

Synthesis, Structures, and Properties of Fused Thiophenes for Organic Field-Effect Transistors

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Abstract: A series of fused thiophenes composed of fused α -oligothiophene units as building blocks, end-capped with either styrene or 1-pentyl-4-vinylbenzene groups, has been synthesized through Stille coupling reactions. The compounds have been fully characterized by means of ^1H NMR spectrometry, high-resolution mass spectrometry, and elemental analysis. The molecules present a *trans-trans* configuration between their double bonds, which has been verified and confirmed by Fourier-transform infrared spectroscopy and single-crystal X-ray diffraction analysis. The X-ray crystal structures showed π -

π overlap and sulfur-sulfur interactions between the adjacent molecules. The decomposition temperatures were all found to be above 300°C, indicating that compounds of this series possess excellent thermal stability. The fact that no phase transition occurs at low temperature indicates that they should be well-suited for application in devices. Moreover, they possess low HOMO energy levels, based on cyclic

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voltammetry measurements, and suitable energy gaps, as determined from their thin-film UV/Vis spectra. Thin-film X-ray diffraction analysis and atomic force microscopy revealed high crystallinity on supporting substrates. In addition, as the substrate temperature has a significant influence on the morphology and the degree of crystallinity, the device performance could be optimized by varying the substrate temperature. These materials were found to exhibit optimal field-effect performance, with a mobility of $0.17\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ and an on/off ratio of 10^5 , at a substrate temperature of 70°C.

Introduction

In recent years, organic field-effect transistors (OFETs), the critical components of future organic electronics, have attracted a lot of interest as a low-cost alternative to conventional silicon transistors for electronic applications.^[1] The design and synthesis of novel materials to improve the key OFET performance, including carrier mobility, on/off ratio, and threshold voltage, are major challenges in organic semiconductor research. Organic semiconductors such as penta-

cene have shown superior field-effect performance and mobilities in excess of $1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$.^[2] Thiophene-based materials have been considered as promising candidates for organic semiconductors and are proposed to have good OFET performance due to various intra- and intermolecular interactions, including weak hydrogen bonding, π - π stacking, and sulfur-sulfur interactions.^[3] Oligothiophenes consisting of α -linked thiophene units (α -oligothiophenes, α -nT) and derivatives thereof have been widely used in OFETs.^[3c, 4] However, these oligomers can easily twist from planarity, thus decreasing conjugation through torsion about single bonds, which may potentially affect the band gap in the solid state.^[5] An effective approach to resolving this problem is to combine the stability of the thiophene ring with the planarity of linear acenes to produce thienoacenes.^[3a, b, 6] Fused thiophenes can be regarded as fused α -oligothiophenes and their derivatives. Linearly condensed thiophenes give the most extended π -conjugation and the highest planarity. In addition, efficient intermolecular S...S interactions in the fused thiophenes may contribute to carrier transport. Therefore, the exploration of organic semiconductors based on fused thiophenes would appear to be highly promising.

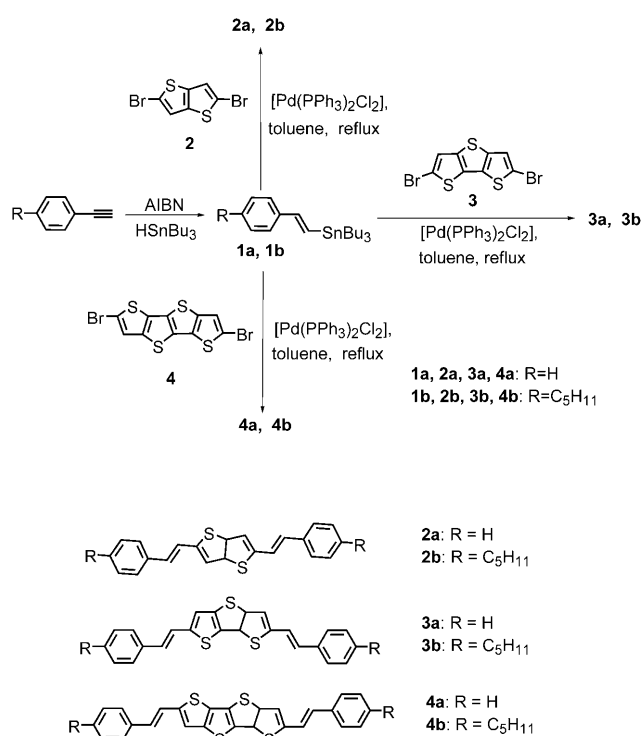
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In our research aimed at finding superior semiconductors, we have focused our attention on fused thiophenes and have successfully synthesized a series of high-performance organic semiconductors.^[7] Fused α -oligothiophenes based on thieno[3,2-*b*]thiophene (TT) and dithieno[3,2-*b*:2',3'-*d*]thiophene (DTT) represent versatile and effective molecular scaffolds in the design of organic semiconductors. However, semiconductors containing thieno[3,2-*b*]thieno[2',3':4,5]-thieno[2,3-*d*]thiophene (TTA) have scarcely been studied.^[7c,8] A series of new organic semiconductors has been synthesized, which have fused α -oligothiophene units as the building blocks, end-capped with either styrene or 1-pentyl-4-vinylbenzene groups. Double bonds in the backbones of these materials facilitate π -electron delocalization and extend the effective conjugation length of the system.^[9] Several research groups have developed semiconductors with high performance by selecting conjugated vinylene-based compounds.^[10] In the current work, some organic semiconductors have been designed and synthesized by varying the degree of fusion in a series of fused thiophenes. The products may represent a new family of candidate materials for use in OFETs. These semiconductors display good polycrystalline film-forming properties, and the molecules are oriented in an orderly manner with a π - π stacking direction parallel to the substrate. Their properties ensure that OFETs based on these materials will exhibit high device performance, which has been verified by device fabrication and measurement. An identical approach has been followed to synthesize six target compounds by Stille coupling reactions.^[11] The building blocks were synthesized in a specific manner by oxidative couplings. Scheme 1 shows the chemical structures of the fused thiophenes end-capped with styrene (**2a**, **3a**, and **4a**) and 1-pentyl-4-vinylbenzene (**2b**, **3b**, and **4b**), and the synthetic route used to obtain them. The products have been characterized by high-resolution mass spectrometry, ¹H NMR spectrometry, Fourier-transform infrared spectroscopy, and elemental analysis. Their photoelectronic properties have been probed by UV/Vis spectrophotometry, fluorescence spectroscopy, and cyclic voltammetry.

Results and Discussion

Synthesis: The key building blocks were synthesized by an approach involving a combination of cross-coupling reactions and oxidative couplings. TT was obtained in 52 % yield in six steps starting from 3-bromothiophene and was converted into 2,5-dibromo-thieno[3,2-*b*]thiophene **2** by treatment with two equivalents of *N*-bromosuccinimide (NBS) in CHCl₃.^[12] DTT was obtained in 25 % yield in two steps from 2,3-dibromothiophene.^[13] The synthetic route used to prepare TTA^[14] started from 3-bromothiophene[3,2-*b*]thiophene.^[12] The same methodology was implemented for the synthesis of 2,6-dibromodithieno[3,2-*b*:2',3'-*d*]thiophene **3**^[13b] and 2,6-dibromodithieno[3,2-*b*]thieno[2',3':4,5]thiophene **4**^[7c] using two equivalents of NBS in CHCl₃. (*E*)- β -Tributyl-



Scheme 1. Synthetic routes to **2a–4a** and **2b–4b**.

