IV-E Molecular Crystals toward Nano-Devices by Use of *d*-π Interaction, Crystal Designing and Optical Doping

After some 30 years' intensive research on molecular charge transfer (CT) salts as potential functional materials, the research field has now gotten ready to examine how to make them into actual devices. Such efforts are concentrated on the developments of organic thin films for field effect transistors and light-emitting devices, both of which are carried out in a number of laboratories and groups with worldwide competitions. In order to examine the potential applicability of molecular materials from a different point of view, we are carrying out basic studies on development and physical properties of molecular CT single crystals. Major part of our study can be classified into three categories; the physical properties of the CT salts including localized spins, crystal designing using poly-carboxylate anions, and device formation by optical doping method.

IV-E-1 Light-Induced Transformation of Molecular Materials into Devices

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([1]Hokkaido Univ.)

[*Adv. Mater.* in press]

Many kinds of molecular solids are now attracting a worldwide interest as promising candidates for advanced materials such as electronic/magnetic/optical devices and energy converters. In particular, semi-conductor diodes based on photovoltaic effect appear one of the most effective ways to utilize molecular materials, if there is an appropriate doping method available. This work concerns a finding of a novel method of (persistent) carrier doping to molecular materials. The method is simple and versatile; just illuminating the desired part of material as long as it contains a photosensitive chemical species in addition to an electroactive one. Although various kinds of photo-excited states reported thus far have typical lifetimes of some hundreds of micro-seconds at longest in general, the doped state survived even several months after the illumination was finished. The experimental results demonstrate that one can control the conducting properties of an arbitrary part of a molecular material using appropriately focussed illumination. In other words, this method opens a new way for making devices and conducting nano-architectures from a wide variety of molecular solids, which have awaited for a space-resolved doping method under a mild condition.

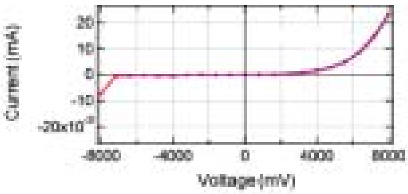

Figure 1. Current-Voltage property curve of the single crystal of Ag(DM)$_2$ after UV-VIS illumination upon only half of it for ~ 21 days.

IV-E-2 Molecular Conductors Containing Photoreactive Species

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[*J. Phys. IV France* **114**, 553–555 (2004)]

In order to examine the possibility of (persistent) carrier doping to molecular crystals by light exposure, some different types of molecular crystals containing photoreactive species are synthesized and characterized. The [Ru(bpy)$_3$]$^{2+}$ cation (bpy = 2,2'-bipyridyl) yielded two different new complexes with [Ni(dmit)$_2$]$^-$ radical species, both of which were structurally characterized and turned out to be band insulators. Methy viologen (MV) has been found to yield a new phase of the complex with [Ni(dmit)$_2$]$^-$, MV[Ni(dmit)$_2$]$_2$. The temperature dependences of electrical resistivity (decreasing with lowering temperature down to 1.0 K) and magnetic susceptibility (Pauli paramagnetism from 300 K to 1.8 K with a hysteresis below ~ 100 K) clearly indicate that this phase is metallic. The thermoelectric power exhibited ~ 0 μVK^{-1} from 300 K–4.2 K. This phase turned out to be metastable, and the crystals gradually turned into insulating ones. The effects of UV-VIS light exposure to the conducting and magnetic properties of Ag(DMe-DCNQI)$_2$ have been studied, and clear differences between the exposed and the pristine crystals were observed. The ESR signal at 3.7 K suggested that the exposed sample should include the Ag(0) species.

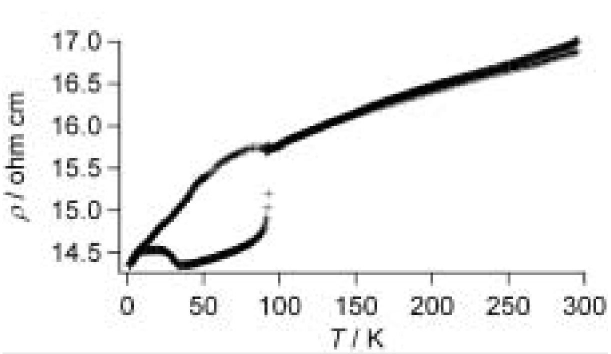

Figure 1. Temperature-dependent electrical resistivity of MV[Ni(dmit)$_2$]$_2$.

IV-E-3 Molecular Unit Based on Metal Phthalocyanine Designed for Molecular Electronics

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[*J. Phys. IV France* **114**, 541–543 (2004)]

We obtained three conducting crystals based on a [Fe^{III}(Pc)$(CN)_2$] molecular unit. All crystals showed a large anisotropic negative magnetoresistance arising from the π-*d* interaction self-contained in the [Fe^{III}(Pc)$(CN)_2$] unit. The anisotropy is attributable to the anisotropic *g*-tensor in the [Fe^{III}(Pc)$(CN)_2$] unit. We also obtained a thin film containing [Fe^{II}(Pc)$(CN)_2$]. The film exhibits photocurrent response for the UV irradiation. These features suggest [M(Pc)$(CN)_2$] molecular unit is a well-designed one for a building block of molecular devices.

