Effects of aromatic spacers on the properties of organic field effect transistors based on π-extended tetrathiafulvalene derivatives†

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Received 10th December 2008, Accepted 10th March 2009
First published as an Advance Article on the web 17th April 2009
DOI: 10.1039/b822159f

OFETs built from extended TTF derivatives containing N-methylpyrrole, furan, thiophene and benzene with meta or para linkages as spacers are presented. The aromatic spacer plays a crucial role in the characteristics and stability of the OFETs. The less conjugated derivative with a meta-benzene moiety as spacer has the best mobility, with a higher on/off ratio and strongly enhanced stability in air.

Organic field-effect transistors (OFETs) are a focus of considerable current technological and fundamental interest.1–3 While pentacene derivatives and thiophene-based π-conjugated systems have been extensively investigated as organic semiconductors for OFET fabrication,4–6 recent works have shown that tetrathiafulvalene (TTF) derivatives are efficient active materials for OFETs.6,7 High hole mobilities have been reported for OFETs based on single crystals,8 thermally evaporated films9–14 and more recently spin-cast films of TTF derivatives.15–17

A major advantage of TTF derivatives resides in their strong propensity to form ordered stacks due to the combined effects of strong π–π and sulfur–sulfur interactions.5,9,18,19 However, the strong donor properties of TTF derivatives make them easy to oxidize and thus relatively unstable under atmospheric conditions.10,12 An important challenge consists of developing stable systems with reinforced intermolecular interactions propitious to good mobility in the materials.

In this context, extended TTF derivatives, built by insertion of a conjugated spacer between two dithiafulvalenyl moieties, show promise as p-semiconductors. Indeed, such systems, already widely developed,20–23 are known to exhibit enhanced interchain interactions due to multiple π–π and chalcogen–chalcogen interactions.24 The electronic properties of extended TTF derivatives can be controlled both by the nature of the conjugating spacer and by substitution of dithiole rings.25 Electron-releasing substituents lead to a decrease of oxidation potential (Eox) whereas electron-withdrawing substituents have the reverse effect. The fusion of a benzene ring with the dithiafulvalenyl moiety results to the second type of effect, as shown by the increase of Eox from 0.40 V for TTF to 0.72 V for dibenzo-TTF.10

In addition, this substituent results in the reinforcement of the intermolecular contacts. On the other hand, it has been shown that the insertion of an aromatic unit between the two dithiafulvalenyl moieties allows large modulations of the electronic properties of the resulting extended TTF. Whereas furan, thiophene or pyrrole rings produce a decrease of Eox, such an effect is not observed for the benzene ring.21 A systematic analysis of the mode of linkage of dithiafulvenyl moieties on a phenyl core has shown that whereas an ortho-linkage leads to compounds that present a rapid structural modification upon oxidation or thermal treatment,25,26 meta- and para-linkages lead to stable systems, with a higher Eox for the meta- than for the para-isomers.

We describe here a series of OFETs in which extended TTFs 1–5 are incorporated as the semiconductor materials. Their performances are strongly dependent on the nature of the spacer and on the linkage mode. Relationships between the molecular structures and the characteristics of the OFETs are highlighted.

Compounds 1–5 were synthesized according to reported procedures,27–30 and their optical and electrochemical data are gathered in Table 1. The UV-Vis spectra of fully conjugated compounds 2–5 present a vibrational fine structure typical of rigid conjugated systems. In contrast, the spectrum of the meta isomer 1 presents a broad structureless absorption band.
with a 50 nm blue shift of $\lambda_{\text{max}}$ as compared to that of the para isomer 2, indicative of a substantial reduction of the effective conjugation (Fig. 1).

As already demonstrated, the first oxidation potential, corresponding to the formation of the radical cation, is strongly dependent on the spacer. Compound 3 presents a first anodic peak potential $E_{\text{pa}} = 0.37$ V. Replacing the N-methyl pyrrole unit by furan and thiophene as in 4 and 5 leads to a positive shift of $E_{\text{pa}}$ to 0.41 V and 0.48 V respectively. A benzene spacer with a para linkage presents a further increase of the oxidation peak at $E_{\text{pa}} = 0.72$ V, while the restricted conjugation between the dithiafulvalenyl groups caused by the meta linkage produces a further positive shift of $E_{\text{pa}}$ to 1.00 V.

