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Combined experimental–theoretical NMR study on 2,5-bis(5-aryl-3-hexylthiophen-2-yl)-thiazolo[5,4-*d*]thiazole derivatives for printable electronics

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Four 2,5-bis(5-aryl-3-hexylthiophen-2-yl)thiazolo[5,4-*d*]thiazole derivatives have been synthesized and thoroughly characterized. The extended aromatic core of the molecules was designed to enhance the charge transport characteristics, and solubilizing hexyl side chains were introduced on the thiophene subunits to enable possible integration of these semiconducting small molecules in printable electronics. Complete elucidation of the chemical structures by detailed one-dimensional/two-dimensional NMR spectroscopy is described, providing interesting input for chemical shift prediction software as well, because limited experimental data on these types of compounds are currently available. Furthermore, theoretical calculations have assisted experimental observations—giving support for the chemical shift assignment and providing a springboard for future screening and predictions—demonstrating the benefits of a coordinated theoretical–experimental approach. Copyright © 2012 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: NMR; ^{1}H and ^{13}C NMR chemical shift assignment; density functional theory calculations; thiazolo[5,4-*d*]thiazoles; chemical shift prediction software; printable electronics

Introduction

The development of organic semiconductors for the active layers of field effect transistors (FETs) has received significant attention during recent years.[1] Carefully designed high-performance organic materials are required to achieve high charge carrier mobilities, on/off current ratios, stability, and processability. π-conjugated small molecules such as thiophene oligomers have been shown to possess excellent charge transport characteristics in FETs. A number of structural modifications have been carried out on such (oligo)thiophene compounds so far.[2] Replacement of some of the thiophene units by thiazolo[5,4-*d*]thiazole (TzTz) fused ring systems is reported to be rather effective, resulting in high charge carrier mobilities.[3] The TzTz moiety possesses some important features toward electronic applications. Thiazolo[5,4-*d*] thiazoles are electron-deficient fused heterocycles with a rigid planar structure, which enables efficient intermolecular π-π overlap, and they show enhanced stability toward oxygen.[4,5] Moreover, functionalized TzTz derivatives are easily prepared starting from the corresponding arylcarbaldehydes (e.g. 3-hexylthiophene-2-carbaldehyde) and dithiooxamide.[6,7]

Unfortunately, non-alkylsubstituted TzTz compounds are very poorly soluble and require vacuum deposition techniques for device fabrication. So far, only a few soluble TzTz semiconducting materials have been reported.[4,5] In a previous work, we have decorated the TzTz core with two 3-hexylthiophene moieties.[8] The substitution with alkyl chains obviously leads to a significantly improved solubility in common organic solvents. Here, an extended series of expanded TzTz chromophores is presented, i.e. **D1–D4** (Scheme 1). Functionalization, purification, and characterization were considerably simplified by the introduction of the solubilizing 3-hexylthiophene subunits, and these molecules can hence be utilized in solvent-based processing techniques toward printable electronics. Furthermore, such TzTz materials are also of particular appeal for integration (as acceptor components) in low bandgap copolymers toward highly efficient organic solar cells. The interest in the TzTz structure in this respect has increased spectacularly, noticeably in the last year.[9]

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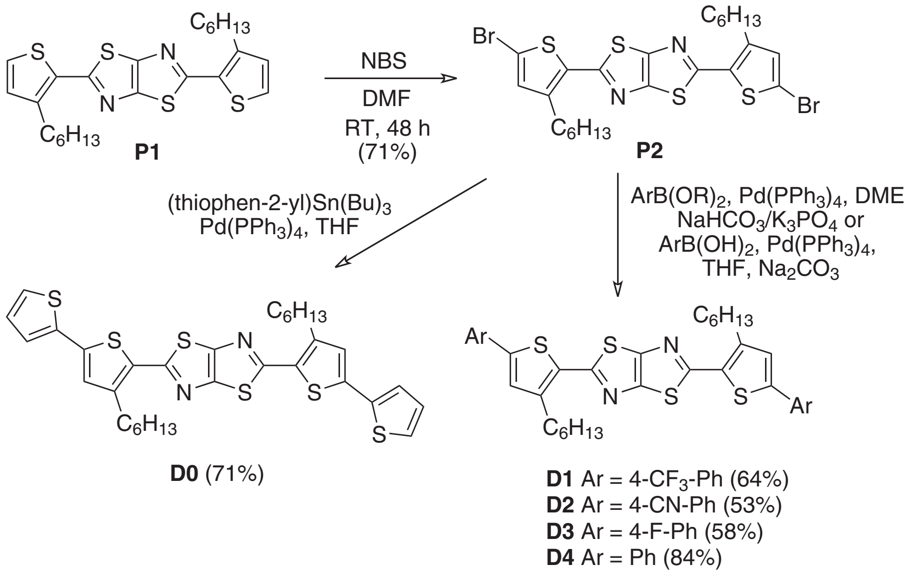

Scheme 1. Synthetic procedures toward TzTz derivatives **D0–D4**.

In this paper, we report the synthesis, detailed hydrogen-1 (^{1}H) and carbon-13 (^{13}C) NMR chemical shift assignment and the correlation of experimental NMR results with theoretical chemical shift calculations for a number of functionalized 2,5-bis(5-aryl-3-hexylthiophen-2-yl)thiazolo[5,4-*d*]thiazole derivatives.

Experimental Section

Synthesis

Detailed synthetic procedures toward TzTz derivatives **D1**, **D2**, and **D3** will be reported elsewhere.[10]

*2,5-Bis(3-hexyl-5-phenylthiophen-2-yl)thiazolo[5,4-d]*thiazole (D4)[11]

Under nitrogen atmosphere, a small amount of Pd(PPh$_3$)$_4$ (6 mg, 5 μmol) was dissolved in tetrahydrofuran (4 ml). 2,5-Bis(5-bromo-3-hexylthiophene-2-yl)thiazolo[5,4-*d*]thiazole (**P2**) (100 mg, 158 μmol), a Na$_2$CO$_3$ solution (2 M, 0.5 ml) and phenylboronic acid (42 mg, 347 μmol) were added to the stirring solution in the mentioned sequence. After heating at reflux temperature for 5 h under nitrogen atmosphere and protected from light, no starting material was observed any more (by thin layer chromatography analysis). After cooling to room temperature, the crude reaction mixture was concentrated under reduced pressure and subsequently diluted with water and CH$_2$Cl$_2$. The organic layer was separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 50 ml). The combined organic layers were washed with a saturated NaHCO$_3$ solution and brine, dried over MgSO$_4$, filtered, and concentrated by evaporation *in vacuo*. The reaction product was purified by gradient column chromatography (silica, eluent CH$_2$Cl$_2$ to CH$_2$Cl$_2$:MeOH 95:5) and recrystallized from ethyl acetate, resulting in 80 mg (84% yield) of red crystalline needles. Gas chromatography–mass spectrometry electron impact (EI): $m/z = 626$ (M$^+$); UV–vis (CHCl$_3$, nm) λ_{max} (log ε) 434 (4.656).

