University of Groningen

Solution-Processable Septithiophene Monolayer Transistor

Defaux, Matthieu; Gholamrezaie, Fatemeh; Wang, Jingbo; Kreyes, Andreas; Ziener, Ulrich; Anokhin, Denis V.; Ivanov, Dimitri A.; Moser, Armin; Neuhold, Alfred; Salzmann, Ingo

Published in:
Advanced materials

DOI:
[10.1002/adma.201103522](https://doi.org/10.1002/adma.201103522)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2012

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Defaux, M., Gholamrezaie, F., Wang, J., Kreyes, A., Ziener, U., Anokhin, D. V., Ivanov, D. A., Moser, A., Neuhold, A., Salzmann, I., Resel, R., de Leeuw, D. M., Meskers, S. C. J., Moeller, M., & Mourran, A. (2012). Solution-Processable Septithiophene Monolayer Transistor. *Advanced materials*, 24(7), 973+. <https://doi.org/10.1002/adma.201103522>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Solution-Processable Septithiophene Monolayer Transistor

Matthieu Defaux, Fatemeh Gholamrezaie, Jingbo Wang, Andreas Kreyes, Ulrich Ziener, Denis V. Anokhin, Dimitri A. Ivanov, Armin Moser, Alfred Neuhold, Ingo Salzmann, Roland Resel, Dago M. de Leeuw, Stefan C. J. Meskers, Martin Moeller, and Ahmed Mourran*

Current efforts towards conjugated organic materials and (opto)electronic devices thereof, strive for the development of efficient photovoltaic cells, bright/multicolour organic light emitting diodes (OLED), or organic light emitting transistors (OLETs), which combine in a single device the electrical switching functionality of a field effect transistor and the capacity of light generation.^[1] In all of these applications, the efficiency of charge transport within the organic layers plays a key role. In an organic thin film field effect transistor (OFET), transport of carriers in the channel between the source and drain electrodes occurs in the first layers of the semiconductor, close to the dielectric layer adjacent to the gate electrode.^[2,3] Thus, the transport property in such a device is very sensitive to molecular packing to the same extent as the interfacial interactions between the three electrode terminals. Down

scaling the semiconducting film to a monolayer reduces the electrical transport to two dimensions. Therefore, any structural imperfection or deficient electrical contacts lead to potential barriers and, hence, to a deteriorated charge carrier mobility.^[4] Often, the mobility in monolayer transistors is orders of magnitude lower than in the corresponding multilayer film.^[5,6] The major problems of polycrystalline films, as obtained usually, is the existence of structural defects and grain boundaries, which act as traps for the charge carriers and therefore considerably reduce mobilities.^[5–7] Liquid crystalline (LC) π -conjugated molecules may alleviate these restrictions.^[8,9] Their capability to self-heal structural defects and form large structurally homogeneous domains is well documented.

Oligothiophenes are a promising class of organic semiconductors, and their derivatives have been employed as active layers in OFETs. Significant research efforts have been devoted to the exploitation of oligothiophene derivatives but only a few examples of oligomers with more than six thiophene rings without solubilizing substituents in the β -position have been reported,^[10–12] in particular because of their extremely low solubility. Examples of LC phases are described in the literature, wherein flexible peripheral substituents are combined with a rigid thiophene core.^[11–13] In this work we report on the crystal structure of α,ω -substituted septithiophenes and we demonstrate that this material is an excellent candidate for the realization of monolayer OFETs. We first assessed the crystal structure of 2-octyldodecyl-disubstituted septithiophene (7T) and revealed the presence of several high temperature transitions between the crystalline and LC phases. We make use of the high solubility of these substituted septithiophenes for accurate control of the surface coverage by a simple spin coating process. The structure of the monolayer was assessed with scanning force microscopy (SFM) and X-ray reflectivity measurements. The process enabled fabrication of monolayer OFETs which exhibit mobilities comparable to or even better than OFETs with vacuum deposited multilayer films. In addition, the orientation and packing of 7T within the (sub)monolayer was probed with time-resolved fluorescence spectroscopy. The 2D packing of the molecules in the monolayer differs from the 3D crystal structure.

