Research Center for Molecular Materials

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

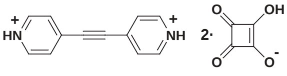
Heterocycles containing sulfur and/or nitrogen atoms are useful as components of functional materials since heteroatoms in their rings are helpful to stabilize ions or ion-radical species, and extended π-conjugation decreases Coulombic repulsion. In addition intermolecular interactions caused by heteroatom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

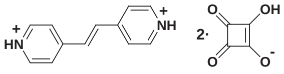
ZAMAN, Md. Badruz; TOMURA, Masaaki; YAMASHITA, Yoshiro[1]
([1]IMS and Tokyo Inst. Tech.)

[*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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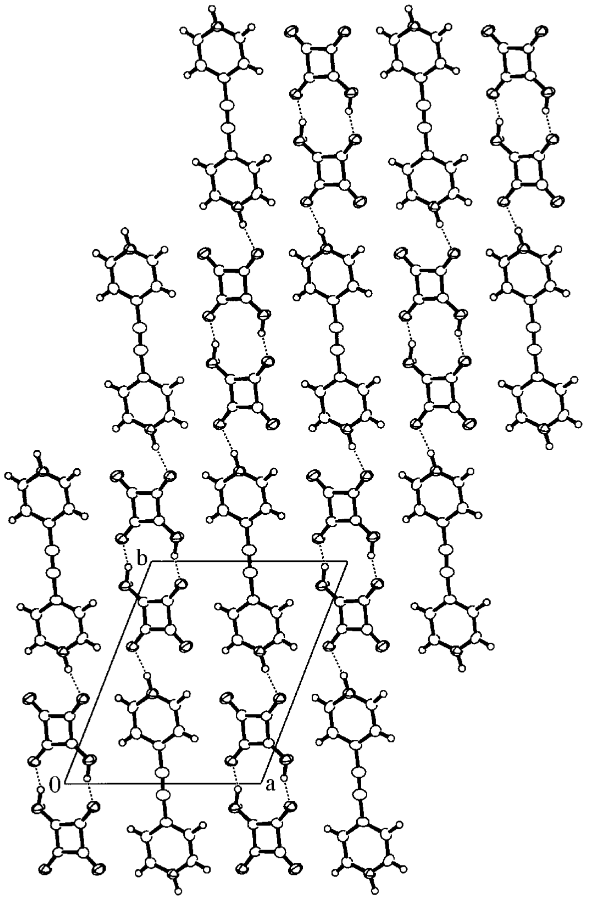


Figure 1. Packing diagram of **1** viewed along the c axis. Dotted lines show the intermolecular hydrogen bonds.

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

AKHTARZZAMAN, Md.[1]**; TOMURA, Masaaki; YAMASHITA, Yoshiro**[2]
([1]GUAS; [2]IMS and Tokyo Inst. Tech.)

[*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* $R^2_1(5)$ 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*.

