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

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

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

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

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

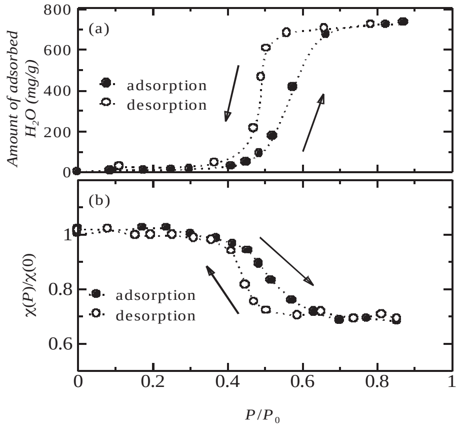

Figure 1. (a) Water adsorption isotherm of ACFs at room temperature, (b) adsorption dependence of the spin susceptivility obtained by ESR measurements. $P_0 \approx 20$ Torr is the saturation pressure of water at room temperature. The spin susceptibilities, $\chi_{\mathrm{spin}}(P)$, were calculated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

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

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

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

IV-F-3 Crystal Structure and Physical Properties of (EDS-TTF)$_2$FeBr$_4$

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

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

IV-F-4 Unconventional TTF-Based Molecular Magnets

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

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

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

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

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

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

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

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

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

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

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

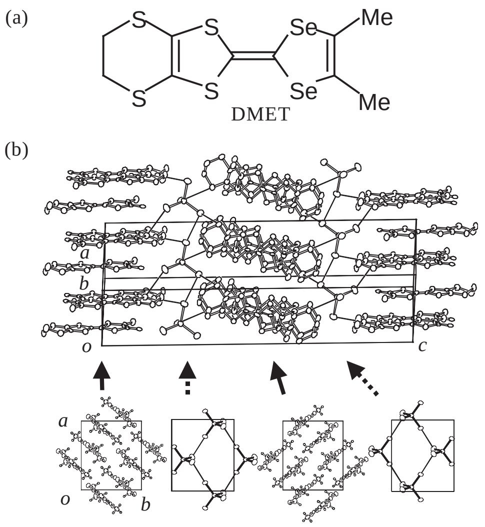

Figure 1. (a) Molecular structure of DMET donor. (b) The crystal structure of $(DMET)_2FeBr_4$. Cross sectional views of donor and anion layers are drawn. Solid lines in the both figures denote close intermolecular B···S and Br···Br contacts.

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

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

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