Thin films of compounds 1–5 were deposited on glass by thermal evaporation under high vacuum and analyzed by X-ray diffraction in reflection mode (Fig. 2 for 1 and Fig. S1† for the other compounds). The diffractograms of films for 1–3 have very well defined sharp reflections up to the sixth order, indicative of highly ordered crystal packing. The $d$ spacing obtained from the first reflection peaks correspond to a monolayer thickness of 2.00 nm for the meta isomer 1, 2.02 nm for the para isomer 2, and 1.94 nm for compound 3. By contrast, the films of 4 and 5 have a multiplicity of peaks, indicating the formation of several crystalline phases. A $d$ spacing of 1.93 nm for the film of 4 is indicated from the position of the (broad) first peak.

Optimization of the geometry of the compounds (density functional theory at the B3LYP/6-31G(d) level) indicates that the molecules have a similar $\delta$-trans conformation with a dihedral angle between the dithiafulvalenyl moieties and the spacer unit less than 15° for 1 and 2 and good planarity for 3–5 with heterocycles as spacers (see Fig. S2†). The longest distance between two opposite hydrogen atoms is about 2 nm, thus suggesting that the different compounds adopt a preferential vertical orientation on the substrate independently of the spacers. It can be noted that for 4 and 5, the calculations for the $\delta$-cis conformation (Scheme 1) lead to a planar structure with short S•••S and S•••O distances between the sulfur atom of the dithiafulvene groups and the chalcogen atom of the central heterocycle. The energy differences between the $\delta$-cis and $\delta$-trans conformations are less than 0.6 kcal mol$^{-1}$, indicating that the two conformations have similar stability in the gas phase. In contrast, 3 has a distorted $\delta$-syn conformation that is 6.4 kcal mol$^{-1}$ higher in energy than the $\delta$-trans conformation. As already demonstrated by X-ray structures, the planar $\delta$-cis conformation of 4 and 5 stabilized by S•••S or S•••O intramolecular interactions can modify the packing of the molecules in the film.\textsuperscript{21}

OFETs were fabricated on an n-doped silicon gate with thermally grown SiO$_2$ as the dielectric using a top-contact configuration. After deposition of the active layer, the gold source and drain electrodes were deposited by evaporation through a mask, leading to a channel of 70 $\mu$m length and 5 mm width. The OFET characteristics were measured at room temperature in a glove box. Under an inert atmosphere, OFETs based on all the compounds present drain current ($I_D$) characteristics with well defined linear and saturation regimes (Fig. 3 for compounds 1 and 2; Fig. S3†). The amplification mode of $I_D$ takes place when the negative gate voltage ($V_g$) increases, as expected for p-type organic semiconductors. The field-effect mobilities ($\mu$) in Table 1 were calculated from both

\begin{table}[h]
\centering
\caption{Optical and electrochemical properties of compounds and performances of OFETs.}
\begin{tabular}{cccccc}
\hline
Cpd & $\lambda_{\text{max}}$ (nm)$^a$ & $\varepsilon$ (L mol$^{-1}$ cm$^{-1}$) & $E_{\text{pa}}$ (V)$^b$ & $\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$) & $I_{\text{on}}/I_{\text{off}}$ \\
\hline
1 & 340 & 7200 & 1.00 & 8.1 $\times$ 10$^{-2}$ & 5 $\times$ 10$^4$ \\
2 & 390 & 8200 & 0.72 & 4.2 $\times$ 10$^{-2}$ & 350 \\
3 & 395 & 8700 & 0.32 & 4.6 $\times$ 10$^{-2}$ & 15 \\
4 & 407 & 8600 & 0.48 & 1.6 $\times$ 10$^{-2}$ & 50 \\
5 & 405 & 8650 & 0.41 & 0.7 $\times$ 10$^{-2}$ & 50 \\
\hline
\end{tabular}
\end{table}

\textsuperscript{a} 10$^{-4}$ M in CHCl$_3$. \textsuperscript{b} Anodic peak potential measured by cyclic voltammery of a 10$^{-3}$ M solution of compound in CH$_2$Cl$_2$ with 0.10 M Bu$_4$NPF$_6$ as supporting electrolyte. Ref. SCE, $v$ = 100 mV s$^{-1}$.

