RESEARCH ACTIVITIES IV
Department of Molecular Assemblies

IV-A Spectroscopic Study of Charge Carriers in Organic Conductors

The low-frequency reflectivity of an organic conductor provides us with a wealth of information on the nature of charge carriers. For instance, the anisotropy of a band structure, bandwidth, effect of electron-electron correlation, and electron-molecular vibration (*e-mv*) coupling parameters can be extracted from the analysis of the reflectivity or optical conductivity curve. We are investigating the polarized reflection spectra of various organic conductors in the spectral region of 50–33000 cm^{-1} and in the temperature range of 6–300 K. Usually the molecular vibrations (local phonons) are screened by strong electronic transition by charge carriers. Therefore, few local phonon bands are detected in the reflection spectrum. In this sense, the Raman spectroscopy is a complementary method to reflection spectroscopy for understanding molecular vibrations in a metallic state. Since some molecules have charge-sensitive vibrational modes, the Raman spectroscopic method is a powerful tool to detect the site-charge distribution (oxidation state of molecule). We are investigating the charge ordering (CO) phenomena in organic conductors using the technique of infrared and Raman spectroscopy. In the organic charge-transfer salts, CO is originated from the localization of the charge carriers. Since the charge carriers in organic crystal is located at the boundary between localized and extended (delocalized) states, CO will be widely found through the phase transition. The charge ordering was first found in inorganic narrow-band systems such as copper, manganese, and vanadium oxides. Recently, CO has been found in several organic conductors, and the electronic phase diagrams of typical organic conductors are re-examined taking CO into account. The CO state is drawing attention, since CO is theoretically considered as being related to the pairing mechanism in superconductivity. The Raman and infrared spectra change dramatically at the CO phase-transition temperature, since CO is accompanied by an inhomogeneous charge distribution. Our goal is the complete understanding of the CO phase transition through the interpretation of the vibrational spectra, and the drawing of a *P-T* phase diagram.

IV-A-1 Charge-Ordering Transition in Two Crystal Modifications of θ-(BEDT-TTF)$_2$TlZn(SCN)$_4$ Studied by Vibrational Spectroscopy

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[*Phys. Rev. B* submitted]

We are systematically investigating the phase diagram of θ-(BEDT-TTF)$_2$MM'(SCN)$_4$ (M = Tl, Rb, Cs; M' = Zn, Co). Subsequently to the thorough study of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$, we investigated the phase transitions of the orthorhombic and monoclinic modifications of θ-(BEDT-TTF)$_2$TlZn(SCN)$_4$ by the method of infrared and Raman spectroscopy with aid of electrical resistivity and x-diffraction experiments. Both modifications showed the phase transitions, which were accompanied by resistivity jumps, structural changes, and charge separation. The temperature dependence of vibrational spectra of orthorhombic salt showed abrupt peak splitting at around 240 K. Below this temperature, the polarization dependence of the infrared and Raman bands of the orthorhombic modification agreed with that of the low-temperature phase of θ-(BEDT-TTF)$_2$RbZn-(SCN)$_4$, which had been elucidated to have a horizontal-type charge-ordering pattern (Figure 1a). The monoclinic salt also showed a resistivity jump at around 165 K. Below this temperature, the polarization dependence of infrared and Raman spectra and the pattern of the satellite peaks in x-ray diffraction were very different from those of orthorhombic modification. Analyzing these results, we concluded that the pattern of the charge order was a diagonal stripe (Figure 1b). The spectral change at the phase transition was rather gradual compared with that of orthorhombic modification. The precursory change was observed in the Raman spectrum above 165 K. This precursor was interpreted as the fluctuation of the site-charge density, namely, the charge carriers move incoherently.

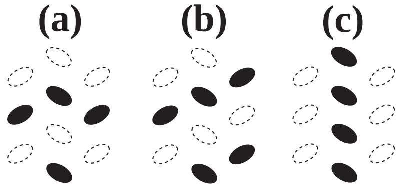

Figure 1. Schematic view of charge-ordered state in θ-type BEDT-TTF sals: (a) horizontal stripe, (b) diagonal stripe, and (c) vertical stripe. The ovals represent the arrangement of the BEDT-TTF molecules in a conducting layer. Above the phase transition temperature, the average charge (+0.5*e*/molecule) is homogeneously distributed at each site, whereas the charges are localized at the sites drawn by solid oval below the phase transition temperature.

IV-A-2 Dynamical Charge Localization in θ-(BEDT-TTF)$_2$MM'(SCN)$_4$ [M = Cs, Rb, Tl, M' = Zn,Co]

SUZUKI, Kenji[1]**; YAMAMOTO, Kaoru;**

YAKUSHI, Kyuya
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The high-temperature phase of θ-(BEDT-TTF)$_2$-MM'(SCN)$_4$ [M = Cs, Rb, Tl, M'=Zn, Co] (hereafter abbreviated as MM') exhibits an unusually broad Raman band. Although this phase is regarded as a metallic state, the temperature derivative of resistivity has a small negative value. The low-temperature phase has been characterized as a charge-ordered state, namely, the localized charge is ordered with a structural distortion. However, the nature of the high-temperature phase is not well understood. We found that the line shape of the Raman band of the charge-sensitive mode at room temperature changed systematically against the bandwidth. Figure 1a shows the line shapes of the Raman band of the charge-sensitive mode of CsZn, RbZn, and TlZn. As the high-pressure narrows the bandwidth in the θ-type BEDT-TTF salts, the various spectra are arranged in the descending sequence of bandwidth from the top to the bottom. In this spectral region, there are two charge-sensitive modes ν_2 and ν_3. We have experimentally and theoretically elucidated that ν_2 splits into two and the highest-frequency ν_3 among the split modes keeps the position, when the charge localization occurs. As shown in Figure 1a, the ν_2 band is broadened and split into two (shown by arrows), when the bandwidth is narrowed. We speculated that the systematic change of the line shape of the Raman band was ascribed to the hopping rate of the localized charge between the adjacent BEDT-TTF molecules. Figure 1b is the simulation of the linewidth based on the two-site motional-narrowing model. The agreement with the experimental results strongly suggests that the charge carrier in the high-temperature phase is not in a coherent state but is incoherently hopping between the adjacent sites in the time scale of a few ps. This state is regarded as a dynamically localized state of charge carrier. This interpretation is consistent with the non-metallic nature of the electrical resistivity.

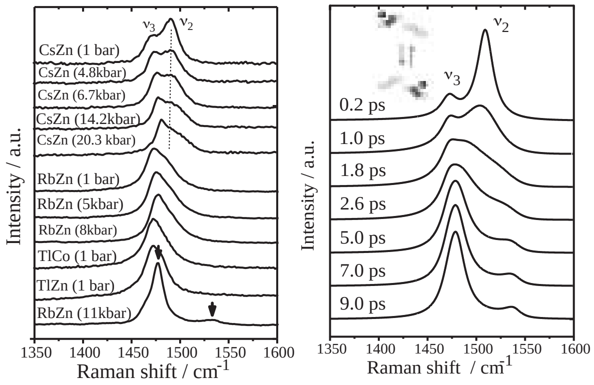

Figure 1. (a) Systematic change of the lineshape of the Raman band (λ_{ex} = 515 nm) of the title compounds at room temperature. The spectra are arranged in a descending order of bandwidth. (b) Raman spectra simulated by using a two-site motional-narrowing model. The time on each spectrum shows the hopping rate between the adjacent sites.

IV-A-3 Activation of Strong Overtone in the IR Spectrum of a Charge-Ordered Organic Conductor

YAMAMOTO, Kaoru; YAKUSHI, Kyuya

The infrared spectrum of charge ordered θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ exhibits a number of additional signals that are not present above the phase-transition temperature. The example of the additional signals is displayed by solid triangles of Figure 1a. Although the bandwidths of the activated signals seem to be of vibrational transitions, their frequencies are out of the characteristic range of ordinary vibrations. To understand the origin of these bands, we calculated the vibrational transition moment using a molecular dimer containing a single radical electron that is distributed asymmetrically as $M^{\rho+}–M^{(1-\rho)+}$. The vibrational transition moment is expressed by the series of the vibronic correction terms. Because the strongest newly activated signal (*ca.* 2750 cm^{-1}) is positioned around the twofold frequency of C=C stretching signal, we performed the numerical calculation including up to the second-order correction. We calculated the ratios of the oscillator strength of two overtones and one combination-tone to the vibronic fundamental. Figure 1b plots the ratios against the ionicity (ρ) at one site. This plot qualitatively explains that the overtones and combination tone are noticeable only when large charge disproportionation ($\rho > 0.8$) takes place.

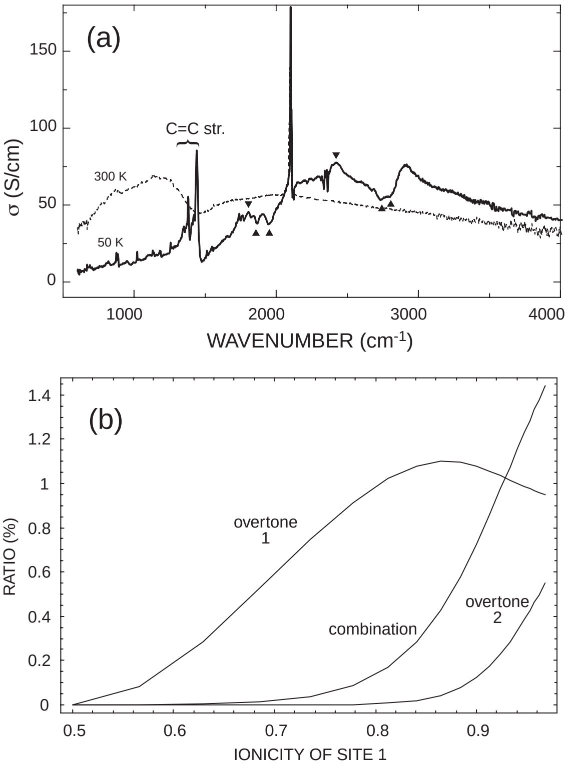

Figure 1. (a) Optical conductivity spectrum of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ above (300 K) and below (50 K) the phase transition temperature. The solid triangles show the vibronic overtones and combination tones. (b) Intensity ratios of overtones and combination tones to the fundamentals are plotted against the site charge (ρ).

IV-A-4 Charge Ordered State in θ-(BEDT-TTF)$_2$Cu$_2$(CN)[N(CN)$_2$]$_2$

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([1]Kyoto Univ.)

θ-type BEDT-TTF salts are systematically studied according to the dihedral angle (φ_d) defined from BEDT-TTF molecules in adjacent BEDT-TTF stacks. In the temperature dependence of electrical resistivity, a metal-insulator transition is observed for the most of θ-salts. With increasing φ_d, the transition temperature increases. This phenomenon can be interpreted from the narrow bandwidth due to the small transfer integral. Theoretical studies predict that these compounds fall down to the charge ordered state since Coulomb repulsions play an important role for such a narrow band system. Among numerous θ-salts, which has been synthesized so far, θ-(BEDT-TTF)$_2$Cu$_2$(CN)[N(CN)$_2$]$_2$ has the largest φ_d (~ 132°). We measured the temperature dependence of Raman spectra below 300 K, and analysed two kinds of C=C stretching modes abbreviated as ν_2 and ν_3. The ν_3 mode exhibited a factor group splitting with decreasing temperature. We were able to apply the factor group analysis exactly the same as those for θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$. This result implied that the system fell down to the horizontally charge-ordered state. Interestingly, the ν_2 mode showed a peak splitting even at 300 K, which is higher than the transition temperature in the resistivity measurement (~ 220 K). This result suggests that the charges are already dynamically localized and the localized charges are incoherently hopping between the adjacent sites at room temperature. We estimated the site charge (ρ) from the peak positions of ν_2. The estimated values were ~ $+0.8_5$ and ~ $+0.1_5$, which were found to be independent of φ_d. Among the four ν_3 modes, the ν_{3D} mode was observed in the lowest energy through an *e-mv* interaction. The peak position of this mode showed a blue shift with the increase of φ_d. This result was explained by the decrease of the transfer integrals along the *a* direction.

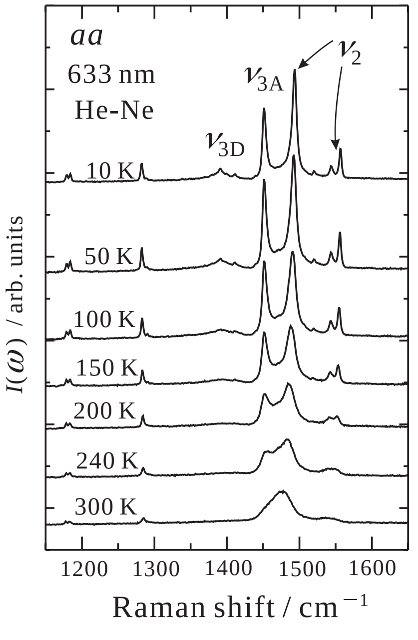

Figure 1. Temperature dependence of the Raman spectrum of θ-(BEDT-TTF)$_2$Cu$_2$(CN)[N(CN)$_2$]$_2$.