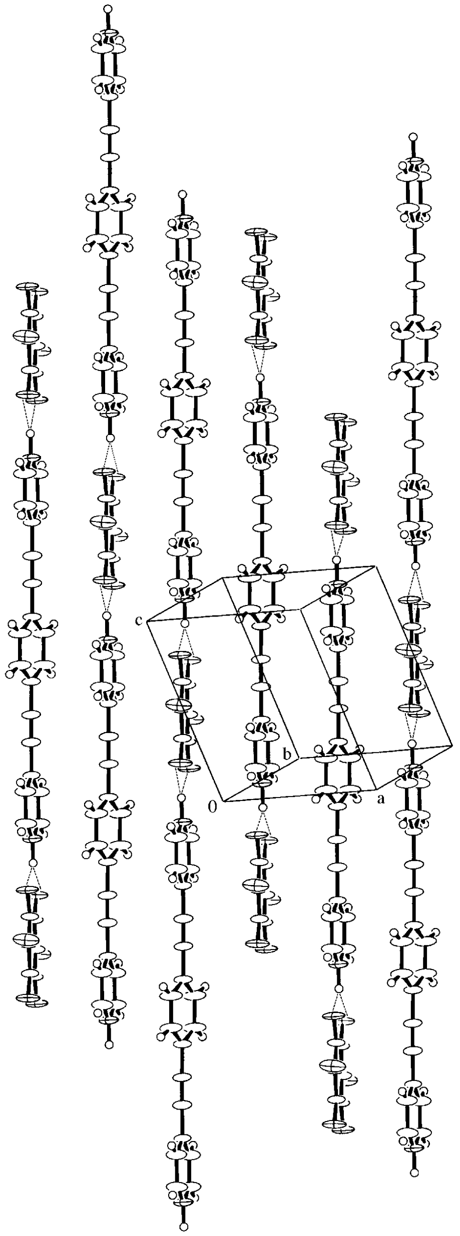


Figure 1. Packing diagram of the title compound. Dotted lines show the intermolecular N–H···O hydrogen bonds.

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

AKHTARZZAMAN, Md.[1]; TOMURA, Masaaki; YAMASHITA, Yoshiro[2]
([1]GUAS; [2]IMS and Tokyo Inst. Tech.)

[*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.

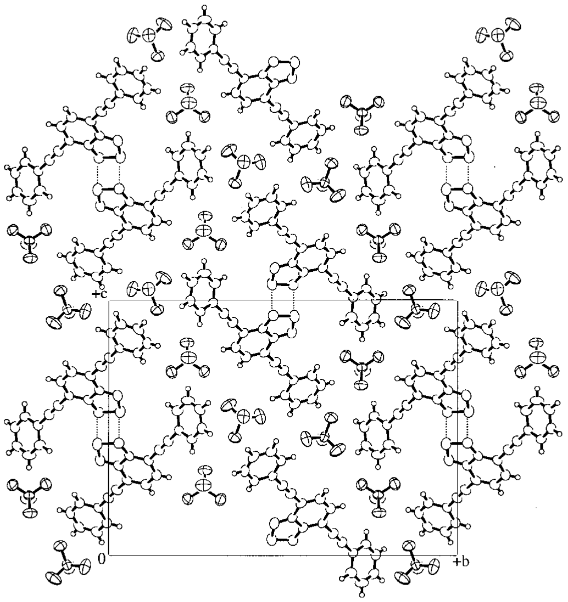


Figure 1. Packing diagram of **2** viewed along the a axis. Dotted lines show the short S···N interheteroatom contacts.

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

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

[*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.

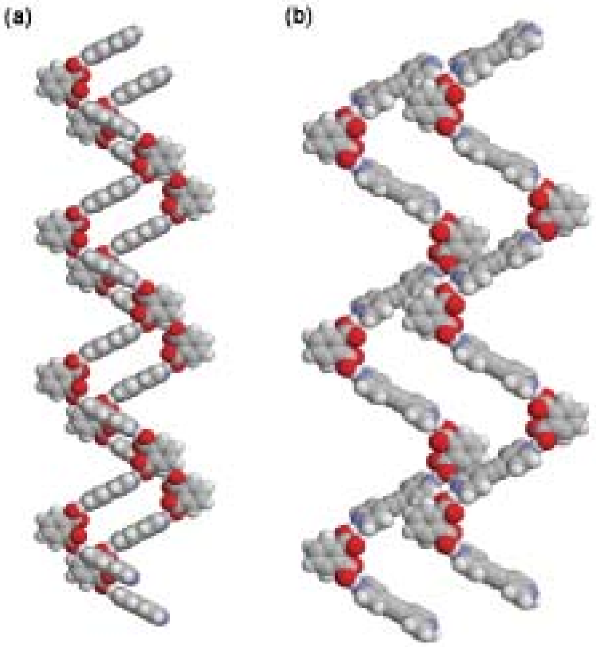


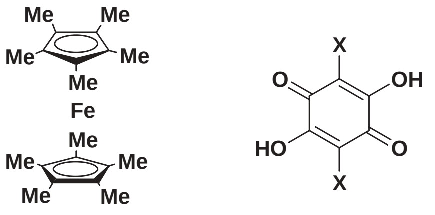
Figure 1. Two one-dimensional zigzag chain structures in the co-crystal of phthalic acid with (a) 4,4’-bipyridine and (b) 4,4’-dipyridylacetylene.