IV-E-4 Anisotropic Giant Magnetoresistance Originating from the π-*d* Interaction in a Molecule

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

[*J. Phys. Chem. Solids* **65**, 749–752 (2004)]

We synthesized TPP[Fe^{III}(Pc)$(CN)_2]_2$, $PTMA_x$ [Fe^{III}(Pc)$(CN)_2$]·*y*(MeCN), and PXX[Fe^{III}(Pc)$(CN)_2$], a new series of charge-transfer salts containing the axially-substituted phthalocyanine (Pc), [Fe^{III}(Pc) $(CN)_2]^-$. In this molecular unit, the π conduction electron derived from the Pc-ring coexists with the *d* electron which is a potential source of a local magnetic moment. Therefore various phenomena associated with the interplay between local magnetic moments and conduction electrons are expected. We observed the giant negative magnetoresistance (GNMR) in all the three salts. The GNMR is highly anisotropic for the magnetic-field direction, and reflects the *g*-tensor anisotropy of the local magnetic moment in the [Fe^{III}(Pc) $(CN)_2]^-$ unit. This indicates that the GNMR in these salts originates from the strong π-*d* interaction in the [Fe^{III}(Pc)$(CN)_2]^-$ unit.

IV-E-5 Novel Phthalocyanine Conductor Containing Two-dimensional Pc Stacks, $[PXX]_2[Co(Pc)(CN)_2]$ (PXX = *peri*-Xanthenoxanthene, $Co(Pc)(CN)_2$ = Dicyano(phthalocyaninato)cobalt(III))

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[*Chem. Lett.* **33**, 128–129 (2004)]

A novel phthalocyanine conductor containing 2-D–stacks of the partially oxidized Co(Pc)$(CN)_2$ units has been obtained by the electrochemical oxidation method with PXX. The crystal is highly conductive ($> 10^3$ Scm^{-1}) at all the temperatures measured ($5 K < T < 300 K$). Though the metallic character becomes clearer compared with the single chain or ladder chain conductors, the 2-D sheet has been found to be still anisotropic.

IV-E-6 Contribution of Degenerate Molecular Orbitals to Molecular Orbital Angular Momentum in Molecular Magnet $Fe(Pc)(CN)_2$

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[*J. Phys. Soc. Jpn.* **72**, 3226–3230 (2003)]

We measured the static magnetic susceptibility and the electron spin resonance of the Fe(Pc)$(CN)_2$ complexes, and investigated the molecular magnetism of the unit Fe(Pc)$(CN)_2$. The magnetic susceptibility shows a highly anisotropic Curie behavior. Based on the electron spin resonance, we found a highly anisotropic *g*-value ($g_1 = 3.62$, $g_2 = 1.11$, and $g_3 = 0.52$) in the molecular unit Fe(Pc)$(CN)_2$. This anisotropy is caused by the molecular orbital angular momentum in the degenerate next highest occupied molecular orbitals of the molecular unit Fe(Pc)$(CN)_2$. Since the molecular unit Fe(Pc)$(CN)_2$ has a unique structure with fourfold symmetry, the molecular orbital angular momentum has a finite value of $l_z \sim +1$ and –1. The anisotropic molecular magnetism of the unit Fe(Pc)$(CN)_2$ contributes the highly anisotropic Curie behavior. The molecular unit Fe(Pc)$(CN)_2$ is a good candidate for a molecular magnet having high magnetic anisotropy.

IV-E-7 Angle-Resolved Mapping of the Fermi Velocity in a Quasi-Two-Dimensional Organic Conductor

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[*Phys. Rev. Lett.* **91**, 216402 (2003)]

We demonstrate a new method for determining the Fermi velocity in quasi-two-dimensional (Q2D) conductors. Application of a magnetic field parallel to the conducting layers results in periodic open orbit quasiparticle trajectories along the Q2D Fermi surface. Averaging of this motion over the Fermi surface leads to a resonance in the interlayer microwave conductivity. The resonance frequency is simply related to the extremal value of the Fermi velocity perpendicular to the applied field. Thus, angle dependent microwave studies enable a complete mapping of the in-plane Fermi velocity. We illustrate the applicability of this method for the highly 2D organic conductor κ-$(BEDT\text{-}TTF)_2I_3$.

