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 (EMV) 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, very few molecular vibrations 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 unconventional superconducting mechanism. The Raman and infrared spectra change dramatically at the CO phase-transition temperature, since CO is accompanied by a charge disproportionation, forming 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 Raman Study of the Charge Ordering in α -(BEDT-TTF)₂I₃ at High Pressure

WOJCIECHOWSKI, Roman; YAMAMOTO, Kaoru; YAKUSHI, Kyuya; KAWAMOTO, Atsushi¹ (¹Hokkaido Univ.)

We have carried out Raman experiments on α -(BEDT-TTF)₂I₃ to investigate the site-charge distribution among BEDT-TTFs in the paramagnetic semimetal-like (PM) and diamagnetic insulating (DI) phases at ambient and quasi-hydrostatic pressures. We focused on the charge-sensitive v_2 and v_3 modes of BEDT-TTF, which are related to the ring and central C=C stretching modes with A_g symmetry. We found a distinctive spectral change associated with metal-insulator phase transition up to 1.5 GPa (above this pressure the DI phase was suppressed).

In the DI phase, v_2 splits into four bands labeled by **c**_{1a}, **c**_{1b}, **c**₂, and **c**₃, which are confirmed by the isotope shift of the central ¹³C=¹³C band). The presence of the four bands of v_2 indicates the presence of the four crystallographically non-equivalent BEDT-TTFs. This observation means that the inversion symmetry characteristic of the PM phase disappears in the DI phase. The magnitude of the observed splitting and the symmetry breaking indicate that charges are disproportionate in so-called horizontal stripes (perpendicular to stacks). Quasi-hydrostatic pressures induce a progressive downshift of **c**_{1a} and **c**_{1b} accompanied with an upshift of **c**₂ and **c**₃, indicating the continuous change of the charge disproportionation (CD) ratio, while the band position is

temperature independent under a constant pressure. Assuming the linear dependence of the v_2 frequency on the ionicity of BEDT-TTF, the CD ratio between the charge-rich and charge-poor sites is evaluated as ca. 0.2e: 0.8e at low pressures, which gradually decreases to ca. 0.3e : 0.7e near 1.5 GPa. The CD ratio decreases and eventually CD is discontinuously suppressed above 1.5 GPa. This is because the transfer integrals (t) increase faster than the inter-site (V) Coulomb repulsions (on-site (U) is pressure independent) as expected. In the PM phase the v_2 mode is split into two a_1 and a_2 bands (for ¹³C substituted sample three bands were observed) indicating not uniform charge distribution among BEDT-TTFs. The charge difference evaluated from the splitting between the $\mathbf{a_1}$ and $\mathbf{a_2}$ bands is small, say 0.4e: 0.6e, which is weekly dependent upon the pressure.



Figure 1. The pressure dependence of the α -(BEDT-TTF)₂I₃ Raman spectra taken at 20 K with 514 nm laser line polarized along b-axis i.e. perpendicular to the stacks.

IV-A-2 Raman Study of the Charge Ordering in α'-(BEDT-TTF)₂IBr₂ at High Pressure

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Raman spectroscopy experiments have been carried out for α' -(BEDT-TTF)₂IBr₂ at ambient and under several quasi-hydrostatic pressures up to 2.3 GPa. We have focused on the charge-sensitive v_2 and v_3 modes of BEDT-TTF', which are related to the rings and central C=C stretching modes with A_g symmetry. We have examined these modes from room temperature to 20 K in order to detect the change in charge-distribution resulting from the structureless phase transition at 250 K at ambient pressure. We first confirmed from the splitting of v_2 ($\mathbf{a_1}$, $\mathbf{a_2}$) and v_3 ($\mathbf{b_1}$, $\mathbf{b_2}$) [See the spectrum at ambient pressure in Figure 1] that this phase transition is characterized as the charge-ordering (CO) phase transition. On increasing pressure, the phase-transition temperature (T_{CO}) decreases monotonously. Eventually above 1 GPa, the Raman spectra characteristic of the CO phase, which consist of two v_2 (**a**₁, **a**₂) and two v_3 (**b**₁, **b**₂), are suppressed in the entire temperature range.

This suggests that inter-stack transfer integrals between BEDT-TTFs increases faster than the inter-site Coulomb repulsion when the unit cell volume is reduced by pressure. In the semiconducting phase of α '-(BEDT-TTF)₂IBr₂, the Raman spectra consist of a rather broad band in contrast to the spectrum of metallic β -(BEDT-TTF)₂IBr₂ or θ -(BEDT-TTF)₂I₃ salts, in which v_2 and v_3 are well separated. We have found that the pressure over 1.8 GPa is required for this compound to reach the uniform charge distribution like metallic salts [See the spectra above 1.8 GPa in Figure 1].



Figure 1. Raman spectra recorded at 100 K under several pressures up to 2.3 GPa, from the (001) crystal face with 514 nm laser line polarized parallel to $[1\overline{1}0]$ *i.e.* perpendicular to BEDT-TTF stacks.

IV-A-3 Charge Ordering in θ-(BEDT-TTF)₂TIM(SCN)₄ (M = Co and Zn) Studied by Vibrational Spectroscopy

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[Synth. Met. to be published]

Mori et al. systematically synthesized the series of θ -(BEDT-TTF)₂*MM*'(SCN)₄, [*M* = Cs, Rb, Tl; *M*' = Co, Zn], (abbreviated as θ -MM'), and proposed the phase diagram which demonstrated the relation between the metal-insulator transition temperature and the dihedral angle between BEDT-TTF molecules in adjacent stacks.¹⁾ Recent experimental and theoretical studies including our research group have manifested that the MI transition of θ -RbM' is caused by the charge ordering (CO). θ -TlM' [M' = Co, Zn] have the largest dihedral angle among the θ -MM' family, which means that theses compounds have the most narrow bandwidth. We examined the Raman and infrared spectra of these two compounds in the temperature range of 50-300 K. Vibrational spectra of θ -TlCo at low temperature suggest the charge ordering with a horizontal stripe accompanying a doubling of the unit cell. θ -TlZn, which has larger dihedral angle, also underwent a charge-ordering phase transition at $T_{\rm CO} = 165$ K. Different from θ -RbZn and θ -TlCo, however, the fluctuation of CO appeared at 240 K, which is much higher than $T_{\rm CO}$. Furthermore, the pattern of v_3 modes is quite different from θ -RbZn, which reflects the structure-sensitive nature of v_3 modes, which was claimed in our preceding paper.2)

References

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- 2) K. Yamamoto, K. Yakushi, K. Miyagawa and K. Kanoda, *Phys. Rev. B* 65, 085110 (2002).

IV-A-4 High-Pressure Raman Study on a 1/3-Filled System (BEDT-TTF)₃CuBr₄

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While most CT salts showing charge ordering (CO) belong to 1/4-filled system, the semiconducting phase of the 1/3-filled system (BEDT-TTF)₃CuBr₄ is identified as the CO state by the X-ray diffraction and Raman measurements. In the present study, we investigated the critical behavior of the charge distribution across the phase boundary between the CO and pressure-induced metallic phases. Figure 1 shows the pressure dependence of the Raman spectrum measured at 150 K. The spectrum showed four bands a₁, a₂, b₁, and b₂ (a₂ and b1 are almost degenerated at ambient pressure). Based on the polarization dependence, we have assigned a_1 and $\mathbf{a_2}$ to ring C=C based stretching-mode v_2 (a_g). Note that the peak separation of \mathbf{a}_1 and \mathbf{a}_2 is gradually reduced as the pressure is increased. Then, the two bands are almost merged into one band close to 1 GPa around which the DC conductivity changes into metallic behavior. Since the frequency of v_2 shifts roughly in proportional to the molecular charge, the approaching of the two bands manifests that the charge disproportionation is continuously suppressed under the application of pressures. It should be important to distinguish whether the pressured-induced phase transformation is a phase transition or crossover phenomena.

