

## IX-I Development of Precisely-Defined Macromolecules and Their Organization on Substrate Surfaces for Planar Molecular-Scale Electronics Circuits

The concept of molecular-scale electronics is now realized for individual components such as wire, diode, switch, and memory cell, but the fabrication of complete molecular-scale circuits remains challenging because of the difficulty of connecting molecular modules to one another. Molecular monolithic technology, which integrates the wiring, transistors and the required passive elements on a single macromolecule, has been proposed as a promising solution to this problem. In this project we have been trying to establish both the architecture of this novel class of macromolecules and the protocols for their purposive organization on metal/semiconductor substrate surfaces.

### IX-I-1 Partially Insulated Molecular Wire as Components for Planar Molecule-Metal Junctions

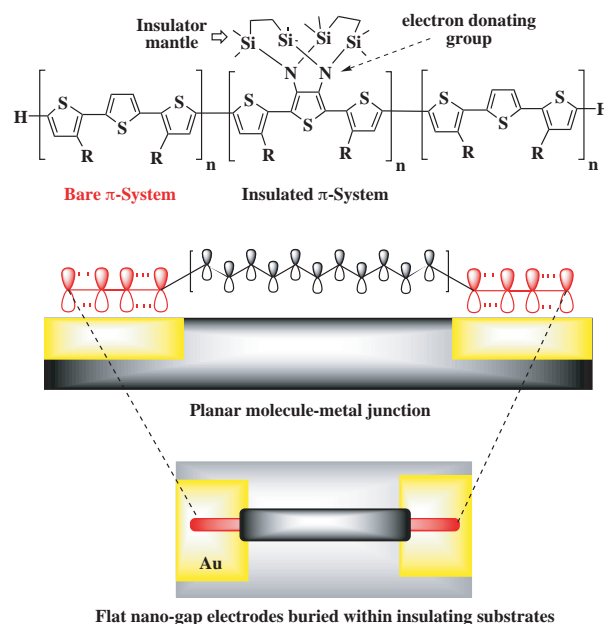
TANAKA, Shoji

We have developed a series of “partially-insulated” multi-nanometer oligothiophenes to investigate systematically the nature of planar molecule-metal junctions as shown in Figure 1. Charge transport at planar junctions will be controlled by the degree of face-to-face interactions between  $\pi$ -system of conjugated molecules and electrode substrate. Therefore, to define exactly the areas of interactions, we have designed these molecules; the main chain consists of bare  $\pi$ -system as “charge-transfer interface” and insulated  $\pi$ -system possessing electron-donating amino groups as “positive charge-retention sites.” Here we describe the electrochemical characterization of these molecules.

Figure 2 shows the cyclic voltammograms of the partially insulated oligothiophenes and the related molecules. In general multi-scan voltammogram of long oligothiophenes ( $> \alpha$ -6T) is well known to be ill defined as shown in the voltammogram of oligomer **1**. The complicated electrochemical behavior can be attributed to severe interchain interactions among the charged long oligomers that induce molecular aggregation and deposition on the electrode. During these processes, charges on an oligomer are dispersed and lost. In contrast, partially insulated oligothiophenes **3,4,6** as well as the fully insulated one **2** afforded reversible steady-state voltammograms. These findings suggest that only a one third coverage of the main chain of the  $\alpha$ -9T-18T is enough to reduce the interchain interactions between the charged species and prevent the aggregation. In the case of oligomer **5**, slight voltammogram deformation, a symptom of aggregation, was observed. This indicates that the steric hindrance of the alkyl substituents on the interchain interactions is minor but not negligible.

Figure 3 shows the differential pulse voltammograms of partially insulated oligothiophenes **2-4**. Judging from the potential difference between the first and second peak, the magnitude of on-site Coulomb repulsion was found to decrease in this order: **4**  $>$  **2**  $>$  **3**. This result may be explained based on the spatial arrangement of the insulated mantle. This component has electron-donating amino groups and tends to attract positive charges. Therefore, separate

arrangement of them in the main chain is expected to isolate positive charges from each other resulting in reduction of on-site Coulomb repulsions as illustrated in Figure 3.