(styryl)stannane (**1a**) was prepared by the reaction of phenylacetylene with tributyltin hydride (Bu₃SnH) catalyzed by azobis(isobutyronitrile) (AIBN).^[15] Similarly, reaction of 4-pentylphenylacetylene with Bu₃SnH in the presence of AIBN gave (*E*)- β -tributyl[2-(4-pentylphenyl)vinyl]stannane (**1b**). The subsequent [Pd(PPh₃)₂Cl₂]-catalyzed Stille couplings of the appropriate stannyl and bromo compounds used to synthesize the six fused thiophenes are shown in Scheme 1. Palladium-catalyzed Stille coupling of **2** with **1a** by refluxing for 12 h in toluene solution afforded **2a** in 70 % yield. Likewise, Stille coupling of **2** with the corresponding **1b** afforded **2b** in 73 % yield. **3a** and **3b** were synthesized through an analogous procedure in 65 and 70 % yield, respectively. **4a** and **4b** derived from TTA were prepared by Stille couplings of **4** with the corresponding compounds **1a** and **1b** in 70 and 63 % yield, respectively. One of the greatest challenges was the purification of the compounds because homo-couplings of the stannyl and bromo compounds occurred as side reactions in all of the syntheses. After the obtained materials had been purified by multiple Soxhlet extraction using methanol and acetone, they were further purified by threefold gradient sublimation under vacuum. They were all obtained as yellow solids and were found to be slightly soluble in THF, chloroform, toluene, and chlorobenzene. Their chemical structures were determined by EI-MS or MALDI-TOF MS, ¹H NMR spectrometry, Fourier-transform infrared (FTIR) spectroscopy, and elemental analyses. Single-crystal X-ray structure determinations of two of the target compounds confirmed the proposed structures.

None of the compounds could be characterized by ^{13}C NMR spectroscopic analysis due to their poor solubility.

Thermal properties: The thermal properties of the new fused thiophenes were evaluated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The onset of decomposition temperatures, **2a** (317°C), **2b** (345°C), **3a** (343°C), **3b** (359°C), **4a** (350°C), and **4b** (389°C), increase with the extent of thiophene ring fusion and on adding the alkyl-substituted groups. There is no doubt that extension of the conjugation of the fused α -oligothiophenes and attachment of the alkyl-substituted groups improved the thermal stability.^[16] The DSC traces of **2a** and **4a** did not show any obvious endothermic peaks between 0 and 285°C in either the heating or cooling cycles, but those of **2b**, **3a**, and **3b** displayed single endothermic peaks at 144°C, 288°C, and 221°C, respectively. The DSC trace of **4b** showed two endothermic melting peaks at 216°C and 265°C. The former was strong with high enthalpy, while the latter was relatively weak with low enthalpy. As identified by polarized optical micrography, some solid–solid phase transitions of **4b** occurred at both endothermic peaks, although an isotropic phase was not observed before the decomposition temperature. The fact that the onset decomposition temperatures of all of the fused thiophenes are above 300°C shows that they have excellent thermal stability, and the absence of any phase transitions at low temperatures indicates that this series of compounds should be well-suited for application in devices.

Molecular and single-crystal structures: The effect of molecular conformation and packing property in single crystals on charge-carrier transport is one of the fundamental issues for organic semiconducting materials. Single crystals of **3a** were obtained by slow evaporation of the volatiles from a solution in methanol/toluene (2:1), while those of **4a** were obtained by slow sublimation in a temperature-gradient furnace. Unfortunately, no single crystals of the compounds **2a**, **2b**, **3b**, and **4b** could be obtained. X-ray diffraction studies were performed on the crystals of **3a** and **4a** to determine their solid-state structures. Figure 1 shows that the molecular structure of **3a** has a twisted geometry, with the central DTT core not lying in the same plane with a torsion angle of 130° along its long axis. The angle by which the benzene rings in **3a** are displaced from the plane of the long axis is 9.86°. In contrast, the molecular backbone of the TTA core in **4a** is almost flat, and the angle by which the benzene rings are displaced from the mean plane is 7.55°. As expected, the geometric structures of **3a** and **4a** display a *trans–trans* configuration between their double bonds, which may increase the mobility of the charge carriers.^[17] We assumed that the other compounds **2a**, **2b**, **3b**, and **4b** would have a similar *trans–trans* molecular configuration, confirmation of which was provided by the results of a subsequent FTIR spectroscopy study. The unit cells of the derivatives are shown in Figure 2. Each unit cell contains two layers along the *c*-axis direction, such that one half of the *c*-axis length,

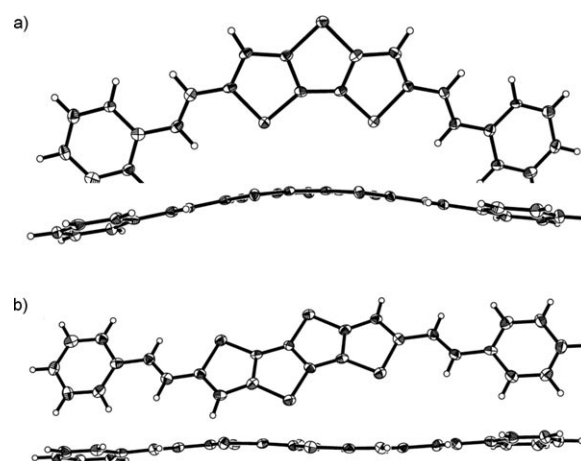


Figure 1. Front and side views of the molecular structures of a) **3a** and b) **4a** with 50% probability ellipsoids.

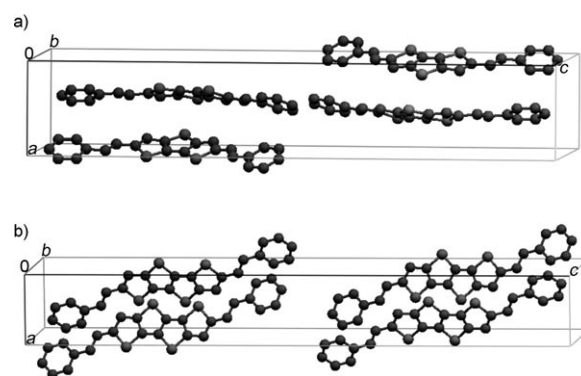


Figure 2. Stereographic views of unit cells of molecules a) **3a** and b) **4a** (hydrogen atoms have been omitted for clarity).

21.14 and 22.90 Å for **3a** and **4a**, respectively, corresponds to the width of each layer. In Figure 3, it can be seen that the molecules are packed to form a sheet-like array, in which short S...S contacts are observed. The intermolecular short S...S contact in the *bc* plane of the sheet-like array of **3a** has a distance of 3.44 Å, while that in the *ac* plane of **4a** has a distance of 3.42 Å. Intermolecular S...S contacts increase the effective dimensionality of the electronic structure and are beneficial to charge transport. The molecular sheets are piled up and form a columnar stacking with an interplanar separation of 2.23 Å (**3a**) in the *b*-axis direction and 2.20 Å (**4a**) in the *a*-axis direction. The interaction between the stacks is reinforced by the close intermolecular S...S contacts. Such packing is similar to that of other fused thiophenes.^[3a,18] Both molecules display a nearly flat, symmetric molecular geometry, which facilitates tight molecular packing. The molecules pack in a herringbone geometry, similar to those of pentacene^[19] and most fused thiophenes,^[20] and the tilt angle between the two molecular planes is 37.13° in **3a** and 43.08° in **4a**.

