21-st Century COE — Kyoto University Alliance for Chemistry

21世紀COE 京都大学化学連携研究教育拠点

Fabrication of New Materials

新規機能性物質の創製

One-day International Workshop

Date: March 6 (Thursday), 2003
Venue: Shiran Kaikan (芝蘭会館 http://www.shirankai.or.jp/facilities/access/index.html)

10:00 - 10:05 Opening Address (Hideki Yamochi)

<< Thin Films >> 10:05 - 10:50 Dr. Adam H. Tracz (Polish Academy of Science)
Crystallization in situ in Polymer Matrix - Towards Fabrication of Applicable Materials based on Organic Conductors and Superconductors

10:50 - 11:20 Dr. Hitoshi Ohnuki (Tokyo University of Mercantile Marine)
Recent Progress in Metallic Langmuir-Blodgett Films based on BEDO-TTF and Fatty Acid

11:20 - 11: 50 Dr. Tatsuo Hasegawa
(National Institute of Advanced Industrial Science and Technology (AIST))
Ambipolar Field Effect Transistors based on Charge-Transfer Crystals with Strongly Correlated Charge Gaps

((Lunch))

<< From Physics >>

13:15 - 13:45 Professor Hiroshi Ito (Nagoya University)
Our Strategies to Develop the Functional Organic Materials

13:45 - 14:15 Professor Hideki Miyaji (Kyoto University)
Crystallization of Polymers –Morphology and Growth Rate–

14:15 - 14:45 Professor Tadaoki Mitani
(Japan Advanced Institute of Science and Technology)
A New Approach to Electronic Devices from Soft Matter Science

((Break))

<< Low Molecular Weight Materials >>

15:15 - 15:45 Professor Koichiro Tanaka (Kyoto University)
Local structure of the photo-induced phase in Fe-spin-crossover system

15:45 - 16:30 Professor Lahcene Ouahab (University of Rennes 1, France)
Conducting Charge-Transfer Complexes having Magnetic Counter Components and the Strategies to Effect the Interplay between them

((Short Break))

16:40 - 17:10 Dr. Kazuo Takimiya (Hiroshima University)
Is Selenium a Good Ingredient for Electronic Molecular Materials?

17:10 - 17:40 Dr. Olga Drozdova
(Kyoto University, Institute for Molecular Science)
Phase Transformation and Optical Properties of κ and β'' Phase of BEDO-TTF Charge Transfer Salts with $CF_3SO_3^-$

17:40 - 17:50 Closing Remarks (Gunzi Saito)

Supported by
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問合せ先：京都大学大学院理学研究科化学専攻 矢持 秀起 ((075)753-4036, yamochi@kuchem.kyoto-u.ac.jp)

Crystallization *in situ* in polymer matrix- towards fabrication of applicable materials based on organic conductors and superconductors.

A.Tracz

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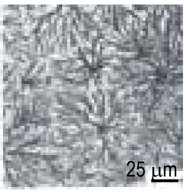
Small size and poor mechanical properties of organic low molecular weight organic conductors and superconductors seriously limits the possibility of their application. Elaboration of simple methods of obtaining these materials in a form more applicable than tiny crystals is therefore of a great importance.

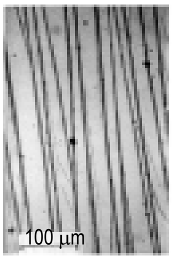
In this lecture various methods of preparation and properties of micro-crystalline networks of organic conductors and superconductors formed by *in situ* crystallization in polymer solution will be reviewed and discussed.

The basic method of obtaining polymer films showing high, isotropic conductivity using a small amount of the CT complex (~ 1 wt. %) is called *reticulate doping* [1]. According to this method the CT complex, dissolved in a polymer solution, crystallizes *in situ* during film casting. Isotropic conductivity of films results from the isotropic network formed of whiskers or dendritic CT complex micro-crystals grown under non-equilibrium conditions during solvent evaporation [2].

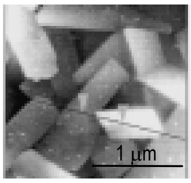


Modification of the *reticulate doping* method so called *zone casting technique* allows the preparation of films showing highly anisotropic electrical and optical properties owing to unidirectional growth of micro-crystals [3] . Amorphous or semicrystalline (e.g. polycarbonate or polypropylene) polymers can be used.