Figure 1. Pressure dependence of the Raman spectrum of $(ET)_3CuBr_4$. The exciting ($\lambda_{ex} = 780 \text{ nm}$) and scattered lights are polarized along the *a** and *c* axes.

IV-A-5 Infrared and Raman Studies of the Charge Ordering in the Organic Semiconductor κ -[(Et)₄N](ET)₄Co(CN)₆·3H₂O

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[Macromolecular Symposia to be published]

Polarized infrared reflectance and Raman spectra of the chare transfer salt κ -[(Et)₄N](ET)₄Co(CN)₆·3H₂O were measured as a function of temperature. The salt undergoes a phase transition at T = 150 K which is related to a charge ordering inside the conducting ET layers. The charge ordering has a considerable influence on vibrational as well as electronic spectra. New vibrational bands related to ET⁺ cations are seen below 150 K. Moreover, formation of a new energy gap (charge gap) in electronic excitation spectrum is observed.

IV-A-6 Charge-Ordering and Magnetic Phase Transitions in θ -(BDT-TTP)₂Cu(NCS)₂

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[Phys. Rev. B to be published]

The charge ordering (CO) in organic charge-transfer (CT) salts draws much attention, since the theoretical studies suggest the relation between the charge fluctuation and the pairing mechanism in superconductivity (SC). The experimental study on charge ordering of organic CT salts has been conducted most intensively in θ -type ET salts. The θ -ET salt is a quarter-filled quasitwo-dimensional (Q2D) system without a dimerized ET unit. In non-dimerized θ -ET salts, the charge localization is accompanied by charge disproportionation (CD) and generates charge-rich and charge-poor sites such as $(0.5+\delta, 0.5-\delta)$. We have discovered such CO phase transition at $T_{CO} \sim 250$ K in non-dimerized Q2D system, θ -(BDT-TTP)₂Cu(NCS)₂.¹⁾ The CO pattern in a variety of ET-based CT salts was theoretically considered. In the framework of mean-field theory, Seo examined the three types of CO patterns, the horizontal, diagonal, and vertical stripes. In this context, the magnetic property gives some information about the CO pattern. The magnetic susceptibility of 30 K < T < 300K follows the Curie-Weiss law with Curie constant of 0.154 emuK/mol and Weiss temperature of -29 K. We roughly estimate the exchange interaction between the localized charges as |J| = 8 K. The single-crystal ESR experiment shows a magnetic phase transition to a spinsinglet state at 5 K. We examined the selection rule of the polarized Raman spectrum. Both the Raman spectra and magnetic properties suggest the vertical stripe along the *b*-axis. In addition to the pattern of CO, we discussed the following three subjects. (1) Through the analysis of the v_2 modes, we presented the parameter CD ratio δ as 0.4. (2) The linewidth of v_2 suggested the charge fluctuation above $T_{\rm CO}$. (3) The structural fluctuation for the doubling of the unit cell was found at 200 K.

Reference

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Figure 1. (a) Temperature dependence of resistivity. (b) Temperature dependence of the frequency of v_2 (solid square) in the (c,c+b) spectrum, v_2 (open circle) in (a,a+b), and v_4 (solid triangle) in (a,a+b). (c) Magnetic susceptibility and ESR intensity. The solid and broken lines are respectively the best-fit curves of the Curie-Weiss model and the Bonner-Fisher model with J = -7.9 K. The low-temperature region of ESR intensity is expanded in the inset. (d) ESR linewidth. Open squares, open triangles, and solid circles respectively correspond to the signals of $H||a^*, H||c$, and H||b. T_{CO} and T_{M} represent the charge-ordering and magnetic phase transition temperatures, respectively.

IV-A-7 Spectroscopic Studies of Charge-Ordering System in Organic Conductors

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[Macromolecular Symposia to be published]

We reviewed our infrared and Raman studies of charge-ordering phase transitions in organic chargetransfer salts. In molecular conductors, the molecular orbital barely overlaps with those of neighbor molecules. Therefore, the transfer integral (t), which contributes to the delocalization of charge, is usually smaller than the on-site (U) and off-site (V) Coulomb interactions that contribute to the localization the charges. Strong correlation effect originates from the comparative magnitude among t, U, and V, and thus many molecular conductors are located at the boundary between a metal (delocalized state) and insulator (localized state). When the charge is localized, the charge often induces a charge disproportionation (CD) and eventually generates an inhomogeneous charge distribution. This localized state is called as a chargeordered (CO) state, since the localized charges often form a new periodic structure. It is well known that the frequency of some C=C stretching modes, for example, in BEDT-TTF show downshift depending upon the degree of oxidation of the molecule. Using the C=C stretching mode as a probe of the oxidation state, we investigate the CO phase transition. We first introduce θ -(BEDT-TTF)₂*MM*'(SCN)₄ (*M* = Rb, Cs, Tl; *M*' = Zn, Co) as typical examples of a charge-ordering system. We apply the same spectroscopic technique to α' - $(BEDT-TTF)_2IBr_2$, θ - $(BDT-TTF)_2Cu(NCS)_2$, and (TTM-TTP)I₃, which show the phase transitions from low-resistivity state to high-resistivity state.

IV-A-8 Charge and Molecular Arrangement in (DI-DCNQI)₂Ag Studied by Vibrational Spectra

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The quasi-one-dimensional (Q1D) radical anion salt (DI-DCNQI)₂Ag (DI-Ag) (Figure 1a) shows antiferromagnetic (AF) ordering below 5.5 K, in contrast to the ordinary Q1D systems that fall down to a spinsinglet state. NMR study proposed that the charge localization (CL) in DI-Ag is the first example of the Wigner crystallization in organic charge-transfer salts. While this proposal has stimulated much interest in the charge-ordering (CO) phenomenon in various strongly correlated systems, no direct evidence has been reported so far for the emergence of CO in the present material. We have suggested via infrared reflectance study that the molecular arrangement is dimerized (short-range order) from room temperature, although the proposed model is based on a uniform molecular stacking. To investigate the charge distribution as well as the molecular arrangement, we measured the temperature dependence of the Raman spectrum.

Figure 1b shows the temperature dependence of the Raman spectrum. Two lines $\mathbf{a_1}$ and $\mathbf{b_1}$ found at room temperature are attributed to a_g type of C=C and C=N stretching modes, respectively. On lowering temperature, the spectrum exhibited additional bands $\mathbf{a_2}$ and $\mathbf{b_2}$ attributable to the vibronic bands of $\mathbf{a_1}$ and $\mathbf{b_1}$. We confirmed that the infrared signals of the C=C and C=N modes appeared at different frequencies from these Raman bands. The present result indicates that the dimerized molecular stack ($4k_F$ bond-order wave (BOW)) transforms into a tetramerized one ($2k_F$ BOW) with an effective inversion center at low temperatures. Hence, the present result suggests that the AF-CL phase should be the $2k_F$ BOW state, rather than the $4k_F$ CDW state (Wigner crystal).

Figure 1. (a) Molecular structure of DI-DCNQI. (b) Temperature dependence of the Raman spectrum measured at ambient pressure. ($\lambda_{ex} = 633$ nm) Dotted line shows guide for eyes.