IV-E-8 Molecular Hexagonal Perovskite: A New Type of Organic-Inorganic Hybrid Conductor

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(*[1]Hokkaido Univ.)*

[*J. Solid State Chem.* **176**, 243–249 (2003)]

An organic charge-transfer (CT) salt (BEDT-TTF)$_3$(MnCl$_3$)$_2$(C$_2$H$_5$OH)$_2$ has been synthesized by a standard electrochemical method. The crystal data are monoclinic, $C2/c$ (#15), a = 38.863(4) Å, b = 6.716(1) Å, c = 23.608(3) Å, β = 115.007(3)°, V = 5584(1) Å^3, and Z = 4. The structure consists of one-dimensional (1D) infinite $\{[\mathrm{MnCl_3}]^-\}_\infty$ magnetic chains and two-dimensional (2D) organic conduction pathways. The former consists of face-sharing octahedra of manganese chloride complex ions, and dominates the magnetic properties of this compound. Such a feature of the crystal structure closely relates to transition metal hexagonal perovskite compounds, all of which are known for frustrated triangular lattices comprised of weakly interacting 1D magnetic chains. The new compound exhibits a high conductivity down to 4 K.

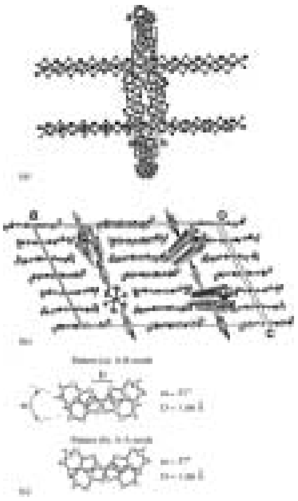

Figure 1. (a) Unit cell viewed down along the c-axis and (b) viewed down along the b-axis. (c) Two molecular overlapping modes of ET. Hydrogen atoms are omitted for clarity except in (c).

IV-E-9 Structure and Physical Properties of Low-Dimensional Molecular Conductors, [PXX][Fe^{III}(Pc)(CN)$_2$] and [PXX][Co^{III}(Pc)(CN)$_2$] (PXX = *peri*-Xanthenoxanthene, Pc = Phthalocyaninato)

MATSUDA, Masaki[1]; ASARI, Takehiro[2]; NAITO, Toshio; INABE, Tamotsu[2]; HANASAKI, Noriaki[1]; TAJIMA, Hiroyuki[1]
([1]Univ. Tokyo; [2]Hokkaido Univ.)

[*Bull. Chem. Soc. Jpn.* **76**, 1935–1940 (2003)]

A novel low-dimensional molecular conductor, [PXX][Fe^{III}(Pc)(CN)$_2$], has been synthesized. This salt contains the magnetic Fe^{III} ion (S = 1/2), and is isomorphous with [PXX][Co^{III}(Pc)(CN)$_2$] which includes the non-magnetic Co^{III} ion. In both salts, the [Mc(Pc)(CN)$_2$] (M = Fe or Co) units form a two-leg ladder chain. The two salts exhibit a similar temperature dependence of the thermoelectric power and a similar reflectance spectrum. The Fe^{III} salt shows semiconducting behavior in its electrical resistivity over the temperature range measured, while the isomorphous Co^{III} salt exhibits metallic behavior in its resistivity above 100 K. The difference in the transport properties between the two salts suggests that the conduction electrons in the Fe^{III} salt are seriously scattered by the local magnetic moment. Spontaneous magnetization is observed below 8 K in the Fe^{III} salt. Upon applying a magnetic field, the resistivity of the Fe^{III} salt drastically decreases below 50 K. The decrease in the resistivity is highly anisotropic to the field orientation. The field orientation dependence is highly consistent with the g-tensor anisotropy in the [Fe^{III}(Pc)(CN)$_2$] unit, suggesting that the negative magnetoresistance originates from the large π-d interaction self-contained in the [Fe^{III}(Pc)(CN)$_2$] unit.

IV-E-10 Torque Study of TPP[Fe(Pc)(CN)$_2$]$_2$ (TPP = Tetraphenyl Phosphonium and Pc = Phthalocyanine)

HANASAKI, Noriaki[1]; MATSUDA, Masaki[1]; TAJIMA, Hiroyuki[1]; NAITO, Toshio; INABE, Tamotsu[2]
([1]Univ. Tokyo; [2]Hokkaido Univ.)

[*Synth. Met.* **137**, 1227–1228 (2003)]

The magnetic torque shows the anomaly around 20 K. The torque curve suggests the antiferromagnetic state in the one-dimensional Fe(Pc)(CN)$_2$ chain. The magnetic easy axis is directed along the CN-ligand in the Fe(Pc)(CN)$_2$ unit. Because of the strong spin-orbit coupling, the next highest occupied molecular orbital is also ordered so that the molecular orbital angular momentum of the neighboring Fe(Pc)(CN)$_2$ unit is antiparallel. We observed the weak ferromagnetism below 6 K. This is ascribed to the canting of the antiparallel moments.

