Research Center for Molecular Materials

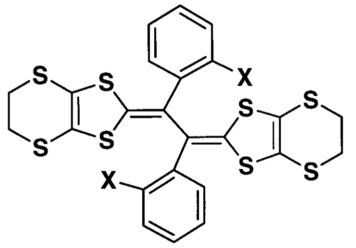
VIII-E Development of Novel Heterocyclic Compounds and their Molecular Assemblies for Advanced Materials

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. Thiophene oligomers with rigid structures were also synthesized for molecular wires.

VIII-E-1 Cation Radical Salts of TTF Vinylogues with Au(CN)$_2$ Anion

YAMASHITA, Yoshiro; TOMURA, Masaaki; IMAEDA, Kenichi

TTF vinylogues bearing substituents have been easily obtained and the TTF skeletons can be planar when the aryl substituents are twisted from the π-conjugated framework. We have now found that TTF vinylogues **1a-c** containing one halogen atom at the ortho position afford cation radical salts [**1**·Au(CN)$_2$] as single crystals when they are electrochemically oxidized in dichloromethane in the presence of Bu$_4$N·Au(CN)$_2$. The X-ray crystal structure analyses of **1b,c**·Au(CN)$_2$ salts were carried out to reveal the unique crystal structures. The molecular and crystal structure of **1b**·Au(CN)$_2$ is shown in Figure 1. The TTF vinylogue skeleton is planar and the phenyl groups are orthogonal from the π-framework. The donor molecules do not take a stacking structure and the 1,3-dithiole parts sandwich the counter anion. The crystal structure of **1c**·Au(CN)$_2$ is very similar to that of **1b**·Au(CN)$_2$. These cation radical salts showed semiconducting behaviour since these have a 1:1 stoichiometry [**1b**·Au(CN)$_2$; $\sigma = 1 \times 10^{-2}$ Scm^{-1}, $E_a = 0.11$ eV, **1c**·Au(CN)$_2$; $\sigma = 5 \times 10^{-3}$ Scm^{-1}, $E_a = 0.11$ eV].



1a; X = F
1b; X = Cl
1c; X = Br

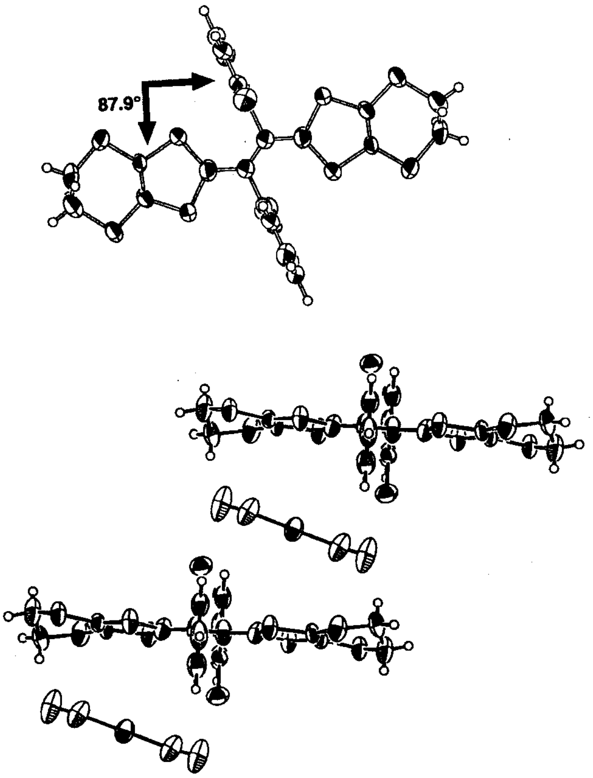


Figure 1. Molecular and crystal structure of **1b**·Au(CN)$_2$.