IV-A-9 Charge Distribution and Molecular Arrangement in the Pressure-Induced Metallic Phase of (DI-DCNQI)₂Ag

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[Synth. Met. submitted]

In contrast to the NMR study which suggests the Wigner-crystal-like charge-ordered state (CO), our previous infrared and Raman study has suggested the important role of lattice modulation rather than the Coulomb interaction for the charge localization (CL) in DI-Ag. It has been confirmed in this compound that the localized charge is released to be metallic at moderate pressures (*ca.* 10 kbar). So the high-pressure experiment will provides crucial data to elucidate the localized state. In the present study, we measured high-pressure Raman spectrum using a sapphire-anvil cell to investigate the pressure dependence of the charge-sensitive C=C and C=N stretching modes.

Figure 1 shows the Raman spectrum observed at 100 K under various pressures. The split phonon bands, (a_1, a_2) and (b_1, b_2) , are respectively assigned to the stretching modes of C=C and C=N. Under the application of pressure, a_2 and b_2 were readily suppressed and almost completely disappeared at *ca*. 1 GPa. Note that a_2 and b_2 do not merge with their parent peaks a_1 and b_1 when they are suppressed. This result indicates that no detectable change occurs in the charge distributions between the localized and metallic states. This result supports our previous conclusion: The localized state of DI-Ag is not regarded as the Wigner crystal but the $2k_F$ BOW state coexisting with SDW.

Figure 1. Pressure dependence of the Raman spectrum of DI-Ag measured at 100 K. ($\lambda_{ex} = 780$ nm)

IV-A-10 Study of the Phase Transitions of (DI-DCNQI)₂M (M = Ag, Li, Cu) through the Analysis of the Temperature Dependent Vibronic and Vibrational Infrared Absorptions

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[J. Solid State Chem. in press]

The temperature dependent phase transitions of 2,5-DI-DCNQI (diiodo-dicyanoquinon-diimmine) title compounds are analyzed by looking at the BOW (bond order wave) and at the CDW (charge density wave) which characterizes the transitions. The analysis is done by studying temperature dependent powder infrared spectra which allow one to have a separate evaluation of both types of contribution to the phase transition of these molecular metals. A model for the spectroscopic infrared features related to the transitions is reported and used for the analysis. It is found that all the title compounds develop a BOW structure at low temperature with characteristics which recall an instability toward a tetramerized $2k_{\rm F}$ periodicity particularly for the Ag and Li compounds. An appreciable CDW amplitude contribution to the transitions is not found in the spectra.

IV-A-11 Development of a High-Pressure Cell for Raman Measurement Using Sapphire Anvil

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[J. Spectrosco. Soc. Jpn. 51, 72 (2002)]

Diamond is most widely used as anvils for a highpressure cell. However, the strong Raman band at 1332 cm⁻¹ of diamond disturbs our Raman study of charge ordering in organic conductors. We can avoid this serious problem by using sapphire anvils, which has been often adopted for the anvil of high-pressure cell. Because sapphire is more brittle than diamond, sapphire anvils are sometimes broken before the pressure is elevated to several GPa. Although a soft gasket can relieve the strain on the anvil surface, the aperture in such gaskets is easily distorted. To prevent the distortion of aperture and the strain on sapphire surface at the same time, we have prepared the following coated gasket. The body of the gasket was made of stainless steel (Inconel 600) plate. The hard plate was covered with copper by means of electroplating. We performed high-pressure Raman measurement using the copper coated Inconel gasket (0.3 mm thick, ϕ 0.5 mm aperture) with sapphire anvils (1.5 mm height, ϕ 1.2 mm culet). Figure 1 of IV-A-9 shows the resultant Raman spectrum measured from the charge-transfer salts DI-Ag. It demonstrates that the coated gasket enables us to generate pressures over ca. 5 GPa without any special modifications for the pressure cell that is designed originally for diamond anvils.

IV-A-12 Optical Study of Two-Dimensional Organic Metal (EO-TTP)₂AsF₆ (EO-TTP=2-(4,5ethylenedioxy-1,3-dithiol-2-ylidene)-5-(1.3dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene)

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[J. Solid State Chem. in press]

The charge-transfer salts of organic electron donor molecules involving TTP skeleton provide an enormous number of stable metals down to low temperature. EO- TTP belongs to the metallic BDT-TTP family with an asymmetric structure, in which ethylenedioxy group is substituted at one of the five member rings. Polarized reflectance spectra were measured on the conductive (010) plane of metallic (EO-TTP)₂AsF₆ single crystal. At room temperature, well-defined plasma edges ap-

peared in both directions parallel (E||a) and perpendicular $(E \perp a)$ to the molecular stack. It was found from the Drude analysis that the effective mass ratio of (EO-TTP)₂AsF₆ was 4 times larger than that of (TMTSF)₂-PF₆ and half of β -(BEDT-TTF)₂I₃ which has a closed Fermi surface. The intra- and inter-stack transfer integrals were estimated from the plasma frequencies in the framework of tight-binding model. Based on these transfer integrals, we suggested that the Fermi surface was open in the k_c direction. Using a generalized Drude model, we obtained the frequency dependence of relaxation rate, which conformed to $\gamma(\omega) = \gamma_0 + b\omega^2$ in the frequency range of 1800-5500 cm⁻¹. This result suggests the view that (EO-TTP)₂AsF₆ has exceptionally weak electron-electron and electron-phonon interaction among organic conductors.

Figure 1. Energy dispersion $E(k_a,k_c)$ in a reciprocal cell and Fermi surface in a Wigner-Seitz cell: (a) $E(k_a,k_c)$ and (b) Fermi surface calculated using the theoretically calculated transfer integrals; (c) $E(k_a,k_c)$ and (d) Fermi surface calculated using the experimentally obtained transfer integrals.

IV-B Microscopic Investigation of Molecular-Based Conductors

The aim of this research is to clarify the electronic states (charge and spin states) of molecular based compounds with curious electronic phases by microscopic point of view. Although the fundamental properties of molecular based conductors have been very well clarified, it is true that there still remain several unsolved questions in the molecular based conductors.

Microscopic investigations are advantageous for understanding the detailed electronic structures of molecular based compounds. To clarify the low temperature electronic states, we performed the NMR, and ESR measurements for molecular based conductors.

IV-B-1 EPR Investigation of the Electronic States in β '-type [Pd(dmit)₂]₂ Compounds (where dmit is the 1,3-dithia-2-thione-4,5-dithiolato)

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[J. Mater. Chem. 11, 2159 (2001)]

Magnetic investigations of organic conductors, β' type [Pd(dmit)₂]₂, have been performed by Electron Paramagnetic Resonance (EPR) measurements. We found that most of them except one compound underwent antiferromagnetic transitions. Although they are isostructural with little differences in lattice parameters, their spin-spin correlations and antiferromagnetic transition temperatures show strong counter ion dependence. The EPR *g*-values of Pd(dmit)₂ cannot be explained within the framework of isolated radical description which is a good approximation for conventional organic conductors. The electronic structures of a series of molecular conductors based on Pd(dmit)₂ at ambient pressure are discussed from microscopic points of view.

IV-B-2 NMR Study of Charge Localized States of (TMTTF)₂Br

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[J. Phys. Chem. Solids 63, 1259 (2002)]

 13 C NMR study was performed for a quasi-onedimensional organic conductor (TMTTF)₂Br using a single crystal in which two central carbon sites of TMTTF molecules were labeled with 13 C. To investigate the relation between the charge localization around 100 K and its magnetic ground state from the microscopic point of view, we measured the NMR spectra and nuclear relaxation. We found slight broadening of the spectra above the magnetic phase transition temperature ($T_N \sim 15$ K). We discuss this anomaly with the newly measured data of uniform susceptibility and ESR.

