

Research Center for Molecular Materials

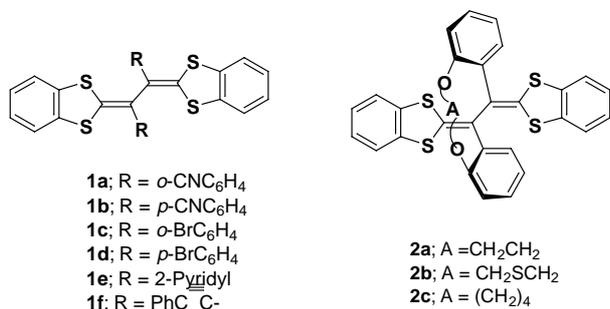
VIII-C Development of Novel Heterocyclic Compounds and Their Molecular Assemblies for Advanced Materials

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

VIII-C-1 Preparation of New TTF Vinylogues Containing Substituents at the Vinyl Positions

YAMASHITA, Yoshiro; TOMURA, Masaaki

TTF vinylogues **1** have a stronger electron-donating ability and reduced on-site Coulomb repulsion owing to the extended π -delocalized system. The physical properties and structures can be tuned by the substituents at the vinyl positions. For example the ortho-substituted phenyl groups can keep the TTF vinylogue skeleton plane by taking twisting conformations, leading to the stable cation radical states.¹⁾ We have now prepared the new derivatives **1** and **2**, and investigated their properties. New compounds **1a–d** possess cyano or bromo substituents which can induce intermolecular interactions. The synthesis is based on oxidative coupling reaction of the corresponding 1,4-dithiafulvenes. **1e** with 2-pyridyl substituents and **1f** with phenylethynyl groups were also synthesized. **1f** has no steric hindrance caused by substituents. Furthermore, we have obtained cyclophane-type molecules **2** which have a bridge between the phenyl substituents. The following oxidation potentials of new molecules were observed. **1a**; 0.61, 0.84, **1b**; 0.64 (2e), **1c**; 0.51, 0.75, **1d**; 0.68 (2e), **1e**; 0.91 (irrev.), **1f**; 0.57, 0.76, **2a**; 0.48, 0.64, **2b**; 0.52, 0.65; **2c**; 0.40, 0.63V vs. SCE.



Reference

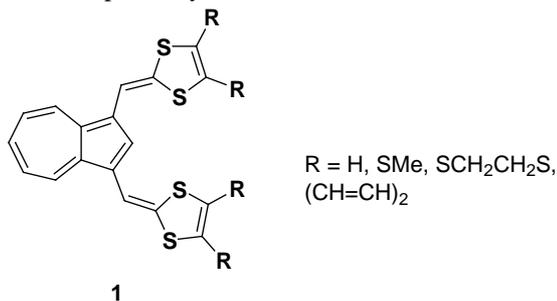
1) Y. Yamashita, M. Tomura, M. B. Zaman and K. Imaeda, *Chem. Commun.* 1657 (1998).

VIII-C-2 Preparation, Structure, and Properties of 1,3-Bis(1,4-dithiafulven-6-yl)azulenes

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FUJIMORI, Kunihide¹
(¹Shinshu Univ.)

Novel bis(1,3-dithiole) electron donors **1** containing an azulene spacer unit were prepared from 1,3-diformylazulene using a Wittig-Horner reaction in 20–85% yields. The first oxidation potentials of **1** are lower than that of TTF, indicating that they are stronger donors than TTF as predicted by the PM3 calculations. In addition to the oxidation waves, they show an irreversible reduction peak at *ca.* –1.4 V. This amphoteric nature is consistent with the absorption data where the longest absorption maxima are observed at 733–762 nm in dichloromethane. The structure features of a benzo-fused derivative were investigated by X-ray analysis. One of the 1,4-dithiafulvenyl groups and the azulene moiety are in almost coplanar, while the other one twists with a torsion angle of 20.8°. The spectroelectrochemical studies on the methylthio derivative reveals that the cation radical and dication state have the longest absorption maxima at 612 and 721 nm, respectively.

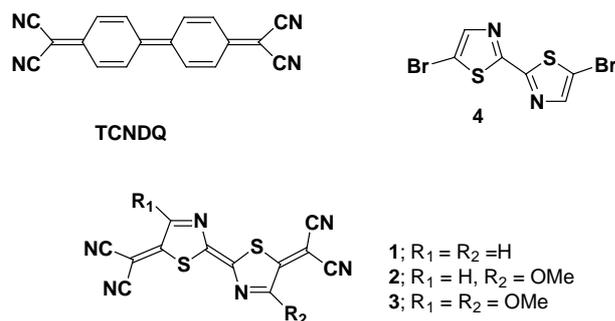


VIII-C-3 Synthesis and Characterization of Novel Strong Electron Acceptors: Bithiazole Analogues of Tetracyanodiphenylmethane (TCNDQ)

