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and the electron donor ability of the thiophene moieties.



The synthesis of extended benzodifuran-thiophene systems connected by azomethine junctions is

described. The electronic properties of these systems, studied by UV-vis spectroscopy and cyclic voltam-

metry, are discussed in relation with the electron withdrawing groups grafted on the benzodifuran unit





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# Extended benzodifuran-thiophene systems connected with azomethine junctions: synthesis and electronic properties



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#### ARTICLE INFO

#### ABSTRACT

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# Introduction

Organic semiconductors based on linearly  $\pi$ -conjugated systems are the focus of considerable interest motivated by their potential applications in large area, lightweight and flexible optoelectronic devices such as organic field-effect transistors (OFET), organic electroluminescent diodes (OLED), and organic photovoltaic cells (OPC).<sup>1–3</sup> For these different applications, the design of new active materials imposes investigations of conjugated systems with specific electronic properties.<sup>4</sup> Benzofuran and benzodifuran moieties have emerged as efficient building blocks for the development of semiconductor materials for organic electronics.<sup>5</sup> Thus polymers or small molecules based on the benzo[1,2-b:4,5b']difuran units (BDF) variously substituted on the benzenic core and/or the furan units (Scheme 1) have been used as active materials in OLEDs and OPCs.<sup>5–11</sup> On the other hand, the donor-acceptor (D/A) approach with electron-donating (D) and electron acceptor (A) blocks inserted in the conjugated backbone is currently one of the most widely investigated materials for the development of electronic plastics.<sup>12–14</sup> Recently many donor–acceptor copolymers containing BDF building blocks were used as donor materials in OPC and power conversion efficiencies above 6% were achieved.<sup>6</sup>

We have recently shown that benzodifuran extended with furan<sup>15</sup> or bithiophene<sup>16</sup> units by azomethine junctions constituted a green approach for synthesizing active materials for OPC.

\* Corresponding author. E-mail address: pierre.frere@univ-angers.fr (P. Frère). Azomethine bonds that are isoelectronic of ethylenic bonds<sup>17</sup> have been used as extended conjugated materials in electrochromic

materials and OPCs.<sup>18–22</sup> As a further step in our contribution of developing donor–acceptor conjugated systems based on BDF, we report here on the synthesis and the electronic properties of extended BDF–thiophene derivatives **1a–d** (Scheme 1). The electron donor ability of the thiophene units was strengthened by hexyloxy groups while electron withdrawing pentafluorophenyl, cyano and butylacetate groups were grafted on the BDF units.

The synthesis of compounds **1a-d** (Scheme 2) is based on the condensation reaction between the diamino derivatives 2 and the thiophene aldehyde **3**. The diamino compounds **2a**-**c** are easily obtained in 30-48% yields by reaction between benzoquinone and cyano derivatives **4a-c** in the presence of aqueous ammonia solution.<sup>15,23-25</sup> For the condensation reaction of diamino **2a-c** with aldehyde derivatives, two different protocols have been employed. With diamino 2a and 2.5 equiv of 2-hexylthiophene-5-carbaldehyde **3a** or 3,4-dihexyloxythiophene-5 carbaldehyde **3b**, the green method using ethyl lactate as the solvent<sup>26</sup> in the presence of a little amount of P2O5 (10% mol) led to compounds 1a and 1b easily purified by precipitation in water in 87% and 80% yields respectively. From diamino 2c bearing an ester group the condensation did not work in ethyl lactate due to trans-esterification reaction giving a mixture of compounds difficult to separate. Thus a second method using trifluoroacetic acid (TFA) as the catalyst has been preferred.<sup>27</sup> Treatment of diamino **2a-c** with 3 equiv of aldehyde **3b** in chloroform in the presence of 10% molar





R Scheme 1. Structure of benzodifuran derivatives.

1b-d

C<sub>6</sub>H<sub>13</sub>



Scheme 2. Synthetic pathway of compounds 1a-d.

of TFA gave after workup and purification by flash chromatography compounds 1b-d in 58-70% yields. Compounds 1b-d present a lower stability than 1a in chlorinated solvents. Thus by NMR, the partial reverse reaction with the formation of the aldehyde and diamino derivatives (about 10% mol) has been observed after one hour in CDCl<sub>3</sub>.

The electronic properties of **1a-d** have been evaluated by theoretical calculations and analyzed by cyclic voltammetry and UVvis spectroscopy. Theoretical and experimental data are gathered in Table 1.

