Conducting Polymers

DOI: 10.1002/ange.200602894

Regiosymmetric Poly(dialkylphenylenedioxythiophene)s: Electron-Rich, Stackable π-Conjugated Nanoribbons**

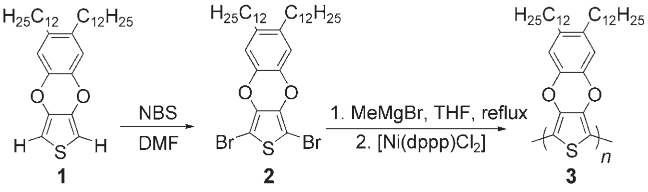
*Christophe R. G. Grenier, Wojciech Pisula, Thomas J. Joncheray, Klaus Müllen, and John R. Reynolds**

Regioregular poly(3-alkylthiophene)s are some of the best-performing semiconducting polymeric materials and are increasingly finding use in device applications such as organic field-effect transistors[1] and photovoltaics,[2] in which their high degree of order yields high charge-carrier mobilities. The more easily oxidized poly(3,4-ethylenedioxythiophene) (PEDOT) has been used as the active material in electrochromic devices, antistatic coatings, and capacitors, and as a hole-injecting layer in organic light-emitting diodes (OLEDs).[3] Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) provides an interesting alternative to indium tin oxide (ITO); it has better mechanical properties, low surface roughness, and allows more facile processing from aqueous dispersions. Although it was used successfully in the fabrication of flexible, all-plastic electrochromic devices,[4] PEDOT:PSS has a relatively low conductivity relative to ITO (100–500 $\mathrm{S\,cm^{-1}}$ vs. 4000 $\mathrm{S\,cm^{-1}}$).[5] It is desirable to synthesize easily oxidizable, low-band-gap conjugated polymers with a high degree of order, useful processability, and flexible mechanical properties.

In recent publications, the groups of both Ritter[6] and Roncali[7] introduced 3,4-phenylenedioxythiophene (PheDOT) as an attractive synthon for obtaining highly ordered polythiophenes, as X-ray crystal structures show that the thiophene and phenylene rings are fully coplanar. This arrangement should provide a strong driving force for a high degree of ordering in the solid state. PheDOT, and more recently its dimer and trimer, were electropolymerized to yield electroactive films.[7,8] As is common with electropolymerized materials, the resulting polymers are insoluble because of strong π-stacking interactions, and therefore cannot be solution-processed.

Herein we report the synthesis of the first soluble and processable polyPheDOT, specifically poly[3,4-(4,5-didodecylphenylene)dioxythiophene] (poly[PheDOT-$(C_{12})_2$]), which is highly ordered. The introduction of two dodecyl side chains induces significant solubility in organic solvents. The self-assembly of the side chains, which extend within the plane of the polythiophene backbone, provides additional order in the solid state.

PheDOT-$(C_{12})_2$ (**1**) was synthesized by using a modified procedure of Roncali and co-workers, who synthesized PheDOT-$(C_6)_2$.[7] Following bromination with *N*-bromosuccinimide to form **2**, the monomer was chemically polymerized by Grignard metathesis (GriM) polymerization (Scheme 1).[9,10] At room temperature, poly[PheDOT-$(C_{12})_2$] (**3**) forms purple colloidal suspensions in toluene, tetrachloroethane, xylenes, and THF. This result is consistent with the presence of strong interchain interactions, which force aggregation. However, upon heating to around 80 °C, poly[PheDOT-$(C_{12})_2$] becomes readily soluble in a variety of aromatic or halogenated solvents. The solubility of the polymer is important, as it enables easy processing and allows the structure of the polymer to be fully characterized (in particular, molecular weight determination). High-temperature gel-permeation chromatography (GPC), carried out at 140 °C in trichlorobenzene, yields $M_n = 14800\ \mathrm{g\,mol^{-1}}$ and a polydispersity of 1.95, which corresponds to a molecular structure of approximately 30 number-average repeat units.



Scheme 1. Synthesis of **3** by Grignard metathesis. NBS = *N*-bromosuccinimide; DMF = *N*,*N*-dimethylformamide; dppp = propane-1,3-diylbis(diphenylphosphine) (full synthetic details for **1**, **2**, and **3** are provided in the Supporting Information).

