Research Center for Molecular Materials

VIII-C 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. In addition, precisely-defined heterocyclic oligomers containing various types of functional units have been developed, which are a promising building blocks for future molecular nanotechnologies.

VIII-C-1 Linear Hydrogen-Bonded Molecular Tapes in the Co-Crystals of Squaric Acid with 4,4'-Dipyridylacetylene or 1,2-Bis(4-pyridyl)ethylene

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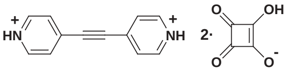
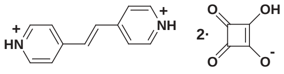
[*Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **57**, 621 (2001)]

The co-crystals of squaric acid with dipyridyl-type ligands, **1** and **2**, are isomorphous and form in the triclinic crystal system. The co-crystals contain linear and flat hydrogen-bonded molecular tape structures along the [120] direction (Figure 1). The squarate monoanions form a rare ten-membered dimer linked by two intermolecular O–H···O hydrogen bonds [2.511(3) Å for **1** and 2.503(2) Å for **2**]. Each component molecule forms a segregated stack along the c axis. The bond lengths of the squarate monoanion indicate the delocalization of the enolate anion.



1



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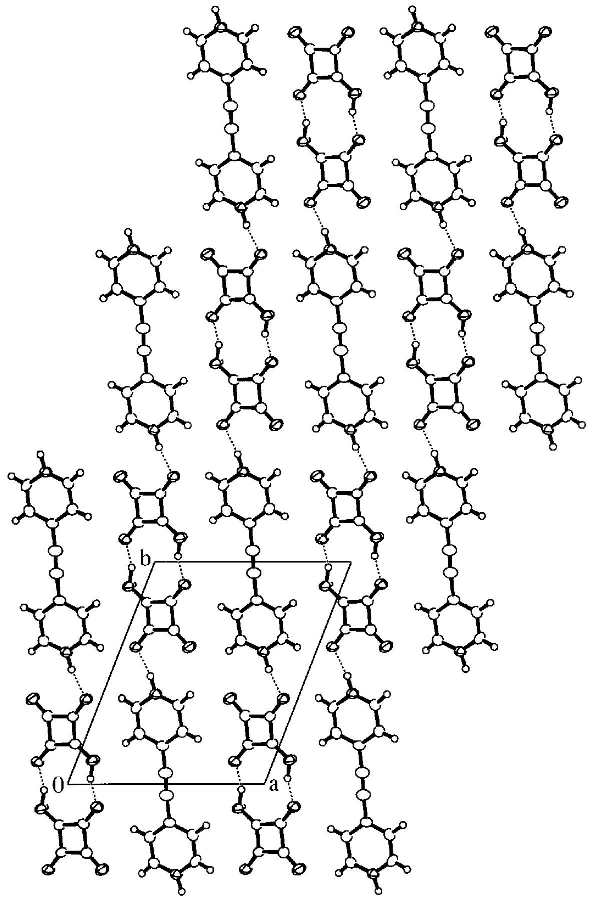

Figure 1. Packing diagram of **1** viewed along the c axis. Dotted lines show the intermolecular hydrogen bonds.

VIII-C-2 One-Dimensional Hydrogen-Bonded Molecular Tapes in 1,4-Bis[(4-pyridinium)ethynyl]-benzene Chloranilate

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[*Acta Crystallogr., Sect. E: Struct. Rep.* **57**, o353 (2001)]

The crystal structure of a 1:1 co-crystal with chloranilic acid and 1,4-bis[(4-pyridyl)ethynyl]benzene contains one-dimensional hydrogen-bonded molecular tapes along the [113] direction, as shown in Figure 1. The molecular tape is nearly flat. The angles between the molecular planes of the chloranilate and the pyridinium ring, and of the pyridinium ring and the benzene ring are 7.3(2)° and 11.8(4)°, respectively. The molecular tapes are connected *via* $R_1^2(5)$ couplings with two intermolecular N–H···O hydrogen bonds [2.609(3) Å and 2.897(4) Å], where both protons of chloranilic acid have transfered to the prydine rings. The overlaps between the chloranilate-pyridinium ring-benzene ring-pyridinium ring-chloranilate are observed in the stacks of the molecular tapes. A short C–Cl··π interaction [Cl···triple bond 3.440(7) Å] exists between the stacks of the molecular tapes. It is 1.7% shorter than the sum of the van der Waals radii of Cl and C*sp*.

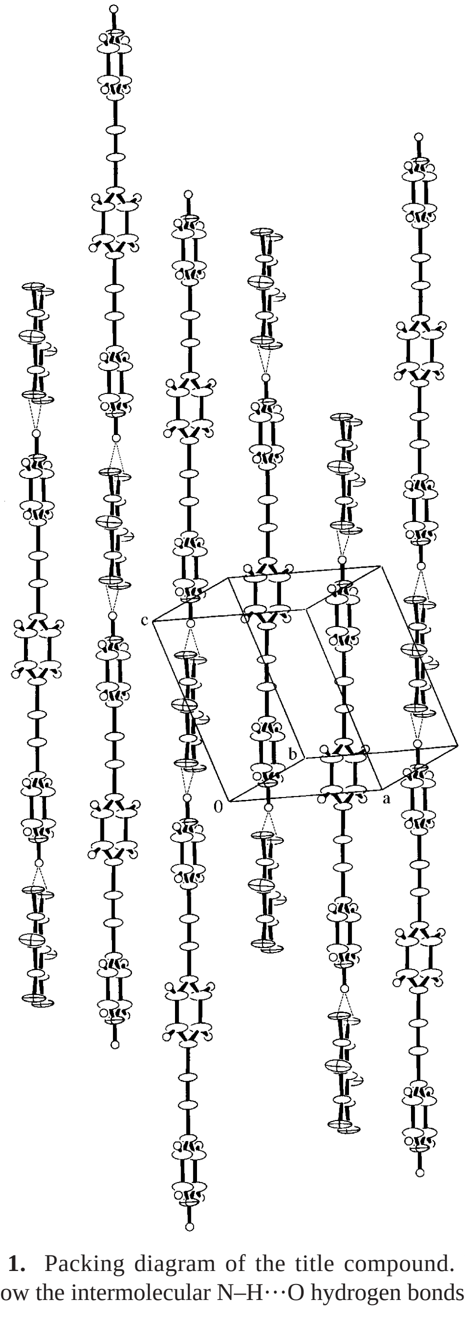

Figure 1. Packing diagram of the title compound. Dotted lines show the intermolecular N–H···O hydrogen bonds.

