DOI: 10.1002/cplu.201200132

Functionalized Dithienylthiazolo[5,4-d]thiazoles For Solution-Processable Organic Field-Effect Transistors

Sarah Van Mierloo,^[a] Karolien Vasseur,^[b] Niko Van den Brande,^[c] Ayse E. Boyukbayram,^[a, d] Bart Ruttens,^[e] Silvio D. Rodriguez,^[f, g] Edith Botek,^[f] Vincent Liégeois,^[f] Jan D'Haen,^[e] Peter J. Adriaensens,^[a] Paul Heremans,^[b] Benoît Champagne,^[f] Guy Van Assche,^[c] Laurence Lutsen,^[h] Dirk J. Vanderzande,^{*[a, h]} and Wouter Maes^{*[a, i]}

A series of 5'-aryl-substituted 2,5-bis(3'-hexylthiophen-2'yl)thiazolo[5,4-*d*]thiazole derivatives was synthesized and these expanded semiconductors were investigated as active materials for solution-processable organic field-effect transistors. Field-effect mobilities of up to 10^{-3} cm²V⁻¹s⁻¹ were obtained, representing the first reasonable FET behavior for highly soluble thiazolo[5,4-*d*]thiazole-based small organic compounds suitable for printable electronics. Thermal and electrooptical material properties were studied by thermogravimetric analy-

Introduction

Organic semiconductors receive significant attention as func tional materials applicable in organic field-effect transistory (OFETs),^[1] organic light-emitting diodes (OLEDs),^[2] and organic photovoltaics (OPV).^[3] Some of the particular features of organ ic materials render them more attractive than their inorganic counterparts for electronic applications requiring large area coverage, structural flexibility, and solution processability. In the design of organic semiconductors, the consideration o molecular properties such as oxidation potentials, electron af finities, and intermolecular π - π interactions is a crucial aspect Several prominent semiconducting materials have been ob tained by structural modifications of oligothiophene deriva tives and their properties have been tuned by introducing par ticular substituents onto the π -conjugated backbone.^[4] Among these thiophene-based (small) molecules, a number of materials containing a thiazolo[5,4-d]thiazole (TzTz) unit have shown high field-effect mobilities when used as active layers in both n- and p-type OFET devices. The TzTz fused heterocycle shows some excellent characteristics toward applications in organic electronics. Its electron-accepting character enhances the stability of the resulting materials toward oxygen. TzTz compounds are generally stable under ambient atmosphere at room temperature over a period of several months. Moreover the TzTz moiety has a rigid planar structure resulting from the fused bicyclic ring system, which leads to efficient intermolecu lar π - π interactions.^[5-7] Finally, 2,5-diaryl-substituted TzTz deriv atives can easily be synthesized starting from the corresponding arylcarbaldehyde compounds and dithiooxamide.^[8,9]

The majority of TzTz molecules reported so far are very poorly soluble in common organic solvents and require vacuum deposition techniques for device fabrication. To be apsis, differential scanning calorimetry, cyclic voltammetry, and UV/Vis spectroscopy. Trends in thermal and optical data were supported by (time-dependent) density functional theory calculations. Additional X-ray diffraction, atomic force microscopy, and scanning electron microscopy studies provided insight in the relationship between the molecular structures, film morphologies, and FET performances. The fibrillar microcrystalline structure observed for the best-performing thienyl-substituted material was linked to the high mobility.

[a]	Dr. S. Van Mierloo, Dr. A. E. Boyukbayram, Prof. Dr. P. J. Adriaensens,
	Prof. Dr. D. J. Vanderzande, Prof. Dr. W. Maes
	Design & Synthesis of Organic Semiconductors (DSOS), Hasselt University Institute for Materials Research (IMO-IMOMEC), Agoralaan 1–Building D 3590 Diepenbeek (Relaium)
	F-mail: wouter maes@uhasselt.be
	dirk vanderzande@uhasselt be
[h]	K Vassour, Brof. Dr. B. Horomans
[D]	IMEC Kaneldreef 75 3001 Leuven (Belaium)
	Department of Metalluray and Materials Engineering KII Leuven
	Kasteelnark Arenbera 44, 3001 Leuven (Belaium)
[6]	N Van den Brande Prof. Dr. G. Van Assche
[C]	Department of Materials and Chemistry
	Physical Chemistry and Polymer Science
	Vrije Universiteit Brussel. Pleinlaan 2. 1050 Brussels (Belaium)
[d]	Dr. A. F. Boyukhayram
[[]]	Department of Chemistry, Karabuk University
	78000 Karabuk (Turkev)
[e]	B. Ruttens, Dr. J. D'Haen
[0]	Electrical and Physical Characterization (ELPHYC)
	Hasselt University, Institute for Materials Research (IMO-IMOMEC)
	Universitaire Campus - Wetenschapspark 1, 3590 Diepenbeek (Belgium)
ſſ	S. D. Rodriauez, Dr. E. Botek, Dr. V. Liégeois, Prof. Dr. B. Champagne
	Laboratoire de Chimie Théorique
	Facultés Universitaires Notre-Dame de la Paix (FUNDP)
	Rue de Bruxelles 61, 5000 Namur (Belgium)
[q]	S. D. Rodriguez
	Medio Ambiente y Energía, Instituto de Química-Física de Materiales
	Universidad de Buenos Aires
	Pabellón II, Ciudad Universitaria, C1428EGA Buenos Aires (Argentina)
[h]	Dr. L. Lutsen, Prof. Dr. D. J. Vanderzande
	IMEC, IMOMEC Ass. Lab.
	Universitaire Campus - Wetenschapspark 1, 3590 Diepenbeek (Belgium)
[i]	Prof. Dr. W. Maes
	Department of Chemistry, Molecular Design and Synthesis, KU Leuven
	Celestijnenlaan 200F, 3001 Leuven (Belgium)
	Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cplu.201200132.

