Structure-reactivity relationships in bithiophenic precursors based on the 3-phenoxythiophene building block

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3-Toluoxythiophene and bithiophenes diversely substituted by toluoxy groups have been synthesized. Theoretical, spectroscopic and electrochemical studies show that the number and position of the phenoxy groups exert a strong influence on the geometry of the ground state and cation radical and determine the reactivity of the latter and hence its aptitude for electropolymerization.

Introduction

Organic materials derived from thiophene-based linear π -conjugated systems are intensively investigated as electrode materials¹ or organic semi-conductors for the realization of devices such as field effect transistors,² light-emitting diodes³ and solar cells.⁴

The development of these various fields creates a continuous demand for the synthesis of new functional π -conjugated structures with tailored chemical, optical or electrical properties. This situation, in turn, generates a need for new synthetic routes, new methods of functionalization and new building blocks.

Among the large number of substituents which have been used for the derivatization of polythiophene (PT),⁵ the phenyl group appears particularly interesting as it represents an interesting platform for further functionalization.^{6–12} Polythiophenes based on monomer containing phenyl groups have been investigated at an early stage of the development of this class of polymers.⁶ In 1990 we described a series of PTs containing substituted phenyl rings, electronically and sterically disconnected from the conjugated system.⁷

In an attempt to develop new analogues of 3,4-ethylenedioxythiophene(EDOT) which could be substituted at sp² carbons we have recently synthesized 3,4-phenylenedioxythiophene (PheDOT) and the corresponding polymers.¹² However, experimental and theoretical results have shown that because of the delocalization of the HOMO over the whole molecule, the introduction of the phenyl ring to form a dioxin-like structure results in a strong stabilization and hence loss of reactivity of the corresponding cation radical.¹²

In a continuation of these investigations we now report the synthesis of precursors of polythiophenes derivatized by phenoxy groups. In addition to the release of the steric constraint associated with the direct connection of a phenyl ring at the 3-position of thiophene, such compounds are expected to contribute to a better understanding of the electronic effects associated with the introduction of phenoxy substituents on the electronic properties and reactivity of the thiophene ring.

3-Toluoxythiophene has already been described by Hellberg *et al.* in a short conference paper, in which it was reported as poorly reactive.¹³ Consequently, we have also synthesized bithiophenes 2, 3 and 4 (Scheme 1) in which the number and position of the phenoxy groups has been varied, and we report here a comparative analysis of their reactivity using cyclic voltammetry and theoretical calculations.

Results and discussion

3-toluoxythiophene 1 was obtained by condensation of p-cresol and 3-bromothiophene in the presence of copper and potassium carbonate.¹⁴ Bromination of 1 with one equivalent of NBS in DMF at 0 °C gave selectively 3-(ptolyloxy)-2-bromothiophene 5 in 77% yield. Treatment of 1 with two equivalents of bromine in a boiling mixture of chloroform and acetic acid gave the dibromo compound 6 in 70% yield. Treatment of 6 with one equivalent of butyllithium at low temperature followed by hydrolysis gave 80% of a 1 : 1 mixture of the 2-bromo and 5-bromo (7) compounds which were separated by chromatography. Oxidative coupling of 1 by successive addition of n-BuLi and CuCl₂ led to bithiophene 3 isolated in 10% yield after recrystallisation in petroleum ether. A Stille coupling of 2-tributylstannylthiophene with compound 5 led to the monosubstituted bithiophene 2 in 65% yield. A symmetrical coupling of the *in situ* generated stannyl derivative of compound 7 in the presence of Pd^{0} (Pd(OAc)₂) and $CuCl_2$ gave bithiophene 4 in 20% yield. All new compounds were satisfactorily characterized by NMR and mass spectrometry.