SUZUKI, Kazuharu; TOMURA, Masaaki;
TANAKA, Shoji; YAMASHITA, Yoshiro

Pyridine analogues of TCNQ are unstable due to the much stronger electron accepting ability. On the other hand, thiophene-TCNQs are generally weak electron acceptors due to the electron donating effect of the thiophene ring. Therefore, we have designed a new

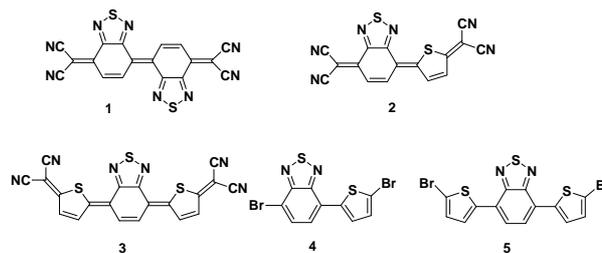
electron acceptor **1**, a TCNDQ analogue containing Nitrogen and Sulfur atoms in the skeleton. **1** was prepared by using Pd-catalyzed coupling reaction of dicyanomethanide to a dibromo precursor **4**. The new acceptor shows a strong electron accepting ability and small on-site Coulomb repulsion. The methoxy derivatives **2** and **3** were also obtained by substitution reaction of **1** with methanol. The reduction potentials of **2** and **3** are lower than that of **1** due to the electron donating methoxy substituents. The X-ray analysis of **1** and **2** has revealed the planar structures containing a double bond with *E*-configuration. The acceptors **1**–**3** have characteristic strong absorptions around 550 nm. **1** afforded several charge transfer complexes with electron donors such as TTF.



VIII-C-4 Heterocyclic TCNQ Analogues Containing Thiophene and Benzothiadiazole Units

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 recently prepared a TCNDQ derivative **1** containing fused thiadiazole rings. As an extension of this work, we have now prepared new π -extended electron acceptors **2** and **3** composed of benzothiadiazole and thiophene units. They were synthesized using the Pd catalyzed reaction of the corresponding dibromides **4** and **5** with malononitrile anion. The absorption maxima of **2** and **3** were observed at 524 and 635 nm in dichloromethane, respectively. **2** shows stepwise one-electron reduction waves at +0.07 and -0.17 V vs. SCE, while **3** shows a one-step two-electron reduction wave at +0.08 V vs. SCE. The values of the first reduction potentials are lower than that of TCNQ, indicating that they are not so strong acceptors. However, they are still stronger acceptors than the corresponding thiophene-TCNQ analogues. The X-ray analysis revealed that **2** has a planar geometry and the central double bond takes a *Z*-configuration. **2** gave various charge transfer complexes and anion radical salts. The Me_4P^+ salt exhibits a high conductivity of 8.4 Scm^{-1} .



VIII-C-5 Crystal Engineering in π -Overlapping Stacks: Unusual One- and/or Two-Dimensional Stacking of π -System in the Crystal Structure of the Cation Radical Salts of Tetrathiafulvalene Vinyllogues

TOMURA, Masaaki; YAMASHITA, Yoshiro

[*CrystEngComm* 14 (2000)]

One- and/or two-dimensional π -overlapping stacks have been found in the crystals of the cation radical salts of the tetrathiafulvalene vinyllogues **1** and **2** having *o*-substituted phenyl groups at the vinyl positions. The packing mode in the two-dimensional π -stacks could be modified depending on the counter anions. We have observed the pseudo two-dimensional stacking and the zigzag two-dimensional stacking with an angle of nearly 90° in the crystal structure of **1**- FeCl_4 and **1**- ReO_4 salts, respectively. In the case of **2**- PF_6 - $(\text{H}_2\text{O})_8$ salt, we have observed not the two-dimensional π - π overlapping stack found in the cation radical salts of **1**, but the one-dimensional stacking of π -system. The one-dimensional overlapping mode of **2** has brought a square grid-like structure (Figure 1) with a void in which eight water molecules are occupied. The 1,3-dithiole rings in **2** are unfavorable for π - π intermolecular interactions due to the less π -delocalization and steric interactions of the ethylenedithio parts compared to those in **1**. This seems to lead to the novel one-dimensional structure, not the two-dimensional one.