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plicable to printing processes and highly attractive for large area coverage at a reasonable cost, solubilizing groups/side chains have to be appended to the extended π -system. Such highly soluble TzTz materials are also of particular appeal for integration (as acceptor components) in low bandgap donor-acceptor copolymers toward the preparation of efficient organic solar cells. The interest in the TzTz structure in this respect has increased spectacularly, noticeably in the last year.^[10]

Herein, a series of highly soluble functionalized TzTz-based semiconductors is presented. Four 2,5-bis-(5'-aryl-3'-hexylthio-phen-2'-yl)thiazolo[5,4-*d*]thiazole (DTTzTz) molecules, **Th-DTTzTz**, **4-CF₃C₆H₄-DTTzTz**, **4-FC₆H₄-DTTzTz**, and **4-CNC₆H₄-DTTzTz** (Scheme 1), were synthesized, in which the two



Scheme 1. Synthetic pathway toward soluble 2,5-dithienylthiazolo[5,4-d]thiazole derivatives. DME = 1,2-dimethoxyethane, DMF = N,N-dimethylformamide, NBS = N-bromosuccinimide, THF = tetrahydrofuran.

3-hexylthiophene units ensure solvent-based processing.^[11] Functionalization, purification, and characterization of the molecules are considerably simplified by their high solubility. The correlation between the molecular structures of the synthesized DTTzTz derivatives, their thermal and (photo)physical properties, spin-coated film morphologies, and FET performances was thoroughly analyzed.

Results and Discussion

Synthesis and (electrooptical) characterization

The novel thiazolo[5,4-*d*]thiazole derivatives have been prepared through a convenient three-step synthetic protocol (Scheme 1). The backbone unit, 2,5-bis(3'-hexylthiophene-2'- yl)thiazolo[5,4-d]thiazole, was synthesized by using the classical condensation approach, treating 3-hexylthiophene-2-carbaldehyde with dithiooxamide.^[8,9] After that, a bromination reaction with NBS was carried out (in DMF), to afford 2,5-bis(5'-bromo-3'-hexylthiophene-2'-yl)thiazolo[5,4-d]thiazole (Br-DTTzTz). 2,5-Bis(4-hexyl-2,2'-bithiophene-5-yl)thiazolo[5,4-d]thiazole (Th-DTTzTz) was then obtained through a Stille cross-coupling rewith tributyl(thiophen-2-yl)stannane $([Pd(PPh_3)_4],$ action THF).^[12] On the other hand, 4-(trifluoromethyl)phenyl-, 4-fluorophenyl-, and 4-cyanophenyl-substituted DTTzTz derivatives (4-CF₃C₆H₄-DTTzTz, 4-FC₆H₄-DTTzTz, and 4-CNC₆H₄-DTTzTz) were synthesized through Suzuki cross-coupling reactions with the respective boronic esters ([Pd(PPh₃)₄], DME, NaHCO₃ or K₃PO₄ base). The use of the K₃PO₄ base provided higher yields for the 4-CNC₆H₄-DTTzTz compound. All DTTzTz compounds were efficiently purified by column chromatography (on silica) and consecutive recrystallizations, and were isolated as red crystals. The materials were found to be stable under ambient atmosphere at room temperature over a period of several months. Owing to the substitution with hexyl side chains, all compounds were nicely soluble in common organic solvents, in particular in chlorinated solvents and ethers.