Theoretical calculations were performed at the ab initio density functional level with the gaussian09 package. Becke's three parameter gradient-corrected functional (B3LYP) with a polarized 6-31G (d,p) was used for the geometrical optimization and for the HOMO and LUMO level determination. The optimized structures of 1a-d present a good planarity of the conjugated systems (Fig. 1). For compounds 1a and 1b, the lateral pentafluorophenyl units show a torsional angle of 50° with the benzodifuran moiety. Between these two compounds, the hexyloxy groups of 1b confer a higher electron donor character than the hexyl groups of 1a leading to a

1d R= COOC<sub>4</sub>H<sub>o</sub>

## Table 1

HOMO and LUMO energy levels, theoretical bandgap  $\Delta E_{i}^{a}$  experimental absorption data<sup>b,c</sup> and cyclic voltammetry data<sup>d</sup> of compounds **1a-d** 

Compounds	HOMO (eV)	LUMO (eV)	$\Delta E_{\text{The}} (\text{eV})$	$\lambda_{\max} (nm)^{b}$	$\Delta E_{\rm Opt}  ({\rm eV})^c$	$Ea_{ox}(V)$	$Ec_{ox}(V)$	$\Delta E_{\rm p}  ({\rm mV})^{\rm g}$	$E_{\rm red}\left(V\right)$
1a	-5.14	-2.48	2.66	476	2.0	1.18 <sup>e</sup>		_	-1.51 <sup>e</sup>
1b	-5.00	-2.34	2.66	479	2.0	0.71 <sup>f</sup>	0.66	50	-1.45 <sup>e</sup>
1c	-5.30	-2.61	2.69	480	2.0	0.91 <sup>f</sup>	0.86	50	-1.38 <sup>e</sup>
1d	-4.97	-2.31	2.66	478	2.0	0.75 <sup>f</sup>	0.71	40	-1.47 <sup>e</sup>

B3LYP/6-31G(d,p).

<sup>b</sup>  $10^{-4}$  mol·l<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>c</sup> Optical band gap calculated from the onset of the absorption band for film deposited on glass.

d  $10^{-3}$  mol·l<sup>-1</sup> 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub>,  $\nu = 100$  mV s<sup>-1</sup>, ref SCE.

Irreversible peak.

f Reversible peak.

<sup>g</sup>  $\Delta E_{\rm p} = {\rm Ea}_{\rm ox} - {\rm Ec}_{\rm ox}$ .



Figure 1. Frontier orbitals of compound 1b.

destabilization both of the HOMO and LUMO levels. For **1c** and **1d**, the cyano and ester groups are in the plane defined by the benzodifuran units (Fig. S1 in Supplementary data). The comparison of the HOMO and LUMO levels of **1b–d** reveals the effect of the electron acceptor characters of the substituent grafted on the benzodifuran unit. Cyano groups procure higher stabilization of the HOMO and LUMO levels than ester and pentafluorophenyl groups. Nevertheless, the replacement of the electron donor groups on thiophene units and electron acceptor groups on the central BDF moiety leads to a translation of the HOMO and LUMO levels with-out modifying the gap between the two levels about 2.7 eV.

As shown in Figure 2 for 1d, the UV-vis absorption spectra of 1a-d in CH<sub>2</sub>Cl<sub>2</sub> exhibit an absorption band with vibronic fine structures that are characteristic of rigid conjugated systems. The substituents grafted on the benzodifuran or thiophene units have a limited effect on the absorption band with  $\lambda_{max}$  in 476–480 nm range. Films of **1a-c** have been deposited on glass by the spin coating technique using chloroform, dried on anhydrous Na<sub>2</sub>CO<sub>3</sub>, as the solvent. The UV-vis absorption spectra of the films present a 90 nm red shift of the absorption bands compared to the solution spectra and an enhancement of the vibronic bands with the apparition of well distinct maxima. Such behavior is characteristic of strong intermolecular interactions without presenting strictly parallel  $\pi$ stacking between the molecules. Annealing tests of the films have been performed at temperatures varying from 70 to 150 °C during 10 min. Except for 1b that presented a rapid degradation of the films from 80 °C, the other derivatives did not show any evolution of the spectra of the films before 130 °C.

The electrochemical properties of 1a-d have been studied by using cyclic voltammetry in  $CH_2Cl_2$  in the presence of  $Bu_4NPF_6$  as

300 350 400 450 500 550 600 650 700 Wavelength (nm)

Figure 2. Normalized UV-vis absorption spectra of 1d in solution in  $CH_2Cl_2$  (solid line) and film of 1d deposited on glass (dashed line).

the supporting electrolyte. The various substituents induce strong modifications of the electrochemical properties. Although diaminoderivative **2a** presents two reversible oxidation waves, compound **1a** shows an irreversible oxidation peak at 1.18 V and compounds **1b–d** with dialkoxythiophene units a reversible oxidation peak at potential inferior to 1V (Fig. 3). Thus, the electron donor effect of alkoxy groups favors the oxidation of **1b–d** and strongly stabilizes the oxidized states. A comparison of the data of compounds **1b–d** shows that the oxidation potentials ranging from 0.71 V for **1b** (R<sub>1</sub> =  $-C_6F_5$ ) to 0.75 V for **1d** (R1 = -COOBut) then to 0.91 V for **1c** (R1 = -CN), follow the electron withdrawing character of the substituents grafted on the central BDF unit.