The above two methods were successfully applied for different 1-D organic conductors e.g. tetrathiatetracene-tetracyanoquinodimethane (TTT-TCNQ).



Two step reticulate doping technique allows the formation of the CT complex micro-crystals within a thin surface layer of the polymer film and thus the material exhibiting the surface conductivity can be obtained [4]. This method has been successfully applied to the important class of 2-D conductors: salts of bis(ethylenediothio)-tetrathiafulvalene) (ET) and bis(ethylenedioxy)-tetrathiafulvalene (BO). Flexible polymer films showing metallic conductivity were obtained using bromine or iodine ET and BO salts [5,6]**.** Characteristic feature of the obtained surface conducting films of ET or BO polyidides is possibility of their further transformation in order to change their properties**.** After annealing the network of α-$(ET)_2I_3$ micro-crystals formed within the surface of polycarbonate films can be converted to the network of α_T-$(ET)_2I_3$; thus polymer films showing an onset to superconductivity below 5K were obtained [5]. The role of the polymer matrix in superconductivity of the systems will be emphasized [7]. Special attention will be paid to the transformations of the micro-crystalline networks by anion exchange (e.g. by intercalation). The latter allows the preparation of transparent colorless films showing metallic conductivity [8].



References.

1. J.K.Jeszka, J.Ulanski, M.Kryszewski, *Nature* 298, 390 (1981)
2. A.Tracz, M. Kryszewski, *Makromol. Chem. Suppl.* 15, 219 (1989)
3. A.Tracz, E.El Shafee, J.Ulanski, J.K.Jeszka, M.Kryszewski, *Synthetic Metals* 97,175 (1990)
4. J.K.Jeszka, A.Tracz, *Polym. Adv.Technol.,* **3**, 139 (1992)
5. E.E. Laukhina , et al. *Synth. Met.,* 69, 797 (1995).
6. S. Horiuchi, H. Yamochi , G. Saito, J.K.Jeszka , A.Tracz , A.Sroczyńska , J.Ulanski, *Mol. Cryst. Liq. Cryst.,* 296, 365 (1997).
7. A. Tracz, *Synthetic Metals* 123 477 (2001)
8. A.Tracz, *J. Appl. Polym. Sci.*, 86, 1465 (2002)

Recent progress in metallic Langmuir-Blodgett films based on BEDO-TTF and fatty acid

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Abstract

A simple method of spreading the mixed chloroform solution of BEDO-TTF and stearic acid provides a metallic Langmuir (L) film on the water surface. Also, the transferred LB films onto a substrate show extremely high d.c. conductivity (80 S/cm at room temperature) together with a stable metallic conducting state down to low temperature ($T \geq 110$ K). These LB films can be useful for the molecular device application.

In the past few years, we have investigated the physical properties of the L film on the water surface and LB films on a substrate, and we have found unusual aspects of these films :

- On the water surface, a creation of small islands is occurred in the first stage, and then a homogeneous L film is formed by coalescence of the islands when the surface area is decreased. In both the islands and the L film, the existence of metallic state was confirmed by optical studies.
- The carboxyl groups of fatty acid act as the counter anions to BEDO-TTF donor molecules. They form hydrogen-bonded carboxylate layer of $(\text{R-COO}\cdots\text{H}\cdots\text{OOC-R})^-$ in the LB films [1]. The detail chemical reactions occurring at the water surface were estimated from the pH and atmosphere dependencies.
- Exposure to UV light causes a transformation of the LB film character from metallic into semiconductive. The transformation is due to a loss of the long range order requiring metallic conduction in the film plane [2]. The phenomena may be useful for processing the LB films to fabricate organic based electronic devices.

References

[1] H. Ohnuki, Y. Ishizaki, M. Suzuki, B. Desbat, P. Delhaes, M. Giffard, T. Imakubo, G. Mabon, and M. Izumi, Materials Science and Engineering C 22, 227 (2002).

[2] Y. Ishizaki, T. Ida, V. M. Yarsev, H. Ohnuki, T. Imakubo, and M. Izumi, Synthetic Metals, in press.

