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n-Type and Ambipolar FET Characteristics Using Pyrazinophenanthrolines Linked with Oligothiophenes

Jun-ichi Nishida,[1] Shigeki Murakami,[1] Hirokazu Tada,[2] and Yoshiro Yamashita*[1]

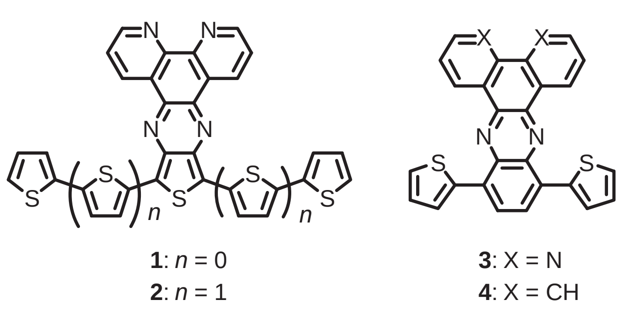
[1]*Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering,*
Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502
[2]*Graduate School of Engineering Science, Osaka University, Machikaneyama, Toyonaka, Osaka 560-8531*

(Received August 7, 2006; CL-060896; E-mail: yoshiro@echem.titech.ac.jp)

Phenanthroline rings were used to generate n-type FET properties for the first time. A FET device based on a pyrazinophenanthroline with a quinquethiophene unit showed clear ambipolar FET characteristics.

Organic thin-film field-effect transistors (OFETs) have attracted much attention because of their potential applications to low-cost electronic devices and their integrated circuits.[1] To date, there are many reports on FETs with p-type characteristics such as pentacene[2] and oligothiophenes[3] with high hole mobilities. Compared to p-type semiconductors, the number of n-type[4] and ambipolar[5,6] semiconductors which can transport both hole and electron is still limited, especially when devices are fabricated by using Au electrodes. The development of good n-type and ambipolar materials is crucial for the fabrication of p–n junction, bipolar transistors,[7] and light emitting FET devices.[5b]

Phenanthroline derivatives have been used as essential ligands in metal complexes which can be applied to catalyst, luminescent materials,[8] and molecular machines like catenanes and rotaxanes. On the other hand, phenanthroline derivatives have been used to transport electrons.[9] The electron mobility of 4,7-diphenylphenanthroline using a time-of-flight (TOF) technique was reported to be $10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ in the amorphous state.[9a] If this ring is introduced to a proper planar π-conjugated core, new donor–acceptor type semiconductors showing n-type and ambipolar FET characteristics would be achieved. Bearing this in mind, we have now designed pyrazinophenanthroline derivatives **1** and **2** linked with oligothiophenes (Chart 1), which have the following advantages. (1) Oligothiophenes are one of the most popular organic materials which work as p-type semiconductors. Modification of terminal positions of oligothiophenes with electron-withdrawing units such as alkylcarbonyl groups,[6a] dicyanomethylene groups,[6b] and fullerene[6c] has afforded interesting amibipolar semiconductors. (2) Phenanthrolines **1** and **2** have a quinonoid structure of a thieno[3,4-*b*]pyrazine unit, which leads to a smaller HOMO–LUMO energy gap than other oligothiophene-[1,10]phenanthroline systems.[10] (3) The phenanthroline ring is introduced as a branch of oligothiophenes, where unsubstituted terminal positions of oligothiophenes can be utilized to further elongate the π-conjugation and polymerize. We report here the synthesis of phenanthroline derivatives **1**–**3** and their physical properties including n-type and ambipolar FET characteristics.



1: *n* = 0
2: *n* = 1

3: X = N
4: X = CH

Chart 1.

Compounds **1** and **2** having a pyrazinophenanthroline unit were prepared by the condensation reaction of 1,10-phenanthroline-5,6-dione with the corresponding diaminoterthiophene[11] and diaminoquinquethiophene in 83 and 77% yields, respectively. Diaminoquinquethiophene was prepared by reduction of dinitroquinquethiophene[12] with $SnCl_2$ in 92% yield. Compound **3** was also prepared from 3,6-dithienyl-1,2-diaminobenzene by the similar condensation in 51% yield. Phenanthrene derivative **4** was also prepared for a comparison. These compounds show high thermal stability and could be purified by sublimation.