VIII-C-3 4,7-Bis[(4-pyridyl)ethynyl]-2,1,3-benzothiadiazole and Its Dipyridinium Diperchlorate

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[*Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **57**, 751 (2001)]

A long, rigid and conjugated bridging ligand, 4,7-bis[(4-pyridyl)ethynyl]-2,1,3-benzothiadiazole **1**, and its dipyridinium salt **2** display the bond alternation in the 2,1,3-benzothiadiazole rings, which suggests their quinonoid character. The dipyridinium dication molecules stack along the a axis and form a dimer with short S···N interheteroatom contacts [3.146(4) Å] between the two 1,2,5-thiadiazole rings. The dimer is surrounded by the perchlorate anions with a large number of intermolecular N–H···O and C–H···O hydrogen bonds, as shown in Figure 1.

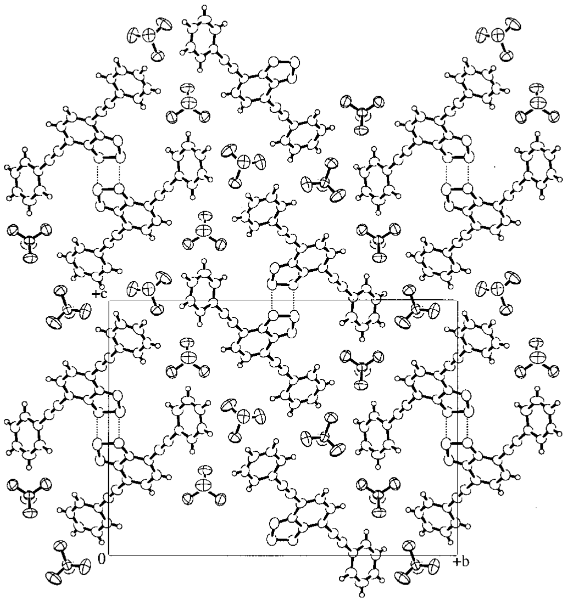

Figure 1. Packing diagram of **2** viewed along the a axis. Dotted lines show the short S···N interheteroatom contacts.

VIII-C-4 One-Dimensional Zigzag Chain Structures with Intermolecular C–H··π and C–H···O Interactions Consisted of Phthalic Acid and Pyridine Derivatives

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[*Chem. Lett.* 532 (2001)]

Crystal structures of co-crystals of phthalic acid with dipyridyl-type ligands, 4,4'-bipyridine or 4,4'-dipyridylacetylene, contain one-dimensional zigzag chain structures connected by intermolecular O–H···N hydrogen bonds. The edge-to-face packing (T-shaped geometry) between phthalic acid and the pyridine rings of the dipyridyl-type ligands is also observed and is stabilized by intermolecular C–H···π and C–H···O interactions. Strong resemblance between the two crystal structures suggests robustness and reproducing ability of the supramolecular synthon formed with phthalic acid and pyridine rings. In this case, a zigzag chain structure seems to be "programmed" to form in a crystal. We have displayed that the supramolecular synthons generated by combination of simple compounds such as phthalic acid and dipyridyl-type ligands can be used in the design of one-dimensional zigzag chain structures and can realize unique preserved crystal structures.

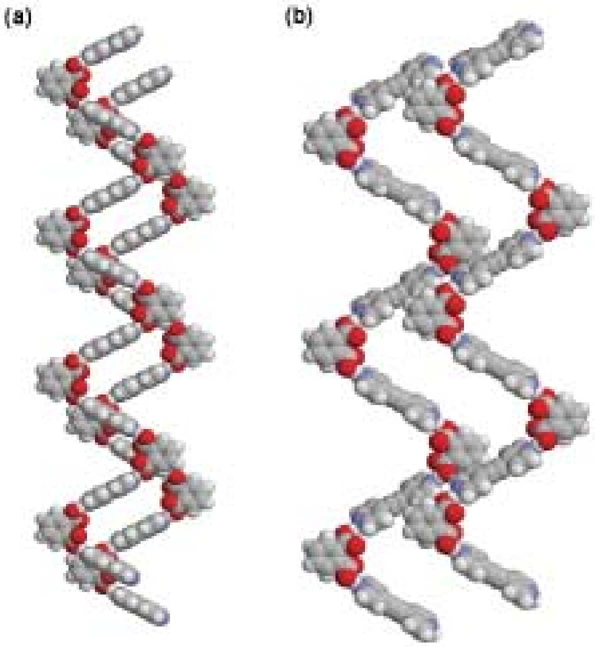

Figure 1. Two one-dimensional zigzag chain structures in the co-crystal of phthalic acid with (a) 4,4'-bipyridine and (b) 4,4'-dipyridylacetylene.

VIII-C-5 Synthesis and Crystal Structures of Decamethylferrocenium Salts of Anilate Anion Derived from Bromanilic Acid, Chloranilic Acid and Cyananilic Acid

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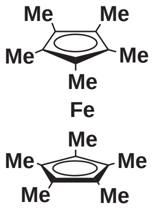
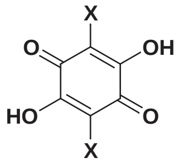
([1]IMS and Tokyo Inst. Tech.)

