Syntheses and Properties of Oligothiophenes with Cyano and Hexyl Groups

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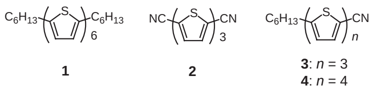
Syntheses of new oligothiophenes which have cyano and hexyl groups at the ends of quarter- and ter-thiophenes are described. The observations of DSC and polarizing microscopy indicate the presence of liquid-crystalline (LC) phases over a wide temperature range. The energy gaps are discussed on the basis of the absorption and photoluminescence (PL) spectra and cyclic voltammetry. Thin films of oligothiophenes fabricated by vacuum deposition are investigated by AFM and XRD measurements.

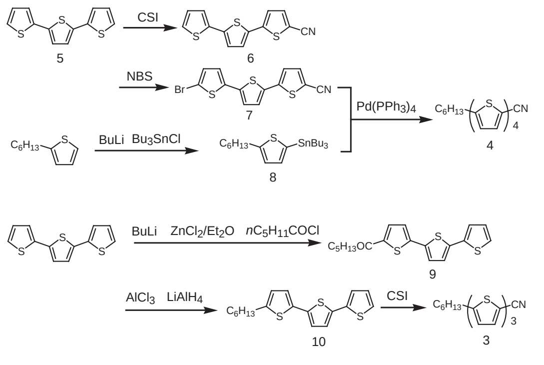
Conjugated oligothiophenes are currently receiving considerable attention as organic semiconductors. Dihexylsexithiophene **1** makes particularly good thin films, which are used as active layers of organic field-effect transistors (OFETs).[1] Recently, we have investigated introduction of cyano groups on tetrathiafluvarenes (TTF) derivatives,[2] and found that such polar groups increase the affinity to SiO_2 substrates and improve the thin-film properties. In this context, we are interested in cyano-substituted oligothiophenes. Cyano terthiophene and dicyanoterthiophene **2** have been reported previously.[3,4] However, unsymmetrically substituted oligothiophenes are not very much explored. In this report, we report the syntheses of olighothiophenes, **3** and **4**,[5] in which not only a cyano group but also a hexyl group are unsymmetrically attached to the α- and ω-terminals of terthiophene and quarterthiophene. These compounds are oligothiophene analogs of the well-known LC materials, cyanobiphenyls (Scheme 1).

The oligothiophenes were prepared according to Scheme 2.[6] A cyano group was attached to terthiophene **5**[7] with the treatment of an equivalent amount of CSI (chlorosulfonyl isocyanate) in THF at −70 °C.[3] After the temperature was allowed to rise to rt, the solvent was evaporated, and the resulting residue was purified with silica gel column chromatography (hexane/CH_2Cl_2), giving a yellow solid **6** (74% yield). **7** was prepared from **6** with the treatment of an equivalent amount of NBS (*N*-bromosuccinimide) in a mixture of CCl_4 and AcOH. After refluxing 30 min, the reaction mixture was washed with water and aqueous Na_2CO_3. After evaporation of the solvent, the residue was purified using silica gel column chromatography (hexane/CH_2Cl_2), giving a yellow solid **7** (97% yield).[3] 2-Hexylthiophene was lithiated by the treatment of BuLi in THF at 0 °C and reacted with Bu_3SnCl at 0 °C, giving a pale yellow oil **8** (81% yield).

A mixture of **7** and **8** was refluxed 24 h in toluene by using $Pd(PPh_3)_4$ as a catalyst. The product was purified with silica gel column chromatography (hexane/CH_2Cl_2) to give a yellow solid **4** (43% yield): mp 220 °C; Mass *m/z* 439, ^{1}H NMR ($CDCl_3$) δ 0.897 (3H), 1.361 (6H), 1.685 (2H), 2.800 (2H), 6.689 (1H), 7.007 (2H), 7.092 (3H), 7.187 (1H), 7.520 (1H); Anal. Calcd for $C_{23}H_{21}N_1S_4$: C, 62.82; H, 4.81; N, 3.19; S, 29.18%. Found: C, 62.69; H, 4.77; N, 3.18; S, 29.60%. IR ν_{max}/cm^{-1}: 792, 847, 1043, 1441, 2218, 2856, 2927.



Scheme 1.



Scheme 2. Synthesis of α,ω-cyanohexylquaterthiophene **4** and α,ω-cyanohexylterthiophene **3**.

Since terthiophene is much more soluble in THF than quaterthiophene, preparation of **3** was achieved by another route described in Scheme 2. Terthiophene was treated by BuLi in THF at −60 °C, and succeeding addition of $ZnCl_2/Et_2O$ and hexanoyl chloride at −30 °C gave a pale yellow solid **9** (27% yield). **10** was prepared from the reduction of **9** by the treatment of $AlCl_3$ and $LiAlH_4$ in distilled diethyl ether and toluene, giving a yellow solid **11** (71% yield).[8] A cyano group was attached to **10** by the treatment of CSI similarly to the preparation of **6**, giving a yellow solid **3** (28% yield): mp 82.5 °C; Mass *m/z* 357, ^{1}H NMR ($CDCl_3$) δ 0.895 (3H), 1.332 (6H), 1.686 (2H), 2.802 (2H), 6.710 (1H), 7.032 (2H), 7.099 (1H), 7.163 (1H), 7.522 (1H); Anal. Calcd for $C_{19}H_{19}N_1S_3$: C, 63.82; H, 5.36; N, 3.92; S, 26.91. Found: C, 64.11; H, 5.38; N, 3.53; S, 26.68%. IR ν_{max}/cm^{-1}: 794, 854, 1043, 1442, 2216, 2925.