Experimental UV/Vis absorption maxima (in CHCl₃ solution) and cyclic voltammetry (CV) data of the DTTzTz derivatives are summarized in Table 1. For the phenyl-substituted compounds

Table 1. Optical and electrochemical data for the dithienylthiazolo[5,4- d]thiazole derivatives.					
DTTzTz	λ_{\max} [nm] (log $arepsilon$) ^[b]	HOMO [eV] ^[c]	LUMO [eV] ^[c]	E_{g}^{EC} [eV]	$E_{g}^{OP} [eV]^{[d]}$
Th ^[a] 4-FC ₆ H ₄ 4-CNC ₆ H ₄ 4-CF ₃ C ₆ H ₄	449 (4.768) 433 (4.714) 445 (4.777) 434 (4.713)	-5.51 -5.66 -5.76 -5.83	-2.92 -3.05 -3.25 -3.04	2.59 2.61 2.51 2.79	2.45 2.52 2.47 2.54
[a] Data taken from a previous study. ^[12] [b] In CHCl., [c] Evaluated from					

a CV study in MeCN: $0.1 \text{ M Bu}_4\text{NPF}_{6r}$ Pt electrode, scan rate 50 mV s^{-1} . [d] Evaluated from the low energy onset of the absorption spectra in CHCl₃.

4-FC₆H₄-DTTzTz, 4-CNC₆H₄-DTTzTz, and 4-CF₃C₆H₄-DTTzTz, the absorption maxima were observed at 433, 445, and 434 nm, respectively, somewhat blue-shifted relative to Th-**DTTzTz** ($\lambda_{max} = 449$ nm). On the other hand, CV measurements (Figure S1 in the Supporting Information) of $4-FC_6H_4$ -DTTzTz, 4-CNC₆H₄-DTTzTz, and 4-CF₃C₆H₄-DTTzTz revealed oxidation peaks at 0.73, 0.83 and 0.90 V, respectively, notably higher than for Th-DTTzTz (0.58 V). These results point to somewhat deeper HOMO levels for the phenyl-substituted materials, thus suggesting that these compounds might have a higher stability toward oxygen. On the other hand, reduction peaks were found at -1.88, -1.68, -1.89, and -2.01 V for $4\text{-FC}_6\text{H}_4$ -DTTzTz, 4-CNC₆H₄-DTTzTz, 4-CF₃C₆H₄-DTTzTz, and Th-DTTzTz, respectively. Similar CV results concerning the incorporation of phenyl substituents have been reported before for TzTz-based semiconductors.^[13]

Density functional theory (DFT) and time-dependent DFT (TDDFT) calculations, summarized in Table 2, supported the experimentally observed changes in optical and electrochemical properties upon replacing the thiophene ring of **Th-DTTzTz** by

Table 2. Ca dithienylth lations.	alculated iazolo[5,4-	optical - <i>d</i>]thiazol	and e deriva	electrochemic tives as obtaine	al data d from TD	for DFT ca	the alcu-
		(C)[b]				= calc	

UTIZIZ	"ge [iiii] ('ge/	Lg [CV]			-g [CV]
Ph ^[a]	484 (1.91)	2.56	-5.20	-2.28	2.92
Th	516 (1.96)	2.40	-5.10	-2.36	2.74
4-FC ₆ H₄	484 (1.91)	2.56	-5.21	-2.30	2.91
4-CNC ₆ H₄	508 (2.17)	2.44	-5.45	-2.65	2.80
$4-CF_3C_6H_4$	492 (2.00)	2.52	-5.36	-2.48	2.88

[a] The phenyl-substituted analogue^[11] was merely used as a reference compound for the theoretical calculations and was not included in the OFET study. [b] Oscillator strength.

substituted phenyl groups. In general, the calculated data reflect the experimentally observed trends rather well. The impact of the nature of the terminal aryl moiety on the frontier orbitals and optical band gaps was further exemplified by the topology of the HOMO and LUMO, which are delocalized over the whole backbone (Figure 1 and Figure S2-S5). These differences in optical and electrochemical properties have then been correlated to the Mulliken charge distribution and therefore to the relative electronegativity of the different substituents (Figure 2). So, the smaller/larger optical and electrochemical gaps are associated with more/less positive thiophene donor rings (directly linked to the TzTz core) and less/more positive substituted terminal arenes, in other words, with a better/smaller distribution of the excess positive charge on the 2+2 external ring units, whereas the central TzTz acceptor moiety bears a negative charge.







Figure 2. Relationship between the wavelength of absorption of the lowest energy optical transition (λ_{ge}) and the charge distribution on the ring moieties.