Design and Synthesis of the Oligothiophene: As described in a previous publication, the introduction of branched alkyl side chains in the α - and ω -positions and the use of a soluble precursor opened synthetic access to long oligothiophenes by the combination of ring-closure and metal catalyzed coupling reactions.^[12b] The 2-octyldodecyl endgroups provide good solubility of 7T (see Figure 1) and have a strong impact on the packing properties of the molecules in bulk and thin film (see below).

Dr. M. Defaux, J. Wang, Prof. M. Möller, Dr. A. Mourran
DWI an der RWTH
Pauwelsstrasse 8, 52056 Aachen, Germany
E-mail: mourran@dw.rwth-aachen.de

Dr. A. Kreyes, Dr. U. Ziener
University of Ulm
Institute of Organic Chemistry III
Albert-Einstein-Alle 11, 89081 Ulm, Germany

Dr. D. V. Anokhin, Prof. D. A. Ivanov
Institut de Sciences des Matériaux de Mulhouse (CNRS LRC 7228)
15 rue Jean Starcky, B.P. 2488, 68057 Mulhouse Cedex
France and Moscow State University
Faculty of Fundamental Physical and Chemical Engineering
119991, Moscow, GSP-1, 1-51 Leninskie Gory, Russia

A. Moser, A. Neuhold, Prof. R. Resel
Institute of Solid State Physics
Graz University of Technology
Petersgasse 16, 8010 Graz, Austria

Dr. I. Salzmann
Institut für Physik
Humboldt Universität zu Berlin, Germany
Newtonstr. 15, 12489 Berlin, Germany

F. Gholamrezaie, Prof. D. M. de Leeuw
Philips Research Laboratories
High Tech Campus 4, 5656 AE Eindhoven
The Netherlands and Molecular Electronics
Zernike Institute for Advanced Materials
University of Groningen
Nijenborgh 4, 9747 AG Groningen, The Netherlands

Dr. S. C. J. Meskers
Molecular Materials and Nanosystems
Eindhoven University of Technology
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

DOI: 10.1002/adma.201103522

Figure 1. a) Molecular structure of 7T and DSC trace recorded during heating of 7T; the inset shows the corresponding cooling curve and the thermal transition temperatures. The *ab* plane of the 7T unit cell at RT (b) and reconstructed electron density profile along the {100}-direction (c). X-ray diffraction patterns recorded at room temperature (d), 100 °C (e) and at 168 °C (f); the fiber axis is vertical.

LC Properties and Structures: Strong π - π interactions and separation between the rigid conjugated backbone and the long flexible chains in the periphery result in the presence of a LC phase. This was corroborated by measuring the specific heat (DSC)^[12a] and by analyzing the temperature dependent X-ray diffraction (XRD) pattern. Indeed, the DSC thermogram of septithiophene depicted in Figure 1 shows three reversible transitions:^[21a] a low temperature thermal event at 65 °C ($\Delta H = 9 \text{ J g}^{-1}$) followed by two consecutive transitions, one at 166 °C ($\Delta H = 39 \text{ J g}^{-1}$) and a clearing transition at 171 °C ($\Delta H = 9.4 \text{ J g}^{-1}$). The enthalpy of transition gives a hint to the existence of a LC phase prior to the isotropic phase. Analysis of the XRD pattern of extruded fibres (Figure 1d-f)^[12a] recorded at different temperatures suggests that at low temperature the compound crystallizes in a triclinic unit cell ($a = 36.8 \text{ \AA}$, $b = 8.90 \text{ \AA}$, $c = 11.34 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 80.4^\circ$, $\gamma = 72^\circ$, $P-1$ symmetry, $V = 1769.3 \text{ \AA}^3$, $\rho = 1.07 \text{ g cm}^{-3}$). The most intense equatorial peak with higher-order reflections up to nine orders is indicative of the presence of a well-ordered layer structure. The interlayer distance, the 100 spacing, of about $34.3 \text{ \AA}$ is shorter than the molecular length in its fully extended conformation (ca. $49 \text{ \AA}$); hence, the molecules must be tilted with respect to the layer plane normal. The inclination of the thiophene core with respect to the layer plane normal was evaluated from the reconstruction of the electron density profile computed from ten orders of the fundamental reflection of the layered structure (Figure 1b,c). It was found that the thickness of the

sublayers with high and low electron densities, corresponding to the thiophene core and alkyl substituents, is 22.8 and $11.5 \text{ \AA}$, respectively. Therefore, the thiophene core is tilted by 15° with respect to the layer plane. The presence of the bulky alkyl chains makes packing of the thiophene cores less dense than in compounds with linear alkyl chains.

