

VIII-G 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.

VIII-G-1 Characterization of Electronic Properties of Molecular Enamel Wires

TANAKA, Shoji

The precisely-defined “insulated molecular wire,” in which rigid insulators are placed around a π -conjugated backbone except the “electrical connections,” is one of the key modules for realizing ultra-dense molecular-scale electronic circuits. The well known approach to this special class of molecular wire is based on the supramolecular complex between π -conjugated oligomers and cyclodextrin molecules. As an alternative approach, we have proposed “molecular enamel wire” concept, in which the insulator mantle is covalently bonded to the backbone. The stability of insulator-attachment of molecular enamel wire will be superior to that of supramolecular wire due to the intrinsic toughness of a covalent bond. So far, we have established the synthetic approaches to molecular enamel wires based on building blocks **1** (Figure 1). Here we report the effects of the insulator mantles on electronic behaviors of these molecular enamel wires.

Figure 2 shows the absorption spectra of the vacuum-deposit thin films of oligomers **2–5** on quartz substrate as well as those in THF. Generally photophysical process of a π -conjugated molecule in solid state is complicated due to the intermolecular π - π interactions. The electronic spectra of the thin film of non-insulated oligothiophenes **2–3** are apparently dissimilar to those in the THF solution. In contrast, the thin film spectra of insulated oligothiophenes **4–5** are nearly identical to the THF solution spectra. These results indicate that the intermolecular π - π interactions are efficiently prevented by the insulator mantle of **4–5**. This conclusion is supported by the electrochemical data. Typical cyclic voltammograms of insulated and non-insulated α -12T derivatives **6–7** are shown in Figure 3. The voltammogram of non-insulated α -12T **6** is broad and ill-defined in contrast to that of insulated α -12T **7**, where three reversible waves are obtained. In general the ill-resolved cyclic voltammogram of long oligothiophenes has its origin in i) adsorption of charged species on the electrode surface and/or ii) π -complex formations such as “ π dimer” and “dimer radical ion.” Therefore the reversible electrochemical behavior of insulated α -12T **7** can be attributed to the steric inhibitions of adsorption and/or complex formation *via* π -system of the oligomers by the insulator mantle.

In conclusion these experimental data clearly demonstrate the availability of our “molecular enamel wire” concept in molecular-scale engineering.

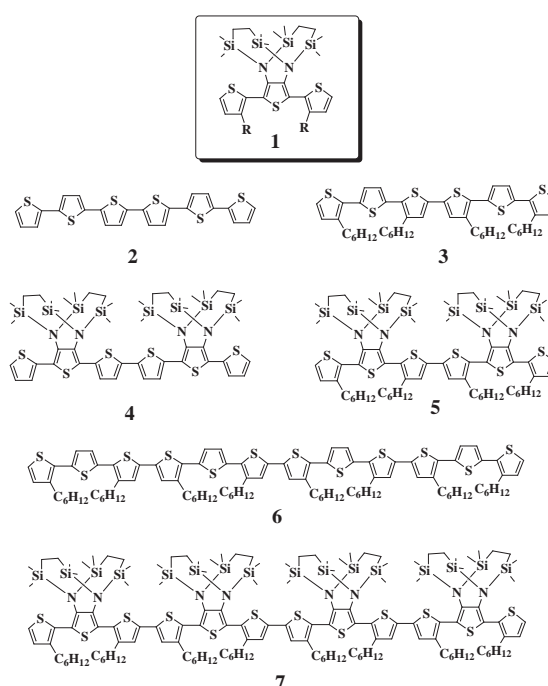


Figure 1. Molecular Structure of oligomers.

