Synthetic routes, characterization, electrochemical and spectral properties of *p*-substituted *N*-phenylpyrroles

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Abstract

A series of *p*-substituted *N*-phenylpyrroles, including 4-(1*H*-pyrrol-1-yl)phenol (**1**), 1-(4-methoxyphenyl)-1*H*-pyrrole (**2**), 1,1'-benzene-1,4-diylbis(1*H*-pyrrole) (**4**), 1,1'-biphenyl-4,4'-diylbis(1*H*-pyrrole) (**5**) and 1-(4-bromophenyl)-1*H*-pyrrole (**3**), was prepared by means of a modified Clauson-Kaas method. Two new symmetrically and asymmetrically end-capped pyrrole thiophenes, namely 1-[4-(thiophen-2-yl)phenyl]-1*H*-pyrrole (**6**) and 1,1'-(bithiophen-5,5''-diyldibenzene-4,1-diyl)bis(1*H*-pyrrole) (**7**) were synthesized by using **3** as a building block and the Stille method as cross-coupling reaction. For both methods, the chemical yields ranged from 36 to 81% and the desired products were characterized by ^{1}H and ^{13}C NMR, IR, and mass spectrometry. Electrochemical properties and UV-visible absorption spectra were also investigated in order to evaluate the substituent electron-donor effects on the physicochemical parameters.

Keywords: *p*-Substituted *N*-phenylpyrroles, end-capped pyrroles and thiophenes, synthesis, electrochemical properties, UV-visible absorption spectra

Introduction

The design of novel, functional, conjugated monomers and oligomers remains an area of intense interest for the electrosynthesis of conducting polymer films. Particular emphasis has been placed on the search for new electron-rich heterocyclic monomers that could serve as building

blocks for the elaboration of conjugated polymers.[1-3] Among these functional heterocyclic monomers, pyrroles are very often used to build up conducting interfaces, since the chemistry of pyrrole derivatives is well-defined, and their chemical or electrochemical polymerization is generally easy, the resulting polymers forming robust and regular films. *N*-Phenylpyrrole (NPPY) can be considered as a particularly interesting compound, due to its important electronic properties enhanced by the conjugation of the phenyl group with the pyrrole ring linked to the nitrogen. For this reason, a number of publications have been devoted to a study of the effect of the phenyl group on the properties of the corresponding polymer [poly(NPPY)].[4-7] For instance, Mangeney *et al*.[4] have investigated the role of a conjugated link in poly(NPPY) between the polypyrrole backbone and the phenyl group. These authors showed that it was possible to obtain polymers with conjugated grafted groups, leading to a new class of materials in which the π-electron density of the active centre might be adjusted without synthesis. Also, the redox switching reaction of conducting polymers was used to modulate the electronic properties of benzene nuclei grafted on the polypyrrole backbone.[5] Moreover, recently, Diaw *et al*.[6,7] have optimized the experimental conditions to electrosynthesize poly-NPPY films in organic and micellar media, and have reported that the presence of traces of pyrrole, during the electropolymerization process, can improve several physicochemical properties of poly-NPPY films.

On the other hand, in order to diversify the structure and, hence, the properties of *p*-conjugated aromatic systems, several research groups have introduced various types of terminal amino groups such as diphenylamino, diamino, carbazolyl, and azaindolyl into the thiophene or benzene ring, for the purpose of end capping oligothiophenes or oligophenylenes.[8] These syntheses are of substantial interest, since the resulting compounds were found to fulfil all the requirements needed to obtain active materials for optoelectronic devices, including high absorptivities, high charge carrier mobilities, good film-forming properties, as well as good thermal- and photo-stabilities. The essential step in the synthesis of the above-mentioned amino end conjugated aromatic systems consisted of a heavy metal-catalyzed coupling reaction of aryl halides and an amine. However, this approach suffers from several drawbacks, such as the use of expensive organometallic catalysts (palladium and ligands) which also are often difficult to synthesize.

Therefore, in this study, we attempted to develop an alternative, easier synthetic approach to synthesize *p*-substituted *N*-phenylpyrroles, based on the introduction of a new amino end-group into the conjugated phenyl group. In order to combine the functional properties of a π-conjugated aromatic system and of pyrrole as end-capped group, we also herein report, for the first time, the synthesis of novel asymmetrically and symmetrically end-capped pyrrole mono- and oligothiophene-phenylenes and we investigated their structure-property relationship. We also characterized all the newly-synthesized compounds (Figure 1) by IR, NMR and mass spectrometry, and we studied their electrochemical and spectral properties. Indeed, these compounds are potential candidates to develop new polymers *via* the electropolymerization of pyrrole, and novel materials for use as active component in organic devices.

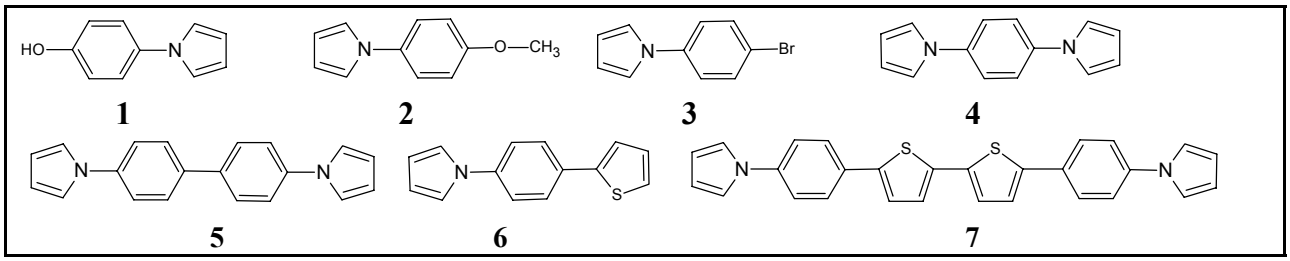


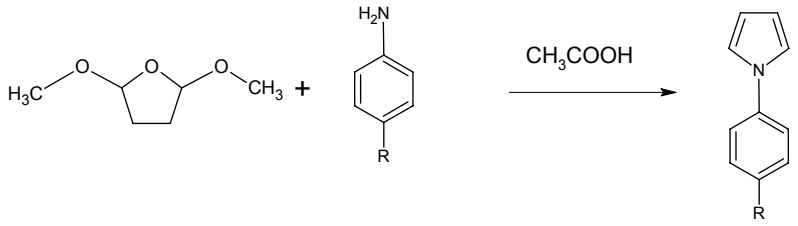
Figure 1. Structures of the synthesized *p*-substituted *N*-phenylpyrrole, and thiophene-*N*-phenylpyrrole, derivatives.

Results and Discussion

Synthesis of *p*-substituted *N*-phenylpyrrole, and thiophene-*N*-phenylpyrrole derivatives

(a) Synthetic route based on a modified Clauson-Kaas procedure

The synthesis of **4** was performed according to the original Clauson-Kaas method, as described earlier.[9] For the preparation of the other *N*-phenylpyrrole derivatives, including **1**-**3** and **5**, we used a synthetic route based on a modified Clauson-Kaas procedure, which is depicted in Scheme 1. The modification involved an improved extraction step in order to recover the products in better yields, since they did not easily precipitate. As can be seen in the Scheme, this synthesis is a multi-step route, starting from a condensation reaction between a *p*-substituted aniline and 2,5-dimethoxytetrahydrofuran in glacial acetic acid under reflux. In the case of *p*-phenylenediamine and benzidine, the target products immediately precipitated. In contrast, when anilines bearing strong electron-donating substituents, such as *p*-methoxyaniline and *p*-hydroxyaniline, were used, the formation of the corresponding *p*-substituted *N*-phenylpyrrole needed several treatments to yield a pure product, as detailed in the Experimental Part. As reported in the literature, the mechanism of this reaction can be described as a succession of three steps, including first, an amine nucleophilic attack in the 2 and 5 position of 2,5-dimethoxytetrahydrofuran, followed by the successive elimination of the two methoxy groups, and, finally, by an intramolecular dehydration of the intermediaries, which affords the desired product.



Scheme 1. Synthetic route to *p*-substituted *N*-phenylpyrroles, based on a modified Clauson-Kaas procedure (R = OH, OCH_3, Br, C_6H_4-4-NH_2).