It was important to identify the configurations of the other four compounds (**2a**, **2b**, **3b**, and **4b**), because isomer-

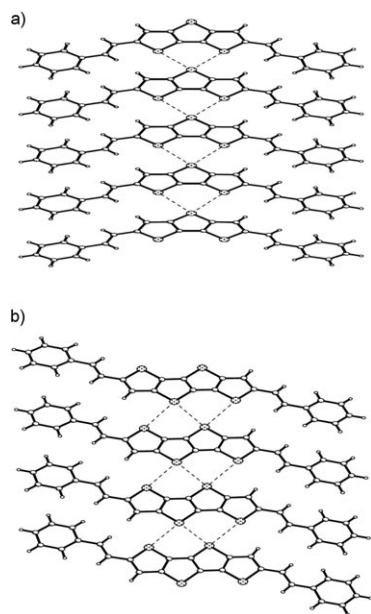


Figure 3. Stacking patterns in the crystals: a) **3a**: view along the *a* axis; b) **4a**: view along the *b* axis. For clarity, only one sheet-like array of molecules ($0.5 < c < 1.0$) is depicted. Intermolecular S...S interactions are indicated with dotted lines.

ization about double bonds often occurs during thermal evaporation and deposition processes. The six compounds were purified by gradient sublimation under vacuum. Therefore, it was necessary to verify that all of the molecules retained the same *trans* configuration. This was confirmed by FTIR spectroscopy (see Figure 4). The FTIR spectra of each of the six molecules featured a strong absorption band at $\approx 946\text{ cm}^{-1}$, which corresponds to an out-of-plane bending vibration of a *trans*-vinylene C–H bond.^[17,21] No bands due to *cis*-vinylene C–H bonds in the region $\approx 882\text{--}862\text{ cm}^{-1}$ were observed in the spectra. It was thus established that all of the compounds exhibit *trans*–*trans* conjugation, which is favorable for ordering in the solid state. This was important and gratifying as even a small percentage of *cis*-isomers may prevent good organization in thin films and hence decrease the mobility of charge carriers. From Figure 4, it can be seen that the monosubstituted phenyl ring (**2a**, **3a**, and **4a**) gives rise to a characteristic absorption band at $\approx 698\text{ cm}^{-1}$, while no band due to the 1,4-disubstituted phenyl ring (**2b**, **3b**, and **4b**) is observed in this region.^[22]

Optical and electrochemical properties: The UV/Vis absorption spectra of the compounds in dilute THF solution and of vacuum-deposited thin films on quartz substrates are shown in Figure 5. In solution, the compounds show redshifts of their absorption peaks with increasing degree of fusion of the α -oligothiophene units. For the compounds sharing the same building block (**2a** and **2b**, **3a** and **3b**, **4a** and **4b**), the absorption spectra in solution of the 1-pentyl-4-vinylbenzene-substituted compounds exhibit a small redshift and a similar peak shape to the spectra of the styrene-substituted compounds. On comparing the solid-state and solution spec-

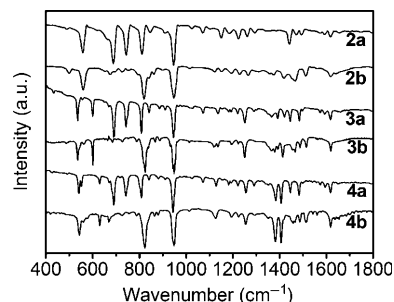


Figure 4. FT-IR spectra of **2a**, **2b**, **3a**, **3b**, **4a**, and **4b**.

tra, the former are blue-shifted because the molecules adopt a herringbone packing motif that leads to H aggregation.^[23,24] This is usually related to excitonic coupling between adjacent molecules in a closely packed structure. We conclude that there are strong interactions between neighboring molecules in the film. The optical band gaps E_g (2.53 eV (**2a**), 2.52 eV (**2b**), 2.40 eV (**3a**), 2.58 eV (**3b**), 2.37 eV (**4a**), and 2.41 eV (**4b**)) were determined by extrapolating the long-wavelength absorption edges, λ_{onset} ($E_g = 1240/\lambda_{\text{onset}}$ eV), of their vacuum-deposited thin-film spectra.

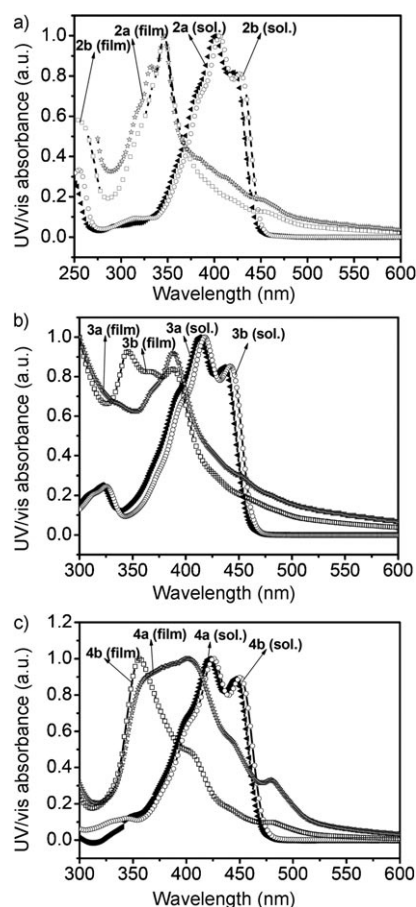


Figure 5. Normalized UV/Vis absorption spectra in THF solution (sol.) and in the solid state (film).

In order to understand the charge-transport properties, to assess the ionization potentials (hole-injecting ability), and to verify the electrochemical stability of the compounds, cyclic voltammetry (CV) measurements were performed. We used a conventional three-electrode cell with Pt working electrodes, a platinum wire counter electrode, and an Ag/AgCl reference electrode in THF solution at room temperature. Compounds **2a–4a** underwent an irreversible oxidation process between 1.13 and 1.16 V, while the oxidations of **2b–4b** were partially reversible and appeared at 0.95 V versus Ag/AgCl. No reduction potentials of the six compounds below zero voltage could be observed, as shown in Figure 6. The ionization potentials (E_{HOMO} ; HOMO: highest occupied molecular orbital) of π -conjugated systems can be estimated by using the equation $E_{\text{HOMO}} = -(4.40 + E_{\text{ox}}^{\text{onset}})$ eV.^[25] $E_{\text{ox}}^{\text{onset}}$ is the onset potential for oxidation. The values of $E_{\text{ox}}^{\text{onset}}$ for **2a**, **2b**, **3a**, **3b**, **4a** and **4b** of 1.03, 0.73, 0.99, 0.82, 0.96, and 0.74 V, corresponding to estimated E_{HOMO} levels of -5.43 , -5.13 , -5.39 , -5.22 , -5.36 , and -5.14 eV, respectively, are indicative of good electrochemical stability. It is worthy of note that these HOMO levels match the work function of gold metal (-5.2 eV), so that hole injection from a gold source electrode in a p-type OFET can be expected to be efficient. All of the studied compounds have lower-lying HOMO energy levels and larger band gaps than pentacene ($E_{\text{HOMO}} = -4.60$ eV, $E_{\text{g}} = 2.21$ eV), suggesting that they should show better stabilities towards oxygen under ambient conditions.^[26]

Studies on thin films: Thin films (of thickness about 50 nm) of the materials on *n*-octadecyltrichlorosilane (OTS)-modified SiO₂/Si substrates at different substrate temperatures were investigated by means of thin-film X-ray diffraction (XRD) analysis and atomic force microscopy (AFM). Figure 7 shows the X-ray diffraction patterns of the six films at different substrate temperatures (T_{sub}), which indicate that they show their best mobilities at 70 °C (for **2a**, **3a**, and **3b**) and 100 °C (for **2b**, **4a**, and **4b**). All of the XRD patterns exhibit strong and sharp diffraction peaks with multiple orders of reflection, which is indicative of a preferred orientation of the molecules in the films with high crystallinity on the substrates. Compared to the pentyl-substituted **2b–4b**, compounds **2a–4a** exhibit stronger and sharper primary peaks, indicating that these molecules are perfectly oriented in the crystal grains. The first strong reflection peak in the XRD pattern of a film of **3a** at $2\theta \approx 4.11^\circ$ corresponds to a d -spacing of 21.4 Å (see Figure 7c), which is coincident with the length of the molecule (21.1 Å) determined by single-crystal XRD experiments. This suggests that the molecules of **3a** are arranged with their long axes almost perpendicular to the substrate, with the π – π stacking direction parallel to the substrate, in which case the charge carriers would transport easily with high mobilities.^[27] The molecules of **4a** pack in the same manner as those of **3a**. The first strong reflection peak in the XRD pattern of a film of **4a** at $2\theta \approx 3.82^\circ$ corresponds to a d -spacing of 23.1 Å, coincident with the length of the molecule (22.9 Å). The diffraction peaks of **3a** and **4a** correspond well with those observed by powder