Ambipolar field-effect transistors on charge-transfer crystals with strongly correlated charge gaps

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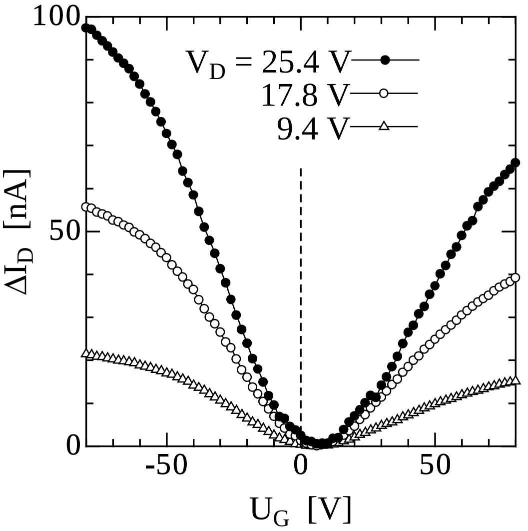
We report ambipolar operations of field-effect transistors (FET) based on organic single crystals of quasi-one-dimensional (Q1D) Mott-Hubbard insulator, (BEDT-TTF)(F_2TCNQ) [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene, F_2TCNQ = difluorotetracyanoquinodimethane]. Vapor phase polymerization of organic diradicals (known as "Parylene" coating) was utilized to deposit gate dielectric layers in the fabrication of field-effect device structures. Since the standard FET equations for unipolar devices were found to be inapplicable to the observed characteristics, we established and utilized symmetric-gate ambipolar FET formula (right panel of the figure) in consideration of the device symmetry of triode FET structures. Fundamental features of the observed Mott insulator FET characteristics, shown in the figure, were well described on this model, though the deviation became prominent at low temperature, which could be ascribed to the interfacial potential effect.



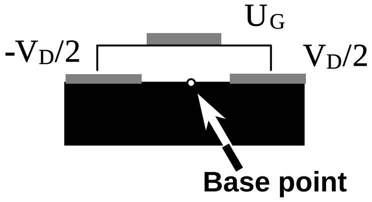


Figure
Transfer characteristics of (BEDT-TTF)(F_2TCNQ) single-crystal MIS-FET at 40K (left), measured in the symmetric-gate configuration, as schematically show in the right panel.

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Our Strategies to Develop Functional Organic Materials

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Our research group studies conducting organic materials with use of following strategies and methods to control electronic states and develop functional materials.

1. Field effect doping

Field effect doping attracts great attention in order to control carrier doping. We have developed Al_2O_3 rf-sputtered films having dielectric constant of 7.3 and breakdown voltage of more than 12 MV/cm. Using this film as gate insulator we fabricated a field effect transistor (FET) on which regioregular poly(3-hexylthiophene) was cast from chloroform solution. The source and drain I-V characteristics at highest gate voltage of -160 V corresponds to an induced carrier density up to 7×10^{12} cm^{-2} with hole mobility of 8×10^{-3} cm^2/Vs. By cooling down to 80 K, induced carrier density decreases by one, and mobility decreases by two orders of magnitude.

2. Unidirectional compression

Unidirectional compression is a useful technique to study electronic phase transitions of low-dimensional materials. For the superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, we observe increase of T_c under compression along c-axis at 1 kbar, correlated with the enhancement of the resistance hump at 90 K. Phase transitions near 210 K between averaged and mixed valence states of Pt-Pt-I chain of the halogen-bridged binuclear metal complex Pt_2(n-BuCS$_2$)$_4$I can be tuned by unidirectional compression parallel and perpendicular to the chain.

3. Combination of functional molecules

Cooperation of functional molecules creates new functions. BEDT-TTF salts having Fe and Mn ions in the counter anion are studied by transport and magnetic measurements in search of π-d interaction. Mixing fullerenes into conjugated polymers facilitates charge separation upon light irradiation and enhances LESR and photoconductivity due to polaron formation.

4. Separating functional moiety with alkyl chains

Conducting and magnetic properties can be tuned by separating the functional moiety with insulating alkyl chains. Studies on conducting BO-fatty acid LB films, regioregular poly(3-alkylthiophene)s, and halogen-bridged binuclear metal complexes Pt_2(alkyl-CS$_2$)$_4$I having different alkyl chains length are underway.