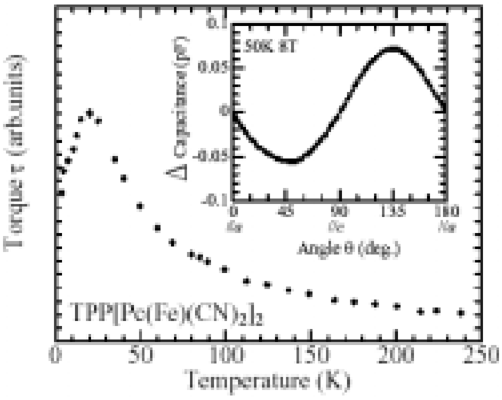

Figure 1. Temperature dependence of the torque. Inset: Torque curve measured under the magnetic field rotated within the *ac* plane.

IV-E-11 Physical Properties of (ET)$_3$(MnCl$_4$)(TCE) and the Related Salts

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AKUTAGAWA, Tomoyuki[1]; HASEGAWA, Tatsuo[1]; NAKAMURA, Takayoshi[1]; HOSOKOSHI, Yuko; INOUE, Katsuya
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[*Synth. Met.* **135-136**, 613–614 (2003)]

The ET salt with a magnetic counter ion $(ET)_3(MnCl_4)(TCE)$ (TCE = 1,1,2-trichloroethane) exhibits pressure-sensitive, complicated electrical behavior due to its semimetallic electronic structure. On the other hand, stronger d-π coupling is suggested in $(ET)_3(MnCl_3)_2(C_2H_5OH)_2$, which has infinite magnetic chains with semimetallic conducting behavior.

IV-E-12 Magnetic Properties of *d*-π Conducting System, $TPP[Fe^{III}{}_xCo^{III}{}_{1-x}(Pc)(CN)_2]_2$

MATSUDA, Masaki[1]; HANASAKI, Noriaki[1]; TAJIMA, Hiroyuki[1]; SAKAI, Fumiko[1]; NAITO, Toshio; INABE, Tamotsu[2]
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[*Synth. Met.* **135-136**, 635–636 (2003)]

We have studied the magnetic susceptibility for one-dimensional system, $TPP[Fe^{III}{}_xCo^{III}{}_{1-x}(Pc)(CN)_2]_2$ ($0.07 \le x \le 1$). At $x = 1$, the system shows anisotropic Curie-Weiss behavior and spontaneous magnetization below 6 K. The temperature below which spontaneous magnetization occurs (T_c) shifts downward with a decrease in Fe^{III} concentration, but is still above 2 K at $x = 0.07$. The anisotropic Curie-Weiss behavior in the susceptibility was observed for all the alloys measured. This magnetic anisotropy was associated with the g-tensor anisotropy in the $[Fe^{III}(Pc)(CN)_2]$ unit.

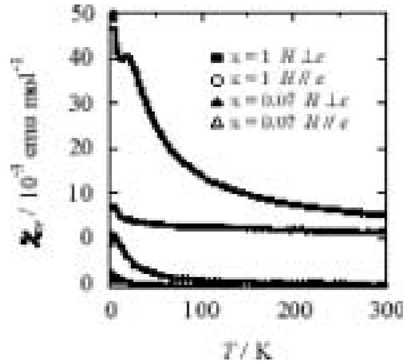

Figure 1. Temperature dependence of the magnetic susceptibility for aligned crystals of $TPP[Fe^{III}{}_xCo^{III}{}_{1-x}(Pc)(CN)_2]_2$ ($x = 1$ and 0.07). The magnetic field was applied perpendicular and parallel to the c-axis. Note the 1×10^{-3} emu mol^{-1} offset for $x = 0.07$.

IV-E-13 Magnetic and Optical Properties of One-Dimensional π-*d* System with Axially Substituted Iron(III) Phthalocyanine

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[*Synth. Met.* **133-134**, 547–548 (2003)]

We have measured the angular dependence of the ESR spectra on $DMDP[Fe^{III}{}_{0.01}Co^{III}{}_{0.99}(Pc)(CN)_2]$ (DMDP = dimethyldiphenylphosphonium, Pc = phthalocyanine), which is the alloy system of magnetic Fe^{III} and non-magnetic Co^{III}. The spectra exhibit giant anisotropic shift in g-value of iron(III). We also report the temperature dependence of the polarized reflectance spectra of one-dimensional conductors, $TPP[Fe^{III}(Pc)(CN)_2]_2$ and $TPP[Co^{III}(Pc)(CN)_2]_2$ (TPP = tetraphenylphosphonium). With lowering the temperature, the plasma edge drastically shifts to a higher wavenumber, and additional dispersion appears around 1600 cm^{-1} and around 3600 cm^{-1} in both salts.