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

ZAMAN, Md. Badruz; TOMURA, Masaaki; YAMASHITA, Yoshiro[1]
([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

TOMURA, Masaaki; YAMASHITA, Yoshiro[1]
([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).

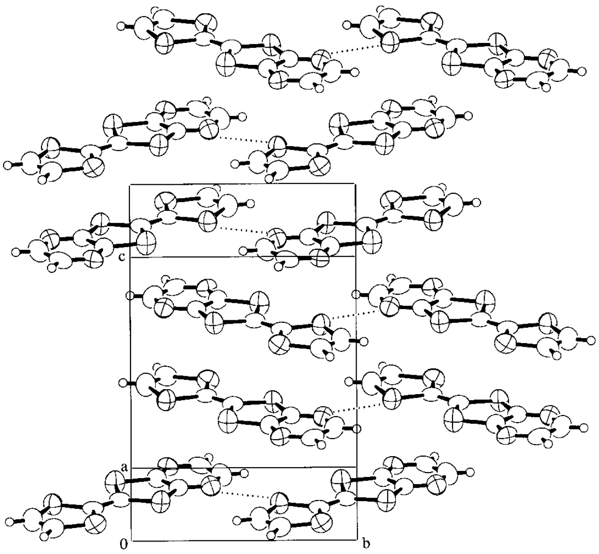


Figure 1. Packing diagram of the title compound. Short S···N interheteroatom contacts are indicated by dotted lines.

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).

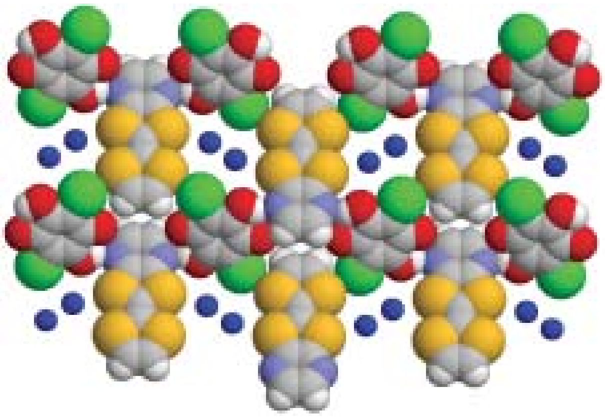


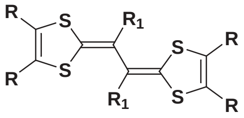
Figure 1. Crystal structure of **1** viewed along the a axis.

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

YAMASHITA, Yoshiro[1]; TOMURA, Masaaki; IMAEDA, Ken-ichi[2]
([1]IMS and Tokyo Inst. Tech.; [2]IMS and Chubu Univ.)

[*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**·$Au(CN)_2 \cdot PhCl$, **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**·$Au(CN)_2 \cdot PhCl$. 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

TOMURA, Masaaki; YAMASHITA, Yoshiro[1]
([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.

