Synthesis and Transistor Properties of Asymmetric Oligothiophenes: Relationship between Molecular Structure and Device Performance

Tae Kyu An,^[a] Sang Hun Jang,^[b] Seul-Ong Kim,^[c] Jaeyoung Jang,^[a] Jihun Hwang,^[a] Hyojung Cha,^[a] Young Ri Noh,^[b] Soon Byung Yoon,^[b] Yong Jin Yoon,^[b] Lae Ho Kim,^[a] Dae Sung Chung,^[d] Soon-Ki Kwon,^[c] Yun-Hi Kim,^{*[b]} Sang-Gyeong Lee,^{*[b]} and Chan Eon Park^{*[a]}



14052 -

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Chem. Eur. J. 2013, 19, 14052-14060

Abstract: A series of three thiophenenaphthalene-based asymmetric oligomers—5-decyl-2,2':5',2":5",2"'-quaterthiophene (DtT), 5-decyl-5"-(naphthalen-2yl)-2,2':5',2"-terthiophene (D3TN), and 5-(4-decylphenyl)-5'-(naphthalen-2-yl)-2,2'-bithiophene (DP2TN)—was synthesized by Suzuki cross-coupling reactions. The long alkyl side chains improved both the solubility of the oligomers in solvents and their tendency to self-assemble. UV/Vis absorption measurements suggested that DtT, D3TN, and DP2TN form H-type aggregates with a face-to-face packing structure. In addition, the three oligomers were found to adopt vertically aligned crystalline structures in films deposited on substrates, as revealed by grazing-

Keywords: aggregation • oligothiophenes • semiconductors • thin films • transistors

FULL PAPER

incidence wide-angle X-ray scattering. These oligomers were used as the active layers of p-type organic field-effect transistors, and the resulting devices showed field-effect mobilities of $3.3 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for DtT, $1.6 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for D3TN, and $3.7 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for DP2TN. The differences in transistor performances were attributed to the degree of π overlap and the morphological differences determined by the molecular structures.

Introduction

During the last decade, numerous conjugated organic oligomers and polymers have been synthesized for use as active materials in organic electronic devices related to low-cost semiconductor applications, such as smart cards, display drivers, and identification tags, which could replace their high-cost inorganic counterparts.^[1] The physical or chemical properties of organic oligomers and polymers can be tuned through molecular design and functionalization, and this is one of the most appealing aspects of these compounds.^[2] Many classes of conjugated oligomers and polymers have been synthesized and their electrochemical properties investigated,^[2a,3] and they were found to display high performance and chemically stable conjugated systems.^[4]

Thiophene-based oligomers, in particular, are considered to be promising candidates for organic semiconducting materials because they form a variety of intra- and intermolecular interactions due to the high polarizability of the electrons of their sulfur atoms. The packing structures of thiophene-based oligomers result in high field-effect mobili-

[a]	T. K. An, J. Jang, J. Hwang, H. Cha, L. H. Kim, Prof. C. E. Park
	Department of Chemical Engineering
	Pohang University of Science and Technology
	POSTECH Organic Electronics Laboratory
	Polymer Research Institute, Pohang, 790-784 (Korea)
	E-mail: cep@postech.ac.kr
[b]	S. H. Jang, Y. R. Noh, S. B. Yoon, Y. J. Yoon, Prof. YH. Kim,
	Prof. SG. Lee
	Department of Chemistry, Gyeongsang National University
	Research Institute of Natural Science (RINS)
	Graduate School for Molecular Materials and Nanochemistry
	Jinju, 660-701 (Korea)
	E-mail: ykim@gnu.ac.kr
	leesang@gnu.ac.kr
[c]	SO. Kim, Prof. SK. Kwon
	School of Materials Science and Engineering
	Gyeongsang National University

- Gyeongsang National University Research Institute for Green Energy Convergence Technology(REGET), Jinju, 660-701 (Korea)
- [d] Prof. D. S. Chung School of Chemical Engineering and Materials Science Chung Ang University Seoul, 156-756 (Korea)
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201302588.

ties.^[5] Many reports have focused on the use of thiophenebased oligomers as the active layers in organic thin-film transistors (OTFTs).^[4,6] In the field of OTFTs, most studies have focused on thiophene-based oligomers with symmetric structures because they yield superior device performances.^[7] By contrast, thiophene-based oligomers with asymmetric structure have not been fully investigated, and many challenges remain in improving the film morphology and device performance.

We recently reported that asymmetric thiophene-based oligomers with cyclohexyl end groups could exhibit decent field-effect mobility values.^[8] Previously, we found that asymmetric oligothiophene derivatives tended to form H-aggregates, whereas symmetric derivatives tended to form Jaggregates. The field-effect mobilities of H-aggregated asymmetric molecules were found to be much higher than those of J-aggregated symmetric molecules. Cyclohexyl end groups are bulky substituents that generate steric hindrance and induce the formation of H-aggregates by pushing the molecules apart.^[9] Such bulky side groups thus prevent close packing of the molecular backbones. Thus, decreasing the steric hindrance in asymmetric molecules is expected to promote efficient molecular packing in the H-aggregated structures and further enhance device performance.