Spray-coated films of poly[PheDOT-$(C_{12})_2$] are electroactive: they switch from dark purple to transmissive green in the oxidized state. Differential-pulse voltammetry (see the Supporting Information) shows a low onset of oxidation at −0.2 V vs. ferrocene/ferrocenium (Fc/Fc$^+$). This value corresponds to a HOMO level at 4.6 eV, which is substantially lower in energy (higher oxidation potential) than neutral PEDOT (4.1 eV).[11] This result is consistent with the trend

---

[*] C. R. G. Grenier, T. J. Joncheray, Prof. Dr. J. R. Reynolds
The George and Josephine Butler Polymer Research Laboratory
Department of Chemistry
Center for Macromolecular Science and Engineering
University of Florida, Gainesville, FL, 32611 (USA)
Fax: (+1) 352-392-9741
E-mail: reynolds@chem.ufl.edu

Dr. W. Pisula, Prof. Dr. K. Müllen
Max-Planck-Institut für Polymerforschung
55128 Mainz (Germany)

[**] The authors thank Dr. Stephen J. Eyles of the University of Massachusetts, Amherst, Mass Spectrometry Facility, who supplied the high-temperature GPC results, and the AFOSR (FA955-06-1-0192) for financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

reported recently for theroretical and experimental studies on the PheDOT dimer and trimer which showed that the phenylene ring decreases the electron release of the oxygen atoms into the thiophene.[8] This higher oxidation potential gives the neutral polymer greater air stability and allows for long-term storage without the need to keep the materials under an inert atmosphere. Spectroelectrochemistry was carried out on a film drop-cast onto an ITO-coated glass slide. As the potential applied to the film is increased to 0.2 V, the π–π* transition is progressively bleached (Figure 1) and two near-infrared optical transitions appear which are characteristic of the polaronic and bipolaronic states. The optical bandgap, determined from the onset of absorption in the spectrum, is estimated at 1.85 eV, which is 0.25 eV higher than that of PEDOT (1.6 eV). The presence of vibronic features in the absorption spectrum reinforces our conclusion that this polymer contains a high degree of order.

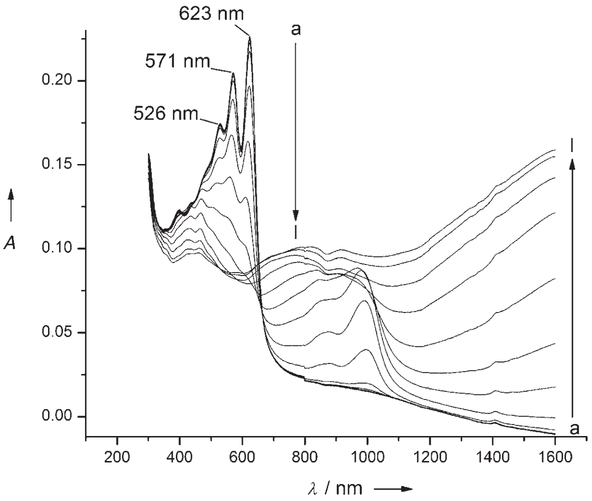


Figure 1. Spectroelectrochemistry of poly[PheDOT-(C_{12})$_2$]. The films were drop-cast from a solution (5 mg mL^{-1}) in hot toluene (100 °C) onto an ITO-coated glass slide. The film was electrochemically oxidized in 0.1 M TBAP/propylene carbonate solution (TBAP = tetrabutylammonium perchlorate). A silver wire was used as a quasi-reference electrode and was calibrated against Fc/Fc$^+$. Applied potentials: a) 0.0, b) +0.1, c) +0.2, d) +0.3, e) +0.4, f) +0.5, g) +0.6, h) +0.7, i) +0.8, j) +0.9, k) +1.0, and l) +1.1 V.

In solution, poly[PheDOT-(C_{12})$_2$] displays a strong thermochromic effect: it changes from dark purple at low temperature to red-orange at higher temperatures. Figure 2 shows the UV/Vis spectrum of a polymer solution in xylenes as it is heated from 25 to 95 °C. The absorption maximum shifts by almost 70 nm (from 614 to 546 nm) as the temperature increases. This thermochromic effect is well known in solutions of poly(3-alkylthiophene)s, but its origin is still controversial. It was first proposed that intramolecular interactions were mainly responsible for the shift in absorption.[12] In this perspective, increasing temperature induces twisting of the polythiophene backbone, which lowers the effective conjugation. However, more recent studies suggested that intermolecular interactions might play a more significant role than originally thought, and that twisting of the conjugated polymer is only responsible for smaller shifts at temperatures above the thermochromic transition.[13] In the case of poly[PheDOT-(C_{12})$_2$], we attribute the thermochromism to the transition from aggregates to isolated, intermolecular planar chains. The presence of vibronic features at high temperature indicates that the chains retain a planar (or highly conjugated) conformation. In poly(3-alkylthiophene)s, the absorption spectrum above the phase transition is broad and featureless, and arises from intrachain twisting of the polythiophene backbone.[14] This difference is consistent with studies on short oligothiophenes with alkyl or alkoxy substituents which show that the presence of the oxygen atoms induces planar conformations of the oligomers. This effect is attributed to the smaller steric demand of the oxygen atom, mesomeric effects, as well as sulfur–oxygen interactions.[15,16]