[*Inorg. Chim. Acta* **318**, 127 (2001)]

Four complexes were synthesized using bis(pentamethylcyclopentadienyl)iron $Fe(C_5Me_5)_2$ as an organometallic donor and three anilic acids (2,5-dibromo-3,6-dihydroxy-1,4-benzoquinone; BA, 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone; CA and 2,5-dicyano-3,6-dihydroxy-1,4-benzoquinone; CNA) as an organic acceptor. The molecular-based structures with different stoichiometric ratios [1:1, 1:1:1(H_2O) and 2:1] of these complexes have been determined by X-ray crystallographic analysis and elemental analysis. These complexes have a one-dimensional alternated stacking arrangement as $D^+A^-D^+A^-$ type. Close contacts between the bromine atoms and oxygen atoms of the BA units are observed in the structure $[Fe(C_5Me_5)_2](BA)$ of 1:1 composition. Interestingly, the structures $[Fe(C_5Me_5)_2](CA)(H_2O)$ and $[Fe(C_5Me_5)_2](CNA)(H_2O)$ of 1:1:1 (H_2O) ratio contain one-dimensional molecular tape structures with the combination of the CA or the CNA units and water molecules *via* O–H···O hydrogen bonds. Different stoichiometric ratios and structures are found from the CNA complexes $[Fe(C_5Me_5)_2](CNA)(H_2O)$ and $[Fe(C_5Me_5)_2]_2(CNA)$.



$Fe(C_5Me_5)_2$



BA: X = Br
CA: X = Cl
CNA: X = CN

VIII-C-6 Tetrathiafulvalene with a Fused Pyrazine Ring

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([1]IMS and Tokyo Inst. Tech.)

[*Acta Crystallogr., Sect. E: Struct. Rep.* **57**, o307 (2001)]

The title compound, 2-(1,3-dithiol-2-ylidene)-2,3-dihydro-1,3-dithia-4,7-diazaindene (pyrazinotetrathiafulvalene) forms a head-to-tail type of π-stacking centrosymmetric dimer with an interplanar distance of 3.59(1) Å. Short S···N interheteroatom contacts [3.10(1) Å] are observed between the two dimers, which form a two-dimensional stacking column along the [101] direction (Figure 1).

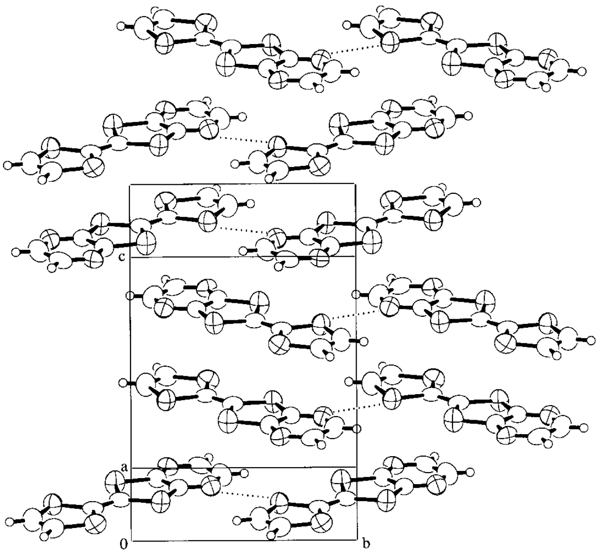

Figure 1. Packing diagram of the title compound. Short S···N interheteroatom contacts are indicated by dotted lines.

VIII-C-7 Hydrogen-Bonded Square Grid-Type Network in the Co-Crystal of Pyrazinotetrathiafulvalene with Chloranilic Acid

TOMURA, Masaaki; YAMASHITA, Yoshiro[1]
([1]IMS and Tokyo Inst. Tech.)

For the development of functional molecular materials, we have designed the hydrogen-bonded square grid-type network using the supramolecular synthon formed with chloranilic acids and heterocyclic compounds with nitrogen. The co-crystal **1** was isolated from an acetone solution of pyrazinotetrathiafulvalene with chloranilic acid. Figure 1 shows the crystal structure of **1**. The square grid-type network with cavities and the segregated unistacks of each molecule are observed. This packing motif is essentially the same as those previously obtained from the co-crystal of chloranilic acid with quinoxaline or phenazine.1) This fact suggests robustness and reproducing ability of the supramolecular synthon formed from chloranilic acid. Moreover, this type of segregated columnar structure is very important for organic conducting materials such as TTF-TCNQ charge transfer complex. The cavities in **1** are occupied by two water molecules. Such guest molecules in the cavities may affect physical properties of organic solids. Crystal data for **1**: $C_{14}H_6Cl_2N_2O_4S_4\cdot(H_2O)_2$, M = 497.35, monoclinic, space group $P2_1/m$, a = 3.867(3), b = 22.419(9), c = 11.675(4) Å, β = 99.27(3)°, V = 999(1) Å^3, Z = 2, T = 296 K, μ(Cu-Kα) = 7.165 mm^{-1}, R_1 = 0.0731 and wR_2 = 0.1841 for 998 data with $I > 2\sigma(I)$.

Reference

1) M. Tomura and Y. Yamashita, *CrystEngComm* 16 (2000).

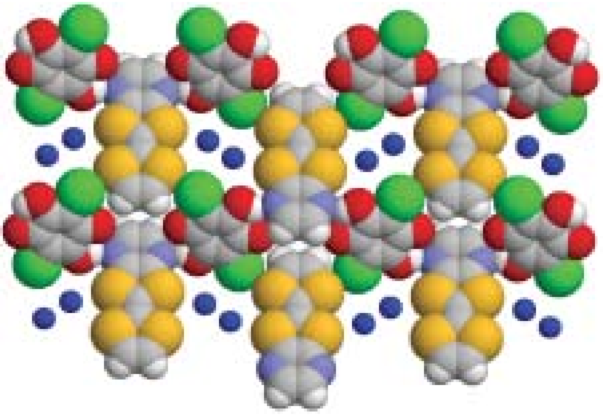

Figure 1. Crystal structure of **1** viewed along the a axis.