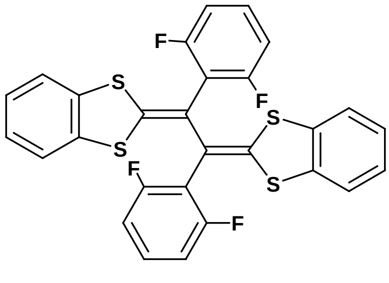
VIII-E-2 Control of Packing Mode in Crystals of Cation Radical Salts of TTF Vinylogues

TOMURA, Masaaki; YAMASHITA, Yoshiro

Molecular and crystal structures of cation radical salts of novel tetrathiafulvalene (TTF) vinylogues with extended π-conjugation and aryl groups in their vinyl part have been studied by X-ray crystallographic analysis. We reported that the unique conformation with a planar TTF vinylogue framework in **1**-PF$_6$ salt causes an interesting two-dimensional stacking mode where one donor molecule bridges two molecules like a brick wall in the crystal.$^{1)}$ We have succeeded in controlling the packing mode in the two-dimensional stack by changing the counter anion. In the case of **1**-FeCl$_4$ salt, we observed a partial two-dimensional stacking in the crystal. On the other hand, the zigzag two-dimensional stacking with an angle of nearly 90° exists in the crystal of **1**-ReO_4 salt, as shown in Figure 1.

Reference

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



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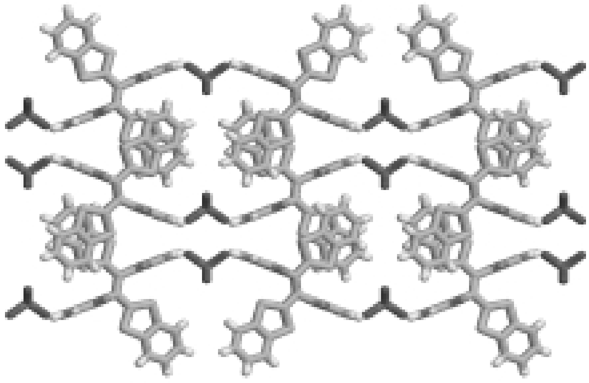
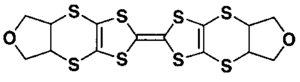


Figure 1. Crystal structure of **1**-ReO_4 salt.

VIII-E-3 Non-Planar BEDT-TTF Derivatives Fused with Tetrahydrofuran Rings Affording Cation Radical Salts with Unusual Structures

YAMASHITA, Yoshiro; TOMURA, Masaaki

Unusual crystal structures are expected from non-planar molecules to avoid steric interactions. Three-component conductors might be prepared from non-planar molecules by inclusion of solvent molecules. We have now designed new electron donors **1** and **2** where tetrahydrofuran (THF) rings are fused to BEDT-TTF. The new donors were prepared using the addition reaction of oligo(1,3-dithiole-2,4,5-trithione) with 2,5-dihydrofuran. The donor **2** gave two cation radical salts [**2**·$Au(CN)_2$ and **2**·PF_6·$(PhCl)_{0.5}$] as single crystals when electrochemically oxidized in chlorobenzene. The salts exhibit semiconducting behavior [**2**·$Au(CN)_2$; $\sigma = 3 \times 10^{-3}$ Scm^{-1}, $E_a = 0.20$, **2**·PF_6·$(PhCl)_{0.5}$; $\sigma = 5 \times 10^{-5}$ Scm^{-1}, $E_a = 0.24$ eV]. The X-ray crystal analyses of these salts revealed their unusual crystal structures. The donor molecule is non-planar and the cis-fused THF ring is like a hook. In **2**·$Au(CN)_2$ one $Au(CN)_2$ anion is sandwithched between the donor molecules. This sandwiched structure is stacked to give a column. In **2**·PF_6·$(PhCl)_{0.5}$, instead of a stacking structure, a complicated molecular network is observed, where one neighboring molecule is highly leaned (77°) and the molecules are combined by short S···S contacts as shown in Figure 1.



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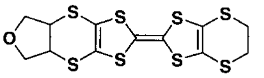

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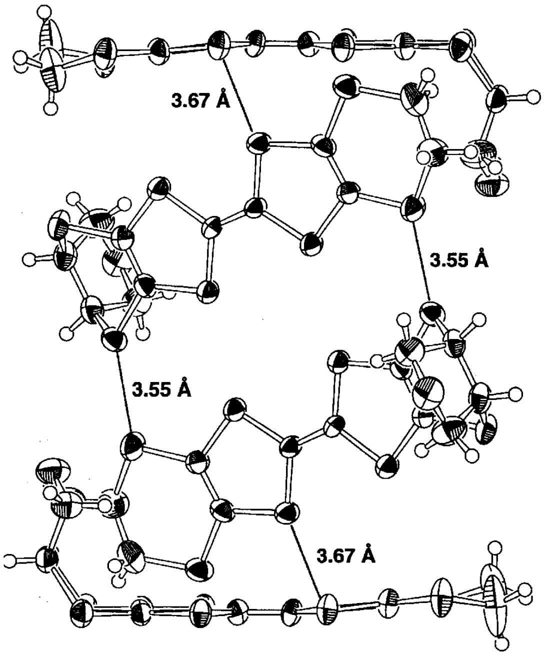
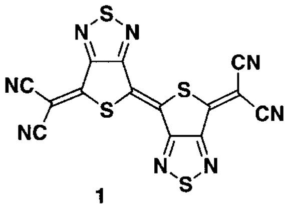