Thermal analysis

The DTTzTz moieties were found to be quite thermally stable, as determined by thermogravimetric analysis (TGA), losing less than 1% of their weight on heating up to 400 °C (Figure S6). The thermal properties of the synthesized compounds were further investigated by differential scanning calorimetry (DSC). The DSC results are depicted in Figure 3 (Th-DTTzTz) and Figure S7 in the Supporting Information. All derivatives displayed pronounced endothermic and exothermic peaks in heating and cooling, ascribed to melting and crystallization, respectively. Th-DTTzTz showed indications of thermally induced side reactions in the DSC experiments. During cooling, crystallization was seen at about 145°C in the first cycle. These crystals melted at about 177 °C in the subsequent heating. When this cooling-heating cycle was repeated, the crystallization peak shifted to lower temperatures, whereas the melting peak remained mostly unchanged, except for a shoulder appearing at lower temperatures. The results after five cycles can be seen in Figure 3 (dashed line). This observation can most likely be explained by a limited amount of undesirable side reactions at more elevated temperatures, as virtually no mass loss is ob-



Figure 1. Sketch of the HOMO (above) and LUMO (below) of the most stable conformer of 4-FC₆H₄-DTTzTz (hexyl side chains were truncated to methyl groups).

Figure 3. DSC thermogram of Th-DTTzTz showing heating and cooling cycles at 20 $Kmin^{-1}$. The dashed line shows the result after 5 cycles.

ChemPlusChem **2012**, 00, 1–9

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served below 400 °C. For comparison, the non-alkylated analogue showed a single high-temperature melting endotherm at 280 °C.^[5a] Introduction of a solubilizing alkyl side chain is indeed expected to lower the T_m value.

The 4-CF₃C₆H₄-DTTzTz material displayed a melting endotherm at 173 °C, whereas the insoluble non-alkylated analogue showed a sharp melting endotherm at 298 °C (Figure S7).^[5c] For **4-FC₆H₄-DTTzTz**, in addition to a melting peak at 188°C and a crystallization peak at 165°C, a broad endotherm and exotherm were noted between -10 °C and 60 °C, in both heating and cooling (Figure S7). This might be ascribed to a transition between a liquid crystalline and crystalline form. Finally, the 4-CNC₆H₄-DTTzTz compound exhibited a sharp exotherm at 161 °C during cooling, in addition to crystallization at 193 °C, adding up to about 54 Jg⁻¹. Upon heating, two very small endothermic peaks were followed by a large melting peak, adding up to 58 Jg^{-1} . At a slower cooling rate of 5 Kmin⁻¹, the exotherm at 161 °C disappeared, but the exothermal enthalpy remained 54 Jg⁻¹. The sharp exotherm at 161 °C probably corresponds to the formation of a less stable polymorph that reorganizes to a more stable form upon heating (Figure S7). In summary, although the four synthesized DTTzTz compounds have the same core structure, their crystallization and melting behavior showed significant differences and is complicated by polymorphism and/or liquid crystalline transitions. The considerably higher transition enthalpy in heating for Th-DTTzTz (50 kJ mol⁻¹) as compared to the other DTTzTz compounds $(22 \text{ kJmol}^{-1} \text{ for } 4-CF_3C_6H_4-DTTzTz, 29 \text{ kJmol}^{-1} \text{ for } 4-FC_6H_4-$ **DTTzTz**, and 39 kJ mol⁻¹ for **4-CNC₆H₄-DTTzTz**) points to a higher crystallinity for Th-DTTzTz (Table S1).

Solution-processed OFET characteristics

Subsequently, the electronic and morphological properties of solution-casted thin films of the functionalized TzTz semiconducting materials were investigated, with the goal to obtain good OFET characteristics. Transistor performance was mainly evaluated by the thin film hole mobility (μ) extracted in the saturation regime and by the threshold voltage (V_T), which are listed in Table 3. For the 4-CNC₆H₄-DTTzTz derivative, several spin-coating conditions were tested (with optimization of concentration, solvent, spin-coating speed, and acceleration), but unfortunately no suitable layers for OFET measurements could be obtained. Although optimized spin-coating conditions were found for $4-CF_{3}C_{6}H_{4}-DTTzTz$ (5 mg mL⁻¹ in 1,2-dichlorobenzene, 3000 rpm, 5000 acc, 60 s), hole mobilities of the films calculated in the saturation regime were found to be only around $2 \times 10^{-6} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. The **4-FC₆H₄-DTTzTz** material showed a slightly better performance for the same optimized spincoating conditions, with a calculated hole mobility of $1 \times$ 10^{-5} cm²V⁻¹s⁻¹. On the other hand, the **Th-DTTzTz** semiconductor afforded a noticeably better FET performance with a hole mobility of $1.58 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (spin-coating conditions: 5 mg mL⁻¹ in 1,2-dichlorobenzene, 3000 rpm, 3000 acc, 60 s).

