Influence of the Substitution Pattern on the Chiroptical Properties of Regioregular Poly(3-alkoxythiophene)s

Marnix Vangheluwe, Thierry Verbiest, and Guy Koeckelberghs*

Laboratory for Molecular Electronics and Photonics, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium

Received October 10, 2007
Revised Manuscript Received November 22, 2007

Substituted polythiophenes, such as poly(3-alkylthiophene)s (**P3AT**s), constitute an important class of soluble, environmentally stable, conjugated polymers.[1] Because 3-substituted thiophene is an asymmetric molecule, regioregularity becomes an important issue in the polymerization of these materials. The regioregularity has a tremendous influence on the properties of these polymers: The larger the degree of regioregularity, the larger the conjugation length, which leads to, for instance, lower bandgaps. Moreover, a regular molecular structure is a requisite for good stacking, from which excellent (chir)optical and electronic properties can arise.[2]

Regioregularity in 3-substituted polythiophenes can be obtained in two ways: either by successive head-to-tail (HT) couplings or by alternating HH and TT couplings. While the synthesis of HT-coupled regioregular polythiophenes requires the use of a regiospecific polymerization method, HH-TT-coupled polythiophenes can conveniently be prepared by condensing the substituted thiophene moiety in a HH or TT fashion to form a symmetric dimer, which can then be polymerized.

Apart from (regioregular) **HT-P3AT**s,[3] also (regioregular) HT-poly(3-alkoxythiophene)s (**HT-P3AOT**s) have been prepared.[4] Compared to **P3AT**s, they show reduced bandgaps and increased stability of their oxidized state. In previous manuscripts, we prepared a chiral, highly regioregular **HT-P3AOT** using a "modified McCullough procedure".[4a] Leclerc et al. prepared (achiral) **HH-TT-P3AOT**s by an oxidative polymerization of a symmetric bithiophene moiety.[5]

In this paper, we report the synthesis of a chiral **HH-TT-P3AOT** (Figure 1). By comparing its chiroptical properties with those of the isomeric **HT-P3AOT**, the influence of the substitution pattern of **P3AOT**s is investigated.

The **HT-P3AOT** was synthesized according to a modified McCullough procedure, as reported earlier.[4a] The abovementioned method renders **P3AOT**s with a very high degree of regioregularity. **HH-TT-P3AOT** was prepared by a polycondensation of dibrominated (**1**) and distannylated (**2**) HH-coupled bithiophenes using a Stille coupling (Scheme 1). $Pd_2(dba)_3$ and $AsPh_3$ were used as a catalyst and ligand, since this system appeared to be the system of choice in analogous polymerizations.[6] The polymer was successively washed with acetone and hexane using a Soxhlet apparatus, extracted with chloroform, precipitated in methanol and finally dried. The yield after purification amounts 66%.

The molecular weight ($\bar{M}_n = 47$ kg·mol^{-1}, $D = 3.0$) for **HH-TT-P3AOT** was determined by GPC using polystyrene standards in THF. In DSC measurements (scan rate: 20 °C/min), no T_g or T_m was observed for **HT-P3AOT**,[4a] while, in contrast, **HH-TT-P3AOT** shows a clear glass transition ($T_g = 135$ °C) and melting peak ($T_m = 214$ °C). Degradation started always >250 °C. Polarized UV−vis spectroscopy, finally, revealed that both polymers were *not* liquid crystalline. We can therefore conclude that **HT-P3AOT** is an amorphous polymer and that **HH-TT-P3AOT** is semicrystalline. This can tentatively be explained by the symmetric nature of **HH-TT-P3AOT**, in contrast to **HT-P3AOT**.