Figure 1. Temperature dependence of spin lattice relaxation rate $1/T_1$ of 13 C NMR. The values are deduced by fitting the experimental recovery data with a single exponential.

Figure 2. Temperature dependence of 13 C NMR spectra of (TMTTF)₂Br above 30 K. The horizontal axis indicates the deviation from 87.25 MHz.

Figure 3. Temperature dependence of the 13 C NMR absorption lines between 17 K and 30 K.

IV-B-3 Magnetic Investigation of Possible Quasi-One-Dimensional Two-Leg Ladder Systems, $(BDTFP)_2X(PhCI)_{0.5}$ (X = PF₆, AsF₆)

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[J. Phys. Soc. Jpn. 71, 2022 (2002)]

ESR and ¹H-NMR investigations of the quasi-onedimensional organic conductors, $(BDTFP)_2X(PhCl)_{0.5}$ ($X = PF_6$, AsF₆), were carried out. The low-temperature physical properties of the title compounds are quite different from each other, although those at R.T. are very similar. The PF₆ salt undergoes a spin-singlet transition around 170 K. On the other hand, the AsF₆ salt shows a discontinuous transition of first order around 230 K, in association with an abrupt jump in the spin susceptibility. The AsF₆ salt shows spin-gap behavior below 50 K, but it undergoes an antiferromagnetic transition at 14 K. The low-temperature electronic states of the title compounds are discussed by microscopic point of view. (a)

Figure 1. Crystal structure of $(BDTFP)_2X(PhCl)_{0.5}$: (a) possible two-leg ladder structures, (b) dimerization along the stacking axes.

Figure 2. Temperature dependence of the ¹H-NMR spinlattice relaxation rate, ¹H- T_1^{-1} , of (BDTFP)₂AsF₆(PhCl)_{0.5} for a single crystal.

IV-B-4 Microscopic Investigation of a New Two-Component Organic Conductor with Itinerant and Localized Spins: (CHTM-TTP)₂TCNQ

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[J. Phys. Soc. Jpn. in press]

Low-temperature electronic phases in a new two-

component organic conductor, a segregated-stack charge-transfer salt called (CHTM-TTP)₂TCNQ, 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, ¹H-NMR, and static susceptibility analyses. We present a microscopic investigation of the two-spin system with itinerant and localized moments.

(a)

Figure 1. (a) Molecular structure of CHTM-TTP. (b) Crystal structure of (CHTM-TTP)₂TCNQ at R.T.

Figure 2. Temperature dependence of the *g* values of $(CHTM-TTP)_2TCNQ$ applying the external static field along the *a* (triangle), b^* (square), and c^* (circle) crystal axes.

IV-B-5 ESR Study of the Charge Ordering States in (TMTTF)₂X

NAKAMURA, Toshikazu

ESR investigations were performed for a series of organic conductors, $(TMTTF)_2X (X = SbF_6, AsF_6, PF_6, ReO_4, ClO_4, SCN, Br)$. The ESR linewidth shows abrupt jumps or humps in the paramagnetic insulating region. The $(TMTTF)_2X$ compounds are roughly divided into three groups in the aspect of the anisotropy of the ESR linewidth at low-temperatures. We discuss the low-temperature charge distributed pattern from the microscopic point of view.

Figure 1 show the temperature dependence of the peak-to-peak ESR linewidth, ΔH_{pp} , of (TMTTF)₂ReO₄. The angular dependence of the $\Delta \hat{H}_{pp}$ for the c^*a plane at 300 K, 170 K and 110 K is shown in the inset of Figure 1. While the ΔH_{pp} reveals the standard anisotropic behavior in the metallic region, that at 110 K follows the formula for dipole-dipole interacted spins. This fact indicates that the electronic dipoles contribute to the ESR linewidth in the low temperature region. Considering the anisotropy of the ESR linewidth, we can estimate the charge distribution patterns in the low temperature phase. According to the experimental result, ΔH_a $>> \Delta H_{b'} \sim \Delta H_{c^*}$, the possible charge ordering pattern is -O-O-o-o- along the stacking axes (O and o indicate the charge rich and poor sites, respectively) with the wave-number, Q = (1/2, 0, 1/2).

Figure 1. Temperature dependence of the peak-to-peak ESR linewidth, $\Delta H_{\rm pp}$, of (TMTTF)₂ReO₄ for a single crystal. The inset shows the angular dependence of the $\Delta H_{\rm pp}$ at 300 K, 170 K and 110K. The static magnetic field applied in the *c*a*-plane.

IV-C Magnetic Organic Superconductors and Related Systems

Molecular materials are expected to play an important role in the future development of electronic devices. For the realization of molecular electronic devices, it is essential to develop a "dual-action system" whose conducting properties can be sharply controlled by external forces. One of the prospective dual-action molecular system is a composite system consisting of organic layers responsible for electron conduction and inorganic layers with localized magnetic moments, whose conductivity can be controlled by tuning magnetic state of the inorganic layers. We have recently discovered the first example of dual-functional magnetic organic conductor whose superconducting state can be sharply switched on or off by controlling the metamagnetic transition of the magnetic anion layers. In addition to the dual functionality of molecular conductors, the field-induced superconductivity of the organic conductors reported by us in 2001 has attracted an increasing interest. In organic systems, there are two well-known conductors showing field-induced superconducting transition: Chevrel type compound $Eu_{0.75}Sn_{0.25}Mo_6S_{7.2}Se_{0.8}$ and heavy Fermion system CePb₃. Unlike these inorganic conductors, λ -(BETS)₂FeCl₄ has an antiferromagnetic insulating ground state. That is, λ -(BETS)₂FeCl₄ is the first conductor exhibiting the insulator \rightarrow metal \rightarrow superconductor transitions with increasing magnetic field. We have recently discovered that the first antiferromagnetic organic superconductor, κ -(BETS)₂FeBr₄ undergoes a field-induced superconductiviting transition. The field-induced superconductivity seems to be a common feature of the organic superconductor with localized magnetic moments in the anion layers.

IV-C-1 An Indication of Magnetic-Field-Induced Superconductivity in a Bi-Functional Layered Organic Conductor, κ-(BETS)₂FeBr₄

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We have investigated BETS conductors, λ - and κ - $(BETS)_2FeX_4$ (X = Cl and Br), and reported several interesting properties, such as the novel magnetic-fieldinduced superconductivity under very high magnetic field (18 T < H < 41 T) in λ -(BETS)₂FeCl₄. Here we report the magnetoresistance of the antiferromagnetic organic superconductor, κ -(BETS)₂FeBr₄ up to 15 T and the observation of the onsets of the magnetic-fieldinduced superconductivity as the cooperative phenomena between the superconductivity and magnetism. As shown in the upper inset of Figure 1, with an increase of the applied magnetic field at 0.58 K, the resistivity suddenly increased at about 1.6 T for the magnetic field applied parallel to the a axis (// easy-axis), and the system recovered its metallic state. These results suggest that the internal field originated from the AF coupling between the π electrons and the ferromagnetically aligned Fe³⁺ spins, which was sharply induced at 1.6 T, destroyed abruptly the superconducting state. In addition, a conspicuous resistivity decrease was observed just below the abrupt resistivity increase at 1.6 T. This decrease around 1.6 T suggests the compensation of the external field by the internal field created by Fe³⁺ spins and the stabilization of the superconducting state. Further anomalies were observed at 10-15 T below 0.75 K both for H//a and H//c as shown in Figure 1. The resistivity changes between 1.19 K (the normal state) and the lowest measured temperatures strongly suggest the onset of the magnetic-field-induced superconductivity around 12.5 T. Because of the existence of the metamagnetic transition which makes this system a dual functional material and gives rise to the fieldinduced resistivity decreases suggesting the stabilization of the superconducting state at two characteristic magnetic fields of 1.6 T and 12.5 T.