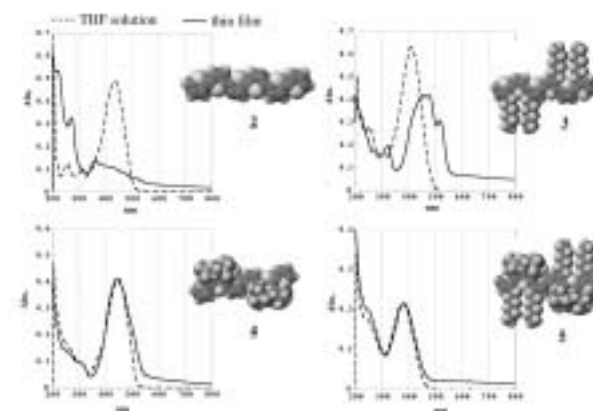


Figure 2. UV/Vis spectra of oligomers.

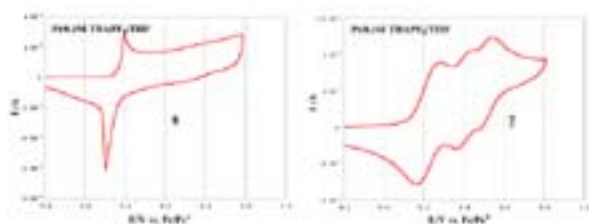


Figure 3. Cyclic voltammograms of oligomers.

VIII-G-2 Combined Spectroscopic and Theoretical Study of Narrow-Bandgap Heterocyclic Cooligomers Containing Alternating Aromatic-Donor and *o*-Quinoid-Acceptor Units

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In this paper we analyze, with the help of Density Functional Theory calculations, the relationship between the molecular structure and the optical and vibrational properties of two narrow-bandgap π -conjugated cooligomers containing an alternating

sequence of aromatic-donor and *o*-quinoid acceptor units. The optimized molecular geometries of these cooligomers reveal that short inter-ring S...N contacts occur in their minimum-energy structure between the two types of constituting units, and that the resulting rigid coplanar arrangement of the rings enhances the degree of π -conjugation and lowers the bandgap.

VIII-G-3 Electrochemical Synthesis and Properties of Poly[1,4-bis(*N*-pyrrolylalkoxy)benzene]s with a Three-Dimensional Crosslinked Structure

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[*Chem. Lett.* 516–517 (2003)]

The title polymers, which were composed of π -conjugated pyrroles and dialkoxybenzene crosslinkers, were prepared by electrochemical polymerization to afford amorphous thin films, which were characterized by cyclic voltammetry (CV), scanning electron microscope (SEM), and redox stability.

VIII-H Development of Novel Heterocyclic Compounds and Their Molecular Assemblies for Advanced Materials

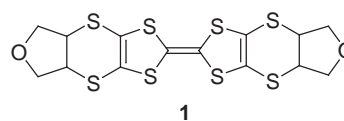
Heterocycles containing sulfur and/or nitrogen atoms are useful as components of functional materials since heteroatoms in their rings are helpful to stabilize ions or ion-radical species, and extended π -conjugation decreases Coulombic repulsion. In addition intermolecular interactions caused by heteroatom 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.

VIII-H-1 Non-Planar BEDT-TTF Derivatives Fused with Tetrahydrofuran Rings Affording Cation Radical Salts with Unusual Crystal Structures

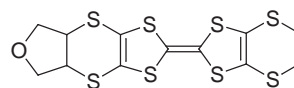
YAMASHITA, Yoshiro¹; TOMURA, Masaaki; IMAEDA, Kenichi²
(¹IMS and Tokyo Inst. Tech.; ²IMS and Chubu Univ.)

[*Mol. Cryst. Liq. Cryst.* **380**, 203–207 (2002)]

The title non-planar electron donors **1** and **2** were prepared by the several steps involving the addition reaction of oligo(1,3-dithiole-trithione) with 2,5-dihydrofuran. They afforded the cation radical salts as single crystals whose unusual crystal structures were revealed by X-ray analysis.