Figure 1. Crystal structure of **2**·PF_6·$(PhCl)_{0.5}$.

VIII-E-4 Bithiophene-TCNQ Analogue with Fused 1,2,5-Thiadiazole Rings

SUZUKI, Kazuharu; TOMURA, Masaaki; YAMASHITA, Yoshiro

Sulfur containing TCNQ analogues are highly polarized and are expected to have strong intermolecular interactions by heteroatom contacts. We have now prepared π-extended electron acceptor **1** containing fused thiadiazole rings and carried out the X-ray structure analysis to reveal the intermolecular interactions. The acceptor **1** was obtained by the reaction of dibromide **2** with tetracyanoethylene oxide (TCNEO) in 3% yield. However, thiophen-TCNQ analogue **3** could not be isolated in this reaction. The mechanism for the formation of **1** is still ambiguous. In the reaction to give **1**, a small amount of new compound **4** was isolated whose structure was determined by X-ray structure analysis. The dibromide **4** gave **1** upon heating, suggesting that **4** is an intermediate to give **1**. The absorption maximum of **1** is observed at 461 nm in dichloromethane. The reduction potential (–0.31 V *vs.* SCE) is lower than that of TCNQ, indicating that the interaction between the dicyanomethylene parts is weak in **1**. The X-ray analysis revealed that **1** forms a molecular assemble by heteroatom interactions. The crystal structure is shown in Figure 1. The planar molecules are combined by short S···N contacts to give a three-dimensional network. The distance of S···N contact (3.18 Å) is shorter than the sum of the van der Waals distances (3.35 Å).



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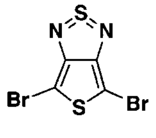

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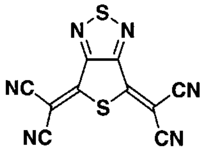

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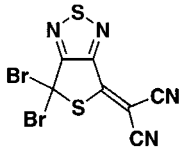

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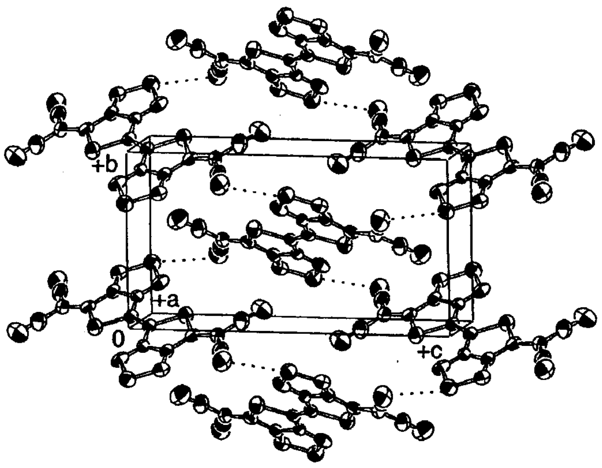

Figure 1. Crystal structure of **1**.

VIII-E-5 First Stable Tetracyanodiphenoquinodimethane with a Completely Planar Geometry: Preparation, X-Ray Structure, and Highly Conductive Complexes of Bis[1,2,5]thiadiazolo-TCNDQ

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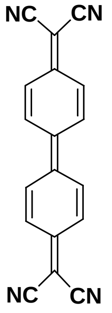
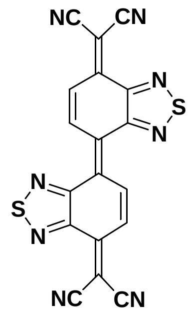
([1]Tohoku Univ.; [2]Hokkaido Univ.)