NMR characterization

All ^{1}H and ^{13}C liquid-state NMR experiments were performed at room temperature on a Varian Inova 300 spectrometer (Agilent Technologies, Santa Clara, California, US) in a 5-mm four-nucleus PFG probe. The chemical shift scales are calibrated to CDCl$_3$: ^{1}H = 7.24 ppm and ^{13}C = 77.70 ppm. The proton spectra were acquired with a 90° pulse of 4.3 μs, a spectral width of 4500 Hz, an acquisition time of 3.5 s, a preparation delay of 8 s and 20 accumulations, processed with a line broadening of 0.2 Hz. The concentration of the samples was ~2 mg/0.7 ml. The carbon spectra were acquired with a 90° pulse of 12 μs, a spectral width of 16500 Hz, an acquisition time of 0.8 s, a preparation delay of 60 s and 2500 accumulations, processed with a line broadening of 3 Hz. Higher concentrations were used for the one-dimensional and two-dimensional spectra with ^{13}C detection. The ^{13}C spin-lattice relaxation time (T_{1C}) decay times were measured by the inversion recovery method, using 17 recovery time increments between 0.01 and 70 s (80 accumulations; preparation delay of 60 s). With regard to DEPT, a full 'ADEPT' editing was performed on the basis of an array of spectra taken with $\theta = 45°$, 90° and 135° as tip angles for the final proton pulse (40 accumulations; preparation delay of 20 s). COSY spectra were taken with 256 indirect time increments (eight accumulations; preparation delay of 2 s). Short-range (direct) HETCOR experiments were acquired with 96 indirect time increments (eight accumulations; preparation delay of 2 s; optimized for $^1J_{C-H} = 140$ Hz). Long-range HETCOR experiments were acquired with 96 indirect time increments (120 accumulations; preparation delay of 10 s; optimized for $^nJ_{C-H} = 8$ Hz).

Computational procedure

The ground state geometries were optimized at the density functional theory (DFT) level of approximation by employing the B3LYP exchange-correlation (XC) functional and the 6-31 G* basis set. For convenience, the *n*-hexyl substituents have been replaced by smaller methyl groups. The chemical shifts (δ) of all systems were calculated as the difference of isotropic shielding constants (σ) with respect to TMS. All σ values were obtained with the B3LYP XC functional and the 6-311 + G(2d,p) basis set together with the Gauge invariant (or including) atomic orbital method to ensure origin independence, following the approach that was employed and tested recently for polyvinyl chloride oligomers, fluoroionophores, and poly(thienylene vinylene) model compounds.[12] As shown in these previous studies as well as in related ones,[13] linear fits between experimental and theoretical δ values of representative model compounds can facilitate the interpretation of the NMR spectra of more complex and larger compounds and can therefore provide a way of correcting the calculated properties from systematic errors. Preliminary investigations on PTV model compounds have been reported before,[12d] and the theoretically estimated δ values were obtained from the calculated values by using the following relationships (in ppm):

$$sp^2 \text{ in } \alpha \quad {}^{13}\mathrm{C}: \delta(\text{estimated}) = 0.8099\delta[\text{IEF}-\text{PCM/B3LYP/6}-311+\text{G(2d, p)}]+15.39 \tag{1a}$$

$${}^{1}\mathrm{H}: \delta(\text{estimated}) = 0.8653\delta[\text{IEF}-\text{PCM/B3LYP/6}-311+\text{G(2d, p)}]+0.67 \tag{1b}$$

$$sp^2 \text{ in } \beta \quad {}^{13}\mathrm{C}: \delta(\text{estimated}) = 0.7618\delta[\text{IEF}-\text{PCM/B3LYP/6}-311+\text{G(2d, p)}]+27.61 \tag{2a}$$

$${}^{1}\mathrm{H}: \delta(\text{estimated}) = 0.8845\delta[\text{IEF}-\text{PCM/B3LYP/6}-311+\text{G(2d, p)}]+0.61 \tag{2b}$$

$$\text{other } sp^2 \; {}^{13}\mathrm{C}: \delta(\text{estimated}) = 0.6510\delta[\text{IEF}-\text{PCM/B3LYP/6}-311+\text{G(2d, p)}]+40.36 \tag{3a}$$

$${}^{1}\mathrm{H}: \delta(\text{estimated}) = 0.8911\delta[\text{IEF}-\text{PCM/B3LYP/6}-311+\text{G(2d, p)}]+0.52 \tag{3b}$$

$$\text{other atoms } {}^{13}\mathrm{C}: \delta(\text{estimated}) = 0.9618\delta[\text{IEF}-\text{PCM/B3LYP/6}-311+\text{G(2d, p)}]-2.66 \tag{4a}$$

$${}^{1}\mathrm{H}: \delta(\text{estimated}) = 0.9451\delta[\text{IEF}-\text{PCM/B3LYP/6}-311+\text{G(2d, p)}]+0.12 \tag{4b}$$