Figure 1. Magnetic field dependence of the magnetoresistance up to 15 T at the indicated temperatures in the figures with an application of the magnetic field in parallel with the *a* axis. The upper inset is the data measured between 0 T and 2 T. The lower insets are the resistivity differences between the data at 1.19 K and one at the lowest measured temperature (0.58 K).

IV-C-2 Dual-Action Molecular Superconductors with Magnetic Anions

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[J. Am. Chem. Soc. 124, 9982 (2002)]

Recently, the reports on the marvelous field-effect switching between insulating and superconducting states, which is the widest possible variation of electrical properties of materials, have attracted an extremely large attention though it has not been reconfirmed yet. We have found that similar switching phenomena can take place in bulk organic superconductors with magnetic anions. It is easily imagined that the superconducting state will be broken if the magnetic moments in the anion layers are forced to orient ferromagnetically. We found that the unprecedented combination of metamagnetism and organic superconductivity is realized in the first antiferromagnetic organic superconductor, ĸ- $(BETS)_2FeBr_4$ (BETS = bis(ethylenedithio) tetraselenafulvalene) and observed the superconducting state to be sharply switched on or off by controlling the magnetic state of the anion layers by external field (the critical magnetic field of metamagnetic transition is 1.6 T). More novel switching phenomena was also found in the other modification of BETS salts. As reported before, the diluted magnetic anion system, λ -(BETS)₂Fe_xGa₁₋ $_x$ Cl₄ (0.35 < x < 0.5) undergoes metal \rightarrow superconductor \rightarrow insulator transitions with lowering temperature ($T_c \approx$ 4 K, $T_{\text{SC}\rightarrow\text{Ins}} \approx 3.4$ K). We measured the magnetoresistance up to 15 T at T < 3.4 K. When magnetic field was applied to the direction perpendicular to the ac conduction plane, the insulator \rightarrow superconductor \rightarrow metal transitions were observed with increasing magnetic field. While for the field perpendicular to the ac conduction plane, the insulator \rightarrow superconductor \rightarrow metal \rightarrow superconductor transitions and insulator \rightarrow superconductor transition took place at 2.5 < T < 3.4 K and T < 2 K, respectively. T-H phase diagram indicates that the field induced superconducting phase appear around 14 T. Owing to the unique phase diagram with narrow superconducting region neighboring both insulating and metallic phases, the sharp insulator \leq superconductor \leq metal switching can be realized by modulating the external magnetic field.

Figure 1. (a) The magnetoresistance of λ -(BETS)₂Fe_{0.4}Ga_{0.6}-Cl₄ up to 15 T at 1.6–3.4 K for the magnetic fields parallel and perpendicular to the conduction plane. (b) An example of the insulator-superconductor-metal triple step switching behavior of λ -(BETS)₂Fe_{0.4}Ga_{0.6}Cl₄ coupled with the periodic modulation of magnetic field around 2.5 T (*H*//*ac* plane) at 3 K.

IV-C-3 A Series of Organic Conductors κ -(BETS)₂FeBr_xCl_{4-x} (0 ≤ x ≤ 4) Exhibiting Successive Antiferromagnetic and Superconducting Transitions

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[Adv. Mater. 14, 1376 (2002)]

In contrast to λ -type salt, where the crystals of λ - $(BETS)_2FeBr_xCl_{4-x}$ are obtained only for small x-range (x < 1.0), Br and Cl atoms are exchanged freely in κ type salts κ -(BETS)₂FeBr_xCl_{4-x} (0 ≤ x ≤ 4). Therefore, the magnetic and superconducting properties of κ -type salt can be changed continuously in the wide range. In this paper, we have examined the x-dependence of the electromagnetic properties of a series of the antiferromagnetic organic superconductors, κ-(BETS)₂FeBr_x- Cl_{4-x} (0 $\leq x \leq 4$). By collecting the experimental results of the electrical resistivities and magnetic susceptibilities, the temperature vs. x-value phase diagram of κ - $(BETS)_2FeBr_xCl_{4-x}$ ($0 \le x \le 4$) was obtained. Both superconducting and antiferromagnetic transition temperatures are lowered with decreasing x. It is interesting that the lattice constants a and c in the conduction plane exhibit small x-dependences, in spite of the strong xdependence of resistivity behavior. In addition, despite of the shortening of the lattice constant along the direction perpendicular to the conduction plane (//b), the magnetic interaction tends to be decreased with increasing the Cl content, suggesting the importance of the intermolecular magnetic interaction through the Br atom.

Figure 1. Temperature dependences of electrical resistivities of κ -(BETS)₂FeBr_xCl_{4-x}. a: x = 4, b: x = 3.86, c: x = 3.54, d: x = 3.43, e: x = 2.96, f: x = 2.82, g: x = 1.69, h: x = 1.04 and i: x = 0. The inset shows the resistivity behavior at low temperature region.

IV-C-4 Magnetic Molecular Conductors Based on BETS Molecules and Divalent Magnetic Anions [BETS = Bis(ethylenedithio)tetraselenafulvalene]

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Several conducting salts based on BETS molecules and divalent magnetic anions such as the $(CoCl_4)^{2-}$, (CoBr₄)²⁻ and (MnBr₄)²⁻ were prepared. Electrocrystallization by using the (CoCl₄)²⁻ anion gave two kinds of crystals. Block-shaped crystals were cleared to be (BETS)₂CoCl₄, which is an insulator with the high-spin state of cobalt 3d spin. On the other hand, the X-ray crystal structure analysis of a plate-shaped crystal of the $(CoCl_4)^{2-}$ salt revealed the system to be κ -(BETS)₄-CoCl₄(EtOH), which is metallic down to 0.7 K. The electronic band structure calculation gave a typical twodimensional cylindrical Fermi surface. However, there is only very weak antiferromagnetic interaction between the s = 3/2 cobalt 3d spins due to its anion-solventintermingled layer structure. On the other hand, the electrocrystallization by using the (MnBr₄)^{2–} anion yielded the plate-shaped black crystals of the (MnBr₄)²⁻ salt. Crystal structure analysis of the (MnBr₄)²⁻ salt showed that the salt is θ -(BETS)₄MnBr₄(EtOH)₂ with alternating the donor and anion/solvent mixed layers. The stacking direction in one donor layer is perpendicular to those of the neighboring layers. The electrical and magnetic properties of the θ -(BETS)₄MnBr₄(EtOH)₂ salt showed the metallic behavior down to ca. 30 K and the paramagnetism of the high-spin manganese 3d spins. Band structure calculation of this salt gave an elliptical cylindrical Fermi surface. Since the Fermi surfaces of the adjacent donor layers are rotated to each other by 90°, the θ -(BETS)₂MnBr₄(EtOH)₂ salt becomes a twodimensionally isotropic metal.

Figure 1. Crystal structure of κ-(BETS)₄CoCl₄(EtOH).

