Improving the Stability of Polymer FETs by Introducing Fixed Acceptor Units into the Main Chain: Application to Poly(alkylthiophenes)

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A concept to improve the air stability of poly(3-hexylthiophene)s (P3HT)s is proposed which is based on the introduction of electron-accepting units in the main chain in order to increase the polymer ionization energy (IE). Following this approach a series of soluble acceptor-containing poly(alkylthiophene)s with varied chemical composition has been synthesized. The structural and optical properties of the new polymers were investigated by differential scanning calorimetry (DSC), X-ray diffraction (XRD) and UV−vis optical absorption methods and the results are discussed in the present paper. The systematic change of the ionization energy relative to the conventional P3HT is measured by ultraviolet photoemission spectroscopy, and supported by quantum-mechanical calculations. Combining the results of these techniques, reveals two main effects that lead to the IE increase: (i) incorporation of acceptor units and (ii) a decreased intermolecular order in acceptor-modified polymers. Finally, the performance of OFETs comprising these new materials was evaluated, corroborating the advantages of the modified polymers with respect to operational and ambience stability.

Introduction

Regioregular poly(3-hexylthiophene) (P3HT)[1] is one of the most attractive soluble conjugated polymers for applications in organic field-effect transistors (OFETs). The self-alignment ability of P3HT facilitates the formation of thin films with well-ordered lamellae of co-facially stacked planarized main chains. This assembly ensures fast charge transport in the layer of the ordered backbones, resulting in the achievement of field-effect charge carrier mobilities as high as 0.1 cm^2/V·s.[2−4]

In spite of the impressive OFET performance of P3HT, the applications are restricted by the susceptibility to p-type doping when exposed to oxygen.[5] Consequently, the polymer conductivity increases, which leads to unfavorable changes in the overall transistor operation in terms of high OFF currents, large positive shift in the onset voltage, and inhibition of the field effect.[6,7] Therefore, during the preparation of devices, special precautions should be taken to exclude the influence of oxygen. Nevertheless, the application potential of P3HT-based transistors has been demonstrated by the realization of fast integrated circuits on flexible polyester films using a low-cost printing technique.[8] In fact, it has been suggested that the top gate device geometry functions additionally as an intrinsic encapsulation ensuring the stability of the P3HT-OFET performance.[9]

To allow a free choice of the device layout and to circumvent the necessity of preventing the contact from oxygen, it is essential to improve the ambience stability of P3HT. This will facilitate true low-cost production processes, establishing the advantages of “polymer electronics” compared to silicon technology. The sensitivity to oxidative doping is closely related to the oxidation potential (or the ionization energy, IE) of the polymer. Therefore, the improvement of ambience stability could be achieved by

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(1) Sirringhaus, H. *Adv. Mater.* **2005**, *17*, 2411.
(2) Bao, Z.; Dodabalapur, A.; Lovinger, A. J. *Appl. Phys. Lett.* **1996**, *69*, 4108.
(3) Chang, J. F.; Sun, B. Q.; Breiby, D. W.; Nielsen, M. M.; Solling, T. I.; Giles, M.; McCulloch, I.; Sirringhaus, H. *Chem. Mater.* **2004**, *16*, 4772.
(4) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685.
(5) Taylor, D. M.; Gomes, H. L.; Underhill, A. E.; Edge, S.; Clemenson, P. I. *J. Phys. D: Appl. Phys.* **1991**, *24*, 2032.
(6) Abdou, M. S. A.; Orfino, F. P.; Son, Y.; Holdcroft, S. *J. Am. Chem. Soc.* **1997**, *119*, 4518.
(7) Meijer, E. J.; Detcheverry, C.; Baesjou, P. J.; van Veenendaal, E.; de Leeuw, D. M.; Klapwijk, T. M. *J. Appl. Phys.* **2003**, *93*, 4831.
(8) Knobloch, A.; Manuelli, A.; Bernds, A.; Clemens, W. *J. Appl. Phys.* **2004**, *96*, 2286.
(9) Rost, H.; Ficker, J.; Alonso, J. S.; Leenders, L.; McCulloch, L. *Synth. Met.* **2004**, *145*, 83.

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increasing the IE value. Among the schemes to modify IE, the most suitable procedures—especially for poly(alkylthiophene)s—are those which retain the self-organization properties. One possible approach involves the manipulation of the effective conjugation length. It can be realized by introducing unsubstituted thiophene rings in the main chain, which increase the rotational degrees of freedom and thereby reduce the structural coplanarity.[10] A different concept is to induce head−head or tail−tail steric interactions between the 3-alkyl chains on adjacent thiophene rings combined with unsubstituted thiophene or naphtalene units in the main polymer chain.[11] Alternatively, the effective conjugation length can be optimized by including less conjugated (or even nonconjugated) units in the main chain.[12] Following this approach, an aromatic heterocycle has been introduced with the advantage of preserving the planar conformation of the backbone.[12] A further interesting method to modify the IE is to include electron-accepting units in the polymer either in the substituents (e.g., electron-withdrawing carboxylate side chains[13]) or in the main chain. The advantage of the latter case is the rather free choice of the donor−acceptor design of the polymer backbone, which facilitates relatively easy control of the oxidation potential. Nevertheless, to our knowledge, there are no reports of employing this concept to improve the ambience stability of soluble polymer materials for applications in field-effect transistors.

In this paper we explore the possibility of optimizing the IE of soluble poly(alkylthiophene)s by introducing electron-accepting units in the main chain, which can also be expected to reduce the structural coplanarity. The polymers were modified using 1,4-dithienyl-2,3,5,6-tetrafluorobenzene (**TFT**) segments fixed in the main chain following the McCullough Grignard metathesis method. **TFT** has been chosen for its strong electron-accepting properties.[14] Fluorinated units have been incorporated in thiophene alternating copolymers with focus on the improvement of the self-assembly and solution processability of the materials.[15] In the present study the **TFT** segments were integrated in the main polymer chain while retaining the regioregularity of the 3-hexylthiophene units. The regioregularity is important for promoting the self-organization tendency and consequently high field-effect mobility values of the modified structures. The **TFT** amount in the main chain was varied in the preparation of several statistical copolymers by which different structure−property relations were obtained. We report in detail the synthesis and the structural and optical characterization of the acceptor-containing poly(alkylthiophene)s. The systematic change of IE of the polymers was determined by ultraviolet photoemission experiments, which was rationalized theoretically by quantum-mechanical calculations. Finally, the OFET performance was studied in comparison to conventional P3HT, emphasizing the advantages of the modified polymers, especially with respect to the operational and ambience stability.

Experiments and Methods Section

General. All reactions were carried under an argon atmosphere. The solvents were used at a commercial p.a. quality. All chemicals are commercially available. The details of the synthesis of the monomers and polymers are available as Supporting Information.

^{1}H and ^{13}C NMR data were obtained using an INOVA 500 spectrometer. Gel permeation chromatographic analysis (GPC) utilized polystyrene (PS) columns (three columns, 5 μm gel, effective molecular weight range 500 to 4×10^6) connected with UV−vis ($\lambda = 254$ nm) and infrared (IR) detection. All GPC analyses were performed on solutions of the polymers in tetrahydrofurane (THF) at 20 °C (concentration of the polymer: ca. 2 g/L). The calibration was based on polystyrene standards with a narrow molecular weight distribution. Elemental analysis was performed on EA 1110 CHNS-O equipment.