VIII-C-8 Hydroxyphenyl Substituted Tetrathiafulvalene Vinylogues Affording Stable Cation Radical Salts with Unusual Crystal Structures

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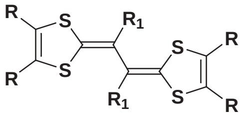
[*Tetrahedron Lett.* **42**, 4191 (2001)]

TTF vinylogues **1** containing hydroxy phenyl groups were newly prepared. They are stronger electron donors than BEDT-TTF and afforded their cation radical salts as single crystals upon electrochemical oxidation. The X-ray crystallographic analyses of the three cation radical salts **1a**·$Au(CN)_2$·PhCl, **1b**·PF_6, and **1c**·$ReO_4\cdot(H_2O)_8$ have revealed their unusual crystal structures, where p-overlapping and hydrogen bonding play a crucial role in constructing them. The TTF vinylogue skeletons of the salts are planar and the phenyl groups are almost orthogonal to them. The two-dimensional π-overlapping1) of the donor molecules was only found in the structure of **1a**·$Au(CN)_2$·PhCl. The structure of **1c**·$ReO_4\cdot(H_2O)_8$ has a one-dimensional grid-like structure with a void.2) In the structures of the three salts, hydrogen bonding between OH groups and counter anions was observed.



1

a; R, R = $(CH{=}CH)_2$, R_1 = *o*-OHC_6H_4
b; R, R = $(CH{=}CH)_2$, R_1 = *p*-OHC_6H_4
c; R, R = SCH_2CH_2S, R_1 = *o*-OHC_6H_4
d; R, R = SCH_2CH_2S, R_1 = *p*-OHC_6H_4
e; R, R = SCH_2CH_2S, R_1 = *o*-$OBzC_6H_4$
f; R, R = SCH_2CH_2S, R_1 = *p*-$OBzC_6H_4$

References

1) Y. Yamashita, M. Tomura, M. B. Zaman and K. Imaeda, *Chem. Commun.* 1657 (1998).
2) M. Tomura and Y. Yamashita, *CrystEngComm* 14 (2000).

VIII-C-9 A Molecule with a C_1-Homobasketane Framework

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([1]IMS and Tokyo Inst. Tech.)

[*Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **57**, 619 (2001)]

We have carried out the X-ray crystallographic analysis of 6-(1,3-benzodithiol-2-ylidene)-5,7-dimethyl-1,2-diphenylpentacyclo[5.4.0.0^{2,5}.0^{3,11}.0^{4,8}]undecane **1**, which is the C_1-homobasketane derivative with a 1,3-dithiole moiety as the redox part. This is the first example of the crystal structure determination of a molecule with a C_1-homobasketane framework. Compound **1** crystallizes in the triclinic crystal system with one molecule in the asymmetric unit. The molecular structure of **1** is shown in Figure 1. The two cyclobutane rings in the cage are in puckered conformation. Due to the enhanced through-bond interaction of phenyl π systems involving a strained σ bond, the (Ph–)C–C(–Ph) bond length is significantly extended to 1.610(3) Å.

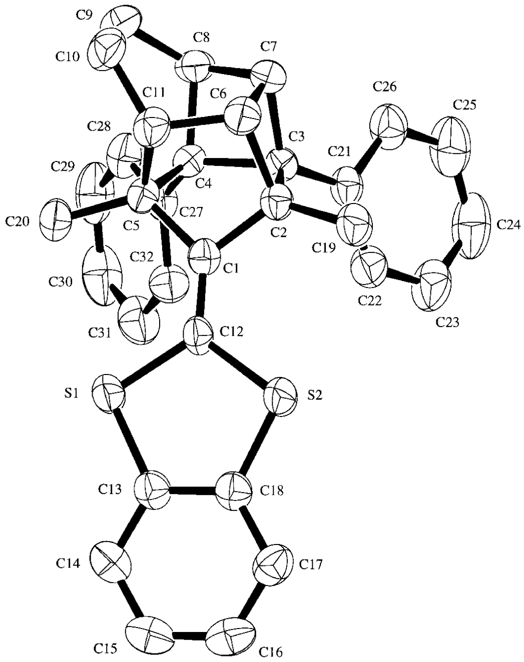


Figure 1. Molecular structure of **1**.

VIII-C-10 Real Space Observation of Individual Conformers of Oligothiophenes on Au(111) Surface

TANAKA, Shoji; YAMASHITA, Yoshiro[1]; YOKOYAMA, Takashi[2]
([1]Tokyo Inst. Tech.; [2]NIMS)

The prototype of a “single molecular device” is now realized for the basic components of digital electronics (rectification, amplification and storage), however, there is still much to be learned about the molecular / supramolecular architecture on solid surface to design practical nanoscopic devices and trier large-scale integration systems. In particular, conformational identification of a π-conjugated molecule has generated a great deal of interest, because the conformational changes in the conjugated skeleton caused by the adsorption on surface will influence appreciably the electronic feature and the self-assembling ability. Here we present a real-space analysis of the molecular conformation and the self-assembling pattern of novel oligothiophenes deposited on the Au(111) surface using UHV low-temperature scanning tunneling microscopy (STM).

The samples are molecular building blocks, **BL-1** and **BL-2**, which have been designed to construct a series of multi-functional molecular wire with insulating mantle as shown in Figure 1. Figure 2a shows the twin-lobe shape of a single **BL-1** molecule, which suggests that this oligomer tends to adsorb with the main-chain parallel to the Au surface. The regular molecular ordering of **BL-1**, however, was not observed as shown in Figure 2b. In the case of the **BL-2**, the STM data shown in Figure 3a reveal that two types of well-ordered domains, *molecular stripes* and *meshes,* evolve on the Au surface. The close-up STM views of these supra-structures as shown Figure 2b-d indicate that the *molecular stripe* and *meshes* consist of *s-trans* and *s-cis* conformer of **BL-2**, respectively. In solution and gas phase, the rapid exchange between the possible conformers of oligomers will occur usually. In molecular crystals, the most stable conformer would be observed predominantly. Our findings demonstrate experimentally that the control of molecular-surface interactions will be one of the key tactics to investigate individual conformers of oligomers and to construct a desired nanostructure based on them.