The first thermal event at 65°C corresponds to a crystal-crystal transition, which does not modify the symmetry of the crystal lattice. At 100°C the unit cell remains triclinic with the following parameters: $a = 36.4 \text{ \AA}$, $b = 9.73 \text{ \AA}$, $c = 6.11 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 75.2^\circ$, $\gamma = 65.9^\circ$, $V = 1869.0 \text{ \AA}^3$, and $\rho = 1.01 \text{ g cm}^{-3}$. However, a slight contraction of the unit cell above 65°C leads to reorganization of the molecules in the unit cell whereby strong and broad off-meridian peaks split into sharp well-defined reflections. Between 166 and 171°C , the compound is in the LC state. It is organized in smectic layers of $33.6 \text{ \AA}$ thickness.

Film Formation: Because of the bulky alkyl substituents, the solubility of the septithiophene is relatively high compared to the unsubstituted one, with a saturation concentration of 3 g L^{-1} in toluene. This concentration is largely sufficient to cast several nanometer thick films. Characterized by SFM, the film's morphology is very homogeneous even on a large scale. The molecules form a layered structure with a $34 \text{ \AA}$ step height. This value is similar to the 100 spacing of the bulk material, as inferred from the XRD pattern discussed previously. Thus in a thick film, the material organizes in layers with the molecules close to the substrate normal.

Figure 2. b) The solution concentration of 7T versus the surface coverage; the film coverage was estimated from the SFM data; 100% coverage is achieved at 0.89 g L^{-1} in toluene. The SFM micrographs (c–e) show the morphology of the monolayer depending on the solution concentration. In addition, in submonolayer coverage of the islands is square shaped and in the upper image (a) the internal sub-structure of the islands with a periodic length of ca. 250 Å is resolved.

To form a physisorbed monolayer it is essential to accurately control the surface coverage. The low nucleation density with pronounced growth rate is a prerequisite to reduce the density of the grain boundaries and to obtain large 2D single crystals. Often non-substituted oligothiophenes exhibit a marked tendency to form 3D layered islands before the monolayer is completed. Only in rare cases is the formation of islands without a closed monolayer observed; in most cases the monolayer is formed followed by the formation of islands. Here, it is demonstrated that septithiophene behaves remarkably differently. Essentially, the surface density of monolayer islands increase linearly with the solution concentration (Figure 2), while the increment is sensitive to the surface energy and processing conditions (e.g., spinning velocity and evaporation rate). On a SiO_2 surface, a complete monolayer was achieved from toluene containing 0.9 g L^{-1} septithiophene. The average island size was ca. $1\text{--}2 \text{ μm}$. Above this concentration, the molecules have a tendency to form multilayer stacks with a well defined thickness of 34 Å . Striking is the rectangular symmetry of the islands which infer their crystalline nature. High resolution SFM imaging allows resolution of the inner superstructure with a 250 Å periodicity (Figure 2). This shape becomes difficult to resolve once the monolayer coverage is reached, likely a result of coarsening of the domains. The superstructure may be the result of two-dimensional organization of the molecules. Indeed, in 3D, 7T crystallizes in multilayer stacks with partial interdigitation of the alkyl chains while the thiophene cores are inclined relative to the

layer plane. However, it will be shown below that in a monolayer, the molecules are tilted at an angle greater than in the 3D crystal. Apparently, the surface force (the confining interface) and lack of interdigitation lead to a large tilt angle, which would weaken the $\pi\text{--}\pi$ interactions. Thus, a balance between geometrical requirements and intermolecular interaction could be the cause of this superstructure.^[14,13a] Additional modeling together with grazing incidence diffraction is required to understand how a monolayer of tilted molecules with a rigid conjugated backbone and long flexible chains in the periphery generates such a superstructure.

