Synthesis of Phenylenevinylene Oligothiophene Derivatives with and without Cyano Side Substitution and Evaluation of Optoelectronic Characteristics

Mizuho Kondo,^{*1} Yukihiro Inoue,¹ Yuki Koeduka,¹ Masahiro Funahashi,² Akira Heya,¹ Naoto Matsuo,¹ and Nobuhiro Kawatsuki^{*1} ¹Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo,

2167 Shosha Himeji, Hyogo 671-2280

²Department of Advanced Materials Science, Faculty of Engineering, Kagawa University,

2217-20 Hayashi-cho, Takamatsu, Kagawa 761-0396

(E-mail: mizuho-k@eng.u-hyogo.ac.jp)

Two types of phenylenevinylene terthiophene with and without cyano side substitution were synthesized to investigate the effect of the molecular structure on optoelectronic properties. The oligothiophene with cyano side substitution exhibited large bathochromic effect and behaved as organic electron acceptors with decrease in field effect conductivity due to increase in dipole moment.

Oligothiophenes have attracted much attention in the fields of organic semiconductors and optoelectronics due to their good processability and tunability of their solid and crystalline state. These compounds have significant potential for use as molecular semiconductors in organic electronics and device applications such as organic field effect transistors (OFETs),¹ photovoltaic solar cells,² and lasers.³ There is a wide range of possibilities for chemical modification; therefore, various oligothiophene derivatives have been synthesized.

In particular, cyanovinyl oligothiophene has a strong electronic push–pull structure with good processability and redox properties,⁴ and has been used as a dye sensitizer in Grätzel-type solar cells.^{2b} Both symmetric and asymmetric cyano-based oligothiophenes have also been used as OFETs with tetracyanoquinodimethane analogs that switch high electron mobility and ambipolar transport properties by changing the incorporation amount of electron-withdrawing (EW) substitution.⁵ Recently, Funahashi and Kato have prepared one cyano-substituted oligothiophene that has liquid-crystalline nanostructures consisting of ionically conductive and electronic charge transport layers by the association of π -conjugated molecules with ionic moieties.⁶ The use of cyano-based terthiophene as a mesogenic unit was reported, although the field effect conductivity of cyanovinyl oligothiophene has not been evaluated to date.

In this work, we prepared two types of phenylenevinylene terthiophene with and without cyano side substitution and evaluated the effect of the molecular structure on optoelectronic properties. To design the molecular structure, enhancement of the thermal properties is necessary in order to utilize wet processes such as spin-casting and drop-casting to make it suitable for industrial applications. Alkyl chain substitution is an effective way to solubilize aromatic compounds; therefore, to utilize substituted compounds for electronic devices, it is necessary to add substituents in an appropriate manner, i.e., without disturbing the electronic properties of the original conjugated core.⁷ In addition, asymmetric structure along the conjugated structure is useful for enhancing the solubility and liquid crystallinity. Consequently, the asymmetric oligothiophene shown in Figure 1 was designed. The synthesis route for the compounds, experimental details, and thermal



Figure 1. Chemical structures, nomenclature, and thermal properties of oligothiophenes used in this study. K: crystal; LC: liquid crystal; I: isotropic.



Figure 2. UV absorption (black) and PL spectra (colored) of **4TTh** (top) and **4CnTTh** (bottom) dissolved in THF (triangles) and DMSO (circles) solvents $(1.2 \times 10^{-5} \text{ M})$ under exposure to 365 nm light. The insets show photographs of the THF (left) and DMSO (right) solutions upon exposure to 365 nm light.

properties are given in the Supporting Information (SI). Figure 2 shows absorption and photoluminescence (PL) spectra of the oligothiophenes dissolved in tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) at a concentration of ca. 1.2×10^{-5} M excited at 365 nm light. The peak wavelengths for absorbance (λ_{abs}), photoluminescence (λ_{PL}), maximum absorption coefficients (ε), and quantum yields (Φ_f) for the solutions under UV irradiation are summarized in Table 1, and excitation spectra are provided in Supporting Information S4 (SI). It has been reported that cyanobased oligothiophene molecules typically exhibit intramolecular charge transfer.⁴ A cyano group located in the α position causes a bathochromic shift; the more polar DMSO stabilizes a strongly charge polarized ground electronic state so that a very large amount of planar conformers should be present in the DMSO solution. As a result, the absorbance is slightly broad due to its intramolecular charge-transfer characteristics, because the planar conformation optimizes the conjugation of thiophene and phenylacetonitryl moieties.⁴ These results suggest that intramolecular charge transfer (ICT) occurred from the conjugated backbone to the cyano branch. The energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were estimated