Differential scanning calorimetry (DSC) analysis was carried out under nitrogen atmosphere using a NETZSCH thermoanalyser 204 at a heating/cooling rate of 10 and 20 K/min.

The UV−vis spectra were recorded on a Perkin-Elmer Lambda 19-UV/Vis/NIR spectrophotometer. The solution spectra were recorded using chloroform as solvent. Thin films for the solid-state measurements were drop-casted or spin-coated from chloroform solutions onto quartz substrates. With adjustment of the solution concentrations and the spinning speed, the resultant film thickness was typically 70 nm for all deposited layers, as measured with a Dektak surface profilometer. The measured spectra were corrected for the transmission of the solvent/substrate.

X-ray diffraction (XRD) investigations[16] were performed with radiation of a fine focus copper tube with nickel filter (wavelength $\lambda = 0.154$ nm). The radiation was collimated by slit systems in both the incident and the reflected beam. The goniometer (HZG-4, Seifert-FPM, Germany) with proportional counter was operated in $\theta-2\theta$ mode with θ steps of 0.01°. The samples were drop-casted from chloroform solutions on glass slides with thickness 200−250 nm. The films have been annealed to promote the chain self-assembly which was found to increase the intensity of the XRD features compared to the as-prepared samples (not shown). The thermal processing has been performed under the same conditions as for the OFET samples (vide infra).

Ultraviolet Photoemission Spectroscopy (UPS). Photoemission experiments were performed at the end station SurICat (beamline PM4) at the synchrotron light source BESSY GmbH.[17] The excitation energy for UPS was 27 eV. The spectra were collected with a hemispherical electron energy analyzer (Scienta SES 100) with an energy resolution of 140 meV (80%−20% intensity drop at the Au Fermi-edge). Polymer thin films were spin-coated ex situ from dilute chloroform solutions (typically 0.1 g/L) onto native oxide covered Si wafers. After introduction into the ultrahigh vacuum system, photoemission spectra were recorded. The secondary electron cutoff was measured with a negative sample bias (−10 V). Each sample was carefully checked for the absence of charging prior to determining ionization energies.

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(10) Ong, B. S.; Wu, Y. L.; Liu, P.; Gardner, S. *J. Am. Chem. Soc.* **2004**, *126*, 3378.

(11) McCulloch, L.; Bailey, C.; Giles, M.; Heeney, M.; Love, I.; Shkunov, M.; Sparrowe, D.; Tierney, S. *Chem. Mater.* **2005**, *17*, 1381.

(12) Heeney, M.; Bailey, C.; Genevicius, K.; Shkunov, M.; Sparrowe, D.; Tierney, S.; McCulloch, I. *J. Am. Chem. Soc.* **2005**, *127*, 1078.

(13) Murphy, A. R.; Liu, J. S.; Luscombe, C.; Kavulak, D.; Frechet, J. M. J.; Kline, R. J.; McGehee, M. D. *Chem. Mater.* **2005**, *17*, 4892.

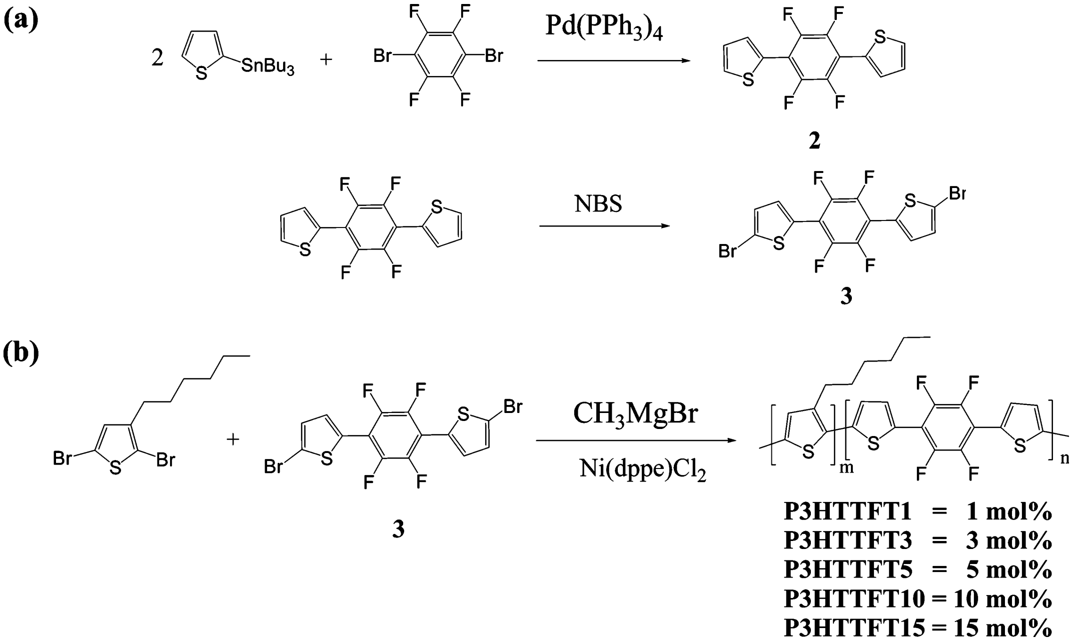
(14) Facchetti, A.; Yoon, M. H.; Stern, C. L.; Katz, H. E.; Marks, T. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3900.

(15) Crouch, D. J.; Skabara, P. J.; Lohr, J. E.; McDouall, J. J. W.; Heeney, M.; McCulloch, I.; Sparrowe, D.; Shkunov, M.; Coles, S. J.; Horton, P. N.; Hursthouse, M. B. *Chem. Mater.* **2005**, *17*, 6567.

(16) Reiche, J.; Pietsch, U.; Fink, H. P.; Lemmetyinen, H. *Acta Polym.* **1992**, *43*, 206.

(17) Vollmer, A.; Jurchescu, O. D.; Arfaoui, I.; Salzmann, I.; Palstra, T. T. M.; Rudolf, P.; Niemax, J.; Pflaum, J.; Rabe, J. P.; Koch, N. *Eur. Phys. J. E* **2005**, *17*, 339.

Scheme 1. (a) Synthesis of the Acceptor Molecule 1,4-Bis(5-bromothien-2-yl)-2,3,5,6- tetrafluorobenzene (Compound 3); (b) Synthesis of the Poly(3-hexylthiophenes) with the 1,4-Dithienyl-2,3,5,6-tetrafluoro-benzene (TFT) Units in the Main Chain by the Grignard Metathesis Method[a]



[a] The percentage indicates the **TFT** content.