IV-A-5 Direct Evidence for the Inhomogeneous Charge Distributions and Charge Re-Distribution in β"-(ET)$_3$(ReO$_4$)$_2$

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The charge disproportionation in organic CT salt is drawing an attention since theoretical studies suggest the relation between charge fluctuation and pairing mechanism in superconductivity. An insulator-superconductor transition is observed for the several β"-type BEDT-TTF salts under the hydrostatic pressure or the ambient pressure. However, a few experimental studies were presented for the charge disproportionation in the insulating phase of BEDT-TTF salts. We measured the infrared and Raman spectra of β"-(BEDT-TTF)$_3$(ReO$_4$)$_2$ below 300 K. We analysed three kinds of C=C stretching modes abbreviated as ν_2, ν_{27} and ν_3. The ν_{27} mode shows triple peaks below 80 K, while ν_{27} exhibits a doublet above 81 K. The phase-transition temperature detected from the vibrational spectra agreed with those determined from the reflectivity and EPR experiments. In the low-temperature phase, the ν_2 mode was also observed as triple peaks. The site charges (ρ) estimated from the frequencies of ν_2 for non-equivalent BEDT-TTF were +0.2, $+0.8_5$ and $+0.9_5$. A mutual exclusion rule between the infrared and Raman spectra was broken for the three ν_3 modes. These results lead to the conclusion that an inversion center is lost below 80 K. This is in agreement with the result of the X-ray structural analysis solved at 22 K. The observed pattern of site charges in the unit cell was reproduced from the mean-field approximation of a Hubbard model. In the high temperature phase, the ν_2 mode was observed as doublets. The estimated ρ are $+0.7_3$ and $+0.5_3$. A mutual exclusion rule was found in the three ν_3 modes. These results imply that an inversion centre is kept above 81 K. This is also in agreement with the result from the X-ray structural analysis solved at 100 K. This inhomogeneous charge distribution above 81 K was reproduced from the mean-field calculation of the Hubbard model with a weak on-site Coulomb energy, where electron and hole pockets still exist in the semi-metallic band. The molecular arrangement slightly changed in this charge-ordering phase transition. This structural change brought about a re-distribution of the localized charge. It is interesting to note that the re-distribution of the charge accompanies the re-distribution of the transfer integrals.

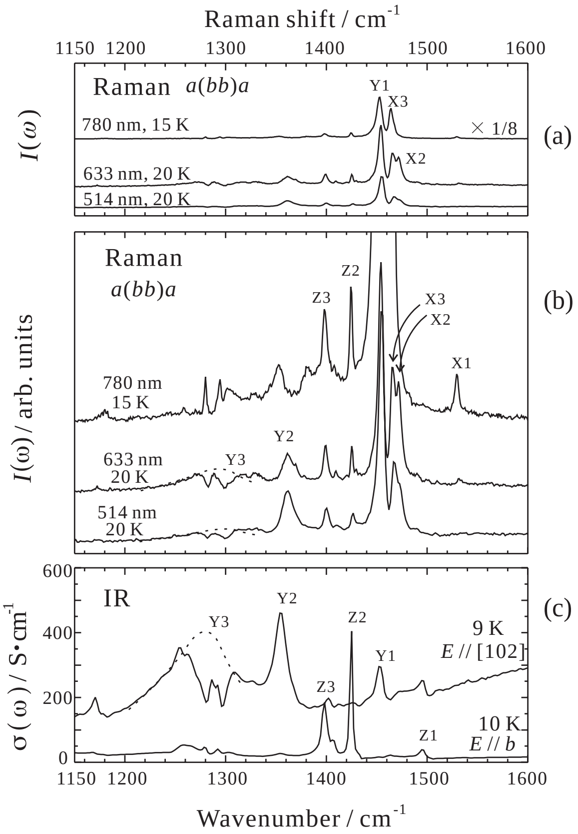

Figure 1. (a) and (b) Raman spectra at the lowest temperature we measured. X, Y and W correspond to the ν_2, ν_3 and ν_{27} modes. (c) Optical conductivity (IR) spectra. Z denotes the ν_{27} mode.

IV-A-6 Inhomogeneous Charge Distributions and Isotope Effect in β”-(BEDT-TTF)$_4$M(CN)$_4$H$_2$O (M = Ni, Pd, Pt) Group

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The charge disproportionation in organic CT salt is drawing attention since theoretical studies suggest the relation between charge fluctuation and pairing mechanism in superconductivity. Various studies have been concentrated on the θ-type BEDT-TTF salts. However, few studies have been presented for β”-type BEDT-TTF salts, although this family has a rich variety of electrical properties including superconductivity. The title compounds are 3/4-filled β”-salts. For M = Pd and Pt, superconductivities are observed under the hydrostatic pressures. No superconductivity is observed for M = Ni salt. However, resistivity curves for three compounds exhibit insulating behaviours under the ambient pressure below ~ 100 K. We studied temperature dependence of vibrational spectra under the ambient pressure. We analysed three C=C stretching modes abbreviated as ν_2, ν_{27} and ν_3. For M = Ni and Pd, ν_2 and ν_{27} have broad linewidth around 300 K. With decreasing temperature down to 10 K, both modes show peak splitting. This observation leads to an separation of charges. The separated site charges (ρ) are ~ +0.3 and ~ +0.7. Since more than two ν_3 modes are observed in the Raman spectra, the space group is changed from $P\bar{1}$ to $P1$ at low temperature. For M = Pt, ν_2 keeps a broad linewidth down to 10 K, but ν_{27} exhibits a peak splitting at 10 K. We also observed Raman spectra for the deuterium substituted M = Pt salt, where all the hydrogen atoms in BEDT-TTF were substituted by deuterium. Interestingly, the spectral shape becomes similar to that of M = Ni salt rather than that of M = Pt salt. Such a drastic isotope effect is firstly observed in β”-salts. Our results demonstrated that M = Pt salt was located at the region close to the phase boundary that separates the insulator, metal, and superconductor phases.

IV-A-7 Dynamical Fluctuation of Site-Charge Density in Metallic β”-(BEDT-TTF)(TCNQ)

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Charge disproportionation (CD) and charge ordering (CO) in organic conductors originate from the localization of charge carriers. CO has been investigated in the insulating states of several charge-transfer salts. We present dynamically fluctuating CD in the metal-like state of the title compound, which are investigated by means of infrared and Raman spectroscopy. β”-(BEDT-TTF)(TCNQ) newly synthesized by Yamamoto *et al.* consists of a segregated stack structure, where TCNQ and BEDT-TTF separately form uniform chains.$^{1),2)}$ This compound is metallic with three resistance anomalies at 175 K, 80 K, and 20 K. We measured the polarized Raman and infrared spectra. First we estimated the charge-transfer degree as 0.5 using the C=C stretching mode (ν_4) of TCNQ. All of the Raman bands of TCNQ are independent of temperature. However, the C=C stretching modes (ν_2 and ν_3) of BEDT-TTF show clear splitting, and the low-frequency component of ν_3 exhibits a broad vibronic feature. This finding indicates that the holes of BEDT-TTF are nearly localized, and thus CD arises near the room temperature. We theoretically investigated the frequency shift and Raman intensity of ν_2 and ν_3 using an asymmetric dimer model, and verified that this observation is consistent with the generation of CD. Very interestingly, the split bands of ν_2 merge into a single broad band, and the broad band is sharpened on lowering temperature. The same phenomenon is found in the infrared-active C=C stretching mode ν_{27} as shown in Figure 1. This temperature dependence is well reproduced by motional narrowing model. This finding implies that the holes in BEDT-TTF chain change the nature at low temperature.

References

1) H. M. Yamamoto, M. Hagiwara and R. Kato, *Synth. Met.* **133-134**, 449 (2003).

2) H. M. Yamamoto, N. Tajima, M. Hagiwara, R. Kato and J.-I. Yamaura, *Synth. Met.* **135-136**, 623–624 (2003).

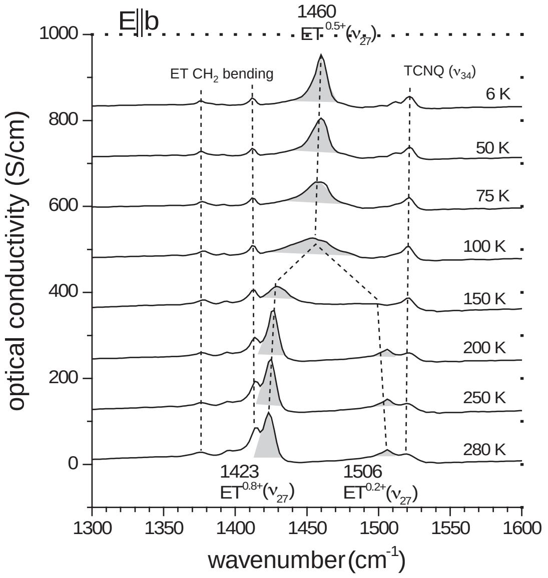

Figure 1. Temperature dependence of the infrared-active C=C stretching mode ν_{27}. The split bands merged at 100 K. This behavior was interpreted based on the motional narrowing model.

IV-A-8 Novel Type of 2k_F Bond-Charge-Density Wave in Quasi-One Dimensional 3/4 Filled (EDO-TTF)$_2$X (X = PF$_6$ and AsF$_6$)

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[*Phys. Rev. B* submitted]

Recently, charge ordering (CO) in organic charge transfer solids (CTS) has received considerable interest. In quasi-1D 1/4-filled organic CTS, a large on-site (U) and inter-site (V) Coulomb repulsion would cause, intuitively, the alternating (Wigner type) pattern of charge distribution '1010' corresponding to a 4k_F CDW. For V smaller than some critical V_c ~ 2t (t being the intra-stack transfer integral) the '0110' ground state (2k_F BCDW-I, Chart 1) can be found, while further small V would lead to 2k_F BCDW-II. Whereas 2k_F BCDW-I was found experimentally in some 1:2 TCNQ salts, 2k_F BCDW-II was characterized for the first time in (EDO-TTF)$_2$X (X = PF$_6$ and AsF$_6$) below T_{MI} (268 K in PF$_6$ and 280 K in AsF$_6$). The stacking-axis optical conductivity spectrum at 300 K is consistent with the weak 4k_F BOW accompanied by *e-mv* coupling (Figure 1a). Below T_{MI} the spectrum is dominated by two charge transfer bands CT$_1$ and CT$_2$ corresponding to the electronic transition from the ground state (mainly, |0110>) to the first (|1100> (55%) and |1010> (41%)) and third (mainly, |0200>) excited states, respectively. The fact that CT$_2$ holds a large fraction of the total spectral weight in the nominally 1/4 filled (EDO-TTF)$_2$X (X = PF$_6$ and AsF$_6$) is unique to 2k_F BCDW-II state and can be explained by a cooperation of large site charge difference and the type of BOW where the largest transfer integral connects two charge-rich sites. From the vibrational analysis of three charge-sensitive C=C stretching modes of EDO-TTF, the site charges below T_{MI} were estimated as +0.04 and +0.96. Besides, there is evidence for strong *e-mv* coupling of the out-of-phase mode of vibration of the central pair of molecules to CT$_2$, in both infrared and Raman spectra. A kind of relationship between the molecular charge, molecular deformation, and intermolecular π-π overlap is thought to play a role in stabilizing the 2k_F BCDW-II state.

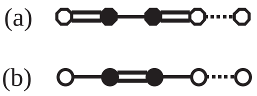

Figure 1. 2k_F BCDW-I (a) and 2k_F BCDW-II (b). Black and white circles represent charge-rich and charge-poor sites, respectively. The double, single and dotted lines denote the bond strength in descending order.

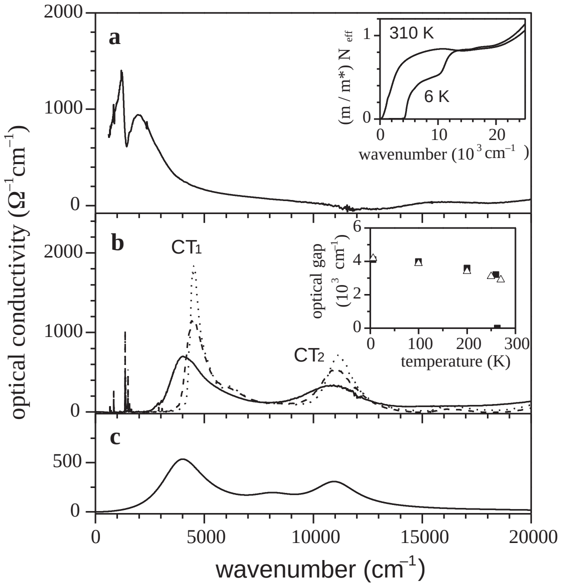

Figure 2. Stacking-axis optical conductivity spectra of (EDO-TTF)$_2$PF$_6$: (a) at 310 K; (b) at 270 K (solid line), 100 K (dashed line), and 6 K (dotted line); (c) spectrum calculated for a symmetric tetramer. Inset in (a) illustrates the sum rule calculation; inset in (b) the temperature dependence of the optical gap.