The chemical yields of formation of the *p*-substituted-*N*-phenylpyrroles were satisfactory, since ranging between 36 and 81% (Table 1). It is worth noting that, for the synthesis of **4** and **5**, the chemical yields were proportional to the number of amino sites transformed into the corresponding pyrrole derivative. Moreover, **4** and **5** were immediately precipitated during the condensation reaction with 2,5-dimethoxytetrahydrofuran. In contrast, in the case of the other *p*-substituted *N*-phenylpyrroles, as stated above, the title compounds were not spontaneously precipitated, and their preparation required longer and more elaborate treatments.

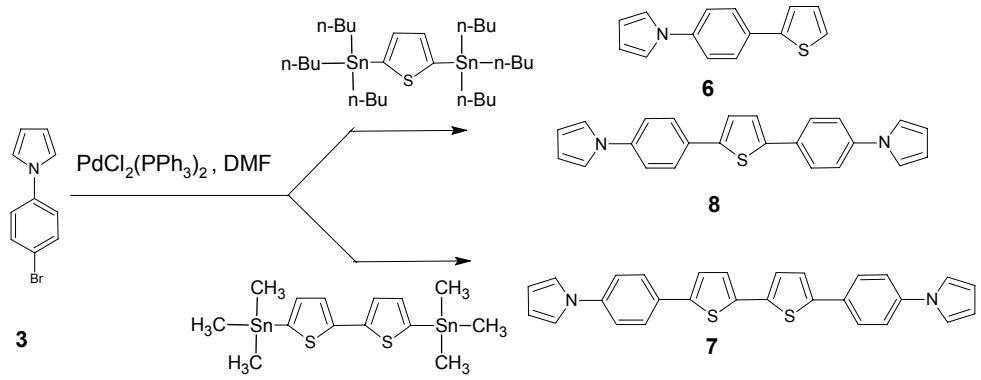
Table 1. Synthesis of the *p*-substituted *N*-phenylpyrroles by the modified Clauson-Kaas method from the corresponding aromatic amines

Aromatic amine	NPPY derivative	Yield (%)
p-phenylene diamine	**4**	36[a]
benzidine	**5**	71
p-anisidine	**2**	65
p-aminophenol	**1**	57
p-bromoaniline	**3**	81

[a] Yields of 41 and 15% were also reported by the Clauson-Kaas method in literature.[9,12]

(b) Synthetic route based on a Stille-type cross-coupling reaction

In order to gain access to the thiophene-*N*-phenylpyrrole derivatives **6** and **7**, possessing a longer chain with a well-defined substitution pattern, it was necessary to initially introduce the desired functional group into smaller building blocks, and then to use these precursors to extend the conjugation length. This was achieved by using the previously-prepared *p*-bromo-*N*-phenylpyrrole (**3**), as the building block, and the Stille procedure as cross-coupling reaction. The Stille-type cross-coupling reaction was carried out in degassed DMF in the presence of dichlorobis(triphenylphosphine)palladium(II) as catalyst. In the case of the synthesis of **6**, we performed the double palladium-catalysed Stille cross-coupling reaction of *p*-bromo *N*-phenylpyrrole with 2,5-bis(tributylstannyl)thiophene, whereas for **7** the Stille reaction was carried out with 5,5′-bis(trimethylstannyl)-2,2′-bithiophene. The distannane thiophene or bithiophene derivatives were used because they can be prepared in a simple and efficient way, and they could be easily purified. For the preparation of **6**, the Stille reaction led, after a chromatographic column purification, to the mono-substituted product in moderate yield (36%), and a trace of the di-substituted product **8** (see Scheme 2). Attempts to improve the yield of di-substituted product **8** by changing the experimental conditions of the reaction were unsuccessful. This result was attributed to the deactivation of the mono-substituted intermediate by the terminal amino group. In contrast, for the synthesis of **7**, when 5,5′-bis(trimethylstannyl)-2,2′-bithiophene was used, the Stille cross-coupling reaction led to the target product **7** in a yield of 61%. The synthetic route for both thiophene-N-phenylpyrrole derivatives **6** and **7** is summarized in Scheme. 2.



Scheme 2. Synthetic route to *p*-thiophene-*N*-phenylpyrrole (**6**) and pyrrole-*N*-phenyl-thiophene-thiophene-*N*-phenylpyrrole (**7**).

Spectroscopic characterization

(a) FT-IR spectral study

The FT-IR data of the *p*-substituted *N*-phenylpyrroles, including the vibration wavenumbers, intensities and assignments of the main IR bands, are given in Tables 2 and 3. As a typical example, Fig 2 shows the partial IR spectra of **6** and **7** in KBr pellets. These spectra were limited to the 600-1600 cm^{-1} region.

For characterization purposes, we have assigned the main IR bands of the *p*-substituted *N*-phenylpyrroles by comparison of our IR data with those of various analogues found in the literature.[10-14] We also compared, whenever it is possible, the IR spectral data of the *p*-substituted *N*-phenylpyrroles with those that we previously reported for unsubstituted NPPY, the parent compound.[6,7]

For all compounds under study, the bands observed within 3150-3100 cm^{-1} and those within 3000-3080 cm^{-1} can be assigned to the υ=C-H stretching vibrations (harmonic) of the pyrrole and phenyl rings, respectively, in agreement with the attribution of bands appearing in the same spectral region for NPPY (Tables 2 and 3).

Table 2. IR wavenumbers (cm^{-1}) and assignments of the main bands of 2, 1, 4 and NPPY in KBr pellets

NPPY[a]	**2**	**4**	**1**	Assignment
Band position (cm^{-1})				
			3426 (vs)	υ=O-H
3151(vw) 3141(w) 3113(vw)	3142(w)	3125(w) 3109(vw)	3143(w) 3100(vw)	υ=C-H pyr harmonic
3062(w) 3046(w) 3019(w)	3014(w)	3073(w) 3047(w)	3039(w)	υ=C-H ar harmonic
--------	2962(w) 2936(vw)	----------	------	υC-H methoxy
1604 (s) 1591(vw)	1592(vw) 1613(vw)	1581(s) conjugation	1604(w) 1637(vw)	υ C=C ar stretch
1513(vs)	1524(vs)	1524(vs) 1490(vs)	1512(vs)	υ C=C ar stretch
1460(s) 1470(s)	1458 (s) 1442 (s)	1472 (w) 1433 (s)	1450(s) 1478(w)	υ C=C ; υC-N pyr
1255 (s)	1247 (s) 1261(s)	1259 (s)	1252 (vs) 1234(vs)	δ =C-H ar in-plane vib 4H 1,4-disub-benzene
1016 (vs) 1071 (s)	1071 (vs) 1017 (vs)	1023 (s) 1071 (s)	1014(vs) 1070 (s)	υ=C-H_α pyr in-plane vib
------	827(vs)	820(vs)	824 (vs)	υ=C-H def out-of-plane 2H 1,4-disub-benzene
720 (vs)	719 (vs)	717 (vs)	718 (vs)	υ=C-Hpy out-of-plane bending vib for 4H
	434 (w)			δCOC out-of -plane
609 (s)	638 (s) 611 (s)	641 (s) 609 (s) 619 (s)	693 (s) 641 (s) 621(s)	δ=C-H ar in-plane

[a] References 6,7.

Table 3. IR wavenumbers (cm^{-1}) and assignments of the main bands of compounds **3**, **5**, **6** and **7** in KBr pellets

7	**3**	**5**	**6**	Assignment
Band position (cm^{-1})				
3140(vw) 3097 (vw)	3129(vw) 3098(w)	3139 (w)	3138 (w) 3101(vw)	υ=C-H pyr harmonic
3065 (w)		3049 (w) 3073 (w) 3042 (w)		υ =C-Har harmonic
1605 (s) conjugation	1593 (s) 1564 (w)	1609 (s) conjugation	1605 (w) conjugation	υ C=C ar stretch vib
1504 (vs) 1573 (w)	1502(vs) 1531 (w)	1511 (vs) 1550 (w)	1508(vs) 1574 (w)	υ C=C ar stretch vib
1478 (w) 1445 (w) 1424 (vw)	1413 (w)	1476(w)	1478(w) 1430 (s)	υ C=C ; υC-N pyr
1250	1249 (vs)	1251 (vs)	1251 (vs)	δ =C-H ar in-plane vib 4H for 1,4-disub benz
1015 (w) 1064 (s)	1017 (s) 1069(vs)	1067(vs) 1017 (s)	1017 (s) 1066(vs)	υ=C-H_α py in-plane deformation
826 (vs)	822(vs)	820(vs)	818(vs)	υ C-H def out-of-plane vib 2H 1,4-disub benz
1536 (s)			1538 (s)	υC=C th in-plane def
722 (vs)	727(vs)	730(vs)	724(vs)	υ=C-H py out-of-plane bending vib for 4H
536			535	C-S-C vib sym alkylth
869 (w) 794			852(w) 835(w)	υC-H vib out-of-plane alkylthiophene
609 (s)	610(s)	612 (s)	609(s)	δC-H ar in-plane

In the case of **1**, in addition to these bands, a wide band, located at 3426 cm^{-1}, was attributed to the υO-H stretching vibration, which confirmed the presence of a hydroxyl group in the phenyl ring, and therefore the formation of the title compound.