Quantum-Mechanical Calculations. The DFT calculations were performed with the Gaussian 98 program package,[18] using a 6-31G* basis set and the B3LYP exchange-correlation functional. This combination has previously been used for similar systems and purpose.[19−23] Ionization energies (IEs) were calculated by subtracting, at the neutral equilibrium geometry, the total energy of the neutral molecule from that of the charged molecule. Transition energies and oscillator strengths were calculated on the basis of the semiempirical Hartree−Fock intermediate neglect of differential overlap (INDO) method.[24,25] Electron correlation effects were included for the excited states via a single configuration interaction (SCI) technique. The CI-active space is given by the N highest occupied orbitals and the N lowest virtual orbitals, where N is the sum of carbon and sulfur atoms in the π-conjugated backbone.

OFET Layout and Measurements. The OFET structures were of a "bottom gate" configuration using heavily doped Si wafers as substrates and common gate electrodes. The gate dielectric was thermally grown directly on the wafer SiO_2 of thickness 230 nm and capacitance 14.6 nF/cm^2. On the top of SiO_2 were deposited the source and drain electrodes (Au) using a photolithographic technique ($L = 10$ μm, $W = 195$ mm). The wafers were carefully cleaned with several solvents, dried under nitrogen flow, and treated with a silylating agent—hexamethyldisilazene (HMDS). Finally, the polymer active layers were spin-coated from chloroform solutions with concentrations of 7−10 mg/mL under inert atmosphere conditions. The final film thickness was about 70 nm. Before electrical characterization, the samples were annealed in an inert atmosphere. Further details of this procedure are available as Supporting Information. No sample encapsulation was used. The OFET characteristics were measured in the dark under glovebox conditions, using two Source-Measure Units 236 combined with a Trigger-Control Unit 2361 and Metrics Software (all three items Keithley Instruments). Usually about 10 transistors were investigated for each polymer type.

Results and Discussion

Acceptor-Containing Monomer and Polymer Synthesis. The integration of the electron-accepting units in the polymer backbone via the McCullough metathesis method requires a bis-bromo-functionalized acceptor monomer. Therefore, the starting molecule was 1,4-bis(5-bromothien-2-yl)-2,3,5,6-tetrafluorobenzene. In the first step, 1,4-dibromo-2,3,5,6-tetrafluorobenzene was coupled with 2-tributylstannylthiophene via refluxing to get 1,4-bisthienyl-2,3,5,6-tetrafluorobenzene (Scheme 1a). The bromination with N-bromosuccineimide (NBS) in dimethylformamide (DMF) leads to the dibromo-functionalized compound 1,4-bis(5-bromothien-2-yl)-2,3,5,6- tetrafluorobenzene (**3**). The product was obtained in very high yields (96%).

The McCullough Grignard metathesis method is well-known to be a very quick and easy approach for the synthesis of regioregular head-to-tail coupled poly(3-alkylthiophenes). Therefore, it has been used for the preparation of the acceptor-modified poly(3-hexylthiophene)s. In the first step, the treatment of 2,5-dibromo-3-hexylthiophene and the acceptor molecule, 1,4-bis(5-bromothien-2-yl)-2,3,5,6- tetrafluorobenzene (**3**), in different ratios with 1 equiv of methylmagnesiumbromide as Grignard reagent results in a magnesium-determined exchange reaction, also referred to

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(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; et al. *GAUSSIAN 98*, Revision A.11; Gaussian, Inc.: Pittsburgh, PA, 2001.
(19) Ando, S.; Ueda, M. *Synth. Met.* **2002**, *129*, 207.
(20) de Bettencourt-Dias, A.; Viswanathan, S.; Ruddy, K. *Cryst. Growth Des.* **2005**, *5*, 1477.
(21) De Oliveira, M. A.; Dos Santos, H. F.; De Almeida, W. B. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3373.
(22) Risko, C.; Zojer, E.; Brocorens, P.; Marder, S. R.; Bredas, J. L. *Chem. Phys.* **2005**, *313*, 151.
(23) Salzner, U.; Lagowski, J. B.; Pickup, P. G.; Poirier, R. A. *J. Comput. Chem.* **1997**, *18*, 1943.
(24) Pople, J. A.; Beveridg, Dl.; Dobosh, P. A. *J. Chem. Phys.* **1967**, *47*, 2026.
(25) Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Muellerwesterhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589.

Table 1. Composition and Properties of the Synthesized Poly(3-hexylthiophenes) with the 1,4-Dithienyl-2,3,5,6-tetrafluorobenzene Units in the Main Chain, Where A_{added} Denotes the Acceptor Amount Added during the Polymerization, $A_{\text{polymer-chain}}$ Refers to the Acceptor Concentration in the Polymer Chain According to an EA Fluorine Determination, and PDI is the Polydispersity

		GPC results			
polymerization	A_{added} [mol %]	M_n [g/mol]	M_w [g/mol]	PDI	$A_{\text{polymer-chain}}$ [mol %]
P3HTTFT1	1.0	22700	35400	1.6	1.1
P3HTTFT3	3.0	19800	28700	1.4	3.0
P3HTTFT5	5.0	14800	22300	1.5	5.1
P3HTTFT10	10.0	14500	21100	1.5	9.5
P3HTTFT15[a]	15.0	n.a.[a]			14.8

[a] GPC measurements not possible when THF is used due to the insufficient solubility of P3HTTFT15 in this solvent.

as Grignard metathesis. In the second step, a catalytic amount of Ni(dppe)Cl_2 was added to initiate the polymerization reaction (see Scheme 1b).

Random copolymers were synthesized with main chains consisting of regioregularly linked 3-hexylthiophene segments and varied amounts of units with strong electron-accepting properties (**TFT**). The fluorine content in the polymers was detected by anion chromatography conductivity detection after chemical suppression. From this characterization, the amount of the 1,4-dithienyl-2,3,5,6-tetrafluorobenzene in each polymer could be calculated.

A summary of the molecular weight data as obtained from the GPC analysis is shown in Table 1. The main tendency observed is a parameter decrease in the modified poly(3-hexylthiophene)s with increasing the concentration of the **TFT** units. The incorporation of a very small amount of the acceptor—1.1 mol % **P3HTTFT1**—resulted in polymers with approximately 120 3-hexylthiophene (3HT) segments regioregularly linked together in the main chain. This value was reduced to 90 for the higher **TFT** concentration of 9.5 mol % in **P3HTTFT10**. A further increase to 14.8 mol % **TFT** in the main chain led to a restricted solubility of the product **P3HTTFT15**. Although this polymer was not completely soluble in tetrahydrofurane, the solubility remained sufficiently high in chloroform, which was therefore used for further investigations. All synthesized polymers were extracted with acetone and hexane to remove the short oligomers. In this way, relatively low polydispersity coefficients around 1.5 were achieved.

Differential Scanning Calorimetry (DSC) Characterization. The thermal properties of the polymers were investigated by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min and a cooling rate of −10 °C/min. The corresponding scans for P3HT and the acceptor-modified P3HTs are shown in Figure 1a. In general, a gradual decrease in the melting and recrystallization temperatures and in the corresponding enthalpies with increasing acceptor content (Figure 1a and Table S1 from the Supporting Information) were observed.