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{Fig_1.png}
\caption{UV-Vis absorption spectra of 1 and 2 (10$^{-4}$ M in CHCl$_3$).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{Fig_2.png}
\caption{X-Ray diffraction of a film of 1 deposited on glass, geometric optimization of 1 and schematic representation of the molecular orientation of 1 on the substrate.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{Scheme_1.png}
\caption{\textit{\delta}-trans and \textit{\delta}-cis conformations for 4 and 5.}
\end{figure}
linear and saturation current regimes with classical equations. Compounds 1–3, with the best structured films, lead to $\mu_E$ values of the same order of magnitude, $\sim 0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. For 4 and 5, which have less homogenous films, the $\mu_E$ values are smaller. In particular, the latter compound shows a mobility less than $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Fig. 4 shows AFM images of thin films of 1 and 2 deposited on Si/SiO$_2$. The films show very similar morphologies, although larger grain sizes are seen with compound 1. Since $\mu_E$ generally increases with grain size, this result is consistent with the larger $\mu_E$ value observed for the meta isomer 1.

Examination of the $I_{\text{on}}/I_{\text{off}}$ ratios, calculated as the ratio of currents by applying gate voltages of $V_g = -60 \text{ V}$ ($I_{\text{on}}$) and $V_g = 0 \text{ V}$ ($I_{\text{off}}$) respectively, reveals considerable differences that are directly correlated with the first oxidation potential of the active compounds (Table 1). Compound 3, which has the lowest oxidation potential, has a low $I_{\text{on}}/I_{\text{off}}$ ratio due to a non-negligible $I_{\text{off}}$ current at a gate voltage $V_g = 0 \text{ V}$. In fact, to observe a null $I_{\text{off}}$ current a positive gate voltage $V_g = +20 \text{ V}$ must be applied. These results suggest the presence of the charge-carriers at $V_g = 0 \text{ V}$ due to the high ease of oxidation of compound 3. Replacing the N-methylpyrrole unit by furan and thiophene (as in 4 and 5) allows one to increase the $I_{\text{on}}/I_{\text{off}}$ ratio up to 50. For compounds with benzene as spacer the ratios are more important, and the meta-linked compound 1 has an $I_{\text{on}}/I_{\text{off}}$ ratio about two orders of magnitude larger than that of the para isomer 2.

The stability of the OFETs towards ambient atmosphere was then tested. OFETs based on compounds 3, 4 and 5 show a complete loss of the field effect after a few minutes in air.

Fig. 3 (bottom) shows the characteristics of OFETs based on compounds 1 and 2 measured after 48 days of storage under ambient atmosphere, compared to the measurement performed in the glove box immediately after fabrication (top). The device based on compound 2 undergoes a dramatic change in its electrical characteristics upon exposure to air, with a decrease of the $I_{\text{on}}/I_{\text{off}}$ ratio from 350 to 4. The strong increase of the $I_{\text{off}}$ current suggests an increase of the hole concentration in the material due to oxidative doping by oxygen. In contrast, long-term exposure to air of OFETs synthesized from compound 1 does not alter the...
Improvement of the stability of the active material under ambient potential induced by the meta or para linkage of the two dithiafulvenyl moieties. After two months of storage under ambient atmosphere, devices fabricated with the meta compound 1 still show a hole mobility of $1.3 \times 10^{-2} \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$ and an $I_{on}/I_{off}$ ratio of $10^4$. Hence the large increase of the oxidation potential induced by the meta linkage leads to a considerable improvement of the stability of the active material under ambient conditions.

Conclusions

The performance of OFETs based on extended TTFs built with various aromatic spacers has been compared. We show the crucial role of the spacers in relation with the electronic properties of the extended TFF and the OFET characteristics. OFETs built from extended TTFs with benzene containing a para or meta linkage or N-methylpyrrole as spacer have higher mobility than compounds based on thiophene and furan as spacers. This result may be attributed to a better vertical self-organisation of the molecules on the substrate when the molecules adopt mainly a $\delta$-trans conformation. The strongest differences between the characteristics concern the on/off ratio and the stability under ambient atmosphere, which can be correlated to the first oxidation potential of the extended TTFs. The performances of OFETs are substantially improved when the oxidation potential of the extended TTFs increases by limiting the conjugation between the two dithiafulvenyl moieties. Thus, the non-conjugated extended TTF 1 leads to OFETs having the best combination of extended properties: higher mobility and $I_{on}/I_{off}$ ratio, and good stability under atmospheric conditions.

Experimental

OFETs were prepared by evaporating a 50 nm thick organic layer onto Si heavily n doped wafers coated with a 200 nm thick SiO$_2$ layer. As source and drain top contacts, 25 nm of Au were evaporated through a shadow mask, defining a channel with 5000 µm width and 70 µm length. The FET characterisation was done either in a glove-box (MBraun, Ar, H$_2$O and O$_2$ less than 0.1 ppm) or under atmospheric conditions using an Agilent 4155C semiconductor parameter analyser. The contacts were tungsten tips (Signatone).

References