 Table 1. Wavelengths of absorption and photoemission spectral peaks, maximum absorption coefficients, and quantum efficiencies for the oligothiophene solutions

Sample	Solvent	$\lambda_{ m abs}{}^{ m a)}$ /nm	$\lambda_{ m em}{}^{ m b)}$ /nm	$\mathcal{E}/M^{-1}cm^{-1}$	$\Phi_{ m f} \ /\%$
4TTh	THF	412	495	83000	3.6
	DMSO	418	501	58000	3.5
4CnTTh	THF	415	443	59000	0.14
	DMSO	427	543	40000	0.025

^aConcentration: $1.2 \times 10^{-5} \text{ mol } \text{L}^{-1}$. ^bExcitation at 365 nm.

from density functional theory (DFT) calculations. The dipole moment of 4CnTTh is 3.97 D, which is approximately five times larger than that of **4TTh** (0.78 D), but the electron clouds in the conjugated backbone are delocalized for the HOMO and LUMO level (Figure S5, SI). The energies of both the HOMO and LUMO of 4CnTTh are lower than those of 4TTh, and the reduction of the LUMO is larger than that of the HOMO, which reduces the energy band. Additionally, the effect of solvent polarity on λ_{abs} was also estimated by time-dependent (TD)-DFT method, and the result is provided in ST1 (SI). Red shift in λ_{abs} is observed and bathochromic effect became larger in 4CnTTh, supporting the experimental results although the change was slight. On the other hand, difference in the photoemission behavior of the oligothiophens was more prominent; the PL spectrum peak of 4CnTTh showed large red shift when it was dissolved in DMSO, while 4TTh showed a slight change. In addition, the photoemission intensity of the 4CnTTh solution is weaker than that of the 4TTh solution, as shown in the inset of Figure 2 and Table 1. Sun et al. reported that ICT was induced in oligothienylene derivatives with electron-withdrawing substitution by polar solvents,8 followed by geometric twisting (TICT).⁹ They also indicated that the PL of the compounds in nonpolar solvents is emitted from the fluorescent states with planar conformations that showed small difference between the compound with and without EW substitution, presuming that the same mechanism occurred in our compounds due to the similarity of chemical structure and the effect of solvent polarity on absorbance and photoemission.

Cyclic voltammetry measurements of the compounds were conducted in CH_2Cl_2 in the presence of n-Bu₄NClO₄ (0.1 M) using Fc/Fc⁺ as an internal standard (Table 2). For compound **4CnTTh**, quasi-reversible one-electron oxidation and one-electron reduction were observed at the half-wave potentials of 0.50 and -1.95 V vs. Ag⁺/Ag, respectively. The cyclic voltammograms for compound **4TTh** indicate only an ambiguous one-electron oxidation at 0.33 V, without any reversible reduction peaks within the electrochemical window of the electrolyte solution (Figure S6, SI). The introduction of the cyano groups at the ethylene linkages reduced the LUMO level, which leads to the expected positive shift of the reduction potential and stable anion species are observed.

The carrier transport characteristics of the oligothiophenes were examined using the time-of-flight (TOF) technique.¹⁰ Transit times were determined from kink points in double logarithmic plots of the transient photocurrent curves. The arrows in Figure 3 indicate the transit times for **4TTh** and **4CnTTh**. The hole mobilities at 50 V are calculated to be 2.1×10^{-2} and 4.6×10^{-3} cm²V⁻¹s⁻¹ for **4TTh** and **4CnTTh**, respectively. The lower field-dependent hole mobility of **4CnTTh** should be attributed to the local electric field produced by dipole moments of the cyano groups of **4CnTTh** molecules. Unlike molecular crystals, disorder

 Table 2. Measured reduction potentials and HOMO and LUMO energies of the oligothiophenes estimated from DFT calculations

	$E_{ m ox}^{ m a)}$ /V	$E_{\rm red}{}^{\rm a)}$ /V	$\Delta E^{\mathrm{a})}$ /eV	HOMO ^{b)} /eV	LUMO ^{b)} /eV	$\Delta E_{\rm DFT}$ /eV
4TTh 4CnTTh	0.33 0.5		 	-4.88 -5.20	-1.95 -2.43	2.93 2.77

^aMeasured in CH₂Cl₂ containing 0.1 M *n*-Bu₄NClO₄ as a supporting electrolyte at room temperature. ^bCalculations were performed using DFT with the restricted B3LYP functional and the 6-31G(d) basis set, as implemented in Gaussian 09.