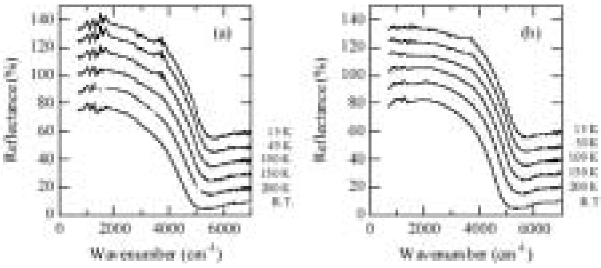

Figure 1. Temperature dependence of the reflectance spectra of $TPP[Fe^{III}(Pc)(CN)_2]_2$ (a) and $TPP[Co^{III}(Pc)(CN)_2]_2$ (b) for the polarized light parallel to the c-axis. In $TPP[M^{III}(Pc)(CN)_2]_2$, $[M^{III}(Pc)(CN)_2]$ units form a one-dimensional regular chain along the c-axis. The 0% level is successively shifted by 10% for clarity.

IV-E-14 One-Dimensional π-*d* Electron System inTPP[Fe(Pc)(CN)$_2$]$_2$, [PXX][Fe(Pc)(CN)$_2$], and (PTMA)$_x$[Fe(Pc)(CN)$_2$]$_y$(CH$_3$CN): Electron Spin Resonance and Negative Magnetoresistance

HANASAKI, Noriaki[1]; MATSUDA, Masaki[1]; TAJIMA, Hiroyuki[1]; NAITO, Toshio; INABE, Tamotsu[2]
([1]Univ. Tokyo; [2]Hokkaido Univ.)

[*Synth. Met.* **133-134**, 519–521 (2003)]

We measured the electron spin resonance and the magnetoresistance in the iron(III) phthalocyanine complexes. The electron spin resonance in $PNP[Fe(Pc)(CN)_2]$ reveals the large anisotropy of the g-value. This is due to the strong spin-orbit coupling in the second HOMO (the third HOMO) hybridizing the d_{yz} (d_{zx}) orbital in the central Fe atom. This anisotropic g-value is consistent with the anisotropy of the magnetic susceptibility and the negative magnetoresistance in $TPP[Fe(Pc)(CN)_2]_2$. We also measured the large negative magnetoresistance in $[PXX][Fe(Pc)(CN)_2]$ and $(PTMA)_x[Fe(Pc)(CN)_2]_Y(CH_3CN)$. The iron(III) phthalocyanine complexes are the good materials for the research of the one-dimensional π-d electron system.

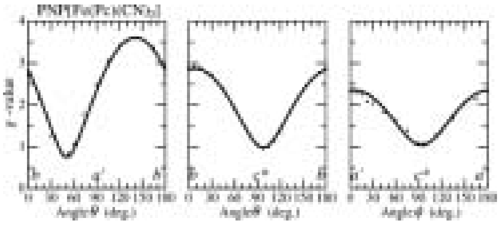

Figure 1. Angular dependence of electron spin resonance in PNP[Fe(Pc)(CN)$_2$].

IV-E-15 Phthalocyanine-Based Multi-Dimensional Conductors

INABE, Tamotsu[1]; ASARI, Takehiro[1]; HASEGAWA, Hiroyuki[1]; MATSUDA, Masaki[1]; GACHO, Eduardo H.[1]; MATSUMURA, Naoko[1]; TAKEDA, Sayaka[1]; TAKEDA, Keiji[1]; NAITO, Toshio
([1]Hokkaido Univ.)

[*Synth. Met.* **133-134**, 515–518 (2003)]

Electrochemical oxidation of [Co^{III}(Pc)X$_2$]$^-$ yields highly conducting partially oxidized salt crystals. Their crystal structures and dimensionality of the π-π interaction (electronic system) vary by the cationic species in the salts; one-dimensional for TPP (tetraphenylphosphonium) or PTMA (phenyltrimethylammonium) cations, and ladder and two-dimensional for the PXX (*peri*-xanthenoxanthene) radical cation. Substitution of the axial group (X) or extension of the π-conjugated macrocycle (Pc) has been found to influence the magnitude of the π-π stacking interactions. Their electrical properties characterized by the conductivity and thermoelectric power measurements are found to be dependent on the dimensionality and the magnitude of π-π stacking interactions.

IV-E-16 ET$_3$(MnCl$_3$)$_2$(EtOH)$_2$: A New Organic Conductor with A Perovskite Structure

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([1]Hokkaido Univ.)

[*Synth. Met.* **133-134**, 445–447 (2003)]

The title salt was obtained as fine black needles from the electrolysis of ET (ET: bis(ethylenedithio)tetrathiafulvalene) with a Mn cluster in 1,1,2-trichloroethane containing 10% of ethanol. The conductivity at room temperature was 25 S cm^{-1} with weakly semiconducting behavior, yet the salt kept a high conductivity down to 4 K (~ 0.1 S cm^{-1}). The manganese(II) chloride anion formed an infinite chain made of face-shared MnCl$_6$ octahedrons, and these chains formed insulating sheets with ethanol molecules between the chains. The ET cation radicals formed α-type conducting sheets between the insulating sheets. Such crystal structure was characterized as that of a typical hexagonal perovskite ABX$_3$, where A equals to a bulky monocation. The magnetic behavior was reproduced by the Curie-Weiss law, which might be attributable to the face-shared MnCl$_6$ octahedron chains.