As discussed in Ref. 12d, a single equation for correcting all ^{1}H or all ^{13}C chemical shifts turns out to be insufficient. First, we have made the distinction between the sp^2 C atoms (and the H atoms linked to them) and the other hybridizations (other atoms). Then, the sp^2 atoms (C and the H attached to them) have been classified into three categories, those of the thiophene rings (where α and β refer to the position with respect to the S atoms) and the other ones (other sp^2). Therefore, for both the H and C atoms, we have four equations, associated with different combinations of hybridization/position, and all the theoretical chemical shifts reported in this paper have been corrected by the appropriate linear regression equation. Solvent (here $CHCl_3$) effects were taken into account within the integral equation formalism of the polarizable continuum model (IEF-PCM)[14] for the calculations of the isotropic shielding constants of all compounds (including TMS). The δ[IEF-PCM/B3LYP/6-311 + G(2d,p)] values consist in the Maxwell–Boltzmann average chemical shifts over the stable conformers on the basis of the energies calculated at the B3LYP/6-31 G* level of theory with the inclusion of solvent effects. Each torsion angle between adjacent rings is characterized by two minima, close to values of 0° and 180°. Therefore, taking into account the molecular symmetry, we end up with 16 conformers for **D0**, but only four for **D1–D4**. The Maxwell–Boltzmann weights are given in the supplementary material Table S1. All calculations were performed using Gaussian09.[15]

Results and Discussion

Synthesis

The common precursor for the reported TzTz semiconductors, 2,5-bis(3-hexylthiophen-2-yl)thiazolo[5,4-*d*]thiazole (**P1**), was synthesized in moderate yield (47%) via a condensation reaction at elevated temperature (200 °C) between dithiooxamide and an excess of 3-hexylthiophene-2-carbaldehyde,[8] prepared according to a modified literature procedure (Scheme 1).[6,7] The resulting product mixture required extensive purification (column chromatography and two successive recrystallizations from ethanol and acetonitrile) to convert the black crude residue into pure yellow crystals of **P1**. After subsequent dibromination with *N*-bromosuccinimide (71% yield), the final TzTz derivatives **D1**, **D2**, **D3**, and **D4** were obtained through Suzuki cross-coupling reactions with the respective boronic acids or esters (Scheme 1).[10] The dithienyl-substituted TzTz counterpart **D0** has previously been prepared by an analogous Stille protocol.[8] The cross-coupling reactions were in general very effective, main product losses occurring during the tedious material purification (by repetitive recrystallization and column chromatography), affording highly pure materials for device applications.

NMR characterization

To confirm the identity and purity of the novel thiazolo[5,4-*d*]thiazole derivatives, they were analyzed by mass spectrometry and NMR.[10] NMR spectroscopy confirmed that TzTz's **D0–D4** were obtained in excellent purity. Complete assignment of the ^{1}H and ^{13}C resonances was achieved by a combination of regular ^{1}H and ^{13}C NMR spectra with attached proton test (APT), DEPT, T_{1C} inversion recovery experiments, COSY, and short/long-range HETCOR experiments. Table 1 presents an overview of all signal assignments for **D0–D4**. The complete NMR analysis of TzTz **D0** has previously been reported.[8] Such a detailed analysis is useful because the obtained chemical shift information can be helpful in further research on TzTz moieties, for instance by implementation in NMR-based prediction software. To date, experimental NMR data on TzTz compounds, and resonance assignments in particular, are very scarce. The chemical structures of TzTz compounds **D1–D4** differ only in the aryl substituents on the thiophene rings. Figure 1 provides an arbitrary numbering scheme for the different carbon and hydrogen atoms of the TzTz derivatives **D0–D4**.

Assignment of the resonances of TzTz ***D1***

In a previous work, all ^{1}H and ^{13}C NMR resonances of the precursors **P1** and **P2**, and TzTz derivative **D0** were assigned.[8] This knowledge readily allowed the assignment of the carbon signals of **D1** at 161.5, 150.9, 144.7 and 133.0 ppm to the non-protonated carbon atoms C2, C1, C4 and C3 of the fixed core, respectively. The presence of the three ^{19}F nuclei on the *para*-trifluoromethyl

Table 1. Chemical shifts (ppm) and assignments of the proton and carbon resonances for thiazolo[5,4-*d*]thiazole derivatives **D0–D4**. The chemical shift scales are calibrated to $CDCl_3$: $^1H = 7.24$ ppm and $^{13}C = 77.70$ ppm. The assignment of the chemical shifts for TzTz **D0** was retrieved from previous work [8]

	D0	**D1**	**D2**	**D3**	**D4**		**D0**	**D1**	**D2**	**D3**	**D4**
	Ar Thien-2-yl	Ar *p*-CF_3-Ph	Ar *p*-CN-Ph	Ar *p*-F-Ph	Ar Ph		Ar = Thien-2-yl	Ar *p*-CF_3-Ph	Ar *p*-CN-Ph	Ar *p*-F-Ph	Ar Ph
Carbon						*Proton*					
C1	150.7	150.9	151.3	150.9	150.7		—	—	—	—	—
C2	161.5	161.5	161.6	161.9	161.8		—	—	—	—	—
C3	131.0	133.0	133.8	131.9	131.7		—	—	—	—	—
C4	144.5	144.7	145.0	145.2	144.7		—	—	—	—	—
C5	127.6	128.3	129.2	127.4	127.3	H-5	7.00 (s)	7.27 (s)	7.30 (s)	7.12 (s)	7.20 (*s*)
C6	137.3	143.9	143.5	144.9	146.1		—	—	—	—	—
C7	31.1	31.2	31.1	31.1	31.2	H-7	2.88 (t)	2.97 (t)	2.96 (t)	2.94 (t)	2.96 (*t*)
C8	30.5	30.4	30.5	30.7	30.5	H-8	1.71 (p)	1.76 (p)	1.75 (p	1.74 (p)	1.75 (q)
C9	30.1	30.1	30.1	30.1	30.1	H-9	1.45 (p)	1.48 (p)	1.47 (p)	1.47 (p)	1.47 (q)
C10	32.3	32.3	32.3	32.4	32.3	H-10	1.34 (m)	1.35 (m)	1.35 (m)	1.35 (m)	1.35 (m)
C11	23.3	23.3	23.3	23.3	23.3	H-11	1.34 (m)	1.35 (m)	1.35 (m)	1.35 (m)	1.35(m)
C12	14.8	14.8	14.8	14.8	14.8	H-12	0.90 (t)	0.90 (t)	0.90 (t)	0.90 (t)	0.90 (t)
C13	139.4	137.3	138.3	130.7 (d)	134.1		—	—	—	—	—
C14	125.2	126.2	126.6	128.3 (d)	126.4	H-14	7.22 (dd)	7.73 (d)	7.72 (d)	7.60 (dd)	7.64 (dd)
C15	128.8	126.6 (q)	133.5	116.8 (d)	129.7	H-15	7.02 (dd)	7.64 (d)	7.67 (d)	7.08 (dd)	7.39 (t)
C16	126.0	130.4 (q)	112.0	163.6 (d)	128.9	H-16	7.24 (dd)	—	—	—	7.31 (t)
C17		124.7 (q)	119.3				—	—	—	—	—