Figure 3. Double logarithmic plots of transient photocurrent curves for hole transport in **4TTh** (A) and **4CnTTh** (B) under various applied voltages in a 4 μ m cell irradiated with 356 nm light. Applied voltage: 50 V (red); 40 V (blue); 30 V (green); 20 V (purple); 10 V (pink); 0 V (black). Black arrows indicate kink point of the photocurrent when the applied voltage was 50 V.

of dipolar moment orientation was generated in LC phase and it remained in the thiophene solid, causing distribution of the HOMO levels. In amorphous organic semiconductors, this distribution of the energy levels of the π -orbitals leads to a decrease in the carrier mobilities and their field- and temperature-dependence.¹¹

Thin films of the oligothiophenes were prepared by sublimation onto quartz substrates, and their surface profiles were investigated. Figure 4A shows an X-ray diffraction (XRD) pattern for **4TTh**, which corresponds to a *d*-spacing of d = 2.38 nm. The **4TTh** film had a small angle reflection at $2\theta = 3.71^{\circ}$, consistent with the molecular length of the **4TTh** molecule (2.39 nm) estimated from DFT calculations. An atomic force microscopy (AFM) image for the 4TTh film is shown on the right side of Figure 4A, where small circular grains ($< 0.2 \,\mu$ m) and a smooth surface ($R_{q} \approx 2.0 \text{ nm}$) were observed. To further evaluate the surface profile of the **4TTh** film, the angular dependency of a probe beam was measured using polarized absorption spectroscopy. The detailed geometry of the optical setup is shown in Figure S1 (SI), and angular-dependent absorption spectra are summarized in Figure S7A (SI). The absorption peak for the film is approximately 343 nm, which is shorter than that for the THF solution, and the absorbance increased with the tilt angle. In addition, the PL spectrum of the substrate was similar to that of solution with low intensity, as displayed in Figure S8 (SI), which indicates that 4TTh aligned normal to the substrate and formed H-aggregation.



Figure 4. XRD patterns (left) and AFM images (right) of (A) 4TTh and (B) 4CnTTh films sublimed on quartz substrates. Scale bar: 1 μ m.



Figure 5. Output (left) and transfer characteristics (right) of topcontact OFETs fabricated with (A) 4TTh and (B) 4CnTTh. $V_{on/off} = 3 \times 10^2$; I_D : drain–source current.

Figure 4B shows an XRD pattern and AFM image for the **4CnTTh** film. In contrast to **4TTh**, a weak and unresolved peak was observed at $2\theta = 3.81^{\circ}$ (2.32 nm), although the AFM image was similar with a slightly rough surface (average grain size: <0.2 µm, $R_q \approx 2.5$ nm). Furthermore, absorption spectroscopy indicated a blue shift, but no obvious angular dependence (Figure S7B, SI). The PL spectrum of the substrate was similar to DMSO solution and reduction of PL intensity was also observed (Figure S8B, SI). The reduction of PL intensity was small in comparison to **4TTh**, suggesting that **4CnTTh** sublimed randomly on the quartz substrate and only a small amount of molecules were aligned normal to the substrate.

The OFET activities of **4TTh** and **4CnTTh** were observed at room temperature using vapor-deposited thin films, and are shown in Figure 5. $V_{\rm th}$ for **4TTh** was 38 V, as estimated from the transfer characteristic displayed in the right figure of Figure 5A, and the mobility was $3.0 \times 10^{-3} \, {\rm V}^{-1} \, {\rm s}^{-1}$, as estimated from the saturated

region for **4TTh** that is lower than TOF measurement due to the existence of disordered regions and the smaller size of grains in the film.^{1c} In contrast, a decrease in output was observed in the saturated region for **4CnTTh**. The field effect mobility was estimated to be 1.6×10^{-4} cm²V⁻¹s⁻¹ in the (quasi) saturated region, which was one order lower than that for **4TTh**, which is consistent with the TOF measurement results (Figure 5B). It can be speculated that the decrease of I_D is due to the lower molecular crystallinity and larger dipole moment of **4CnTTh** molecules. In comparison to the previous oligothiophene derivatives with cyano substitution,⁵ the incorporation amount of EW is not enough to induce electron mobility, causing reduction of the LUMO level and hole mobility.