Several bands occurring in the 1609-1581 cm^{-1} and the 1574-1490 cm^{-1} regions can be attributed to the phenyl υC=C stretching vibrations. These bands were characterized by intensity changes and slight wavenumber shifts, depending apparently on the electron-donor or electron-acceptor effects of the phenyl ring substituents.

In the case of **6**, **7**, **5** and **4**, it only one band was found in the 1605-1581 cm^{-1} region, and two bands in the second region at around 1500 cm^{-1}, whereas, in contrast, for the remaining compounds, two bands were observed near 1600 cm^{-1}, and one band at around 1500 cm^{-1}. This significant difference of spectral behaviour is probably due to the considerable increase of conjugation occurring in the case of the former series of compounds, for which the *para*-substituents of the phenyl ring were heteroaromatic groups, namely pyrrole and thiophene.

The bands located in the 1498-1424 cm^{-1} region are due to the C=C pyrrolic ring stretching vibrations.[12] The very strong or strong bands appearing in the 1247-1261 cm^{-1} region for all *p*-substituted *N*-phenylpyrrole derivatives were assigned to the δ =C-H in- plane bending vibrations of four adjacent hydrogen atoms of a 1,4-disubstituted phenyl ring.

For characterization purposes, it is particularly interesting to interpret the bands occurring in the 1100-600 cm^{-1} region. Two relatively strong bands located at 1013-1017 and 1063-1071 cm^{-1} were attributed to the δC-H in-plane bending vibrations in the α-position of the *N*-substituted pyrrole rings. Also, the strong or very strong band which was observed at 720-730 cm^{-1} corresponded to the in-phase δ=CH out-of-plane bending vibration of four adjacent hydrogen atoms of the pyrrole ring, confirming the absence of substituents on the ring.

In addition, the presence of a very strong band located near 820 cm^{-1} in the spectra of all *p*-substituted *N*-phenyl-pyrroles, but not in that of the unsubstituted NPPY, revealed the existence of δ=C-H out-of-plane bending vibrations of two adjacent hydrogen atoms of a 1,4-disubstituted phenyl ring. This result confirmed the presence of two substituents in the *para* position of the *N*-phenyl group of all pyrrolic compounds under study. The wavenumber and intensity of this band also slightly changed with the nature of the *para*-substituent.

Moreover, in the case of **2**, we observed the υC-H harmonic stretching vibration of methyl group near 2960 and 2940 cm^{-1} and the δC-O-C vibration at around 434 cm^{-1}, which indicated the presence of a methoxy group.

In the specific cases of **6** and **7**, the presence of a band located near 1538 cm^{-1}, attributed to the υC=C stretching vibration of a thiophene ring, added to two bands appearing at around 852 and 835 cm^{-1}, assigned to the δ C-H out-of-plane bending vibration of the thiophene group, confirmed the formation of the title products.[14]

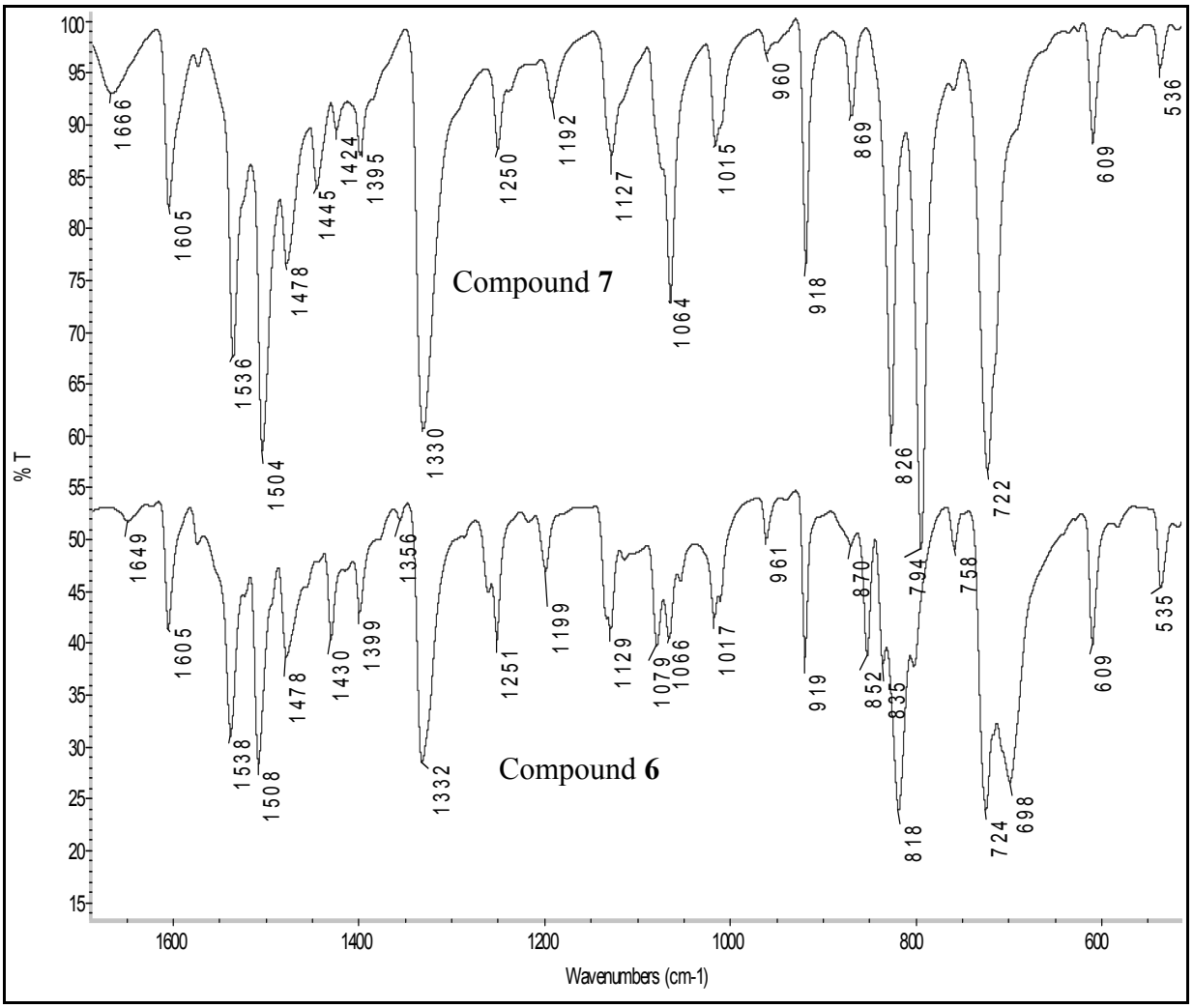


Figure 2. Partial FT-IR spectra of compounds **6** and **7** in KBr pellets.

(b) NMR spectral study

The ^{1}H and ^{13}C NMR spectra of the series of *p*-substituted *N*-phenylpyrroles under study were investigated for characterization purposes. The NMR data are reported in detail in the Experimental Section. They confirmed the identity of the synthesized compounds.