In the present study, we designed and synthesized three asymmetric alkylated thiophene-naphthalene oligomers with the aim of improving the intermolecular ordering in the thin-film state: 5-decyl-2,2':5',2":5",2"'-quaterthiophene 5-decyl-5"-(naphthalen-2-yl)-2,2':5',2"-terthiophene (DtT), (D3TN), and 5-(4-decylphenyl)-5'-(naphthalen-2-yl)-2,2'-bithiophene (DP2TN). The lipophilic alkyl chain at the α position of the oligothiophene was expected to reduce the steric hindrance relative to the cyclohexyl group and facilitate self-organization and molecular packing between adjacent molecules by van der Waals interactions.^[10] UV/Vis absorption and grazing-incidence wide-angle X-ray scattering (GIWAXS) analyses indicated that DtT, D3TN, and DP2TN tend to form H-aggregates with vertical orientation on substrates. The ratio of H- to J-aggregates and the distinct differences among the film morphologies in the three oligomers were correlated with high field-effect mobilities of up to $3.7 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in OTFTs based on DP2TN. These values represent a twofold improvement over those reported

previously for asymmetric oligothiophenes with cyclohexyl groups under identical conditions of fabrication and measurement.^[8]

Results and Discussion

Synthesis and characterization: The synthetic strategy is illustrated in Scheme 1. The asymmetric thiophene-naphthalene oligomers DtT, D3TN, and DP2TN were synthesized by palladium-catalyzed Suzuki cross-coupling reactions. Compounds 3 and 4 were prepared from the 2,2-bithiophene (1), which was prepared according to the literature.^[3a] 2-Decylthiophene (5) was synthesized by the reaction of ortholithiated thiophene with 1-bromodecane and was used for the synthesis of the boronic ester 6.^[3b] 4-Bromodecylbenzene (7) was readily available by Friedel-Crafts acylation of bromobenzene, followed by a Wolff-Kishner reduction.^[11] Compound 7 was then esterified with 2-isopropyl-4,4,5,5-tetramethyl-1,2,3-dioxabolane in the presence of nBuLi to give 8.

Compound 9 was synthesized by a Suzuki cross-coupling reaction between 2-bromonaphthalene and boronic ester 4. Subsequent bromination with N-bromosuccinimide gave 10. The target materials DtT, D3TN, and DP2TN were synthesized by Suzuki cross-coupling reactions in the presence of Aliquat 336 as a phase-transfer catalyst in toluene in yields of 75, 65, and 70%, respectively. The structures of compounds DtT, D3TN, and DP2TN were confirmed by ¹H NMR, IR, and HRMS analysis. They exhibited good solubilities in organic solvents, such as chlorinated solvents, THF, and toluene, at room temperature.

Thermal and electrochemical properties: The thermal behavior of the compounds was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. The TGA and DSC results are shown in Figures S1 and S2 in the Supporting Information and are summarized in Table 1. A weight loss of 5 % was observed at T_{5d} =281, 246, and 346 °C for DtT, D3TN, and DP2TN, respectively. Thermogravimetric analysis re-



14054 ·

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1. Physical properties of DtT, D3TN, and DP2TN.

Compound	λ_{ab} solution ^[a]	s [nm] film ^[b]	$T_{\rm m}/T_{\rm 5d}$ [°C] ^[c]	E_{g} [eV] ^[d]	HOMO [eV] ^[e]	LUMO [eV] ^[f]
DtT	397	268, 339	160/281	2.55	-5.29	-2.74
D3TN	400	261	93/246	2.48	-5.33	-2.85
DP2TN	388	254, 280, 313	246/345	2.51	-5.35	-2.84

[a] Measured in a dilute CHCl₃ solution. [b] Measured in film state on quartz-crystal substrate. [c] Obtained from DSC and TGA measurements under N₂ at a heating rate of 10 °Cmin⁻¹. [d] Estimated from the onset of the absorption spectra (E_g =1240/ λ_{onset}). [e] Calculated by using the empirical equation: HOMO = $-(4.4+E_{ox,onset})$. [f] Calculated by using the relation LUMO = HOMO + E_g .

vealed the oligomers had sufficient thermal stability for use in OTFT applications. The DSC data revealed major endothermic melting peaks at 93 °C for D3TN and 246 °C for DP2TN, and the corresponding major exothermic crystallization peaks were observed at 73 °C for D3TN and 243 °C for DP2TN. For DtT, the two endothermic peaks (130, 160 °C) corresponded to the major exothermic crystallization transitions (85, 156 °C).

The electrochemical behavior of the asymmetric thiophene–naphthalene oligomers was investigated by cyclic voltammetry. The cyclic voltammograms of the oligomers were recorded in a 1.0×10^{-3} M CHCl₃ solution containing 0.1 M Bu₄NClO₄. The HOMO energy levels of DtT, D3TN, and DP2TN were estimated classically from $E_{\text{ox,onset}}$ to be -5.29, -5.33, and -5.35 eV, respectively, from the relation $E_{\text{HOMO}}/\text{eV} = -(E_{\text{ox,onset}} + 4.4)$.^[12] The correlation between the HOMO level and optical bandgap energy E_{g} of each UV/ Vis absorption spectrum ($E_{\text{g}} = E_{\text{HOMO}} - E_{\text{LUMO}}$) was used to calculate the LUMO energy levels as -2.74, -2.85, and -2.84 eV, respectively (see Figure S3 in the Supporting Information). The optical bandgaps E_{g} and HOMO and LUMO energy levels of DtT, D3TN, and DP2TN are listed in Table 1.

UV/Vis absorption spectroscopy: The UV/Vis absorption spectra of DtT, D3TN, and DP2TN in chloroform and in thin films are shown in Figure 1 and are summarized in Table 1. The absorption peaks of all three compounds in the thin-film state were found to be blueshifted relative to the peaks observed in the solution state. These spectral shifts were thought to be due to formation of H-aggregate-type molecular packing structures^[13] and are correlated with the particular molecular packing structures and the potential energies associated with the intermolecular interactions.^[14] The potential energy of interaction between two molecules is a function of their relative dipole configurations and orientations, assuming that the molecules can be approximated as point dipoles.^[14a] A simplified expression for the potential energy of interaction between two dipoles is given by Equation (1) because, as shown in Figure S4(a) of the Supporting Information, $\boldsymbol{\mu}_1 \cdot \mathbf{r} = \mu_1 r \cos \theta$ and $\boldsymbol{\mu}_2 \cdot \mathbf{r} = \mu_1 r \cos \theta$.^[8]

$$V = \frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2}{4\pi\varepsilon_0 r^3} - 3\frac{(\boldsymbol{\mu}_1 \cdot \mathbf{r})(\boldsymbol{\mu}_2 \cdot \mathbf{r})}{4\pi\varepsilon_0 r^5} = \frac{\mu_1 \mu_2 (1 - \cos^2 \theta)}{4\pi\varepsilon_0 r^3}$$
(1)