IV-A-9 Raman Spectra of (Me$_2$-DCNQI)$_2$Cu$_x$Li$_{1-x}$ (0 ≤ x ≤ 1)—Evidence for Charge Separation at Room Temperature in a One-Dimensional Conductor Having a Quarter-Filled Band

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[*J. Phys. Soc. Jpn.* **71**, 1956–1964 (2002)]

In the title alloys, the charge density on Me$_2$-DCNQI is expected to be varied as a function of x. These alloys are classified into three groups within $0 \le x \le 1$. For $x >$ 0.29, the alloy is classified into three-dimensional metal down to the liquid helium temperature. For $x \le 0.14$, a (metal-)insulator-insulator transition is observed in the resistivity measurement, and the system falls down to a non-magnetic insulator below 60 K. For $0.14 < x \leq 0.29$, the system keeps a paramagnetic behaviour down to the liquid helium temperature, although a metal-insulator transition is observed in the resistivity measurement. Both groups ($x \leq 0.29$) are one-dimensional conductors. Observed physical properties for $x \leq 0.29$ around room temperature are interpreted in two different ways. One is a lattice dimerization through electron-phonon interaction, and another is the charge separation through Coulomb repulsion(s). Although the optical conductivity spectrum supports the latter, no direct evidence has been obtained. Raman spectroscopy is a powerful tool to evaluate the charge density on organic molecules. We have measured the Raman spectra of $(Me_2\text{-DCNQI})_2Cu_xLi_{1-x}$ ($0 \leq x \leq 1$) at room temperature, 200 K, 100 K and 5 K. The Raman band assigned to the a_g ν_{R8} fundamental mode (outer-ring C=N stretching) down-shifts with an increase of x and exhibits a remarkable split for $0 \leq x \leq 0.29$. This frequency shift is attributable to the change of a charge density on a Me_2-DCNQI molecule. From the split of the ν_{R8} Raman band, it is concluded that charge disproportion occurs in $(Me_2\text{-DCNQI})_2Cu_xLi_{1-x}$ ($x \leq 0.29$) even at room temperature, where the system exhibits a metallic behaviour.

IV-A-10 Vanadyl Phthalocyanine as a High-Pressure Sensor

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The ruby fluorescence is a useful pressure sensor, which is commonly used in transparent high-pressure cell, such as diamond and sapphire anvil cells. Since this fluorescence is located at around 694 nm, it appears at around 1400 cm^{-1} in a Raman spectrum when HeNe laser (632.8 nm) is used as an exciting light. Since the strong fluorescence is close to the frequency of the C=C stretching mode, it disturbs the measurement of the Raman bands, even if the focused HeNe laser is not directly irradiated to the ruby. In order to avoid this problem, we looked for some vibrational modes of vanadyl phthalocyanine as a pressure sensor, and examined the pressure dependence of these Raman bands. Among the strong Raman bands of vanadyl phthalocyanine, the breathing mode of macrocycle at around 835 cm^{-1} showed a large blue shift upon applying high pressure. On the other hand, the C–H bending mode at around 1002 cm^{-1} showed no shift at all. Therefore, the frequency difference $\Delta\omega$ between the CH stretching and breathing modes was used as a scale to measure the pressure. Since both modes showed similar temperature dependence, the frequency difference was independent of temperature as shown in Figure 1. We proposed the equation to relate $\Delta\omega$ to P, which was shown in the inset of Figure 1.

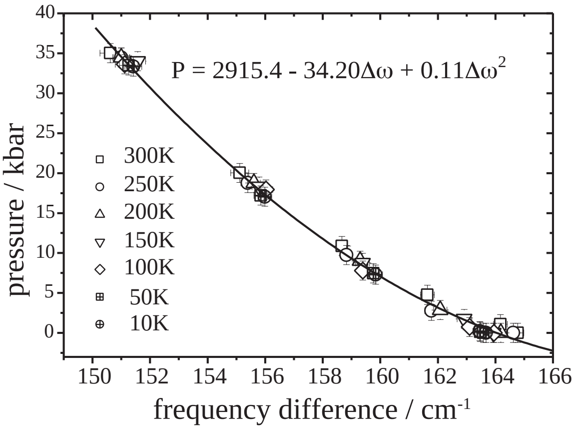

Figure 1. Pressure dependence of the frequency difference $\Delta\omega$ between the C–H bending mode (~ 1002 cm^{-1}) and the breathing mode of macrocycle (~ 835 cm^{-1}) in the Raman spectrum at various temperatures.

IV-A-11 Charge Ordering in the κ-Phase BEDT-TTF Salts with $Co(CN)_6$ and $Fe(CN)_6$ Anions Studied by Infrared and Raman Spectroscopy

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([1]IMS and IMP, Poland; [2]IMP, Poland; [3]LCSIM-CNRS, France)

[*C. R. Acad. Sci. (Paris) Chimie* **3/6**, 395–403 (2003)]

We studied the temperature dependence of the Raman scattering spectra of two semiconducting isostructural charge-transfer salts κ-$[Et_4N](BEDT\text{-}TTF)_4M(CN)_6\cdot 3H_2O$ (M = Co^{III}, Fe^{III}) within the region of C=C stretching vibrations (1200–1700 cm^{-1}). Moreover, polarized reflectance spectra (600 to 10000 cm^{-1}) of the Co^{III} salt were recorded as a function of temperature and compared with previous infrared studies of the Fe^{III} salt. Both salts undergo a phase transition at T = 150 K related to a charge ordering inside the conducting BEDT-TTF layers. Due to the charge ordering new vibrational bands corresponding to BEDT-TTF^{+1} cations are recorded both in Raman and infrared spectra. Infrared electronic bands also experience strong modifications at 150 K: a new energy gap is formed and a new charge-transfer band in the near-infrared region is observed. The most important difference is that the charge redistribution in Fe^{III} salt is developed gradually below about 240 K, whereas in Co^{III} salt this is an abrupt process related to the phase transition at 150 K.

IV-B Magnetic Resonance Studies for Molecular-Based Conductors

Molecular based conductors are one of the extensively studied materials. The development of the understanding of the electronic phases of these materials enables us systematic investigations of low-dimensional highly correlated electrons systems.

Magnetic resonance investigations are powerful microscopic investigations; they are advantageous for studying the fundamental electronic properties and for understanding the detailed electronic structures of molecular based compounds. Competition of the electronic phases in molecular based conductors has attracted much attention. Investigation of such electronic phases in molecular based conductors is important to understand the unsolved fundamental problems in the field of solid state physics.

In this project, we performed the ESR, and NMR measurements for molecular based conductors to clarify the low temperature electronic states.

IV-B-1 Low-Temperature Electronic Phases of EDT-TTF Based Molecular Conductors

NAKAMURA, Toshikazu

[*Mol. Cryst. Liq. Cryst.* **380**, 233–237 (2002)]

Magnetic investigation was carried out for low temperatures electronic phases in (EDT-TTF)$_2$AuBr$_2$, which undergoes an SDW transition at 16 K. In the SDW phase, we observed an abrupt change of ^{1}H-NMR absorption line around 6 K where the ^{1}H-NMR spin-lattice relaxation rate shows an anomalous second-peak. The electronic phase is discussed by microscopic point of view.

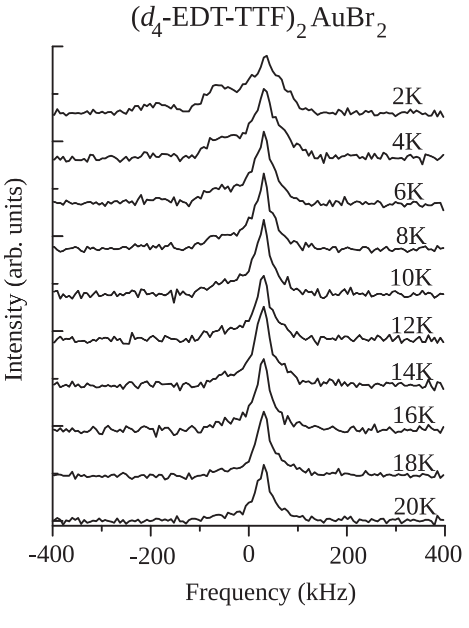

Figure 1. Temperature dependence of the ^{1}H-NMR absorption lines of the (d_4-EDT-TTF)$_2$AuBr$_2$ single crystal.

IV-B-2 Microscopic Investigation of a New Two-Component Organic Conductor with Itinerant and Localized Spins: (CHTM-TTP)$_2$TCNQ

NAKAMURA, Toshikazu; TANIGUCHI, Masateru[1]; MISAKI, Yohji[1]; TANAKA, Kazuyoshi[1]; NOGAMI, Yoshio[2]
([1]Kyoto Univ.; [2]Okayama Univ.)

[*J. Phys. Soc. Jpn.* **71**, 2208–2215 (2002)]

Low-temperature electronic phases in a new two-component organic conductor, a segregated-stack charge-transfer salt called (CHTM-TTP)$_2$TCNQ, are investigated. The ESR g tensor analyses indicate that there exist itinerant CHTM-TTP spins and localized TCNQ spins at R.T. The temperature dependence of the physical parameters reveals that this salt undergoes two drastic, successive phase transitions at low temperatures. The effective moment of the localized TCNQ spins decreases at the 245 K transition and completely disappears at the transition around 195 K. These curious physical properties are explained by the drastic changes in the electronic states of the two different types of spins. The spin susceptibility was decomposed into the contribution of each of the two spin species by using ESR, ^{1}H-NMR, and static susceptibility analyses. We present a microscopic investigation of the two-spin system with itinerant and localized moments.

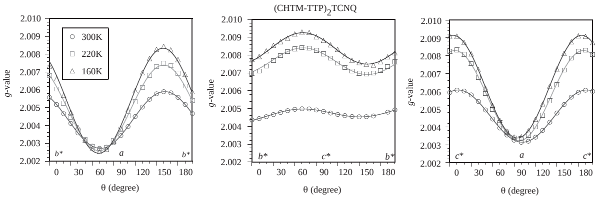

Figure 1. Angular dependence of the g values of (CHTM-TTP)$_2$TCNQ at 300 K (circle), 220 K (square) and 150 K (triangle), applying the static field static field within the ab^*, b^*c^*, and c^*a planes, respectively. The solid curves are the least square fits to the measured data using the standard anisotropic g tensor equation.

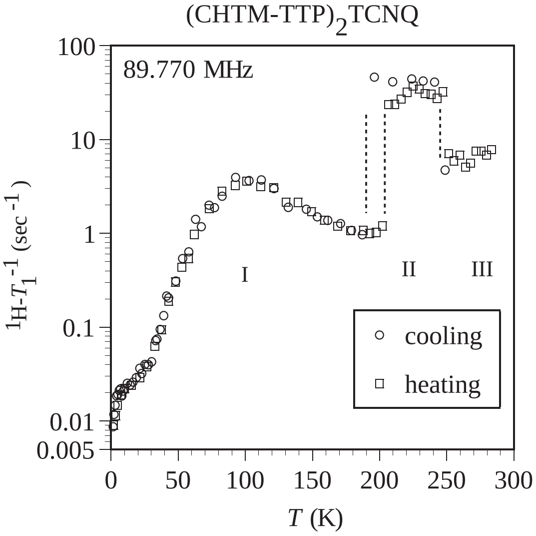

Figure 2. Temperature dependence of the ^{1}H-NMR spin-lattice relaxation rate, $T_1{}^{-1}$, of (CHTM-TTP)$_2$TCNQ, operated at 89.770 MHz, using a polycrystalline sample.

IV-B-3 *g*-Tensor Analyses of β'-Type Pd(dmit)$_2$ Metal Complexes

NAKAMURA, Toshikazu; TAKAHASHI, Toshihiro[1]; AONUMA, Shuji[2]; KATO, Reizo[2,3]
([1]Gakushuin Univ.; [2]Univ. Tokyo; [3]IMS and Inst. Phys. Chem. Res.)

[*Mol. Cryst. Liq. Cryst.* **379**, 53–58 (2002)]

ESR measurements and *g*-tensor analyses were performed for metal complexes, β'-type Pd(dmit)$_2$. The ESR *g*-values of β'-type Pd(dmit)$_2$ are found to be beyond one radical description which is a good approximation for conventional molecular based conductors. In this paper we focus on the anomalous behavior of the ESR *g*-values in β'-type Pd(dmit)$_2$. We discuss the possible explanation of the electronic structure of β'-type Pd(dmit)$_2$ metal complexes from microscopic points of view.