XRD, revealing that the molecules in the films pack in the same manner as in the crystalline state. This orientation is known to be favorable for achieving high mobility since the stacking structure increases the intermolecular π -overlap^[28] and the stacking direction is also consistent with the direction of current flow.^[29] We assume that **2a** adopts a similar thin-film structure because the monolayer thickness of films (19.5 Å) determined by thin-film XRD measurements is coincident with the length of the molecule (19.5 Å) calculated by ChemDraw 3D and optimized by Material Studio 3.0. However, the tilt angles of films of **2b–4b** deposited from the vapor phase are not easily deduced from the X-ray diffractograms because of the absence of the first reflection peak. Figure 8 shows atomic force microscopy

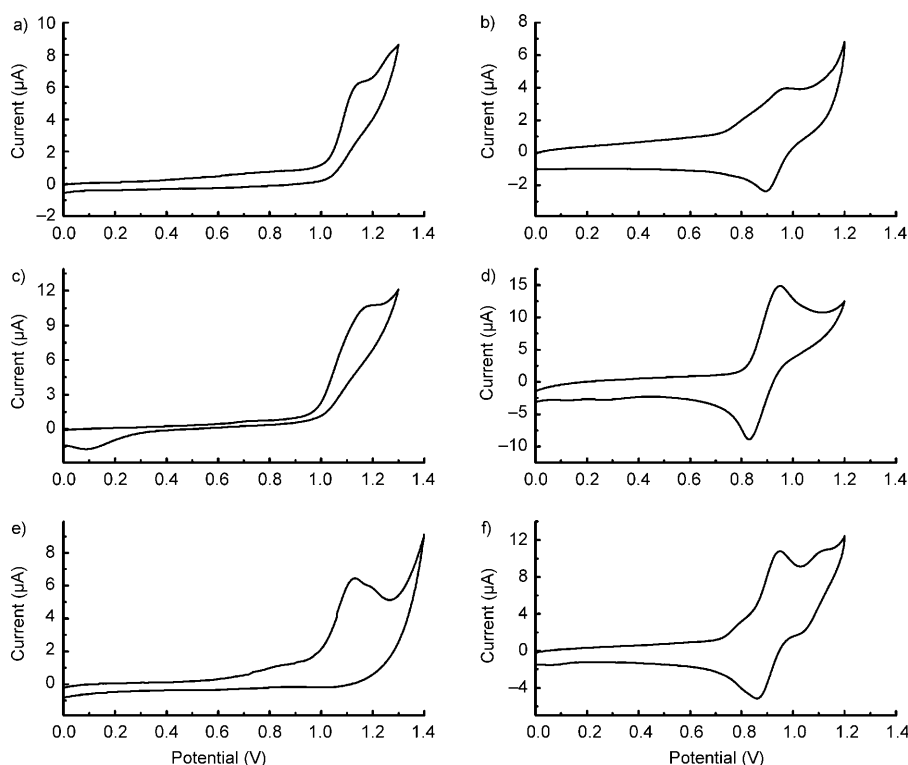


Figure 6. Cyclic voltammograms measured at a scan rate of 100 mV s^{−1} in 0.1 M Bu₄NPF₆ in THF. a) **2a**, b) **2b**, c) **3a**, d) **3b**, e) **4a**, f) **4b**.

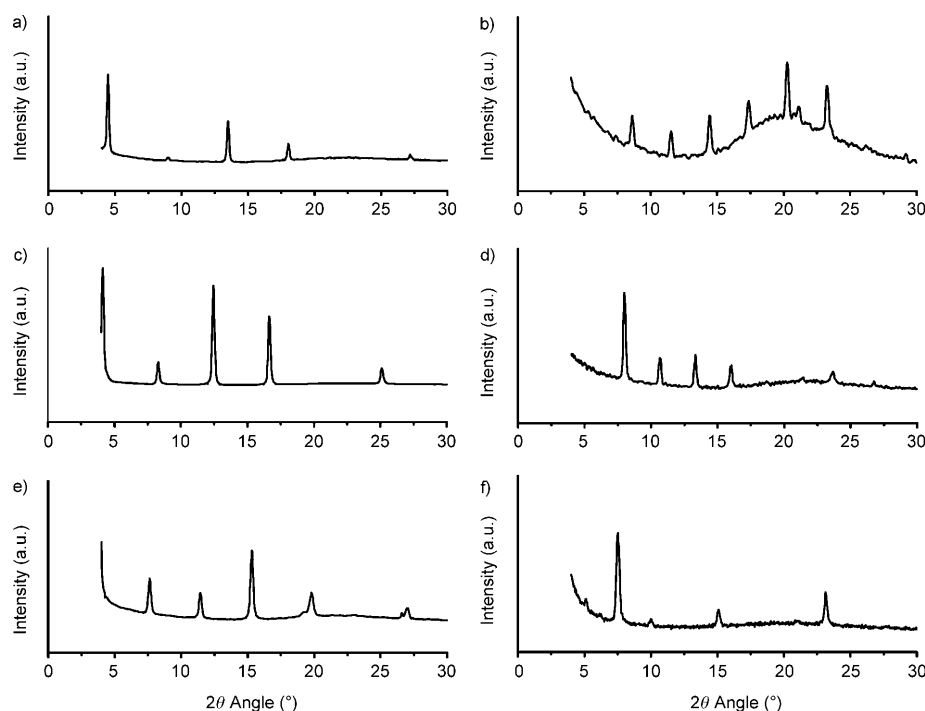


Figure 7. Thin-film X-ray diffractograms of a) **2a** ($T_{\text{sub}}=70^{\circ}\text{C}$), b) **2b** ($T_{\text{sub}}=100^{\circ}\text{C}$), c) **3a** ($T_{\text{sub}}=70^{\circ}\text{C}$), d) **3b** ($T_{\text{sub}}=70^{\circ}\text{C}$), e) **4a** ($T_{\text{sub}}=100^{\circ}\text{C}$), and f) **4b** ($T_{\text{sub}}=100^{\circ}\text{C}$).

(AFM) images of thin films deposited on SiO_2/Si substrates. The AFM images of **2a–4a** all show plate-like grains consisting of flat terraces. In particular, the thin film of **3a** was seen to consist of large plate-like and interconnected polycrystalline grains of several microns on the substrate at 70°C , which should facilitate carrier transport and thus result in superior transport properties. For the alkyl-substituted compounds **2b–4b**, the AFM image of **3b** reveals a mixture of rod-like and plate-like grains. The grain sizes of **2b** and **4b** are smaller and inter-grain connection is less extensive than that in **3b**. This trend in the morphologies is consistent with the fluctuation trends in the μ_{FET} values, those of **2a–4a** being higher than those of the alkyl-substituted **2b–4b** (the μ_{FET} values are in the order: **2a** $\approx$ **2b**, **3a** $>$ **3b**, **4a** $>$ **4b**).

OFET device performance: Devices were fabricated by vacuum deposition on OTS-treated SiO_2/Si substrates at various temperatures. Their performances were measured in a top-contact configuration (drain and source electrodes deposited above the semiconductor) with Au electrodes. The performances were measured in air and the results are shown in Table 1. Typical field-effect transistor output and transfer characteristics using **3a** as the active semiconductor are presented in Figure 9. All of the OFET devices exhibited p-type operation.