substituent, affording quadruplet ^{13}C resonance patterns under broadband proton-decoupling, was very helpful for further assignments. The nonprotonated carbon atom C17 has a chemical shift at 124.7 ppm (split into a quadruplet with lines at 130.1, 126.5, 122.9, and 119.2 ppm due to the direct $^1J_{C-F}$ coupling with coupling constant of 272 Hz). The $^2J_{C-F}$ coupling of 33 Hz was also clearly identifiable in the quadruplet with chemical shift of 130.4 ppm (131.1, 130.6, 130.2, and 129.8 ppm) arising from C16. Finally, a $^3J_{C-F}$ coupling of 3.5 Hz allowed to locate the chemical shift of C15 at 126.6 ppm (Fig. 2). The proton signal at 7.64 ppm could be assigned to H-15 via a short-range (^1J or direct coupling) HETCOR experiment.

The aromatic region of the ^1H NMR spectrum presents three resonance patterns corresponding to the ten aromatic protons of **D1**: an AB-system[16] consisting of H-15 (7.64 ppm) and H-14 (7.73 ppm; $^3J = 9.0$ Hz) and a singlet resonance at 7.27 ppm from the thiophene protons H-5. A short-range HETCOR experiment then allowed to determine the chemical shifts of C5 (128.3 ppm) and C14 (126.2 ppm). This left only two unidentified chemical shifts (137.3 and 143.9 ppm) for two nonprotonated aromatic carbons, C6 and C13. A long-range HETCOR experiment (Fig. 3) showed a clear correlation between H-15 and the carbon signal at 137.3 ppm which can only arise from the ^3J-coupling between H-15 and C13. Indeed, H-15 is too far (four bonds) from C6 to show

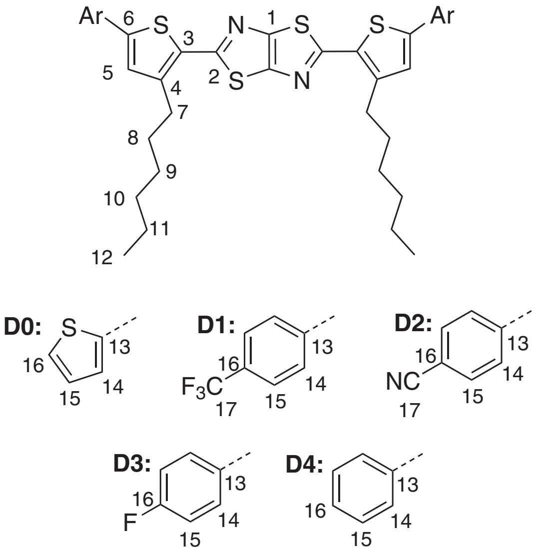

Figure 1. Arbitrary numbering scheme for 2,5-bis(5-aryl-3-hexylthiophen-2-yl)thiazolo[5,4-*d*]thiazole derivatives **D0–D4**. The different carbon atoms are numbered from C1 to C17, and the different hydrogen atoms are labeled accordingly from H-5 to H-16.

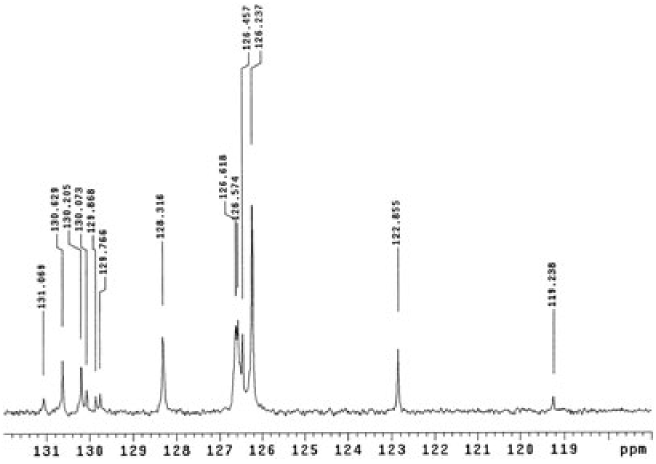

Figure 2. Part of the aromatic region of the ^{13}C NMR spectrum of **D1**.

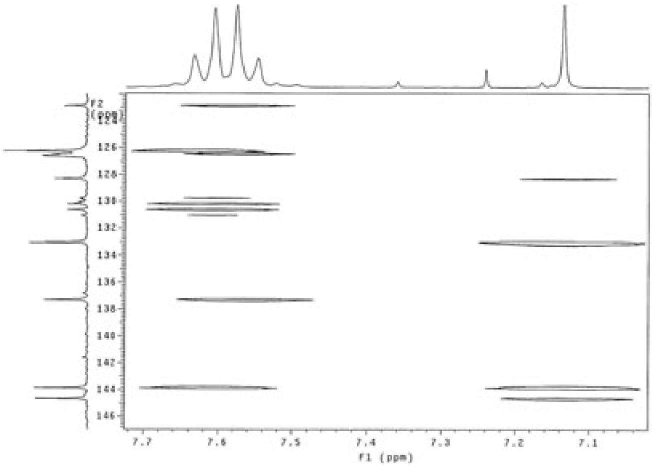

Figure 3. Long-range HETCOR ($J = 8$ Hz) spectrum of **D1**.

