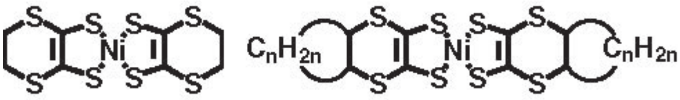
Metal bis-dithiolene complexes have been intensively studied as conducting materials. Among them, acceptor type complexes provide various anion radical salts which exhibit superconducting and metallic behavior [1]. On the other hand, neither a metal nor a superconductor has been obtained from donor type complexes except for a salt of [Ni(dddt)$_2$] [2]. In this work, we examined modification of the dddt complex with terminal cycloalkane rings, and developed [Ni(Cn-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 [Ni(C3-dddt)$_2$]$_3$(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

P11.01.33

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Crystal structures of indenofluorenediones and diindenopyrazinediones showing FET characteristics

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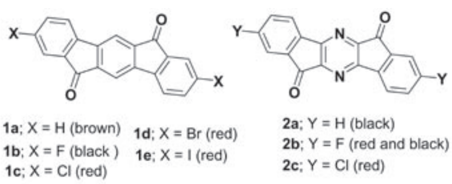
We have found indeno[1,2-b]fluorene-6,12-diones **1** and diindeno[1,2-b;1',2'-e]pyrazine-6,12-diones **2** are attractive n-type semiconductors for organic field-effect transistors (OFETs),[1)] whose crystal structures and colors are dependent on the halogen substituents introduced at the terminal positions. 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.



Molecular structures and crystal colors

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 (BTBN)$_8$ C$_6$H$_{14}$ with a size of ca. 0.1 x 0.1 x 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.

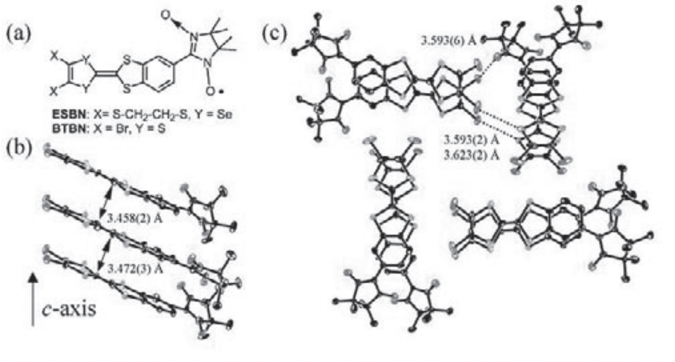

Fig 1. Crystal structure of BTBN:Tetragonal, $P4_2/n$, $a = b = 33.327(4)$, $c = 7.617(1)$Å, $Z = 16$
(a) Molecular structure of ESBN and BTBN (b) Staking of BTBN along the c axis
(c) Arrangement of BTBN in the ab plane

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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