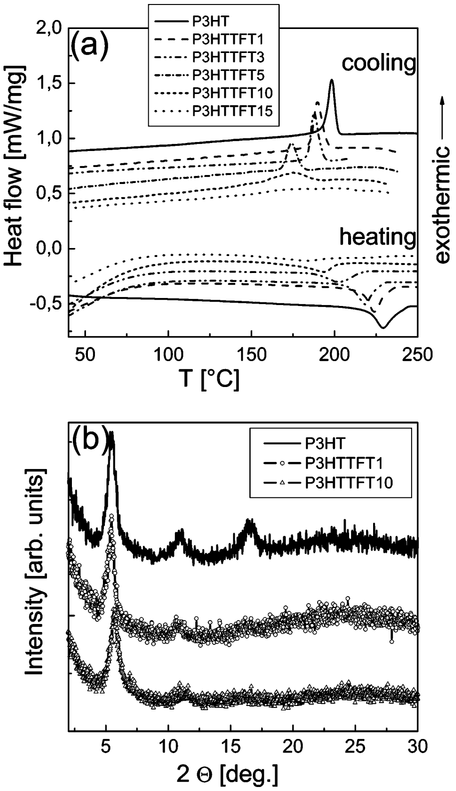

Figure 1. (a) DSC scans of P3HT and the modified poly(alkylthiophenes) containing different concentrations of the electron-accepting unit **TFT**; (b) X-ray diffraction patterns of films prepared by drop casting from chloroform solutions and subsequent annealing of P3HT, **P3HTTFT1**, and **P3HTTFT10** (corresponding **TFT** amount: 0, 0.1.1, and 9.5 mol %).

Clear exothermic and endothermic peaks at relatively high temperatures were observed in the DSC measurements for the modified P3HTs with a low degree of acceptor content. Especially for **P3HTTFT1** (1.1 mol %) and **P3HTTFT3** (3.0 mol %), the enthalpies of melting and crystallization are in the range of the unmodified P3HT.[26] This indicates that these polymers retain the ability for a chain self-assembly and the formation of a crystalline morphology. However, when the **TFT** concentration is further increased, as in the polymer **P3HTTFT10** (9.5 mol %), the melting and crystallization take place at lower temperatures combined with less defined phase transition peaks. This is not unexpected, considering the higher degree of structural disorder due to the polymer design. The effect becomes more pronounced in the compound **P3HTTFT15** (14.8 mol %), resulting in amorphous behavior with no distinct transitions in the DSC scans.

X-ray Diffraction (XRD). X-ray diffraction (XRD) experiments were performed to estimate the correlation between the acceptor concentration and the resulting solid-state microstructure in terms of chain self-assembly and crystallinity. As a comparison to P3HT, two of the new synthesized polymers were investigated—**P3HTTFT1** and **P3HTTFT10**—as a representative for the cases of low and high **TFT** concentration in the main chain.

Results from XRD measurements are depicted in Figure 1b. All three polymers exhibit highest intensity in the low-angle diffraction peaks with indices *h*00 which are known to correspond to the direction along the side chains.[4] The P3HT film showed clearly resolved reflections of first, second, and third order at 2θ angles of 5.4°, 10.9°, and 16.7°, respectively. This closely resembles the literature data for layers of highly regioregular P3HT prepared and measured

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(26) Yang, H. C.; Shin, T. J.; Yang, L.; Cho, K.; Ryu, C. Y.; Bao, Z. N. *Adv. Funct. Mater.* **2005**, *15*, 671.

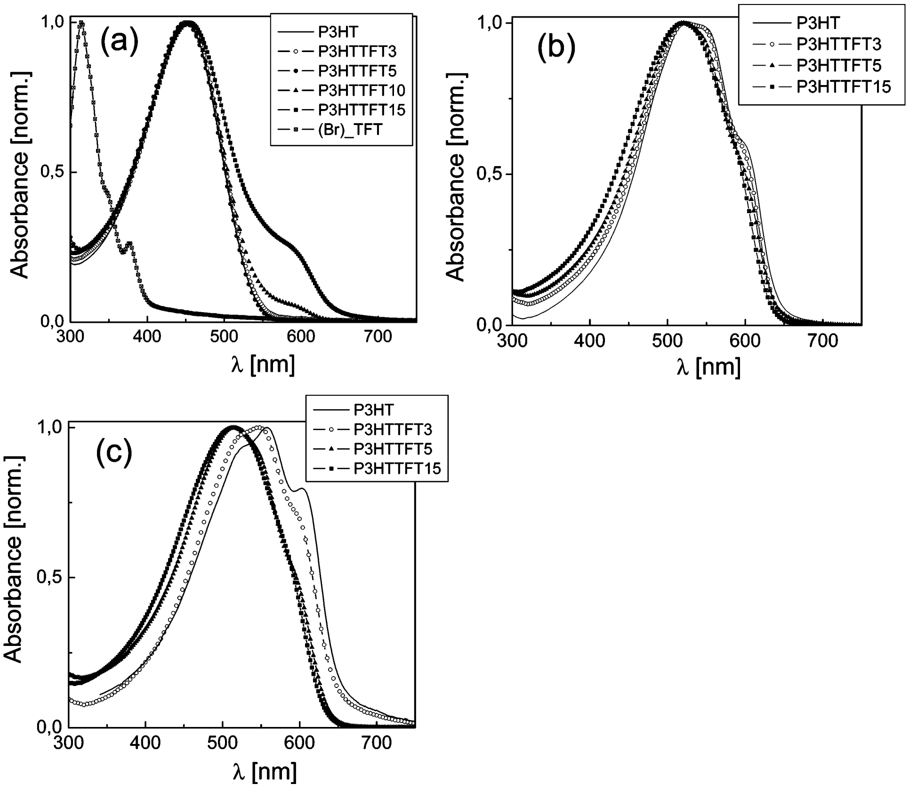

Figure 2. (a) Normalized absorption spectra measured in diluted chloroform solutions of the modified poly(alkylthiophene) polymers in comparison with the conventional P3HT. The absorption of the electron-acceptor unit (Br)_**TFT** in chloroform solution (compound 3 in Scheme 1) is also shown in the plot; (b) solid-state absorption spectra prepared by spin coating and drop casting (c) of the modified poly(alkylthiophene)s (**P3HTTFT3**, **P3HTTFT5**, and **P3HTTFT15**) in comparison with the corresponding P3HT spectra.

in a similar way.[2,27] It is associated with a film morphology with well-ordered lamellae formed by stacks of planarized thiophene main chains regularly spaced by the hexyl substituents. The corresponding interlamellar spacing in our case was calculated to be 1.6 nm using the standard diffraction equation. The XRD pattern of **P3HTTFT1** is similar to that of P3HT. However, higher diffraction orders were less pronounced, with the concomitant disappearance of the (300) reflection. This effect was also observed in the **P3HTTFT10** samples. Moreover, the (100) reflection maximum shifted to 5.8°, indicating a decreased interlamellar spacing in conjunction with the higher content of unsubstituted **TFT** segments in the **P3HTTFT10** main chain. The absence of higher diffraction orders in the XRD patterns has also been reported for poly(alkylthiophene) layers and related to a lower structural regioregularity of the polymers[4,27] or to film processing conditions detrimental to the degree of solid-state order.[3,26] Since all samples in our case were prepared in essentially a similar way, the observed effect—especially at high concentration of the electron-accepting units—can be attributed to a deviation from chain planarity and a suppressed regular three-dimensional lamellae assembly. Interestingly, the XRD data imply a similar loss of structural order for **P3HTTFT1 and P3HTTFT10** (i.e., 1.1 and 9.5 mol %). The increased disorder in the alkylthiophene backbones, which contain **TFT** segments, has already been discussed above for the DSC measurements.