X-Ray diffraction[†]

The crystallographic structure of compound $\mathbf{3}$ has been analyzed on a single crystal. This derivative crystallizes in

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[†] Orange prism (0.62 × 0.33 × 0.19 mm³), C₁₁H₉O₁S₁, M_r = 189.24, orthorhombic, space group *Pbcn*, *a* = 19.056(2) Å, *b* = 7.536(1) Å, *c* = 13.524(1) Å, *V* = 1942.1(4) Å³, *Z* = 8, *T* = 293 K, ρ_{calc} = 1.294 g cm⁻³, μ (Mo K α) = 0.287 mm⁻¹, *F*(000) = 792, θ_{min} = 2.91°, θ_{max} = 25.81°, 10599 reflections collected, 1859 unique (R_{int} = 0.0741), restraints/ parameters = 0/154, *R*1 = 0.0461 and w*R*2 = 0.1163 using 1139 reflections with *I* > 2 σ (*I*), *R*1 = 0.0776 and w*R*2 = 0.1290 using all data, GOF = 0.971, -0.185< $\delta \rho < 0.297$ e Å⁻³. CCDC reference number 263331. See http://dx.doi.org/10.1039/b502164b for crystal-lographic data in CIF or other electronic format.





the orthorhombic *Pbcn* space group and the formula of the structure corresponds to half a molecule. As shown in Fig. 1, the bithiophene system adopts a fully planar geometry with the



Fig. 1 ORTEP view of bithiophene 3

two thiophene units in an *anti* conformation. The non-bonded S–O distances (~2.90 Å), are considerably shorter than the sum of the van der Waals radii of sulfur and oxygen (3.35 Å), thus confirming the occurrence of non-covalent S–O intramolecular interactions which stabilize the planar conformation of bithiophene, as observed for many EDOT-based π -conjugated systems.¹⁵ Due to steric interactions between periplanar hydrogens, the phenyl rings are not coplanar with the bithiophene system and form a dihedral angle of 65° with the latter.

UV-visible spectroscopy

Fig. 2 shows the UV–vis absorption spectra of compounds 2-4 in methylene chloride. The spectrum of compound 4 shows a broad structureless absorption band consistent with a high degree of rotational freedom around the inter-ring single bond. The spectrum of compound 2 exhibits a discernible vibronic fine structure with shoulders around 300 and 330 nm which suggest a more rigid structure due to intramolecular S–O interactions. This trend becomes more apparent in the spectrum of compound 3 which shows a better resolved fine structure as expected for stronger S–O interactions.



Fig. 2 UV-vis absorption spectra in CH_2Cl_2 . Long dashed: 4, short dashed: 2, solid line: 3.

Compound 4 shows the most red shifted λ_{max} at 323 nm suggesting a more delocalized π -electron system than for compounds 2 and 3 which have practically the same λ_{max} at 311 and 312 nm.

Electrochemistry

The electrochemical properties of compounds 1–4 have been analyzed by cyclic voltammetry in acetonitrile using Bu_4NPF_6 as electrolyte. The anodic peak potentials (E_{pa}) corresponding to oxidation to the corresponding cation radicals are listed in Table 1. As expected bithiophenes 2–4 have E_{pa} values lower than compound 1, and compounds 3 and 4 with two phenoxy substituents show less positive E_{pa} values than the monosubstituted bithiophene 2. The data in Table 1 also show that compound 3, with phenoxy groups at the inner β -positions of the bithiophene structure, presents a lower E_{pa} value than compound 4.

Electro-oxidation of compound 1 leads to the appearance of a blue coloration on the anode surface but no polymer deposition occurs. A similar behaviour is observed for compounds 2 and 3 although the latter compound presents the lowest oxidation potential of the series.

Application of repetitive potential scans to a 0.05 M solution of compound **4** in methylene chloride leads to a typical potentiodynamic electropolymerization curve with the progressive development of a broad redox system corresponding to the doping/undoping process of the growing polymer in the 0.50 to 1.00 V region (Fig. 3).

Table 1 Calculated HOMO and LUMO energy level and anodicpeak potentials^b for compounds 1, 3 and 4^a

	$E_{\rm pa}/{\rm V}$	HOMO/eV	LUMO/eV
1	1.83	-5.78	-0.37
2	1.22		
3	1.02	-5.26	-1.10
4	1.19	-5.65	-1.42
a Cal			

^a Calculated on 3-phenoxythiophene instead of 3-toluoxythiophene. ^b Ref Ag.AgCl, in 0.10 M Bu₄NPF₆/CH₂Cl₂.