1



2

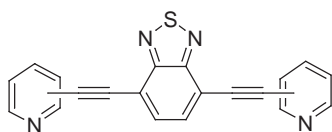
VIII-H-2 Synthesis and Characterization of New π -Conjugated Molecules Containing Bis(ethynylpyridine) Units with a Benzothiadiazole Spacer

AKHTARUZZAMAN, Md.¹; TOMURA, Masaaki; ZAMAN, Md. Badruz²; NISHIDA, Jun-ichi¹; YAMASHITA, Yoshiro³
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³IMS and Tokyo Inst. Tech.)

[*J. Org. Chem.* **67**, 7813–7818 (2002)]

Three novel 4,7-bis(*n*-pyridylethynyl)-2,1,3-benzothiadiazoles (*n* = 2, 3 and 4) were synthesized by using the Sonogashira cross-coupling reaction of 4,7-dibromo-2,1,3-benzothiadiazole with the corresponding ethynylpyridines in the presence of a Pd(II) catalyst. The viologen analogues were also prepared by methylation of pyridyl nitrogen atoms. X-ray structure analysis of these compounds revealed the linear molecular structures with unusual columnar crystal structures. Insertion of a benzothiadiazole moiety into the acetylene-pyridine skeleton brings about a large increase in electron affinity and the bispyridyl compounds obtained here show high fluorescence quantum yields.



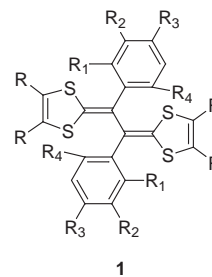
2,2'-dipyridyl, 3,3'-dipyridyl, 4,4'-dipyridyl

VIII-H-3 Preparation and Structures of Dication Salts of Phenyl Substituted TTF Vinyllogues

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[*J. Solid State Chem.* **168**, 427–432 (2002)]

Some TTF vinyllogues **1a–l** containing phenyl groups at the vinyl positions were synthesized. The redox properties were investigated by cyclic voltammograms, showing that they are strong electron donors and the Coulomb repulsion is decreased in the dication states. Some of the donors afforded their dication salts as single crystals by electrochemical oxidation or the reaction with CuCl₂. X-ray structure analysis has revealed that the dication molecules have structures with planar TTF vinyllogue units and twisted phenyl groups. The crystal structures are unusual to avoid the steric interactions of the phenyl groups.



1

	R,R	R ₁	R ₂	R ₃	R ₄
1a	(CH=CH) ₂	H	H	H	H
1b	(CH=CH) ₂	F	H	H	F
1c	(CH=CH) ₂	H	H	Cl	H
1d	(CH=CH) ₂	CN	H	H	H
1e	(CH=CH) ₂	H	H	CN	H
1f	(CH=CH) ₂	OCH ₂ O		H	H
1g	SCH ₂ CH ₂ S	F	H	H	F
1h	SCH ₂ CH ₂ S	Cl	H	H	H
1i	SCH ₂ CH ₂ S	CN	H	H	H
1j	SCH ₂ CH ₂ S	H	H	CN	H
1k	SCH ₂ CH ₂ S	OCH ₂ O		H	H
1l	H, H	F	H	H	F

VIII-H-4 Unsymmetrical Tetrathiafulvalene with a Fused 1,2,5-Thiadiazole Ring and an Ethylenedioxy Group

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(¹IMS and Tokyo Inst. Tech.)

[*Acta Crystallogr., Sect. E* **59**, o145–o147 (2003)]

In the crystal structure of the title compound, 4,5-ethylenedioxy[1,2,5]thiadiazolotetrathiafulvalene, C₈H₄N₂O₂S₅, a large number of short intermolecular S...S contacts are observed [3.519(5)–3.610(5) Å]. The molecules stack along the *c* axis in a face-to-face fashion.