IV-B-4 Possible Charge Ordering Patterns of the Paramagnetic Insulating States in (TMTTF)$_2$*X*

NAKAMURA, Toshikazu

[*J. Phys. Soc. Jpn.* **72**, 213–216 (2003)]

ESR investigations were performed for a series of quasi-one-dimensional organic conductors, (TMTTF)$_2$*X*. The ESR linewidth shows abrupt jumps or humps in the paramagnetic insulating region. The (TMTTF)$_2$*X* salts are roughly divided into three groups according to the anisotropy of the ESR linewidth at low temperatures. In this paper, we discuss the possible charge-ordered patterns of three typical salts (*X* = ReO$_4$, SbF$_6$ and Br) from the microscopic point of view.

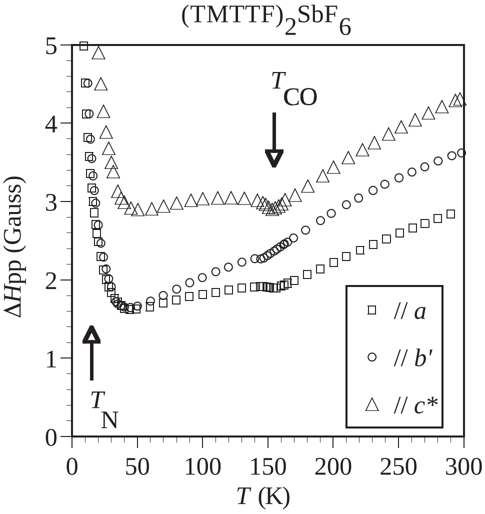

Figure 1. Temperature dependence of the peak-to-peak ESR linewidth, Δ*H*pp of (TMTTF)$_2$SbF$_6$ for a single crystal. The arrows indicate the charge-ordering and antiferromagnetic transitions.

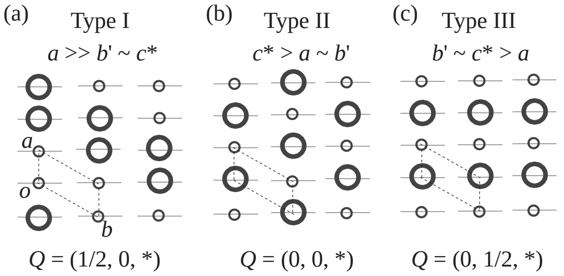

Figure 2. Schematic of possible charge-ordering patterns in the conducting *ab'* planes of TMTTF compounds: (a) Type I (ReO$_4$, ClO$_4$), (b) Type II (SbF$_6$, AsF$_6$) and (c) Type III (Br).

IV-B-5 NMR Investigation of (TMTTF)$_2$*X*: Charge Configurations and Spin Dynamics

FUJIYAMA, Shigeki; NAKAMURA, Toshikazu

[*Synth. Met.* **133-134**, 67–68 (2003)]

We performed ^{13}C NMR study for a quasi-one-dimensional organic conductor (TMTTF)$_2$Br. Although the resistivity has its minimum value around 100 K, the NMR spectra showed no significant change down to 30 K. Instead, we found slight broadening of the spectra above the magnetic phase transition temperature (T_{N} ~ 15 K). Similar anomaly is also observed for the uniform susceptibility (χ_s).

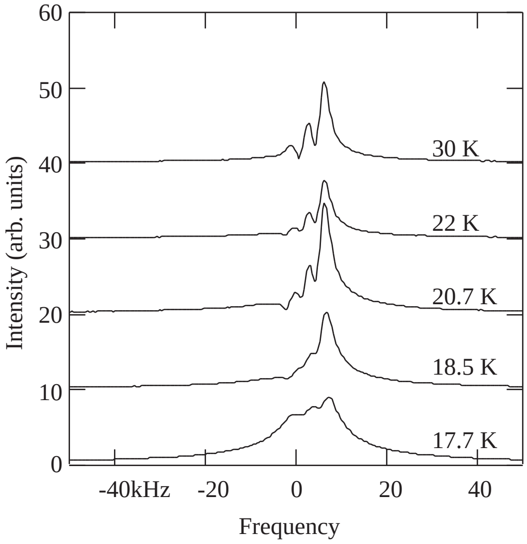

Figure 1. Temperature dependence of the ^{13}C NMR absorption line below 30 K.

IV-C Development of Multi-Functional Molecular Conductors

The molecules are usually assembled by weak intermolecular interactions and tend to retain their isolated electronic states even in the crystalline state. Consequently, the multi-functional systems may be constructed by assembling various molecules with different characters. Thus, the molecules are considered to be suitable building blocks for the bottom-up construction of the systems where various functions coexist and interplay with each other.

Recently, “dual-action system” such as magnetic molecular conductors has attracted a considerable interest. Though there exist well-known systems such as the paramagnetic organic superconductor and the ferromagnetic organic metals, there seems almost no significant interactions between conduction parts and magnetic parts. In contrast, we have discovered several novel organic superconductors exhibiting remarkable electro-magnetic properties originating from π-d coupling. κ-(BETS)$_2$FeBr$_4$ and κ-(BETS)$_2$FeCl$_4$ are the first and the second antiferromagnetic organic superconductors, respectively. Furthermore, κ-(BETS)$_2$FeBr$_4$ exhibits a metamagnetic (antiferromagnetic → ferromagnetic) transition around 1.6 T to give rise to a sharp switching behavior between superconducting and metallic states by tuning the external field around 1.6 T. In addition, due to the π-d interaction, a field-induced superconducting transition was observed around 12.5 T. But this is not the first observation of field-induced superconductivity in the organic conductors. We have previously reported the field-induced superconductivity in λ-(BETS)$_2$FeCl$_4$. Owing to the relatively large π-d interaction, λ-(BETS)$_2$FeCl$_4$ shows the field-induced superconductivity around 33 T, though the ground state is a π-d coupled antiferromagnetic insulating state. Moreover, the analogous system with diluted magnetic moments, λ-(BETS)$_2$Fe$_x$Ga$_{1-x}$Cl$_4$ ($0.35 < x < 0.5$) undergoes the successive metal → superconductor → insulator transitions with decreasing temperature. The electromagnetic properties of these BETS conductors gave clear examples of organic conductors showing the π-d coupling. Besides these conductors, we have recently tried to develop another type of magnetic molecular conductors by using the π donor molecules incorporating stable organic radicals. When the magnetic anions such as FeCl$_4^-$ are adopted as counter anions, the magnetic organic conductors with two kinds of spin systems will be prepared where a variety of novel electromagnetic properties will be expected.

Until quite recently, it has been long believed that all the molecular metals are constructed of more than two chemical species because the intermolecular charge transfer phenomena have been used to generate charge carriers. The best example may be the first organic superconductor, (TMTSF)$_2$PF$_6$ where the hole carriers are generated in TMTSF columns by the charge transfer from TMTSF to PF$_6^-$ (TMTSF → TMTSF$^{+0.5}$). Due to the charge transfer, the molecular metals have the character of ionic crystals. But we have recently developed molecular metals consisting of neutral single-component molecules where intermolecular charge transfer cannot be considered. More recently, the experimental evidence for the existence of Fermi surfaces in this single-component molecular crystal was obtained. The discovery of the single-component molecular metal disclosed the amphibious molecular crystal consisting of neutral single-component molecules and possessing 3D Fermi surfaces.

IV-C-1 Highly Conducting Crystals Based on Single-Component Gold Complexes with Extended-TTF Dithiolate Ligands

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(*[1]Univ. Tokyo; [2]Nagoya Univ.*)

[*J. Am. Chem. Soc.* **125**, 1486 (2003)]

We have recently found the first metallic crystal consisting of neutral transition metal complex molecules with extended-TTF (tetrathiafulvalene) ligands, [Ni(tmdt)$_2$]$^{0+}$ (tmdt = trimethylenetetrathiafulvalenedithiolate) with metallic behavior down to very low temperature. In terms of valence electrons, the neutral bis(dithiolato)gold complex is isoelectronic to the planar bis(dithiolato)nickel monoanion complex with one unpaired electron per molecule, which makes the electromagnetic properties of the neutral gold complex very attractive. It has been thought that these unpaired electrons or holes in the bis(dithiolato)gold complexes have a possibility to form a metallic band. We have prepared the crystals composed of single-component gold complexes with extended-TTF ligands, [Au(dmdt)$_2$]$^{0+}$ (dmdt = dimethyltetrathiafulvalenedithiolate) and [Au(tmdt)$_2$]$^{0+}$ and examined their structural, electrical and magnetic properties. Since the crystals were very small, the synchrotron radiation X-ray powder experiments were performed by using the imaging plate detectors and the Large Debye-Scherrer camera at the facility SPring-8 BL02B2. Although the sufficient diffraction patterns could not be obtained on [Au(dmdt)$_2$], an ideal X-ray powder pattern was obtained on [Au(tmdt)$_2$], which revealed [Au(tmdt)$_2$] to be isostructural to [Ni(tmdt)$_2$]. The crystal structure was successfully analysed by a self-consistent iterative analysis of a combination of the maximum entropy method (MEM) and Rietveld analysis. The lattice constants of [Au(tmdt)$_2$] are: $a = 6.4129(1)$ Å, $b = 7.5514(2)$, $c = 12.1543(3)$, $\alpha = 90.473(3)°$, $\beta = 96.698(2)$, $\gamma = 103.008(3)$, $V = 569.21(2)$ Å^3. The high conductivity of compacted crystalline powder sample (≈ 15 S cm^{-1} at room temperature) and the XPS and NEXAFS measurements suggested [Au(tmdt)$_2$] to be essentially a metal. The temperature dependence of ESR intensity showed that [Au(tmdt)$_2$] undergoes a magnetic transition around 100 K with keeping the highly conducting states. To our knowledge, there has been no molecular conductor exhibiting magnetic transition at the temperature as high as 100 K. The SQUID measurements suggested the magnetic transition to be antiferromagnetic one.

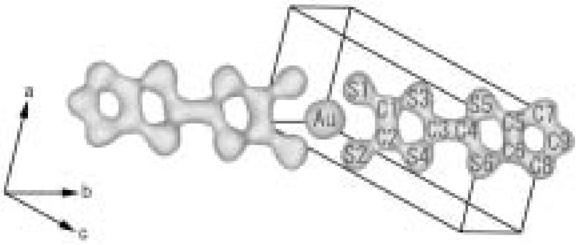
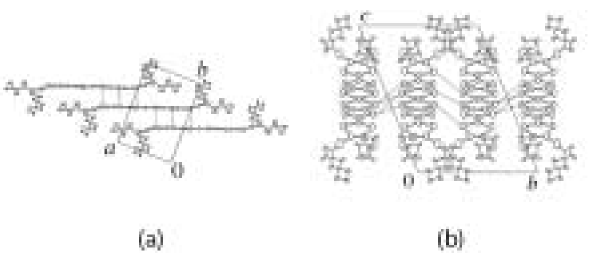


Figure 1. Structure of [Au(tmdt)$_2$] determined by MEM/Rietveld analysis of X-ray powder patterns.

IV-C-2 Structure and Physical Properties of Palladium Complexes with Extended-TTF Dithiolate Ligands

SUZUKI, Wakako[1]; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]; HASEGAWA, Ami[2]; MIYAMOTO, Takeshi[2]; KOBAYASHI, Hayao
([1]Univ. Tokyo; [2]Kitasato Univ.)

In the course of the studies on the development of single-component molecular metals, new dithiolato palladium complexes with an extended-TTF (tetrathiafulvalene) ligand (^{n}Bu$_4$N)[Pd(C3-tdt)$_2$](**1**) and [Pd(C3-tdt)$_2$] ((C3-tdt)$^{2-}$ = dipropylthiotetrathiafulvalenedithiolate)(**2**) were prepared and their crystal structures were determined. The electrochemical properties of **1** were investigated by cyclic voltammetry technique at 20 °C and scan rate of 200 mVs^{-1}. The cyclic voltammogram measured in dimethylformamide showed three pairs of reversible redox waves. The first, second and third potentials are –0.92, –0.30 and +0.47 V *vs.* Ag/AgCl, respectively. The first, second and third waves correspond to three electrons, two electrons and one electron oxidation, respectively, leading [Pd(C3-tdt)$_2$]$^{2-}$ to [Pd(C3-tdt)$_2$]$^{4+}$. The crystal structures of **1** and **2** were examined. **2** has three-dimensional S···S short contacts even though **2** has large steric hinderence through large propylthio groups. The molecular structure is almost planar except for four propylthio groups and more planar than that in **1**. The magnetic susceptibility of (^{n}Bu$_4$N)[Pd(C3-tdt)$_2$] gave good agreement with Bonner-Fisher model (J = –16 K), which suggests [Pd(C3-tdt)$_2$] anions form approximately a one-dimensional antiferromagnetic chain. On the other hand neutral [Pd(C3-tdt)$_2$] was found to be a semiconductor with a room temperature conductivity of 10^{-2} S·cm^{-1}.



(a) (b)

Figure 1. Crystal structure of [Pd(C3-tdt)$_2$] (**2**) projected onto (a) the *ac*-plane and (b) the *bc*-plane.