Polymer Crystallization -Morphology and Growth Rate-

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For polymers as well as low molecular weight materials, crystallization mechanisms have been investigated through the morphology and growth rate of crystals. Polymers crystallizes usually to form thin plates (lamella) as thin as 10 nm with the chain axis perpendicular to the lamellar surface. Hence the thickness of the lamellar crystals is the most important quantity describing the morphology specific to polymer crystals. The thickness l decreases with supercooling [1],

$$l = \frac{2\sigma_e}{\Delta g} + \delta l, \qquad (1)$$

where σ_e is the surface free energy of lamellar surface, Δg is the difference of free energies between crystal and liquid, namely the driving force for crystallization, which is proportional to supercooling ΔT at low supercoolings, and δl is a constant. Since the first term in Eqn. (1) is an equilibrium thickness, the lamellar thickness of a growing crystal must be thicker by δl than that in equilibrium. Another feature specific to polymer crystallization is the ΔT dependence of growth rate of crystals. The dependence is independent of the morphology of crystals; for both faceted and rounded crystals (Figure 1), the growth rate G observed can be expressed as follows,

$$G = G_0 \exp\{-U / R(T - T_v)\} \exp(-K / T\Delta T) \qquad (2)$$

where G_0 is a factor almost independent of ΔT, the second factor is the Vogel-Fulcher factor for viscosity, and the last is the surface kinetic factor derived from the nucleation theory of Lauritzen-Hoffman [1].

In the present workshop, we firstly review the experimental evidences of morphology and growth rate at high supercoolings for isotactic polystyrene and at high crystallization temperatures for isotactic poly-4-methylpentene-1. Secondly, crystallization in nm-thick films of polystyrene is shown [2]. On the basis of the traditional theory of crystal growth, we demonstrate the specific feature of the morphology and growth rate observed in polymer crystallization. Unifying nucleation regime and rough surface regime in the light of Eqn. (1), we propose a crystallization kinetics [4] taking account of the entropic barrier which was originally proposed by Sadler [3] for polymer crystallization.

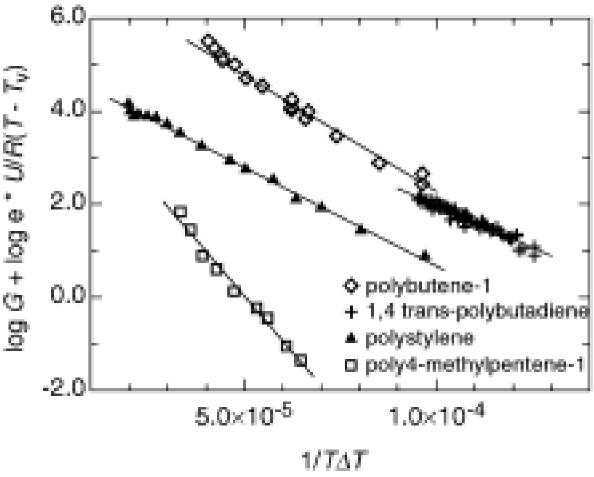


Figure 1. The supercooling (ΔT) dependence of growth rate (G): The plot of {log G + log(e) $U/R(T - T_v)$} vs. $1/T\Delta T$.

References

[1] . Hoffman, J.D.; Davis,G.T. and Lauritzen, Jr. J.I. The Rate of Crystallization of linear Polymers with Chain Folding. In *Treatise on Solid State Chemistry*; Plenum Press; New York, 1976;Vol.3, 497-614.

[2] Taguchi, K.; Miyaji, H.; Izumi, K.; Hoshino, A.; Miyamoto, Y.; Kokawa, R. Crystal Growth of Isotactic Polystyrene in Ultrathin Films: Film Thickness Dependence. J. Macromol. Sci. Phys.**2002**, B41, 1033-1042