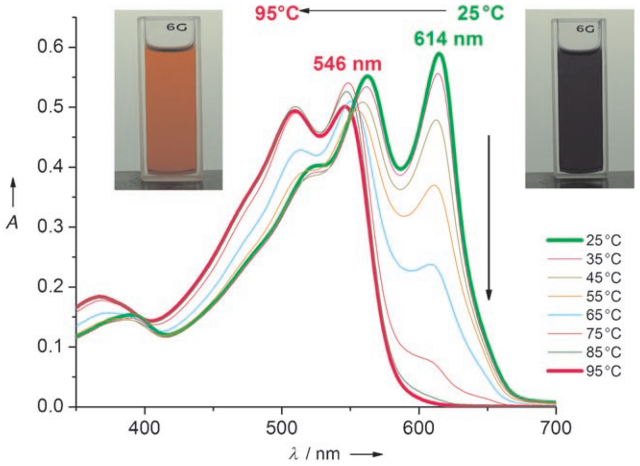


Figure 2. Solution thermochromism of poly[PheDOT-(C_{12})$_2$] (6×10^{-5} M, relative to the repeat unit) in xylenes. Pictures show the solution at 25 °C (right) and 95 °C (left).

The conformation of the polymer chains in the processing solution (aggregated versus isolated chains) plays an important role in the solid-state ordering. AFM imaging was carried out for films spin-coated onto mica from either hot (130 °C) or cold (25 °C) solutions of *ortho*-dichlorobenzene (ODCB). The films spin-coated from the hot ODCB solution yield a nanofibrillar structure (Figure 3). The average height of the fibrils is 3 nm, a value slightly lower than, but close to, the polymer chain width for a conformation in which the thiophene rings are in a *trans* conformation and the dodecyl chains are extended. This lower value is not surprising given that at high temperature in ODCB the dodecyl chains are disordered. During spin-coating of the hot solution, the fast evaporation of the solvent does not allow the side chains to order properly. The fibrils are estimated to have widths of about 10 nm (after correction for the lateral tip broadening effect[17]), which is consistent with the estimated length of the polymer chains in their fully extended conformation. From these data, we propose that the material forms ribbons of π-stacked polymer chains, whereby the polymer chains are arranged perpendicular to the plane of the substrate (Figure 3). Similar self-assembled nanostructures have been

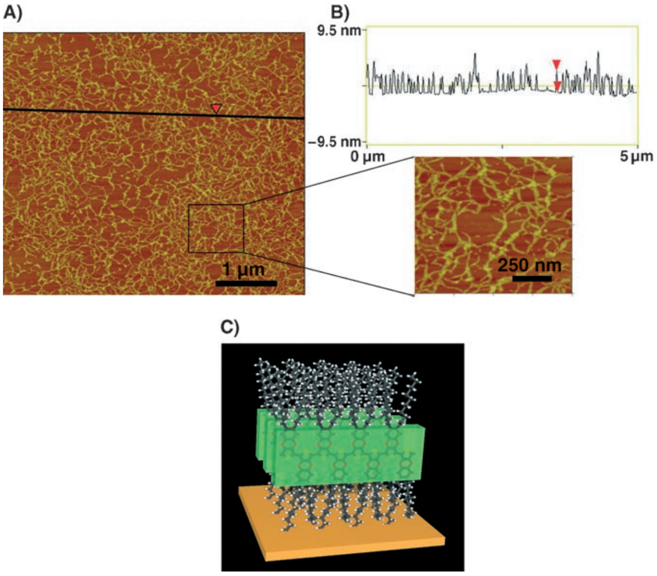


Figure 3. A) AFM image (5×5 µm^2) of poly[PheDOT-(C$_{12}$)$_2$] spin-coated on mica from hot ODCB (C=0.2 mg mL^{-1}); B) cross-sectional analysis and magnification (1×1 µm^2). The fibril marked by the red arrow in the surface profile has a height of 3.2 nm; C) proposed 3D model of the arrangement of nanoribbons on the mica surface.

