VIII-F Development of Precisely-Defined Macromolecules and their Organization on Substrate Surfaces for 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-F-1 Design and Synthesis of Molecular Junction and Anchor Modules for Multi-Function Integrated Macromolecules

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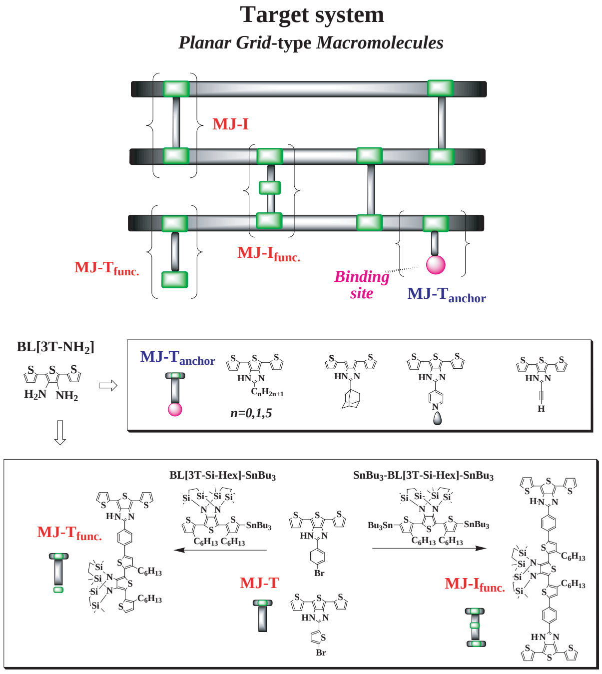
The design of "planar and multi-function integrated" π-conjugated macromolecules has been a subject of intensive research in the field of molecular electronics, because of their potential applications as basic components for future IT hardware such as ultra-dense molecular-scale quantum computers. In order to establish the architecture for this class of tailor-made macromolecules, we have developed various types of molecular building blocks and characterized them on substrate surfaces based on the high-resolution STM experiments combined with their bulk-level properties. Here we describe the synthesis of i) "molecule-anchor modules" for setting the molecular systems on metal/semiconductor substrate, and ii) "molecule-junction modules" for constructing planar grid-type molecular frameworks. Scheme 1 shows the synthetic pathways to these modules. Purification of these molecules was achieved by gel permeation chromatography. The purity of the obtained compounds was clearly reveled by MALDI-TOF mass spectroscopy using dithranol as matrix.



Scheme 1.

VIII-G 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-G-1 Crystal Engineering Using Anilic Acids and Dipyridyl Compounds through a New Supramolecular Synthon

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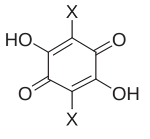
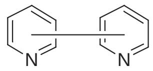
[*J. Org. Chem.* **66**, 5987 (2001)]

The anilic acids, 2,5-dihydroxy-1,4-benzoquinone **1a**, 2,5-dibromo-3,6-dihydroxy-1,4-benzoquinone (bromanilic acid; **1b**), 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid; **1c**), and 2,5-dicyano-3,6-dihydroxy-1,4-benzoquinone (cyananilic acid; **1d**), were cocrystallized with rigid organic ligands containing two pyridine rings, 2,4-bipyridine **2a**, 4,4'-bipyridine **2b**, 1,2-bis(2-pyridyl)-ethylene **3a**, 1,2-bis(4-pyridyl)ethylene **3b**, 2,2'-dipyridylacetylene **4a**, 3,3'-dipyridylacetylene **4b**, and 4,4'-dipyridylacetylene **4c**. Fourteen complexes **5**–**18** were obtained as single crystals, and their crystal structures were successfully determined by X-ray analysis. All complexes except those with **2a** are 1 : 1 and are composed of an infinite linear or zigzag tape structure, the formation of which is ascribed to intermolecular O–H···N, N^+–H···O, or N^+–H···O^- hydrogen bonds or a combination of these between the anilic acids and the dipyridyl compounds. In the complexes **5** and **6**, no infinite tape structure is observed although the molecular units connected by a similar hydrogen-bonding pattern are formed. For the 1 : 1 complexes, we have found two types of stacking arrangements, segregated stacks (**7**, **9**, **12**–**15**, **18**) and alternated ones (**8**, **10**, **11**, **16**, **17**). In the complexes of **1c** with the series of dipyridylacetylenes **4** (**14**, **15**, **17**), the neutral, dication, and monocaction states are formed depending on the nitrogen positions, which can be attributed to the different basicity of the pyridyl groups.