Fig. 3 Top: potentiodynamic electropolymerization of **4**, 0.05 M in 0.1 M Bu_4NPF_6/CH_2Cl_2 scan rate 100 mV s⁻¹. Bottom: CV of poly(**4**) in 0.10 M Bu_4NPF_6/CH_3CN , scan rate 100 mV s⁻¹.

The CV of the resulting polymer recorded in a monomerfree electrolytic medium exhibits a broad redox system with a main anodic peak at 0.70 V followed by a shoulder around 1.00 V. The *ca.* 300 mV negative shift of the potential of the main anodic peak compared to poly(bithiophene)⁵ reflects the electron-releasing effect of the phenoxy group. The polymer film shows a good stability and no change in electroactivity (as expressed by the amount of charge reversibly exchanged) was observed after 100 cycles at 100 mV s⁻¹ in either acetonitrile or water.

Note that these results agree well with the observations of previous works of Heinze and coworkers on oligothiophenes substituted by methoxy and methylsulfanyl groups.^{16–18}

Theoretical studies

In order to elucidate the behaviour of the oxidized species, we have undertaken theoretical calculations. *Ab initio* quantum calculations have been performed on compounds 1–4 with the Gaussian 98^{19} package of programs at a hybrid density functional theory²⁰ (DFT) level. Calculations have been done using the restricted B3LYP/6-31G* function for neutral states and at the U-B3LYP/6-31G* level for the cation radical states.^{21,22}

HOMO, LUMO levels of neutral molecules 1, 3 and 4 are collected in Table 1. Although compound 4 presents a torsion of 32.5° between the thiophene cycles, the move of the phenoxy groups from outer to inner position leads to a planarization of the conjugated systems for derivative 3 which shows a dihedral angle of only 4.8° . In addition to the X-ray structure for the solid state and UV–vis spectroscopy for the diluted solution, calculations for the gas phase show again the key role of the oxygen atoms at the inner position for stabilizing the planar conformation of bithiophenic system by S…O intramolecular interactions. Consequently, the HOMO level of derivative 3 is higher than the one of 4. These results are well correlated with



the electrochemical properties which show that compound **3** is easier to oxidize.

The oxidation to radical cation is accompanied by structural change. For both compounds, the cation radical adopts a planar geometry with the largest SOMO coefficients located on the carbons of the bithiophene system forming the pathway linking the two oxygen atoms. The analysis of the geometries of radical cations shows that for the two radical cations, as expected for a pseudo-quinoid structure, the central C-C bond is shortened. On the other hand, the C-O bonds lengths linking thiophene cycles with phenoxy groups are also shortened indicating a localization of the positive charge on an oxygen atom. Such structures are consistent with an important contribution of the mesomeric forms A and B (Scheme 2) for radical cations 3 and 4. The cation radical of compound 3 possess a maximum density of unpaired electrons on the internal part of the molecule which does not favour the coupling reaction. On the contrary, the outer localization of toluoxy groups of 4^+ allows delocalization of unpaired electrons on the whole bithiophene skeleton, including the terminal position which favours polymerization.

Conclusion

To summarize, 3-toluoxythiophene and three bithiophenes diversely substituted by toluoxy groups have been synthesized. The crystal structure of one of the bithiophenes reveals short non-bonded sulfur-oxygen distances indicating that the intra-molecular non-covalent interactions, already observed in many conjugated systems containing 3,4-ethylenedioxythiophene¹⁵ or methoxythiophene units²³, also occur in some 3-phenoxy-thiophene-based compounds.

Ab initio quantum calculations performed with a hybrid density functional theory have shown that the introduction of phenoxy groups markedly affects the geometry of the ground state and the energy level of the frontier orbitals. Futhermore,

theoretical calculations show that the number and position of the phenoxy groups exert a strong influence on the reactivity of the cation radical. Thus, whereas the introduction of phenoxy groups at the inner β -positions of the bithiophene structure suppresses the aptitude of the cation radical to polymerize, their grafting at the outer β -positions of bithiophene has the reverse effect by increasing the SOMO coefficient at the 2,5' coupling positions, in agreement with experimental results.