Optical Properties. The optical properties of the polymers were investigated by UV−vis spectroscopy in solution and in the solid state (Figure 2).

The spectra measured in diluted chloroform solutions of the modified poly(alkylthiophene)s with low **TFT** content were structureless with a maximum at 450 nm, and thereby essentially similar to the conventional P3HT[27,28] (Figure 2a). The increase of the acceptor concentration does not affect the position of the main absorption maximum. However, in **P3HTTFT10** and **P3HTTFT15** it is accompanied by the appearance of an additional long wavelength shoulder. It should be noted that the position of this spectral feature remains constant when the solution spectra were recorded in solvents of varied polarity, such as *m*-xylene and chlorobenzene. A possibility for this observation made at increased **TFT** concentrations in the polymers could be a molecular interaction taking place between the fluorine and the π-electron system.[29] Quantum-chemical calculations (described below) indicate that the appearance of the shoulder cannot be associated with a ground-state charge-transfer process, which would typically lead to a red shift of the absorption peak (e.g., when the donor and acceptor concentrations become comparable as in push−pull systems). This finding is consistent with previous calculation results concerning the limited ability of fluorine to form strong interactions with hydrogen when attached to aliphatic or

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(27) Chen, T. A.; Wu, X. M.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.

(28) Zen, A.; Pflaum, J.; Hirschmann, S.; Zhuang, W.; Jaiser, F.; Asawapirom, U.; Rabe, J. P.; Scherf, U.; Neher, D. *Adv. Funct. Mater.* **2004**, *14*, 757.

(29) Kawahara S.-i.; Tsuzuki, S. T. U. *J. Phys. Chem. A* **2004**, *108*, 6744.

aromatic compounds.[15] In this way our new materials are essentially different from the polymers developed for organic photovoltaic applications with alternating donor−acceptor (D-A) segments linked in the main chain leading to a charge-transfer effect and band gap lowering. Examples of polythiophenes of D−A architecture reported in the literature[30,31] demonstrate a red shift in the absorption onset typically by 100 nm in solution and up to 150 nm in the solid state. These features are absent in our polymers; in fact, the solid-state spectra indicate even a slight increase in the optical band gap at high acceptor concentrations (vide infra). Therefore, we note that by the random introduction of the acceptor moiety in the polymer chain the aim is to influence exclusively the IE value of the resultant polymers to facilitate the stability against the unwanted oxidation effect in the OFET applications.

The absorption of the poly(alkylthiophene) thin films has been found to depend strongly on the processing conditions.[32] Therefore, spin coating as well as drop casting were used for the thin film deposition. As can be seen from Figures 2b and 2c, the UV−vis characteristics of the modified structures depend on the incorporated **TFT** amount. In particular, the spin-coated films prepared from **P3HTTFT1** (not shown) and **P3HTTFT3** retain the main characteristics of P3HT with high degree of regioregularity.[27,28] Notably, when compared to the measurements in solution, the solid-state spectra exhibit a large bathochromic shift combined with a vibronic splitting (maximum at 522 nm, shoulders at 550 and 600 nm; cf. Figure 2b). These features indicate the presence of highly ordered and planarized $\pi-\pi$ main chains. The effect was promoted in the drop-casted layers (Figure 2c) where longer relaxation times were allowed for the transfer from liquid into the solid phase, thereby facilitating the backbone self-assembly.[32] Consequently, the spectra showed a further red shift of about 10 nm and a better resolved vibronic splitting. In addition, the maximum shifts from the (0-2) vibronic band to the lower energy transition (0-1) positioned at 547 nm in the case of **P3HTTFT3** (Figure 2c). This characteristic has been related to the improved molecular order in the layers.[33] In contrast, the solid-state absorption of the polymers with **TFT** concentration equal to or above 5.1 mol % showed almost no fine structure and there was no particular difference between the films processed by spin coating or drop casting (Figures 2b and 2c). These results indicate the perturbation of the planar conformation of the main chains probably caused by the presence of the electron-accepting units. As discussed in the chemical characterization section, the number of 3-hexylthiophene rings linked together is gradually reduced in the **TFT**-containing polymers, which also changes the backbone conformation. The solid-state band gap of our samples can be accessed using the tangential through the long wavelength absorption edge. A comparison between the spectra of P3HT and **P3HTTFT15** drop-casted layers (Figure 2c) reveals an onset shift of about 25 nm. This corresponds to an energy gap increase by 0.08 eV. Consequently, an improvement in the environmental stability can be expected in polymers with high **TFT** concentration. Nevertheless, for device performance optimization it is important to clarify to which extent the restricted chain planarity or a possible reduction of the effective conjugation length of the individual chains influence charge transport properties.

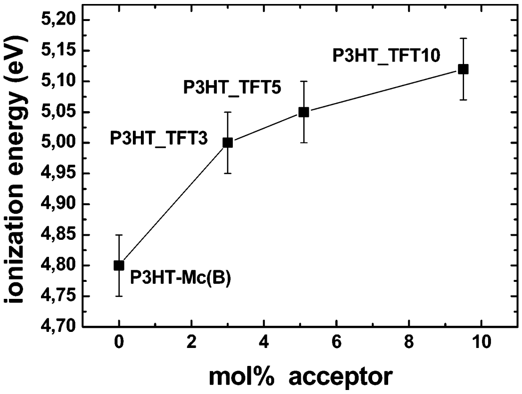

Figure 3. Ionization energy of P3HT-based polymer thin films for increasing acceptor concentration determined by UPS.

Measurement of the Ionization Energies. Ultraviolet photoemission spectroscopy was used to measure the ionization energies of a series of **P3HTTFT** copolymers. Ionization energies were obtained by subtracting the full width of the energy distribution curve (kinetic energy difference between the valence band onset and the secondary electron cutoff) from the photon energy.[34] Values for IE obtained in this way are summarized in Figure 3. We measured a total change in IE of 0.3 eV when going from pure P3HT to the copolymer containing 9.5 mol % of **TFT** (**PHTTFT10**).

Calculation of the Ionization Energies and the Absorption Spectra. To study the influence of the tetrafluorobenzene on the IE and the optical properties of **P3HTTFT** copolymers, calculations were performed on model molecules A, B, and C (Scheme 2) with R being either hydrogen or a methyl group. Molecule A is an oligothiophene and serves as a model for P3HT. Molecule B is an oligothiophene, where a terminal thiophene ring was substituted with a **TFT** unit, and the influence of the **TFT** unit on the conjugation of the molecule is minimal. Molecule C is an oligothiophene, where a center thiophene ring was substituted with a **TFT** unit, thus allowing study of its influence on the conjugation. We investigate model systems consisting of 9 rings and 13 rings to obtain tetrafluorobenzene to thiophene ratios similar to **P3HTTFT15** and **P3HTTFT10**, respectively. Unless explicitly stated, results for the 9-ring systems are presented. For analyzing the optical properties and the IEs of the copolymer in the film, coplanar conformations of the oligomers were assumed. To describe the optical properties in solution, twisted geometries were considered (for details see Supporting Information).