a correlation.[17] The remaining carbon signal at 143.9 ppm correlates with H-5 and H-14, confirming its assignment to C6. Figure 3 shows additional confirmative correlations (e.g. C4–H5, C3–H5, C16–H14, C17–H15) which are not discussed in detail. The assignment of the alkyl side chain carbon atoms was based on COSY and short-range HETCOR experiments as described in our previous paper.[8] Most assignments could be confirmed by T_{1C} experiments (Table 2). Taking the through-space dipole–dipole interaction as the main mechanism for relaxation, the T_{1C} relaxation of small molecules in solution (situated in the so-called extreme narrowing region) is mainly determined by the correlation time of motion (τ_c) and the distance to surrounding proton magnetic dipoles ($1/T_{1C}$ has a $1/r^6$ dependency to proton spins). Proton magnetic moments induce, due to molecular motions, local oscillating magnetic fields in the neighborhood of the carbon atoms, the source of T_{1C} relaxation.[18] With regard to the nonprotonated TzTz core carbon atoms (C1, C2, C3, C4, and C6—with similar τ_c), the decay times are determined by the spatial distance to the nearest protons (a longer distance corresponding to a longer decay time). With regard to the carbon atoms of the mobile hexyl side chains (with a similar distance to protons), the closer the carbon is situated toward the end of the side chain, the longer its relaxation decay time will become because of less restricted conformational motions.[13] This is obvious for C7 and C12 which have the shortest and longest T_{1C} decay time of the side-chain carbon atoms, respectively. The short-range HETCOR spectrum allowed the assignment of the proton signals of the bonded protons, and this was confirmed by a COSY experiment.

*Assignment of the resonances of TzTz **D2***

Carbon peaks at 151.3, 161.6, 133.8, and 145.0 ppm could be assigned to C1, C2, C3, and C4, respectively, on the basis of the previous attributions for the precursors **P1** and **P2** and the TzTz derivative **D0**.[8] The aromatic region of the ^{1}H NMR spectrum again showed three resonance patterns corresponding to the ten aromatic protons of **D2**: an AB-system consisting of H14/H15 (7.72/7.67 ppm; $^3J = 9$ Hz) and a singlet resonance at 7.30 ppm for the thiophene protons H-5. A short-range HETCOR experiment allowed to assign the carbon signal at 129.2 ppm to C5 (128.3 ppm). This left six aromatic carbon atoms at 143.5, 138.3, 126.6, 133.5, 112.0, and 119.3 ppm, for which an APT spectrum (and integration) showed that the signals at 126.6 and 133.5 ppm arose from methine carbon atoms. On the basis of the chemical shift and T_{1C} decay time, the carbon signal at 143.5 ppm could be assigned to C6. Indeed, the long-range HETCOR experiment (Fig. 4) revealed a ^3J coupling between this carbon resonance and the proton resonance at 7.72 ppm, next to a ^2J coupling with the proton resonance at 7.30 ppm (H-5). This allowed to assign the proton signal at 7.72 ppm to H-14. Confirmation could be found in C4 (145.0 ppm), which only correlates to H-5 because it is too far (5 bonds) from H-14. The remaining

Table 2. ^{13}C spin-lattice relaxation time (T_{1C}) relaxation decay times (s), determined by the inversion recovery method, for the carbon atoms of thiazolo[5,4-*d*]thiazole derivatives **D0–D2** and **D4**. T_{1C} data for TzTz **D0** were retrieved from previous work[8]

	D0	T_{1C}	**D1**	T_{1C}	**D2**	T_{1C}	**D4**	T_{1C}
	Ar = Thien-2-yl	(s)	Ar *p*-CF$_3$-Ph	(s)	Ar *p*-CN-Ph	(s)	Ar Ph	(s)
Carbon								
C1	150.7	9.3	150.9	8.55	151.3	11.32	150.7	10.28
C2	161.5	6.7	161.5	6.00	161.6	7.29	161.8	6.81
C3	131.0	7.8	133.0	6.82	133.8	8.67	131.7	8.32
C4	144.5	3.3	144.7	2.74	145.0	3.64	144.7	3.80
C5	127.6	0.40	128.3	0.23	129.2	0.35	127.3	0.43
C6	137.3	6.1	143.9	3.85	143.5	5.48	146.1	4.65
C7	31.1	0.50	31.2	0.39	31.1	0.43	31.2	0.48
C8	30.5	0.71	30.4	0.51	30.5	0.55	30.5	0.69
C9	30.1	1.00	30.1	0.73	30.1	0.86	30.1	0.96
C10	32.3	1.67	32.3	1.24	32.3	1.50	32.3	1.58
C11	23.3	2.32	23.3	1.95	23.3	2.28	23.3	2.35
C12	14.8	3.12	14.8	2.95	14.8	2.97	14.8	2.98
C13	139.4	4.00	137.3	2.51	138.3	4.05	134.1	3.62
C14	125.2	0.63	126.2	0.41	126.6	0.52	126.4	0.76
C15	128.8	0.63	126.6 (q)	0.46	133.5	0.46	129.7	0.69
C16	126.0	0.41	130.4 (q)	3.42	112.0	3.98	128.9	0.41
C17			124.7 (q)	4.26	119.3	1.32		

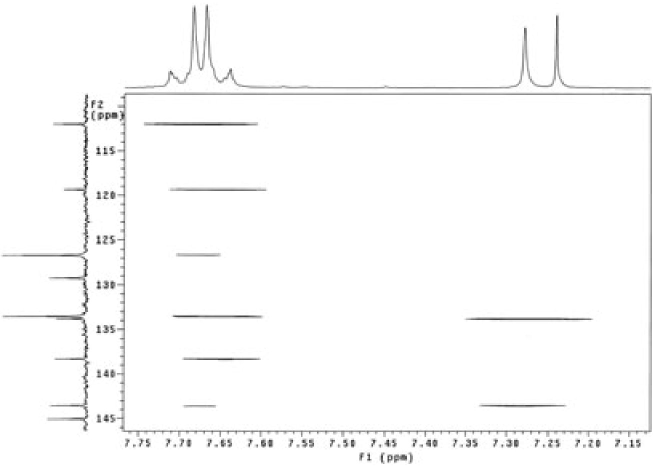

Figure 4. Long-range HETCOR ($J = 8$ Hz) spectrum of **D2**.