It was observed that the OFET performance of each compound depended on the temperature of the substrate. When **2b** was deposited at a substrate temperature of 100°C , the resultant device showed a mobility of $0.04\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Re-

cently, better performance of **2b**, with a mobility of up to $0.15\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, has been obtained at $T_{\text{sub}}=60^{\circ}\text{C}$.^[30] Although the introduction of alkyl chains at the longitudinal ends of semiconducting molecules has previously proved to be a promising approach for improving OFET characteristics,^[31] in our case, the *n*-pentyl groups had no beneficial effect on performance. The styrene end-capped fused thiophenes (**3a**, **4a**) exhibited superior device performance compared to the corresponding 1-pentyl-4-vinylbenzene end-capped fused thiophenes (**3b**, **4b**) under the same device fabrication conditions. For example, the best OFET of **3a** exhibited a μ_{FET} more than ten times higher than that of **3b** (0.17 versus $0.013\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), while the μ_{FET} of **4a** was four

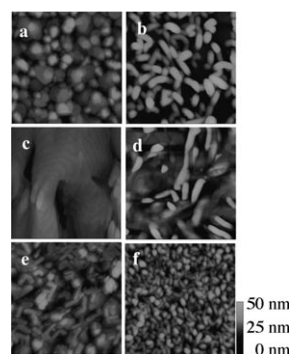


Figure 8. $2\times 2\text{ }\mu\text{m}^2$ AFM images at different substrate temperatures: a) **2a** ($T_{\text{sub}}=70^{\circ}\text{C}$), b) **2b** ($T_{\text{sub}}=100^{\circ}\text{C}$), c) **3a** ($T_{\text{sub}}=70^{\circ}\text{C}$), d) **3b** ($T_{\text{sub}}=70^{\circ}\text{C}$), e) **4a** ($T_{\text{sub}}=100^{\circ}\text{C}$), and f) **4b** ($T_{\text{sub}}=100^{\circ}\text{C}$).

times that of **4b** (0.06 versus $0.014\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), which may be attributed to the more effective π -conjugation and closer π - π overlap in the former. As is well known, the morphologies of thin films dramatically influence device performances. This is consistent with the aforementioned thin-film XRD and AFM images, which indicate superior film morphology and molecular order in the non-alkyl-substituted compounds compared to the alkyl-substituted compounds. Devices fabricated from **3a** at $T_{\text{sub}}=70^{\circ}\text{C}$ showed a best hole mobility of $0.17\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and an on/off ratio of 10^5 in a saturation regime. It is accepted that the charge carrier transport in OFETs is dominated by highly ordered thin films with large interconnected polycrystalline grains. At $T_{\text{sub}}=70^{\circ}\text{C}$, all diffraction peaks became stronger and sharp-

Table 1. Field-effect transistor characteristics: the carrier mobility μ_{FET} , on/off current ratio $I_{\text{on/off}}$, and threshold voltage V_{T} of materials deposited at different substrate temperatures T_{sub} .

Material	T_{sub} [°C]	μ_{FET} [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]	$I_{\text{on/off}}$	V_{T} [V]
2a	20	0.03	10^5	−21.0
	70	0.04	10^5	−11.0
	100	0.04	10^5	−11.5
2b	20	0.013	4×10^6	−1.6
	70	0.018	3×10^4	−9.1
	100	0.04	10^6	+0.8
3a	20	0.08	10^5	−6.1
	70	0.17	10^5	−10.1
	100	0.07	10^5	−9.7
3b	20	6.2×10^{-3}	10^5	−1.1
	70	0.013	2×10^4	−6.4
	100	9.4×10^{-3}	10^4	−4.2
4a	20	0.02	10^4	−9.5
	70	0.03	10^4	−10.0
	100	0.06	10^5	−8.7
	120	0.02	10^4	−15.4
	150	0.017	10^4	−20.2
4b	20	0.01	10^5	+1.0
	70	0.017	10^5	−17.8
	100	0.014	10^4	−3.5
	120	0.008	10^4	+5

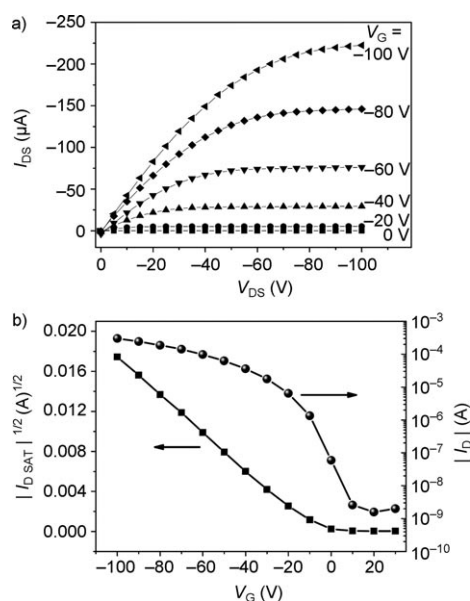


Figure 9. a) Output and b) transfer characteristics of OFET devices based on **3a** at $T_{\text{sub}} = 70^\circ\text{C}$ at different gate voltages.

er, and, at the same time, the AFM images revealed that the grain size increased and the intergrain connection was improved, indicative of improved ordering in the films. Both AFM and thin-film XRD showed that the films of **3a** deposited at $T_{\text{sub}} = 70^\circ\text{C}$ had the best film morphology and molecular ordering, consistent with the highest μ_{FET} obtained under these conditions. When the substrate temperature was increased to 100°C , the molecules of **3a** formed larger assemblies on the substrate and simultaneously some boundaries between the grains were formed, which probably led to

a lowering of the charge transport, as manifested in a decrease in mobility to $0.07 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.

Conclusions

In conclusion, we have synthesized a new series of oligomers based on thieno[3,2-*b*]thiophene, dithieno[3,2-*b*:2',3'-*d*]thiophene, and thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene, end-capped with either styrene or 1-pentyl-4-vinylbenzene groups, by means of Stille coupling reactions. Their chemical structures, which feature a *trans-trans* configuration between the double bonds, have been determined by Fourier-transform infrared spectroscopy and single-crystal X-ray diffraction analysis. Investigation of their physicochemical properties has indicated that they are more stable than pentacene. They have been used as p-type semiconductors for organic field-effect transistors, which showed a high mobility of $0.17 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and a large on/off ratio of 10^5 .

Experimental Section

General: Chemicals were purchased from Aldrich or Alfa Aesar and were used as received. Solvents and other common reagents were obtained from the Beijing Chemical Plant. ^1H NMR (300 MHz) and ^1H NMR (400 MHz) spectra were obtained on Bruker DMX-300 and DMX-400 NMR spectrometers, respectively, using tetramethylsilane as an internal standard. Mass spectra were determined on a Micromass GCT-MS spectrometer. Elemental analyses were performed with a Carlo Erba model 1160 elemental analyzer. TGA measurements were carried out on a TA SDT 2960 instrument under a dry nitrogen flow, heating from room temperature (RT) to 550°C at a rate of $10^\circ\text{C min}^{-1}$. DSC analyses were performed on a TA DSC 2010 instrument under a dry N_2 flow, heating from RT to 300°C at a rate of $10^\circ\text{C min}^{-1}$. Electronic absorption spectra were measured on a Jasco V570 UV/Vis spectrophotometer. Emission spectra were recorded on a Hitachi F-4500 fluorescence spectrometer. FT-IR spectra were determined using a Perkin-Elmer Tensor 27 spectrometer with samples in KBr pellets. Cyclic voltammetric measurements were carried out at RT in a conventional three-electrode cell using Pt button working electrodes of diameter 2 mm, a platinum wire counter electrode, and an Ag/AgCl reference electrode, with a 0.1 mol L^{-1} solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in tetrahydrofuran (THF) as the electrolyte, using a computer-controlled CHI660C instrument. Thin-film X-ray diffraction measurements were made in the reflection mode at RT using a 2 kW Rigaku X-ray diffraction system. The films were also imaged in air using a Digital Instruments Nanoscope III atomic force microscope operated in tapping mode.