The DSC of **3** and **4** indicate the presence of mesophases as shown in Figure 1, particularly for **4**. Observation under a polarizing microscope for **3** shows the phase sequence as I:85 °C:N:76 °C:Cry. Phase transitions of **4** are observed at I:220 °C:N:188 °C:SmA:185 °C:SmX:70–80 °C:Cry. The transitions of I–N and N–SmA are clearly observed in the DSC measurement. The transition of SmX–Cry is identified with a polarizing microscope by the appearance of cracks in the crystal phase, but is not detected in the DSC measurement. Although dicyanoterthiophene shows a nematic phase only monotropically between 205 and 178 °C,[4] dihexyl-quaterthiophene exhibits a smectic phase in a wide temperature range between 84 and 179 °C.[9] The present monohexyl compound **4** shows a fairly stable mesophases which are comparable to the dihexyl compound. The increased number of thiophene rings seems to enhance the

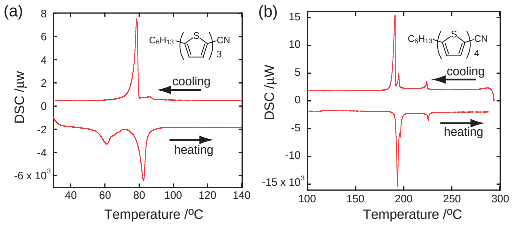


Figure 1. DSC of (a) **3** and (b) **4**.

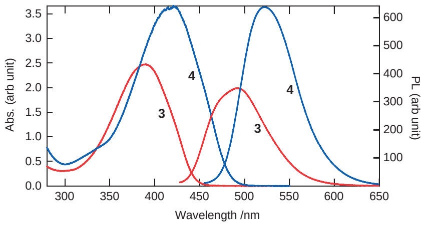


Figure 2. Absorption and PL Spectra of **3** and **4**.

stability of LC phases. A similar stability of LC phases has been observed in cyano biphenyl LC compounds.

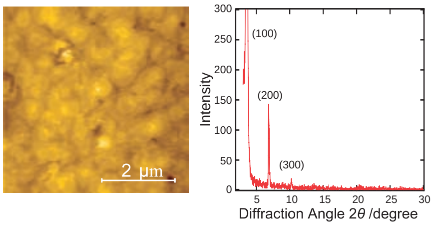
Cyclic voltammetry of **3** exhibits two reversible oxidation waves at $E_{1/2} = 1.22$ and 1.47 V (vs. Ag/AgCl in PhCN), and one reversible reduction wave at $E_{1/2} = -0.94$ V. Compound **4** also shows two reversible oxidation waves at $E_{1/2} = 1.03$ and 1.22 V, and one reversible reduction wave at $E_{1/2} = -0.94$ V. Redox potentials of **2** have been reported to be $E_{1/2} = 1.50$ V for oxidation, and $E_{1/2} = -1.41$ V for reduction (vs SCE).[10] These results indicate that the energy gaps are 2.16, 1.97, and 2.91 eV for **3**, **4**, and **2**, respectively. In comparison with those of unsubstituted terthiophene and quaterthiophene (2.47 and 2.21 eV),[11] addition of a cyano group to one end of oligothiophenes reduces the energy gap, while the substitution to the both ends enlarges the energy gap.

Absorption and PL spectra of these materials measured in CCl_4 are shown in Figure 2. The absorption maxima are observed at 390 and 421 nm for **3** and **4**, respectively. The cyano group of **3** induces a bathochromic shift of 35 nm relative to the unsubstituted terthiophene **5** (355 nm), whereas the absorption maximum of **3** is not much different from that of the dicyano analog **2** (385 nm).[3] The PL maxima are 481 and 513 nm. HOMO–LUMO gaps of **3** and **4** obtained from the absorption edges are 2.79 and 2.55 eV, respectively, in consistent with the CV results.

AFM images and XRD patterns of thin films of **4** formed on SiO_2 substrates at rt and 80 °C by vacuum deposition are shown in Figure 3. Improvement of thin-film morphology is observed with increasing the substrate temperature. In particular, screw dislocation appears in the AFM image for the thin film deposited at 80 °C. The step size observed in Figure 3(b) is estimated to be 2.6 nm. The step size is in good agreement with the layer thickness evaluated from the XRD peaks, 2.54 nm. Since the molecular length is 2.55 nm, this indicates that the oligothiophene molecules are standing almost perpendicular to the substrate with the tilt angle of 5 °.

Unfortunately, these compounds have not worked as organic transistors, but show anomalous transport properties in the time-of-flight measurements; ionic conduction for **3** and non ionic conduction for **4**.[12]

(a) Substrates temperature : rt



(b) Substrates temperature : 80°C

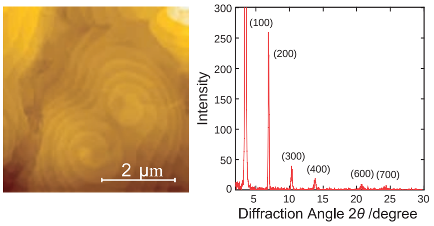


Figure 3. AFM images and XRD patterns of thin-film **4**.

In conclusion, we have prepared α, ω-cyanohexyl-terthiophene and quaterthiophene. These compounds have liquid-crystalline phases, and form good thin films on SiO_2, where the molecules are almost perpendicular to the substrates.

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