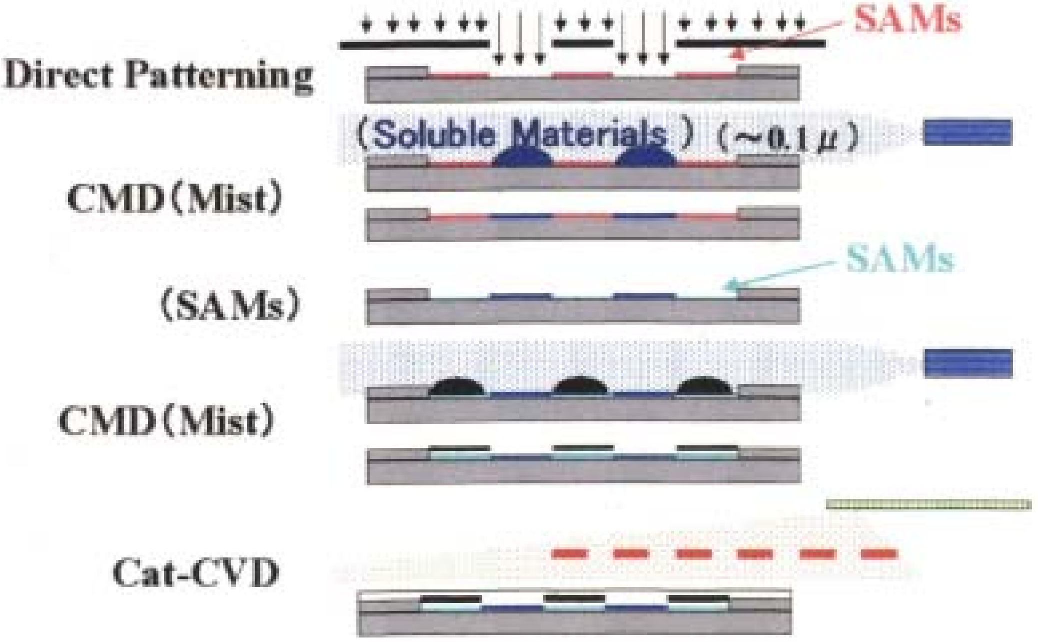
[3] Sadler, D.M. Roughness of Crystal Growth Faces of Polymer Crystals: Evidence from Morphology and Implications for Growth Mechanisms and Types of Folding. Polymer **1983,** 24, 1401-1409.

[4] Miyaji, H. ; Miyamoto, Y. ; Taguchi, Ken ; Hoshino, A. ; Yamashita, M. ; Sawanobori, O. ; Toda, A. Morphology, Growth Rate and Lamellar Thickness of Polymer Crystals. J. Macromol. Sci. Phys.**2003** (in press).

A New Approach to Electronic Devices from Soft Matter Science

T. Mitani (JAIST)

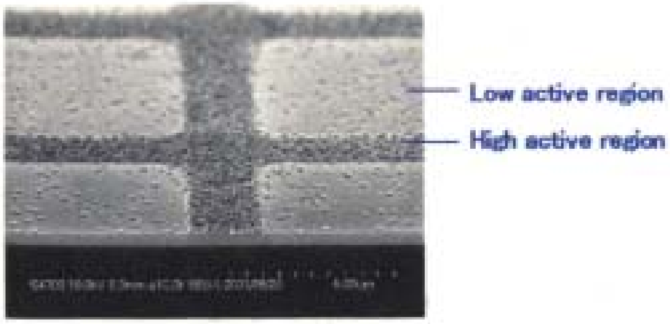
Processing of LSI System



Area-selective Deposition of nano-materials

CVD patterning of Cu

((trimethyle vinyl silyl) hexaflurro acetyl acetonato Cu(I))



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Local structure of the photo-induced phase in Fe-spin-crossover system

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Recently, cooperative phenomena such as a photo-induced phase transition (PIPT) triggered by electronic excitation attract much attention, offering promising opportunities, in materials science, to find a variety of novel physical properties and functions.[1], [Fe II (2-pic)$_3$]Cl$_2$EtOH (2-pic=2-aminomethyl-pyridine, hereafter abbreviated as Fepic) is a typical spin-crossover complex which shows a thermally induced first-order phase transition from a low-spin (LS, S=0) to a high spin (HS, S=2) state.. In the spin-crossover complex, the cooperative spin coupling and lattice interaction induce first-order phase transitions at critical temperatures around 120 K, a photo-induced LS to HS phase transition in Fe-pic has been observed, which exhibited nonlinear characteristics such as threshold light intensity, incubation period and phase separation [2]. We recently found broken symmetry in the photo-induced phase below 40 K using resonant Raman spectroscopy [3]. The result means that PIHS may not be the same with thermally induced HS phase that is quenched into low temperature. Symmetry breaking could occur since structural relaxation of excited state may proceed with symmetric and non-symmetric normal coordinates. We made an in-situ x-ray absorption spectroscopy (XAS) study of Fe-pic under light irradiation at low temperature to probe the local structure of photo-induced phase and nature of symmetry breaking. We found that the metal-ligand distance undergoes a remarkable change upon the diamagnetic (S=0) to paramagnetic (S=2) transformation induced by visible light (532nm). Indication of symmetry breaking was observed not in the nearest neighbor but in the next-nearest metal-ligand correlation. The photo-induced strained ligand molecule is discriminated from the thermally induced relaxed state as shown in Fig.1. Broken symmetry observed in the photo-induced phase is ascribed to the strained ligand molecule.