Remarkable differences in the absorption spectra of the compounds **1**–**3** were observed. Phenanthroline derivative **3** having a quinoxaline ring shows a strong absorption at 317 and 482 nm ascribed to the π–π transition and the intramolecular charge transfer (CT), respectively. The similar intramolecular CT band of **1** with a thieno[3,4-*b*]pyrazine ring appeared at 655 nm. This red-shift of absorption maxima of ca. 170 nm is attributed to the quinonoidal structure of the thienopyrazine unit, because the similar red-shift is observed between the corresponding dithienylthienopyrazine (529 nm) and dithienylquinoxaline (405 nm).[13] The introduction of the phenanthroline ring in **1** brings about a large red-shift. Increase of the number of thiophene units causes a further red-shift in **2**, whose CT band appeared at 727 nm. These results indicate that phenanthrolines linked with oligothiophenes have a small HOMO–LUMO energy gap. Phenanthrene derivative **4** showed a small blue-shift of the CT band (467 nm) compared with **3** (see Supporting Information).[14]

HOMO and LUMO energy levels were investigated by cyclic voltammetry. All of the voltammograms exhibited one reversible reduction wave and the potentials are summarized in Table 1. The reduction potential of **3** with a quinoxaline ring was observed at -1.16 V, which is higher than that of **4**. This shift can be attributed to the electron-accepting property of the phenanthroline ring. The replacement of the quinoxaline ring by the thienopyrazine ring increases the electron-accepting properties as found in **1** and **2**. Interestingly, the elongation of the thiophene unit in **2** led to a higher reduction potential (-0.83 V). On the other hand, oxidation peaks were also observed in these compounds **1**–**4**. The oxidation peak potential of **1** ($+0.80$ V) was observed at a lower potential than that of

Table 1. Absorption maxima[a] and redox potentials[b] of **1–4**

Compound	$\lambda_{\max}$/nm	$E_{1\mathrm{red}}$	$E_{1\mathrm{pa}}$[c]
1	359 (4.73), 655 (3.74)	−0.92	+0.80
2	396 (4.62), 727 (4.05)	−0.83	+0.46
3	317 (4.63), 482 (3.81)	−1.16	+1.05
4	315, 467[d]	−1.29	+0.65

[a]In CH_2Cl_2. [b]E/V vs SCE, n-Bu_4NPF_6 in CH_2Cl_2, scan rate 100 mV/s, Pt electrode. [c]Irreversible peaks, peak potentials. [d]Low solubility.

3. This result suggests that the thienopyrazine unit lowers the HOMO–LUMO energy gap. Increase of the number of thiophene rings is also effective to lower the oxidation potentials resulting in large red-shifts of the absorption maxima.

OFETs using pyrazinophenanthrolines **1–3** and **4** were fabricated on SiO_2/n-Si substrates by a high vacuum evaporation method with bottom contact geometry with Au electrodes. The FET measurements were carried out under a high vacuum condition without exposure to air. The substrate was kept at room temperature and no attempts were made to optimize the performances. All of the new phenanthroline derivatives **1–3** exhibited n-type FET characteristics. Phenanthroline **1** with a terthiophene unit showed a higher electron mobility than **3** (mobility and on/off current ratio of **1**; $2 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ and 200, of **3**; $3 \times 10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ and >1000). Furthermore, a clear difference was observed between **1** and **3**. Thus, the device based on **1** showed a weak ambipolar-like property, while **3** showed only n-type characteristics (Supporting Information).[14] A device based on **2** with a quinquethiophene unit exhibited clear ambipolar transport as shown in Figure 1. The field-effect mobilities of electron and hole are $6 \times 10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ (on/off 730) and $1 \times 10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ (on/off 70), respectively. Although the quinquethiophene unit is introduced in **2**, the electron mobility is still higher than the hole mobility, indicating that the phenanthroline ring has a strong effect to generate n-type FET properties. Further elongation of the thiophene unit would improve the carrier mobilities. On the other hand, phenanthrene derivative **4**, which shows the similar X-ray diffraction pattern in reflection mode (XRD) to **3**, did not show the FET property under the same conditions. This result indicates that the phenanthroline ring is essential for making active conducting channels.

In this communication, unique pyrazinophenanthroline derivatives with extended π-conjugation have been successfully prepared to show n-type FET characteristics. A phenanthroline derivative linked with a quinquethiophene moiety gave an ambipolar FET device. Further extention of this work by polymerization, protonation and metal complexation formation of the compounds is now in progress.

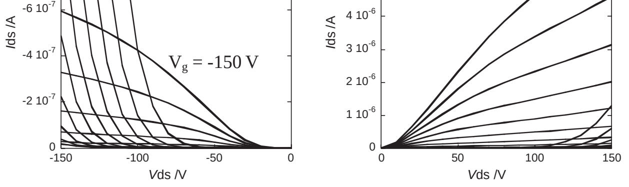


Figure 1. Drain current (I_{ds}) versus drain voltage (V_{d}) plots for the film of **2** as (a) p-type and (b) n-type characteristics. Gate voltages were 0–150 V from bottom to top curves in increments of 10 V.

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14 Detailed experimental procedure, OFET device fabrication procedure, UV–vis spectra of compounds **1–4**, cyclic voltammograms of **1–4**, FET performances of **1–3** and X-ray diffraction pattern (XRD) of **3** and **4** are available in Electronic Supporting Information, which is available electronically on the CSJ-Journal website, http://www.csj.jp/journals/chem-lett/.