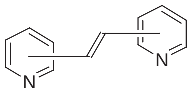
1

1a; X = H
1b; X = Br
1c; X = Cl
1d; X = CN



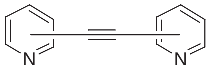
2

2a; 2,4-bipyridine
2b; 4,4'-bipyridine



3

3a; 1,2-bis(2-pyridyl)ethylene
3b; 1,2-bis(4-pyridyl)ethylene



4

4a; 2,2'-dipyridylacetylene
4b; 3,3'-dipyridylacetylene
4c; 4,4'-dipyridylacetylene

5; complex between **1b** and **2a**
6; complex between **1c** and **2a**
7; complex between **1a** and **2b**
8; complex between **1c** and **2b**
9; complex between **1c** and **3a**
10; complex between **1b** and **3b**
11; complex between **1c** and **3b**
12; complex between **1a** and **4c**
13; complex between **1b** and **4a**
14; complex between **1c** and **4a**
15; complex between **1c** and **4b**
16; complex between **1b** and **4c**
17; complex between **1c** and **4c**
18; complex between **1d** and **4c**

VIII-G-2 Bis(tetra-n-butylammonium) Bis(2-dicyanomethylene-4,5-dimercapto-1,3-dithiole)nickel(II)

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[*Acta Crystallogr., Sect. E* **58**, m133 (2002)]

We have carried out the X-ray crystallographic analysis of the title dithiolato-nickel complex derived from 2-dicyanomethylene-4,5-dimercapto-1,3-dithiole (dcndmdt) ligand.[1)] This ligand in the nickel complex has peripheral heteroatoms and extended π-conjugated systems. In the nickel complex, [Ni(dcndmdt)$_2$](n-Bu$_4$N)$_2$, the centrosymmetric dianion is flat. The nickel atom has square-planar coordination, with Ni–S bond lengths of 2.1836(16) and 2.1940(18) Å.

Reference

1) M. Tomura and Y. Yamashita, *J. Mater. Chem.* **5**, 1753 (1995).

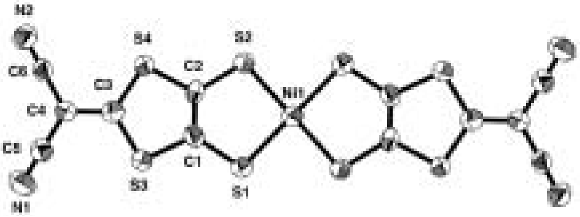

Figure 1. Molecular structure of the dianion in [Ni(dcndmdt)$_2$](n-Bu$_4$N)$_2$.

VIII-G-3 ^{1}H NMR Analysis and Crystal Structures of 1,1',3,3'-Tetramethyl-2,2'-bi-1*H*-Imidazolium Bis(tetraphenylborate): Ion-Associative Interactions Containing Ketone, Aldehyde, and Nitrile

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[*Chem. Lett.* 622 (2002)]

According to ^{1}H NMR analysis of 1,1',3,3'-tetramethyl-2,2'-bi-1*H*-imidazolium bis(tetraphenylborate) **1** in acetone and acetonitrile, high magnetic field shifts of the chemical shifts were observed. The facts are ascribable to ion association between the biimidazolium dication and BPh$_4$ anions. The crystals of **1** included some kinds of ketone, aldehyde, and nitrile as guest molecules to afford unique molecular aggregations. The biimidazolium dication is surrounded by four BPh$_4$ anions and is in a specific cyclic environment arising from eight phenyl groups, as shown in Figure 1. The molecular arrangements of the biimidazolium dication in the crystals can be controlled by the guest molecules.

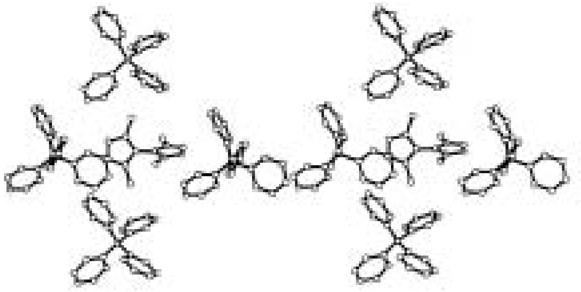

Figure 1. Stereo view of the packing mode of **1**·cyclohexanone.