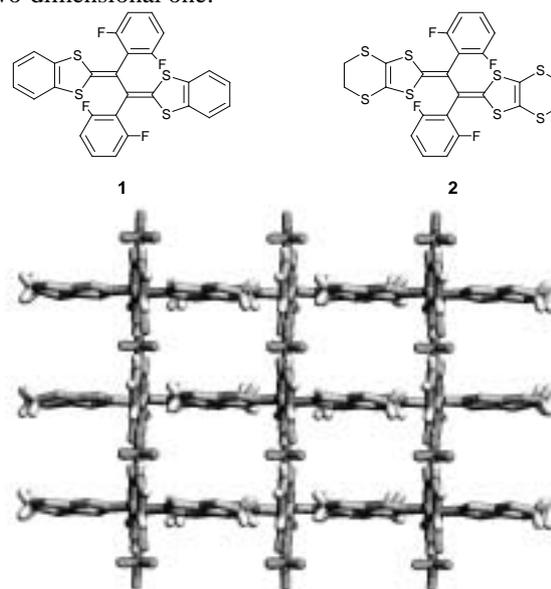


Figure 1. Crystal structure of **2**- PF_6 - $(\text{H}_2\text{O})_8$ salt viewed along the *c* axis. The water molecules are omitted for clarity.

VIII-C-6 One-Dimensional Supramolecular Tapes in the Co-Crystals of 2,5-Dibromo-3,6-dihydroxy-1,4-benzoquinone (Bromanilic Acid) with Heterocyclic Compounds Containing a Pyrazine Ring Unit

TOMURA, Masaaki; YAMASHITA, Yoshiro

[*CrystEngComm* 16 (2000)]

The design of new molecular architectures for crystal engineering has generated great interest in recent years. We have carried out co-crystallization of 2,5-dibromo-3,6-dihydroxy-1,4-benzoquinone (bromanilic acid) with heterocyclic aromatic compounds, phenazine, quinoxaline and pyrazine. The X-ray crystallographic analyses of the co-crystals suggest the supramolecular synthon formed with bromanilic acid and the heterocyclic compounds can yield the robust one-dimensional supramolecular tapes (Figure 1) and realize preserved interesting crystal structures.

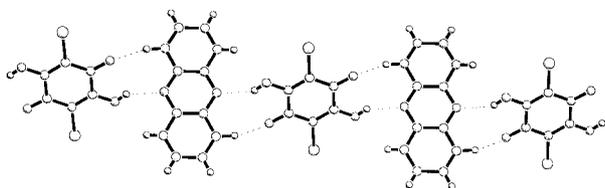


Figure 1. One-dimensional tape in the co-crystal of bromanilic acid with phenazine.

VIII-C-7 A Decamethylferrocene [Fe(C₅Me₅)₂] and Chloranilic Acid (CA) Complex with Hydrogen Bonded Supramolecular Structure between CA and H₂O

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(¹Dhaka Univ.)

[*CrystEngComm* 9 (1999)]

The chloranilic acid as acceptor (A) has been used to prepare crystalline materials with organometallic decamethylferrocene as donor (D). The structure was obtained by single crystal X-ray analysis and the stoichiometric ratio [D:A:H₂O = 1:1:1] was confirmed by elemental analysis. These analyses reveal the molecular complex as [Fe(C₅Me₅)₂]⁺[CA]⁻[H₂O]. The water molecules in this crystal act as cohesive elements by connecting the anions through O–H...O hydrogen bonds to form an infinite one-dimensional supramolecular structure along the b axis (Figure 1). This solid-state structural aspects of DA solids has interesting, highly charged ground states, which are not commonly observed in Fe(C₅Me₅)₂ complexes due to the paucity of stability and highly charged species.



Figure 1. View of the hydrogen bonded network with CA and H₂O molecule.

VIII-C-8 New Hydrogen Bond Donor-Acceptor Pairs between Dipyriddylacetylenes and 2,5-Dichloro-3,6-dihydroxy-1,4-benzoquinone

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

[*Org. Lett.* 2, 273 (2000)]

The crystalline donor-acceptor hydrogen bonding complexes between 2,5-chloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid, H₂CA) and dipyriddylacetylenes (DPA) [2,2'-DPA, 3,3'-DPA and 4,4'-DPA] were prepared and crystal structures were revealed by X-ray analysis. The structures of the complexes are formed by intermolecular hydrogen bonding interactions and demonstrate three beautiful supramolecular architectures based on a new common supramolecular synthon (Figure 1), which allows controlling the crystal structures, ionicity and stacking arrangements.

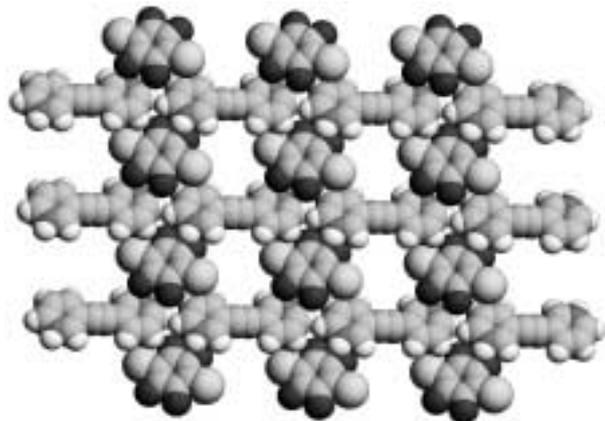


Figure 1. Square grids structure of [CA]²⁻[3,3'-H₂DPA]²⁺·(H₂O)_{3,3} complex. The water molecules are omitted for clarity.