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(30) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 5065.

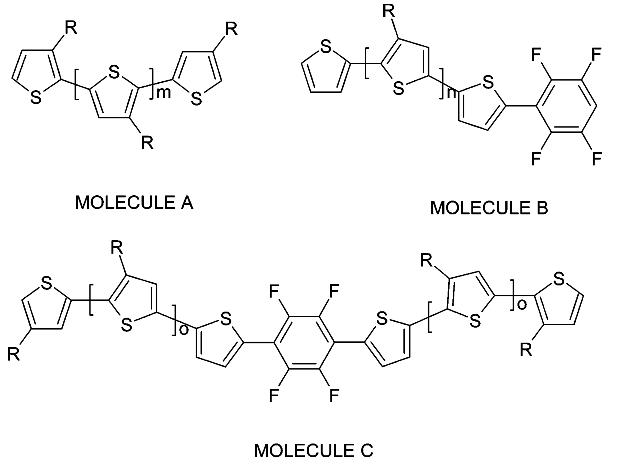
(31) Jayakannan, M.; Van Hal, P. A.; Janssen, R. A. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2360.

(32) Wang, G. M.; Swensen, J.; Moses, D.; Heeger, A. J. *J. Appl. Phys.* **2003**, *93*, 6137.

(33) Heil, H.; Finnberg, T.; von Malm, N.; Schmechel, R.; von Seggern, H. *J. Appl. Phys.* **2003**, *93*, 1636.

(34) Kahn, A.; Koch, N.; Gao, W. Y. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 2529.

Scheme 2. Model Oligomers Used for the Calculation of the Ionization Energy of the P3HT and P3HTTFT Copolymer



[a] Molecules A, B, and C have been calculated as 9-ring systems ($m = 7$, $n = 6$, $o = 2$) and molecules A and B as 13-ring systems ($m = 11$, $o = 4$). The side chain R can be hydrogen or methyl groups.

Table 2. HOMO Orbital Energy E_{Homo}, Ionization Potential IP, Transition Energies E_{ex}, and Oscillator Strength (osc. str.) of the Model Molecules

molecule	E_{ex} [eV]/E_{ex} [nm]	osc. str.	E_{Homo} [eV]	IP [eV]
	Planar			
A (R=H)	2.18/ 567	3.29	−4.70	−5.55
B (R=H)	2.18/ 567	3.29	−4.78	−5.65
A (R=CH_3)	2.12/585	3.24	−4.42	−5.24
B (R=CH_3)	2.11/587	3.23	−4.57	−5.41
C (R=CH_3)	2.24/552	3.28	4.72	−5.52
	Twisted			
A (R=CH_3)	2.24/553	3.04	−4.51	−5.33
C (R=CH_3)	2.30/538	3.14	−4.78	−5.58
	13-Ring Planar			
A (R=CH_3)	2.00/619	4.56	−4.37	−5.03
C (R=CH_3)	2.08/594	4.63	−4.57	−5.22

In Table 2, we show the transition energies and oscillator strengths of the lowest[35] excited states calculated at the INDO/SCI level for planarized and twisted (fully optimized) conformations of the oligomers. The states are strongly optically allowed, have a $\pi-\pi^*$ character, and are dominated by a single excited determinant, where one electron is promoted from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital). The absorption energy for molecule A (R = H) is 2.18 eV for the coplanar geometry in good agreement with previous work,[36] where also the systematic underestimation of INDO/SCI excitation energies relative to experiments on thiophenes has been discussed.

The main conclusions from the calculations are as follows: (i) As long as the conjugation of the oligothiophene chain is preserved (i.e., comparing model systems A and B), there is virtually no shift in the energy of the first excited state upon replacement of a thiophene unit with **TFT** (both the occupied and unoccupied orbitals are stabilized by the same amount). This is in full agreement with the experimental observations in Figure 2, where the main absorption feature does not shift. (ii) The calculations show no indication of a low-energy feature below the main absorption peak, even at the highest **TFT** concentrations considered. This supports the notion that the long wavelength shoulder observed in the experiment is most likely not related to an intrinsic property of the polymer chain, but rather to the formation of aggregates (vide supra). (iii) The calculated red shift between twisted and planar conformers (on the order of 0.1 eV) is significantly smaller than the experimental shift between solution and film, which is between 0.3 and 0.5 eV (depending on the sample). This indicates that in films intermolecular interactions have a more profound impact than a mere planarization of the chains, with the effect being stronger in pristine P3HT. (iv) Incorporating the **TFT** unit into the center of the model system does reduce the effective conjugation (i.e., leads to a blue shift of the lowest excited state by 0.06 eV in the twisted and 0.13 eV in the planar conformations).

Table 2 also contains the IEs and the energies of the highest occupied molecular orbitals, E_{HOMO}. The magnitude of the HOMO energy is systematically smaller than the IE. This is typical for DFT and the relationship between the two energies was previously discussed for the chosen methodology (in the context of LUMO energies and electron affinities).[22]

Three factors having an influence on IE can be identified: (i) The accepting properties of the **TFT** ring increases the IE by 0.10 eV, which can be seen by comparing molecules A (R = H) and B (R = H); (ii) with the incorporation of each acceptor unit, the chain also contains three fewer alkyl chains. A comparison of molecule A (R = H) with A (R = CH_3) shows that the methyl side chains decrease the IE by about 0.3 eV due to their electron-donating character. Therefore, the difference in IE of molecule A (R = CH_3) and molecule B (R = CH_3) is 0.08 eV larger than that for the model systems without the methyl group; (iii) the **TFT** unit disturbs the conjugation when placed in the center of the model molecule C (R = CH_3). This causes a further increase of IE by about 0.12 eV. As discussed in the Supporting Information, this number can be regarded as an upper limit of the effect associated with the reduced conjugation and the effect should, in fact, be significantly smaller in a real thin film polymer sample.

When reducing the acceptor concentration from 16 to 10 mol % (9-ring system compared to 13-ring system), the **TFT** to thiophene ratio changes from 1:8 to 1:12 and the change in IE can be expected to be roughly proportional to this ratio. Indeed, calculations on A (R = CH_3) and C (R = CH_3) with 13 rings show a reduced difference in IEs of 0.19 eV compared to 0.30 eV for the 9-ring system. Correspondingly, for a 13-ring model with **TFT** at the end rather than in the center, the expected difference in IEs should be around 0.12 eV.

This change in IE is clearly smaller than the experimentally observed increase of 0.3 eV from P3HT to **P3HTTFT10**. The deviation between the experiment on solid samples and

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(35) Only the lowest excited states are relevant for the description of the optical spectra shown in Figures 3 and 4, s.f.a.t.m., the next states are about 0.4−0.5 eV higher in energy and show negligible oscillator strength. The third excited state in each molecule is 1 eV higher than the lowest one and, therefore, out of the considered energy range.