IV-C-3 Single-Component Molecular Crystal with Three-Dimensional Fermi Surfaces

TANAKA, Hisashi[1]; TOKUMOTO, Madoka[1]; ISHIBASHI, Shouji[1]; GRAF, David[2]; CHOI, Eun S.[2]; BROOKS, James S.[2]; YASUZUKA, Shyuma[3]; OKANO, Yoshinori; KOBAYASHI, Hayao; KOBAYASHI, Akiko[4]
([1]AIST; [2]Florida State Univ.; [3]Natl. Inst.Mater. Sci.; [4]Univ. Tokyo)

Recently a considerable attention has been attracted to the unconventional conducting molecular systems such as single component molecular conductors, nanowires , molecular wire junctions and even DNA. Though the intriguing reports on new types of molecular systems are rapidly increasing in number, there seem to be many systems whose origins of the charge carriers and/or transport mechanisms still remain unclear. The single-component molecular crystal, we reported recently, consisting of neutral metal complex molecules [Ni(tmdt)$_2$] (tmdt = trimethylenetetrathia-fulvalenedithiolate) exhibits metallic behavior down to 0.6 K, but without Fermiological evidence of metallic nature. In order to prove definitely the existence of an amphibious molecular crystal consisting of single-component neutral molecules and possessing metal electrons, the torque magnetometry measurements of de Haas van Alphen oscillatory signals in a single crystal of [Ni(tmdt)$_2$] were performed by using a sensitive microcantilever at low temperatures in high magnetic fields to 45 T. Because of very small size of the crystals (of order 130 × 100 × 20 μm^3, and 0.5 μg in mass), we employed a commercial microcantilever for atomic force microscope (AFM). A simple resistance bridge circuit was used to cancel the background resistance of the two piezoresistive sensing cantilevers on the AFM assembly. The observed signals for all directions of magnetic field revealed unambiguously the presence of three-dimensional Fermi surfaces for both electrons and holes, which correspond well to the band structure calculated by local density approximation (LDA) and *ab initio* plane-wave norm-conserved pseudopotential method.

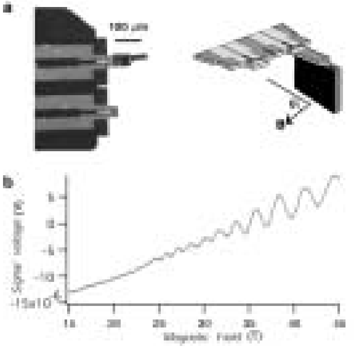


Figure 1. (a) AFM cantilever for torque magnetometry, (b) The raw torque magnetometer signal *versus* the applied magnetic field showing de Haas van Alphen oscillation of the single-component molecular metal, Ni(tmdt)$_2$.

IV-C-4 Infrared Electronic Absorption in Single-Component Molecular Metal

KOBAYASHI, Akiko[1]; SASA, Masaaki[1]; SUZUKI, Wakako[1]; FUJIWARA, Emiko[1]; TANAKA, Hisashi[2]; TOKUMOTO, Madoka[2]; OKANO, Yoshinori; FUJIWARA, Hideki; KOBAYASHI, Hayao
([1]Univ. Tokyo; [2]AIST)

[*J. Am. Chem. Soc.* in press]

It is commonly accepted that the electronic energy of a molecule is much higher than the vibrational energy of a molecule. If a molecule with electronic excitation in the *infrared* (*ir*) region can be designed, then the molecular system is expected to have unprecedented electronic properties. In order to develop a metallic crystal consisting of single-component molecules, we have tried to synthesize molecules with unprecedentedly low electronic excitations (or unprecedentedly small HOMO-LUMO gaps). In fact, as reported before, we could find the first single-component molecular crystal with stable metallic state down to 0.5 K. If our molecular design is correct, the transition metal complex molecules with extended TTF ligands (L) will have very small HOMO-LUMO gap. We have synthesized and examined the electronic absorption spectra of the crystals of $M(L)_2$[M = Ni, Pd; L = tmdt (trimethylenetetrathiafulvalenedithiolate), dmdt (dimethyl-tetrathiafulvalenedithiolate), ptdt (propylenedithiotetrathia-fulvalenedithiolate) and dt (tetrathiafulvalenedithiolate)]. Since a suitable solvent was not found, the *visible* (*vis*) and *ir* spectra were measured on crystalline powder samples. $Ni(tmdt)_2$ and $Ni(dmdt)_2$ exhibited the broadest absorption maxima around 2200 cm^{-1}. To our knowledge, this is the smallest electronic absorption energy ever reported for single-component closed-shell molecular systems. Although the electronic absorptions around 2200 cm^{-1} of $Ni(tmdt)_2$ and $Ni(dmdt)_2$ seem to suggest an extremely small HOMO-LUMO gap, the $M(L)_2$ peaks blue shifted as the semiconducting properties of the crystal increased, which indicates that the band structure plays a crucial role. Based on the extended-Hückel tight-binding band parameters, the electronic spectra were calculated. The good agreement between observed and calculated spectra shows that the single-component molecular conductors are composed of molecules with unprecedentedly small HOMO-LUMO gaps.

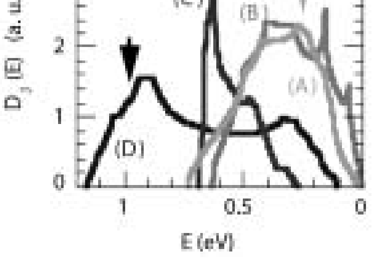


Figure 1. The calculated joint density of states $D_J(E)$: (A) $Ni(tmdt)_2$, (B) $Ni(dmdt)_2$, (C) $Ni(ptdt)_2$, and (D) $Pd(dt)_2$. The *E*-dependence of $D_J(E)$ is consistent with the observed electronic absorption spectra for each system. The arrows indicate the energy of observed absorption maxima.

IV-C-5 A Novel TTP Donor Containing a PROXYL Radical for Magnetic Molecular Conductors

FUJIWARA, Hideki; LEE, Ha-Jin; KOBAYASHI, Hayao; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

[*Chem. Lett.* 482 (2003)]

The development of new electron donors for molecule-based conductors involving a magnetic centre are of quite interest to investigate the interplay between the π conducting electrons generated by an oxidation and the localized radical spins, and several donors containing a stable radical have been synthesized to try for novel conducting-magnetic bifunctional materials. Among them, to realize the metallic conductivity, we focused on the molecules with TTP skeleton [TTP = 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene], which was regarded as a series of promising donors for the realization of stable metallic states. We synthesized a novel electron donor consisting of the TTP framework and a stable PROXYL radical part **1** and cleared its structure and physical properties. Furthermore, we reported the physical properties of its ClO_4^- and $FeCl_4^-$ salts. Among them, the $FeCl_4^-$ salts of **1** (D:A ratio ≈ 1:0.46) showed the highest conductivity record (1.1 S cm^{-1}) in the cation radical salts based on the donors containing stable organic radicals reported so far, even though it was measured on compressed pellets. This salt showed semiconducting behavior, however, the activation energy is quite small value of 0.02 eV. Therefore, the electrical conductivity of this salt can be considered to be essentially metallic if we could measure the conductivity using its single crystals. The χT values of this salt around room temperature correspond to the sum of the contributions from one PROXYL radical, high spin Fe^{3+} and conduction electrons, suggesting the coexistence of these three different magnetic moments. These results indicate that this salt is possibly the first example of paramagnetic organic metal with the coexistence of the conduction electrons and two kinds of the localized spins.

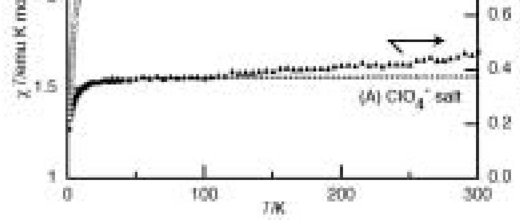


Figure 1. Magnetic properties of the cation radical salts of **1**.

IV-C-6 Synthesis, Structures and Physical Properties of a New Organic Conductor Containing a Stable PROXYL Radical

FUJIWARA, Hideki; LEE, Ha-Jin; CUI, Heng-Bo; KOBAYASHI, Hayao; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

We have reported several π-extended donor molecules containing a stable organic radical part, and recently, we have discovered highly conducting cation radical salts by use of the bis-fused TTF skeleton called as TTP containing a PROXYL radical substituent. However we could not clear the crystal structures of the cation radical salts based on such TTP-based donor molecules because it was difficult to obtain suitably large crystals for crystallographic analysis so far. Very recently, we succeeded in the structure analysis of a quite small crystal of the AsF_6^- salt of a newly synthesized cyclopenteno-fused TTP derivative **1** carrying a stable PROXYL radical part by using a new X-ray diffractometer equipped with the confocal X-ray mirror system and the CCD detector. The AsF_6^- salt has a 4:1 stoichiometry of D:A. As shown in Figure 1, the TTP skeleton of the donor molecules formed the π-conduction layer along the *ab*-plane and the PROXYL radical parts of both the donors and the AsF_6^- anions formed the insulating layers sandwiched by the donor layers. The donor layer has a quite unique structure and each the donor molecules (A and B) constructed independent one-dimensional stackings I and II in the donor layer. Reflecting strong one-dimensionality of the intermolecular interactions along the *b*-axis, the calculated Fermi surface also indicates the one-dimensional electronic structure of this salt. Above 100 K, the χT values are larger than the value for one S = 1/2 spin per one donor molecule (0.375 emu K mol^{-1}), suggesting a small contribution from conduction electrons. That is, the localized spin of the PROXYL radical part and π conduction electrons seem to coexist at higher temperature. This salt showed relatively high room temperature conductivity of 1 S cm^{-1} and semiconducting temperature dependence of resistivities with a very small activation energy of 0.046 eV.

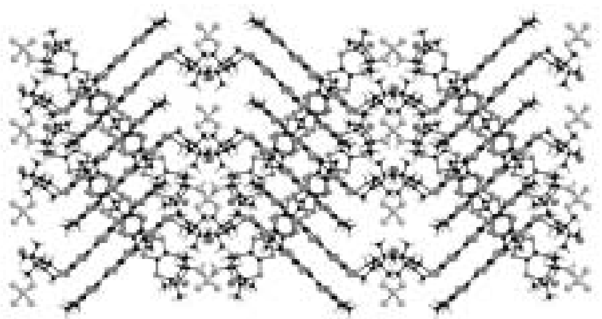


Figure 1. (a) Crystal structure of the AsF_6^- salt of **1** projected on to the *bc*-plane.

IV-C-7 Crystal Structures and Physical Properties of New Magnetic Conductors Based on π-Donor Molecule Containing a Stable Organic Radical

LEE, Ha-Jin; CUI, Heng-Bo; FUJIWARA, Hideki; KOBAYASHI, Hayao; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

In the research for new molecular-based organic conductors, a considerable interest has been focused on the development of molecular conductors and superconductors containing magnetic transition metal anions to investigate the intrerplay between conduction electrons and localized magnetic moments in organic conductors. From this point of view, several donors containing a stable organic radical part such as TEMPO and NN, have been prepared with the aim of developing novel organic conducting-magnetic multifunctional materials and organic ferromagnetic metals. We have recently reported highly conducting radical salts, for example, the $FeCl_4^-$ (1:0.46) salt (σ_{RT} = 1 Scm^{-1}) of the donor (TTP-proxyl (**1**)) based on the bi-fused TTF skeleton named as TTP containing a PROXYL radical. However we could not solve the crystal structure of these cation radical salts because it was impossible to obtain single crystals suitable for crystallographic analysis. In this paper, we reported the preparation of the $FeCl_4^-$ and $GaCl_4^-$ salts of the donor **1**, which have a 1:1 stoichimoetry, and examined their structure, and magnetic and conductivity properties. Overall temperature dependence of the **1**·$FeCl_4$ indicates typical semiconducting behavior with an activation energy of *ca.* 0.13 eV. The room temperature electrical conductivity of this salt is low, with a value of about 10^{-3} Scm^{-1}, due to the 1:1 stoichiometry and strongly dimerized structure. The χT value of **1**·$FeCl_4$ at room temperature is 4.65 K·emu·mol^{-1} and slightly lower than 4.75 K·emu·mol^{-1} expecting from the sum of the contribution form one PROXYL radical (S = 1/2; 0.375 K·emu·mol^{-1}) and high spin Fe^{3+} (S = 5/2; 4.375 K·emu·mol^{-1}), and the value slightly increases as temperature decreases to 50 K.