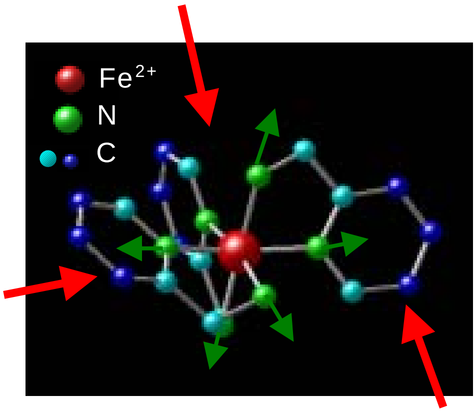

Fig.1 Schematic picture of the strained ligand molecule in the photo-induced state.

[1]. Photoinduced Phase Transitions ed. by Nasu, K., Phase Transition vol. 74 (2001), Gordon and Breach Publishers, Malasia.
[2]. Ogawa, Y., Koshihara, S., Koshino, K., Ogawa, T., Urano, C. and Takagi, H., Phys. Rev. Lett. 84, 3181-3184 (2000).
[3]. Tayagaki, T. and Tanaka, K., Phys. Rev. Lett. 86, 2886-2889 (2001).

Conducting charge-transfer complexes having magnetic counter components and the strategies to effect the interplay between them.

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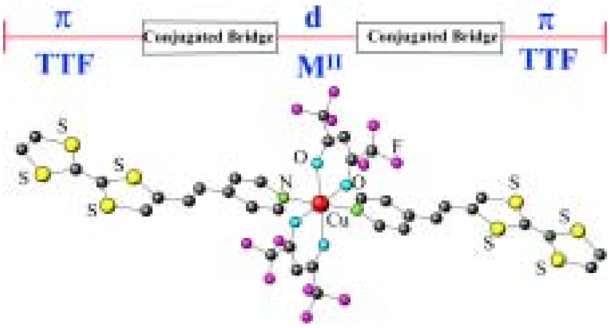
In the last few years an increased interest was devoted to hybrid organic-inorganic multifunctional molecular materials aiming to obtain synergy between two physical properties. For the particular class of materials combining electrical conductivity and magnetic interactions, it is hopped to achieve magnetic coupling between the localized spin of the inorganic part through the mobile electrons of the organic part via the so-called π-d interactions. In order to match this mechanism, we are investigating in our group materials where the two systems interact through space or through a covalent link. We will present in this contribution some of our results according to these ideas i.e. (i) we discuss materials based on functionalized organic donors and paramagnetic coordination complexes with π ligands such as $M^{III}(L)X_4$ [M= Fe, Cr; X= NCS^- or CN^-], the two components might interact through S•••S or -N•••I- contacts and π-π overlaps; in this context materials with canted weak ferromagnetism were obtained. (ii) We present novel paramagnetic coordination complexes [1] containing TTF's as ligands (see figure) as well as their radical cation salts [2]. In these molecular bricks, namely $[M(hfac)_2](TTF\text{-}py)_2$, M= Cu^{II}, Mn^{II}, hfac= hexafluoroacetylacetonate; TTF-py= 4-(2-tetrathiafulvalenyl-ethenyl)pyridine the conducting and the magnetic systems are covalently linked through a conjugated bridge. This might constitute a new approach in the realization of interations between conducting electrons and localized spins.



[1] F. Iwahori, L. Ouahab, S. Golhen, J.P. Sutter, R. Carlier, *Inorg. Chem.*, 2001, *40*, 6541

[2] F. Setifi, L. Ouahab, S. Golhen, Y. Yoshida, G. Saito, *Inorg. Chem.*, 2003, *in press*

Is Selenium a Good Ingredient for Electronic Molecular Materials?

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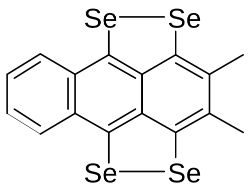
For the development of electronic molecular materials e.g. organic metals, superconductors, and organic field-effect-transistors, sulfur-containing molecules such as tetrathiafulvalenes (TTFs) and thiophene derivatives have played an important role. Substitution of sulfur atoms in such molecules by selenium atoms has been regarded as an effective way to improve the physical properties owing to enhanced intermolecular interaction through nonbonded Se–Se contacts in the solid state. In general, however, difficulties in synthesizing selenium-containing molecules compared to the sulfur counterparts are often problematic.

