

Metal bis-dithiolene complexes have been intensively studied as conducting materials. Among them, acceptor type complexes provide various anion radical salts which exhibit superconducting and metallic behavior [1]. On the other hand, neither a metal nor a superconductor has been obtained from donor type complexes except for a salt of $[\text{Ni}(\text{dddt})_2]$ [2]. In this work, we examined modification of the dddt complex with terminal cycloalkane rings, and developed $[\text{Ni}(\text{C}_n\text{-dddt})_2]$ ($n = 3, 4, 5, 6$) to expand the materials chemistry of the donor type complexes. In the crystals of the neutral complexes, the cycloalkane rings exhibited various conformations which would affect physical properties in their cation radical salts. We succeeded in electrochemical crystallization of new cation radical salt $[\text{Ni}(\text{C}_3\text{-dddt})_2]_3(\text{BF}_4)_2$. Other salts were also obtained by the similar procedures. We will discuss their electrical property based on the crystal structure.

[1] R. Kato, *Chem. Rev.*, 104 (2004) 5319.

[2] L. A. Kushch *et al.*, *J. Mater. Chem.*, 5 (1995) 1633.



Keywords: condensed matter, conducting materials, complexes

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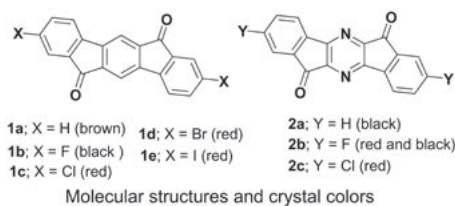
Crystal structures of indenofluorenediones and diindenopyrazinediones showing FET characteristics

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We have found indeno[1,2-b]fluorene-6,12-diones **1** and diindenopyrazinediones **2** are attractive n-type semiconductors for organic field-effect transistors (OFETs),¹⁾ whose crystal structures and colors are dependent on the halogen substituents introduced at the terminal positions. After sublimation of the crude product of **2a** with a pyrazine and no halogen groups, black crystals were obtained. On the other hand, in the case of compound **2b** with fluorine atoms, red crystals as well as black ones were obtained. We have succeeded in carrying out X-ray analyses of both single crystals and found the overlap patterns of the molecules are considerably different. In the red crystal only a half of the molecule is overlapped, whereas in the black crystal the whole molecule is involved in the overlap. The films of these derivatives deposited on SiO_2/Si substrates were investigated by X-ray diffraction in reflection mode (XRD). In the XRD measurement of **2b**, a clear difference depending on the crystal morphology was observed. We will discuss here about the relationship between the crystal structures and film morphologies.

(1) *Chem. Mater.* **2008**, in press.



Keywords: organic semiconductors, field-effect transistors,

polymorphism

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Genuine organic crystal exhibiting giant negative magnetoresistance

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A coexisting system of conductivity and magnetism consisting of a genuine organic material has become one of the current targets in the field of "molecular magnetism". Here we prepared a new type of the spin-polarized donor, BTBN, in which two bromine atoms are introduced at the dithiole ring to increase the intra- and inter-columnar interactions of donor units. The novel donor radical formed needle crystals of $(\text{BTBN})_8 \text{C}_6\text{H}_{14}$ with a size of ca. $0.1 \times 0.1 \times 5$ mm, including n-hexane in a channel structure. BTBN stacks along the c axis with the interplanar distance of 3.458(2) and 3.472(3) Å. The charge transfer band of the polycrystalline sample extended over to ca. 1400 cm^{-1} , suggesting a narrow gap between the valence and the conduction bands. This neutral crystal turns out to exhibit the negative magnetoresistance of -70 % at 5 K under 9 T. We found that the source drain current (IDS) of BTBN on a surface-oxidized silicon wafer increased by the application of both negative and positive gate voltage (VG). Moreover, the IDS values increased appreciably (ca. three times) when the external magnetic field of 5 T is applied at 2 K.

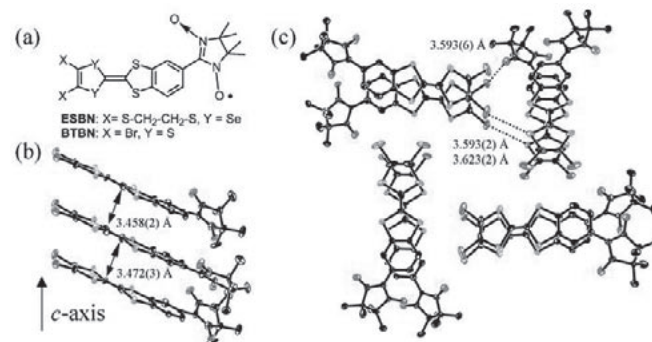


Fig. 1. Crystal structure of BTBN: Tetragonal, $P4_2/m$, $a = b = 33.327(4)$, $c = 7.617(1)$ Å, $Z = 16$
(a) Molecular structure of ESNB and BTBN (b) Stacking of BTBN along the c axis
(c) Arrangement of BTBN in the ab plane

Keywords: donor radical, negative magnetoresistance, field effect transistor

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Development of organic NLO materials for terahertz-wave generation