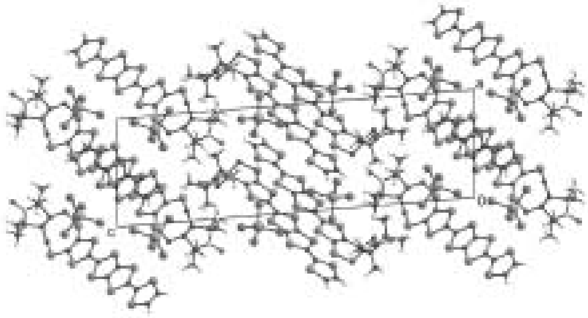


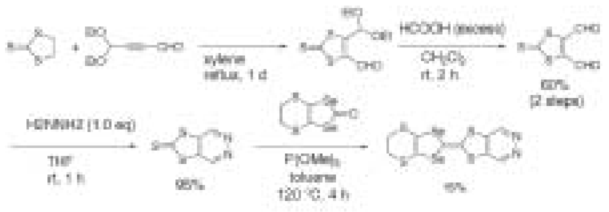
Figure 1. Crystal structure of the $FeCl_4^-$ salt of **1** projected onto the *ac*-plane.

IV-C-8 An Unsymmetrical Donor Fused with Pyridazine Ring

OTSUBO, Saika; TAKAHASHI, Kazuyuki; CUI,

Heng-Bo; FUJIWARA, Hideki; KOBAYASHI, Hayao; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

We have reported that the interaction between π conduction electrons and *d* magnetic anions plays an important role to realize novel electro-magnetic properties such as unprecedented superconductor-to-insulator transition and magnetic field-induced superconductivities of λ- and κ-type BETS salts containing high-spin Fe^{3+} ions. In order to enhance the interaction between donor and anion layers, we have prepared an EDST analogue fused with a pyridazine ring. The new thione unit, pyridazino-1,3-dithiole-2-thione was synthesized in 57% yield (3 steps). The new donor (**1**) was prepared by a phosphite-mediated cross-coupling reaction of the thione unit with 4,5-ethylenedithio-1,3-diselenol-2-one in 16% yield (Scheme 1). The cyclic voltammogram shows one reversible and one irreversible waves. The first and the second oxidation potentials were +0.86 and +1.21 V *vs.* Ag/AgCl, respectively. The crystal structure of the ReO_4^- salt showed that the D:A ratio was 1:1 and the donor molecules formed dimer with a head-to-tail overlap mode. There were anions between the donor dimers and no columnar structure was observed.



Scheme 1. Synthetic route of **1**.

IV-C-9 Structural, Electrical and Magnetic Properties of a Series of Molecular Conductors Based on BDT-TTP and Lanthanoid Nitrate Complex Anions [BDT-TTP = 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6- tetrathiapentalene]

CUI, Heng-Bo; OTSUKA, Takeo; KOBAYASHI, Akiko[1]; TAKEDA, Naoya[1]: ISHIKAWA, Masayasu[1]; MISAKI, Yohji[2]; KOBAYASHI, Hayao
([1]Univ. Tokyo; [2]Kyoto Univ.)

[*Inorg. Chem.* **42**, 6114 (2003)]

The crystals of a series of novel molecular conductors, which are based on π donor molecules BDT-TTP [2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene] with a tetrathiapentalene skeleton and lanthanide nitrate complex anions $[Ln(NO_3)_x]^{3-x}$ (Ln = La, Ce, (Pr), Tb, Dy, Ho, Er, Tm, Yb, and Lu) with localized 4*f* magnetic moments, were synthesized. Except for the Ce complex, the salts were composed of $(BDT\text{-}TTP)_5[Ln(NO_3)_5]$ and were isostructural. Even though the Ce crystal had a different composition, $(BDT\text{-}TTP)_6[Ce(NO_3)_6](C_2H_5OH)_x$ ($x \approx 3$), the crystals all had the space group, $P\bar{1}$. Previously, we reported the crystal structures and unique magnetic properties of $(BDT\text{-}TTP)_5[Ln(NO_3)_5]$(Ln = Sm, Eu, Nd, Gd). Thus by combining the results of this work with previous one, we for the first time succeeded to obtain a complete set of organic conductors composed of the identical π-donors (BDT-TTP in this case) and all the lanthanide nitrate complex anions (except the complex with Pm^{3+}). The crystals were all metallic down to 2 K. Electronic band structure calculations resulted in two-dimensional Fermi surfaces, which was consistent with their stable metallic states. Except the Lu complex, which lacked paramagnetic moments, the magnetic susceptibilities were measured on the six heavy lanthanide ion complex salts by a SQUID magnetometer (Ln = Tb, Dy, Ho, Er, Tm, and Yb). The large paramagnetic susceptibilities, which were caused by the paramagnetic moments of the rare-earth ions, were obtained. The Curie-Weiss law fairly accurately reproduced the temperature dependence of the magnetic susceptibilities of $(BDT\text{-}TTP)_5[Ho(NO_3)_5]$ in the experimental temperature range (2–300 K) and a comparatively large Weiss temperature ($|\theta|$) was obtained [θ(Ho) = –15 K]. The fairly strong intermolecular magnetic interaction between Ho^{3+} ions, which was suggested by the $|\theta|$-value, is inconsistent with the traditional image of strongly localized 4*f* orbitals shielded by the electrons in the outer 5*s* and 5*p* orbitals.

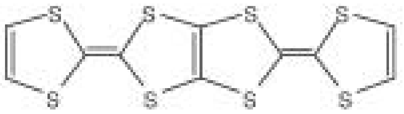


Figure 1. BDT-TTP [2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene].

IV-C-10 Anomalous 1:1 Salt with Metallic State down to 15 K, $(BETS)GaBr_4$

CUI, Heng-Bo; OKANO, Yoshinori; FUJIWARA, Hideki; KOBAYASHI, Hayao; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

Except for a few conductors such as $(TTM\text{-}TTP)I_3$ with metallic state down to 160 K, almost all the 1:1 salt of π donors (D) and inorganic anions (A) have been considered to become insulators due to the large on-site Coulomb interactions. However, we have recently found a 1:1 salt of BETS (= bis(ethylenedithio)tetraselenafulvalene) and $GaBr_4^-$ with high room-temperature conductivity of about 20 S cm^{-1}. The resistivity decreased slowly but almost linearly with lowering temperature and increased rapidly below *ca.*15 K (T_{MI}). That is, $(BETS)GaBr_4$ is the anomalous 1:1 salt with stable metallic state down to about 15 K. The crystal has a very simple and unique structure. The lattice constants are: a = 7.050 Å, b = 8.489, c = 24.142, α = 85.63°, β = 83.79, γ = 68.85, V = 1338.5 Å^3, Z = 1. Similar to usual organic metals with the composition of D_2A, the crystal contains donor and anion layers. But due to 1:1 stoichiometry, the donor and anion layers are arranged as, DAADAA··· along the *a* direction. Considering the Coulomb repulsion between anions, this arrangement seems to be very unusual. In fact, $(BETS)FeBr_4$ has a completely different molecular arrangement, despite that the 2:1 salts of $(BETS)_2FeBr_4$ and $(BETS)_2GaBr_4$ take the isomorphous structures to each other. Band structure calculation gave 2D electron and hole Fermi surfaces. ESR measurements suggested that the spin susceptibility, line width and *g*-value change their temperature dependencies around T_{MI}. The susceptibility increased below T_{MI} shows the low-temperature insulating state to be paramagnetic.

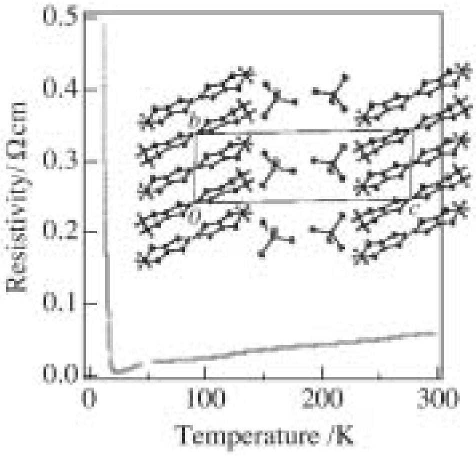


Figure 1. Crystal structure and temperature dependence of resistivity of $(BETS)GaBr_4$.

IV-C-11 High Pressure Effect on Conducting Behavior of an Antiferromagnetic Superconductor κ-$(BETS)_2FeBr_4$

OTSUKA, Takeo; FUJIWARA, Hideki; KOBAYASHI, Hayao; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

κ-$(BETS)_2FeBr_4$, were found to show a unique successive phase transition from paramagnetic metal to antiferromagnetic metal to antiferromagnetic superconductor with lowering temperature. Recently, even the magnetic field induced superconductivity was discovered around 12.5 T. In order to acquire the key to solve the mechanism of these unique electro-magnetic properties, we measured the conduction behavior of this complex under high pressure.

At ambient pressure, a kink anomaly of the resistivity was observed at 2.4 K which is related with the Néel order of Fe^{3+} moments. Resistivity decrease at 1.4 K corresponds to the onset of superconducting phase transition. The pressure dependencies of T_N and T_C (onset) are summarized in Figure 1. The gradual increase of T_N could be attributed to the contraction of the lattice, which will be consequent on the increase of the magnetic interactions. On the other hand, the T_C decreases with increasing pressure, and around 3.5 kbar sharply shifted off lower than 0.6 K, which is the lowest measurement temperature. It is normal that the superconducting phase is suppressed by pressure, because of the stabilization of metallic state at high pressure. Although our preliminary experiments up to 15 T could not find the onset of reentrant field-induced superconducting state, the high-pressure resistivity behaviors under magnetic field will be informative for the understanding of the superconductivity of this unique *d*-π system.

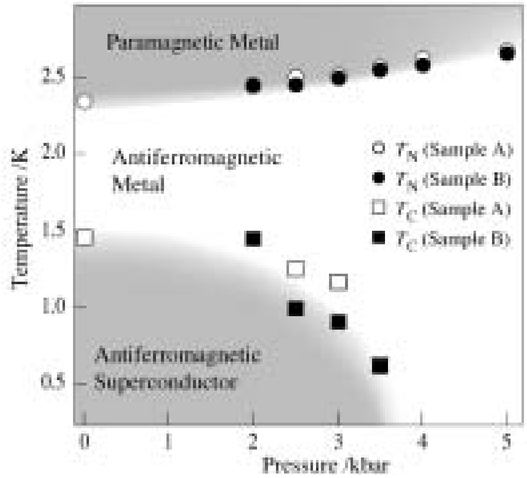


Figure 1. Pressure-temperature phase diagram of κ-$(BETS)_2FeBr_4$.

IV-D Development of Multi-Functional Porous Molecular Materials

The synthesis of new materials with new functions is the most important driving force for advancing molecular material sciences. The molecules are the smallest functional units of the materials and have been regarded as suitable building brocks for the bottom-up construction of multifunctional nano-systems. Recently, a large interest seems to be concentrated to the development of new functional molecular systems. Though increasing numbers of various intriguing molecular conducting systems such as molecular wires, atomic wires embedded in nano-porous molecular materials, molecular wire junctions and even DNA have been reported recently, there seems to be many systems whose underlying sciences seem to be very ambiguous. On the other hand, physics and chemistry of the bulk systems with typical electronic functions such as molecular superconductors and molecule-based magnets have been intensively studied in the last two decades. The *bi*functional molecular systems such as magnetic organic conductors have been developed by combining π donor molecules responsible for the electron conduction and magnetic anions, from which novel molecular systems exhibiting remarkable electro-magnetic properties such as field-induced superconductivity and switchable superconductivity coupled with metamagnetism of the anion part, have been discovered recently. However, an innovative progress seems to be needed for further studies on the traditional molecular conducting systems. The recent progress in the development of the supramolecular systems seems to suggest a way to develop completely new types of multi-functional molecular systems. Nanoporous supramolecular systems have aroused rapidly growing interest because of their abilities on the constructions of potential hydrogen storage materials, gas sensors, molecular nano-devices, *etc*. We have recently launched to try to develop new molecular systems with multi-functionality by combining nano-porous frameworks and suitable guest molecules.

IV-D-1 Manganese(II)-Formate–a 3D Porous Homometallic Ferrimagnetic Diamond Network with Nodes of Mn-Centered $MnMn_4$ Tetrahedron

WANG, ZheMing; ZHANG, Bin; FUJIWARA, Hideki; KOBAYASHI, Hayao; KURMOO, Mohamedally[1]
([1]*Inst. Physique Chimie Matériaux Strasbourg)*

[*Chem. Commun.* in press]

Microporous coordination framework solids with high stability have been the focus of intense research activity because of their potential applications, associated with the porosity, in many fields. Chemists have been trying to add functionalities in addition to the porosity, such as magnetism, to these materials; thus new multifunctional materials are expected. We have examined a new form of metal(II)-formate. The novel 3D porous homometallic ferrimagnets based on manganese(II) with formate as the connector, $[Mn_3(HCOO)_6](CH_3OH)(H_2O)$ **1**, its desolvated form $[Mn_3(HCOO)_6]$ **2**, and the dioxane-inclusion compound **3**. Formic acid is the smallest and simplest carboxylic acid. It can form either a one-atom or a three-atom connector. The materials show a highly stable, unprecedented diamondoid framework based on octahedrally coordinated Mn-centered $MnMn_4$ tetrahedral nodes, and display porosity for guest exchange and 3D long-range magnetic ordering. At room temperature, **1** has a χT value of 12.41 cm^3Kmol^{-1}. The behavior is that of a ferrimagnet, with a minimum in χT at 21 K. The minimum χT reaches 6.53 cm^3Kmol^{-1} at 21 K then gradually rises to 12.24 cm^3Kmol^{-1} at 11.5 K. After that it rises sharply to the maximum of 374.4 cm^3Kmol^{-1} at 7.0 K. This work demonstrates a new, simple and easy approach to obtain magnetically porous materials.