IV-C-5 Crystal Structure of BETS²⁺ Dication Salt (BETS)TICI₅ and Formal Charge Dependence of Bond Lengths of BETS^{+Q} (Q = 0-2)

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It is necessary to find out the BETS salt with higher oxidation state of BETS for getting the relation between bond lengths and formal charge (Q) of BETS (BETS^{+Q}). But the molecular structure of BETS with oxidation state greater than +1 has not been reported so far. Thin, black plate (BETS)TlCl₅ crystal was got from electrocrystallization method. The composition was determined by EDS (Energy Dispersive X-ray Spectrometer). The crystal has a triclinic unite cell and the cell param-

eters are: a = 9.052(3) Å, b = 10.542(3) Å, c = 6.210(1)Å, $\alpha = 103.56(2), \beta = 100.76(2), \gamma = 67.07(2)^{\circ}, V =$ 527.6(2) $Å^3$. Donors are packed with side-by-side mode to form segregated column along b axis. The linear $[TlCl_5]^{2-}$ unit with octahedral $[TlCl_6]$ unit shared an apex along *a* axis in the crystal. The Tl–Cl bond lengths are in the range 2.416(3)-2.692(3) Å which are consistent with the length of Tl³⁺–Cl. There are short contacts between S...S and S...Se atoms in the BETS columns and donor-anion contacts between Cl-...Se, Cl…S atoms. The C-H…Cl hydrogen bonds also exist as shown in Figure 1. The crystal is an insulator and shows paramagnetic behavior from 300 K to 1.9 K. Combining the data of the bond lengths of various charge-transfer salts of BETS with different oxidation states (BETS^{+Q}), we can get a relation of $Q = 10.76 - 9.58\delta$, and $\delta = (b + 10.76)$ (c) - (a + d), where a, b, c, d are the bond lengths of TTF core.

Figure 1. Packing diagram of (BETS)TlCl₅ viewed along *c* axis

IV-C-6 Charge-Transfer Salt of $[C_{12}H_8S_4Se_4Cl_2]FeCl_4\cdot C_6H_5Cl$

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Crystals of the title salt were obtained electrochemically. The donor $C_{12}H_8Cl_2S_4Se_4$: 2,2'-(1,2-dichoroethanediyli-dene)bis(4,5-dithiolene-1,3-diselena) was formed from BETS under high voltage. The cell parameter is: a = 8.669(4), b = 30.571(1), c = 10.388(4) Å, $\beta =$ $102.13(4)^\circ$, V = 2691.5(6) Å³, $P2_1/n$, Z = 4. Except ethylene groups, all the atoms of the donor are coplanar with the maximum derivation of 0.09 Å. The donor molecules form dimers. FeCl₄⁻ anions and C₆H₅Cl molecules are in the intersticial positions between the deimers. C₆H₅Cl plane is perpendicular to that of dimer. The crystal is a semiconductor and shows paramagnetic behavior.

Figure 1. Molecular configuration.

IV-C-7 A New Charge-Transfer Salt of (BETS)₄Fe₂(C₂O₄)₅

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The preparation, crystal structure and physical properties of charge-transfer salt based on BETS molecules and metal oxalate counter ions (BETS)₄Fe₂-(C₂O₄)₅ were examined. There are two phases. One is monoclinic $P2_1/n$ and the cell parameters are a = 17.078(4), b = 11.180(2), c = 19.975(5) Å, $\beta = 102.026(5)^\circ$, V = 3730.3(15) Å³. The other takes C2/m space group and the lattice constants are a = 23.3982(7), b = 11.1365(4), c = 16.9771(7), $\beta = 123.798(1)^\circ$, V = 3676.2(2) Å³. In these two phases, Fe₂(C₂O₄)₅ groups

and BETS molecules are arranged in "checker board" mode. In the $P2_1/n$ phase, BETS molecules are packed with the longest directions parallel to [101] direction. The formal charge of BETS is +1. The crystal showed a semiconductor-to-insulator transition around 80 K. There are antiferromagnetic interaction between Fe(III) ions. The χ vs. *T* curve gave g = 2.0 and J = -6.1 cm⁻¹.

Figure 1. The $\chi_{\rm M}T$ vs T curve of BETS₄Fe₂(C₂O₄)₅ (magnetic field = 1000 Oe). The solid line represents the best fit using the Heisenberg isotropic exchange model for a linear dimer Fe^{III}–Fe^{III}.

IV-D Development of New Conducting Molecular Materials

Molecule can be regarded as the smallest nano-system where various functions can be assembled. Although physics and chemistry of the bulk systems with typical electronic functions such as molecular superconductors and molecule-based magnets have been developed greatly in the last two decades, the development of the basic science of the "nano-molecular systems" seems to be insufficient. It seems that many fascinating ideas on the electronically functional molecular systems such as molecular circuit remain to be realized for a long time. Although present our starting point seems to be rather trivial, we hope to contribute in future to make a bridge between the well-established field of bulk molecular functions. Presently we are trying to develop new types of molecular systems with novel electrobic functions. The "dual-functional" magnetic conductors exhibiting superconductors composed of single-component molecules and (2) pure organic magnetic metals.

IV-D-1 Development of Conducting Crystals Based on Single-Component Transition Metal Complex Molecules with Extended-TTF Ligands

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Until quite recently, it was believed that molecular conductors consist of more than two chemical species. Charge transfer between molecules comprising conduction bands and another chemical species has been considered indispensable to generate charge carriers. However, we have prepared the crystal of a neutral complex, $[Ni(tmdt)_2]^{0+}$ (tmdt = trimethylenetetrathia-

fulvalenedithiolate), and found that it is highly conducting (400 Scm⁻¹ at room temperature) and metallic behavior down to 0.6 K. Besides Ni(tmdt)₂, various molecular conductors composed of neutral transition metal complex molecules with extended TTF-like ligands such as ptdt, dmdt and tmdt were developed (M = Ni, Pd, Pt, Cu, Co, Au; ptdt = propylenedithiotetrathiafulvalenedithiolate, dmdt = dimethyltetrathiafulvalenedithiolate, tmdt = trimethylenetetrathiafulvalenedithiolate). The synthetic works were made under strictly inert atmosphere because these metal complexes were very sensitive to oxygen. By electrochemical oxidation, black microcrystals of the neutral complexes were obtained. Since only very small single or powder crystals were obtained, the resistivity measurements were made on the compressed powder

samples. However, as shown in Table1, many crystals with very high conductivities were discovered: for example, [Ni(tmdt)₂], 250 Scm⁻¹; [Ni(dmdt)₂], 200 Scm⁻¹; [Pd(dmdt)₂], 150 Scm⁻¹.

 Table 1. Single-component molecular conductors based on metal complexes with extended-TTF ligands

complex	starting material (Me_N)_[Ni04md0_2]	ei(300 K) (compactionpellet sample)		
[Ni(dmdt) ₂]		200 Scirc1	Metallic down to 230 K	
[Pd(dradi)_1]	$(Me_4N)_2[Pd(drad)_2]$	150 Scm ⁺	Semiconductor	
[Ni(Ind() ₂]	(Me ₄ N) ₂ [Ni(Imdt) ₂]	250 Scm ⁺	Metallic down to 70 K	
[Coulding]	(Me ₄ N) ₂ [Coolmit() ₂]	0.05 Scm ⁻⁷	Semiconductor Ea=85 meV	
[Coundo ₂]	(Me ₄ N) ₂ [CocundO ₂]	1.5 Scm ⁻¹	Semiconductor Ec:24 meV	
(Ca(dendi)_2)	(McaN);[Cu(dmd0)]	1.2 Scm ⁻¹	Semiconductor Earf() meV	
[Cu(indi)_]	(Me ₄ N) ₂ [Cu(indi) ₂]	5.1 Son ⁺¹	Semiconductor Ecold neV	
[Autombb]	(Me ₄ N) ₂ [Au(tmdt) ₂]	4 Scm ⁻¹	Semiconductor Ext21 meV	
[Autimits]	(Mc_N)-[Au(dmilt)-]	14 Sem ¹	(Metallic)	
[Ni(d) ₂]	(Me4N03[Ni(dt)2]	16 Sem ⁻¹	Semiconductor Ea-35 meV	
[Pd(dO ₂]	$(Me_4N)_2[Pd(dt)_2]$	0.3 Scm ⁻¹	Semiconductor Eu-94 meV	
[Ni(cod) ₂]	(Bu_N)_[Ni(codt)_]	8 Son ⁺	Metallic down to 120 K	
[Cold(lg]	(Me_N)_[Co(dt)_]	195cm+	(Metallic)	