The ^{1}H chemical shift (δ) values are given in Table 4 for the different pyrrolic protons of the various synthesized compounds. The phenyl *para*-substituents were found to induce significant downfield shifts of the pyrrole α-protons of the NMR spectra. These chemical shift values decreased progressively in the order: **5** > **4** >**3** >**1** = **2**. The detailed analysis of the sequence of pyrrole α-proton chemical shifts confirmed the existence of electronic interactions, including important mesomeric effects, of the phenyl substituents with the pyrrole ring, similar to those observed in the case of the ^{1}H NMR spectra of *ortho*-substituted *N*-phenylpyrroles.[15]

Table 4. Effect of substituent on the ^{1}H NMR chemical shifts (δ) of the *p*-substituted *N*-phenylpyrroles[a]

Compound / δ (^{1}H)	$H_{2,5}$	$H_{3,4}$
2	6.99	6.31
1	6.99	6.32
3	7.04	6.33
4	7.08	6.35
6	7.11	6.36
5	7.14	6.38
7	-	6.39

[a]NMR spectra performed in $CDCl_3$. Chemical shift (δ) values expressed relative to tetramethylsilane (TMS).

Electrochemical properties

The electrochemical behaviour of 10^{-5} M **1, 2, 6, 4, 5, 7** and NPPY was studied by cyclic voltammetry (CV) in a 0.1 M tetrabutylammoniun hexafluorophosphate (Bu_4NPF_6) dry acetonitrile solution. The potential was linearly scanned between 0.0 and 1.5 V/SCE, at scan rates (*v*) ranging from 50 to 500 mV/s. The voltammograms obtained during the potentiodynamic electro-oxidation of **6** on a Pt electrode (Fig 3) were found to exhibit three anodic waves located at about 0.8, 1.1, and 1.3 V/SCE, attributed respectively to the thiophene, pyrrole and benzene oxidation.

We have summarized in Table 5 the oxidation potential (E_{ox}) values of the various compounds under study, with their attribution to the redox processes at the various oxidation sites (pyrrole, thiophene, benzene). As can be seen, a potential decrease of the E_{ox} values ranging from about 0.1 to 0.3 V/SCE was observed relative to the anodic peak of the unsubstituted NPPY (Table 5) when an electron-donating substituent (OMe, OH, thiophene) was grafted at the *para*-position of the phenyl group. The decrease of potential was correlated to the importance of the substituent electron-donating and conjugative effects. Therefore, our results can be interpreted in terms of an increase of conjugative effects of the *para* substituents on the phenyl ring, also producing an electronic interaction with the pyrrole ring. Indeed, as previously pointed out by Just *et al*.,[16] the conjugation interaction occurring between the *p*-substituted phenyl and the pyrrole groups might influence the electron density distribution on the pyrrole ring, modifying the oxidation potential.

Table 5. Substituent effect on the oxidation potential (E_{ox}, V/SCE) of the *p*-substituted *N*-phenylpyrroles under study

Compound	E_{ox} (V/SCE)
NPPY[a]	1.1 [a,b] reversible
	1.45 [b,c] irreversible
2	1.0[b] reversible
	1.3[c] irreversible
1	0.9[b] reversible
	1.3[c] irreversible
4	0.85[b] reversible
	1.25[c] irreversible
6	0.8[b] reversible
	1.1[c] irreversible
	1.3[d] irreversible
5	0.84[b] reversible
	1.20[c] irreversible
7	0.45 reversible

[a] From ref 6. [b] Pyrrole oxidation. [c] Benzene oxidation. [d] Thiophene oxidation.

In the case of **6**, the Fig 3 insert shows a linear variation of the intensity of the three anodic peaks located at 1.3, 1.1, and 0.8 V/SCE, (corresponding respectively to the thiophene, benzene and pyrrole ring oxidation) with the scan rate square root ($v^{1/2}$), which indicates that the redox process on all three oxidation sites of **6** is controlled by the electroactive monomer diffusion in solution.[17] The same behaviour was observed for the **2**, **7** and **4** species.

For the pyrrole end-capped compounds (**4**-**7**), the oxidation potential was a function of the nature of the aromatic bridge, as expected. Indeed, the E_{ox} value was found to decrease with the chain-length increase, due to the extension of the π-conjugated system. Thus, compounds **4** and **5** exhibited two oxidation waves, corresponding respectively to the oxidation of pyrrole and benzene rings. The first oxidation potential at 0.84-0.85 V/SCE, attributed to the peripheral pyrrole units, did not change significantly with the number of conjugated units incorporated between the pyrrole rings. In contrast, the increased conjugation length (from phenyl to biphenyl in **4** and **5**) resulted in a slight decrease of the second oxidation potential (from 1.25 to 1.20 V/SCE), corresponding to the oxidation process occurring on the aromatic bridge.

Also, the oligomer **7**, which had the longest conjugation length, presented a completely different electrochemical behaviour relative to the other compounds, with a voltammogram possessing only a wide, single reversible oxidation wave appearing at an E_{ox} value of about 0.45 V/SCE, attributed to the oxidation processes taking place in the whole pyrrole end-capped oligophenyl-thiophene π-conjugated core system (Fig 4).

A similar trend, namely the oxidation potential lowering with increasing conjugation length, has been also noted by several authors in the case of multi-triarylamine-substituted-carbazole end-capped oligothiophenes,[8a] N-7-azaindolyl oligothiophenes,[8e] and diphenylamino end-capped oligofluorenylthiophenes.[8f]

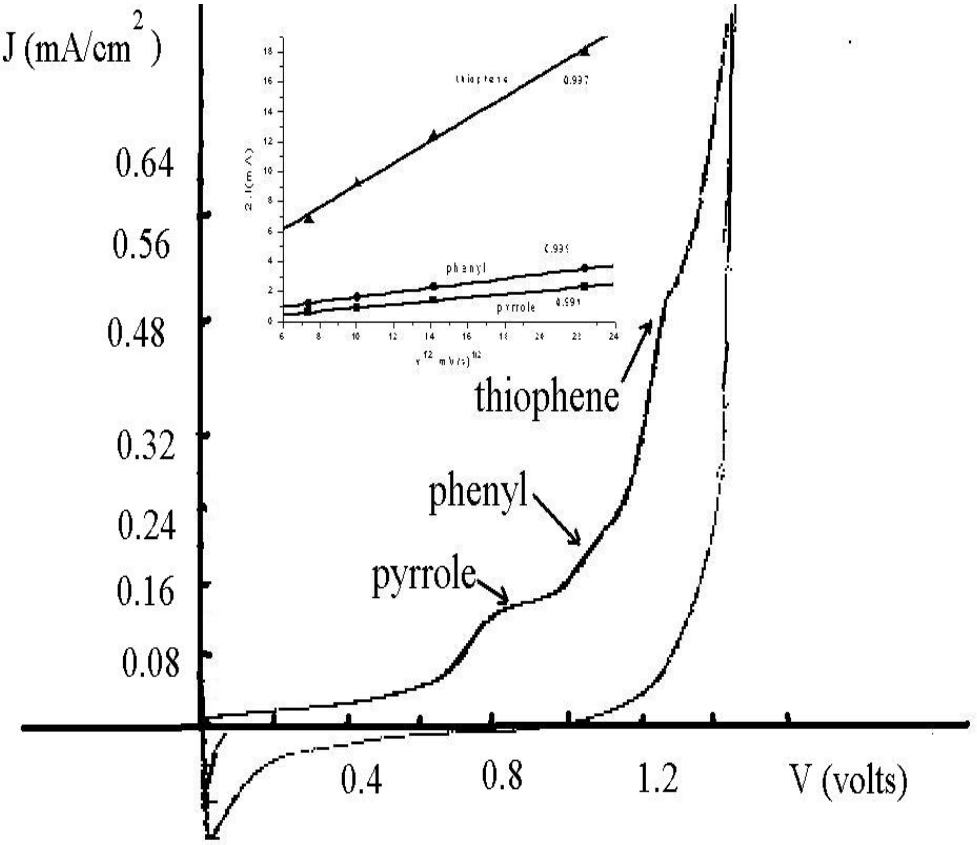


Figure 3. Cyclic voltammograms of a 10^{-5} M **6** + 0.1 M $TBAPF_6$ acetonitrile solution on a Pt electrode. Scan rate v = 100 mV/s. Potential range 0.0-1.5 V/SCE. Insert: Variation of the **6** anodic peak intensity with the scan rate square root.