Equation (1) describes the energy of a system as a function of the molecular configuration. A shift in the peak positions can indicate the nature of the molecular packing structure in the film state. A

FULL PAPER

molecular packing structure in the film state. A blueshift in the main absorption peaks in the UV/ Vis absorption spectrum of the solid state relative to the peaks of a dilute solution could indicate a tendency for the molecules to stack in parallel, and a red shift in the UV/Vis absorption spectra could indicate a tendency for the molecules to stack in a head-to-tail arrangement.^[14] The exciton theory pre-



Figure 1. UV/Vis absorption spectra of a) DtT, b) D3TN, and c) DP2TN in chloroform solution or the film state.

dicts that the excitonic state of a molecular aggregate will be split into two energy levels due to the interactions between adjacent dipoles. One state will be higher and the other lower than the energy of the monomer system, as shown in Figure S4(b) in the Supporting Information, depending on the interaction between the transition dipoles.^[15]

The spectral shifts observed in thin films of DtT, D3TN, and DP2TN arose from changes in the energy levels due to the molecular packing geometry. The degree of π overlap between neighboring molecules is believed to be central to enhancing the field-effect mobilities of molecular semiconductors.^[16] H-aggregates show a large degree of π overlap between contiguous molecules as a result of the face-to-face packing structure. Specific molecular configurations were identified by deconvoluting the observed absorption peaks by using the software program Peakfit, supplied by Jandel Sci. The best-fit mode was selected for baseline fitting, and resolved UV/Vis absorption peaks were determined by fitting two mixed Gaussian-Lorentzian peaks. The optimal solution was selected on the basis of the R^2 value of the fit and yielded $R^2 > 0.98$ for all peaks (see Figure S5 in the Supporting Information). The structural models were determined on

Chem. Eur. J. 2013, 19, 14052-14060

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

the basis of the following two considerations: 1) the magnitude of the absorption peak shift observed in the thin films relative to the solution state, and 2) the fraction of peaks that were blueshifted. Deconvolution of the absorption peaks observed in the film state revealed that the magnitude of the peak shift and the fraction of blueshifted peaks were similar in D3TN and DP2TN (Table 2). The integral of the

Table 2. Data of resolved UV/Vis absorption spectra.

DtT		D3TN		DP2TN	
peak [nm]	fraction [%]	peak [nm]	fraction [%]	peak [nm]	fraction [%]
267	41.1	258	35.4	254	35.0
342	26.0	284	23.6	281	27.1
391	15.0	316	14.1	308	12.7
442	9.21	344	10.6	328	10.6
496	5.46	379	7.57	360	4.84
527	3.21	415	5.36	388	4.16
		457	3.39	419 451	3.14 2.38

area under the deconvoluted peaks revealed that the fractions of molecules present in the H-aggregate state in the DtT, D3TN, and DP2TN films were 67.1, 91.27, and 90.24%, respectively. Thus, the degree of H-aggregation in the DtT film was not as high as in the other two materials (Table 2 and Figure S5 in the Supporting Information). In other words, the lattices composed of DtT included fewer H-aggregated crystalline structures than those of the other two materials.

The microstructures of the three designed semiconductors were further investigated by examining the molecular packing structures by GIWAXS. The GIWAXS data for the three semiconductors suggested that the packing structures in all three films were consistent with an orthorhombic crystal structure. As shown in Figure 2 and Figure S6 in the Supporting Information, D3TN and DP2TN formed a molecular packing structure that was more ordered than that formed by DtT. The XRD patterns for the D3TN and DP2TN films showed much more developed diffraction patterns, including high-order peaks, compared to DtT and reported previously quaterthiophenes with cyclohexyl groups (CE4T and CB4T).^[8] This investigation implied that D3TN and DP2TN show more extensive long-range intermolecular interactions

or a higher degree of molecular ordering than DtT and asymmetric quaterthiophenes with cyclohexyl groups.^[17]

More detailed information about the crystalline structures of the DtT, D3TN, and DP2TN films was obtained by extracting the out-of-plane and in-plane scattering profiles from the GIWAXS patterns (Figure 2) along the $\alpha_{\rm f}$ direction at $2\theta_f = 0^\circ$ and the $2\theta_f$ direction at $\alpha_f = 0.16^\circ$. The out-ofplane scattering profiles revealed interlayer distances in the DtT, D3TN, and DP2TN films of 28.8, 32.1, and 32.7 Å, respectively (Supporting Information Figure S6). The theoretical molecular lengths (derived by using the HyperChem software package) were 27.8, 29.9, and 30.7 Å, respectively. A comparison of the values obtained from the GIWAXS analysis and those obtained from the theoretical calculations suggested that DtT, D3TN, and DP2TN were vertically aligned in a face-to-face packing structure on the substrate.^[18] The in-plane scattering profiles of DtT, D3TN, and DP2TN (Figure S6(d) of the Supporting Information) revealed that the (010) peak in the patterns of the DtT film (observed at 18.26°) corresponded to a π - π stacking distance of 4.35 Å. In the D3TN film (observed at 18.69°), this peak corresponded to a π - π stacking distance of 4.25 Å, and in the DP2TN film (observed at 18.54°) to a π - π stacking distance of 4.28 Å.^[19]

OTFT behavior: The potential utility of the three oligomers as organic semiconductors was tested by fabricating top-contact OTFTs based on these materials by using a solution process. As shown in Figure 3, OTFT devices composed of DtT, D3TN, and DP2TN showed typical p-channel responses, and the output curves showed saturation behavior. The field-effect mobilities of the devices were 3.3× $10^{-3} \, \mathrm{cm}^2 \, \mathrm{V}^{-1} \, \mathrm{s}^{-1}$ $(I_{\rm on}/I_{\rm off} = 5.13 \times 10^5)$ for DtT, $1.6 \times$ $10^{-2} \,\mathrm{cm}^2 \,\mathrm{V}^{-1} \,\mathrm{s}^{-1}$ ($I_{\mathrm{on}}/I_{\mathrm{off}} = 5.70 \times 10^5$) for D3TN, and 3.7×10^5 $10^{-2} \,\mathrm{cm}^2 \,\mathrm{V}^{-1} \,\mathrm{s}^{-1}$ ($I_{\rm on}/I_{\rm off} = 5.70 \times 10^6$) for DP2TN in the saturation regime. Structural and morphological analyses based on the UV/Vis absorption spectrum, GIWAXS studies, and AFM measurements revealed differences between the OTFT behaviors.