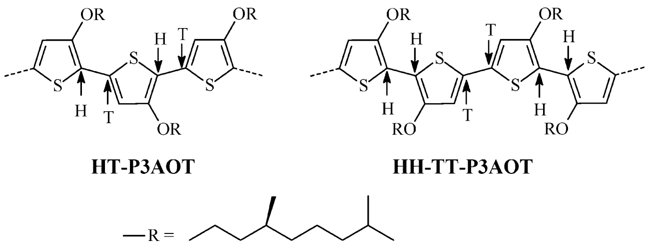
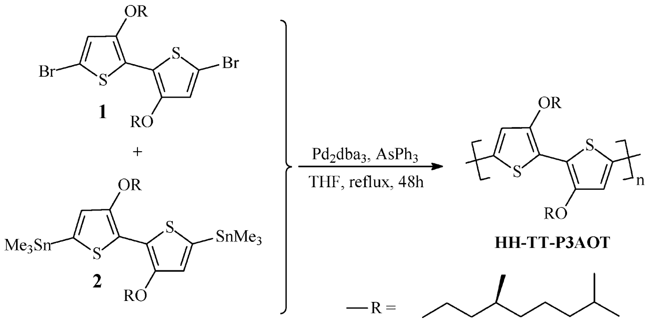


Figure 1. General structure of **HT-P3AOT** and **HH-TT-P3AOT**.

Scheme 1. Synthesis of HH-TT-P3AOT



A representative UV−vis spectrum in chloroform of both polymers is presented in Figure 2A,C. Both polymers exhibit fairly large λ_{max}, indicating that conjugation is not or only slightly limited by twists along the polymer backbone. It is worthwhile to note that the λ_{max} of the (chemically) prepared **HH-TT P3AOT** (583 nm) is significantly higher than the oxidatively prepared (achiral) **HH-TT P3AOT** (~545 nm) by Leclerc et al.[5]

The planarity of the polymer backbone can be attributed to S−O interactions, which hold two adjacent thiophene moieties in a more or less fixed, planar conformation. The rigidity of the polymer was also confirmed by fluorescence spectroscopy, which reveals that the polymer adopts a rigid conformation in solution. The Stokes shifts of **HT-P3AOT** and **HH-TT-P3AOT** are respectively 494 cm^{-1} and 1847 cm^{-1}. This values are comparable with those of rigid conjugated polymers, such as poly(dithienopyrrole)s (~2000 cm^{-1})[7] and ladder-type polymers (~2000 cm^{-1}).[8] Also the fwhm$_{em}$ is quite low: 1541 cm^{-1} and 1105 cm^{-1} for respectively **HT-P3AOT** and **HH-TT-P3AOT**. From these data it is clear that both polymers are present in solution as highly conjugated rigid rods. The quantum yields are very low (0.25% and 7.12% for respectively **HT-P3AOT** and **HH-TT-P3AOT**). Upon addition of a nonsolvent, the polymers aggregate, resulting in a quenching of the fluorescence.

In a poor solvent mixture (chloroform/methanol (5/5)), solvent-induced aggregation occurs and a red-shift (~40 nm) is observed for both polymers, together with the appearance of a vibronic fine-structure.[9] It is clear that for **HT-P3AOT,** this fine-structure is limited to rather small shoulders, while for **HH-**

---

* Corresponding author. E-mail: guy.koeckelberghs@chem.kuleuven.be.