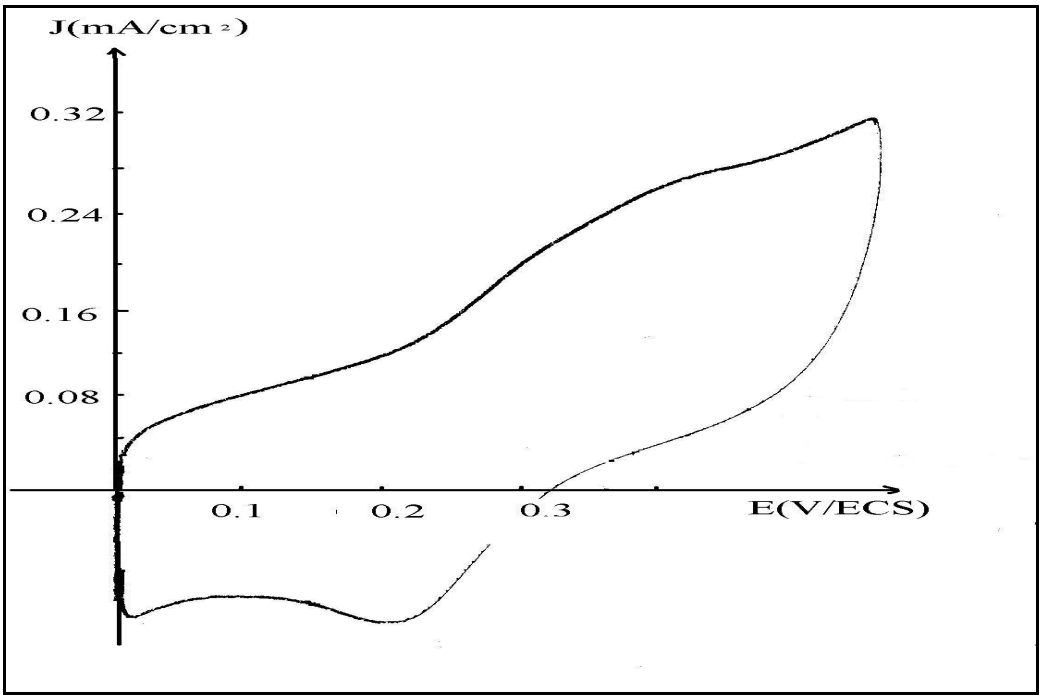


Figure 4. Cyclic voltammogram of a 10^{-5} M **7** + 0.1 M $TBAPF_6$ acetonitrile solution on a Pt electrode. Scan rate v = 100 mV/s.

UV-visible absorption spectral properties

The UV-visible absorption spectra of **1**, **2**, **4, 5, 6** and **7** were investigated at room temperature in several solvents of different polarities, such as cyclohexane, 1,4-dioxane, DMF, DMSO and/or ethanol (Table 6 and Figures 5 and 6). The electronic absorption spectral behaviour was rather complex and varied significantly with the type of *p*-substituted phenyl group located on the pyrrole ring.

The spectra of **1** and **2** presented a similar shape, with the presence of two overlapped absorption bands at around 246-268 nm (maximum) and 281-290 nm (shoulder) in polar solvents (DMSO, DMF) (Figure 5), whereas these bands were considerably blue shifted in non-polar cyclohexane at about 203-217 nm and 245-249 nm. The shortest-wavelength band, which possessed the highest molar absorption coefficients (log ε = 4.17-4.89), and the longest wavelength shoulder with smaller molar absorption coefficients (ε = 3.69-4.42) can be attributed, respectively, to the π→π* ^1B and $^1L_a/^1L_b$ electronic transitions, due to the conjugated *p*-substituted *N*-phenylpyrrole system. In agreement with this result, unsubstituted NPPY displayed an absorption maximum in the same spectral region (260 nm in 1,2-dichloroethane,[18] 252 nm in acetonitrile and 267 nm in DMF.[19])

In the case of the oligophenylene-type compounds, symmetrically end-capped with pyrrole groups, such as **4** and **5**, a single, wide band appeared at 277-278 nm for the former compound, and at 302-313 nm for the latter one, with large molar absorption coefficients (respectively, log ε = 4.26-5.14 and 4.82-4.93). This band was attributed to the π→π* $^1L_a/^1L_b$ electronic transition of the oligophenylene skeleton. As can be seen in Figure 5, the rather strong absorption

maximum red-shift ($\Delta\lambda_A$ = 24-26 nm), and the increase of ε_{max} which were observed upon increasing the phenylene chain length from one to two units can be attributed to the concomitant extension of the conjugated aromatic system. Relatively similar results were reported in the case of the optical properties of symmetrically diphenylamino-end-capped oligophenylenes possessing longer chains (four to six phenylene groups) than our compounds.[8c]

The asymmetrically and symmetrically end-capped pyrrole mono- and oligothiophene phenyl derivatives, **6** and **7**, displayed a wide absorption band with maximums located at 295-308 nm for the former compound and 395-396 nm for the latter one, and very large molar absorption coefficients (respectively, log ε = 4.12-4.91 and 5.03-5.36). This band was attributed to the $\pi\rightarrow\pi^*$ electronic transition of the entire conjugated backbone. Very considerable red-shifts ($\Delta\lambda_{max}$ = 87-101 nm, according to the solvent), were observed upon going from **6** to **7** (Figure 6). Obviously, the length of the thiophene chain plays an important role in this dramatic red-shift of the λ_{max} values, because of the resulting increase of the size of the conjugated system. Indeed, it is worthwhile to note that, similarly, smaller red-shifts of the absorption and photoluminescence bands were observed when the number of thiophene moieties increased in the case of diphenylamino end-capped oligofluorenylthiophenes,[8f] α,α'-diphenylamino-capped oligothiophenes[8d] and multi-triarylamine-substituted carbazole-oligothiophenes,[8a] and were attributed to an increased effective conjugation length. Moreover, a significant red-shift of the λ_{max} values of the absorption band of the pyrrole mono- and oligothiophenes under study was also observed, relative to that of the corresponding non-pyrrole-capped oligothiophene-phenyl derivatives. For example, **7** exhibited an absorption maximum at 395 nm in DMSO (Figure 6), whereas 2,2'-bithiophene, 5,5'-diphenyl, its non-pyrrole-capped homologue, displayed an absorption peak at 376 nm in a dilute chloroform solution.[8g] The red-shift value of $\Delta\lambda_{max} \sim 20$ nm, observed for the spectrum of **7** relative to that of its non-pyrrole-capped homologue, can be attributed to the incorporation of the strongly electron-donating pyrrole group at both ends, resulting either into its full conjugation with the polyene π system and π-electronic delocalization over the entire conjugated backbone of **7**, or into the behaviour of pyrrole as an electron-rich substituent, in the case of a perpendicular configuration of the pyrrole ring relative to the π system.

Table 6. Electronic absorption spectral properties of **1**[a], **2**[a], **4**[a], **5**[a], **6**[a] and **7**[a] in various solvents

Compound	Solvent[b]	λ_A, nm (log ε)[c]
	Cyclohexane	217 (4.89) 245 (4.42)
1	Ethanol	246 (4.43) 284 sh (3.89)
	DMF	267 (4.17) 289 sh (3.74)
	DMSO	260 (4.33) 290 sh (3.78)
	Cyclohexane	203 (4.53) 249 sh (4.39)
2	1,4-dioxane	246 (4.23)
	DMF	268 (4.83) 281 sh (4.75)
	DMSO	262 (4.44) 289 sh (3.85)
	Cyclohexane	212 (4.71) 302 (4.91)
6	DMF	308 (4.12) 347 sh (3.39)
	DMSO	295 (4.55) 350 sh (3.78)
	Cyclohexane	277 (4.26)
	1,4-dioxane	277 (5.14)
4	DMF	277 (4.55)
	DMSO	261 sh (4.67) 278 (4.81)
	DMF	303 (4.82)
5	DMSO	302 (4.93)
	DMF	308 (4.96) 395 (5.03)
7	DMSO	308 (4.23) 396 (5.64)

[a] The concentrations were, respectively, 10^{-5} M for **1**, **2** and **4**, 10^{-6} M for **5** and **6**, and 10^{-7} M for **7.**

[b] Solvents are listed in the order of increasing dielectric constant.