X-ray diffraction measurements: X-ray crystal structure determinations were carried out in reflection mode using a Rigaku MM-007 X-ray diffraction system ($\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). The data were collected at 113 K, and the structure was solved by direct methods using SHELXS-97 and refined by using the SHELXL-97 program. Colorless prismatic crystals of **3a** were obtained by slow evaporation of the volatiles from a solution in methanol/toluene (2:1). Crystallographic data for **3a**: crystal size: $0.14 \times 0.12 \times 0.08 \text{ mm}^3$; monoclinic; $P2_1/n$; $Z = 4$; $a = 7.3557(18)$, $b = 6.0295(14)$, $c = 42.272(8) \text{ \AA}$; $V = 1872.7(7) \text{ \AA}^3$; $\rho_{\text{calcd}} = 1.421 \text{ g cm}^{-3}$; final $R = 0.0789$, $wR = 0.1896$; $\text{GoF} = 1.093$ with $I > 2.00\sigma(I)$. Yellow platelet crystals of **4a** were obtained by slow sublimation in a temperature-gradient furnace. Crystallographic data for **4a**: crystal size: $0.12 \times 0.10 \times 0.02 \text{ mm}^3$; monoclinic; $P2_1/c$; $Z = 4$; $a = 5.8990(18)$, $b = 7.401(2)$, $c = 45.799(13) \text{ \AA}$; $V = 1998.9(10) \text{ \AA}^3$; $\rho_{\text{calcd}} = 1.517 \text{ g cm}^{-3}$; final $R = 0.0697$, $wR = 0.1391$; $\text{GoF} = 0.985$ with $I > 2.00\sigma(I)$. CCDC-711682 (**3a**) and

711683 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Device fabrication: OFET devices were made by subliming the molecules (film thickness: 50 nm) onto OTS-modified SiO₂/Si substrates, followed by Au deposition through a shadow mask to define the source and drain electrodes. Prior to the deposition, OTS was deposited by placing the SiO₂ substrates in a vacuum oven saturated with OTS vapor for 3 h. The performances were measured in a top-contact configuration (drain and source electrodes deposited above the semiconductor). Gold source and drain contacts (50 nm) were deposited onto the organic layer through a shadow mask. The channel length (*L*) and width (*W*) were 3000 and 50 μm, respectively. The OFET characteristics of the devices were determined at room temperature in air by using a Hewlett–Packard 4140B semiconductor parameter analyzer. The mobilities in the saturation regime were determined using Equation (1):

$$I_{DS} = (\mu_{FET} W C_i / 2L) (V_G - V_T)^2 \quad (1)$$

where *I*_{DS} is the drain-source current in the saturated regime, μ_{FET} is the field-effect mobility, *W* is the channel width, *L* is the channel length, *C_i* is the capacitance of the SiO₂ dielectric layer, *V_G* is the gate voltage, and *V_T* is the threshold voltage.

2,5-Distyrylthieno[3,2-*b*]thiophene (2a): Phenylacetylene (2.24 g, 20.0 mmol), Bu₃SnH (5.8 g, 20.0 mmol), AIBN (0.20 g), and dry toluene (100 mL) were placed in a three-necked flask equipped with a condenser. The mixture was heated at 90 °C under a nitrogen atmosphere for 12 h and then cooled to room temperature. The yellow solution of (*E*)-β-tributyl(styryl)stannane thus obtained was used directly for the next step without further purification. (*E*)-β-Tributyl(styryl)stannane, 2,5-dibromothieno[3,2-*b*]thiophene (1.49 g, 5 mmol), and [Pd(PPh₃)₂Cl₂] (3 mol %) were mixed in dry toluene (150 mL). Nitrogen was bubbled through the mixture for 15 min and then it was refluxed under a nitrogen atmosphere for 3 days. Thereafter, the mixture was cooled to room temperature and anhydrous methanol (100 mL) was added. The precipitate formed was collected by filtration and washed with dilute acid (5 % HCl), water, methanol, and finally three times with acetone to remove the starting material as well as the monosubstituted by-product. The material was further purified by three sublimations to afford **2a** as a bright-yellow solid (1.2 g, 70 %). ¹H NMR (400 MHz, [D₈]THF, 27 °C, TMS): δ = 7.52–7.51 (d, 4H, *J*(H,H) = 7.6 Hz), 7.41–7.37 (d, 2H, *J*(H,H) = 16.0 Hz), 7.33–7.31 (t, 4H, *J*(H,H) = 14.0 Hz), 7.30 (s, 2H), 7.23–7.19 (t, 2H, *J*(H,H) = 15.0 Hz), 6.98–6.94 ppm (d, 2H, *J*(H,H) = 16.0 Hz); MS (EI): *m/z* (%): 344 (100) [*M*⁺]; elemental analysis calcd (%) for C₂₂H₁₆S₂: C 76.70, H 4.68, S 18.62; found: C 76.54, H 4.64, S 18.63.

2,5-Bis[2-(4-pentylphenyl)vinyl]thieno[3,2-*b*]thiophene (2b): 4-Pentylphenylacetylene (6.88 g, 40.0 mmol), Bu₃SnH (11.6 g, 40.0 mmol), AIBN (0.20 g), and dry toluene (100 mL) were placed in a three-necked flask equipped with a condenser. The mixture was heated to 90 °C under a nitrogen atmosphere for 12 h and then cooled to room temperature. The yellow solution of (*E*)-β-tributyl[2-(4-pentylphenyl)vinyl]stannane thus obtained was used directly for the next step without further purification. **2b** was prepared according to the procedure described for **2a** by Stille coupling of 2,5-dibromothieno[3,2-*b*]thiophene with (*E*)-β-tributyl[2-(4-pentylphenyl)vinyl]stannane in the presence of [Pd(PPh₃)₂Cl₂] (3 mol %) and was isolated as a yellow solid (1.77 g, 73 %). ¹H NMR (300 MHz, [D₈]THF, 57 °C, TMS): δ = 7.44–7.41 (d, 4H, *J*(H,H) = 9.0 Hz), 7.36–7.31 (d, 2H, *J*(H,H) = 15.0 Hz), 7.26 (s, 2H), 7.17–7.14 (d, 4H, *J*(H,H) = 9.0 Hz), 6.95–6.90 (d, 2H, *J*(H,H) = 15.0 Hz), 2.63–2.58 (t, 4H, *J*(H,H) = 7.5 Hz), 1.68–1.60 (m, 4H), 1.50–1.29 (m, 8H), 0.93–0.88 ppm (t, 6H, *J*(H,H) = 7.5 Hz); MS (MALDI-TOF): *m/z*: calcd for C₃₂H₃₆S₂: 484.8; found: 484.9; elemental analysis calcd (%) for C₃₂H₃₆S₂: C 79.29, H 7.49, S 13.23; found: C 78.91, H 7.44, S 13.44.

2,5-Distyryldithieno[3,2-*b*:2',3'-*d*]thiophene (3a): **3a** was prepared according to the procedure described for **2a** by Stille coupling of 2,6-dibromodithieno[3,2-*b*:2',3'-*d*]thiophene with (*E*)-β-tributyl(styryl)stannane. **3a** was isolated as a yellow solid (1.3 g, 65 %). ¹H NMR (300 MHz, [D₈]THF, 57 °C, TMS): δ = 7.56–7.54 (d, 4H, *J*(H,H) = 7.9 Hz), 7.47–7.41

(t, 2H, *J*(H,H) = 18.8 Hz), 7.40 (s, 2H), 7.36–7.31 (t, 4H, *J*(H,H) = 15.0 Hz), 7.25–7.21 (t, 2H, *J*(H,H) = 14.0 Hz), 7.04–6.98 ppm (d, 2H, *J*(H,H) = 16.0 Hz); MS (EI): *m/z* (%): 400 (100) [*M*⁺]; elemental analysis calcd (%) for C₂₄H₁₆S₃: C 71.96, H 4.03, S 24.01; found: C 71.80, H 4.11, S 13.70.