10.1021/ma702262j CCC: $40.75

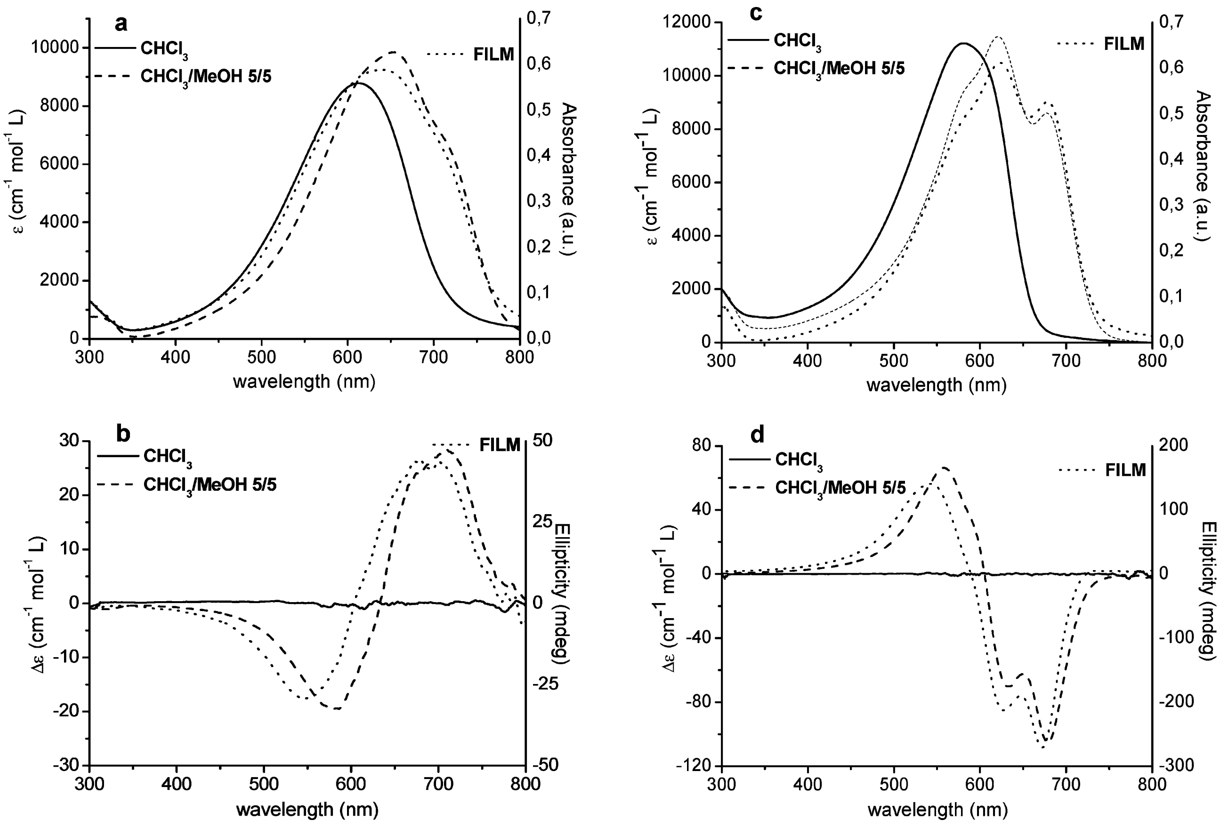


Figure 2. UV−vis (a) and CD-spectra (b) of **HT-P3AOT**; UV−vis (c) and CD-spectra (d) of **HH-TT-P3AOT**.

TT-P3AOT, this fine-structure is much more defined. Moreover, a distinct, quite sharp, low-energy band at 678 nm appears for **HH-TT-P3AOT**, which is absent for **HT-P3AOT**. In the CD spectra of both polymers (Figure 2B,D), a bisignate Cotton effect in the $\pi-\pi^*$ transition appears, albeit of different sign for both polymers. The relative difference in circular absorption, as defined by $g_{\mathrm{abs}} = \Delta\epsilon/\epsilon$, mounts $3 \cdot 10^{-3}$ for **HT-P3AOT** ($\lambda = 568$ nm) and $1 \cdot 10^{-2}$ for **HH-TT-P3AOT** ($\lambda = 548$ nm). Just as for the UV−vis spectra, the CD spectrum of **HH-TT-P3AOT** shows a more distinct vibronic fine-structure than **HT-P3AOT**. Interestingly, a (negative) *monosignate* band ($g_{\mathrm{abs}} = 1.3 \cdot 10^{-2}$) corresponding to the low-energy band at 678 nm of **HH-TT-P3AOT**, is observed.

