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Preparation, Spectral Properties, and Electron Affinity of Bis(thiadiazolo)quinoxaline and Bis(thiadiazolo)phenanthroquinoxaline as n-Type Semiconductors

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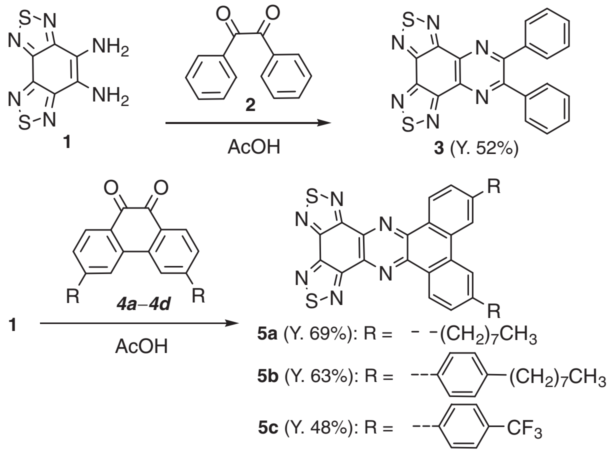
Bis(thiadiazolo)phenanthroquinoxaline and bis(thiadiazolo)quinoxaline derivatives were prepared as a new candidate of n-type semiconductors and their electronic properties were investigated by spectroscopic and electrochemical measurements. The bis(thiadiazolo)phenanthroquinoxaline having the trifluoromethyl groups indicates n-type characteristic in an organic field-effect transistor.

Organic semiconductors have been of much interest in recent years in view of their application to carrier-transporting materials in organic light-emitting diodes, organic field-effect transistors (OFETs), and photovoltaics.[1] p-Type semiconductor has been extensively studied and has excellent characteristics. In contrast, n-type semiconductor is relatively rare and has unsatisfactory performance.[2] Electron-deficient heteroaromatics have been used as a central core of the n-type semiconductor because of their high electron affinity.[3–5] Thus, creation of a new heteroaromatic as an n-type semiconductor is one of the most important tasks in organic material science.

Recently, we have studied n-type semiconductor hexaazatriphenylenes, which are composed of three electron-deficient pyrazine rings.[6] We noticed that a new n-type semiconductor can be created by replacement of the pyrazine ring with another electron-deficient heteroaromatic ring. In this new strategy, we have designed new heteroaromatics bis(thiadiazolo)quinoxaline (BTQ) and bis(thiadiazolo)phenanthroquinoxaline (BTPQ), in which two thiadiazole rings are used instead of the pyrazine rings. Electron affinity of the thiadiazole ring is comparable to that of the pyrazine ring.[4,5,7] In the synthetic strategy, we use the accumulated knowledge in our hexaazatriphenylene chemistry, because the BTQ and BTPQ molecules would be obtained from diaminobenzobis(thiadiazole) that is a synthetic intermediate of the hexaazatriphenylenes.[6] In this letter, we report the preparation of BTPQs and BTQ, and their spectral properties, electron affinity, and OFET characteristics.[8]

The BTQ **3** with phenyl groups was prepared by condensation reaction of benzil (**2**) with diaminobenzobis(thiadiazole) **1** (Scheme 1). Similarly, the BTPQs **5a** bearing octyl groups, **5b** bearing 4-octylphenyl groups, and **5c** bearing 4-(trifluoromethyl)phenyl groups were obtained from the corresponding phenanthrenequinones **4a**, **4b**, and **4c**, respectively (Scheme 1). The BTQ and BTPQs were identified on the basis of spectroscopic methods and elemental analysis.



Scheme 1. Preparation of BTQ and BTPQs.

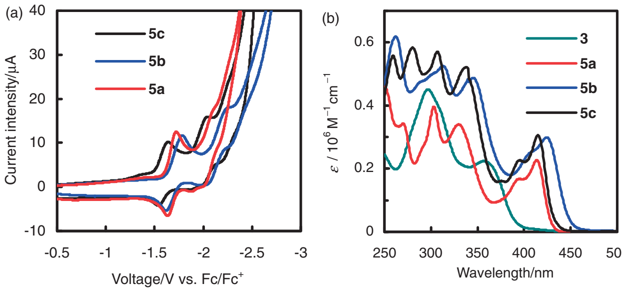


Figure 1. (a) Cyclic voltammograms of **5a**, **5b**, and **5c** in dichloromethane (5×10^{-4} M) in the presence of tetrabutylammonium tetrafluoroborate (0.1 M). (b) UV–vis spectra of **3**, **5a**, **5b**, and **5c** in dichloromethane (1.0×10^{-5} M).