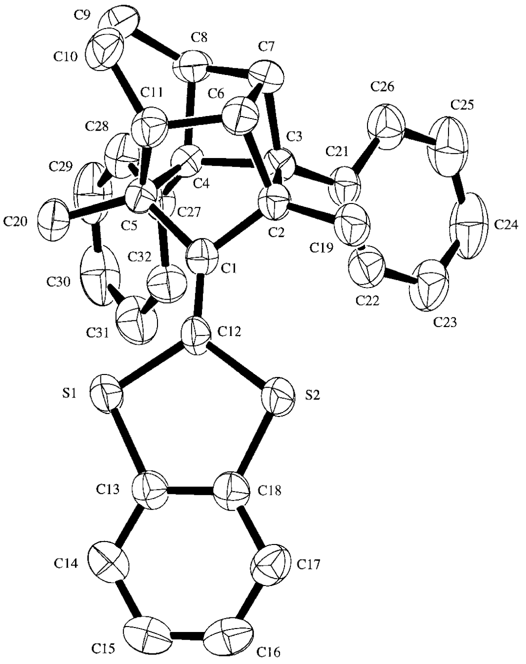


Figure 1. Molecular structure of **1**.

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.

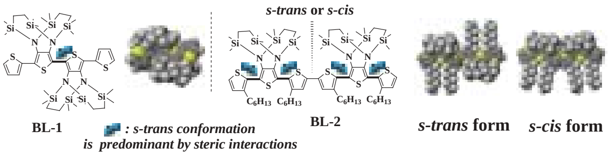
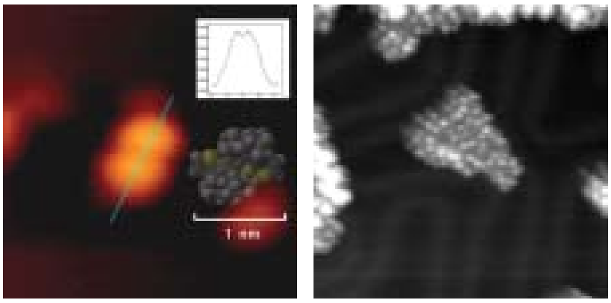


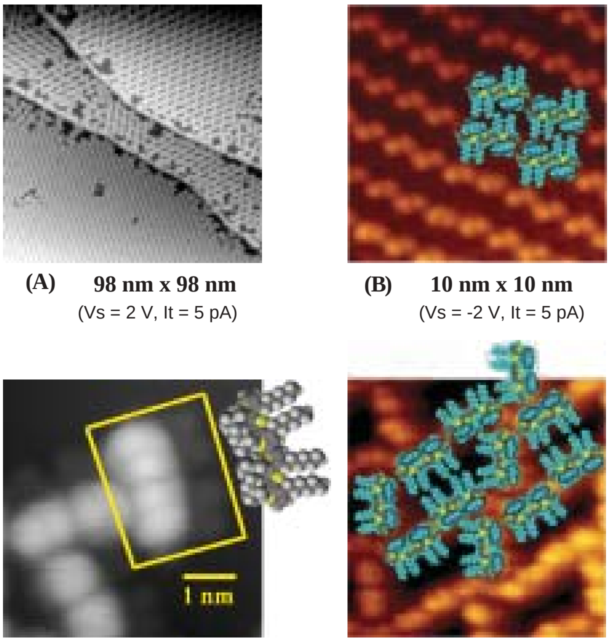
Figure 1. Molecular structure of **BL-1** and **BL-2**.



(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)

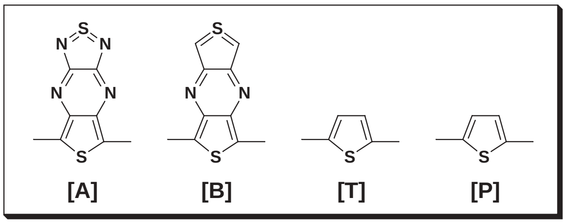
Figure 3. STM images of **BL-2** on Au(111) surface at 63 K.

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

TACHIBANA, Masamitsu[1]; TANAKA, Shoji; YAMASHITA, Yoshiro[2]; YOSHIZAWA, Kazunari[3]
([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

WADA, Yasuo[1]; TSUKADA, Masaru[2]; FUJIHIRA, Masamichi[3]; MATSUSIGE, Kazumi[4]; OGAWA, Takuji[5]; HAGA, Masa-aki[6]; TANAKA, Shoji
([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.