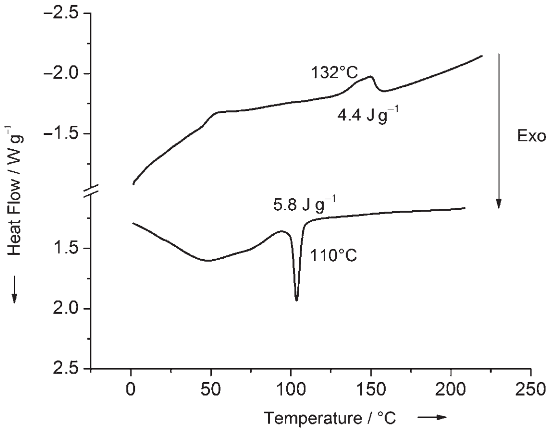


Figure 4. DSC plot (2nd scan) of poly[PheDOT-(C$_{12}$)$_2$]. The sample was heated and cooled at a rate of 10 K min^{-1}.

proposed for alkyl-substituted poly(phenyleneethynylene) (PPE), polyfluorene copolymers, and poly(3-alkylthiophene)s.[18] For the films obtained by spin-coating from a cold ODCB solution, we observed the formation of aggregates that were heterogeneous in both structure and size (see the Supporting Information). This result can be explained by comparison with the solution thermochromism results described above. Similar to the behavior in xylenes solution, the polymer chains in ODCB form stable colloidal suspensions of aggregates at room temperature. During spin-coating of this solution, the solvent evaporates, and the concentration of the aggregates increases, which leads to their collapse into larger, ill-defined structures. This difference of morphology is an important result, as order within crystalline domains, and order of the crystalline domains with respect to one another, have dramatic consequences on charge mobilities, as previously shown in regioregular poly(3-hexylthiophene).[19]

The thermal behavior of poly[PheDOT-(C$_{12}$)$_2$] in the solid state was investigated. Thermogravimetric analysis shows that the polymer is thermally stable up to 300 °C under both oxygen and nitrogen. After the polymer was conditioned by ramping the temperature at 10 K min^{-1} up to 220 °C and cooling to 0 °C, the second differential scanning calorimetry (DSC) scan shows an endothermic transition at 132 °C on heating and an exothermic transition at 110 °C on cooling (Figure 4). The small phase-transition enthalpy suggests that there is little structural rearrangement during the transition. We assign this thermal transition to the melting and recrystallization of the side chains. No further transitions corresponding to a melting of the crystalline regions are observed. This observation confirms the presence of strong intermolecular π–π-stacking interactions, as expected from the planarity of the monomer. As mentioned earlier, sulfur–oxygen interactions and mesomeric effects contribute to rigidification of the planar conformation of the phenylene dioxythiophene backbone. As a result, only the transition corresponding to the melting of the side chains is observed.

The organization of poly[PheDOT-(C$_{12}$)$_2$] in the solid state was investigated by using two-dimensional wide-angle X-ray scattering (2D-WAXS) measurements. The samples were prepared by shear-alignment at 150 °C with a home-built mini-extruder.[20] At ambient temperatures, the 2D pattern displayed sharp and distinct reflections, which indicate a well-ordered structure of the conjugated polymer with a pronounced alignment of the chains in the extrusion direction. (Figure 5 a). The equatorial small-angle reflection is related to a lateral distance of 3.88 nm of the polymer chains. This relatively large distance is in good accordance with the polymer configuration (Figure 5 b), in which the monomer units are arranged in one plane to form a lamella structure of rigid, stacked conjugated chains. Additional higher-order equatorial reflections, positioned at multiple angle values, confirms the well-defined order of the filament. The wide-angle reflection, positioned also in the equatorial plane of the X-ray pattern, is assigned to the π-stacking distance of

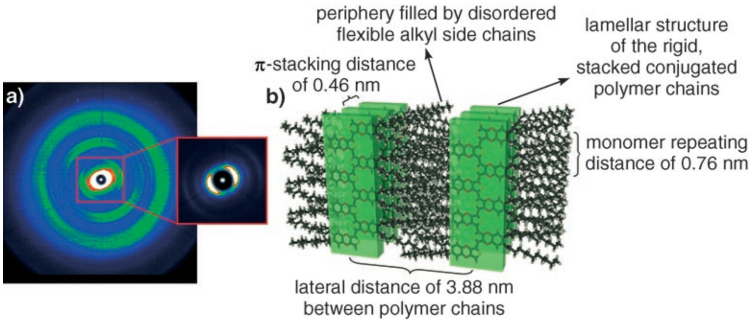


Figure 5. a) 2D-WAXS pattern at 30 °C (the inset displays the small-angle reflections at a lower contrast) and b) packing of poly[PheDOT-(C$_{12}$)$_2$] as indicated by the X-ray results.