IV-D-2 A Conducting Crystal Based on a Single-Component Paramagnetic Molecule [Cu(dmdt)₂] (dmdt = dimethyltetrathiafulvalene dithiolate)

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By the realization of single-component molecular metals, the possibility of the development of the new types of molecular conductors has been extended. For example, it will be possible to develop metallic molecular magnets based on single-component molecules containing magnetic ions such as Cu^{2+} and Co^{2+} , where the intermolecular magnetic interactions are mediated by π conduction electrons. We have examined the crystal structure, electrical resistivity and magnetic properties of crystal of $[Cu(dmdt)_2]^{0+}$ (dmdt = dimethyltetrathiafulvalenedithiolate), to contribute to clarify the possibility of single-component magnetic molecular conductors. The resistivity measurements on the compaction pellet sample showed fairly high conductivity though the quality of the crystals was poor (about 3 Scm⁻¹ at room temperature) and the activation energy was very small ($\approx 40 \text{ meV}$). The temperature dependence of the susceptibility was completely fitted by a Curie-Weiss plot ($\chi_{rt} = 1.09 \times 10^{-3} \text{ emu mol}^{-1}$, C = 0.33emu·K·mol⁻¹, $\theta = -4.2$ K). The Curie constant suggests the existence of 84% of S = 1/2 spin moments (estimated on the basis of a g-value (2.035) obtained by EPR experiments). These results suggest the possibility of the development of the single-component magnetic conductor. The comparison of the bond lengths of [Cu- $(dmdt)_2]^{0+}$ and $[Cu(dmdt)_2]^{2-}$ showed that by the oxidation from (2-) to (0+), all the C=C bonds become longer, indicating that the LUMO has bonding character on each C=C bond (see Table 1). On the other hand, except the bond h showing very small positive change, S–C bonds tend to be shortened, suggesting antibonding character of LUMO on C–S bonds. Large changes in the bonds b and c indicate the large amplitude of LUMO on the S and C atoms in the central five-membered ring. These features are in good agreement with the general features of the calculated molecular orbitals reported previously.

Table 1. The average bind lengths (Å) of $[Cu(dmdt)_2]^n$ ($n = 2^{-}, 0^{+}$)

	$\begin{bmatrix} \mathbf{c}_{\mathbf{u}} \begin{pmatrix} \mathbf{a}, \mathbf{S}, \mathbf{b}, \mathbf{d}, \mathbf{S}, \mathbf{e}, \mathbf{g}, \mathbf{S}, \mathbf{b}, \mathbf{M} \mathbf{e} \\ \mathbf{c}_{\mathbf{u}} \begin{pmatrix} \mathbf{c}, \mathbf{c}, \mathbf{c}, \mathbf{c}, \mathbf{c}, \mathbf{c} \\ \mathbf{c}, \mathbf{c}, \mathbf{c}, \mathbf{c}, \mathbf{c} \\ \mathbf{S}, \mathbf{c}, \mathbf{c}, \mathbf{c}, \mathbf{c} \\ \mathbf{M} \mathbf{e} \end{pmatrix}_{\mathbf{r}} \end{bmatrix}^{\mathbf{u}}$				
	n=2-	n=0+	Δ		
a	2.287(1)	2.282(1)	-5		
b	1.738(3)	1.683(1)	-55		
0	1.341(4)	1.414(9)	73		
d	1.766(3)	1.743(4)	-23		
e	1.756(3)	1.738(4)	-18		
1	1.342(5)	1.361(1)	19		
8	1,758(3)	1.737(4)	-21		
h	1.748(3)	1.762(4)	14		
1	1.330(5)	1.353(9)	23		

IV-D-3 Novel π -Electron Donors for Magnetic Conductors Containing a PROXYL Radical

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[Chem. Lett. 1048 (2002)]

Development of magnetic conductors bearing both conductivity and magnetism has recently played a quite important role in the research of the multifunctionality of organic molecular materials. Recently, we synthesized several new donors containing a TEMPO radical and reported the structures and physical properties of their cation radical salts. Among them, we synthesized the donors 1 and 2 consisting of a TTF moiety and a PROXYL (2,2,5,5-tetramethylpyrrolidin-1-yloxyl) radical part because the PROXYL radical is quite stable to air and heat and the corresponding donor molecules will have a relatively small steric hindrance due to the symmetrical structure and smaller size of the PROXYL radical than that of the TEMPO radical. An X-ray crystal structure analysis revealed the structure of 1. We also clarified the magnetic and electrochemical properties of novel TTF donors 1 and 2 containing a PROXYL radical. Furthermore we prepared the iodine complex of the ethylenedithio derivative 1 and cleared that the salt has 1:1 ratio (donor: I_3^-) and showed insulating conducting behavior and disappearance of the cation radical moments probably due to the strong singlet formation although the PROXYL radical part showed independent behavior with a weak antiferromagnetic interaction.

Figure 1. Structure of 1, 2.

IV-D-4 Novel TTP Donors Containing a PROXYL Radical for Magnetic Molecular Conductors

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The development of new electron donors 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 bifunctional materials. We synthesized novel electron donors 1 and 2 consisting of the TTP framework and a stable PROXYL (2,2,5,5tetramethyl-pyrrolidin-1-yloxyl) radical part as racemic mixtures, where TTP framework was developed by Y. Misaki *et al.* and regarded as a series of promising donors for the realization of stable metallic states. We cleared the structures of the TTP derivatives containing a PROXYL radical 1 and 2 and investigated the magnetic and electrochemical properties of these donors. Furthermore, we prepared the cation radical salts of these donors and studied their electrical and magnetic properties. Among them, the FeCl₄⁻ salts of 1 showed the highest conductivity (1 Scm^{-1}) in the cation radical salts based on the donors containing a localized radical spin. The χT values of this salt around room temperature correspond to the sum of the contributions from one PROXYL radical, high spin Fe³⁺ and small amount of conducting electrons from the cation radical moments, suggesting the coexistence of these three different magnetic moments.

Figure 1. Structure of 1 and 2.

IV-D-5 Synthesis and Physical Properties of New Molecular Conductors Based on Lanthanoid Nitrate Complex Anions

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Molecular conducting salts based on BDT-TTP [2,5bis(1,3-dithiol-2-ylidene)-1,3,4,6- tetrathiapentalene] donor molecules and lanthanide nitrato complex anions $[Ln(NO_3)_5]^{-2}$. (Ln = Tb, Dy, Ho, Er, Tm, Yb and Lu) were synthesized as plate-shaped crystals whose compositions are (BDT-TTP)₅[Ln(NO₃)₅] and they are all isostructural. All these crystals were metallic down to 2K. The electronic band structure calculation gave a two-dimensional Fermi surface that explained their stable metallic states. Magnetic susceptibility measurements of the seven salts [Ln(NO₃)₅]⁻² (Ln = Tb, Dy, Ho, Er, Tm, Yb and Lu) showed paramagnetic moments on rare-earth ions which were superimposed on the Pauli paramagnetism of metallic π electrons. Especially, the magnetic susceptibilities of the (BDT-TTP)₅[Ho(NO₃)₅] and (BDT-TTP)₅[Tm(NO₃)₅] salts showed that there seem to be some antiferromagnetic interactions. On the other hand, the Weiss temperatures for (BDT-TTP)₅[Ln(NO₃)₅] (Ln = Tb, Dy, Er and Yb) salts are rather small.