X-Ray Reflectivity (XRR): The molecular packing and the position of the long axes of the thiophene core relative to the dielectric surface plane are important for optoelectronic properties of the septithiophene monolayers. For this purpose the layer structure of the monolayer perpendicular to the substrate surface was investigated by XRR.

XRR experiments were executed for three films spun from solutions with concentrations of 0.5 , 0.9 , and 1.0 g L^{-1} and for a fourth sample, spun from a 0.9 g L^{-1} solution and subsequently solvent annealed. The XRR data were fitted to determine the structure of the monolayer.^[15] A three-layer model was used to account for the different electron densities of the alkyl chains and the thiophene backbone (Figure 3). The XRR fits confirm that the films are monolayers and reveal the thicknesses of the individual sublayers. The best fit was obtained for the solvent annealed 0.9 g L^{-1} sample showing that the three-layer model is the right choice. Total electron densities of 0.43 Å^{-3} were found for the thiophene layer and 27 and 0.29 Å^{-3} for the top and bottom alkyl layer, respectively. A thickness of 20.5 Å was obtained for the thiophene layer and 9.3 or 11.3 Å for the alkyl layers; the roughnesses between the layers are around 2 Å . An estimation of the tilt angles of the thiophene backbone and alkyl chains with respect to the substrate surface normal (Figure 3) can be calculated from the sub-layer thicknesses and the length of the molecular building blocks. For the solvent annealed

Figure 3. X-ray reflectivity data for the monolayer. The data (symbols) are presented together with the best fit to a three-layer model (red line). The scheme depicts the sublayer's structure as obtained by the fit.

Figure 4. Linear and saturated transfer characteristic of a 7T spin-coated monolayer field-effect transistor. The channel length is 40 μm and the channel width is 1000 μm . To prevent parasitic leakage currents, a ring geometry was used. The inset shows the linear and saturated mobility.

sample the long molecular axis of the 7T is tilted with an angle of approximately 40° with respect to the substrate surface.

Electrical and Optical Characterization: The microstructure of thin films and single crystals of conjugated oligomers such as oligothiophenes, oligophenylenes, and oligophenylene-vinyls is based on stacked layers in which the long molecular axes are parallel to each other with a herringbone configuration. The overlap between the π -orbitals favors charge transport. Here we investigate the electrical transport in monolayer field-effect transistors and the molecular packing by optical spectroscopy.

In general, transistors are annealed prior to the measurements at 130°C to remove any residual water and solvent. However, the 7T molecules exhibit a transition at 65°C , limiting the annealing temperature to 60°C . As a result, a small hysteresis at high source-drain bias and a relatively large parameter spread is observed. In **Figure 4**, a typical transfer characteristic for a ring transistor with a channel length of 40 μm and a channel width of 1000 μm are presented. The transfer curve shows a current modulation of five decades. The inset shows that the linear mobility is about $1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ which is an order higher than the mobility of the bulk drop-cast films ($\sim 2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The mobility, however, is comparable to that measured in quinquethiophene (5T) self assembled monolayer field-effect transistors (SAMFETs) ($2 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^[7] The mobility is thermally activated. The activation energy as obtained from temperature dependent mobility measurements $\mu_{\text{FET}} = \mu_0 \exp(-E_a/kT)$ amounted to 60 to 90 meV, in good agreement with the activation energy obtained for 5T SAMFETs of 80 meV. The value of the activation energy indicates that the transport could still be trap limited by, for example, grain boundaries.

Figure 5. a) Fluorescence (F) and fluorescent excitation (FE) spectra of 7T molecules in MeTHF. The blue lines represent measurements in solution at 293 K, the red dashed curves at 80 K. b) Fluorescence and excitation spectra of a fully covered ($0.9 \text{ g L}^{-1} = 100\%$ film) 7T monolayer on quartz (blue solid lines). The black line shows the extinction of the 100% film measured at zero angle of incidence. c) Fluorescence intensity of partially covered, $0.5 \text{ g L}^{-1} = 50\%$ film and fully covered 100% 7T monolayers on quartz.