[*Tetrahdron Lett.* **40**, 1175 (1999)]

The title tetracyanodiphenoquinodimethane (TCNDQ) derivative **1** was newly designed and prepared as a novel component for highly conductive organic materials. This is the first stable TCNDQ derivative which is a π-extended electron acceptor. The synthesis was achieved by using Pd(0)-catalyzed reaction of the corresponding diiodo compound with $NaCH(CN)_2$ followed by oxidation. Introduction of thiadiazole rings into the TCNDQ skeleton leads to large stabilization in the neutral state. X-ray analysis has revealed the unique structure, where interatomic interactions (CH···N, S···N) play an important role in determining the molecular and crystal structure. The novel electron acceptor shows strong electron affinity (E_{red} = +0.33, +0.12 V *vs.* SCE in CH_2Cl_2) comparable with that of TCNQ, and gave highly conductive charge transfer complexes and anion radical salts.



TCNDQ



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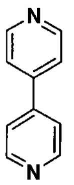
VIII-E-6 Novel Supramolecular Synthon in Crystal Engineering: Ionic Complexes of 4,4’-Bipyridine and 1,2-Bis(2-pyridyl)ethylene with 2,5-Dichloro-3,6-dihydroxy-1,4-benzoquinone

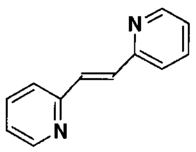
ZAMAN, Md. Badruz; TOMURA, Masaaki; YAMASHITA, Yoshiro

[*Chem. Commun.* 999 (1999)]

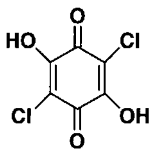
In order to develop a new type of hydrogen-bonding system, we have selected bipyridine (BPY) and 1,2-bis(2-pyridylethylene) (2-PDE) as proton acceptor, and chloranilic acid (2H-CLA) as proton donor. The complexes were prepared by reacting BPY and 2-PDE with an equal amount of 2H-CLA in acetone and/or a mixture of acetone-MeOH. The crystal structure analysis revealed that molecular complexes $[BPY\text{-}2H]^{2+}[CLA]^{2-}$ **1** and $[2\text{-}PDE\text{-}2H]^{2+}[CLA]^{2-}$ **2** are formed where proton transfer occurs. The component molecules are combined via three-center hydrogen bonded interactions to build a linear molecular chain for **1** and a zigzag molecular tape for **2**. The structure of **1** is shown in Figure 1. In both **1** and **2**, bifurcated interionic [N^+-H···O^- and N^+-H···O] hydrogen bonds between the nitrogen atoms of the cations and the two oxygen atoms from the anions are observed. This is a new supramolecular synthon motif. In complex **1** alternating DA-type pairs of the cation and anion molecules are observed in the stacking, while complex **2** has a segregated stacking assembly as DD- and AA-type pairs.



BPY



2-PDE



2H-CLA

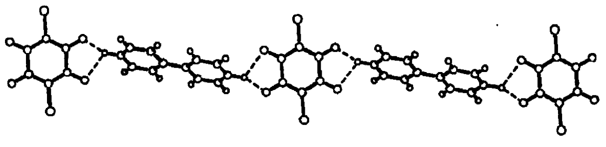


Figure 1. Hydrogen bonding in **1**.

VIII-E-7 Design and Synthesis of Soluble Linear Macromolecules with Highly Extended π-Conjugated Backbone

TANAKA, Shoji; YAMASHITA, Yoshiro

The development of soluble linear macromolecules with highly extended π-conjugated system is of crucial importance to establish the structure-conductance relationship in ballistic-type molecular electric wires. Although the introduction of alkyl substituents into the main chain is an effective method to improve the solubility, this modification often results in conjugation defects in the main chain due to the enhanced inter-unit steric repulsion. Here we report on a tactics in molecular design to do well both in solubility and π-conjugation of linear oligomers. We have synthesized a series of mixed oligomers **1-5**. All of the alkyl-substituted oligomers are more soluble in CH_2Cl_2, $CHCl_3$, and THF compared with the unsubstituted ones. As shown in Figure 1, the hexyl substitution on **1a** induces only a small blue shift of the absorption maximum, indicating a tiny loss of conjugation in spite of the long alkyl-chain substitution. These results suggest that **1b** unit can be used as a building block for soluble and effectively π-conjugated macromolecules. Along this line, we have obtained soluble highly oligomers **1c-d**. The red shift values induced by the chain extension (**1b** → **1c** → **1d**) are significantly higher than the shift value of the related oligomers (**3c** → **3d**). This supports the highly extended π-conjugation in the main chain of **1c-d**.