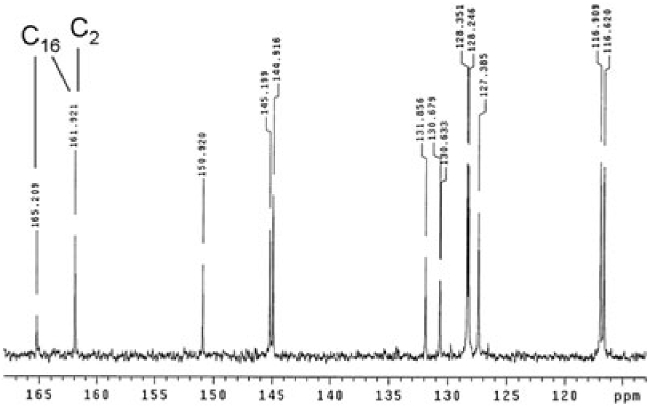

Figure 5. Aromatic region of the ^{13}C NMR spectrum of **D3**.

aromatic proton signal at 7.67 ppm could then be assigned to H-15. The carbon signals at 126.6 and 133.5 ppm could be attributed to C14 and C15, respectively, on the basis of a short-range HETCOR experiment. Taking the electron-withdrawing effect of the –CN functional group into account, the reduced electron density at C15 corresponds with its downfield chemical shift (as compared with C14). In the long-range HETCOR experiment, the ^{13}C signal at 112.0 ppm presented a correlation with H14 (7.72 ppm; ^3J coupling) and H-15 (7.67 ppm; ^2J coupling) and therefore could be assigned to C16 (Fig. 4). In agreement with previous TzTz derivatives, C13 could be assigned to the carbon signal at 138.3 ppm, whereas C17 resonates at 119.3 ppm. The latter is fully in agreement with literature.[19] Figure 4 shows additional confirmative correlations (e.g. C17-H15, C14-H14, C15-H15, C3-H5, C13-H5) which are not discussed further in detail. The alkyl side-chain assignment was again based on COSY, short-range HETCOR, and T_{1C} experiments, as reported earlier and previously.[8]

*Assignment of the resonances of TzTz **D3***

As 4-fluorophenyl-substituted TzTz **D3** was found to be somewhat less soluble in $CDCl_3$, NMR spectra were acquired at a slightly elevated temperature (45 °C). The carbon peaks at 150.9, 161.9, 131.9, and 145.2 ppm could be attributed to the fixed core carbon atoms C1, C2, C3, and C4, respectively, based on the T_{1C} relaxation data (Table 2) and previous assignments.[8] The ^{19}F nucleus gave rise to doublet resonance patterns in the proton-decoupled ^{13}C NMR spectrum (Fig. 5). The nonprotonated carbon atom C16 appeared as a doublet (165.2 and 161.9 ppm) with chemical shift centered at 163.6 ppm because of a direct $^1J_{C\text{–}F}$ coupling of 248 Hz (remark that the signal of C2 overlaps with the high-field line of the doublet). C15 also showed a doublet with chemical shift centered at 116.8 ppm (116.9 and 116.6 ppm) because of a $^2J_{C\text{–}F}$ coupling of 22 Hz. Furthermore, C14 and C13 could be attributed to the doublets with chemical shifts at 128.3 and 130.7 ppm, based on their $^3J_{C\text{–}F}$ and $^4J_{C\text{–}F}$ couplings of 8.5 and 3.4 Hz, respectively (Fig. 5). Taking the electron-donating effect of the –F functional group into account, the increased electron density at C15 corresponds with its low-frequency chemical shift (as compared with C14). C5 was the only protonated aromatic carbon atom remaining and could hence easily be assigned by DEPT to the signal at 127.4 ppm. A short-range HETCOR correlated C5 to the proton singlet of H-5 at 7.12 ppm.

The alkyl side-chain assignment was again based on COSY, short-range HETCOR, and T_{1C} experiments. The only remaining carbon signal at 144.9 ppm therefore corresponded to C6. Besides the H-5 singlet, the aromatic region of the ^{1}H NMR spectrum showed two additional resonance patterns, originating from the *p*-F-Ph ring protons, which could be assigned on the basis of the *J* coupling patterns: a doublet of doublets at 7.60 ppm ($^3J_{H\text{–}H} = 9$ Hz, $^4J_{H\text{–}F} = 6$ Hz) and an 'apparent' triplet at 7.08 ppm ($^3J_{H\text{–}H}$ and $^3J_{H\text{–}F} = 9$ Hz; overlap with H-5 at 7.12 ppm). The short-range HETCOR experiment (Fig. 6) confirmed these assignments: the carbon signal at 116.8 ppm (C15) correlated with the 7.08 ppm 'triplet' of H-15, whereas the 128.3 ppm peak (C14) correlated with the double doublet at 7.60 ppm of H-14.

*Assignment of the resonances of TzTz **D4***

The carbon resonances at 161.8, 150.7, 131.7, and 144.7 ppm are again attributed to the fixed TzTz core carbon atoms C1, C2, C3, and C4, respectively, based on the T_{1C} relaxation data (Table 2) and previous assignments for **D0**.[8] The aromatic region of the ^{1}H NMR spectrum showed four resonance patterns originating from the four aromatic protons of **D4**, which could easily be interpreted on the basis of *J* coupling patterns and integration values; the doublet at 7.65/7.62 ppm ($^3J = 7.3$ Hz, 4H) to H-14, the triplet centered at 7.39 ppm ($^3J = 7.3$ Hz, 4H) to H-15 and the triplet

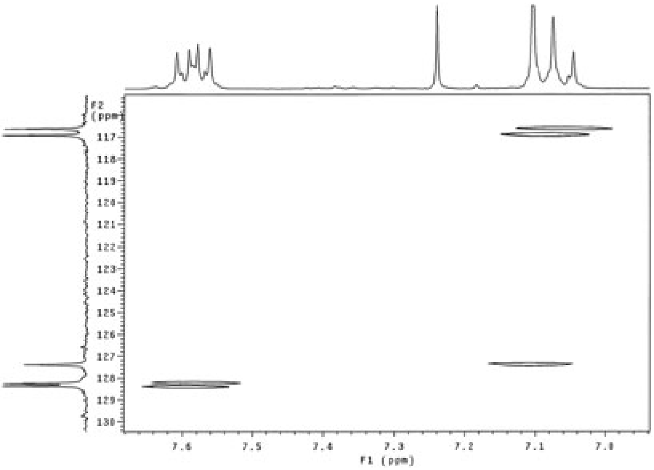

Figure 6. Short-range HETCOR ($J = 140$ Hz) spectrum of **D3**.