Experimental

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE DRX 500 spectrometer operating at 500.13 and 125.7 MHz; δ are given in ppm (relative to TMS) and coupling constants (J) in Hz. Mass spectra were recorded under EI or FAB mode on a VG-Autospec mass spectrometer, under MALDI-TOF mode on a MALDI-TOF-MS BIFLEX III Bruker Daltonics spectrometer or under positive electrospray (ESI) on a JMS-700 JEOL mass spectrometer of reversed geometry. UV-visible optical data were recorded with a PerkinElmer lambda 19 spectrophotometer. IR spectra were recorded on a PerkinElmer model 841 spectrophotometer, samples being embedded in KBr discs or thin films between NaCl plates. Melting points were obtained from a Reichert-Jung Thermovar hot-stage microscope apparatus and are uncorrected. Column chromatography purifications were carried out on Merck silica gel Si 60 (40-63 µm).

Electrochemical experiments were performed with a EG&G 273 potentiostat in a standard three-electrode cell using an Ag/AgCl reference electrode. The solutions were degassed by argon bubbling and experiments were carried under an argon blanket. The working electrode was a 1 mm Pt disk sealed in glass. Tetrabutylammonium hexafluorophosphate (Fluka puriss) was used as received.

3-(p-Tolyloxy)2-bromothiophene 5

3-(*p*-tolyloxy)thiophene (1) (1 g, 5.3 mmol) was dissolved in 20 mL of dry DMF under a nitrogen atmosphere at 0 °C, in the dark. Then, one equivalent of freshly recrystallized NBS dissolved in 20 mL of DMF was added dropwise. After 2 h stirring at 0 °C, and 2 h at room temperature, 150 mL of water was added and the mixture was extracted with diethyl ether. The organic phase was washed with water and dried over MgSO₄. After evaporation of the solvent, purification by column chromatography (silica gel, petroleum ether) gave 77% of compound **5** as a colorless oil. ¹H NMR (CDCl₃): 7.23 (d, 1H, ³J = 5.88); 7.11 (d, 2H, ³J = 8.54); 6.87 (d, 2H, ³J = 8.54); 6.66 (d, 1H, ³J = 5.87); 2.32 (3H). ¹³C NMR (CDCl₃): 155.3; 151.3; 132.6; 130.1; 124.8; 121.0; 116.7; 97.7; 20.6.

3-(p-Tolyloxy)-2,5-dibromothiophene 6

3-(*p*-Tolyloxy)thiophene (1) (0.5 g, 2.6 mmol) was dissolved in a mixture of 30 mL of chloroform and 30 mL of acetic acid. Then, 2.2 equivalent of bromine dissolved in chloroform was added dropwise and the mixture was refluxed overnight. The mixture was poured into 300 mL of ethyl acetate, the organic phase was washed with water and aqueous NaHCO₃ to neutrality and dried on MgSO₄. After evaporation of the solvent column chromatography (SiO₂, petroleum ether) gave 70% of compound **5** as a colorless oil. ¹H NMR (CDCl₃): 7.12 (d, 2H, ³*J* = 8.37); 6.89 (s, 1H); 6.88 (d, 2H, ³*J* = 8.37); 6.66 (s, 1H); 2.33 (s, 3H), together with 10% of 3-(4-(bromomethyl)-phenoxy)-2,5-dibromothiophene as a white solid, 78 °C, ¹H NMR (CDCl₃) 7.35 (d, 2H, ³*J* = 8.64); 6.89 (s, 1H); 6.93 (d, 2H, ³*J* = 8.64); 6.72 (s, 1H); 4.49 (s, 2H), mp 78 °C

4-(pTolyloxy)-2-bromothiophene 7

Dibromo compound **6** (0.6 g, 1.7 mmol) was dissolved in 30 mL of dry diethyl ether under a nitrogen atmosphere and cooled to -78 °C. After addition of one equivalent of *n*-BuLi the mixture was stirred for 1 h at -78 °C. After addition of a mixture of water/methanol and a return to room temperature, the organic phase was washed with water and dried on MgSO₄. After evaporation of the solvent and chromatography (silica gel, petroleum ether) the target compound was isolated in 40% yield together with 40% of 3-(*p*-tolyloxy)bromothiophene. ¹H NMR (CDCl₃): 7.14 (d, 2H, ³J = 8.33); 6.95 (d, 2H, ³J = 8.47); 6.83 (d, 1H, ⁴J = 1.84); 6.40 (d, 1H, ⁴J = 1.78); 2.34 (s, 3H). ¹³C NMR (CDCl₃): 154.8; 154.0; 133.4; 130.2; 123.3; 118.3; 111.8; 106.9; 20.7.