To investigate the molecular packing in the 7T monolayer we measured fluorescence, excitation and extinction, and time-resolved fluorescence spectra. The fluorescence and the fluorescence excitation of a dilute solution (10^{-5} M) of the 7T molecules dissolved in 2-MeTHF is shown in **Figure 5a**. The spectra were measured at room temperature (solid lines) and at a low temperature of about 80 K (dashed line) in the glassy state of the solvent. The dilute solution shows a very bright fluorescence with an onset at 2.35 eV. The spectrum at room temperature shows a characteristic vibronic fine structure that becomes more pronounced at low temperature in frozen 2-MeTHF. The excitation spectrum shows an onset at 2.4 eV. At room temperature the vibronic fine structure is hardly resolved, only a broad structure remains with a maximum near 2.6 eV. **Figure 5a** shows a pronounced vibronic fine structure at low temperature, 80 K. The difference originates from the torsional flexibility around the single bonds joining the thiophene rings. The significant thermal population of the non-planar conformation of the 7T moiety causes the loss of fine structure at room temperature.

The fluorescence, excitation, and extinction spectra of the fully covered 7T monolayer, spin-coated on a quartz substrate, are shown in Figure 5b. The film obtained with 0.9 g L^{-1} , corresponding to 100% coverage, shows the onset of fluorescence at 2.2 eV with a maximum intensity at about 2.0 eV. The excitation spectrum displays an onset at 2.3 eV with a maximum intensity near 2.66 eV. The extinction spectra do not show a strong dependence on the angle of incidence. The spectra exhibit the same shape as the excitation spectrum. The transition dipole moment for the lowest energetically allowed optical transition of the 7T moiety, S_0-S_1 , is oriented along the long axis of the molecule. The substantial extinction measured under a zero degree angle of incidence indicates that the thiophene core is not perpendicular to the surface but tilted. It is well-known that, in first approximation, the dipole strength of an absorption band is conserved when comparing isolated and interacting molecules.^[16] This allows us to obtain an estimate of the tilt angle of molecules by evaluating the area under the absorption curve and comparing this with the isotropically averaged dipole strength of the isolated molecules as observed in 2-MeTHF solution. For compound 7T in 2-MeTHF we obtain a dipole strength of 120 D^2 and hence a transition dipole moment of 9.5 D when including a correction for the Lorentz local field in the solvent ($n = 1.49$) cage around the molecule.^[17] For the fully covered film we find that the projection of the transition dipole moment in the plane of the film along the surface direction amounts to 10.85 D . This implies an angle between the transition dipole moment of the molecule and direction perpendicular to the surface of approximately 60° . The tilt is different to that derived from XRD measurement as discussed above. We note that the excitation spectra at low temperature are similar to that at room temperature. Small changes, however, are observed in the emission spectra. The intensity ratio of the vibronic bands slightly depends on temperature. A new peak appears that may indicate temperature induced reorganization. Data are shown in the Supporting Information.^[18]

The spectra of the isolated molecules are different from that of a fully covered monolayer. The maximum in the excitation of the film is blue-shifted with respect to that of a single molecule. Furthermore the onset of the 0–0 fluorescence is red-shifted, and the ratio of the 0–0 and 0–1 vibronic bands is larger in the film than for the single molecule. The differences indicate that the 7T molecules in the film are packed into H aggregates.^[19] The 0–0 transition then is partially forbidden and the fluorescence is red-shifted and dominated by the 0–1 vibronic transition. Similarly, the extinction is blue-shifted.

The H aggregate packing is supported by the intensity of the fluorescence. Single molecules exhibit a bright fluorescence. The emission in thin films is optically forbidden and, therefore, the intensity of thin films is orders of magnitude lower than expected from the fluorescence quantum efficiency of single molecules. We note that the fluorescence intensity scales with coverage. Figure 5c shows that the fluorescent intensity of a 0.5 g L^{-1} (50% coverage) film is almost half of that of the fully covered film. This clearly shows that the fluorescence originates from the monolayer islands and that a contribution from single molecules in between the islands to the fluorescence can be disregarded.

The fluorescence decay was measured at room temperature for isolated molecules and thin films. The fluorescence of single molecules decays exponentially with time irrespective of emission wavelength. The decay time is 1.3 ns. The decay of thin films does not depend on the coverage. The decay time is about 0.5 ns, ruling out the presence of isolated molecules in the films. The shorter decay time in the film indicates the presence of additional photophysical decay pathways, possibly involving intermolecular charge transfer interactions. The decay time does not depend on the emission wavelength. Hence the emission in the partially and fully covered films originates from the same type of H aggregates.