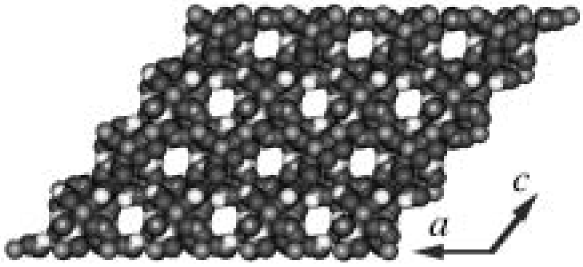


Figure 1. The space filling view of the framework with empty channels. The channels are occupied by methanol and water in **1** or dioxane in **3**.

IV-D-2 Magnetic Coordination Network Embedded in Polyiodide Matrix

WANG, ZheMing; ZHANG, Bin; OTSUKA, Takeo; FUJIWARA, Hideki; KOBAYASHI, Hayao; FUJIWARA, Emiko[1]**; YAN, Chunhua**[2]
([1]Univ. Tokyo; [2]Peking Univ.)

Crystal engineering of coordination networks has become a rapidly developing research area because of its importance in fundamental research and producing novel smart materials. Various bridging ligands have been employed to construct coordination networks. When they are neutral, the resultant networks are positive. Thus counter charged parts, *i.e.*, anions, coordinating directly to metal ions or acting as guest, are necessary to keep the whole system neutral, which have a strong influence on determining the structures of the produced network. Sometimes, the positive coordination networks can provide temprates for the formation of anion frameworks to produce, for example, novel organic-inorganic hybrid materials). However, to the best of our knowledge, polyiodides, a class of interesting and unique anionic species, have never been introduced in the crystal engineering of coordination networks.

In this work, we employ 4,4’-bipyridine-N,N’-dioxide (dpdo) to build the first series of architectures with positive coordination network and polyiodide, $[M(dpdo)_3](I_7)_2$, **1**, **2**, **3**, and **4** for M = Mn, Co, Ni, and Zn respectively, and examined their unusual structural and magnetic properties. All the compounds are isomorphic. As expected, the structure is composed of positive three-dimensional coordination network $[M(dpdo)_3{}^{2+}]_\infty$ of six-connected M nodes and the heptaiodide I_7^- anions. The Mn, Co, and Ni compounds show weak ferromagnetism due to anti-symmetric exchange interaction between magnetic metal ions. The critical temperatures, T_c’s, are 5.7, 4.8 and 8.2 K for **1**, **2** and **3**, respectively. Thus, we have successfully developed a series of new magnetic and non-magnetic compounds by the assembly of positive coordination network with polyiodide through the concept of crystal engineering. The compounds with M^{2+} ions (M = Mn, Co, Ni) exhibit not only unusual structural characteristics, *i.e.*, the interwoven of 3D coordination network with polyiodide matrix, but also weak ferromagnetism.

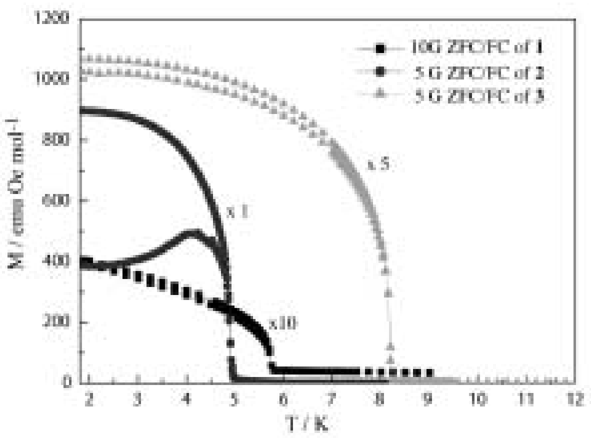


Figure 1. Zero-field (ZFC) and field-cooled (FC) *M*-*T* under low-field for **1**, **2** and **3**.

IV-E Control of Electronic States in Molecular Conductors with Chemical and Physical Methods

The electronic state of the molecular conductor is quite sensitive to molecular arrangement and orientation that are governed by the inter-molecular interaction. Design of the inter-molecular interaction is indispensable in the rational development of molecular conductors to still higher forms. An introduction of supramolecular chemistry is a possible solution to this problem. We have developed various molecular conductors containing supramolecular assemblies based on two types of supramolecular interactions, the iodine-based halogen bond and the tellurium-based secondary bond. It has been demonstrated that the supramolecular interaction has the ability to tune the molecular arrangement and orientation and thus provides a route for the formation of novel molecular materials.

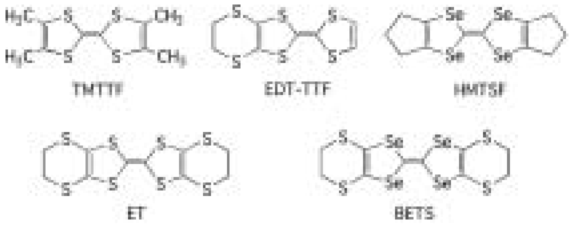
On the other hand, the electronic state of molecular conductors can be quite sensitive to the pressure (including chemical pressure) application. Recent development of the uniaxial stress and strain methods has enabled selective or anisotropic regulation of the inter-molecular interaction and has provided a powerful means to search for novel electronic states. We have examined the uniaxial strain effect and have found unusual electronic states in the organic narrow-gap semiconductor, the supramolecular conductor, and the two-dimensional strongly correlated system based on the metal dithiolene complex.

IV-E-1 Structural and Physical Properties of New Conducting Cation Radical Salts with Te-Based Counter Anions, Tetraiodotellurate(II) and Hexaiododitellurate(II)

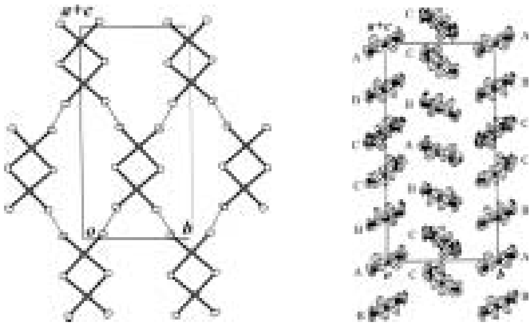
FUJIWARA, Masahiro[1]; TAJIMA, Naoya[2]; IMAKUBO, Tatsuro[2]; TAMURA, Masafumi[2]; KATO, Reizo
(*[1]Univ. Tokyo; [2]RIKEN)*

[*J. Solid State Chem.* **168**, 396–407 (2002)]

We have prepared and characterized several cation radical salts of organic donors (TMTTF, EDT-TTF, ET, BETS and HMTSF; scheme) with two novel planar Te-based dianions, TeI_4^{2-} and $Te_2I_6^{2-}$. $(ET)_5Te_2I_6$ **1** and $(BETS)_5Te_2I_6$ **2** are isostructural. In these $Te_2I_6^{2-}$ salts, intermolecular short I···I contacts form a supramolecular corrugated anion sheet (Figure 1a). Donor arrangement is similar to the α-type (Figure 1b). With lowering temperature, the resistivity of **1** shows a gradual increase followed by a sharp upturn at 110 K. **2** is metallic down to 120 K and shows a gradual increase of the resistivity followed by a clear transition to an insulating state around 60 K. Crystal structure of $(ET)_4TeI_4$ **3** is based on the “herring bone” arrangement of ET molecules similar to the α-type. **3** shows a semiconductive behavior around room temperature followed by a transition to an insulating state at 210 K. $(EDT\text{-}TTF)_4TeI_4$ **4**, a semiconductor, exhibits a unique two-dimensional arrangement of dimerized EDT-TTF molecules.



Scheme 1. Molecular structures of organic donors used in this work.



(a) (b)

Figure 1. Crystal structure of **1**: a) $Te_2I_6^{2-}$ anion network. b) end-on projection of ET molecules.

IV-F Electronic and Magnetic Properties of π-Electron-Based Molecular Systems

π-electrons are an interesting building block in architecting functionalized electronic and magnetic molecular systems. We have focused on nano-sized graphite and TTF-based organic charge transfer complexes, in which π-electrons play an important role, in developing new types of molecular electronic systems. In nanographene, single layer nanographite, which is defined as flat open π-electron system having edges and contrasted to closed π-electron systems of fullerenes and carbon nanotubes, non-bonding π-electronic state appearing around the Fermi level generates unconventional nanomagnetism. We have found an interesting magnetic switching effect in a nanographite network operated by water-adsorption/desorption processes. A combination of TTF-based π-electron donor and counteranion having localized spins is a useful way in producing molecular magnetic conductors, which are expected to have properties different from traditional metal magnets featured with *s*-*d* interaction. Under this scheme, we have developed a new class of TTF-based organic magnetic conductors. The interaction between the conducting π-electrons of donors and the localized *d*-electrons of magnetic anions are found to show interesting interplay between magnetism and electron transport.

IV-F-1 Drastic Effect of Water-Adsorption on the Magnetism of Carbon Nanomagnets

SATO, Hirohiko[1]; KAWATSU, Naoki[1]; ENOKI, Toshiaki; ENDO, Morinobu[2]; KOBORI, Ryoji[3]; MARUYAMA, Satoshi[3]; KANEKO, Katsumi[3]
([1]Tokyo Inst. Tech.; [2]Shinshu Univ.; [3]Chiba Univ.)

[*Solid State Commun.* **125**, 641–645 (2003)]

Activated carbon fibers (ACFs), composed of nanometer-size fragments of graphite (nanographites), show π-electron-based paramagnetism. Measurements of ESR and magnetic susceptibility revealed that adsorption of water molecules drastically suppresses the paramagnetism of ACFs. Considering also the structural change, this is interpreted in terms of a crossover from a paramagnetic state to a low-spin state of each nanographite due to a structural change of nanographite-network caused by internal pressure of adsorbed water molecules. This phenomenon serves us as a new method for in situ controlling of the condensed state of electrons in soft materials.

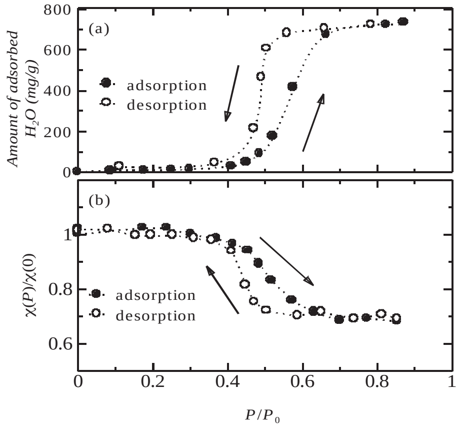


Figure 1. (a) Water adsorption isotherm of ACFs at room temperature, (b) adsorption dependence of the spin susceptivility obtained by ESR measurements. $P_0 \approx 20$ Torr is the saturation pressure of water at room temperature. The spin susceptibilities, $\chi_{\mathrm{spin}}(P)$, were calculated from the peak heights and the line widths.

IV-F-2 Ferromagnetic Interaction and Metallic Conductivity of Radical Ion Salts $(\mathrm{DIEDO})_2\mathrm{M(mnt)}_2$ (M = Ni, Pt)

NISHIJO, Junichi[1]; OGURA, Eiji[2]; YAMAURA, Jun-ichi[3]; MIYAZAKI, Akira[1]; ENOKI, Toshiaki; TAKANO, Takahiko[2]; KUWATANI, Yoshiyuki[2]; IYODA, Masahiko[2]
([1]Tokyo Inst.Tech.; [2]Tokyo Metropolitan Univ.; [3]Univ. Tokyo)

[*Synth. Met.* **133-134**, 539–541 (2003)]

$(\mathrm{DIEDO})_2\mathrm{M(mnt)}_2$ (M = Ni, Pt; DIEDO = 4,5-diiodo-4',5'-ethylenedioxytetrathiafulvalene; mnt: maleonitriledithiolate) composed of transition metal complexes and iodine-bonded donor have a unique structure featured with strong coordination-bond-like interaction between iodo group of donor and cyano group of anion. It consists of two donor chains sandwiched between anion chains. The salts are metallic down to 100 K, followed by an onset of a metal-insulator (M-I) transition. T_{MI} becomes lowered at high pressures (21 K at P > 11 kbar). The magnetic susceptibility suggests the presence of ferromagnetic interactions ($J \sim 20$ K) between localized magnetic moments of $\mathrm{M(mnt)}_2^{-}$, which interact with conduction electrons. The origin of ferromagnetic interactions is explained by McConnell's first model and small overlaps between SOMOs of $\mathrm{M(mnt)}_2^{-}$.