Figure 4 shows the obtained transfer characteristics for the **Th-DTTzTz** device, with I_{d} , V_{DS} , and V_{GS} values representing the

Table 3. Organic field-effect transistor characteristics of bottom contact devices made from the DTTzTz derivatives.					
DTTzTz	Hole mobility (μ) [cm ² V ⁻¹ s ⁻¹]	$I_{\rm on}/I_{\rm off}$ ratio	Threshold voltage $[V_T]$		
Th 4-FC ₆ H ₄ 4-CF ₃ C ₆ H ₄	$ \begin{array}{r} 1.58 \times 10^{-3} \\ 1 \times 10^{-5} \\ 2 \times 10^{-6} \end{array} $	10⁵ 10⁴ 10³	1.4 -3.4 -2.2		



Figure 4. FET characteristics for a bottom contact device made from **Th-DTTzTz**: I_d and $I_d^{-1/2}$ versus V_{GS} plots at $V_{DS} = -20$ V.

source-drain current, source-drain voltage, and gate voltage, respectively. It must be emphasized that, despite the rather poor film-forming characteristics inherent to small molecules, the **Th-DTTzTz** films showed reasonably high hole mobilities. For the analogous non-alkylated Th-DTTzTz material, processed by vacuum deposition, a mobility of $0.02 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ was reported, that is, one order of magnitude higher.^[5e] From a structural point of view, the best result for the **Th-DTTzTz** derivative does not come as a real surprise, as the additional thiophene unit is expected to increase the hole affinity. On the other hand, film morphology and crystallinity also have a major impact on device performance, and the noticeable differences in thermal properties within the DTTzTz series already hinted to large differences in crystallization tendencies.

Morphology studies

To investigate the molecular organization of the DTTzTz molecules on the transistor surface and evaluate a possible correlation with the observed hole mobilities, X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM) studies were carried out. The observed XRD diffraction patterns are shown in Figure 5. The results were quite similar to earlier reported data for the unsubstituted analogues.^[5a,C] The thin films of **Th-DTTzTz** displayed high crystallinity, with a strong primary diffraction peak, pointing to an ordered crystalline structure. This high crystallinity is likely to be the reason for the high hole mobility observed. On the other hand, the



Figure 5. XRD patterns of thin films of 4-CNC₆H₄-DTTzTz (15.23 nm, red), 4- $\textbf{CF}_{3}\textbf{C}_{6}\textbf{H}_{4}\textbf{-}\textbf{DTTzTz}$ (14.25 nm, green), $\textbf{4-FC}_{6}\textbf{H}_{4}\textbf{-}\textbf{DTTzTz}$ (25.75 nm, black), and Th-DTTzTz (23.60 nm, blue).

crystallinity of the 4-CF₃C₆H₄-DTTzTz and 4-FC₆H₄-DTTzTz derivatives was rather poor, whereas the 4-CNC₆H₄-DTTzTz film showed even less evidence of a crystalline phase.

Figure 6 and Figure 7 show optical microscope and SEM images obtained for the different spin-coated films, revealing large differences in morphology. The Th-DTTzTz films showed



Figure 6. Optical microscope (left) and SEM (right) images of spin-coated thin films of Th-DTTzTz.



Figure 7. SEM images of thin films of 4-CF₃C₆H₄-DTTzTz, 4-FC₆H₄-DTTzTz, and 4-CNC₆H₄-DTTzTz.

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an anisotropic fibrillar morphology (Figure 6). On the other hand, SEM images of solution-processed thin films of 4-CF₃C₆H₄-DTTzTz, 4-FC₆H₄-DTTzTz, and 4-CNC₆H₄-DTTzTz indicated a very different topography, characterized by the presence of partially connected domains, creating a large number of grain boundaries (Figure 7). These morphologies are in sharp contrast to the one observed for Th-DTTzTz, and this profound difference was further confirmed by AFM measurements (Figure 8). The trend in morphology could clearly be



Figure 8. AFM images $(5 \times 5 \ \mu m^2)$ of spin-coated thin films of the DTTzTz derivatives on SiO_2 with a root-mean-square (rms) roughness of (a) 1.9 nm, (b) 0.8 nm, (c) 3 nm, and (d) 1.2 nm.

correlated to the electrical characteristics: the 4-CF₃C₆H₄-DTTzTz, 4-FC₆H₄-DTTzTz, and 4-CNC₆H₄-DTTzTz films were characterized by the absence of crystals on the micrometer scale and exhibited quite poor hole mobilities, whereas the high mobility Th-DTTzTz film showed a fibrillar microcrystalline texture. The significantly higher hole mobility in this case might be related to the presence of intergranular charge transport paths, as boundaries along the fibrils could provide a smaller barrier to charge transport.^[14] The thin films were proven to be (oxidatively) stable, as essentially identical SEM images were obtained after storage for two months.