[c] Absorption band wavelengths (λ_A). The underlined wavelength values correspond to the maxima of the respective spectra. sh = shoulder. The logarithms of molar absorption coefficients, ε (in M^{-1} cm^{-1}) are given in parenthesis. Wavelength precision ± 1 nm.

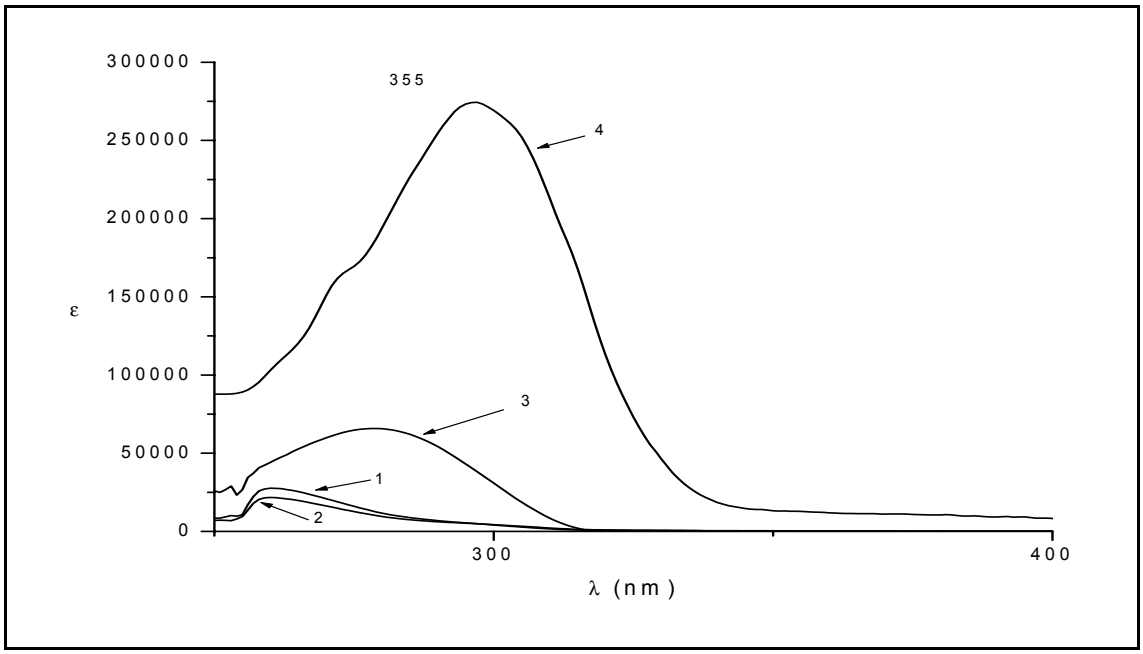


Figure 5. UV-vis absorption spectra of solutions of: 1) **2** (10^{-5} M), 2) **1** (10^{-5} M), 3) **4** (10^{-5} M), and 4) **5** (10^{-6} M) in dimethylsulfoxide (DMSO) at room temperature.

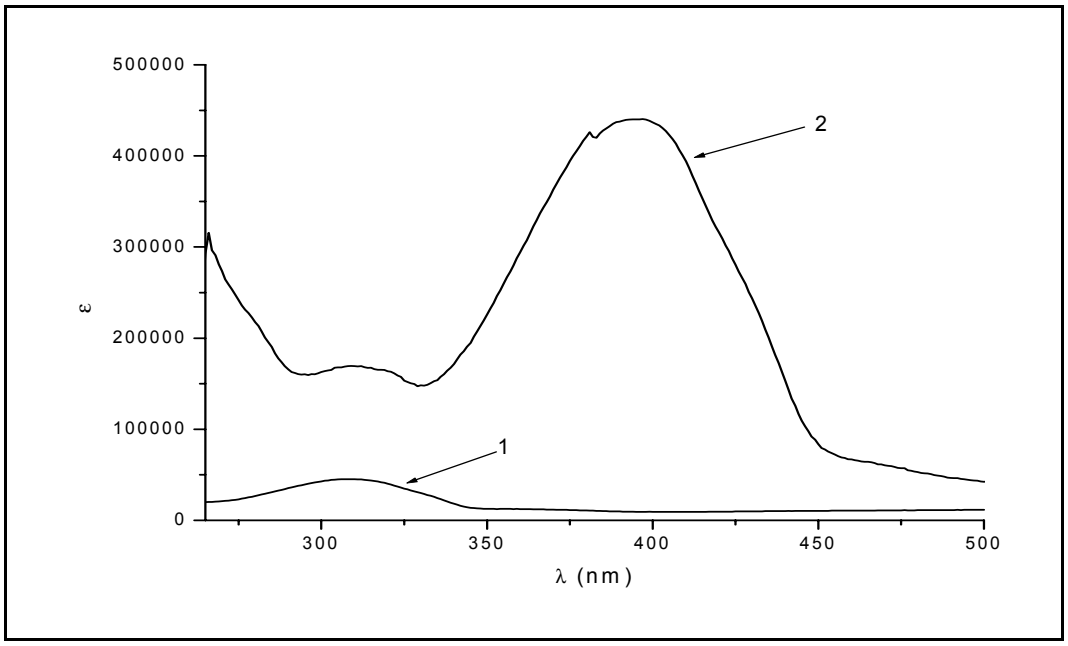


Figure 6. UV-vis absorption spectra of solutions of 1) **6** (10^{-6} M) and 2) **7** (10^{-7} M) in DMSO at room temperature.

Conclusions

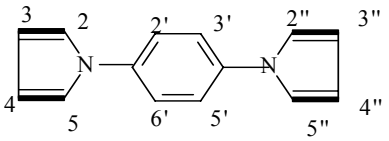
In this work, we have reported on the synthesis, characterisation and functional properties of a series of *p*-substituted *N*-phenylpyrroles by means of a modified Clauson-Kaas method, leading to yield new dipyrrole end-capped phenylene monomers and oligomers. We have shown the importance of the pyrrole moiety in its use as an active component in organic devices by studying the effects of substituents and of the chain length on the electrochemical and absorption spectral properties of these pyrrole end-capped compounds (**1**, **2**, **4**, **5**). To integrate the functional properties of the *p*-conjugated system and pyrrole as end-capped, we have also performed herein the first syntheses of new symmetrically and asymmetrically end-capped pyrrole mono- and oligothiophenes (**6**, **7**) as well as the investigation of the structure-functional property relationship. Concerning the electrochemical properties, we have demonstrated that, in the case of all pyrrole end-capped compounds under study (**4**, **5**, **6**, **7**), the oxidation potential was a function of the nature of the aromatic bridge, and that the E_{ox} value significantly decreased with the chain-length increase, due to the extension of the π-conjugated system. In addition, we have found for these same compounds rather strong absorption maximum red-shifts, and important increases of the ε_{max} values of the UV-visible spectra upon increasing the phenylene and/or thiophene chain length from one to two units, which was attributed to the concomitant extension of the conjugated aromatic system. The comparison of the electrochemical and spectral properties of these pyrrole end-capped phenylene compounds and end-capped pyrrole mono- and oligothiophenes to those of the corresponding N-carbazole end-capped oligothiophene-fluorenes, N-7-azaindolyl oligothiophenes, and diphenylamino end-capped oligophenylenes allowed us to conclude to the great interest of the pyrrole moiety for applications aimed to develop organic devices with useful electronic and photonic properties. Therefore, based on the present investigation, we feel that these end-capped pyrrole compounds should be very interesting candidates to prepare new polymer materials *via* their electropolymerization for use as active component in organic devices, possessing important electrochemical and optical characteristics.