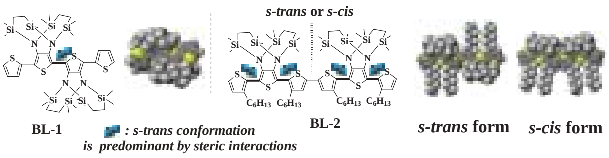
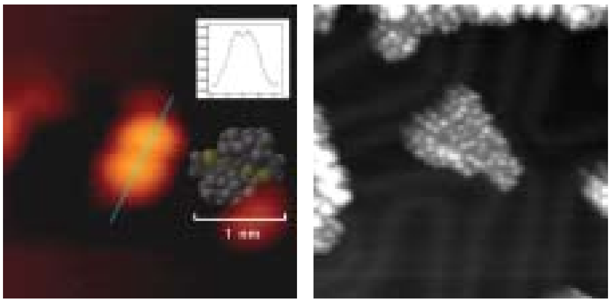


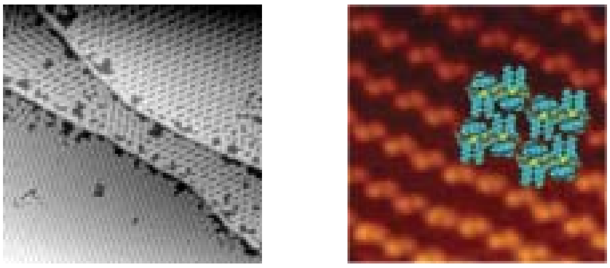
Figure 1. Molecular structure of **BL-1** and **BL-2**.



(A) **3.3 nm x 3.3 nm**
(Vs = -2.5 V, It = 5 pA)

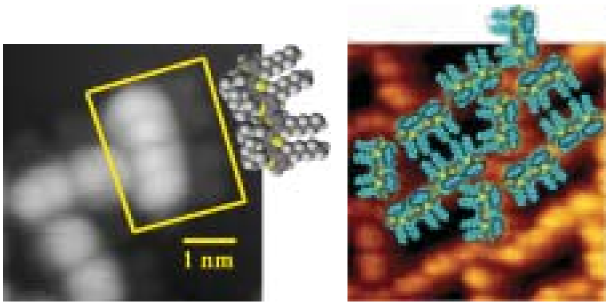
(B) **23.5 nm x 23.5 nm**
(Vs = -2.5 V, It = 5 pA)

Figure 2. STM images of **BL-1** on Au(111) surface at 63 K.



(A) **98 nm x 98 nm**
(Vs = 2 V, It = 5 pA)

(B) **10 nm x 10 nm**
(Vs = -2 V, It = 5 pA)



(C) **5nm x5 nm**
(Vs = -2 V, It = 30 pA)

(D) **10 nm x 10 nm**
(Vs = -2 V, It = 5 pA)

Figure 3. STM images of **BL-2** on Au(111) surface at 63 K.

VIII-C-11 Small Bandgap Polymers Involving Tricyclic Nonclassical Thiophene as a Building Block

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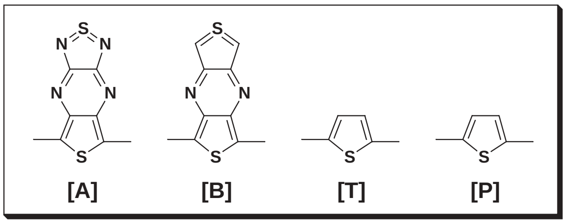
([1]Kyoto Univ.; [2]Tokyo Inst. Tech.; [3]Kyushu Univ.)

[*J. Phys. Chem. B* submitted]

The band electronic structures of one-dimensional polymers composed of thiophene, pyrrole, and tricyclic nonclassical thiophenes ([1,2,5]thiadiazolo[3,4-*b*]-thieno[3,4-*e*]pyrazine and dithieno[3,4-*b*:3',4'-*e*]-pyrazine) **1–2** are calculated and analyzed at the extended Hückel level of theory, with the development of highly conducting polymers in mind. The tricyclic nonclassical thiophenes that can impose quinoid-type characters to the resulting polymers are effective building blocks for the preparation of small bandgap polymers. Calculated bandgaps are discussed in view of the frontier crystal orbitals and the bond length alternation of the polymers. The homopolymer of [1,2,5]thiadiazolo[3,4-*b*]thieno[3,4-*e*]pyrazine **1a** that is predicted to have a bandgap of 0.1 eV is a good candidate for an intrinsic conducting polymer without dopants.



1a: $[A]_n$ 1b: $[AT]_n$ 1c: $[AP]_n$ 1d: $[ATT]_n$ 1e: $[APP]_n$

2a: $[B]_n$ 2b: $[BT]_n$ 2c: $[BP]_n$ 2d: $[BTT]_n$ 2e: $[BPP]_n$

Figure 1. Polymers composed of thiophene, pyrrole, and tricyclic nonclassical thiophenes.

VIII-C-12 Prospects of Single Molecule Devices for Future High Performance Infromation Technologies

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([1]Hitachi Ltd., Adv. Res. Lab.; [2]Univ. Tokyo; [3]Tokyo Inst. Tech.; [4]Kyoto Univ.; [5]Ehime Univ.; [6]Chuo. Univ.)