In summary we have demonstrated that 2-octyldodecyl-disubstituted septithiophene is capable of forming crystalline and liquid crystalline phases. In 3D, 7T crystallizes in multilayer stacks with partial interdigitation of alkyl chains while the thiophene cores are inclined relative to the layer plane. However, in a monolayer, the molecules are tilted at an angle greater than in the 3D crystal. The bulkiness of the endgroups enhances the solubility and allows for solution deposition and self-assembly of an electrically connected monolayer. The process resulted in monolayers with high mobility and on–off current modulation in a field effect transistor. Moreover, spectroscopic signatures of the monolayer could be recorded and are consistent with those expected from a closely packed layer of tilted molecules. Differences in spectroscopic properties of the monolayer and isolated molecules in solution provide evidence for delocalization of the excitation through intermolecular interactions within the layer.

Experimental Section

Film Preparation and Microscopy: The desired amounts of 7T were weighed into a brown GC vial and HPLC grade toluene was added according to the target concentration. The mixture was stirred under room temperature overnight, a transparent yellow solution was obtained, and it was filtered through a $0.2 \mu\text{m}$ PTFE syringe filter before use. Silicon wafers were cleaned by sonication in isopropyl alcohol for 5 min, dried with air stream, and activated in UV/O_2 for 12 min. 7T thin films were prepared by placing a drop of solution onto a cleaned silicon wafer and spin coated at a spinning rate of 2500 rpm for 30 s (Convac 1001S, Germany). The surface coverage was controlled by concentration.

The morphology of the 7T thin films was investigated by a tapping mode SFM (NanoScope V, Digital Instruments Veeco Instruments, Santa Barbara, CA) under ambient conditions. Commercially available standard silicon cantilevers (PPP-SEIH-W from Nanosensors) with a spring constant of $5-37 \text{ N m}^{-1}$ and an oscillation frequency of $\sim 125 \text{ kHz}$ were used. Data analysis was performed using Digital Instruments software, NanoScope Analysis, version 1.10.

Differential Scanning Calorimetry (DSC): DSC measurements were performed on a Netzsch DSC 404 instrument under the protection of a N_2 stream. About 1 mg of 7T was sealed in an aluminum pan, and heated to 200°C and kept at that temperature for 2 min to erase the thermal history, and then cooled to -70°C at a rate of $10^\circ\text{C min}^{-1}$. Afterwards the sample was heated to 200°C at a rate of $10^\circ\text{C min}^{-1}$ again to determine the melting behavior of the compound.

X-Ray Diffraction (XRD): XRD experiments were conducted on the ID01 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble) using X-ray photons with energy of 10 keV. During measurements, the samples were placed in a chamber with Kapton windows equipped with a computer-controlled heating/cooling stage. The diffraction patterns were collected using a 2D photon-counting pixel detector MAXIPIX. Raw images were corrected for dark current, flat field;

the image distortion correction was performed using special calibration frames. The sample-to-detector distance was calibrated using several diffraction orders of Ag behenate powder.

X-Ray Reflectivity (XRR): XRR measurements were performed at the W1 beamline at the synchrotron radiation source HASYLAB (Hamburg, Germany) using a wavelength of $\lambda = 0.118$ nm. The samples were measured under a helium atmosphere to avoid radiation damage. The XRR data was fitted with the software package GenX.^[15]

Electrical and Optical Characterization: Spin-coated monolayers of 7T molecules were prepared on heavily doped silicon wafers acting as the common bottom gate covered with a 200 nm layer of thermally grown SiO₂. The gold source and drain contacts were defined by conventional photolithography. Ti (10 nm) was used as an adhesion layer. Normally HMDS was applied to passivate the SiO₂ gate dielectric. However, the presence of HMDS led to crystallization of the 7T molecules. Therefore, prior to spin-coating the monolayer, any HMDS and all organic contaminants were removed by 10 min UV-ozone treatment. The monolayer could be applied by spin-coating 7T molecules from a toluene solution of 1 mg mL⁻¹ at 2000 rpm for 30 s with an acceleration of 600 rpm s⁻¹. AFM experiments have shown that the morphology of the monolayer on the patterned SiO₂ is similar to that on bare silicon. The electrical transport was measured using a HP 4155C semiconductor parameter analyzer in a vacuum of 10⁻⁶ mbar.