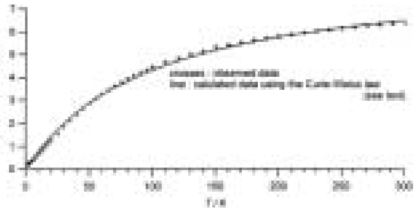

Figure 1. Temperature dependence of the magnetic susceptibility of (ET)$_3$(MnCl$_3$)$_2$(C$_2$H$_5$OH)$_2$.

IV-E-17 Hydrogen-Bond Networks of Mellitate Anions ([C$_6$(COO)$_6$H$_{6-n}$]$^{n-}$) in Salts with Pyridine Derivatives

KOBAYASHI, Norihito[1]; NAITO, Toshio; INABE, Tamotsu[1]
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[*Bull. Chem. Soc. Jpn.* **76**, 1351–1362 (2003)]

Single crystals of mellitate anion ([C$_6$(COO)$_6$H$_{6-n}$]$^{n-}$) salts with 3-aminopyridinium, [3-NH$_2$C$_5$H$_4$NH$^+$]$_3$[C$_6$(COO)$_6$H$_3$$^{3-}$] (**1**), 4-methylpyridinium, [4-CH$_3$C$_5$H$_4$NH$^+$]$_2$[CH$_3$C$_5$H$_4$N]$_2$[C$_6$(COO)$_6$H$_4$$^{2-}$] (**2**), [4-CH$_3C_5H_4NH^+$]$_2$[C$_6(COO)_6H_4$$^{2-}$]·2CH$_3$OH (**3**), pyridinium, [C$_5$H$_5$NH$^+$]$_2$[C$_6$(COO)$_6$H$_4$$^{2-}$]·2H$_2$O (**4**), 3-methylpyridinium, [3-CH$_3$C$_5$H$_4$NH$^+$]$_2$[C$_6$(COO)$_6$H$_4$$^{2-}$] (**5**), [3-CH$_3C_5H_4NH^+$]$_5$[C$_6(COO)_6H_3$$^{3-}$][C$_6(COO)_6H_4$$^{2-}$]·CH$_3$OH (**6**), and isoquinolinium, [C$_9$H$_7$NH$^+$]$_2$[C$_6$(COO)$_6$H$_4$$^{2-}$]·CH$_3$OH (**7**), [C$_9H_7NH^+$]$_2$[C$_9H_7NH_{0:5}$$^{0.5+}$][C$_6(COO)_6H_{3.5}$$^{2.5-}$]·CH$_3$OH (**8**) have been structurally characterized. In these crystals, strong hydrogen-bonds between the mellitate anions are formed. Various arrangements that depend on the deprotonation number, *n*, have been found. All hydrogen-bonds found between the anions are combinations of a carboxy and a carboxylato group. The "triangular hydrogen-bond" unit between the anions, in which three anions are connected by the three hydrogen-bonds to form a triangle, in the salt with $n = 3$, induces the two dimensional (2-D) sheet self-organizing structure in this crystal. "Dual hydrogen-bond" units between the anions, in which two pairs of the hydrogen-bonds connect the neighboring anions, have been found in the salts with $n = 2$ or 2.5. The repetition of the co-planer "dual hydrogen-bond" induces the anion one-dimensional (1-D) belt structure, while the combination of the standing and co-planer "dual hydrogen-bond" units induces the 2-D grid structure. These 2-D grids are further linked by hydrogen-bonds to form a channel. In all the salts ($n = 3, 2, 2.5$), the counter cation molecules are arranged in the space defined by the anion network.

IV-E-18 Crystal Design of Cation-Radical Salts Based on the Supramolecular Self-Organizing Arrangement of Mellitate Anions

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([1]Hokkaido Univ.)

[*J. Phys. IV France* **114**, 449–453 (2004)]

Mellitate anions form hydrogen-bonding infinite networks in the salts with pyridinium cations. The network pattern depends on the number of deprotonation (n) from the mellitic acid; for n = 3, triangular hydrogen-bond units form a two-dimensional sheet, while for n = 2, dual hydrogen-bond units induce one-dimensional belts or two-dimensional grids. These self-organizing properties have been utilized for the crystal design of the TTF-type radical cation salts. Crystallization with TMTTF gave two kinds of crystals. One of the radical cation salt crystals consists of channel network of the anions and one-dimensional columns of TMTTF in the channels. In the other TMTTF salt, the anions with n = 1 form a two-dimensional sheet with methanol molecules. The TMTTF radicals are packed between the sheets with their molecular planes parallel to the anion planes.