Experimental Section

General Procedures. 2,5-dimethoxytetrahydrofuran (Aldrich), *p*-phenylenediamine (Avogado), acetic acid (Aldrich), benzidine (Aldrich), *p*-anisidine (Aldrich), *p*-aminophenol (Avogado), *p*-bromoaniline (Aldrich), petroleum ether (Prolabo), 1,4-dioxane (sds), cyclohexane (sds), ethanol (Prolabo), acetonitrile (Aldrich), dimethylsulfoxide (Arcos), dimethylformamide (ucb-Laboratoires Standa), tetrabutylammonium hexafluorophosphate (Avogado), and dichlorobis(triphenylphosphine)palladium(II) (Aldrich) were used as received. 2,5-bis(tributyl stannylthiophene and 5,5′-bis(trimethylstannyl)-2,2′-bithiophene were prepared by means of the Pelter method.[20]

Preparation of 1,1'-benzene-1,4-diylbis(1*H*-pyrrole) (4). The condensation reaction of 6.46 ml of 2,5-dimethoxytetrahydrofuran (0.050 mol) and 2.70 g of *p*-phenylenediamine (0.025 mol) was achieved in 100 ml of glacial acetic acid solution under reflux at 120 °C. A precipitate was immediately formed. Five minutes later, 50 ml of acetic acid were added, and then, ten minute afterwards, 1 g of carbon black was added to discolour the compound. After five minutes, heating was discontinued and the hot liquid was filtered through filter paper without suction. The filtrate was left standing for three hours at room temperature, whereby, the formation of light brown crystals was observed. The light brown crystals were filtered off, washed with acetic acid and ether and dried. Crystallization from acetic acid afforded 1.87 g (36 %) of **4**, mp 229 °C (literature: 228 °C[16]).

^{1}H NMR spectrum (200 MHz, $CDCl_3$):

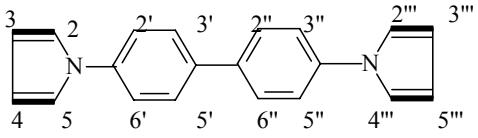


δ 7.08 (app t, J = 2.1 and 2.2 Hz, 2H, $H_{2,5}$), 6.4 (app t, J = 2.1 and 2.2 Hz, 2H, $H_{3,4}$), 7.4 (s, 4H, $H_{2',6',3',5'}$)

^{13}C NMR (200 MHz, $CDCl_3$) δ: 138.6 ($C_{1'}$, $C_{4'}$), 121.5 ($C_{2'}$, $C_{3'}$, $C_{5'}$, $C_{6'}$), 119.3 ($C_{2,5}$), 110.6 ($C_{3,4}$). IR spectrum (KBr): 3125; 3109, 3073; 3047; 1581 ;1526; 1472; 1482; 1433; 1388; 714; 1068; 1023; 641; 609; 619; 543. For $C_{14}H_{12}N_2$ [mass spectrum calc: 208.263; found: 209 (100), 179 (20), 177 (3), 153 (11), 141 (9.09), 116 (25), 105 (25), 89 (24), 76 (23), 63 (20), 57 (15), 51 (15), 39 (48), 32 (60)] calc.: C 80.74, H 5.81, N 13.45% found: C 80.17, H 5.80, N 13.21%

Preparation of 1,1'-biphenyl-4,4'-diylbis(1*H*-pyrrole) (5). By using the same procedure as for the synthesis of the previous compound, the reaction mixture of 1.4 ml of 2,5-dimethoxytetrahydrofuran (0.010 mol), 4.60 g of benzidine (0.005 mol) and 100 ml of glacial acetic acid provided 1.1 g of brown crystals of **5** (71%), mp > 260 °C.

^{1}H NMR spectrum (200 MHz, $CDCl_3$):



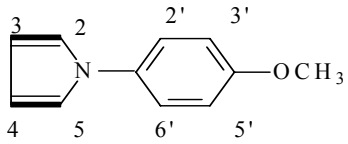
δ 7.14 (app t, J = 2.1 and 2.2 Hz, 2H, $H_{2,5}$), 6.38 (app t, J = 2.0 and 2.1 Hz, 2H, $H_{3,4}$), 7.48 (d, J = 8.5 Hz, 2H, $H_{2',6'}$), 7.68 (d, J = 8.4 Hz, 8H, $H_{3',5'}$).

IR spectrum (KBr,): 3139; 3049; 3073; 3042; 1609; 1511; 1476;1553; 1408; 820; 1067; 730; 612; 516. For $C_{20}H_{16}N_2$ [mass spectrum calc: 284.360] calc.: C 84.48, H 5.67, N 9.85% found: C 83.17, H 5.43, N 9.52%

Preparation of 1-(4-methoxyphenyl)-1*H*-pyrrole (2). A mixture of 6.46 ml of 2,5-dimethoxytetrahydrofuran (0.050 mol), 6.07 g of *p*-anisidine (0.025 mol) and glacial acetic acid

(100 ml) was refluxed at 120 °C for 30 min. Five minutes after the reflux began, 50 ml of glacial acetic acid were added, and ten minutes later 1g of carbon black was added. The resulting hot solution was filtered through paper without suction and left at room temperature for 4 h. There was no crystal formation. The solvent was removed *in vacuum* and the residue was dissolved in 100 ml of petroleum ether. The mixture was filtered and the solvent was evaporated under reduced pressure; the resulting residue was dissolved in 100 ml of petroleum ether and washed with 200 ml of a 1 M sodium hydroxide solution. The mixture was decanted, and the yellow organic solution was isolated, dried with anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The pure, yellow title compound (5.6 g) was obtained (65%), mp 112 °C (literature: 104-108°C[21]).

^{1}H NMR spectrum (200 MHz, $CDCl_3$):

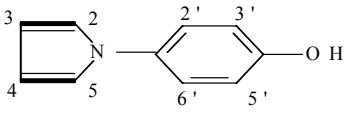


δ (s, 3.83, 3H, CH_3O); 6.99 (app t, *J*= 2.1 and 1.9 Hz, 2 H, $H_{2,5}$); 6.31 (app t, *J*= 2.2 and 2.1 Hz, 2H, $H_{3,4}$), 6.96 (d, *J*= 8.4 Hz, 4H, $H_{2',6',3',5'}$) 7.33 (d, *J*= 8.9 Hz, 2H, $H_{3',5'}$).

^{13}C NMR spectrum (200 MHz, $CDCl_3$) δ: 157.6 ($C_{4'}$), 122.2 ($C_{2'}$, $C_{6'}$), 119.7 ($C_{2,5}$), 114.6 ($C_{3'}$, $C_{5'}$), 109.8 ($C_{3,4}$), 55.5 (CH_3O). IR spectrum (KBr): 3142; 3014; 2962; 2936; 1591; 1525; 1563; 1458; 1442; 1402; 870; 827; 804; 1071; 1030; 721; 610. For $C_{11}H_{11}NO$ [mass spectrum calc: m: 173.214; found: 173 (100), 158 (85), 130 (50), 116 (6), 103 (29), 87 (14), 77 (52), 63 (29), 57 (18), 51 (34), 39 (31), 32 (54)] calc.: C 76.28, H 6.40, N 8.09, O, 9.24% found: C 75.17, H 6.16, N 8.11, O 9.81%

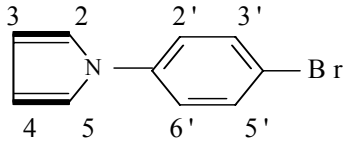
Preparation of 4-(1*H*-pyrrol-1-yl)phenol (1). A mixture of 6.46 ml of 2,5-dimethoxytetrahydrofuran and 5.45 g of *p*-aminophenol, equimolar (0.050 mol) solution in 100 ml of glacial acetic acid, was refluxed at 120 °C for 30 min. Five minutes after the reflux began, 50 ml of glacial acid acetic were added, and ten minutes later 1 g of carbon black was added. The resulting hot solution was filtered through filter paper without suction, and left at room temperature for 4 h. There was no crystal formation. The solvent was removed *in vacuum* and the residue was dissolved in 100 ml of petroleum ether. The mixture was filtered and the solvent was evaporated under reduced pressure; the resulting residue was dissolved in 100 ml of petroleum ether and washed with 200 ml of a 1 M sodium hydroxide solution. The mixture was decanted, and the red organic solution was isolated, dried with anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. We obtained 4.60 g of red crystals of **1** (55 %), mp 120 °C.