Fluorescence spectra were recorded using a continuous wave spectrophotometer (Edinburg Instruments F900). Measurements at room temperature were performed in inert atmosphere (N₂), low temperature spectra were taken using a cryostat. Spectra were corrected for the wavelength dependence of the sensitivity of the detection channel. Fluorescence lifetimes were obtained through single photon counting.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors gratefully acknowledge support of the present work by the Deutsche Forschungsgemeinschaft projects MO982/2-1 and Z1567/4-1. They thank W. Caliebe from HASYLAB (Hamburg, Germany) for the experimental support. DVA, LV and DAI acknowledge the French Agence Nationale de la Recherche (SPIRWIND project of the HABISOL program and T2T project of the Blanc International program) and Russian Ministry of science and education (project for financial support of leading scientists No.G34.31.0055 from 19.10.2011) for financial support. The authors are grateful for the excellent technical support of the ID01 beamline of the ESRF (Grenoble, France) and especially to Peter Boesecke for his assistance during measurements.

Received: September 13, 2011

Published online: January 19, 2012

- [1] a) M. Pope, C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, 2nd ed., Oxford University Press, New York **1999**; b) F. A. Hegmann, *Phys. Canada* **2003**, 59, 127; c) M. E. Gershenson, V. Podzorov, A. F. Morpurgo, *Rev. Mod. Phys.* **2006**, 78, 973; d) B. Oregan, M. Grätzel, *Nature* **1991**, 353, 737; e) R. F. Service, *Science* **2004**, 306, 2034; f) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* **1990**, 347, 539; g) J. Godlewski, M. Obarowska, *Opto-Electron. Rev.* **2007**, 15, 179; h) M. Muccini, *Nat. Mater.* **2006**, 5, 605.
- [2] G. Horowitz, R. Hajlaoui, H. Bouchriha, R. Borguiga, M. Hajlaoui, *Adv. Mater.* **1998**, 10, 923.
- [3] F. Dinelli, M. Murgia, P. Levy, M. Cavallini, F. Biscarini, D. M. De Leeuw, *Phys. Rev. Lett.* **2004**, 92, 116802.
- [4] a) X. Guo, M. Myers, S. Xiao, M. Lefenfeld, R. Steiner, G. S. Tulevski, J. Tang, J. Baumert, F. Leibfarth, J. T. Yardley, M. L. Steigerwald, P. Kim, C. Nuckolls, *Proc. Natl. Acad. Sci. U.S.A.* **2006**, 103, 11452; b) G. S. Tulevski, Q. Miao, M. Fukuto, R. Abram, B. Ocko, R. Pindak, M. L. Steigerwald, C. R. Kagan, C. Nuckolls, *J. Am. Chem. Soc.* **2004**, 126, 15048; c) M. Mottaghi, P. Lang, F. Rodriguez, A. Rumyantseva, A. Yassar, G. Horowitz, S. Lenfant, D. Tondelier, D. Vuillaume, *Adv. Funct. Mater.* **2007**, 17, 597.
- [5] R. Ruiz, A. Papadimitratos, A. C. Mayer, G. G. Malliaras, *Adv. Mater.* **2005**, 17, 1795.
- [6] B.-N. Park, S. Seo, P. G. Evans, *J. Phys. D* **2007**, 40, 3506.
- [7] E. C. P. Smits, S. G. J. Mathijssen, P. A. van Hal, S. Setayesh, T. C. T. Geuns, K. A. H. A. Mutsaers, E. Cantatore, H. J. Wondergem, O. Werzer, R. Resel, M. Kemerink, S. Kirchmeyer, A. M. Muzafarov, S. A. Ponomarenko, B. de Boer, P. W. M. Blom, D. M. de Leeuw, *Nature* **2008**, 455, 956.