**Figure 1.** Molecular structure of partially insulated oligothiophenes.

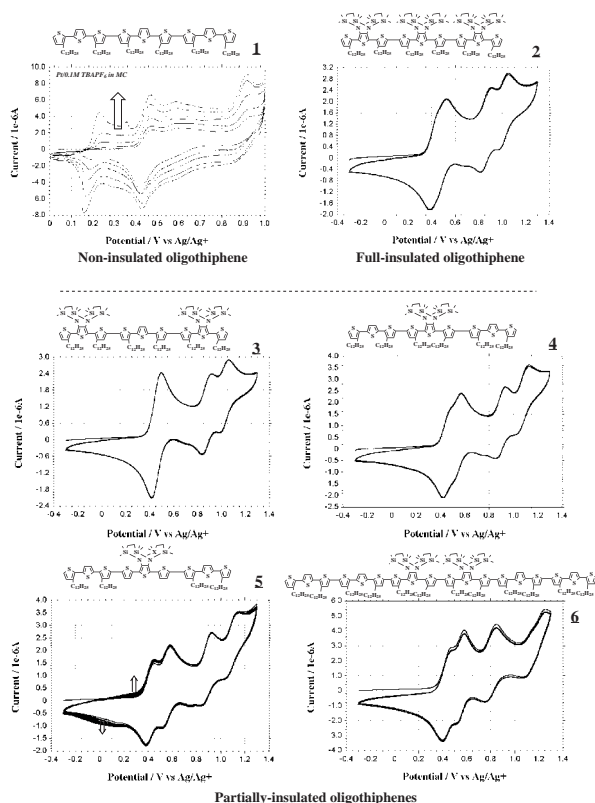


Figure 2. Cyclic voltammograms of oligothiophenes.

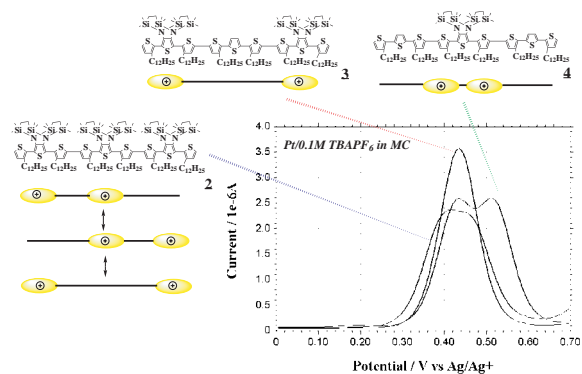


Figure 3. Differential pulse voltammograms of oligothiophenes.

## IX-J Development of Novel Heterocyclic Compounds and Their Molecular Assemblies for Advanced Materials

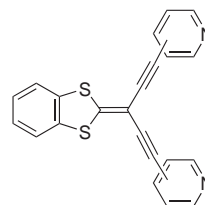
Heterocycles containing sulfur and/or nitrogen atoms are useful as components of functional materials since heteroatoms in their rings are helpful to stabilize ions or ion-radical species, and extended  $\pi$ -conjugation decreases Coulombic repulsion. In addition intermolecular interactions caused by heteroatom contacts can be expected to form novel molecular assemblies. In this project new electron acceptors, donors, and donor-acceptor compounds based on heterocycles such as 1,2,5-thiadiazole and 1,3-dithiole were synthesized and their properties including those of the charge-transfer complexes or ion-radical salts were investigated. Unique crystal structures were constructed by using weak intermolecular interactions such as hydrogen bonding or heteroatom contacts.

### IX-J-1 Preparation, Structures and Properties of Novel 1,3-Dithiol-2-Ylidene Derivatives Containing Bis(ethynylpyridine) Units

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[*Tetrahedron Lett.* **44**, 6845–6848 (2003)]

1,3-Dithiol-2-ylidene derivatives containing bis(ethynylpyridine) units were synthesized using a Pd-catalyzed reaction of the corresponding dibromide. X-Ray crystal analysis revealed unique crystal structures depending on the aromatic groups. The absorption spectra and redox properties indicated intramolecular charge-transfer interactions between the 1,3-dithiole unit and the pyridyl parts.



2-dipyridyl, 3-dipyridyl, 4-dipyridyl

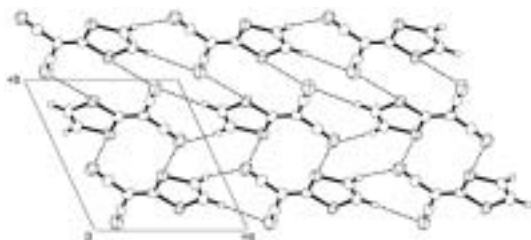
### IX-J-2 (1,3-Dithiol-2-ylidene)propanedinitrile

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(<sup>1</sup>IMS and Tokyo Inst. Tech.)

[*Acta Crystallogr., Sect. E* **59**, o1941–o1943 (2003)]

In the crystal structure of the title compound,  $C_6H_2$

$N_2S_2$ , there is a tape structure, as a result of C–H...N hydrogen bonds is found. The molecules stack along the [120] direction in a head-to-tail fashion.