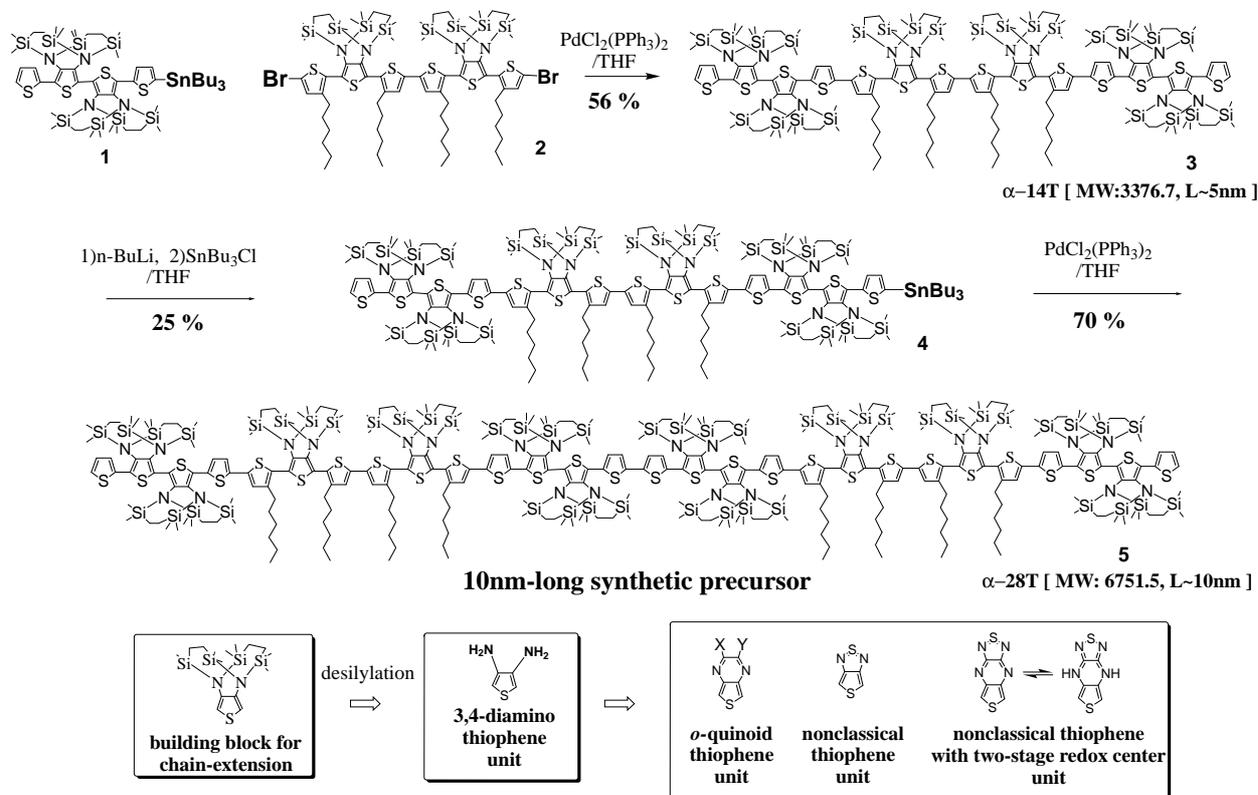
VIII-C-9 Novel Synthetic Approach to 5–10 nm Long Functionalized Oligothiophenes

TANAKA, Shoji ; YAMASHITA, Yoshiro

The development of precisely-defined oligomers with extended π -conjugation length comparable to the inter-electrode gap currently made by nano-patterning techniques (5–10 nm gap) has generated a great deal of interest. The reason for this is that highly oligomers of this class will become an important tool for providing specific information on the parameters controlling the long-distance electron-tunneling through a single molecular wire. Here we will report a new synthetic approach to a series of precisely defined 5–10 nm long oligothiophenes, using N-silyl-protected 3,4-

diaminothiophene as a key building unit. Scheme 1 shows the synthetic pathways for α -14T (**3**: $l \sim 5$ nm) and α -28T (**5**: $l \sim 10$ nm) derivatives. Purification of all oligomers (**1–5**) was achieved by preparative gel permeation chromatography, and the purity was clearly revealed by MALDI-TOF mass spectrometry in the

positive ion and linear detection mode using dithranol as matrix. The desilylation and further chemical modifications of the N-silyl-protected 3,4-diaminothiophene moieties of the obtained oligomers will afford various types of 5–10 nm long functionalized oligomers.



Scheme 1.