(36) Cornil, J.; Beljonne, D.; Bredas, J. L. *J. Chem. Phys.* **1995**, *103*, 842.

Table 3. OFET Performance Summary of the TFT-Containing Polymers in Terms of Saturation Field-Effect Mobility (μ), ON/OFF Ratio, Onset Voltage (V_0), Threshold Voltage (V_T), and Threshold Voltage Shift (ΔV_T) after Three Successive Scans of the Transfer Characteristics in the Saturation Regime

polymer	μ [cm^2/V·s]	ON/OFF	V_0 [V]	V_T [V]	ΔV_T [V]
P3HT	4.0×10^{-2}	1×10^4	10	−10	−4 to −6
P3HTTFT1	3.2×10^{-2}	1×10^4	10	−10	−1 to −2
P3HTTFT3	1.2×10^{-2}	3×10^4	10	−12	−1 to −2
P3HTTFT5	4.5×10^{-3}	2×10^5	5	−14	−1 to −2
P3HTTFT10	1.1×10^{-3}	2×10^5	2	−15	−2 to −3
P3HTTFT15	7.0×10^{-4}	3×10^5	0	−15	−1 to −2

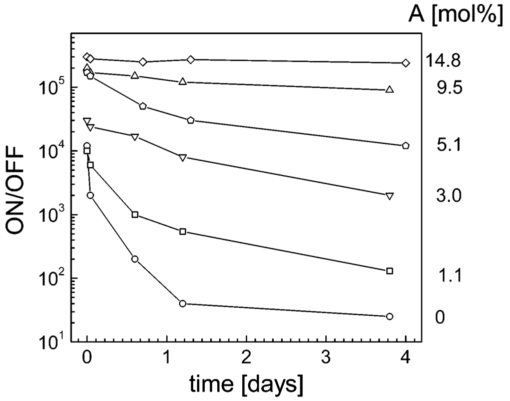

Figure 4. Change in the ON/OFF ratio values of OFET devices based on P3HT and the acceptor-modified polymers due to air exposure for 4 days. A [mol%] refers to the **TFT**-acceptor amount in the polymer chain.

the calculations for isolated molecules becomes even bigger for a reduced acceptor concentration of 3 mol % in **P3HTTFT3** (with an average **TFT** to thiophene ratio of 1/34). While in the experiment the change in IE amounts to about 0.2 eV, only 0.05−0.07 eV can be expected from a linear extrapolation based on the ring ratios (vide supra). This implies that the steep increase of the IE at low **TFT** concentrations in Figure 3 is not intrinsic to the individual chain, but likely a consequence of a modified film morphology caused by the **TFT** segments, as discussed in the X-ray section. Only at larger acceptor concentrations a more significant contribution to the increase in IE stems from intrachain effects.

OFET Characterization. The field-effect behavior of the acceptor-containing poly(alkylthiophene)s was investigated in comparison to conventional P3HT. In all cases, a typical p-type field-effect performance in the accumulation regime was observed, with well-pronounced linear and saturation operational regimes. An example of the output characteristics measured for P3HT and the modified polymer **P3HTTFT3** is available as Supporting Information. The field-effect mobility values for the samples have been calculated from the transfer characteristics in the saturation regime using the standard transistor equations. The OFET performance of the **TFT**-modified polymers in comparison to that of P3HT is summarized in Table 3.

The P3HT results for the field-effect mobility and the ON/OFF ratio are in the range of literature data for similar polymers (i.e., regioregularity and molecular weight) and comparable sample configuration and preparation conditions.[2,3] The OFET performance of P3HT reflects the pronounced chain self-assembly leading to a crystalline film morphology and is consistent with the above discussed characterization by DSC, UV−vis, and X-ray methods. These properties were essentially preserved for **P3HTTFT1** and **P3HTTFT3** with low **TFT** concentrations in the main chain. Consequently, the corresponding mobility data were in the range of 10^{-2} cm^2/V·s, comparable to that of P3HT. The increase of the **TFT** amount in the backbone led to reduced structural/morphological quality and resulted in a mobility decrease by 1 order of magnitude for **P3HTTFT5** and to 7×10^{-4} cm^2/V·s for **P3HTTFT15**. The observed trend follows the correlation between solid-state morphology and mobility reported for poly(alkylthiophene)s.[2,3,11−13,32] The mobility value of 1.1×10^{-3} cm^2/V·s achieved for **P3HTTFT10** is in the range of the results obtained by application of acceptor group in the side chains and using a bottom contact OFET configuration [μ: (2.0 to 3.2) $\times 10^{-3}$ cm^2/V·s[13]]. The authors demonstrate a further increase in the mobility by application of top-contact OFET layout or by promoting the crystalline order using a modified polymer structure. Nevertheless, in the latter case the polymer was reported to be of a low solubility in organic solvents at room temperature. We expect that our results for the field-effect mobility can be improved by a transfer to top-contact OFET layout, which supports a better chain ordering compared to the bottom-contact devices, especially for HMDS-treated SiO$_2$ gate dielectric. In addition, the concept that we propose allows for further improvement of the mobility values by applying acceptor units which maintain the planarity of the main chain. At the same time, however, it is important to find the best possible compromise between the crystallinity and processability of the resultant polymer structures.

The ON/OFF ratio values increase by 1 order of magnitude in the presence of **TFT** units in the main chain. This indicates the high degree of purity in the new synthesized polymers. The onset voltage data (V_0) reported in Table 3 were determined from the logarithmic plot of the transfer characteristics. Threshold voltage (V_T) values were obtained from the square root plot ($|I_{S-D}|^{0.5}$ vs V_G). Upon increasing the **TFT** amount, the V_0 values were reduced and consequently V_T shifts in the negative direction. The two quantities depend on the flat band voltage, the intrinsic and (unintentional) doping-induced charge density, and the presence of traps at the interface between the polymer and the gate dielectric layers.[37]

An important issue of polymer transistor performance is the operational stability of V_T. This was investigated by performing three successive scans of the transfer characteristics in forward and reverse gate voltage bias and recording the corresponding V_T changes. Two such examples for P3HT and **P3HTTFT3** are available as Supporting Information. The measured V_T shift (ΔV_T) for the different polymer devices is collected in Table 3. Notably, the negative shift of V_T was smaller in the presence of electron-accepting units in the main chain. The negative V_T shift for OFETs after prolonged operation has been discussed in terms of mobile ions drift in the gate dielectric under the application of a gate field,[38] in correlation with the device processing,[39] or

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(37) Horowitz, G.; Hajlaoui, R.; Bouchriha, H.; Bourguiga, R.; Hajlaoui, M. *Adv. Mater.* **1998**, *10*, 923.

(38) Zilker, S. J.; Detcheverry, C.; Cantatore, E.; de Leeuw, D. M. *Appl. Phys. Lett.* **2001**, *79*, 1124.