- [8] a) A. J. J. M. van Breemen, P. T. Herwig, C. H. T. Chlon, J. Sweelssen, H. F. M. Schoo, S. Setayesh, W. M. Hardeman, C. A. Martin, D. M. de Leeuw, J. J. P. Valetton, C. W. M. Bastiaansen, D. J. Broer, A. R. Popa-Merticaru, S. C. J. Meskers, *J. Am. Chem. Soc.* **2006**, 128, 2336; b) S. A. Ponomarenko, E. A. Tatarinova, A. M. Muzafarov, S. Kirchmeyer, L. Brassat, A. Mourran, M. Moeller, S. Setayesh, D. de Leeuw, *Chem. Mater.* **2006**, 18, 4101.
- [9] I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, L. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabiny, R. J. Kline, M. D. McGehee, M. F. Toney, *Nat. Mater.* **2006**, 5, 328.
- [10] a) D. J. Gundlach, *Nat. Materials* **2007**, 6, 173; b) F. Garnier, A. Yassar, R. Hajlaoui, G. Horowitz, F. Deloffre, B. Servet, S. Ries, P. Alnot, *J. Am. Chem. Soc.* **1993**, 115, 8716; c) M. Berggren, D. Nilsson, N. D. Robinson, *Nat. Mater.* **2007**, 6, 3.
- [11] S. Westenhoff, A. Abrusci, W. J. Feast, O. Henze, A. F. M. Kilbinger, A. P. H. J. Schenning, C. Silva, *Adv. Mater.* **2006**, 18, 1281.
- [12] a) A. Kreyes, M. Amirkhani, I. Lieberwirth, R. Mauer, F. Laquai, K. Landfester, U. Ziener, *Chem. Mater.* **2010**, 22, 2079; b) S. Ellinger, U. Ziener, U. Thewalt, K. Landfester, M. Moeller, *Chem. Mater.* **2007**, 19, 1070; c) A. Kreyes, M. Amirkhani, I. Lieberwirth, R. Mauer, F. Laquai, K. Landfester, U. Ziener, *Chem. Mater.* **2010**, 22, 6453.
- [13] a) T. Yasuda, H. Ooi, J. Morita, Y. Akama, K. Minoura, M. Funahashi, T. Shimomura, T. Kato, *Adv. Funct. Mater.* **2009**, 19, 411; b) M. A. Hempenius, B. M. W. Langeveld-Voss, J. A. E. H. van Haare, R. A. J. Janssen, S. S. Sheiko, J. P. Spatz, M. Möller, E. W. Meijer, *J. Am. Chem. Soc.* **1998**, 120, 2798; c) S. Ellinger, A. Kreyes, U. Ziener, C. H-Richter, K. Landfester, M. Moeller, *Eur. J. Org. Chem.* **2007**, 34, 5686; d) O. Lengyel, W. M. Hardeman, H. J. Wondergem, D.-M. de Leeuw, A. J. J. M. van Breemen, R. Resel, *Adv. Mater.* **2006**, 18, 896; e) H. Wada, T. Taguchi, M. Goto, T. Kambayashi, T. Mori, K. Ishikawa, H. Takezoe, *Chem. Lett.* **2006**, 35, 280; f) S. Ponomarenko, S. Kirchmeyer, *J. Mater. Chem.* **2003**, 13, 197.
- [14] A. Mourran, B. Tartsch, M. Gallyamov, S. Magonov, D. Lambrev, B. I. Ostrovskii, I. P. Dolbnya, W. H. de Jeu, M. Moeller, *Langmuir* **2005**, 21, 2308.
- [15] M. Björck, G. Andersson, *J. Appl. Crystallogr.* **2007**, 40, 1174.
- [16] N. Harada, K. Nakanishi, *Circular Dichroic Spectroscopy: Exciton Coupling in Organic Stereochemistry*; University Science Books: Mill Valley, CA, Oxford University Press, Oxford, UK **1983**.
- [17] J. Michl, E. W. Thulstrup, *Spectroscopy with Polarized Light*, VCH Publishers, New York **1986**.
- [18] R. N. Marks, R. H. Michel, W. Gebauer, R. Zamboni, C. Taliani, R. F. Mahrt, M. Hopmeier, *J. Phys. Chem. B* **1998**, 102, 7563.
- [19] E. Da Como, M. A. Loi, M. Murgia, R. Zamboni, M. Muccini, *J. Am. Chem. Soc.* **2006**, 128, 4277.