As the number of molecules stacked in parallel increased, producing a large total area corresponding to a high degree of π -overlap, the hole movement among adjacent molecules improved.^[1b] The large π -overlap area in the H-type aggregates produced higher field-effect mobilities in the devices



Figure 2. GIWAXS patterns for thin films prepared from a) DtT, b) D3TN, and c) DP2TN.

prepared from these materials. The crystalline DtT thin films included a lower fraction of Haggregated crystalline structures and a higher fraction of J-aggregated crystalline structures compared to the D3TN and DP2TN films, and thus DtT is engaged in less intermolecular π overlap. Much more developed diffraction patterns were observed from the D3TN and DP2TN films than from the

14056 -

FULL PAPER



Figure 3. Transfer and output characteristics of OTFTs based on DtT (a and b), D3TN (c and d), and DP2TN (e and f).

DtT film along the out-of-plane direction, that is, D3TN and DP2TN showed more extensive long-range intermolecular order than DtT. The π - π stacking distance in DtT was slightly longer than those observed in D3TN and DP2TN; therefore, DtT displayed a lower field-effect mobility than D3TN and DP2TN.

The surface morphologies of the DtT, D3TN, and DP2TN films were studied by AFM (Figure 4). The AFM images of the DtT and D3TN films exhibited a multi-separated smallcrystalline structure, whereas the DP2TN film morphology exhibited large terracelike crystalline structures that revealed several continuous layers and partial layer-by-layer growth. The charge-carrier transport properties of an OTFT are significantly influenced by the film morphology of the active layer, because the grain boundaries usually promote trap formation and limit charge-carrier hopping between crystal domains.^[20] The crystalline domains in the DP2TN film were connected seamlessly in the as-cast film, and the connectivity among crystals in the DP2TN film was better than in the other films. Consistent with the highly connected surface morphology and high fraction of H-aggregates, the DP2TN film displayed the highest fieldeffect mobility among the three H-aggregated films.[21]

Conclusion

Three novel thiophene-naphthalene-based asymmetric oligomers were synthesized in an effort to improve the performance of solution-processed OTFTs prepared from these materials by introducing appropriate alkyl groups through a Suzuki coupling reaction. The introduction of a linear alkyl group increased both the solubility of the synthesized oligomers in common organic solvents and the wettability on octyltrichlorosilane-treated SiO₂. The molecular aggregation type and crystalline packing structures of the oligomers were investigated by optical, morphological, and crystallographic analyses. Adjacent molecules in the DtT,

D3TN, and DP2TN films stacked in a parallel fashion in the thin-film state, and this indicated the formation of H-aggregates. The linear alkyl group promoted the formation of H-aggregates by reducing steric hindrance relative to the bulky cyclohexyl end-capping groups. The self-organization among molecules and the crystallinity in the thin films were improved relative to previously reported asymmetric oligomers with cyclohexyl side groups. The DP2TN-based OTFT yielded the highest field-effect mobility $(3.7 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ among the three H-aggregated compounds, twice the value obtained from the previously reported asymmetric thiophene-based oligomers with cyclohexyl end groups.

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 4. Height-mode AFM images of a) the DtT film, b) the D3TN film, and c) the DP2TN film. The vertical scales in a), b), and c) represent 30, 20, and 40, respectively.

Experimental Section

Materials: All reagents and solvents were purchased from Aldrich, Alfa, Acros, or Lancaster. THF and diethyl ether were distilled over sodium in the presence of benzophenone to remove residual water.^[22] Toluene was distilled over calcium hydride prior to use to ensure that it was anhydrous. Chloroform, dichloromethane, and methanol were used without further purification. Spectroscopic-grade chloroform (Aldrich) was used to measure the UV/Vis absorption spectra of the samples. The reagents bithiophene, 2-(5-decylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, and 2-(4-decylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were synthesized according to known procedures.^[3a,b]

Measurements: The ¹H NMR spectra were recorded on a Bruker AM-200 spectrometer. Chemical shifts are reported in parts per million (ppm) with TMS as internal standard. IR spectra were measured with a Bomen Michelson series FTIR spectrometer. A Jeol JMS-700 high-resolution mass spectrometer (HRMS) was used to obtain the mass spectra of the samples. The UV/Vis absorption spectra were measured at room temperature with a Shimadzu UV-2201 double-beam spectrophotometer on thin-film samples deposited on quartz crystal substrates by a spin-coating method. The melting points were determined by using an Electrothermal Mode 1307 digital analyzer and are uncorrected. Thermogravimetric analysis (TGA) was performed under nitrogen with a TA Instruments 2050 thermogravimetric analyzer. Samples were heated at a 10°Cmin⁻¹ from 30 to 700 °C. Differential scanning calorimetry (DSC) studies were carried out under nitrogen by using a TA Instruments 2100 differential scanning calorimeter. Samples were heated from 30 to 300 °C at a10°Cmin⁻¹. Cyclic voltammograms (CV) of the samples were recorded by using an Epsilon E3 instrument at room temperature in a 0.1 M solution of tetrabutylammonium perchlorate (Bu_4NCIO_4) in acetonitrile under a nitrogen atmosphere at a scan rate of 50 mVs⁻¹.