IV-E-19 Network Formation of Mellitate Anions ($[C_6(COO)_6H_{6-n}]^{n-}$) in the Salts with Piperidinium Derivatives and *o*-Phenylenediammonium

KOBAYASHI, Norihito[1]; INABE, Tamotsu[1]; NAITO, Toshio
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Single crystals of mellitate anion ($[C_6(COO)_6H_{6-n}]^{n-}$) with piperidinium $[C_5H_{10}NH_2{}^+]_3[C_6(COO)_6H_3{}^{3-}]$ (**1**) and $[C_5H_{10}NH_2{}^+]_2[C_6(COO)_6H_4{}^{2-}]\cdot CH_3OH\cdot 3H_2O$ (**2**), with 1-methylpiperidinium $[C_5H_{10}NHCH_3{}^+]_2[C_6(COO)_6H_4{}^{2-}]\cdot 2H_2O$ (**3**), and with *o*-phenylenediammonium $[C_6H_4(NH_3)_2{}^{2+}]_2[C_6(COO)_6H_2{}^{4+}]\cdot 2CH_3OH$ (**4**) have been prepared and structurally characterized. In all of the salts, two-dimensional (2D) networks of mellitate anions were formed due to the strong self-organization of the anion. In **1**, a 2D hexagon-type network of hydrogen-bond has been observed to form among the anions. This is characteristic of the mellitate anions with n = 3 (n: deprotonation number from the acid). In other salts, a 2D anion network containing either water molecules or $-NH_3$ groups commonly formed. Since the network pattern occurs with different cation species, this hydrogen-bonding unit was determined to be dominant in the n = 2 anion with water and the n = 4 anion with $-NH_3$ species.

IV-E-20 Physical Properties of Electrically Conducting and Stable Molecular Neutral Radical Solid $[Co(2,3\text{-}Nc)(CN)_2]CH_3CN$ (2,3-Nc = 2,3-Naphthalocyanine)

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[*J. Porphyrins. Phthalocyanines.* in press]

Solid state properties of dicyano(2,3-naphthalocyaninato)cobalt(III) neutral radical crystal, $[Co(2,3\text{-}Nc)(CN)_2]CH_3CN$, were characterized by the measurements of the resistivity under high pressure and under uniaxial strain, thermoelectric power, magnetic susceptibility, ESR and polarized reflectance spectra. The title compound exhibited thermally activated-type electrical conductivity along the *c*-axis. The room temperature (RT) resistivity ρ_{RT} along the *c*-axis and activation energy E_a rapidly decreased with increasing pressure. The temperature-dependent thermoelectric power S was that of a typical one-dimensional (1D) semiconductor. However the high absolute value of S suggested that this electronic system should be strongly correlated. Although the electrical resistivity exhibited monotonical temeperature-dependence, the magnetic susceptibility clearly indicated a Peierls-type transition and marked fluctuation from RT. Both of Peierls-type transitions and fluctuations are characteristic phenomena to 1D conductors. Furthermore ESR spectra manifested that the Peierls-type transition occurred at 100 K. The inconsistency between the electrical behaviour (without a phase-transition) and magnetic behaviour (with a phase-transition) indicates the separation of the degrees of freedom in spin and charge (spin-charge separation) of this material. Spin-charge separation is a theoretically predicted phenomenon peculiar to the 1D conductors with strong correlation. The reflectance spectra were quantitatively explained by a 1D Hubbard model, and manifested the existence of a structural fluctuation of this material from RT. Based on these observed physical properties it is concluded that $[Co(2,3\text{-}Nc)(CN)_2]CH_3CN$ is a strongly correlated 1D semiconductor with a Mott-Hubbard type energy gap and characterised with a fluctuation and spin-charge separation.

IV-E-21 Structural, Electrical and Magnetic Properties of $\alpha\text{-}(ET)_7[MnCl_4]_2\cdot(1,1,2\text{-}C_2H_3Cl_3)_2$ (ET = bis(ethylenedithio)tetrathiafulvalene)

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A new charge-transfer salt of ET with a chloromanganate(II) complex anion has been synthesized and characterized by X-ray structural analysis, resistivity measurements, magnetic susceptibility, electron spin resonance (ESR) and extended Hückel tight biding band calculation. The crystal has a sheet structure comprised of α-type two-dimensional (2D) donor arrangement in the *bc*-plane and insulating sheets of discrete $[MnCl_4]^{2-}$ anions and $1,1,2\text{-}C_2H_3Cl_3$ (TCE) molecules. Its conducting property exhibits considerable anisotropy, which is of effectively metallic along the *b*-axis down to 1.2 K under 2.9 kbar and higher pressure. The magnetic susceptibility is approximately reproduced by the Curie-Weiss law with the Weiss temperature $\theta = -(1.35 \pm 0.07)$ K from 2–300 K. ESR measurements revealed that the π-electron system in this salt exhibits Pauli paramagnetism at least at 3.6– ~ 50 K. The band calculation suggests that the HOMO (the highest occupied molecular orbital) band has extremely small dispersion almost solely along the b^*-axis with a simple one-dimensional (1D) Fermi surface. Considering all the data above, it is concluded that this salt has unusually stable and narrow 1D metallic band structure, which is a rare example even in a great number of molecular conducting salts reported to date.