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4-dimethylamino-N-methyl-4-stilbazolium tosylate (DAST) is a well-known organic nonlinear optical material for emitting high-power and broadband terahertz (THz) wave. However, it had nearly reported about the crystals of DAST-derivative materials and their properties as a THz wave source. In this study, we designed new DAST-derivative materials, grew these crystals, and investigated their THz-wave properties. We synthesized various DAST-derivative materials such as 1-methyl-4-{2-[4-hydroxyphenyl]ethenyl}pridinium p-toluenesulfonate (MC-pTS), new material named bis[1-methyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}pridinium]terephthyanate (BDAS-TP), and so on. Then we prepared their solutions with methanol solvent, and grew their crystals by using slow-cooling process. Fig. 1 shows the obtained crystals of MC-pTS and BDAS-TP. By using a femtosecond laser, we found BDAS-TP crystal can generate broadband THz-wave.

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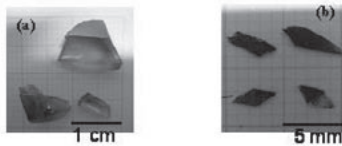


Fig.1 Crystals of DAST derivatives (a) MC-pTS (b) BDAS-TP

Keywords: laser and nonlinear optical materials, organic chemistry, crystal growth from solution

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Neutron and X-ray powder diffraction investigation of LaMnO_3

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The parent compound LaMnO_3 of the hole-doped colossal magneto-resistance (CMR) materials crystallizes in the orthorhombic space group Pbnm. The structure consists of MnO_6 octahedra that are distorted due to the Jahn-Teller effects. Below $T_O = 750$ K LaMnO_3 has an orbital ordered state that consists of the Mn^{3+} eg orbitals in an alternate staggered pattern in the a-b plane that repeats itself along the c axis. This type of orbital order induces A-type antiferromagnetic (AF) ordering below $T_N = 141$ K and coexists with it. In the A-type AF phase the ferromagnetic a-b plane are stacked antiferromagnetically along the c-axis. We have investigated the orbital order-disorder transition in LaMnO_3 by high temperature X-ray powder diffraction with synchrotron radiation and also neutron powder diffraction. The unit cell volume of LaMnO_3 increases with increasing temperature and at higher temperature it starts decreasing in a narrow temperature range below $T_O = 750$ K, and then undergoes a volume collapse at T_O . The Pbnm symmetry of LaMnO_3 is retained above T_O although the unit cell becomes pseudo-cubic. We have constructed a theory of this phase transition by a model Hamiltonian involving the pseudo-spin of Mn^{3+} eg states, the staggered JT distortion and the volume strain coordinate. We also investigated the magnetoelastic effect at the antiferromagnetic phase transition

in LaMnO_3 by neutron powder diffraction. The lattice parameters a decreases with temperature up to $T_N = 141$ K and then abruptly starts increasing whereas the lattice b shows the opposite effect. The third lattice parameter c and the unit cell volume show only weak anomalies close to T_N . We interpreted these results in terms of a spin-lattice coupling Hamiltonian and have extracted the coupling constant.

Keywords: orbital ordering, antiferromagnetic ordering, magneto-elastic effect

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Tuning magnetic interaction in orthorhombic neodymium-yttrium manganites $\text{Nd}_{1-x}\text{Y}_x\text{MnO}_3$

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By lowering the Mn-O-Mn bond angle in LnMnO_3 with $\text{Ln}=\text{La-Ho}$ the Neel-temperature decreases and at $\text{Ln}=\text{Tb}$ the A-type antiferromagnet transforms to an incommensurate (IC) spin-spiral phase for $\text{Ln}=\text{Gd,Tb,Dy}$. The spin-spiral breaks both inversion and time reversal symmetry leading to a strong coupling between magnetism and ferroelectric polarization. We investigate the evolution of the crystal and magnetic structure from the A-type phase to the IC spin spiral phase by systematically replacing neodymium by yttrium in NdMnO_3 resulting to a decrease of the tolerance factors to values similar to that for multiferroic TbMnO_3 . One advantage of this approach is that the tolerance factor can be tuned and that neodymium and yttrium are not high neutron absorbing elements in sharp contrast to other rare earths like Gd, Dy and Eu. Compositions $x=0.0$ to 0.6 have been prepared, neutron and x-ray powder diffraction patterns were measured as well as the magnetic properties. It can be shown that by decreasing the tolerance factor that way, similar effects can be seen as with varying the ionic size of the rare earth ions. For example we found that between $0.4 < x < 0.6$ the incommensurate phase co-exists with the A-type antiferromagnetic phase and with $x=0.6$ and higher the system is only incommensurate and seemingly multiferroic.

Keywords: manganites, multiferroics, NdYMnO_3

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Superstructures in $\text{RBaCo}_2\text{O}_{5.5}$ (R=Nd, Tb) as seen from reciprocal space mapping

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In $\text{RBaCo}_2\text{O}_{5.5}$ (R= rare earth element) the Co^{3+} ions can be found in either low spin state, an intermediate spin state or in a high spin state. Providing that the energy difference between these states is small, i.e. $\sim k_B T$, different electronic and vibrational degeneracy may lead, via an entropy factor, to a temperature induced spin-