0.46 nm of the polymer chains, whereas the low-intensity anisotropic halo is assigned to the poorly ordered alkyl side chains, which fills the periphery between the rigid conjugated units. The meridional reflection corresponds to a period of 0.76 nm and therefore to every second monomer unit along the polymer backbone being in an identical arrangement, as illustrated in Figure 5b.

The organization of the polymer changed slightly above the phase transition of 132 °C (see the Supporting Information). The shape and intensity of the equatorial reflections were unchanged, but the reflections were shifted to lower angles indicating smaller lateral distances of 3.15 nm at the higher-temperature phase. Such a decrease in distance between rigid, well-packed polymer chains might be explained by the melting of the alkyl substituents. Indeed, the diffuse anisotropic halo is characteristic for the melting of the alkyl side chains. The change of the side-chain dynamics does not affect the correlations between the repeat units along the polymer chain, but does lead to an increase of their steric demand and thus to a hindrance of the polymer stacking. This change is reflected by the lowered intensity of the reflection corresponding to the stacking distance; the full intensity was recovered upon cooling the sample back to 30 °C.

In conclusion, the new, electron-rich, electroactive soluble polymer with a regiosymmetric structure poly[PheDOT-$(C_{12})_2$] was synthesized by chemical polymerization. The polymer possesses a high degree of intra- and interchain order, both in solution and the solid state. At high temperature in ODCB or xylenes, the polymer possesses a planar conformation, which leads to aggregation at low temperature. Spin-coating from a hot ODCB leads to the formation of nanoribbons. Structural investigation by 2D-WAXS of mechanically aligned filaments revealed a pronounced 2D organization of the conjugated polymer. Strong correlations along the polymer backbone and between the polymer chains were observed. Because the order of conjugated polymers, as organic semiconductors, is an essential requirement for charge-carrier transport, and thus for their implementation in electronics, this work has shown that poly[PheDOT-$(C_{12})_2$] is a promising candidate for device applications.

Received: August 10, 2006

Keywords: conducting materials · pi interactions · polymers · self-assembly · thermochromism

---

[1] a) H. C. Yang, T. J. Shin, L. Yang, K. Cho, C. Y. Ryu, Z. N. Bao, *Adv. Funct. Mater.* **2005**, *15*, 671 – 676; b) C. Tanase, E. J. Meijer, P. W. M. Blom, D. M. de Leeuw, *Phys. Rev. Lett.* **2003**, *91*, 216601; c) G. M. Wang, J. Swensen, D. Moses, A. J. Heeger, *J. Appl. Phys.* **2003**, *93*, 6137 – 6141; d) K. Kaneto, *Thin Solid Films* **2001**, *393*, 249 – 258; e) H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, *Synth. Met.* **2000**, *111*, 129 – 132; f) H. Sirringhaus et al., *Nature* **1999**, *401*, 685 – 688; G. Horowitz, *Adv. Mater.* **1998**, *10*, 365 – 377; g) H. Sirringhaus, N. Tessler, R. H. Friend, *Science* **1998**, *280*, 1741 – 1744.

[2] a) F. Padinger, R. S. Rittberger, N. S. Sariciftci, *Adv. Funct. Mater.* **2003**, *13*, 85 – 88; b) X. Yang, J. Loos, S. C. Veenstra, W. J. H. Verhees, M. J. Wienk, J. M. Kroon, M. A. J. Michels, R. A. J. Janssen, *Nano Lett.* **2005**, *4*, 579 – 583; c) M. Reyes-Reyes, K. Kim, D. L. Carroll, *Appl. Phys. Lett.* **2005**, *87*, 083506; d) W. L. Ma, C. Y. Yang, X. Gong, K. Lee, A. J. Heeger, *Adv. Funct. Mater.* **2005**, *15*, 1617 – 1622; e) G. Li, V. Shrotriya, J. S. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Nat. Mater.* **2005**, *4*, 864 – 868;.