Vacuum sublimed OFET

For comparison, the most promising molecule from the series, Th-DTTzTz, was also deposited by thermal evaporation in an ultra-high vacuum chamber at a base pressure below 5× 10⁻⁸ Torr. The temperature of the evaporation cell varied between 200 and 220 °C. Transistors were fabricated and were subjected to a surface treatment with pentafluorobenzenethiol and deposition of a self-assembling monolayer of phenylethyltrichlorosilane (PETS). The hole mobilities calculated in the saturation regime were found to be $2 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. Without applying a surface treatment, hole mobilities of only $6 \times$ $10^{-6} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ were achieved. The hole mobility of $1.58 \times$ 10⁻³ cm²V⁻¹s⁻¹ generated in the solution-processed OFET could hence not be reached by vacuum deposition of the

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same material. Although XRD studies showed a high degree of crystallinity in the vacuum deposited films (Figure S8), the SEM images revealed a high number of grain boundaries owing to the presence of a large amount of nanosized domains (Figure 9). These nanocrystals probably result in a reduced mo-



Figure 9. Vacuum sublimed Th-DTTzTz film imaged by (a) AFM (5×5 μm^2), displaying a rms roughness of 14 nm, (b) SEM, (c) 3D AFM.

bility as compared to the fibrillar microcrystals obtained after spin-coating. Furthermore, it cannot be excluded that side reactions occurring during vacuum deposition of the **Th-DTTzTz** material between 200 and 220 °C (compared to the much "softer" conditions for solution processing), as observed in the DSC experiment (Figure 3), might also be (partly) responsible for this reduced mobility.

Conclusion

Aiming for small organic compounds suitable for printable electronics, we have synthesized a family of highly soluble 2,5dithienylthiazolo[5,4-d]thiazole semiconducting materials by a convenient three-step protocol, and studied their thermal, optical, and electrochemical properties. The FET devices were fabricated from these materials by spin-coating active layers from solutions in dichlorobenzene. Despite some difficulties in film formation, the bithiophene-substituted TzTz material (Th-DTTzTz) exhibited a fairly high hole mobility of 1.58× 10^{-3} cm²V⁻¹s⁻¹, thus making it a suitable candidate for solution-processable organic field-effect transistors. The alkyl-substituted Th-DTTzTz showed better self-organization when deposited from solution compared to vacuum deposited layers, resulting in higher hole mobilities. This higher mobility might be linked to the microcrystalline fibrillar structure observed for the solution-casted film, whereas vacuum deposition of the same material afforded a film with multiple nanocrystalline domains. These results clearly show the major effects of both (subtle) structural modifications in organic semiconducting materials and the applied processing conditions on final device performances.

Experimental Section

Materials and methods

Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. NMR chemical shifts (δ , in ppm) were determined relative to the residual CHCl_3 absorption (7.24 ppm) or the $^{13}\mathsf{C}$ resonance shift of CDCl₃ (77.7 ppm). Mass spectra were run using a Thermo Finnigan LCQ Advantage apparatus (electrospray ionization, ESI). Solution UV/Vis absorption measurements were performed at a scan rate of 600 nm min⁻¹ in a continuous run from 200 to 800 nm. Infrared spectra were collected with a resolution of 4 cm^{-1} (16 scans) using films drop-casted on a NaCl disk from a CHCl₃ solution. The XRD measurements were performed with a Bruker D8 discover diffractometer under θ -2 θ conditions. The system works in parafocusing geometry using a Göbel mirror (line focus, mostly $Cu_{K\alpha 1}$ and $Cu_{K\alpha2}$ rays). The X-rays are detected by a 1D detector. Electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 30 potentiostat/galvanostat using 0.1 M Bu₄NPF₆ in anhydrous MeCN as the electrolyte under N2. A three-electrode microcell was utilized containing an Ag/AgNO3 reference electrode (0.1 $\ensuremath{\mathsf{M}}$ AgNO3 and 0.1 $\ensuremath{\mathsf{M}}$ Bu4NPF6 in MeCN), a platinum counter electrode and an indium tin oxide (ITO) coated glass substrate as the working electrode. The respective monomers were dissolved to their maximum solubility in the electrolyte solution. Cyclic voltammograms were recorded at a scan rate of 50 mV s⁻¹. For the conversion to eV, all electrochemical potentials were referenced to a known standard (ferrocene/ferrocenium in MeCN, 0.05 V versus Ag/AgNO₃), which in MeCN solution is estimated to have an oxidation potential of -4.98 V versus vacuum. The DSC measurements were performed at 20 Kmin⁻¹ in aluminum crucibles on a TA Instruments Q2000 Tzero DSC equipped with a refrigerated cooling system (RCS), using nitrogen (50 mLmin⁻¹) as a purge gas. TGA experiments were performed at 50 Kmin⁻¹ in platinum crucibles on a TA Instruments Q5000 TGA using nitrogen (50 mLmin⁻¹) as a purge gas. FET transistors were made on a highly doped Si n^{++} common gate substrate on which 120 nm SiO₂ was thermally grown. Afterwards, Au source/drain bottom contacts were defined by a lift-off process. The measured transistors had a channel width (W) of 5000 µm and a channel length (L) of 10 µm. Substrate cleaning consisted of subsequent rinsing with detergent, deionized water and acetone, followed by submersion in isopropanol. Finally, a 15 min UV-O3 treatment was applied prior to depositing the nicely soluble compounds at room temperature by spin-coating. The FET characteristics were then determined inside a glove box under N₂ with a Hewlett Packard Agilent 4156. SEM images were recorded with a FEI Quanta 200 FEG scanning electron microscope. The topography of the spin-coated and sublimed films was studied by AFM, using a Picoscan PicoSPM LE scanning probe microscope in tapping mode.