centered at 7.31 ppm ($^3J = 7.3$ Hz, 2H) to H-16. The COSY spectrum revealed cross-peaks confirming these assignments. The only remaining aromatic proton signal could be observed as a singlet resonating at 7.20 ppm and corresponded to the thiophene protons (H-5). From the short-range HETCOR experiment (Fig. 7), it could be derived that the methine carbon signals at 129.7, 128.9, 127.3, and 126.4 ppm belong to C15, C16, C5, and C14, respectively. This left two unassigned aromatic carbon signals at 146.1 and 134.1 ppm. A long-range HETCOR experiment (Fig. 8) further revealed that the aromatic carbon signal at 146.1 ppm is coupled with both H-14 and H-5, allowing to assign it to C6 as C4 is too remote (five bonds) from H-14. C4 only correlates to the aromatic proton H-5. The remaining carbon signal at 134.1 ppm could then be attributed to C13. The assignment of the alkyl side-chain carbon resonances was based on the same protocol as described earlier for **D1–D3**.

In general, only subtle changes in NMR chemical shifts were observed for the TzTz core and hexyl side-chain carbon atoms of the differently substituted 2,5-dithienyl-TzTz derivatives **D0–D4** (Table 1). The most noticeable difference is the deshielding of the thiophene proton for *p*-CF$_3$-phenyl and *p*-CN-phenyl derivatives **D1** and **D2**, as compared with the reference compound **D4**, and the upfield shift for the *p*-F-phenyl TzTz **D3** (Table 1). More pronounced differences were, of course, observed within the respective aryl substituents, most notably for the *ipso* and *ortho* aromatic carbon resonances, reflecting the nature of the appended functional groups.

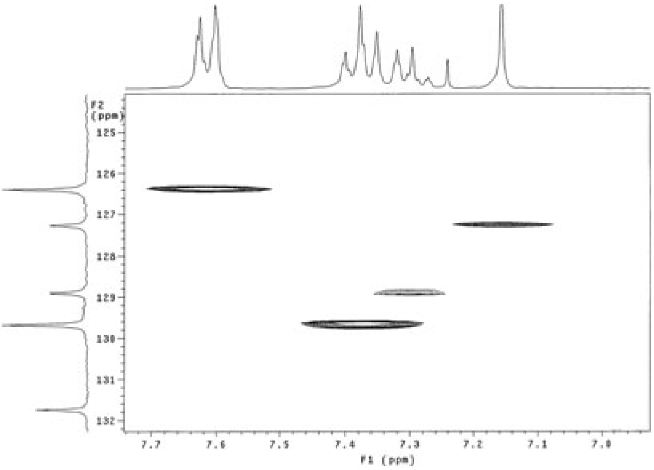

Figure 7. Short-range HETCOR ($J = 140$ Hz) spectrum of **D4**.

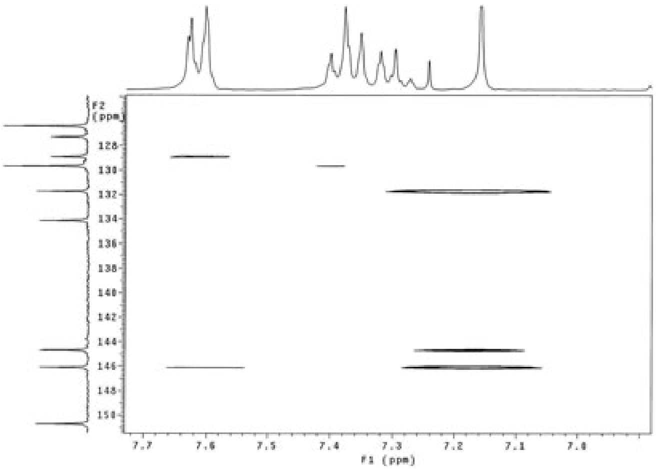

Figure 8. Long-range HETCOR ($J = 8$ Hz) spectrum of **D4**.

Theoretical characterization

Table 3 presents the calculated chemical shifts as well as the corrected mean absolute errors (CMAE), obtained after using Eqs 1–4 (in the Experimental section), with respect to the experimental values given in Table 1. The calculated values are in good agreement with the experimental data and confirm the chemical shift assignments. More precisely, when the chemical shifts display a dependence with respect to the substituents (aromatic carbon atoms C5, C6, C13, C14, C15, and C16), the calculations correctly reproduce the chemical shift trends, demonstrating they account for different electron donating and withdrawing effects. This is further illustrated in Table 4 where the differences of the calculated chemical shifts for derivatives **D1–D3** are reported (the differences between the experimental data are also given in parentheses) with respect to derivative **D4** (Ar = Ph), which is taken as a reference. For instance, C16 becomes more deshielded in derivative **D3** because of the inductive attractor effect of the F atom, whereas it becomes more shielded in derivative **D2** because of anisotropy of the triple C–N bond. The change of chemical shifts of C15 can be explained by the mesomeric donor (derivative **D3**) and attractor (derivative **D2**) effects. There are also a number of cases where the differences between the experimental and calculated values remain large, even after linear regression correction, but they can be explained to a large extent. δ(C4) is underestimated because the hexyl chain is replaced by a methyl group in the calculations. For C16 and C17, the predictions are also of lesser quality as a result of the close proximity to heteroatoms, especially the electron withdrawing F and CN groups, and the fact that our approach has not been fitted specifically for these carbon atoms. However, the CMAE values are smaller than 3.0 ppm for ^{13}C NMR and smaller than 0.1 ppm for ^{1}H NMR, which is a double support for the experimental assignment and the method reliability.