Synthesis of 5-decyl-2,2'-bithiophene (2): *n*-Butyllithium (1.6 M in hexane, 11.3 mL, 18.04 mmol) was added dropwise to a solution of 2,2'-bithiophene **(1,** 3.0 g, 18.04 mmol) in THF (75 mL) at -78 °C over 20 min. After 1 h, 1-bromodecane (3.95 mL, 18.04 mmol) was added to the solution. The reaction mixture was then warmed to room temperature, stirred for another 2 h, and poured into water. The mixture was extracted with diethyl ether and dried over magnesium sulfate, and the solvent of the organic layer was evaporated. The crude product was purified by column chromatography on silica gel with hexane as eluent to give a blue oil. Yield: 5.6 g (97%). ¹H NMR (300 MHz, CDCl₃): δ =7.21–7.20 (d, 1H, *J*=4.2 Hz), 7.16–7.15 (d, 1 H, *J*=2.58 Hz), 7.05–7.02 (m, 2 H), 6.74–6.72 (d, 1 H, *J*=3.4 Hz), 2.84 (t, 2 H, *J*=7.6 Hz), 1.77–1.69 (m, 2 H), 1.40–1.35 (m, 17 H), 0.96 ppm (t, 3 H, *J*=5.8 Hz); ¹³C NMR (75 MHz, CDCl₃): δ =145.4, 138.0, 134.8, 127.7, 124.7, 123.7, 123.4, 123.0, 32.0, 31.7, 30.2, 29.7, 29.6, 29.5, 29.4, 29.2, 22.8, 14.2 ppm; EIMS: *m/z* (%): 306 (100) [*M*⁺].

Synthesis of 5-bromo-5'-decyl-2,2'-bithiophene (3): 5-Decyl-2,2'-bithiophene (2, 0.72 g, 2.35 mmol) was dissolved in dichloromethane (12 mL) and cooled over an ice bath. *N*-Bromosuccinimide (0.42 g, 2.35 mmol) dissolved in chloroform (10 mL) was added dropwise to the reaction mixture. The reaction mixture was then warmed to room temperature, stirred for another 1 h, and poured into water. The mixture was extracted with dichloromethane and dried over magnesium sulfate, and the solvent of the organic layer was evaporated. The crude product was purified by column chromatography on silica gel with hexane as eluent to give a blue oil. Yield: 0.62 g (68 %). ¹H NMR (300 MHz, CDCl₃): δ = 6.99 (t, 2H, *J* = 3.2 Hz), 6.90–6.87 (d, 1H, *J* = 3.8 Hz), 6.74–6.73 (d, 1H, *J* = 3.5 Hz), 2.84 (t, 2H, *J* = 7.6 Hz), 1.77–1.69 (m, 2H), 1.40–1.35 (m, 17H), 0.96 ppm (t, 3H, *J* = 5.8 Hz); ¹³C NMR (75 MHz, CDCl₃): δ = 145.8, 139.7, 133.9, 130.5, 124.8, 123.7, 123.0, 110.2, 32.2, 31.8, 30.2, 29.7, 29.6, 29.5, 29.4, 29.2, 22.8, 14.2 ppm; EIMS *m/z* (%): 386 (100) [*M*⁺].

Synthesis of 2-(2,2'-bithiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4): *n*-Butyllithium (2.5 M in hexane, 24.1 mL, 60.15 mmol) was added dropwise to a solution of 2,2'-bithiophene (1, 10 g, 60.154 mmol) in THF (120 mL) at -78 °C and the mixture stirred for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12.0 mL, 60.15 mmol) was added to the reaction mixture dropwise over 20 min. The reaction mixture was then warmed to room temperature, stirred for 3 h, and poured into water (150 mL). The reaction mixture was extracted with diethyl ether and dried over magnesium sulfate, and the solvent of the organic layer was evaporated. The crude product was purified by column chromatography on silica gel with hexane as eluent to give a blue oil. Yield: 9.2 g (53 %). ¹H NMR (300 MHz, CDCl₃): δ =7.59–7.58 (d, 11H, *J*=3.6 Hz), 7.29–7.25 (m, 3H), 7.06–7.03 (m, 1H), 1.39 ppm (s, 12H); ¹³C NMR (75 MHz, CDCl₃): δ =144.2, 138.0, 137.3, 128.0, 125.1, 125.0, 124.4, 84.2, 24.8 ppm; EIMS *m/z* (%): 292 (100) [*M*⁺].

Synthesis of 5-decyl-2,2':5',2":5",2"'-quaterthiophene (DtT): Sodium carbonate solution (2m, 4 mL) and then Aliquat 336 (1.2 g, 2.96 mmol) were added to a mixture of 3 (0.88 g, 2.28 mmol) and 4 (0.67 g, 2.30 mmol) in toluene (16 mL). The reaction mixture was deoxygenated with a stream of nitrogen, and [Pd(PPh₃)₄] (0.13 g, 0.11 mmol) was added under nitrogen at room temperature. The reaction mixture was heated to 90 °C for 2 d, cooled to room temperature, and poured into methanol (30 mL). The precipitate was filtered off and washed with water and 5% HCl. The crude solid was washed sequentially with water, methanol, and acetone. The crude product was purified by Soxhlet extraction (silica gel, toluene) and recrystallized from toluene to give a pale vellow-green powder. Yield: 0.8 g (75%). ¹H NMR (300 MHz, CDCl₃): $\delta = 7.25 - 7.23$ (d, 1 H, J=5.12 Hz), 7.20-7.19 (d, 1H, J=2.81 Hz), 7.11-7.00 (m, 6H), 6.71-6.70 (d, 1H, J=3.49 Hz), 2.84 (t, 2H, J=7.56 Hz), 1.73 (m, 2H), 1.29 (m, 14H), 0.92 ppm (t, 3H, J=6.6 Hz); EIMS m/z (%): 470 (100) $[M^+]$; HRMS (ESI) calcd. for $C_{26}H_{30}S_4$ [M⁺]: 470.123; found: 470.1229.