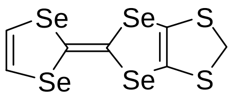
In the last decade, the author has been engaged in synthetic studies of selenium-containing molecules and successfully developed interesting systems as follows:

1. Dimethylteteraselenoanthracene (DMTSA) producing highly conducting organic metal with 1:1 donor/anion ratio.[1]
2. Methylenedithiotetraselenafulvalene (MDT-TSF) and related compounds: novel selenium analogues of TTF affording unique organic superconductors with an incommensurate anion lattice.[2]
3. Oligoselenophenes up to the pentamer: structurally well-defined selenophene oligomers showing high filed-effect mobilities.[3]

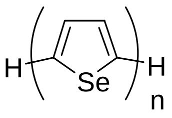
With the synthetic chemistry and unique properties of these molecules, the potential of selenium-containing molecules in this field will be discussed.



DMTSA



MDT-TSF



oligoselenophenes (n = 3–5)

References

1. K. Takimiya, A. Ohnishi, T. Otsubo, F. Ogura, K. Kawabata, K. Tanaka, M. Mizutani, *Bull. Chem. Soc. Jpn*. **1994**, *67*, 766.
2. K. Takimiya, Y. Kataoka, Y. Aso, T. Otsubo, H. Fukuoka, S. Yamanaka, *Angew. Chem., Int. Ed.* **2001**, *40*, 1122.
3. Y. Kunugi, K. Takimiya, K. Yamane, K. Yamashita, Y. Aso, T. Otsubo, *Chem. Mater*. **2003**, *15*, 6.

Phase transformation and optical properties of κ and β'' phase of BEDO-TTF charge transfer salts with $CF_3SO_3^-$

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BEDO-TTF is an electron donor molecule, which in complexes with various acceptors produced a large number of stable organic metals. The major packing motif was that of β'' type promoting a large 2D π-orbital overlap. However, from the point of view of synthesizing novel organic superconductors the κ type has shown to be effective in the complexes of a related donor BEDT-TTF. So far only one κ type salt was reported among BEDO-TTF complexes, κ-(BEDO-TTF)$_2$CF$_3$SO$_3$, which was not superconducting at AP [1]. Besides the κ type, the same synthetic procedure gave a different salt, β''-(BEDO-TTF)$_2$CF$_3$SO$_3$(C$_4$H$_8$O)$_{0.5}$ with a comparable to the κ type dc conductivity [1]. In this work, we studied IR reflectivity, Raman spectra, and electrical conductivity under high pressure of β'' and κ type BEDO-TTF salts with $CF_3SO_3^-$.

(1) Electrical resistivity under high pressure:

- β''-(BEDO-TTF)$_2$CF$_3$SO$_3$(C$_4$H$_8$O)$_{0.5}$ was found to be metallic at all pressures up to 1 GPa, no phase transition around 250 K (as reported in [1]);
- κ-(BEDO-TTF)$_2$CF$_3$SO$_3$ showed a “hump” typical of κ-BEDT-TTF salts, which disappeared at pressures above 600 MPa and the sample became metallic with positive curvature (dR/dT). No superconductivity was found down to the lowest temperature of PPMS.

(2) IR reflectivity

- κ-(BEDO-TTF)$_2$CF$_3$SO$_3$ shows monotonous growth of the Drude term in the reflectivity spectra down to 5.2 K suggesting metallic, gapless nature of the compound.
- During the measurement we have noticed a significant change of the IR reflectivity of the samples of β'' type under the influence of vacuum. Further investigations found that β'' phase undergoes an irreversible transformation into a κ type while kept under vacuum of ~10^{-3} Pa at 293 K for 12 hours and then at 343 K for 2 hours. Further treatment did not induce any more change in the optical spectra. Though the newly obtained structure was inevitably disordered, it possessed its own well-defined optical axes with anisotropy in both electronic and vibrational spectra resembling that found in κ-(BEDO-TTF)$_2$CF$_3$SO$_3$. This suggests existence of a long order in the molecular (BEDO-TTF) orientation similar to that in κ-phase.

Ref.: [1] M. Fettouhi, L. Ouahab, D. Serhani, J.-M. Fabre, L. Ducasse, J. Amiell, R. Canet, P. Delhaes. J. Mater. Chem. 3 (1993) 1101-1107.