IV-E-22 New Binuclear Copper Complexes [(9S3)Cu(CN)Cu(9S3)]X$_n$ (X = BF$_4$, n = 1; X = TCNQ, n = 2) (9S3 = 1,4,7-trithiacyclononane): Syntheses, Crystal Structures and Magnetic Properties

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The binuclear Cu complexes of 1,4,7-trithiacyclononane (9S3) with an inorganic anion (BF_4^-) and with an organic radical anion TCNQ$^-$ (7,7',8,8'-tetracyanoquinodimethanide) were synthesized and their molecular and crystal structures were examined in connection with each magnetic property. A new complex cation [Cu(9S3)CN(9S3)Cu] varied its charges and magnetic properties depending on the counter anions; [Cu(9S3)CN(9S3)Cu](BF_4) (**1**) was obtained as diamagnetic colorless crystals, while [Cu(9S3)CN(9S3) Cu]$(TCNQ)_2$ (**2**) was obtained as dark blue crystals with antiferromagnetic property. Complex **1** crystallized in the monoclinic space group $C2/c$ with a = 26.863(2), b = 7.0878(5), c = 13.4864(8) Å, β = 116.318(2)°. Complex **2** crystallized in the triclinic space group $P\bar{1}$ with a = 12.521(1), b = 20.2698(8), c = 8.0205(4) Å, α = 100.688(4), β = 93.846(5), γ = 94.953(4)°. Both complexes were comprised of cyano-bridged two Cu(9S3) ions with tetrahedral coordination geometry. The X-ray structural study revealed that **1** had two crystallographically equivalent Cu(I) centers, while **2** had two crystallographically independent Cu(I/II) sites. The two Cu(I/II) sites could not be distinguished from the X-ray structural study. As for **2** the IR spectra showed that both crystallographically independent TCNQ species were monoanions and were strongly dimerized due to pstacking, which well explained their diamagnetic contribution to the magnetic susceptibility and the highly insulating property of this salt. The temperature-dependent magnetic susceptibility of **2** showed a deviation from the Curie-Weiss behavior around 60 K, which indicated a strong antiferromagnetic intermolecular interaction between the copper complexes and that such intermolecular interaction should partly occur *via* the TCNQ radical anion dimer.

IV-E-23 Charge Disproportionation and Anomalous Giant Magnetoresistance in a One-Dimensional Conductor, TPP[Co(Pc)(CN)$_2$]$_2$

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Magnetoresistance study on the charge transfer salts of [Fe(Pc)$(CN)_2$] revealed various interesting phenomena, such as anisotropic giant negative magnetoresistance, weak ferromagnetism, and anisotropic Curie-Weiss magnetic susceptivility.[1)] These interesting phenomena originate from the orbital magnetic moment remaining in the [Fe(Pc)$(CN)_2$] unit, and the d-π interaction inherently existing in this unit. Contrary to the [Fe(Pc)$(CN)_2$] salts, physical properties of the [Co(Pc)$(CN)_2$] salts have not been investigated in detail. In this paper, we report the magnetotransport and NQR studies on TPP[Co(Pc)$(CN)_2$]$_2$ salts. This salt is a one-dimensional conductor, where the partially oxidized [Co(Pc)$(CN)_2$] units stack uniformly along the c-axis. The salt exhibits Pauli-paramagnetic susceptibility. The electrical resistivity is semiconducting with a very small activation energy less than 0.01 eV. Interestingly, this salt exhibits very large positive magnetoresistance at low-temperature ($\Delta R(8\ T)/R(0\ T) \sim 6$). Moreover, the field orientation dependence is quite small below 10 T. These facts indicate that the magnetoresistance in this salt is not an ordinary orbital effect. In order to examine the mechanism of the anomalous magnetoresistance, we have measured ^{59}Co NQR spectra. We found a sign of charge disproportionation at 1.8 K. On the basis of magnetotransport (B < 38 T), NQR and NMR (B < 16 T) measurements, we will discuss the anomalous electronic state of this salt.

Reference

1) For example see, N. Hanasaki *et al.*, *Phys. Rev. B* **62**, 5839–5842 (2000).

IV-E-24 A New Optical Doping Method toward Molecular Electronics

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This work concerns a finding of a novel method of (persistent) carrier doping to molecular materials. The method is simple and versatile; just illuminating the material as long as it contains a photosensitive chemical species in addition to an electroactive one. Although various kinds of photo-excited states reported thus far have typical lifetimes of some hundreds of microseconds at longest in general, the doped state survived even a week after the illumination was finished. The experimental results demonstrate that one can control the conducting properties of an arbitrary part of a molecular material using appropriately focussed illumination. In other words, this method opens a new way for making devices and conducting nano-architectures from a wide variety of molecular solids, which have awaited for a space-resolved doping method.