2,6-Bis[2-(4-pentylphenyl)vinyl]dithieno[3,2-*b*:2',3'-*d*]thiophene (3b): **3b** was prepared according to the procedure described for **2b** by Stille coupling of 2,6-dibromodithieno[3,2-*b*:2',3'-*d*]thiophene with (*E*)-β-tributyl[2-(4-pentylphenyl)vinyl]stannane in 70 % yield (1.89 g). ¹H NMR (300 MHz, [D₈]THF, 27 °C, TMS): δ = 7.46–7.43 (d, 4H, *J*(H,H) = 9.0 Hz), 7.39–7.34 (d, 2H, *J*(H,H) = 15.0 Hz), 7.35 (s, 2H), 7.18–7.15 (d, 4H, *J*(H,H) = 9.0 Hz), 6.99–6.94 (d, 2H, *J*(H,H) = 15.0 Hz), 2.63–2.58 (t, 4H, *J*(H,H) = 7.5 Hz), 1.65–1.58 (m, 4H), 1.36–1.29 (m, 8H), 0.93–0.88 ppm (t, 6H, *J*(H,H) = 7.5 Hz); MS (MALDI-TOF): *m/z*: calcd for C₃₂H₃₆S₃: 540.8; found: 540.9; elemental analysis calcd (%) for C₃₄H₃₆S₃: C 75.50, H 6.71, S 17.79; found: C 75.43, H 6.83, S 17.33.

2,6-Distyrylthieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene (4a): **4a** was prepared according to the procedure described for **2a** by Stille coupling of 2,6-dibromothieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene with (*E*)-β-tributyl(styryl)stannane. **4a** was isolated as a yellow solid (1.60 g, 70 %). HRMS (MALDI): *m/z*: calcd for C₂₆H₁₆S₄: 456.0135; found: 456.0138; elemental analysis calcd (%) for C₂₆H₁₆S₄: C 68.38, H 3.53, S 28.09; found: C 68.33, H 3.51, S 27.89.

2,6-Bis[2-(4-pentylphenyl)vinyl]thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene (4b): **4b** was prepared according to the procedure described for **2b** by Stille coupling of 2,6-dibromothieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene with (*E*)-β-tributyl[2-(4-pentylphenyl)vinyl]stannane. **4b** was isolated as a yellow solid (1.88 g, 63 %). ¹H NMR (300 MHz, [D₈]THF, 57 °C, TMS): δ = 7.43–7.40 (d, 4H, *J*(H,H) = 9.0 Hz), 7.33–7.28 (d, 2H, *J*(H,H) = 15.0 Hz), 7.36 (s, 2H), 7.17–7.14 (d, 4H, *J*(H,H) = 9.0 Hz), 7.00–6.95 (d, 2H, *J*(H,H) = 15.0 Hz), 2.64–2.59 (t, 4H, *J*(H,H) = 7.5 Hz), 1.72–1.62 (m, 4H), 1.37–1.29 (m, 8H), 0.92–0.88 ppm (t, 6H, *J*(H,H) = 6.0 Hz); MS (MALDI-TOF): *m/z*: calcd for C₃₂H₃₆S₄: 596.9; found: 596.8; elemental analysis calcd (%) for C₃₂H₃₆S₄: C 72.43, H 6.08, S 21.49; found: C 72.54, H 6.15, S 21.24.

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- [1] a) H. E. A. Huitema, G. H. Gelinck, J. B. P. H. van der Putten, K. E. Kuijk, C. M. Hart, E. Cantatore, P. T. Herwig, A. J. J. M. van Breen, D. M. de Leeuw, *Nature* **2001**, *414*, 599; b) P. Mach, S. J. Rodriguez, R. Nortrup, P. Wiltzius, J. A. Rogers, *Appl. Phys. Lett.* **2001**, *78*, 3592–3594; c) U. Mitschke, P. Bäuerle, *J. Mater. Chem.* **2000**, *10*, 1471–1507; d) B. Crone, A. Dodabalapur, A. Gelperin, L. Torsi, H. E. Katz, A. J. Lovinger, Z. Bao, *Appl. Phys. Lett.* **2001**, *78*, 2229–2231; e) M. Mushrush, A. Facchetti, M. Lefenfeld, H. E. Katz, T. J. Marks, *J. Am. Chem. Soc.* **2003**, *125*, 9414–9423.
- [2] a) H. E. Katz, *Chem. Mater.* **2004**, *16*, 4748–4756; b) H. Klauk, M. Halik, U. Zschieschang, G. Schmid, W. Radlik, W. Weber, *J. Appl. Phys.* **2002**, *92*, 5259–5263; c) T. W. Kelley, L. D. Boardman, T. D. Dunbar, D. V. Muires, M. J. Pellerite, T. P. Smith, *J. Phys. Chem. B* **2003**, *107*, 5877–5881; d) C. D. Sheraw, L. Zhou, J. R. Huang, D. J. Gundlach, T. N. Jackson, M. G. Kane, I. G. Hill, M. S. Hammond, J. Campi, B. K. Greening, J. Francl, J. West, *Appl. Phys. Lett.* **2002**, *80*, 1088–1090; e) Y.-Y. Lin, D. J. Gundlach, S. F. Nelson, T. N. Jackson, *IEEE Electron Device Lett.* **1997**, *18*, 606–608.
- [3] a) X.-C. Li, H. Sirringhaus, F. Garnier, A. B. Holmes, S. C. Moratti, N. Feeder, W. Clegg, S. J. Teat, R. H. Friend, *J. Am. Chem. Soc.*

