δm.

The electronic spectra (diffuse reflectance) of neutral polymers were recorded on a Perkin-Elmer Lambda 15 spectrophotometer. Reflection−absorption IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer.

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