Synthesis of 5-(naphthalen-2-yl)-2,2'-bithiophene (9): Sodium carbonate solution (2M, 24 mL) and then Aliquat 336 (12.8 g, 31.7 mmol) were added to a solution of 2-bromonaphthalene (5.05 g, 24.39 mmol) and compound 4 (7.2 g, 24.63 mmol) in toluene (150 mL). The reaction mixture was deoxygenated with a stream of nitrogen, and $[Pd(PPh_3)_4]$ (1.4 g, 24.63 mmol)

14058 -

FULL PAPER

1.22 mmol) was added under nitrogen at room temperature. The reaction mixture was heated to 90 °C for 3 d under nitrogen, cooled to room temperature, and poured into methanol (30 mL). The precipitate was filtered off and washed with water and 5% HCl. The crude solid was washed sequentially with water, methanol, and acetone. The crude product was purified by Soxhlet extraction (silica gel, toluene) and recrystallized from toluene to give a pale yellow powder. Yield: 5.0 g (70%). ¹H NMR (300 MHz, CDCl₃): δ = 8.06–8.05 (d, 1H, *J* = 1.2 Hz), 7.89 (s, 1H), 7.86 (s, 1H), 7.83–7.82 (d, 1H, *J* = 1.6 Hz), 7.78–7.43 (dd, 1H, *J* = 1.8, 1.8 Hz), 7.52–7.48 (m, 2H), 7.39–7.37 (d, 1H, *J* = 3.8 Hz), 7.28–7.24 (m, 2H), 7.29–7.21 (d, 1H, *J* = 3.8 Hz), 7.10–7.07 ppm (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 128.6, 128.0, 127.9, 127.7, 126.7, 126.0, 124.7, 124.5, 124.1, 124.0, 123.7 ppm; EIMS: *m/z* (%): 292 (100) [*M*⁺].

Synthesis of 5-bromo-5'-(naphthalen-2-yl)-2,2'-bithiophene (10): Compound 9 (2.49 g, 8.07 mmol) was dissolved in DMF (15 mL), the solution cooled over an ice bath, and NBS (1.45 g, 8.15 mmol) in DMF (10 mL) added dropwise under nitrogen. The reaction mixture was then warmed to room temperature, stirred for 15 h, and poured into methanol (30 mL). The precipitate was filtered off and washed with water and 5% HCl. The crude solid was washed with water, methanol, and acetone. The crude product was purified by recrystallization from toluene to give a yellow powder. Yield: 1.50 g (50%). ¹H NMR (300 MHz, CDCl₃): δ = 8.06 (s, 1H), 7.90–7.84 (m, 3H), 7.76 (dd, 1H, *J*=3.84 Hz), 7.04 (d, 1H, *J*=3.84 Hz), 7.01 ppm (d, 1H, *J*=3.81 Hz); EIMS *m/z* (%): 371 (100 [*M*⁺].

Synthesis of 5-decyl-5"-(naphthalen-2-yl)-2,2':5',2"-terthiophene (D3TN): Sodium carbonate solution (2 M, 4 mL) and then Aliquat 336 (0.33 g, 0.81 mmol) were added to a solution of 10 (0.6 g, 1.62 mmol) and 6 (0.62 g, 1.78 mmol) in toluene (16 mL) under nitrogen. The mixture was deoxygenated with a stream of nitrogen, and [Pd(PPh₃)₄] (37 mg, 0.032 mmol) was added under nitrogen at room temperature. The reaction mixture was heated to 90 °C for 2 d under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol (30 mL). The precipitate was filtered off and washed with water and 5% HCl. The crude solid was washed with water, methanol, and acetone. The crude product was then purified by Soxhlet extraction (silica gel, toluene) and recrystallized from toluene to give a pale orange powder. Yield: 0.54 g (65%). ¹H NMR (300 MHz, CDCl₃): $\delta = 8.05$ (s, 1H), 7.89–7.83 (m, 3H), 7.77–7.73 (m, 1H), 7.52–7.50 (m, 2H), 7.39–38 (d, 1 H, J = 3.82 Hz), 7.20–7.19 (d, 1 H, J = 3.80 Hz), 7.14–7.13 (d, 1 H, J =3.76 Hz), 7.05–7.04 (d, 1H, J=3.78 Hz), 7.03–7.02 (d, 1H, J=3.56 Hz)6.72-6.71 (d, 1H, J=3.56 Hz), 2.84 (t, 2H, J=7.57 Hz), 1.71 (m, 2H), 1.29 (m, 14H), 0.93 ppm (t, 3H, J=6.67 Hz); EIMS m/z (%): 514 (100) $[M^+]$; HRMS (ESI) calcd for $C_{32}H_{34}S_4$ $[M^+]$: 514.1823; found: 514.1825.

5-(4-decylphenyl)-5'-(naphthalen-2-yl)-2,2'-thiophene Synthesis of (DP2TN): Sodium carbonate solution (2 M, 24 mL) and then Aliquat 336 (0.36 g, 0.88 mmol) were added to a solution of **10** (0.65 g, 1.75 mmol) and 8 (0.66 g, 1.93 mmol) in toluene (16 mL) under nitrogen. The mixture was deoxygenated with a stream of nitrogen, and [Pd(PPh₃)₄] (46 mg, 0.04 mmol) was added under nitrogen at room temperature. The mixture was heated to 90°C for 2 d under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol (30 mL). The precipitate was filtered off and washed with water and 5%HCl. The crude solid was washed with water, methanol, and acetone. The crude product was purified by Soxhlet extraction (silica gel, toluene) and by recrystallization from toluene to give a pale orange powder. Yield: 0.57 g (70%). ¹H NMR (300 MHz, CDCl₃): $\delta = 8.06$ (s, 1 H), 7.89 (m, 3H), 7.78–7.75 (d, 1H, J=8.19 Hz), 7.56–7.46 (m, 4H), 7.39–7.38 (d, 1H, J = 2.68 Hz), 7.23–7.22 (d, 51 H, J = 5.10 Hz), 2.67 (t, 2H, J = 7.44 Hz), 1.68 (m, 2H), 1.29 (m, 14H), 0.92 ppm (t, 3H, J=6.18 Hz); EIMS m/z (%): 508 (100) $[M^+]$; HRMS(ESI) calcd for $C_{34}H_{36}S_2$ $[M^+]$: 508.2258; found: 508.2256.