Bisignate Cotton effects, with a zero-crossing near $\lambda_{\max}$, are indicative for chiral exciton coupling, which can be attributed to the chiral, supramolecular stacking of coplanar strands.[10] This supramolecular stacking has also been observed for other conjugated polymers, such as **HT-P3ATs**[11] and poly(3,4-dialkoxythiophene)s.[12] Concerning the low-energy band with corresponding monosignate Cotton effects, it should be noted that the same chiroptical behavior has also been observed for chiral poly(phenylene ethynylene)s PPEs.[13] In these polymers, the additional absorption band with corresponding monosignate Cotton effect is explained by helically twisted bundles of planar chains.

In order to further examine the chiroptical behavior of the two polymers, a dilution experiment was carried out (Figure 3). Therefore, the UV−vis and CD spectra in a chloroform/methanol (7/3) mixture—in which spectra, intermediate between those of pure chloroform and a chloroform/methanol (5/5) mixture, were present—were recorded for different polymer concentrations. From Figure 3, it is clear that both the bisignate Cotton effects of both polymers, located at the $\pi-\pi^*$ transition, and the monosignate Cotton effect, corresponding to the 678 nm band of **HH-TT-P3AOT**, are concentration dependent and must, therefore, arise from intermolecular effects. This experiment again confirms that the bisignate Cotton effect is due to chiral exciton coupling of aggregated polymer strands. On the other hand, it is also clear that the 678 nm absorption band cannot be due to a twisted, helical conformation of the polymer backbone itself, since in that case, a concentration independent chiroptical effect is expected. Moreover, the monosignate Cotton effect, arising from this helical backbone conformation, would be present in its $\pi-\pi^*$ transition and not in a separate band.

We propose that, analogous to PPE, the 678 nm band originates from a chiral (helical) supramolecular structure, composed of multiple polymer strands. Since this band is not due an electronic transition of a single polymer strand which couples with the transition of a another polymer strands (exciton coupling), not a bisignate, but a monosignate Cotton effect corresponding to this transition is expected. The presence of a chiral, well ordered (supramolecular) structure in **HH-TT-P3AOT** and the absence thereof in **HT-P3AOT** is also confirmed by the more defined vibronic fine-structure in the UV−vis and CD spectra of **HH-TT-P3AOT** and its strong tendency to crystallize (see DSC). Whether this band corresponds to a real electronic absorption or is rather due to scattering, is not clear at this moment.

Next, the chiroptical properties in film were studied. The films were spincoated from chloroform-solution ($c = \sim 12$ mg/mL, entry 3 in Table 1). The bandgaps were calculated from the onset of the absorption band and mount 1.6 and 1.7 eV for **HT-P3AOT** and **HH-TT P3AOT** respectively. Their UV−vis and CD spectra correspond well with those in a poor solvent mixture (Figure 2). Consequently, the films can be regarded as composed of the same aggregates that were present in a poor solvent mixture and the chiroptical behavior can be expected to be the same. However, although the shape of the CD and UV−vis spectra are the same, the g_{abs} values of the films seemed to differ significantly (see Table 1, entry 3). To further examine this,