VIII-G-4 4,7-Diiodo-2,1,3-Benzothiadiazole and 7,7'-Diiodo-4,4'-bis(2,1,3-benzothiadiazole)

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([1]GUAS; [2]IMS and Inst. Res. Innov.; [3]IMS and Tokyo Inst. Tech.)

[*Acta Crystallogr., Sect. C: Cryst. Stuct. Commun.* **58**, o373 (2002)]

The title compounds, 4,7-diiodo-2,1,3-benzothiadiazole **1** and 7,7'-diiodo-4,4'-bis(2,1,3-benzothiadiazole) **2** crystallize in the $P2_1/a$ and the noncentrosymmetric $Fdd2$ space group, respectively. In the crystal structures of **1**, a large number of short S···N and I···I contacts, and a planar I_4 square cluster are observed, as shown in Figure 1. The angle between the planes for the two 2,1,3-benzothiadiazole rings of **2** is 48.4(1)°, and short and linear N···I contacts [3.333(8) Å] exist in the crystal of **2**.

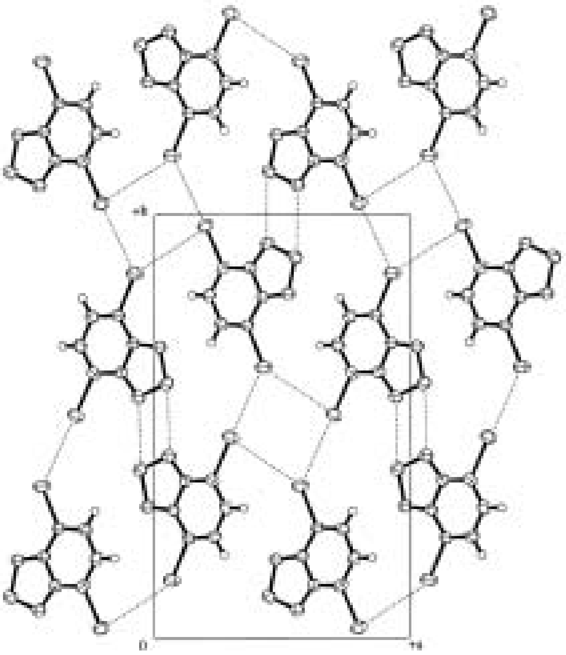

Figure 1. Packing diagram of **1** viewed along the c axis. Dotted lines show the short S···N and I···I contacts.

VIII-G-5 Synthesis and Properties of π-Extended TTF Analogues and Their Cation Radical and Dication Salts

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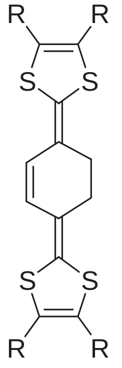
[*Mol. Cryst. Liq. Cryst.* **376**, 19 (2002)]

New bis(1,3-dithole) electron donor **1** containing a cyclohexene unit were prepared using a Wittig-Honer reaction and a cycloreversion reaction. The tetramethyl derivative afforded the highly conductive cation radical salts as single crystal whose unusual crystal structures were revealed by X-ray crystallographic analysis.



a: R = H
b: R = CH_3
c: R,R = SCH_2CH_2S
d: R,R = benzo

1

VIII-G-6 Synthesis and Structure of Bi- and Terthiophene Derivatives Having 4-Pyridylethynyl Substituents

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Conjugated organic oligomers are gaining increasing attention as new and promising materials in the field of molecular electronics. We have synthesized the title compounds, which are able to coordinate with metals and perform intermolecular interaction *via* hydrogen bonding, using the Sonogashira reaction. The X-ray crystallographic analyses of them revealed that the centrosymmetric bithiophene derivative has the *anti* conformation, whereas the crystallographically independent terthiophene derivative has *anti-cis* conformation. All thiophene and pyridine rings in the two derivatives are almost coplanar.

Figure 1. Molecular packing of 5,5''-bis[(4-pyridyl)ethynyl]-2,2':5',2''-terthiophene viewed along the *b* axis.