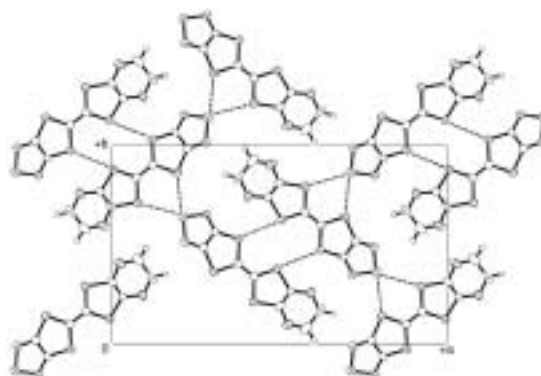


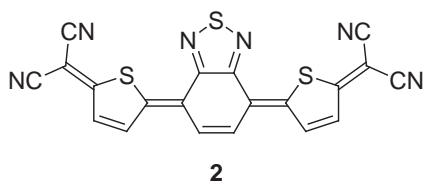
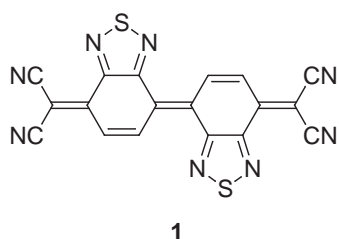
Figure 1. Packing diagram of the title compound viewed along the *c* axis. Dotted lines indicate the short intermolecular S...S contacts.

VIII-H-5 Novel Electron Acceptors Containing Nitrogen, Sulfur-Heterocyclic Units

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[*Synth. Met.* **133-134**, 341–343 (2003)]

A tetracyanodiphenoquinodimethane (TCNDQ) analog **1** containing fused thiadiazole rings is a stronger electron acceptor than tetra-cyanoquinodimethane (TCNQ). The single crystals of this TCNDQ analog were found to exhibit semiconductive behaviors as a single component whose structures were revealed by X-ray structure analysis. The anion radical salts with Et₄N and Me₄P ions were obtained as single crystals by electrochemical reduction. They are 1:1 salts and showed semiconductive behaviors. The structures include tape-like networks formed by S...N contacts. Furthermore, one of the benzothiadiazole rings was replaced with a thiophene unit to give new π -extended quinonoid acceptors **2** which are highly polarized and exhibit their absorption maxima above 500 nm.

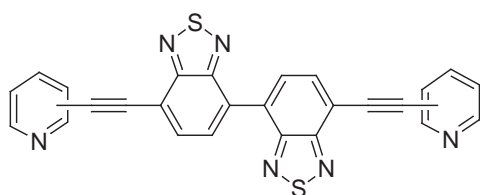


VIII-H-6 Linear Molecules with Ethynylpyridine and Bisbenzothiadiazole Units

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[*Synth. Met.* **137**, 873–874 (2003)]

7,7'-Bis(pyridylethynyl)-4,4'-bis(2,1,3-benzothiadiazole) derivatives were synthesized using the Sonogashira reaction. X-ray crystallographic analysis of the 4,4'-dipyridyl derivative revealed the linear molecular structure with an unusual tape-like crystal structure. They show high electron affinity and fluorescence with large Stokes shifts. The viologen analogues were also prepared by methylation of the pyridyl nitrogen atoms.



3,3'-dipyridyl, 4,4'-dipyridyl

VIII-H-7 Hydrogen Bonding Networks Consisted of Conjugation-Extended 4,4'-Bipyridines and Chloranilic Acid

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[*Supramol. Chem.* **15**, 239–243 (2003)]

Hydrogen-bonding networks of π -extended 4,4'-bipyridines, 2,5-di(4-pyridyl)thiophene **1**, 2,5-di(4-pyridyl)furan **2** and 1,4-di(4-pyridyl)benzene **3** with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid, **CA**) have been investigated. The dipyrindyl compounds afforded three complexes, (dication of **1**)·(monoanion of **CA**)₂, (dication of **2**)·(dianion of **CA**)·(MeOH) and **3**·(dication of **3**)·(dianion of **CA**)·(H₂O)₆ with **CA**. X-ray structure analyses revealed the formation of unusual molecular tape and sheet structures involving N–H...O, O–H...O, C–H...O and N–H...N hydrogen bonds, where the aromatic spacer groups play an important role in constructing the unique crystal structures.