[*Jpn. J. Appl. Phys.* **39**, 3835 (2000)]

Current information technologies use semiconductor devices and magnetic/optical discs, however, it is foreseen that they will all face fundamental limitations within a decade. This paper reviews the prospects and problems of single molecule devices, including switching devices, wires, nanotubes, optical devices, storage devices and sensing devices for future information technologies and other advanced applications in the next paradigm. The operation principles of these devices are based on the phenomena occurring within a single molecule, such as single electron transfer, direct electron-hole recombination, magnetic/charge storage and regand-receptor reaction. Four possible milestones for realizing the Peta (10^{15})-floating operations per second (P-FLOPS) personal molecular supercomputer are described, and the necessary technologies are listed. These include, (1) two terminal conductance measurement on single molecule, (2) demonstration of two terminal molecular device characteristics, (3) verification of three terminal molecular device characteristics and (4) integration of the functions of "molecular super chip." Thus, 1000 times higher performance information technologies would be realized with molecular devices.

VIII-D Designing Artificial Photosynthesis at Molecular Dimensions

Photosynthesis is one of the finest piece of molecular machinery that Nature has ever created. Its ultrafast electron transfer and following well-organized sequence of chemical transformation have been, and will continue to be, challenging goals for molecular scientists. We are trying to mimic the function of photosynthesis by assembling molecular units that perform individual physical/chemical action. The molecular units include porphyrins, redox active organic molecules, and transition metal complexes. Our ultimate goal is to design artificial molecular systems that effect multiple chemical reactions triggered by light on the basis of molecular rationale.

Last year we focused our attention on combining "redox pool" with photoinduced electron transfer.

VIII-D-1 Synthesis and Photochemical Reactions of Multistep Redox Polymer Containing Porphyrin and Metalocenes

HINO, Takami[1]; ITO, Hajime; NAGATA, Toshi
([1]Kyoto Univ.)

Photoinduced electron transfers involving porphyrins are widely studied, but utilizing the high-energy radical ion pairs for driving chemical reactions remains to be a great challenge. One of the missing features in artificial photosynthetic models based on organic molecules is the function of redox pool—that receives the oxidizing and/or reducing equivalents from the photogenerated ion pairs and retains them sufficiently long until the substrates for chemical reactions are ready. This feature is essential for photosynthetic processes to be successful, because the photogenerated high-energy states are otherwise too short-lived to cooperate with (comparatively slow) chemical reactions. In biological systems various electron-carrying substances (proteins like soluble cytochromes, or cofactors like quinones) play the role, whereas in many artificial systems solid particles with electronic band structure (metal or semiconductor nanoparticles) do that. It should be an important research topic to develop redox pools with organic and organometallic substances and utilize in molecule-based artificial photosynthetic systems.

With this goal in mind, we prepared polysiloxanes containing ferrocene and porphyrin moieties (Figure 1). The ferrocenes are present in 20-fold excess of porphyrins, so that they can serve as 'electron pool' that retains photogenerated holes on porphyrin moieties.

The desired polymer **1** was prepared by hydrosilylation of a mixture of vinylferrocene and (4-pentenyloxy)phenyl substituted porphyrin with poly(methylhydro)siloxane catalyzed by hexachloroplatinic acid (Figure 2). Purification by reprecipitation from tetrahydrofuran/methanol followed by gel permuation chromatography yielded the product with reasonably narrow size distribution ($M_w/M_n = 1.4$). The cyclic voltammogram of **1** is shown in Figure 3; a large peak of ferrocenes and two small peaks of porphyrins are observed as expected.

The photoreaction of **1** with quinones were examined. We previously reported the reductive silylation of quinones photocatalyzed by porphyrins (H. Ito, T. Hino, T. Nagata, submitted; see also Annual Review 2000). As the photoreduced product of quinones are trapped by silylating reagents, this reaction can be used to continuously pick up electrons from donor molecules. Indeed, irradiation with visible light of a mixture of the polymer **1**, 2,3,5,6-tetramethyl-1,4-benzoquinone, Me_3SiCl and pyridine in tetrahydrofuran/N,N-dimethylformamide gave the oxidized form of **1** (*i.e.* the ferrocene moieties were converted to ferrocenium) together with the reduced product, 2,3,5,6-tetramethyl-1,4-bis(trimethylsiloxy)benzene (Figure 4). The full identification, as well as the follow-up chemistry (*i.e.* reducing back to the original form) of the oxidized form of **1** is currently under way.

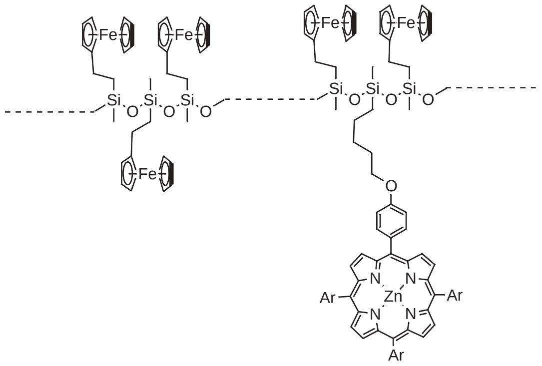

Figure 1. A redox polymer with a photoactive moiety.

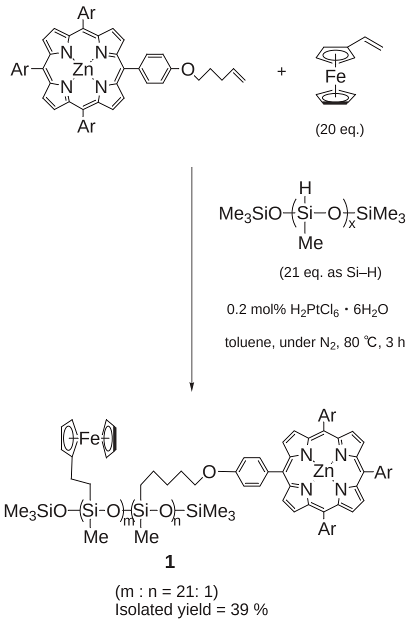

Figure 2. The synthesis of polymer **1**.