Conclusion

A series of soluble aryl-substituted 2,5-dithienylthiazolo[5,4-*d*]thiazole semiconductors was efficiently synthesized by Suzuki cross-coupling reactions. Complete NMR chemical shift assignment for these materials was accomplished by means of a number of one-dimensional and two-dimensional NMR experiments. Computational chemistry has been used as an additional tool to confirm the experimental NMR data. The calculated chemical shift trends are generally consistent with the inductive, mesomeric, and anisotropic effects imposed by the substituents, and a few signatures were identified enabling straightforward screening of various (unknown) TzTz compounds in the future. The gathered chemical shift data are of relevance for chemical shift prediction software, because limited experimental data on TzTz derivatives are currently available. This will be particularly interesting because a spectacular increase in the application of TzTz semiconducting molecules can be seen from literature in the last year, notably in organic photovoltaics. The acquired knowledge will also strongly support further (ongoing) research within our groups on TzTz-

Table 3. Theoretical chemical shifts (ppm) for thiazolo[5,4-*d*]thiazole derivatives **D0–D4**. TMS was taken as a reference and its calculated σ values are 31.31 ppm and 183.33 ppm for ^{1}H and ^{13}C, respectively. All values have been calculated at the IEF-PCM/B3LYP/6-311 + G(2 d,p) level of theory with CHCl$_3$ as a solvent and have been corrected by the linear regression Eqs 1–4. The differences between the calculated and experimental (Table 1) chemical shifts are given in parentheses

	D0	D1	D2	D3	D4		D0	D1	D2	D3	D4
	Ar = Thien-2-yl	Ar *p*-CF$_3$-Ph	Ar *p*-CN-Ph	Ar *p*-F-Ph	Ar Ph		Ar = Thien-2-yl	Ar *p*-CF$_3$-Ph	Ar *p*-CN-Ph	Ar *p*-F-Ph	Ar Ph
Carbon						*Proton*					
C1	149.8 (−0.9)	150.4 (−0.5)	150.6 (−0.7)	149.8 (−1.1)	149.8 (−0.9)		—	—	—	—	—
C2	158.8 (−2.7)	159.3 (−2.2)	159.3 (−2.3)	159.2 (−2.7)	159.2 (−2.6)		—	—	—	—	—
C3	131.9 (+0.9)	135.2 (+2.2)	136.0 (+2.2)	133.6 (+1.7)	133.5 (+1.8)		—	—	—	—	—
C4	140.7 (−3.8)	140.1 (−4.6)	140.5 (−4.5)	140.4 (−4.8)	140.6 (−4.1)		—	—	—	—	—
C5	129.1 (+1.5)	130.5 (+2.2)	131.4 (+2.2)	129.4 (+2.0)	129.8 (+2.5)	H-5	7.11 (+0.11)	7.33 (+0.06)	7.36 (+0.06)	7.16 (+0.04)	7.19 (−0.01)
C6	139.4 (+2.1)	143.2 (−0.7)	142.7 (−0.8)	144.4 (−0.5)	145.5 (−0.6)		—	—	—	—	—
C13	138.0 (−1.4)	135.3 (−2.0)	135.8 (−2.5)	130.3 (−0.4)	132.5 (−1.6)		—	—	—	—	—
C14	126.4 (+1.2)	126.4 (+0.2)	126.5 (−0.1)	127.9 (−0.4)	126.9 (+0.5)	H-14	7.36 (+0.14)	7.74 (+0.01)	7.73 (+0.01)	7.63 (+0.03)	7.64 (+0.00)
C15	129.2 (+0.4)	126.9 (+0.3)	132.2 (−1.3)	119.7 (+2.9)	128.4 (−1.3)	H-15	7.03 (+0.01)	7.63 (−0.01)	7.69 (+0.02)	7.16 (+0.08)	7.48 (+0.09)
C16	126.5 (+0.5)	129.8 (−0.6)	115.9 (+3.9)	153.5 (−10.1)	128.1 (−0.8)	H-16	7.31 (+0.07)				7.46 (+0.15)
C17		129.4 (+4.7)	120.6 (+1.3)				—	—	—	—	—
CMAE	1.5	1.8	2.0	2.7	1.7		0.08	0.02	0.03	0.05	0.07

CMAE, corrected mean absolute errors.

Table 4. Differences of the theoretical chemical shifts (ppm) between thiazolo[5,4-*d*]thiazole derivatives **D1–D3** and **D4** (taken as a reference). All values have been calculated at the IEF-PCM/B3LYP/6-311 + G(2d,p) level of theory with CHCl$_3$ as a solvent and have been corrected by the linear regression Eqs 1–4. Bold (italic) values represent important deshielding (shielding) effects with respect to the chemical shifts of **D4** (Ar Ph). The corresponding experimental values are given in parentheses

	D1	D2	D3		D1	D2	D3
	Ar *p*-CF$_3$-Ph	Ar *p*-CN-Ph	Ar *p*-F-Ph		Ar *p*-CF$_3$-Ph	Ar *p*-CN-Ph	Ar *p*-F-Ph
Carbon				*Proton*			
C1	0.6 (+0.2)	0.8 (+0.6)	0.0 (+0.2)		—	—	—
C2	0.1 (−0.3)	0.1 (−0.2)	0.0 (+0.1)		—	—	—
C3	**1.8 (+1.3)**	**2.5 (+2.1)**	0.2 (+0.2)		—	—	—
C4	−0.5 (+0.0)	−0.1 (+0.3)	−0.2 (+0.5)		—	—	—
C5	0.7 (+1.0)	**1.6 (+1.9)**	−0.4 (+0.1)	H-5	**0.14 (+0.07)**	**0.18 (+0.10)**	−0.03 (−0.08)
C6	*−2.2 (−2.2)*	*−2.8 (−2.6)*	*−1.0 (−1.2)*		—	—	—
C13	**2.9 (+3.2)**	**3.3 (+4.2)**	*−2.2 (−3.4)*		—	—	—
C14	−0.5 (−0.2)	−0.4 (+0.2)	**1.1 (+1.9)**	H-14	0.09 (+0.09)	0.08 (+0.08)	−0.02 (−0.04)
C15	*−1.5 (−3.1)*	**3.8 (+3.8)**	*−8.7 (−12.9)*	H-15	**0.15 (+0.25)**	**0.21 (+0.28)**	*−0.33 (−0.31)*
C16	**1.7 (+1.5)**	*−12.2 (−16.9)*	**25.4 (+34.7)**		—	—	—

based semiconductors and narrow bandgap copolymers toward applications in organic electronics.

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