Synthesis

2,5-Bis(5'-bromo-3'-hexylthiophene-2'-yl)thiazolo[5,4-*d*]thiazole (**Br-DTTzTz**) and 2,5-bis(4-hexyl-2,2'-bithiophene-5-yl)thiazolo[5,4-*d*]thiazole (**Th-DTTzTz**) were synthesized according to a previously reported procedure.^[12] Material identity and purity for both compounds were confirmed by m.p., MS, ¹H, and ¹³C NMR analysis.

4,4,5,5-Tetramethyl-2-[4-(trifluoromethyl)phenyl]-1,3,2-dioxaborolane was synthesized according to a literature procedure.^[15] Material identity and purity were confirmed by MS and ¹H NMR analysis.

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2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was synthesized according to a literature procedure.^[16] Material identity and purity were confirmed by MS and ¹H NMR analysis.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile was synthesized according to a literature procedure.^[16] Material identity and purity were confirmed by MS and ¹H NMR analysis.

2,5-Bis[5'-(4-fluorophenyl)-3'-hexylthiophen-2'-yl]-thiazolo[5,4-d]thiazole (4-FC_eH₄-DTTzTz). General procedure: A solution of 2-(4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.480 a, 1.76 mmol) in DME (15 mL) was added dropwise to a stirring mixture of 2,5-bis(5'-bromo-3'-hexylthiophene-2'-yl)thiazolo[5,4-d]thiazole (0.450 g, 0.706 mmol) and $[Pd(PPh_{3})_{4}]$ (0.033 g, 28 $\mu mol)$ in DME (20 mL) at ambient temperature. Subsequently, a NaHCO₃ solution (1 m, 25 mL) was added. After stirring for 24 h at 60 °C under N₂ and protected from light, the reaction mixture was diluted with water (50 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (3×50 mL). The combined organic layers were washed with a saturated NaHCO₃ solution and brine, dried over MgSO₄, and concentrated by evaporation in vacuo. The reaction product was purified by column chromatography (silica, eluent hexanes/ethyl acetate 95:5) and recrystallized from ethanol, resulting in red crystals of pure $4-FC_6H_4-DTTzTz$ (0.250 g, 53%). ¹H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 7.60$ (dd, J(H,H) = 9/6 Hz, 4 H), 7.08 (t, J(H,H) = 9 Hz, 4 H), 7.12 (s, 2 H), 2.94 (t, J(H,H) = 8 Hz, 4 H), 1.79-1.69 (m, 4H), 1.49-1.43 (m, 4H), 1.37-1.32 (m, 8H), 0.90 ppm (t, J(H,H) = 7 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃, 25 °C): $\delta = 163.6$, 161.9, 150.9, 145.2, 144.9, 131.9, 130.7, 128.3 (CH), 127.4 (CH), 116.8 (CH), 32.4 (CH₂), 31.1 (CH₂), 30.7 (CH₂), 30.1 (CH₂), 23.3 (CH₂), 14.8 ppm (CH_3); UV/Vis (CHCl_3): λ_{max} (log $\epsilon)\!=\!433$ nm (4.714); MS (ESI): m/z 663 $[M + H^+]$.

2,5-Bis(3'-hexyl-5'-[4-(trifluoromethyl)phenyl]thiophen-2'-yl)thiazolo-[5,4-*d*]thiazole (4-CF₃C₆H₄-DTTzTz). Synthesized according to the general procedure: 4,4,5,5-tetramethyl-2-[4-(trifluoromethyl)phen-yl]-1,3,2-dioxaborolane (1.076 g, 3.96 mmol), 2,5-bis(5'-bromo-3'-hexylthiophene-2'-yl)thiazolo[5,4-*d*]thiazole (1.00 g, 1.58 mmol), [Pd(PPh₃)₄] (0.073 g, 63 µmol), DME (20 + 80 mL), NaHCO₃ (1 м, 65 mL); 0.698 g of red crystals (58% yield). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.73 (d, *J*(H,H) = 9 Hz, 4H), 7.64 (d, *J*(H,H) = 9 Hz, 4H), 7.27 (s, 2H), 2.97 (t, *J*(H,H) = 8 Hz, 4H), 1.81–1.71 (m, 4H), 1.49–1.45 (m, 4H), 1.38–1.33 (m, 8H), 0.90 ppm (t, *J*(H,H) = 6.9 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 161.5, 150.9, 144.7, 143.9, 137.3, 133.0, 130.4, 128.3 (CH), 126.6 (CH), 126.2 (CH), 124.7, 32.3 (CH₂), 31.2 (CH₂), 30.4 (CH₂), 30.1 (CH₂), 23.3 (CH₂), 14.8 ppm (CH₃); UV/Vis (CHCl₃): λ_{max} (log ε) = 434 nm (4.713); MS (ESI): *m/z* 763 [*M* + H⁺].