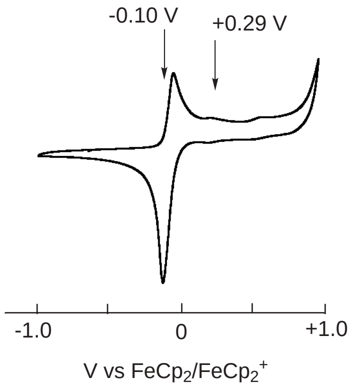

Figure 3. The cyclic voltammogram of polymer **1**. Conditions: CH_2Cl_2 with 0.1 M Bu_4NClO_4, Pt working electrode.

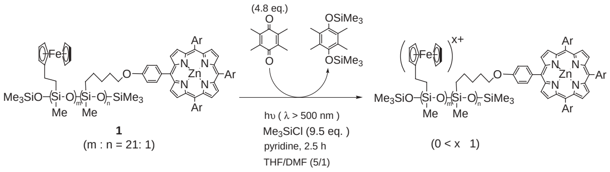

Figure 4. The photoreaction of polymer **1** with quinone and Me_3SiCl.

VIII-E Development of New Metal Complexes as Redox Catalysts

Redox catalysis is an important field of chemistry which translates a flow of electron into chemical transformation. It is also one of the requisites for artificial photosynthesis. This project of ours aims at developing new metal complexes that perform redox catalysis at low overpotential. Last year we focused our attention to developing terdentate ligands with strong donor character. 2,2’:6’,2”-Terpyridine has been the ligand of choice in this field, but our study has now revealed that 2,2’:6’,2”-terpyridine-1,1”-dioxide is also a good candidate for developing new catalysts.

VIII-E-1 Synthesis of Terpyridine-based Binary Ligands and Their Metal Complexes

ITO, Kaname; NAGATA, Toshi; TANAKA, Koji

[*Inorg. Chem.* in press]

In recent years, metal complexes of 2,2’:6’,2”-terpyridine (terpy) and their derivatives are gaining considerable attention as electrochemical catalysts. Derivatives of terpyridine are particularly suitable for electrocatalytic applications because they are chemically robust and form stable complexes with a wide variety of transition metals. On the other hand, the syntheses of terpyridine derivatives are often so troublesome that it is difficult to tune the electrochemical behavior of the metal complexes.

The *N*-oxides of pyridines are promising ligands that are easily derived from pyridine compounds by one-step peracid oxidation. Metal complexes of pyridine *N*-oxide and 2,2’-bipyridine 1,1”-dioxide are numerous, whereas the *N*-oxides of terpyridine have been much less studied. Only a few reports were published on the metal complexes of 2,2’:6’,2”-terpyridine 1,1’,1”-trioxide ($terpyO_3$).

We prepared a series of first-row transition metal complexes of 2,2’:6’,2”-terpyridine 1,1”-dioxide ($terpyO_2$) are reported. Four new bis complexes $[M(terpyO_2)]X_2$ (M = Mn(II), Fe(II), Co(II) and Ni(II); X = ClO_4^- and BF_4^-) and one mono complex $[Cu(terpyO_2)(H_2O)](ClO_4)_2$ were isolated and characterized, and electrochemical properties were examined. The crystal structure of the Fe(II) complex $[Fe(terpyO_2)_2](ClO_4)_2$ is shown in Figure 1. The ligands have non-planar conformations with an approximate C_2 symmetry, which makes the overall symmetry of the complex cation approximately D_2. The Ni(II) complex $[Ni(terpyO_2)_2](ClO_4)_2$ was isostructural with the Fe(II) complex. The X-ray structure of the Cu(II) complex was also examined (Figure 2), and it was revealed that the Cu(II) ion was square-planar with the terdentate $terpyO_2$ ligand whose conformation was similar as in the Fe(II) and Ni(II) complexes.

The cyclic voltammograms of the four bis complexes revealed that the M(III)/M(II) redox potentials of the Mn(II), Fe(II) and Ni(II) complexes showed negative shifts (–0.77 to –0.24 V) compared to the terpyridine complexes, whereas the potential of the Co(II) complex showed a slightly positive shift (+0.03 V). The Fe(II) complex is particularly interesting, because the low $E_{1/2}$ value and the ease of ligand exchange (revealed by ESI-MS) make the complex promising for application as a redox catalyst. Also worth noting is the Mn(II) complex, for which another reversible wave corresponding to the Mn(IV)/Mn(III) couple was observed. The electrocatalytic properties of the $terpyO_2$ complexes is now being investigated.

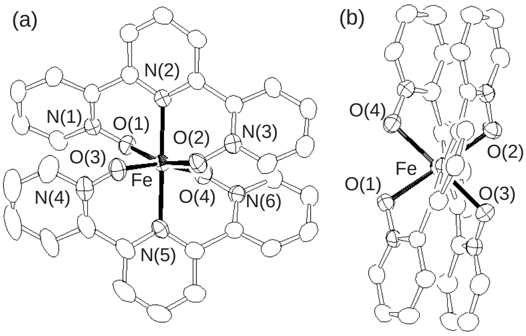

Figure 1. ORTEP view (50% probability ellipsoids) of the complex cation $[Fe(terpyO_2)_2]^{2+}$.

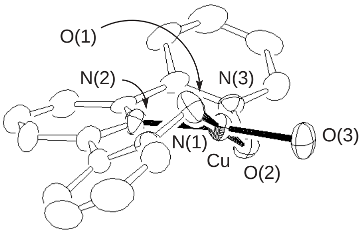

Figure 2. ORTEP view (50% probability ellipsoids) of the complex cation $[Cu(terpyO_2)(H_2O)]^{2+}$.

VIII-F Development of Organic n-Type Semiconductors for Molecular Thin-Film Devices

Organic light-emitting diodes (OLEDs) and field-effect transistors (FETs) based on π-conjugated oligomers have been extensively studied as molecular thin-film devices. Organic n-type semiconductors with low electron-injection barriers and high electron mobilities are required for highly efficient OLEDs and n-type FETs. Radical anions of an n-type semiconductor have to be generated easily at the interface with a metal electrode (electron injection), and electrons must move fast in the layer (electron mobility). Compared with organic p-type semiconductors, organic n-type semiconductors for practical use are few and rather difficult to develop. Recently, we found that perfluorinated oligomers are efficient electron-transport materials for OLEDs.