Device fabrication: Top-contact OTFTs were fabricated on a common gate of highly n-doped silicon with a 300 nm-thick thermally grown SiO_2 dielectric layer. The cleaned substrates were modified with a hydrophobic octyltrichlorosilane (OTS) monolayer by dipping the substrates in an sol-

ution of OTS in toluene at room temperature for 90 min.^[9b] In ambient air, solutions of the organic semiconductors were spin-coated at 2000 rpm from 0.7 wt% chloroform solutions to form thin films with a nominal thickness of 30-40 nm, as confirmed by using a surface profiler (Alpha Step 500, Tencor). Gold source and drain electrodes were evaporated on top of the semiconductor layers (100 nm). For all measurements, we used channel lengths (L) of 160 μ m and channel widths (W) of 1600 μ m. The electrical characteristics of the FETs were measured in air by using Keithley 2400 and 236 source/measure units. Field-effect mobilities were extracted in the saturation regime from the slope of the source-drain current. XRD studies were performed using the 3C beamline at the Pohang Accelerator Laboratory (PAL). The measurements were carried out with a sample-to-detector distance of 136 mm. Data were typically collected for ten seconds by using an X-ray radiation source of $\lambda = 0.138$ nm and a 2D charge-coupled detector (CCD, Roper Scientific, Trenton, NJ, USA). The incidence angle a_i of the X-ray beam was set to 0.14°, which is intermediate between the critical angles of the films and the substrate (a_{cf} and α_{α}).

Acknowledgements

S.-G.L. is grateful to the National Research Foundation of Korea (NRF) (Grant No. 2010-0023775) for financial support. This work was also supported by a NRF grant funded by the Korean government (MSIP) (NRF-2009-0079630).

- a) S. Wang, P. K. L. Chan, C. Wah Leung, X. Zhao, *RSC Adv.* 2012, 2, 9100–9105; b) D. S. Chung, T. K. An, C. E. Park, H.-J. Yun, S.-K. Kwon, Y.-H. Kim, *Appl. Phys. Lett.* 2012, *101*, 193304–193304; c) P. Sonar, S. P. Singh, Y. Li, Z.-E. Ooi, T.-j. Ha, I. Wong, M. S. Soh, A. Dodabalapur, *Energy Environ. Sci.* 2011, *4*, 2288–2296; d) M. Turbiez, P. Frère, M. Allain, C. Videlot, J. Ackermann, J. Roncali, *Chem. Eur. J.* 2005, *11*, 3742–3752.
- [2] a) Q. Tang, H. Li, M. He, W. Hu, C. Liu, K. Chen, C. Wang, Y. Liu, D. Zhu, Adv. Mater. 2006, 18, 65–68; b) H. K. Tian, J. W. Shi, B. He, N. H. Hu, S. Q. Dong, D. H. Yan, J. P. Zhang, Y. H. Geng, F. S. Wang, Adv. Funct. Mater. 2007, 17, 1940–1951; c) P. Sonar, S. P. Singh, S. Sudhakar, A. Dodabalapur, A. Sellinger, Chem. Mater. 2008, 20, 3184–3190; d) Y. Zhang, Z. Zhao, X. Huang, Y. Xie, C. Liu, J. Li, X. Guan, K. Zhang, C. Cheng, Y. Xiao, RSC Adv. 2012, 2, 12644–12647; e) K. H. Jung, S. Y. Bae, K. H. Kim, M. J. Cho, K. Lee, Z. H. Kim, D. H. Choi, D. H. Lee, D. S. Chung, C. E. Park, Chem. Commun. 2009, 0, 5290–5292.
- [3] a) N.-X. Wang, Synth. Commun. 2003, 33, 2119–2124; b) S. Barlow, S. A. Odom, K. Lancaster, Y. A. Getmanenko, R. Mason, V. Coropceanu, J.-L. Brédas, S. R. Marder, J. Phys. Chem. B 2010, 114, 14397–14407; c) A. R. Murphy, J. Liu, C. Luscombe, D. Kavulak, J. M. J. Fréchet, R. J. Kline, M. D. McGehee, Chem. Mater. 2005, 17, 4892–4899.
- [4] W. Tang, S. P. Singh, K. H. Ong, Z.-K. Chen, J. Mater. Chem. 2010, 20, 1497–1505.
- [5] a) G. Barbarella, M. Zambianchi, L. Antolini, P. Ostoja, P. Maccagnani, A. Bongini, E. A. Marseglia, E. Tedesco, G. Gigli, R. Cingolani, *J. Am. Chem. Soc.* **1999**, *121*, 8920–8926; b) M. Halik, H. Klauk, U. Zschieschang, G. Schmid, S. Ponomarenko, S. Kirchmeyer, W. Weber, *Adv. Mater.* **2003**, *15*, 917–922.
- [6] a) P. C. Chang, J. Lee, D. Huang, V. Subramanian, A. R. Murphy, J. M. J. Fréchet, *Chem. Mater.* **2004**, *16*, 4783–4789; b) S. E. Fritz, S. Mohapatra, B. T. Holmes, A. M. Anderson, C. F. Prendergast, C. D. Frisbie, M. D. Ward, M. F. Toney, *Chem. Mater.* **2007**, *19*, 1355–1361.
- [7] a) S. Allard, M. Forster, B. Souharce, H. Thiem, U. Scherf, Angew. Chem. 2008, 120, 4138-4167; Angew. Chem. Int. Ed. 2008, 47, 4070-4098; b) R. P. Ortiz, J. Casado, V. Hernández, J. T. L. Navarrete, J. A. Letizia, M. A. Ratner, A. Facchetti, T. J. Marks, Chem. Eur. J. 2009, 15, 5023-5039; c) M. Defaux, F. Gholamrezaie, J. Wang, A. Kreyes, U. Ziener, D. V. Anokhin, D. A. Ivanov, A. Moser, A. Neu-