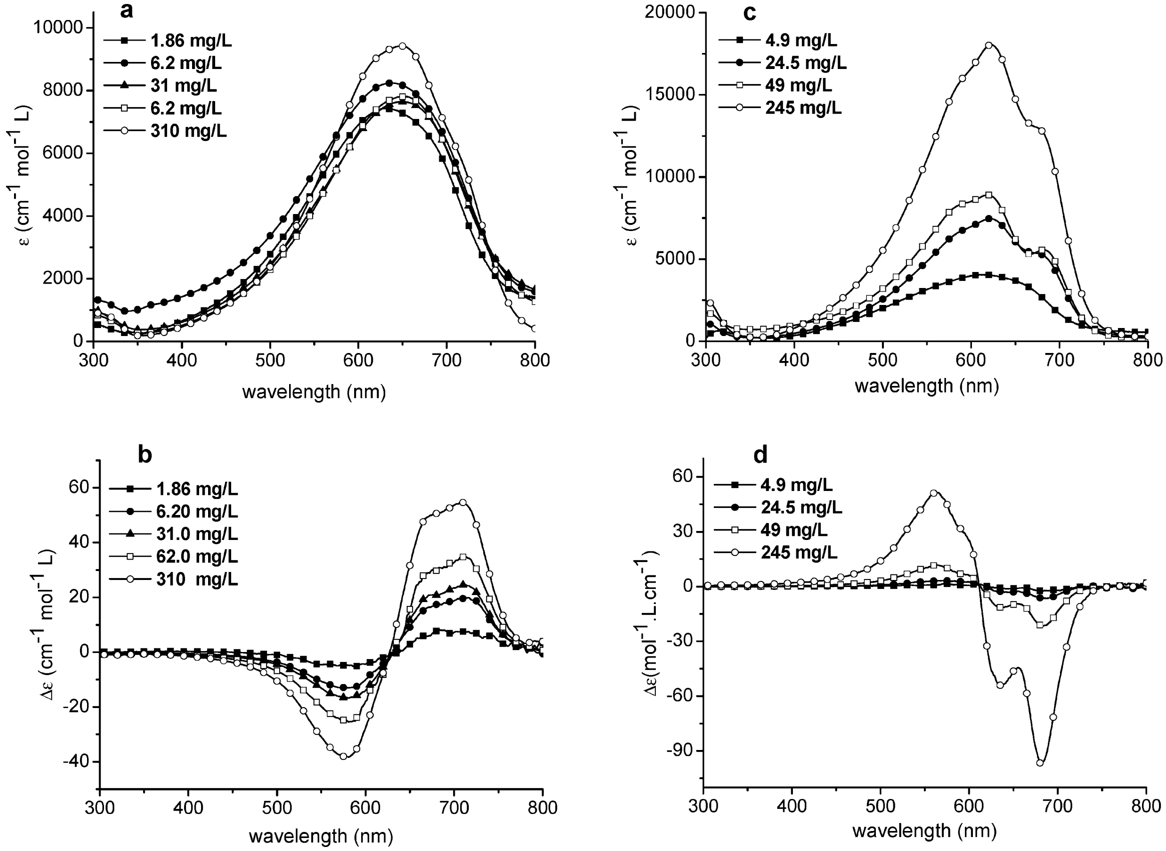


Figure 3. Concentration dependence in a chloroform/methanol (7/3) mixture of (a) UV−vis and (b) CD spectra of **HT-P3AOT** and (c) UV−vis and (d) CD-spectra of **HH-TT-P3AOT**.

Table 1. g_{abs} **Values of the Polymers before and after Annealing (1 min at 220 °C) as a Function of Film Thickness**

HT-P3AOT			HH-TT-P3AOT		
entry	abs_{max}	$\lvert g_{abs}\rvert$ ($\lambda = 550$ nm)/ 10^{-3} before/after annealing	abs_{max}	$\lvert g_{abs}\rvert$ ($\lambda = 545$ nm)/ 10^{-3} before/after annealing	$\lvert g_{abs}\rvert$ ($\lambda = 678$ nm)/ 10^{-3} before/after annealing
1	0.13	0.38/4.6	0.20	8.6/0.80	10/1.3
2	0.30	0.62/21	0.35	11/2.3	11/0.49
3	0.62	2.1/33	0.64	12/24	14/52
4	1.8	6.5/*a*	1.5	7.4/*a*	9.0/*a*