In summary, two types of phenylenevinylene terthiophene were prepared. Oligothiophene with the cyano side group exhibited large bathochormic effect with low quantum yields and behaved as organic electron acceptors in solution state, while it showed p-type conductivity when an OFET was fabricated. The oligothiophenes examined in this study exhibited liquid-crystalline properties; therefore, improvement of the hole mobility could be expected with the use of an alignment layer,¹² and this is currently under investigation.

This work was supported in part by a Grant-in-Aid for Young Scientists B (No. 25810079) from the Japan Society for the Promotion of Science.

Supporting Information is available electronically on J-STAGE.

References

- a) A. R. Murphy, J. M. J. Fréchet, *Chem. Rev.* 2007, 107, 1066.
 b) *Handbook of Thiophene-Based Materials: Applications in Organic Electronics and Photonics*, ed. by I. F. Perepichka, D. F. Perepichka, Wiley, New York, 2009. doi:10.1002/9780470745533. c) F. Zhang, M. Funahashi, N. Tamaoki, *Org. Electron.* 2009, 10, 73.
- a) M. K. R. Fischer, I. López-Duarte, M. M. Wienk, M. V. Martínez-Díaz, R. A. J. Janssen, P. Bäuerle, T. Torres, *J. Am. Chem. Soc.* 2009, *131*, 8669. b) M. K. R. Fischer, S. Wenger, M. Wang, A. Mishra, S. M. Zakeeruddin, M. Grätzel, P. Bäuerle, *Chem. Mater.* 2010, *22*, 1836.
- 3 D. Pisignano, M. Anni, G. Gigli, R. Cingolani, M. Zavelani-Rossi, G. Lanzani, G. Barbarella, L. Favaretto, *Appl. Phys. Lett.* 2002, *81*, 3534.
- 4 S. R. González, J. Orduna, R. Alicante, B. Villacampa, K. A. McGee, J. Pina, J. S. de Melo, K. M. Schwaderer, J. C. Johnson, B. A. Blackorbay, J. J. Hansmeier, V. F. Bolton, T. J. Helland, B. A. Edlund, T. M. Pappenfus, J. T. L. Navarrete, J. Casado, *J. Phys. Chem. B* 2011, *115*, 10573.
- 5 X. Cai, M. W. Burand, C. R. Newman, D. A. da Silva Filho, T. M. Pappenfus, M. Bader, J. L. Bredas, K. R. Mann, C. D. Frisbie, *J. Phys. Chem. B* **2006**, *110*, 14590.
- 6 S. Yazaki, M. Funahashi, J. Kagimoto, H. Ohno, T. Kato, J. Am. Chem. Soc. 2010, 132, 7702.
- 7 M. Lu, S. Nagamatsu, Y. Yoshida, M. Chikamatsu, R. Azumi, K. Yase, *Chem. Lett.* 2010, 39, 60.
- 8 G.-J. Zhao, R.-K. Chen, M.-T. Sun, J.-Y. Liu, G.-Y. Li, Y.-L. Gao, K.-L. Han, X.-C. Yang, L. Sun, *Chem. -Eur. J.* **2008**, *14*, 6935.
- 9 Z. R. Grabowski, K. Rotkiewicz, Chem. Rev. 2003, 103, 3899.
- 10 a) R. G. Kepler, *Phys. Rev.* **1960**, *119*, 1226. b) M. Funahashi, F. Zhang, N. Tamaoki, J. Hanna, *ChemPhysChem* **2008**, *9*, 1465.
- a) A. Hirao, H. Nishizawa, *Phys. Rev. B* **1996**, *54*, 4755. b) T. Nagase,
 H. Naito, *J. Appl. Phys.* **2000**, *88*, 252. c) H. lino, J. Hanna, *Jpn. J. Appl. Phys.* **2006**, *45*, L867.
- 12 T. Fujiwara, J. Locklin, Z. Bao, Appl. Phys. Lett. 2007, 90, 232108.