- 1998, 120, 2206–2207; b) M. He, F. Zhang, *J. Org. Chem.* **2007**, 72, 442–451; c) H. K. Tian, J. W. Shi, B. He, N. H. Hu, S. Q. Dong, D. H. Yan, J. P. Zhang, Y. H. Geng, F. S. Wang, *Adv. Funct. Mater.* **2007**, 17, 1940–1951; d) E. A. Marseglia, F. Grepioni, E. Tedesco, D. Braga, *Mol. Cryst. Liq. Cryst.* **2000**, 348, 137–151.
- [4] a) H. K. Tian, J. W. Shi, D. H. Yan, L. X. Wang, Y. H. Geng, F. S. Wang, *Adv. Mater.* **2006**, 18, 2149–2152; b) H. E. Katz, J. G. Laquindanum, A. J. Lovinger, *Chem. Mater.* **1998**, 10, 633–638; c) M.-H. Yoon, A. Facchetti, C. E. Stern, T. J. Marks, *J. Am. Chem. Soc.* **2006**, 128, 5792; d) B. S. Ong, Y. Wu, P. Liu, S. Gardner, *Adv. Mater.* **2005**, 17, 1141–1144; e) X. Cai, C. P. Gerlach, C. D. Frisbie, *J. Phys. Chem. C* **2007**, 111, 452–456.
- [5] a) X. N. Zhang, M. Köhler, A. J. Matzger, *Macromolecules* **2004**, 37, 6306–6315; b) H. E. Katz, Z. Bao, S. L. Gilat, *Acc. Chem. Res.* **2001**, 34, 359–369; c) N. DiCésare, M. Belletête, A. Donat-Bouillud, M. Leclerc, G. Durocher, *Macromolecules* **1998**, 31, 6289–6296.
- [6] X. N. Zhang, A. J. Matzger, *J. Org. Chem.* **2003**, 68, 9813–9815.
- [7] a) Y. M. Sun, Y. Q. Ma, Y. Q. Liu, Y. Y. Lin, Z. Y. Wang, Y. Wang, C.-a. Di, K. Xiao, X. M. Chen, W. F. Qiu, B. Zhang, G. Yu, W. P. Hu, D. B. Zhu, *Adv. Funct. Mater.* **2006**, 16, 426–432; b) K. Xiao, Y. Liu, T. Qi, W. Zhang, F. Wang, J. Gao, W. Qiu, Y. Ma, G. Cui, S. Chen, X. Zhan, G. Yu, J. Qin, W. Hu, D. Zhu, *J. Am. Chem. Soc.* **2005**, 127, 13281–13286; c) Y. Liu, Y. Wang, W. Wu, Y. Liu, H. Xi, L. Wang, W. Qiu, K. Lu, C. Du, G. Yu, *Adv. Funct. Mater.* **2009**, 19, 772–778.
- [8] H. H. Fong, V. A. Pozdin, A. Amassian, G. G. Malliaras, D.-M. Smilgies, M. He, S. Gasper, F. Zhang, M. Sorensen, *J. Am. Chem. Soc.* **2008**, 130, 13202–13203.
- [9] a) G. Distefano, M. D. Colle, D. Jones, M. Zambianchi, L. Favaretto, A. Modelli, *J. Phys. Chem.* **1993**, 97, 3504–3509; b) E. Orti, P. M. Viruela, J. Sanchez-Marín, F. Tomas, *J. Phys. Chem.* **1995**, 99, 4955–4963; c) J. Roncali, *Chem. Rev.* **1997**, 97, 173–205.
- [10] a) H. Meng, F. Sun, M. B. Goldfinger, F. Gao, D. J. Londono, W. J. Marshall, G. S. Blackman, K. D. Dobbs, D. E. Keys, *J. Am. Chem. Soc.* **2006**, 128, 9304–9305; b) H. Klauk, U. Zschieschang, R. T. Weitz, H. Meng, F. Sun, G. Nunes, D. E. Keys, C. R. Fincher, Z. Xiang, *Adv. Mater.* **2007**, 19, 3882–3887; c) F. Cicoira, C. Santato, A. Dadvand, C. Harnagea, A. Pignolet, P. Bellutti, Z. Xiang, F. Rosei, H. Meng, D. F. Perepichka, *J. Mater. Chem.* **2008**, 18, 158–161; d) C. Videlot-Ackermann, J. Ackermann, H. Brisset, K. Kawamura, N. Yoshimoto, P. Raynal, A. El Kassmi, F. Fages, *J. Am. Chem. Soc.* **2005**, 127, 16346–16347.
- [11] a) L. San Miguel, A. J. Matzger, *Macromolecules* **2007**, 40, 9233–9237; b) P. Espinet, A. M. Echavarren, *Angew. Chem.* **2004**, 116, 4808–4839; *Angew. Chem. Int. Ed.* **2004**, 43, 4704–4734; c) X. J. Zhang, Y. Qu, L. J. Bu, H. K. Tian, J. P. Zhang, L. X. Wang, Y. H. Geng, F. S. Wang, *Chem. Eur. J.* **2007**, 13, 6238–6248.
- [12] a) S.-H. Jung, H. K. Kim, S.-H. Kim, Y. H. Kim, S. C. Jeoung, D. Kim, *Macromolecules* **2000**, 33, 9277–9288; b) L. S. Fuller, B. Iddon, K. A. Smith, *J. Chem. Soc. Perkin Trans. 1* **1997**, 3465–3470.
- [13] a) F. Allared, J. Hellberg, T. Remonen, *Tetrahedron Lett.* **2002**, 43, 1553–1554; b) J. Frey, A. D. Bond, A. B. Holmes, *Chem. Commun.* **2002**, 2424–2425.
- [14] a) Y. Mazaki, K. Kobayashi, *Tetrahedron Lett.* **1989**, 30, 3315–3318; b) N. Sato, Y. Mazaki, K. Kobayashi, T. Kobayashi, *J. Chem. Soc. Perkin Trans. 2* **1992**, 765–770; c) H. Lumbroso, J. M. Catel, G. Le Coustumer, C. G. Andrieu, *J. Mol. Struct.* **1999**, 513, 201–218.
- [15] C. Rim, D. Y. Son, *Org. Lett.* **2003**, 5, 3443–3445.
- [16] J. H. Gao, L. Q. Li, Q. Meng, R. J. Li, H. Jiang, H. X. Li, W. P. Hu, *J. Mater. Chem.* **2007**, 17, 1421–1426.
- [17] N. Drolet, J. F. Morin, N. Leclerc, S. Wakim, Y. Tao, L. Mario, *Adv. Funct. Mater.* **2005**, 15, 1671–1682.
- [18] a) Y. Mazaki, K. Kobayashi, *J. Chem. Soc. Perkin Trans. 2* **1992**, 761–764; b) J. J. Morrison, M. M. Murray, X. C. Li, A. B. Holmes, S. C. Morratti, R. H. Friend, H. Sirringhaus, *Synth. Met.* **1999**, 102, 987–988; c) J. E. Anthony, *Chem. Rev.* **2006**, 106, 5028–5048.
- [19] a) S. T. Bromley, M. Mas-Torrent, P. Hadley, C. Rovira, *J. Am. Chem. Soc.* **2004**, 126, 6544–6545; b) J. Cornil, J. Ph. Calbert, J. L. Bredas, *J. Am. Chem. Soc.* **2001**, 123, 1250–1251; c) S. E. Fritz, S. M. Martin, C. D. Frisbie, M. D. Ward, M. F. Toney, *J. Am. Chem. Soc.* **2004**, 126, 4084–4085.
- [20] a) L. San Miguel, W. W. Porter III, A. J. Matzger, *Org. Lett.* **2007**, 9, 1005–1008; b) X. N. Zhang, A. P. Côté, A. J. Matzger, *J. Am. Chem. Soc.* **2005**, 127, 10502–10503.
- [21] S. Son, A. Dodabalapur, A. J. Lovinger, M. E. Galvin, *Science* **1995**, 269, 376–378.
- [22] Y. K. Jhon, J. J. Semler, J. Genzer, *Macromolecules* **2008**, 41, 6719–6727.
- [23] X. N. Zhang, J. P. Johnson, J. W. Kampf, A. J. Matzger, *Chem. Mater.* **2006**, 18, 3470–3476.
- [24] a) T. Kono, D. Kumaki, J.-i. Nishida, T. Sakanoue, M. Kakita, H. Tada, S. Tokito, Y. Yamashita, *Chem. Mater.* **2007**, 19, 1218–1220; b) S. Tirapattur, M. Belletête, N. Drolet, M. Leclerc, G. Durocher, *Chem. Phys. Lett.* **2003**, 370, 799–804; c) J. H. Park, D. S. Chung, J. W. Park, T. Ahn, H. Kong, Y. K. Jung, J. Lee, M. H. Yi, C. E. Park, S. K. Kwon, D. D. Shim, *Org. Lett.* **2007**, 9, 2573–2576.
- [25] a) X. Gao, W. Wu, Y. Liu, S. Jiao, W. Qiu, G. Yu, L. Wang, D. Zhu, *J. Mater. Chem.* **2007**, 17, 736–743; b) J. L. Brédas, R. Silbey, D. S. Boudreaux, R. R. Chance, *J. Am. Chem. Soc.* **1983**, 105, 6555–6559.
- [26] H. Meng, M. Bendikov, G. Mitchell, R. Helgeson, F. Wudl, Z. Bao, T. Siegrist, C. Kloc, C.-H. Chen, *Adv. Mater.* **2003**, 15, 1090–1093.
- [27] L. San Miguel, W. W. Porter III, A. J. Matzger, *Org. Lett.* **2007**, 9, 1005–1008.
- [28] M. DeLongchamp, S. Sambasivan, D. A. Fischer, E. K. Lin, P. Chang, A. R. Murphy, J. M. J. Fréchet, V. Subramanian, *Adv. Mater.* **2005**, 17, 2340–2344.
- [29] F. Valiyev, W.-S. Hu, H.-Y. Chen, M.-Y. Kuo, I. Chao, Y.-T. Tao, *Chem. Mater.* **2007**, 19, 3018–3026.
- [30] P. Liu, Y. Wu, H. L. Pan, Y. N. Li, S. Gardner, B. S. Ong, S. P. Zhu, *Chem. Mater.* **2009**, 21, 2727–2732.
- [31] a) M. Halik, H. Klauk, U. Zschieschang, G. Schmid, S. Ponomarenko, S. Kirchmeyer, W. Weber, *Adv. Mater.* **2003**, 15, 917–922; b) H. Meng, F. Sun, M. B. Goldfinger, G. D. Jaycox, Z. Li, W. J. Marshall, G. S. Blackman, *J. Am. Chem. Soc.* **2005**, 127, 2406–2407.

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