hold, I. Salzmann, R. Resel, D. M. de Leeuw, S. C. J. Meskers, M. Moeller, A. Mourran, Adv. Mater. 2012, 24, 973–978; d) H. Meng, F. Sun, M. B. Goldfinger, G. D. Jaycox, Z. Li, W. J. Marshall, G. S. Blackman, J. Am. Chem. Soc. 2005, 127, 2406–2407; e) Y. Nicolas, P. Blanchard, J. Roncali, M. Allain, N. Mercier, A.-L. Deman, J. Tardy, Org. Lett. 2005, 7, 3513–3516; Y. Chen, H. Chang, H. Tian, C. Bao, W. Li, D. Yan, Y. Geng, F. Wang, Org. Electron. 2012, 13, 3268–3275.

- [8] S.-O. Kim, T. K. An, J. Chen, I. Kang, S. H. Kang, D. S. Chung, C. E. Park, Y.-H. Kim, S.-K. Kwon, *Adv. Funct. Mater.* **2011**, *21*, 1616– 1623.
- [9] a) J. Locklin, D. Li, S. C. B. Mannsfeld, E.-J. Borkent, H. Meng, R. Advincula, Z. Bao, *Chem. Mater.* **2005**, *17*, 3366–3374; b) T. K. An, S.-H. Hahn, S. Nam, H. Cha, Y. Rho, D. S. Chung, M. Ree, M. S. Kang, S.-K. Kwon, Y.-H. Kim, C. E. Park, *Dyes Pigm.* **2013**, *96*, 756–762.
- [10] a) C. D. Dimitrakopoulos, B. K. Furman, T. Graham, S. Hegde, S. Purushothaman, *Synth. Met.* **1998**, *92*, 47–52; b) H. E. Katz, A. Dodabalapur, L. Torsi, D. Elder, *Chem. Mater.* **1995**, *7*, 2238–2240; c) R. Bourguiga, F. Garnier, G. Horowitz, R. Hajlaoui, P. Delannoy, M. Hajlaoui, H. Bouchriha, *Eur. Phys. J. Appl. Phys.* **2001**, *14*, 121–125.
- [11] M. Wehmeier, M. Wagner, K. Müllen, Chem. Eur. J. 2001, 7, 2197– 2205.
- [12] H.-S. Kim, Y.-H. Kim, T.-H. Kim, Y.-Y. Noh, S. Pyo, M. H. Yi, D.-Y. Kim, S.-K. Kwon, *Chem. Mater.* 2007, 19, 3561–3567.
- [13] a) H. Menzel, B. Weichart, A. Schmidt, S. Paul, W. Knoll, J. Stumpe, T. Fischer, *Langmuir* 1994, 10, 1926–1933; b) L. Zhang, L. Tan, Z. Wang, W. Hu, D. Zhu, *Chem. Mater.* 2009, 21, 1993–1999.
- [14] a) F. C. Spano, Acc. Chem. Res. 2010, 43, 429–439; b) F. Meinardi, M. Cerminara, A. Sassella, R. Bonifacio, R. Tubino, Phys. Rev. Lett.

2003, 91, 247401; c) F. C. Spano, Annu. Rev. Phys. Chem. 2006, 57, 217–243.

- [15] X. Zhang, J. P. Johnson, J. W. Kampf, A. J. Matzger, *Chem. Mater.* 2006, 18, 3470–3476.
- [16] D. S. Chung, J. W. Park, J.-H. Park, D. Moon, G. H. Kim, H.-S. Lee, D. H. Lee, H.-K. Shim, S.-K. Kwon, C. E. Park, *J. Mater. Chem.* 2010, 20, 524–530.
- [17] a) M. C. Hwang, J.-W. Jang, T. K. An, C. E. Park, Y.-H. Kim, S.-K. Kwon, *Macromolecules* **2012**, *45*, 4520–4528; b) N. An, Y. Shi, J. Feng, D. Li, J. Gao, Y. Chen, X. Li, *Org. Electron.* **2013**, *14*, 1197– 1203.
- [18] a) S. W. Lee, S. J. Lee, S. G. Hahm, T. J. Lee, B. Lee, B. Chae, S. B. Kim, J. C. Jung, W. C. Zin, B. H. Sohn, M. Ree, *Macromolecules* **2005**, *38*, 4331–4338; b) T. J. Shin, H. Yang, M.-M. Ling, J. Locklin, L. Yang, B. Lee, M. E. Roberts, A. B. Mallik, Z. Bao, *Chem. Mater.* **2007**, *19*, 5882–5889.
- [19] D. Choi, B.-S. Jeong, B. Ahn, D. S. Chung, K. Lim, S. H. Kim, S. U. Park, M. Ree, J. Ko, C. E. Park, ACS Appl. Mater. Interfaces 2012, 4, 702–706.
- [20] a) T. Yamada, T. Hasegawa, M. Hiraoka, H. Matsui, Y. Tokura, G. Saito, *Appl. Phys. Lett.* **2008**, *92*, 233306–233303; b) G. Generali, F. Dinelli, R. Capelli, S. Toffanin, F. di Maria, M. Gazzano, G. Barbarella, M. Muccini, J. Phys. Chem. C **2011**, *115*, 23164–23169.
- [21] a) G. Horowitz, M. E. Hajlaoui, R. Hajlaoui, J. Appl. Phys. 2000, 87, 4456–4463; b) J. H. Schon, B. Batlogg, J. Appl. Phys. 2001, 89, 336– 342.
- [22] H. Andringa, J. Hanekamp, L. Brandsma, Synth. Commun. 1990, 20, 2349–2351.

Received: July 4, 2013 Published online: September 17, 2013