^{1}H NMR spectrum (200 MHz, $CDCl_3$):



δ (s, 5.2, 1H OH); 6.99 (app t, *J*= 2.2 Hz, 2 H, $H_{2,5}$); 6.32 (app t, *J*= 2.2 Hz, 2H, $H_{3,4}$); 6.90 (d, *J*= 8.9 Hz, 2H, $H_{2',6'}$); 7.28 (d, *J*= 8.8 Hz, 2H, $H_{3',5'}$).
^{13}C NMR spectrum (200 MHz, $CDCl_3$) δ: 153.6 ($C_{4'}$), 134.7 ($C_{1'}$), 122.4 ($C_{2'}$, $C_{6'}$), 119.7 ($C_{2,5}$), 116.1 ($C_{3'}$, $C_{5'}$), 109.9 ($C_{3,4}$). IR spectrum (KBr): 3426; 3143; 3100; 3039; 1604; 1562; 1534; 1521; 1478; 1413; 1070; 1014; 824; 718; 693; 641; 621. For $C_{10}H_9NO$ [mass spectrum calc: 159.187; found 159 (100), 131 (37), 103 (14), 77 (12), 51 (13)] calc.: C 75.45, H 5.70, N 8.80, O 10.05% found: C 74.12, H 5.26, N 8.86, O 11.10%

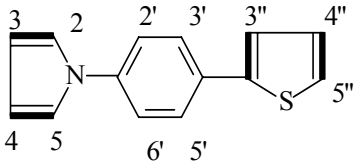
Preparation of 1-(4-bromophenyl)-1*H*-pyrrole (3). Using the same procedure than above-described in the case of **2** and **1**, the condensation of 6.46 ml of 2,5-dimethoxytetrahydrofuran (0.050 mol) and 8.82 g of *p*-bromoaniline (0.050 mol) led to pure, dark-brown crystals of 9.0 g of 1-(4-bromophenyl)-1*H*-pyrrole (81%), mp 107° (literature: 95-96 °C[21]).
^{1}H NMR spectrum (200 MHz, $CDCl_3$):



δ 7.04 (app t, *J*= 2.1 and 1.9 Hz, 2 H, $H_{2,5}$), 6.33 (app t, *J*= 2.2 Hz, 2H, $H_{3,4}$), 7.29 (d, *J*= 8.9 Hz, 2H, $H_{2',6'}$), 7.55 (d, *J*= 8.9 Hz, 2H, $H_{3',5'}$).
^{13}C NMR spectrum (200 MHz, $CDCl_3$) δ: 139.8 ($C_{1'}$), 132.6 ($C_{3'}$, $C_{5'}$), 121.9 ($C_{2'}$, $C_{6'}$), 119.2 ($C_{2,5}$), 118.9 ($C_{4'}$), 111 ($C_{3,4}$). IR spectrum (KBr): 3129; 3098; 1593; 1500; 1450; 1371; 1325; 822; 1069; 1017; 919; 729; 663; 610; 512. For $C_{10}H_8BrN$ [mass spectrum calc.: 222.98; found: 223 (100), 221 (99), 142 (31), 115 (81)] calc.: C 54.08, H 3.63, Br 35.98, N 6.31% found: C 53.90, H 3.59, Br 34.79, N 6.39%

Preparation of 1-[4-(thiophen-2-yl)phenyl]-1*H*-pyrrole (6). 4.11 g of 2,5-bis(tributyl stannyl)thiophene (0.0062 mol) were added, under argon atmosphere, to a solution of 2.77 g of 1-(4-bromophenyl)-1*H*-pyrrole (0.0124 mol) in distilled DMF (100 ml) in a three-neck, round bottomed flack containing 5% of dichlorobis(triphenylphosphine)palladium(II) as catalyst. The reaction mixture was stirred for 15 minutes at room temperature under nitrogen atmosphere, and then heated at 80°C overnight. The solvent was evaporated under vacuum; the residue was twice washed with 100 ml of petroleum ether, and then subjected to purification by column chromatography [30-cm column, silica gel, elution first with petroleum ether, then with a petroleum ether-chloroform (1/2 v/v) mixture]. It afforded 0.50 g of **6** (36%), mp 204 °C.

^{1}H NMR spectrum (200 MHz, $CDCl_3$):

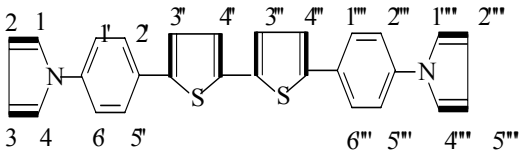


δ 6.36 (app t, *J*= 2.2 Hz, 2H, $H_{3,4}$), 7.10 (app t, *J*= 2.2 Hz, 2H, $H_{2,5}$) 7.42 (d, *J*= 8.7 Hz, 2H, $H_{2',6'}$), 7.68 (d, *J*= 8.8 Hz, 2H, $H_{3',5'}$). 7.1-7.35 (m, 3H, $H_{3",4",5"'}$)

IR spectrum (KBr): 3138; 3101; 3057; 3021; 1605; 1574; 1538; 1508; 1478; 1430; 1066; 1017; 852; 835; 818; 758; 724; 698; 610. For $C_{14}H_{11}NS$ [mass spectrum calc: 225.314; found 225 (100), 198 (40), 181 (15), 172 (23), 166 (45), 152 (25), 139 (11), 115 (59), 99 (64), 89 (339), 63 (24), 51 (43)] calc.: C 74.63, H 4.93, N 6.22, S 14.22% found: C 73.47, H 4.71, N 5.80, S 15.02%.

Preparation of 1,1'-(bithiophen-5,5''-diyldibenzene-4,1-diyl)bis(1*H*-pyrrole) (7). 4.71 g of 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (0.0096 mol) were added, under argon atmosphere, to a solution of 6.80 g of 1-(4-bromophenyl)-1*H*-pyrrole (0.031 mol) in DMF (100 ml) in a three-neck, round-bottomed flask containing 5% of dichlorobis(triphenylphosphine) palladium(II) as catalyst. The reaction mixture was stirred for 15 minutes at room temperature under nitrogen atmosphere, and then heated at 90 °C overnight. The solvent was evaporated under vacuum and the residue was washed with acetone (2 x 100 ml) and filtered. Pure, red-yellow powder of 3.01 g of **7** were obtained (61%), mp > 260 °C.

^{1}H NMR spectrum (200 MHz, $CDCl_3$):



δ 6.39 (app t, *J*= 2.1 and 2.2 Hz, 2H, $H_{3,4}$), 7.48 (d, *J*= 8.7 Hz, 2H, $H_{2',6'}$), 7.71 (d, *J*= 8.4 Hz, 2H, $H_{3',5'}$). 7.08-7.35 (m, 4H).

IR spectrum (KBr): 3138; 3101; 3066; 3032; 1605; 1574; 1536; 1504; 1478; 1446; 1425; 1399; 1331; 1064; 1016; 869; 827; 818; 759; 723; 698; 609. For $C_{28}H_{20}N_2S_2$ [mass spectrum calc: 448.612; found: 450 (14), 449 (32), 448 (100), 383 (5), 281 (2), 224 (15), 207.00 (5), 186 (3), 97 (3), 83 (3.00) 73 (3), 69 (4), 60 (6) 55 (6)] calc.: C 74.97, H 4.49, N 6.24, S 14.30% found: C 73.53, H 4.09, N 5.33, S 13.29%

Electrochemical measurements

Electrochemical measurements were carried out in a one-compartment, three-electrode glass cell at room temperature with an EG&G Parr model 362 potentiostat/galvanostat, the electrochemical

curves being recorded on a Kipp & Zonen BD90 x-y recorder. The working electrode was a platinum disk (disk area 12.56 10^{-2} cm^2) and the counter-electrode was an iron stainless grid. The potentials were measured relative to saturated calomel electrode (SCE). 0.1 M tetrabutylammonium hexafluorophosphate dry acetonitrile solutions were used for all electrochemical measurements.

Spectral measurements

All infrared (IR) absorption spectra were recorded on a Magna-IR 860 FT-IR spectrometer (Nicolet Instrument Corp. Madison, WI), at a 2 cm^{-1} spectral resolution. The transmittance absorption spectra of the monomers were carried out in KBr pellets, using a standard DTGS detector, by collecting 50 scan. All ^1H NMR spectra were obtained in $CDCl_3$ using a 200 MHz Bruker spectrometer. UV-vis absorption spectra were performed in various organic solvents with a Lambda 2 Perkin Elmer UV-vis spectrometer. The molecular weights and the mass spectra of monomers were determined with a Finnigan MAT ITD 800 mass spectrometer with electronic impact (70 eV). All spectral measurements were performed at room temperature.

Acknowledgements

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