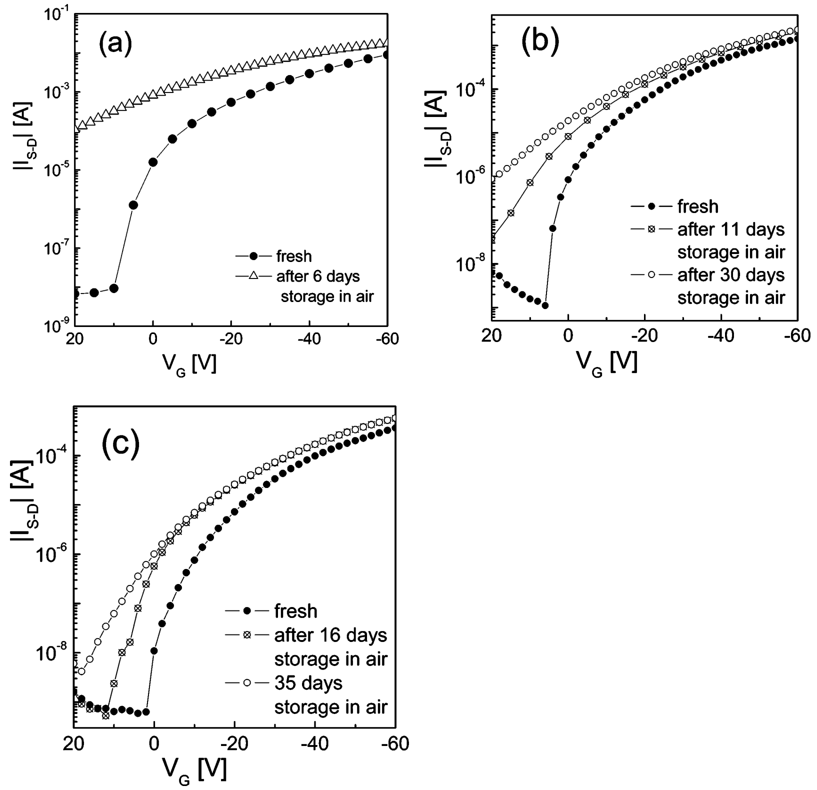

Figure 5. Transfer characteristics recorded at a source-drain voltage of −60 V of transistor devices based on P3HT (a), **P3HTTFT5** (b), and **P3HTTFT10** (c), measured on fresh samples and after their storage in air.

by trapping of charge carriers within the polymer active layer near the interface to the gate.[40] Since the device layout, preparation, and the measurement procedures were identical for all our devices, the observed improved V_T stability is specific to the **TFT**-modified polymers, representing a significant improvement in view of practical applications.

A key parameter aimed at with our acceptor modification of the poly(alkylthiophene) main chain is an improvement of the ambience stability of the transistor performance. Therefore, the device characteristics were measured after different storage periods in air without exposing the samples to light. A comparative plot of the changes in the ON/OFF ratio after ambient exposure of about 4 days for samples of varied **TFT** concentration is shown in Figure 4. The data summarized in the plot exhibit a gradual improvement of the stability toward oxygen-related doping with increasing **TFT** addition. This effect is indeed consistent with the increase in the thin film polymer IE for higher **TFT** concentrations. A comparison between the transfer characteristics of the OFETs based on P3HT, **P3HTTFT5**, and **P3HTTFT10** after prolonged air storage is shown in Figure 5a−c, respectively. Apparently, air exposure for 6 days drastically reduced the field-effect operation of P3HT devices. Note samples were not encapsulated. The deteriorating ambience effect was suppressed in the **P3HTTFT5**-OFETs. This tendency became even more prominent for **P3HTTFT10** and **P3HTTFT15** (the latter is available as a Supporting Information). Indeed the most prominent improvement of the OFET stability has been achieved at higher **TFT** concentrations. This result is probably because during the environmental stability OFET tests the new synthesized copolymers apart from the contact with oxygen have been under the influence of several additional factors, such as the air humidity and the voltage stress during the device operation. In this connection the IE value of the polymers determined by the photoemission measurements (vide supra) represents one property contributing to the overall OFET-ambience stability.

In the case of **P3HTTFT10** (Figure 5c), a positive V_T shift by 16 V was observed, possibly due to p-type doping in air,[37,41] however, at a significantly lower rate than that for P3HT. The field-effect mobility slightly increased from 1.1×10^{-3} to 1.8×10^{-3} cm^2/V·s. The effect can be explained in terms of the field-effect mobility dependence on the charge density[7] that increases due to the oxygen-induced p-doping of the polymer layer. In addition, our experiments showed that a prolonged shelf storage, even under inert atmosphere conditions, increases the mobility of the polymers by 10−20%. This effect was observed in all compounds except the amorphous **P3HTTFT15**. The origin is not yet fully clarified; probably long-term morphology changes (i.e., crystallization processes) take place in the active polymer layer. A more conclusive interpretation of the result may be obtained by further tests such as capacitance−frequency and capacitance−voltage in combination with morphology investigations which are beyond the scope of this paper. The corresponding ON/OFF ratio remained high, 2×10^4. In this way the overall

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(39) Gomes, H. L.; Stallinga, P.; Dinelli, F.; Murgia, M.; Biscarini, F.; de Leeuw, D. M.; Muck, T.; Geurts, J.; Molenkamp, L. W.; Wagner, V. *Appl. Phys. Lett.* **2004**, *84*, 3184.

(40) Torres, I.; Taylor, D. M.; Itoh, E. *Appl. Phys. Lett.* **2004**, *85*, 314.

(41) Scheinert, S.; Paasch, G.; Schrodner, M.; Roth, H. K.; Sensfuss, S.; Doll, T. *J. Appl. Phys.* **2002**, *92*, 330.

OFET performance was significantly better preserved in the **TFT**-containing polymers, demonstrating their improved resistance against the unwanted ambient influence.

Conclusions

It was shown that poly(3-hexylthiophene)s with different amounts of tetrafluorobenzene as an electron-accepting unit in the main chain can be successfully synthesized via the McCullough metathesis method. Random copolymers were prepared with varied **TFT** inclusion between 1.1 and 14.8 mol %. The structure−property relations as a function of the **TFT** content were investigated by means of DSC, UV−vis, X-ray, and photoemission methods. The film morphology exhibited a higher degree of disorder as the acceptor concentration increased, resulting in lower field-effect mobility values. The ionization energy increased from 4.8 eV for P3HT to 5.1 eV for the copolymer with 9.5 mol % acceptor concentration. Density functional theory based calculations support the notion that both the changes in the optical as well as electronic properties upon increasing the **TFT** content are mainly related to morphological effects induced by the **TFT** units and only to a lesser extent a direct consequence of their electron-accepting properties. The observed increase of IE resulted in a significant improvement in the ambience stability of the resultant transistor devices, which makes the current polymers, especially the compounds of higher **TFT** concentrations, attractive candidates, e.g., for integrated circuit fabrication by printing techniques, where tight encapsulation of the active layer is not a feasible option.

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Supporting Information Available: Details of the monomer and polymer synthesis; table summarizing the DSC data; details concerning the quantum-mechanical calculations—the geometry of the molecules and conjugation interruption for the copolymer and the model molecules; description of the OFET sample preparation; plots of the output characteristics and transfer characteristics of P3HT in comparison with those of **P3HTTFT3**; ambience stability data of **P3HTTFT15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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