IV-F-3 Crystal Structure and Physical Properties of $(\mathrm{EDS\text{-}TTF})_2\mathrm{FeBr}_4$

MIYAZAKI, Akira[1]; ENOKI, Toshiaki[2]
([1]Tokyo Inst. Tech.; [2]IMS and Tokyo Inst. Tech.)

[*Synth. Met.* **133-134**, 543–545 (2003)]

Crystal structure, transport and magnetic properties of $(\mathrm{EDS\text{-}TTF})_2\mathrm{FeBr}_4$ (EDS-TTF: ethylenediselenotetrathiafulvalene) are reported. Between one-dimensional columns of donors and quasi square-lattices of FeBr_4 anions, close Br···Se van der Waals contacts and CH···Br type hydrogen bonds are observed. This salt shows high room-temperature conductivity and metal-insulator transition at *ca.* 250 K (σ_{RT} = 400 S cm^{-1}, E_A = 380 K). The magnetic susceptibility obeys the Curie-Weiss law (C = 4.58 emu K mol^{-1}, Θ = –0.9 K) without showing any magnetic transition down to 1.8 K. The weak π-*d* interaction can be due to the small contribution of Se 4*p* orbitals to the HOMO of EDS-TTF.

IV-F-4 Unconventional TTF-Based Molecular Magnets

ENOKI, Toshiaki; YAMAZAKI, Hisashi[1]; OKABE, Kazuki[1]; ENOMOTO, Kengo[1]; KATO, Takehiko[1]; MIYAZAKI, Akira[1]; OGURA, Eiji[2]; KUWATANI, Yoshiyuki[2]; IYODA, Masahiko[2]
([1]Tokyo Inst.Tech.; [2]Tokyo Metropolitan Univ.)

[*Synth. Met.* **133-134**, 296–272 (2003)]

Unconventional magnetic features are reported in charge-transfer complex-based molecular magnets. Quasi-1D metals $(DMET)_2FeBr_4$, $(EDTDM)_2FeBr_4$ and semiconductor $(EDS\text{-}TTF)_2FeBr_4$ are isostructural with alternating stacking of donor π-electron conducting sheets and square lattice *d*-spins of $FeBr_4^-$ anion sheets. The former two undergo an SDW transition at 15–40 K. For $(DMET)_2FeBr_4$, the magnetoresistance is strongly affected by Fe^{3+} spin arrangement, suggesting strong π–*d* interaction. Quasi-1D metal $(EDO\text{-}TTFBr_2)_3I_3$ undergoes an MI transition around T_{MI} ~ 150 K. The susceptibility is featured with 1D antiferromagnetic (AF) system with fractional magnetic moments. It takes a 3D AF ordered state below T_N = 15 K. The co-existence of metallic conduction and localised moments evidences features of strongly correlated electron system in the MI boundary.

IV-F-5 Novel π-*d* Interaction System $(DMET)_2FeCl_4$

ENOMOTO, Kengo[1]; MIYAZAKI, Akira[1]; ENOKI, Toshiaki[2]
([1]Tokyo Inst. Tech.; [2]IMS and Tokyo Inst. Tech.))

[*Synth. Met.* **135-136**, 561–562 (2003)]

The structure of $(DMET)_2FeCl_4$ is featured with an alternate stacking of quiasi-1D chain-based donor sheets and magnetic Fe^{3+} (S = 5/2) sheets. At ambient pressure, the salt shows metallic behavior down to ~ 100 K with the pressure of a resistivity anomaly around 7 K, at which the susceptibility has a broad maximum of magnetic short-renge ordering in the Fe^{3+} magnetic sheet of *d*-electrons. An antiferromagnetic transition takes place at T_N = 2.8 K. The large Weiss temperature Θ = –11 K and the field dependant anomalies in the magnetoresistance, which indicate the presence of a strong antiferromagnetic interation, suggest that the donor π-electrons mediate the interlayer interaction between the Fe^{3+} magnetic layers.

IV-F-6 Novel Magnetism of $EDO\text{-}TTFX_2$ Salts (X = Br, I),

ENOKI, Toshiaki; YAMAZAKI, Hisashi[1]; NISHIJO, Junichi[1]; UGAWA, Kouhei[2]; OGURA, Eiji[2]; KUWATANI, Yoshiyuki[2]; IYODA, Masahiko[2]; SUSHKO, Yuri V.[3]
([1]Tokyo Inst. Tech.; [2]Tokyo Metropolitan Univ; [3]Univ. Kentucky)

[*Synth. Met.* **137**, 1173–1174 (2003)]

Charge transfer complexes of $EDO\text{-}TTFX_2$(X = Br, I) form low-D structures featured with coordination-like bond formation of *X* with counter anions, giving unconventional magnetic conductive systems with magnetic anions. $(EDO\text{-}TTFI_2)_2M(mnt)_2$(M = Pt, Ni) are 1D conductors interacting with ferromagnetic 1D $M(mnt)_2$ chains. Applying pressure gives a unique ferromagnetic domain formation, 2D $(EDO\text{-}TTFBr_2)_2\text{-}FeBr_4$ is metallic, where 1D $FeBr_4$ chains taken an antiferromagnetic transition at a very high T_N(= 13.5 K) with a short-range-order effect around the resistivity minimum (30 K), suggesting the pressure of strong π-*d* interaction.

IV-F-7 Electronic and Magnetic Properties of Organic Conductors $(DMET)_2MBr_4$ (M = Fe, Ga)

ENOMOTO, Kengo[1]; YAMANAKA, Jun-Ichi[2]; MIYAZAKI, Akira[1]; ENOKI, Toshiaki
([1]Tokyo Inst. Tech.; [2]Univ. Tokyo)

[*Bull. Chem. Soc. Jpn.* **76**, 945–959 (2003)]

$(DMET)_2MBr_4$ (M = Fe, Ga) are isostructural organic conductors whose crystal structure consists of an alternate stacking of quasi one-dimensional chain-based donor layers and anion square lattices. The resistivity, ESR, magnetic susceptibility, magnetization, and magnetoresistance of these salts were investigated in order to clarify the correlation between the electronic structure and the magnetism. The electronic structures of both salts are metallic down to T_{MI} ~ 40 K, below which a Mott insulating state is stabilized, accompanied by an SDW transition at T_{SDW} ~ 25 K. The $FeBr_4$ salt with Fe^{3+} (S = 5/2) localized spins undergoes an antiferromagnetic transition at T_N = 3.7 K. In the $FeBr_4$ salt, the magnetization curves, which show field-direction-dependent anomalies in addition to a spin-flop transition, are demonstrated to have a participation of donor π-electron spins in the magnetization processes. The field dependence of the magnetoresistances below T_N tracks faithfully that of the magnetization, where the donor π-electrons and Fe^{3+} *d*-electrons are responsible for the former and the latter, respectively. This clearly demonstrates the presence of the π-*d* interaction that plays an important role in the interplay between electron transport and magnetism.

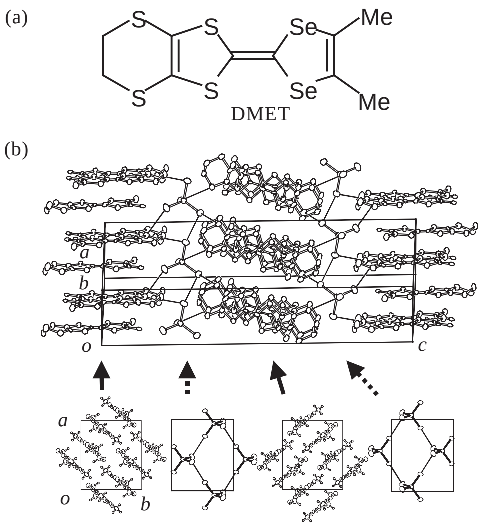


Figure 1. (a) Molecular structure of DMET donor. (b) The crystal structure of $(\mathrm{DMET})_2\mathrm{FeBr}_4$. Cross sectional views of donor and anion layers are drawn. Solid lines in the both figures denote close intermolecular B···S and Br···Br contacts.

IV-F-8 Structure and Electronic Properties of a Nongraphitic Disordered Carbon System and Its Heat-Treatment Effects

TAKAI, Kazuyuki[1]; OGA, Meigo[1]; SATO, Hirohiko[1]; ENOKI, Toshiaki; OHKI, Yoshimasa[2]; TAOMOTO, Akira[2]; SUENAGA, Kazutomo[3]; IIJIMA, Sumio[3]
([1]Tokyo Inst. Tech.; [2]Matsushita Electric Industrial Co., Ltd.; [3]Meijo Univ.)

[*Phys. Rev. B* **67**, 214202 (11 pages) (2003)]

The heat-treatment effect on electronic properties is investigated in relation to structural change for pulsed-laser-deposited amorphous carbon thin films having sp^2/sp^3 ratio ≈ 9. The heat treatment at temperatures 200–400 °C increases conductivity and modifies the hopping conduction mechanism at low temperatures, resulting in the generation of a Coulomb gap at E_F. This is attributed to the heat-treatment-induced modification of the disorder nature of the structure from atomic-scale sp^2/sp^3 disorder to a disordered graphitic sp^2-domain network by the migration of sp^3 defects. In the heat-treatment temperature region above 600 °C, where the structure is featured with graphitic sp^2 domains, considerably small positive thermoelectric power is suggestive of carrier compensation by the competition of hole and electron carriers that originate from the inhomogeneous charge distribution caused by the difference of Fermi levels among graphitic sp^2 domains. In the high-heat-treatment-temperature region 800–1100 °C, the formation of an infinite percolation path network of the graphitic sp^2 domains induces an insulator-to-metal transition, where the electron transport in the sp^2-rich metallic state is featured by weakly temperature-dependent conductivity with majority hole and minority electron carriers. ©2003 *The American Physical Society*

IV-G Development of Molecular Materials Containing Photo-Reactive Species

The molecular materials are considered to be good candidates for advanced functional materials such as (nano-)devices. Their outstanding advantages include the wide variety of substances, possibility of molecular-level fine design, softness of lattices and unique and varied crystal structures. On the other hand, the physical properties of the molecular materials significantly depend on their crystal structures. The crystal structures are, however, not predictable or controllable thus far. Sometimes a pair of molecular materials with very similar crystal structures to each other exhibit qualitatively different physical properties for various or unknown reasons. Additionally many of the molecular charge-transfer salts are very difficult to change their Fermi level by standard methods of doping. Consequently one can hardly choose an appropriate molecular crystal which has favorable physical properties (band-filling) and a crystal structure with an enough good quality and sufficient size for study or other practical purposes. If one can obtain molecular radical salts with a photo-redox-reactive species, one could dope it by irradiation of light (permanent photo carrier injection) without unexpected structural change using solid state in situ reaction. In order to pursue a new possibility of molecular materials, we have started to develop molecular radical salts with photo-reactive species.

IV-G-1 Metastable State of MV[Ni(dmit)$_2$]$_2$ (MV = Methyl Viologene, dmit = 1,3-dithiol-2-thione-4,5-dithiolate)

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[to be published]

MV[Ni(dmit)$_2$]$_2$ has long attracted a special attention of several different research groups in terms of the strong photo-induced redox ability peculiar to MV. Yet most of the electrical, structural or optical data are based on the powder sample, and few details are known on its physical properties. We have recently obtained the single crystals of this material, and found that there exists a new phase as a metastable state. The fresh single crystals of the title compound exhibited clear metallic conductivity down to 1 K with anomaly below 100 K. The magnetic susceptibility was well described by Pauli paramagnetism with a small anomaly below 100 K corresponding to the electrical behavior. The thermoelectric power was constantly ~ 0 μVK^{-1} from RT–4 K, which is consistent with the fact that this material has a half-filled (“compensated”) electronic band strucuture. The crystal consists of mixed stacking of [Ni(dmit)$_2$]$^-$ (A) and MV^{2+} (D) by repeating unit of D–A–A. The intermolecular interactions between A’s are very weak but isotropic. This phase could be one of the rare examples of molecular version of naturally occurring (main group) metallic elements in that weak and isotropic inter-site interactions favor the metallic nature against correlation effect. The light irradiation effects on its electrical and magnetic properties are under study.

IV-G-2 Electrical Behavior of UV-VIS Irradiated Ag(DMe-DCNQI)$_2$

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The UV-VIS (200–1100 nm) irradiation effect on the electrical behavior of the title compound was examined with its single crystals and clear difference has been found depending on the duration of irradiation. The longer the irradiation time was, the higher RT resistivity it exhibited. The whole temperature-dependence also changed. With irradiation a sudden but small resistivity increase appeared well higher temperature than its original metal-insulator transition (100 K), and this temperature rapidly moved toward room temperature. These irradiation effects has been confirmed to be intrinsic by comparing the results of parallel measurements of non-irradiated samples. The overall behavior can be featured by sum of original bulk behavior (major part) and new metallic behavior with a possible transition at higher temperature (minor part). Further details are now under study.