[a] Ellipticity is outside the scale of the apparatus

three additional films of each polymer were spincoated from different concentration ($c = \sim 3$, 6, and 23 mg/mL, entry 1, 2, and 4, respectively), in order to obtain films of different thickness. The UV−vis and CD spectra of the films before and after annealing were recorded (see Supporting Information) and their g_{abs} values were calculated (Table 1). Since the thickness of the films scales with their absorbance, it can be derived from Table 1 that the film thickness was increased roughly by a factor 10. If the Cotton effects are due to pure circular dichroism, i.e., the statistical difference of absorption of left and right circularly polarized light, as is the case for **HT-P3ATs**,[14] the g_{abs} values are independent of the film thickness. It is clear that the g_{abs} values of both **HT-P3AOT** and **HH-TT-P3AOT** are thickness dependent. Craig et al. have observed the same behavior in films of chiral polyfluorenes.[15] They have demonstrated that—apart from "real" circular dichroism—also contributions of "pseudo" circular dichroism are present, which increase the measured CD. Since the contribution from pseudo circular dichroism increases with the film thickness, only from (very) thin films the "real" g_{abs} values will be obtained. Note that the very high g_{abs} values of **HH-TT-P3AOT** are among the highest reported. Moreover, these values can relatively easy be increased by increasing the film thickness.

Because of the presence of the electrondonating alkoxy-substituents, the polymers can easily be oxidized, which is reflected in their low peak anodic potential (E_{pa}), peak cathodic potential (E_{pc}) and half wave potential ($E_{1/2}$).[16] The oxidation of both polymers is pseudo-reversible. The polymers remain oxidized in both film and solution for several days and can be back reduced without any degradation.

In conclusion, we have prepared a chiral **HH-TT-P3AOT** and have studied the influence of the substitution pattern on the (chiroptical) properties of regioregular **P3AOT**. Regioregular **HH-TT-P3AOT** is a semicrystalline material, while the isomeric regioregular **HT-P3AOT** is amorphous. UV−vis and CD spectra of **HH-TT-P3AOT** display an additional absorption band with a corresponding monosignate Cotton effect, which can be ascribed to the supramolecular organization of **HH-TT-P3AOT**.

Acknowledgment. We are grateful to the Katholieke Universiteit Leuven (GOA), the Fund for Scientific Research (FWO−Vlaanderen), Toyota Motor Company Europe, and the Air Force Office of Scientific Research, Air Force Material Command, USAF, under Grant No. FA8655-07-1-3004 for financial support. The authors thank Jan Ramaekers for his help with polarized UV−vis spectroscopy. G.K. is a postdoctoral fellow of the Fund for Scientific Research (FWO−Vlaanderen).

Supporting Information Available: Text giving experimental details and the synthesis of **HH-TT-P3AOT** and figures giving a polarized UV−vis photo of **HH-TT-P3AOT**, the fluorescence quenching of **HH-TT-P3AOT**, the solvatochromism of **HT-P3AOT** and **HH-TT-P3AOT**, influence of annealing on the CD-spectrum of a **HH-TT-P3AOT** film, the thickness dependence of CD of the polymer films, the oxidation behavior in solution and films of **HH-TT-P3AOT** and CV and GPC traces of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) McCullough, R. D.; Ewbank, P. C. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A.. Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; pp 225−258.

(2) (a) 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* (*London*) **1999**, *401*, 685−688. (b) Bao, Z.; Dodabalapur, A.; Lovinger, A. J. *Appl. Phys. Lett.* **1996**, *69*, 4108−4110. (c) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741−1744.

(3) (a) McCullough, R. D.; Lowe, R. L.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904−912. (b) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608−11609. Lowe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250−253. (c) Chen, T.; Wu, A. X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233−244.

(4) (a) Koeckelberghs, G.; Vangheluwe, M.; Samyn, C.; Persoons, A.; Verbiest, T. *Macromolecules*, **2005**, *38*, 5554−5559. (b) Koeckelberghs, G.; Vangheluwe, M.; Van Doorsselaere, K.; Robijns, E.; Persoons, A.; Verbiest, T. *Macromol. Rapid Commun.* **2006**, *27*, 1920−1925. (c) Sheina, E. E.; Khersonsky, S. M.; Jones, E. G.; McCullough, R. D. *Chem. Mater.* **2005**, *17*, 3317−3319.