Moreover the analysis of the oxidation processes shows that the difference  $\Delta E_{\rm p}$  between the anodic (Ea<sub>ox</sub>) and the cathodic (Ec<sub>ox</sub>) peaks of the reversible oxidation waves is 70–80 mV for **2a** and decreases to 40–50 mV for **1b–d**. Thus for **2a**, the values of  $\Delta E_{\rm p}$  are superior to 60 mV indicating that the two oxidation waves correspond to mono electronic process with the successive formation of radical-cation and dication. For **1b–d**, the  $\Delta E_{\rm p}$  values are smaller than 60 mV expected for a mono-electronic process and we can stipulate that the oxidation of compounds **1b–d** gives directly the dication state.<sup>28,29</sup>

By comparison with the diamino benzodifuran derivatives, the lengthening of the conjugated chain with the azomethine junctions isoelectronic of ethylenic bonds<sup>17</sup> leads to a large electronic delocalization.<sup>30,31</sup> Thus thiophene–imine–benzodifuran–imine–thiophene systems correspond to a large extended conjugated system favouring the access to the dication state. On the other hand, as already observed for extended oligothiophenes based on ethylene-dioxythiophene (EDOT) units,<sup>32</sup> alkoxy groups grafted



**Figure 3.** Voltamperogramms of **2a** (red), **1b** (blue) and **1c** (black),  $10^{-3}$  mol·l<sup>-1</sup> in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub>,  $\nu$  = 100 mV·s<sup>-1</sup>, E (V) versus SCE.



Figure 4. (Top) Theoretical structure of dication  $1b^{2^*}$ . (Bottom) Limit structure of dication  $1b-d^{2^*}$ .

on terminal thiophene cycles stabilize the dication state by localizing the positive charge of dication on oxygen atoms.

To know the possible molecular structure of dications 1b<sup>2+</sup>, theoretical calculations were performed with the same base as the neutral compound. The analysis of the bond lengths (Table S1 and Fig. S2) shows that the oxidation of **1b** to dication results in a transition from aromatic to guinonoid structure of the dibenzofuran units and in an inversion of the single and double bonds for the imine junctions (Fig. 4 top). Furthermore, comparison of the C-O bond lengths in the neutral **1b** and di-cationic **1b<sup>2+</sup>** (Table S1) shows that whereas the outer C–O bond lengths are slightly decreased from 1.360 to 1.345 Å, the decrease of the length of the inner C–O length to 1.316 Å suggests that the  $(-C=O^+-)$ mesomeric form (Fig. 4 bottom) contributes to de-localization of the positive charges. Finally, both the lengthening of the conjugated systems and the localization of the positive charges on the external positions strongly stabilize the dication state by a decrease of the on-site coulombic repulsion, thus justifying the direct two electronic process for oxidation of 1b-d. Moreover such a dication state presents higher stability than radical cation because subsequent coupling reaction is not possible.<sup>33,34</sup>

All the compounds were found to be irreversibly reduced. The reduction potentials for compounds **1b** and **1d** were -1.45 and -1.47 V, respectively. For **1c** with the most electron withdrawing groups (—CN) the reduction potential rises to -1.38 V indicating a higher stabilization of the LUMO level as indicated by the theoretical calculations.

In summary, a new series of extended benzodifuran-thiophene derivatives connected by azomethine junctions has been synthesized. It has been evidenced that the raising of the electron acceptor character of groups grafted on the central benzodifuran unit stabilized both the HOMO and the LUMO levels without modifying the band gap of the molecules. On the other hand, alkoxy groups grafted on the external thiophene units enhance the donor character of the molecules and strongly stabilize the positive charges of the oxidized state thus allowing the direct formation of the dication state. These results show that a judicious choice of electron acceptor and donor grafted on the benzodifuran and thiophene units allows a fine tuning of the electronic properties of these extended materials. Conjugated polymers based on various thiophene-imino-BDF building blocks for developing materials for OPCs are now underway and will be reported in future publications.

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### Supplementary data

Supplementary data (Figs. S1 and S2, Table S1, experimental procedures, characterizations, <sup>1</sup>H and <sup>13</sup>C NMR of new compounds) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.07.030. These data include MOL files and InChiKeys of the most important compounds described in this article.

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