High electron affinity as well as electrochemical stability are studied by cyclic voltammetry (Figure 1a).[9,10] In **5a**–**5c**, two or three quasi-reversible reduction potentials were observed around −1.6 to −2.2 V (vs. Fc/Fc$^+$). The first reduction potentials (−1.59 to −1.70 V) in **5a**–**5c** shift more positive compared to those (−1.7 to −1.8 V) of hexaazatriphenylene derivatives[6e] bearing the three pyrazine rings, indicating the good electron affinity in the BTPQ system bearing the two thiadiazole rings and the one pyrazine ring. An enhancement in the electron affinity is observed in **5c** bearing the electron-withdrawing trifluoromethyl groups: the first reduction potential (−1.59 V) in **5c** shifts more positive compared to that (−1.70 V) in **5b** bearing the electron-donating octyl groups. In **5a**–**5c**, no oxidation potential was observed in the cyclic voltammogram (≈1.5 V), indicating the n-type semiconducting nature of BTPQs.

In MALDI-TOFMS of **3** and **5a**–**5c**, dimeric aggregate species were detected.[9] In addition to the parent ions of **3**

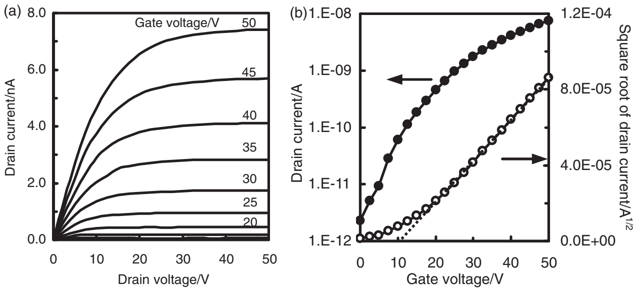


Figure 2. (a) Drain current–voltage relationship within the gate voltage range from 0 to 50 V for an OFET based on **5c**. (b) Transfer characteristics (at a drain voltage of 50 V) of the OFET.

(m/z 398), **5a** (m/z 620), **5b** (m/z 772), and **5c** (m/z 684), significant peaks are seen at a multiple of the parent ion to 796, 1240, 1544, and 1368, respectively. The self-assembling aggregative nature is suitable for the electron carrier-transporting.[11]

In dichloromethane, **5a**, **5b**, and **5c** show absorption bands at 414, 424, and 415 nm, respectively (Figure 1b). The bands in **5a**–**5c** shift bathochromically compared to the band (357 nm) of **3** because of the expanding of the π-electron system. Emission bands were observed in the blue light region at 431 nm for **3**, 433 nm for **5a**, 472 nm for **5b**, and 434 nm for **5c**.[9] Moderate fluorescence quantum yields (Φ_{FL}) were provided from the BTPQ system: Φ_{FL} of 0.19 in **5a**, 0.53 in **5b**, and of 0.36 in **5c**. In contrast, low value of Φ_{FL} was given in **3** to be 0.026. Thus, the BTPQ molecules can be expected also to be blue light emitting materials.[12]

In the absorption bands, significant bathochromic shift upon going from solution to thin film state was observed in **3** and **5a**–**5c**.[9] For example, in **5c** the band shifts from 415 nm in the solution state to 427 nm in the film state. The bathochromic shifts found in the film state indicate that the BTQ and BTPQ molecules are self-assembled to form an aggregate, as suggested in MALDI-TOFMS.

HOMO and LUMO levels in the film state were estimated from the absorption tails and the ionization potentials.[9] The energy gap between HOMO and LUMO levels in **5b** is smaller than that of **5a**, indicating that in **5b** the introduced phenyl groups decrease the LUMO level (-3.26 eV) and increase the HOMO level. In **5c**, both the HOMO and LUMO levels decrease because of the introduction of the trifluoromethyl groups. The lowering LUMO level (-3.70 eV) in **5c** is suitable for the electron injection and the subsequent electron-transport in OFET.

As a preliminary test to check the n-type semiconducting nature, we fabricated an OFET devise of **5c**, expected to be the most effective example. The drain current–voltage relationship indicates an n-channel behavior (Figure 2a). From the plot of the square root of the drain current versus the gate voltage, the field-effect electron mobility was calculated to be 1.3×10^{-5} cm^2 V^{-1} s^{-1} with a threshold voltage of 11 V and an on/off ratio of 3.3×10^3 (Figure 2b).

In conclusion, we have created new heteroaromatics bis(thiadiazolo)quinoxaline and bis(thiadiazolo)phenanthroquinoxaline having the high electron affinity, which are new candidates for electron-transporting materials.

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