4,4'-[5,5'-(Thiazolo[5,4-d]thiazole-2,5-diyl)-bis(4-hexylthiophene-5,2diyl)]dibenzonitrile (4-CNC₆H₄-DTTzTz). Synthesized according to the general procedure: 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)benzonitrile (0.420 g, 1.83 mmol), 2,5-bis(5'-bromo-3'-hexylthiophene-2'-yl)thiazolo[5,4-d]thiazole (0.230 g, 0.367 mmol). $[Pd(PPh_{_{3}})_{_{4}}]$ (0.017 g, 15 $\mu mol), DME$ (20 + 50 mL), $K_{_{3}}PO_{_{4}}$ (0.260 g, 1.25 mmol), eluent hexanes/CHCl₃ 20:80; 0.159 g of red crystals (64% yield). ¹H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 7.72$ (d, J(H,H) = 9 Hz, 4 H), 7.67 (d, J(H,H) = 9 Hz, 4 H), 7.30 (s, 2 H), 2.96 (t, J(H,H) = 7.8 Hz, 4 H), 1.80-1.70 (m, 4 H), 1.50-1.45 (m, 4 H), 1.37-1.32 (m, 8H), 0.90 ppm (t, J(H,H) = 6.9 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 161.6, 151.3, 145.0, 143.5, 138.3, 133.8, 133.5 (CH), 129.2 (CH), 126.6 (CH), 119.3, 112.0, 32.3 (CH₂), 31.1 (CH₂), 30.5 (CH₂), 30.1 (CH₂), 23.3 (CH₂), 14.8 ppm (CH₃); IR (NaCl): $\nu_{max} = 2956/2925/2855$ (s, saturated C-H), 2220 cm⁻¹ (m, CN); UV/Vis (CHCl₃) λ_{max} (log ε) = 445 nm (4.777); MS (ESI): *m/z* 677 [*M*+H⁺].

Acknowledgements

We gratefully acknowledge the IWT (Institute for the Promotion of Innovation by Science and Technology in Flanders) for financial support through the SBO-project 060843 "PolySpec". We also acknowledge the European ONE-P project for grant agreement no. 212311, which facilitates the IMEC-IMOMEC collaboration. Furthermore, we gratefully thank BELSPO in the frame of the IAP P6/27 and Phase VII/FS2 networks as well as MINCyT and FRS-FNRS for supporting the Buenos Aires-Namur scientific cooperation. The computational calculations were performed on the Interuniversity Scientific Computing Facility (ISCF) installed at the Facultés Universitaires Notre-Dame de la Paix (FUNDP, Namur, Belgium), for which we acknowledge financial support from the FRS-FRFC (convention no. 2.4.617.07.F), and from the FUNDP. V.L. thanks the FRS-FNRS for his postdoctoral research position. N.V.d.B. and W.M. thank the FWO (Fund for Scientific Research-Flanders) for a doctoral and postdoctoral research mandate, respectively.

Keywords: conducting materials • field-effect transistors • organic electronics • thiazolo[5,4-*d*]thiazoles • thin film morphology

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Received: May 24, 2012 Published online on ■■ ■, 0000

FULL PAPERS

On the move: A series of dithienylthiazolo[5,4-*d*]thiazole (DTTzTz) semiconductors has been synthesized and investigated as active materials in solution-processed organic field-effect transistors. Spin-coated films of one of the derivatives showed a micrometer scale fibrillar texture and high field-effect mobilities $(10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ were observed. This molecule represents the first example of a highly soluble DTTzTz-based small organic compound for which a reasonable FET behavior was observed.



S. Van Mierloo, K. Vasseur, N. Van den Brande, A. E. Boyukbayram, B. Ruttens, S. D. Rodriguez, E. Botek, V. Liégeois, J. D'Haen, P. J. Adriaensens, P. Heremans, B. Champagne, G. Van Assche, L. Lutsen, D. J. Vanderzande,* W. Maes*



Functionalized Dithienylthiazolo[5,4d]thiazoles For Solution-Processable Organic Field-Effect Transistors