(5) (a) Cloutier, R.; Leclerc, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1194−1195. (b) Faïd, K.; Cloutier, R.; Leclerc, M. *Macromolecules* **1993**, *26*, 2501−2507.

(6) Koeckelberghs, G.; Vangheluwe, M.; Persoons, A.; Verbiest, T. *Macromolecules*, **2007**, *40*, 8142−8150.

(7) (a) Ogawa, K.; Rasmussen, S. C. *Macromolecules* **2006**, *39*, 1771−1778. (b) Koeckelberghs, G.; De Cremer, L.; Persoons, A.; Verbiest, T. *Macromolecules* **2007**, *40*, 4173−4181.

(8) Nehls, B. S.; Galbrecht, F.; Brauer, D. J.; Lehmann, C. W.; Scherf, U.; Farrell, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5533−5545.

(9) Spectra showing the solvatochromism are incorporated as Supporting Information, Figure 3a,b.

(10) Langeveld-Voss, B. M. W.; Beljonne, D.; Shuai, Z.; Janssen, R. A. J.; Meskers, S. C. J.; Meijer, E. W.; Brédas, J.-L. *Adv. Mater.* **1998**, *10*, 1343−1348.

(11) (a) Bouman, M. M.; Havinga, E. E.; Janssen, R. A. J.; Meijer, E. W. *Mol. Cryst. Liq. Cryst.* **1994**, *256*, 439−448. (b) Langeveld-Voss, B. M. W.; Bouman, M. M.; Christiaans, M. P. T.; Janssen, R. A. J.; Meijer, E. W. *Polym. Prepr.* **1996**, *37*, 499−500. (c) Langeveld-Voss, B. M. W.; Waterval, R. J. M.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules* **1999**, *32*, 227−230. (d) Bidan, G.; Guillerez, S.; Sorokin, V. *Adv. Mater.* **1996**, *8*, 157−160.

(12) (a) Lermo, E. R.; Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Meijer, E. W. *Chem. Commun.* **1999**, 791−792. (b) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Christiaans, M. P. T.; Meskers, S. C. J.; Dekkers, S. C. J.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118*, 4908−4909. (c) Grenier, C. R. G.; George, S. J.; Meijer, E. W.; Reynolds, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 10694−10699.

(13) (a) Fiesel, R.; Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Scherf, U.; Bunz, U. H. F. *Macromol. Rapid Commun.* **1999**, *20*, 107−111. (b) Wilson, J. N.; Steffen, W.; McKenzie, T. G.; Lieser, G.; Oda, M.; Neher, D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2002**, *124*, 6830−6831. (c) Babudri, F.; Colangiuli, D.; Di Bari, L.; Farinola, G. M.; Omar, O. H.; Naso, F.; Pescitelli, G. *Macromolecules* **2006**, *39*, 5206−5212.

(14) Lakhwani, G.; Koeckelberghs, G.; Meskers, S. C. J.; Janssen, R. A. J. *Chem. Phys. Lett.* **2007**, *437*, 193−197.

(15) Craig, M. R.; Jonkheim, P.; Meskers, S. C. J.; Schenning, A. P. H. J.; Meijer, E. W. *Adv. Mater.* **2003**, *15*, 1435−1438.

(16) The CV measurements were done in acetonitrile with Bu_4NBF_4 (0.1 M) as the supporting electrolyte under argon atmosphere with a scan rate of 50 mV/s. **HT-P3AOT:** E_{pa} = 0.42 V, E_{pc} = 0.35 V, $E_{1/2}$ = 0.38 V. **HH-TT-P3AOT:** E_{pa} = 0.46 V, E_{pc} = 0.25 V, $E_{1/2}$ = 0.36 V.

MA702262J