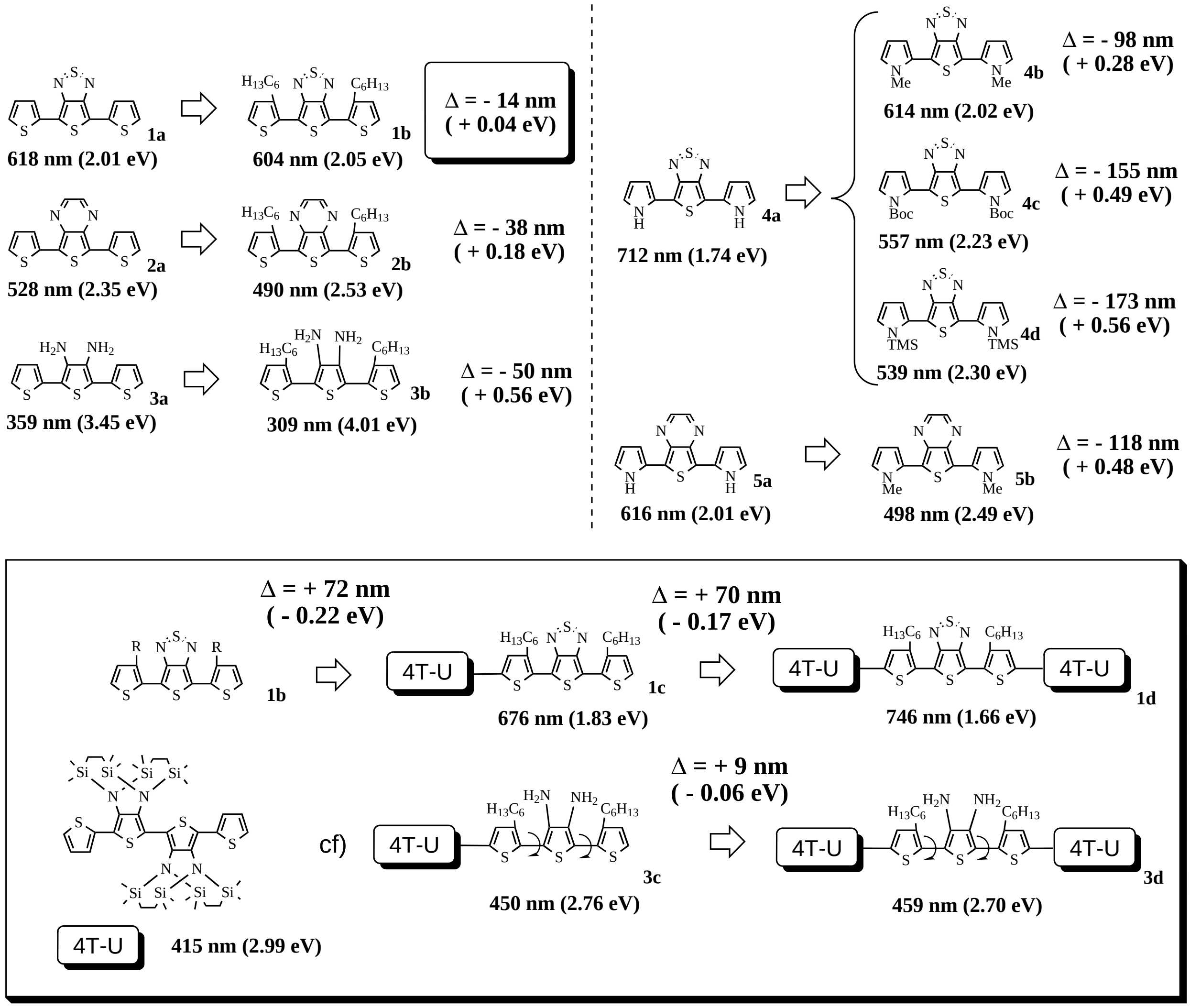


Figure 1. Substituent effects on the absorption maximum of the obtained mixed oligomers.