VIII-F-1 Tetradecafluorosexithiophene: The First Perfluorinated Oligothiophene

SAKAMOTO, Youichi; KOMATSU, Shingo; SUZUKI, Toshiyasu

[*J. Am. Chem. Soc.* **123**, 4643 (2001)]

Perfluoro-a-sexithiophene (**PF-6T**) was synthesized by the fluorination of thienyllithiums with *N*-fluoro-*N*-(phenylsulfonyl)benzenesulfonamide and the Stille and Ullmann couplings. **PF-6T** is an orange crystalline solid and slightly soluble in $CHCl_3$ and aromatic solvents such as toluene. Its structure was determined by EI-MS, elemental analysis, and X-ray crystallography. **PF-6T** exhibits bluish-green photoluminescence in solution and an orange emission in the solid state. A sharp melting endotherm was observed at 286 °C by DSC. The differential pulse voltammogram (DPV) in 1,2-dichlorobenzene showed that the redox potentials of **PF-6T** shifted positively relative to α-sexithiophene (**6T**). Single crystals of **PF-6T** were successfully grown by slow sublimation at 270 °C under a flow of 1 atm of argon. The structure of **PF-6T** is *all-trans* and planar as observed for **6T**. **PF-6T** adopts a π-stack structure with face-to-face molecules. This is quite different from the herringbone structure of **6T**, in which π-π interactions between neighboring molecules are minimized to reduce the repulsion between π-orbitals. High electron mobility is expected along the π-π stacking direction. Fabrication of n-type FETs with this new material is currently underway.

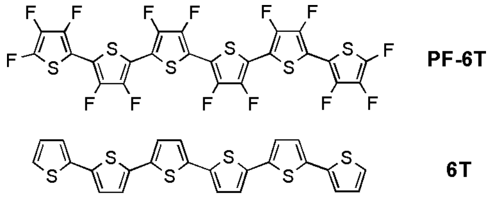

Figure 1. Perfluoro-α-sexithiophene and α-sexithiophene.

VIII-F-2 Highly Efficient Phosphorescence from Organic Light-Emitting Devices with an Exciton-Block Layer

IKAI, Masamichi[1]; TOKITO, Shizuo[1]; SAKAMOTO, Youichi; SUZUKI, Toshiyasu; TAGA, Yasunori[1]
(*[1]Toyota Central R&D Labs.)*

[*Appl. Phys. Lett.* **79**, 156 (2001)]

One of the keys to highly efficient phosphorescent emission in organic light-emitting devices is to confine triplet excitons generated within the emitting layer. We employ “starburst” perfluorinated phenylenes ($C_{60}F_{42}$) as a both hole- and exciton-block layer, and a hole-transport material 4,4’,4”-tri(*N*-carbazolyl) triphenylamine as a host for the phosphorescent dopant dye in the emitting layer. A maximum external quantum efficiency reaches to 19.2%, and keeps over 15% even at high current densities of 10–20 mA/cm^2, providing several times the brightness of fluorescent tubes for lighting. The onset voltage of the electroluminescence is as low as 2.4 V and the peak power efficiency is 70–72 lm/W, promising for low-power display devices.

VIII-G The Effects of the 2D Spin-Echo NMR Experiment on a Solid-State Homonuclear Spin-1/2 Pair

The 2D spin-echo NMR experiment can reintroduce the influence of homonuclear dipolar interactions average out by magic-angle sample spinning (MAS).

VIII-G-1 Novel Structure Discovered on Two-Dimensional Spin-Echo NMR Spectra for a Homonuclear Spin-1/2 Pair in Rotating Solids

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([1]Tokyo Univ. Agric. Tech.; [2]Kyoto Univ.)

Two-dimensional (2D) spin-echo NMR experiments have been carried out on polycrystalline [2,3-$^{13}C_2$]-*L*-alanine under magic-angle sample spinning (MAS) conditions, so that two unusual resonance lines emerged along the F_1 axis. Theoretically it was found that the line positions were determined by the sample spinning frequency and the isotropic chemical-shift difference (*Chem. Phys. Lett.* **305**, 35 (1999)). Stimulated by the result, we carried out the 2D NMR experiment using a sufficiently small t_1 increment in order to enlarge the spectral width of the F_1 domain. As a result, we found many more resonance lines on a spectrum sliced along the F_1 axis. The line distribution had a very unique and interesting structure. To elucidate the line positions theoretically, the signal for the 2D spin-echo experiment performed with any t_1 increment was calculated analytically for a homonuclear two-spin-1/2 system undergoing MAS. We showed that virtually six resonance lines (exactly twelve resonance lines) occurred on a spectrum sliced along the F_1 axis. In addition, it was demonstrated that the intensities of some resonance lines were largely dependent on the dipolar interaction. The 2D spin-echo experiment for a solid-state homonuclear two-spin system was found to have the capability of extracting information concerning the dipolar tensor under MAS conditions.

VIII-H Rotational Echo Double Resonance (REDOR) Experiments with Overtone Adiabatic Inversion Pulses

The effect of overtone adiabatic inversion pulse on solid-state ^{14}N spins was investigated.

VIII-H-1 The Observation of REDOR Phenomenon for Solid-State ^{13}C-^{14}N spin Systems with the Help of Overtone Adiabatic Inversion Pulses

KUWAHARA, Daisuke

We applied overtone adiabatic inversion pulses to ^{13}C-^{14}N spin systems in powdered *L*-alanine undergoing MAS in order to observe REDOR phenomenon. The damping of ^{13}C resonance line intensities was compared with that corresponding to the REDOR experiments with normal RF pulses having a constant frequency. We tried to establish the theoretical treatment for the REDOR experiments with adiabatic inversion pulses.