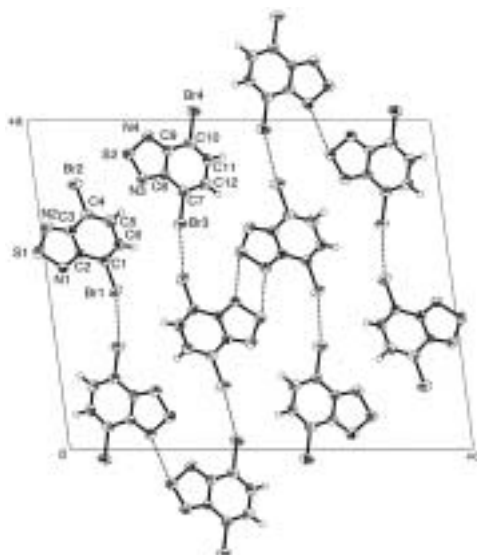
**Figure 1.** Packing diagram of the title compound viewed along the *c* axis. Dashed lines show the intermolecular S...N and C–H...N contacts.

### IX-J-3 Crystal Structure of 4,7-Dibromo-2,1,3-Benzothiadiazole, $C_6H_2Br_2N_2S$

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[*Z. Kristallogr. NCS* **218**, 555–556 (2003)]

The title compound crystallizes in a centrosymmetric  $P2_1/c$  space group with two crystallographically independent molecules in the asymmetric unit. The considerable shortenings of the C1–C6, C4–C5, C7–C12 and C10–C11 bonds are observed. Such double bond fixation suggests the quinonoid character of the 2,1,3-benzothiadiazole ring. Short S...N and Br...Br intermolecular heteroatom contacts are found in the crystal. The S...N [3.226(4) and 3.238(4) Å] and the Br...Br [3.542(1) and 3.662(1) Å] distances are 3.4–3.7% and 1.0–4.3% shorter than the sum of the corresponding van der Waals radii, respectively.



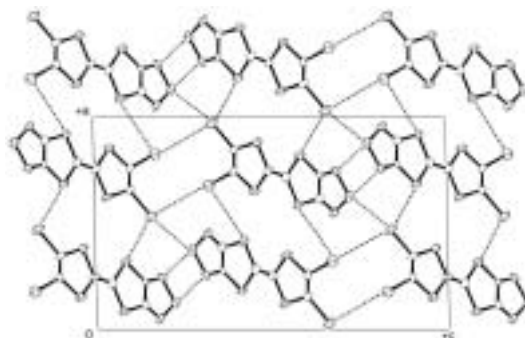
**Figure 1.** Packing diagram of the title compound viewed along the *b* axis. Dashed lines show the short intermolecular S...N and Br...Br contacts.

### IX-J-4 4,5-Diiodo[1,2,5]thiadiazolotetrathiafulvalene

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[*Acta Crystallogr., Sect. E* **60**, o63–o65 (2004)]

In the crystal structure of the title compound, 5-(4,5-diiodo-1,3-dithiol-2-ylidene)-1,3-diaza-2,4,6-trithiapentalene,  $C_6I_2N_2S_5$ , a large number of short intermolecular heteroatom contacts, such as S...N, S...S, S...I, N...I, and I...I, are observed. The molecules, which are planar within 0.051 Å, stack along the *b* axis in a head-to-head fashion.



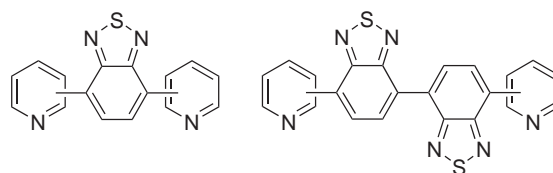
**Figure 1.** Packing diagram of the title compound viewed along the *b* axis. Dashed lines indicate the short intermolecular S...N, S...I and I...I contacts.

### IX-J-5 Synthesis and Characterization of Novel Dipyrindylbenzothiadiazole and Bisbenzothiadiazole Derivatives

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[*J. Org. Chem.* **69**, 2953–2958 (2004)]

Novel dipyrindyl compounds containing a mono- and bisbenzothiadiazole unit were synthesized using the Stille coupling reaction. Their pyridinium salts, viologen analogues, were also prepared by the N-alkylation. The X-ray crystallographic analysis of the compounds containing a benzothiadiazole ring revealed nonplanar molecular structures and unique crystal structures depending on the nitrogen positions. The dipyrindyl compounds are efficient fluorophores with high electron affinity. The derivative afforded complexes with chloranilic acid and cyanuric acid composed of hydrogen bonding networks. The methyl viologen analogues showed two-stage one-electron reduction waves.



2,2'-dipyrindyl, 3,3'-dipyrindyl, 4,4'-dipyrindyl