Figure 1. Crystal structure of (BDT-TTP)₅[*M*(NO₃)₅].

IV-E Control of Intermolecular Interactions 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. This means that we change our viewpoint from the molecule to the *supramolecular synthon*. Tellurium has a strong tendency to form secondary bonds in crystalline compounds. We have used the tellurium-based secondary bond as a supramolecular synthon in anion radical salts.

On the other hand, the electronic state of molecular conductors can be quite sensitive to the pressure application if they are situated near the phase boundary and are soft enough to allow appreciable changes of molecular arrangement and orientation. The application of hydrostatic pressure has played significant roles in changing electronic states of low-dimensional molecular conductors. Furthermore, recent development of the uniaxial stress and strain methods have enabled selective or anisotropic regulation of the intermolecular interaction and provided a powerful means to search for novel electronic states. We have examined the uniaxial strain effect in the twodimensional strongly correlated system based on the metal dithiolene complex.

IV-E-1 Unique Structural and Physical Properties of $Ni(dmit)_2$ Anion Radical Salts Characterized by Short Te...S Contacts, where dmit = 1,3-dithiole-2-thione-4,5-dithiolate

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Five new Ni(dmit)₂ anion radical salts, [Me₃Te]-[Ni(dmit)₂]₂ **1**, [Me₃Te][Ni(dmit)₂]₃·acetone **2**, α -[MOT][Ni(dmit)₂]₂ **3**, β -[MOT] [Ni(dmit)₂]₂ **4** and γ -[MOT][Ni(dmit)₂]₂ **5** (MOT = 1-oxa-4-methyl-4-telluracyclohexane), have been prepared by the galvano-static electrolysis (Scheme). X-ray crystal structure analyses show that all the salts are characterized by short Te···S contacts (3.41 ~ 3.85 Å) between the anions and cations. Each salt shows unique molecular packing of the Ni(dmit)₂ units. Electronic structures deeply depend on these unique molecular arrangements. Among them, **1** and **3** show metallic behavior (down to 60 and 160 K, respectively) and the resistivity of **4** is almost independent from the room temperature and increases moderately below 40 K.

This work has revealed that the Te(IV)-based cations have an ability to induce novel arrangements of the Ni(dmit)₂ units through the intermolecular Te...S contacts. Our results would open a way to the feasible control of the arrangement of the Ni(dmit)₂ anion radical by tuning cations with various shapes.

Scheme 1. Molecular structures of $Ni(dmit)_2$, Me_3Te^+ , and MOT^+ .

IV-E-2 Uniaxial Strain Effect in the Two-Dimensional Strongly Correlated System, β' -(CH₃)₄As[Pd(dmit)₂]₂ (dmit = 1,3-dithiol-2thione-4,5-dithiolate)

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The molecular conductor β' -(CH₃)₄As[Pd(dmit)₂]₂ is a two-dimensional strongly correlated system based on the dimer structure (Figure 1). At low temperature, this system is a Mott insulator under ambient and hydrostatic pressure conditions. The electrical resistivities of this system have been measured under uniaxial strain along all three crystallographic axes. When the strain is applied parallel to the b axis within the a-bconducting layer, the non-metallic behavior is readily suppressed and superconductivity appears at 4 K under 7 kbar (Figure 2). On the other hand, small strain around 2 kbar along both the *a*- and *c*-axis directions effectively enhances the non-metallic behavior. With further increase of the strain, the non-metallic behavior is suppressed, but cannot be removed even at 15 kbar. These unusual results suggest the crucial role of intra- and inter-dimer interactions that affect the band width and the effective on-site Coulomb interaction.

Figure 1. (a) Molecular structure of $Pd(dmit)_2$. (b) Crystal structure of β '-(CH₃)₄As[Pd(dmit)₂]₂.

Figure 2. Temperature-dependence of the resistivity (ρ) under the uniaxial strain along the *b* axis. The inset shows the resistivity under the magnetic field parallel to the *c** direction at 7 kbar.

IV-F Synthetic Approach Toward Single Molecular Transistors

Organic molecules are promising candidates for nano size transistor in two categories of the electronic devices. One is single electron transistor, in which the molecules are used as discrete charge pools. The merit of using organic molecules in this style of devices is that molecules have precise size with determinate electronic states providing stable electronic properties. The other is single molecular field effect transistor, molecules working as the electronic conductor. In this case, resonant tunneling mechanism is expected to work, and the molecular orbital engineering can be utilized in designing complex electronic circuits. In order to realize these appealing devices, we have been constructing optimized nano electrodes and optimized molecules.

IV-F-1 Synthesis of Novel Ruthenium Complexes Optimized for Molecular Single Electron Transistor

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Single electron transistors utilize the Coulomb blockade phenomena with nano size particles as the charge pool. The blockade energy is definitely determined only by the size of the particles, and in order to possess enough energy to work at room temperature the size should be not more than 1 nm. It is still difficult to make this size of nano particles with perfectly same radius. We hope that by using metal complex molecules as the charge pool bearing definite redox states, the blockade energies are controlled by the redox potentials, which are determined by the molecular structure.

The molecule prepared have ruthenium complex moiety in the center, which is protected by a dendrimer layer. The protecting layer provides the tunneling barrier to prevent direct contact between each molecule and of the molecule with the electrodes. The carboxylic group at the surface of the molecule will work as the anchor to the doped silicon electrodes.

IV-F-2 Preparation of Porphyrin Wires Optimized for Molecular Field Effect Transistors

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Although several reports of "single molecular electronic devices" have already published, no one has succeeded the electronic measurement with observing the molecules between the electrodes. We aimed molecular wires that are visible with atomic force microscopy (AFM) even on the rough surface of the nano gap electrodes.

The molecules prepared are porphyrin derivatives that have two meso aryl groups with dendrimers at three and five positions and two ethynyl groups at the remaining meso positions. Molecular mechanics calculations showed that the diameter of the wire is about 5–6 nm that will be easily observed on the rough surface of the nano gap electrodes.

IV-F-3 Synthesis of Octopus Shaped Self Standing Molecular Jacks

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[to be published]

Thiol (-SH) / gold electrodes are the most often used combination for "single molecular electronics" to connect the molecule to the electrodes. The limitations of this combination are (1) electronic contact of this bond is not ideal and significant electronic barrier exist between the molecule and the electrode, (2) the space per molecule is small and a large number of molecules can be connected even to the nano scale electrodes, which disturb the measurements of single molecule.

We have prepared porphyrin derivatives with four meso aryl groups, whose three and five positions are substituted with long alkyl chains with disulfide groups at the ends. The disulfide groups will work as the anchor of the molecule to fix them to gold electrodes. The diameter of the molecule is about 10 nm. So, if the surface area of the nano electrodes is 30×30 nm, only nine molecules can be adsorbed on the surface at the maximum. By introducing rhodium metal in the center of the porphyrin molecule, axial rigands can be connected to the metal that will be the molecular wire standing perpendicularly to the electrode surface.