[3] a) S. Kirchmeyer, K. Reuter, *J. Mater. Chem.* **2005**, *15*, 2077 – 2088; b) L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J. R. Reynolds, *Adv. Mater.* **2000**, *12*, 481 – 494.

[4] a) A. A. Argun, A. Cirpan, J. R. Reynolds, *Adv. Mater.* **2003**, *15*, 1338 – 1341; b) P. Andersson, D. Nilsson, P. O. Svensson, M. X. Chen, A. Malmstrom, T. Remonen, T. Kugler, T. Berggren, *Adv. Mater.* **2002**, *14*, 1460.

[5] J. Ouyang, C.-W. Chu, F.-C. Chen, Q. Xu, Y. Yang, *Adv. Funct. Mater.* **2005**, *15*, 203 – 208.

[6] J. Storsberg, D. Schollmeyer, H. Ritter, *Chem. Lett.* **2003**, *32*, 140 – 141.

[7] S. Roquet, P. Leriche, I. F. Perepichka, B. Jousselme, E. Levillain, P. Frere, J. Roncali, *J. Mater. Chem.* **2004**, *14*, 1396 – 1400.

[8] I. F. Perepichka, S. Roquet, P. Leriche, J. M. Raimondo, P. Frere, J. Roncali, *Chem. Eur. J.* **2006**, *12*, 2960 – 2966.

[9] R. S. Loewe, P. C. Ewbank, J. S. Liu, L. Zhai, R. D. McCullough, *Macromolecules* **2001**, *34*, 4324 – 4333.

[10] B. D. Reeves, C. R. G. Grenier, A. A. Argun, A. Cirpan, T. D. McCarley, J. R. Reynolds, *Macromolecules* **2004**, *37*, 7559 – 7569.

[11] The HOMO level was estimated by $E_{\mathrm{HOMO}} = E_{\mathrm{onset}}$ (vs. Fc/Fc$^+$) + 4.8 eV.

[12] a) S. D. D. V. Rughooputh, S. Hotta, A. J. Heeger, F. J. Wudl, *J. Polym. Sci. Part B* **1987**, *25*, 1071 – 1078; b) K. Faid, M. Frechette, M. Ranger, L. Mazerolle, I. Levesque, M. Leclerc, T. A. Chen, R. D. Rieke, *Chem. Mater.* **1995**, *7*, 1390 – 1396.

[13] a) J. J. Apperloo, R. A. J. Janssen, P. R. L. Malenfant, J. M. J. Frechet, *Macromolecules* **2000**, *33*, 7038 – 7043; b) S. Yue, G. C. Berry, R. D. McCullough, *Macromolecules* **1996**, *29*, 933 – 939.

[14] M. Leclerc, M. Frechette, J. Y. Bergeron, M. Ranger, I. Levesque, K. Faid, *Macromol. Chem. Phys.* **1996**, *197*, 2077 – 2087.

[15] M. Turbiez, P. Frere, M. Allain, C. Videlot, J. Ackermann, J. Roncali, *Chem. Eur. J.* **2005**, *11*, 3742 – 3752.

[16] a) N. Di Cesare, M. Belletete, G. Durocher, M. Leclerc, *Chem. Phys. Lett.* **1997**, *275*, 533 – 539; b) C. Roux, J.-Y. Bergeron, M. Leclerc, *Makromol. Chem.* **1993**, *194*, 869 – 877.

[17] P. Samori, V. Francke, T. Mangel, K. Müllen, J. P. Rabe, *Opt. Mater.* **1998**, *9*, 390 – 393.

[18] a) P. Samori, V. Francke, K. Müllen, J. P. Rabe, *Thin Solid Films* **1998**, *336*, 13 – 15; b) D. H. Kim, Y. D. Park, Y. Jang, S. Kim, K. Cho, *Makromol. Chem. Rapid Commun.* **2005**, *26*, 834 – 839; c) M. Surin, D. Marsitzky, A. Grimsdale, K. Müllen, R. Lazzaroni, P. Leclere, *Adv. Funct. Mater.* **2004**, *14*, 708 – 715; d) P. Leclere, et al., *Eur. Polym. J.* **2004**, *40*, 885 – 892.

[19] H. Yang, T. J. Shin, L. Yang, K. Cho, C. Y. Ryu, Z. Bao, *Adv. Funct. Mater.* **2005**, *15*, 671 – 676;.

[20] W. Pisula, Z. Tomovic, C. Simpson, M. Kastler, T. Pakula, K. Müllen, *Chem. Mater.* **2005**, *17*, 4296 – 4303.