3-(p-Tolyloxy)-2-(thiophen-2-yl)thiophene 2

Compound 5 (0.6 g, 2.2 mmol) was dissolved in dry toluene and the solution was carefully degassed with dry nitrogen. After addition of 2-tributylstannylthiophene (1.2 g,1.5 eq) and 30 mg of freshly recristallized Pd(PPh₃)₄, the mixture was refluxed overnight under a nitrogen atmosphere. After evaporation of the solvent, the residue was dissolved in 50 mL of ethyl acetate and stirred for 30 min with 50 mL of saturated sodium fluoride. The organic phase was washed with water and dried on MgSO₄. After removal of the solvent, column chromatography (SiO₂, petroleum ether) gave 65% of the target compound as a colourless oil. ¹H NMR (CDCl₃) 7.26 (d*d, 1H, ³J = 3.48, ⁴J = 0.96); 7.19 (d*d, 1H, ³J = 5.11, ⁴J = 0.96); 7.11 (d, 2H, ³J = 8.55); 7.09 (d, 1H, ³J = 5.69); 6.99 (d, 1H, ³J = 5.1, ³J = 3.6); 6.93 (d, 2H, ³J = 8.55); 6.72 (d, 2H, 3J = 5.48); 2.34 (s, 3H). MS (TOF): M+ 271.8 (cal. 272.03).

3-(p-Tolyloxy)-2-(3-(p-tolyloxy)thiophen-2-yl)thiophene 3

Compound 1 (0.5 g, 2.6 mmol) was dissolved in 30 mL of dry diethyl ether under a nitrogen atmosphere and cooled to -78 °C. After addition of one equivalent of *n*-BuLi the mixture was stirred for 1 h at 78° and copper chloride (1.2 equivalent) was added in one portion. After stirring overnight at room temperature, the mixture was washed with water and dried on MgSO₄. After evaporation of the solvent, the residue was recrystallised in petroleum ether to give compound 4 in 10% yield, mp 150 °C. ¹H NMR (CDCl₃): 7.11 (m, 3H); 6.93 (d, 2H, ³J = 8.50); 6.71 (d, 1H, ⁴J = 5.55); 2.32 (s, 3H). M S (TOF): M+ 377.9 (cal 378.07).

4-(p-tolyloxy)-2-(4-(p-tolyloxy)thiophen-2-yl)thiophene 4

4-(*p*-Tolyloxy)-2-bromothiophene 7 (0.2 g 0.74 mmol) was dissolved in 30 mL of dry diethyl ether at -78 °C. After dropwise addition of 1.1 equivalent of *n*-BuLi the mixture was

stirred for 30 min at this temperature and 1.5 equivalent of tributylstannyl chloride was added. The brown-red solution immediately turned orange. After return to room temperature and removal of the solvent, the residue was dissolved in 15 mL of ethyl acetate and stirred for 45 min with 20 mL of a saturated aqueous solution of sodium fluoride. After flash filtration onto celite, the organic phase was washed with water and dried on MgSO₄. After evaporation of the solvent, the crude stannic derivative was dissolved in dry THF and two equivalent of CuCl₂ and a catalytic amount of Pd(OAc)₂ (5% mol.) were added. The mixture was stirred overnight under nitrogen at room temperature. After filtration on celite and evaporation of the solvent, column chromatograpy (silica gel, petroleum ether) gave 30 mg (20%) of the target compound as a light yellow solid, mp $\sim 100 \,^{\circ}\text{C}(\text{dec})^{-1}\text{H NMR}$ (CDCl₃): 7.15 (d, 4H, ${}^{3}J = 8.55$); 7.15 (d, 4H, ${}^{3}J = 8.45$); 6.92 (d, 2H, ${}^{4}J = 1.49$; 6.41 (d, 2H, ${}^{4}J = 1.44$); 2.34 (s, 6H). MS (TOF): M+ 378.8 (cal 378.07).

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