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Molecular Design for Organic Conductors and Ambipolar Organic Transistors

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THESIS OUTLINE

In this thesis, several organic conductors and semiconductors are prepared from the viewpoint of the material design, and the structural and physical properties are investigated as a basic study concerning to the organic molecules used in organic electronics.

In Chapter II, *t*-butyl substituted tetrathiafulvalene (*t*-Bu_2TTF) is prepared. *t*-Bu_2TTF shows strong electron donating ability and high solubility. Although the crystal density is remarkably reduced, the crystal has a relatively simple herringbone structure. In the tetracyanoquinodimethane (TCNQ) complex, (*t*-Bu_2TTF)(TCNQ), each column is separated by the *t*-butyl groups to construct a highly one-dimensional system. (*t*-Bu_2TTF)(TCNQ) shows the partial charge transfer of 0.86 and room-temperature conductivity of 7 S cm^{-1}.

In Chapter III, the charge-transfer salt of benzoselenobenzoselenophene (BSBS), $(BSBS)_2TaF_6$, is investigated. $(BSBS)_2TaF_6$ is isostructural to the sulfur analogue, benzothienobenzothiophene (BTBT), $(BTBT)_2PF_6$, but the one-dimensional anisotropy is not clearly reduced in comparison with the BTBT salt. Nonetheless, the resistance jump temperature is reduced to 90 K from 150 K, and the increase of the low-temperature resistance is diminished, though the room-temperature conductivity is not as high as that of the BTBT salt. The spin susceptibility shows a clear drop below 50 K, which indicates that the low-temperature insulating state has essentially singlet nature.

In Chapter IV, neutral thiophene-dithiolate gold(IV) complexes with methyl [AuMe] and ethyl [AuEt] groups are prepared. Although the methyl substitution does not improve the crystallinity, [AuEt] improves the solubility, and produces good-quality single crystals for the first time among the neutral thiophene-dithiolate gold complexes. [AuMe] and [AuEt] show semiconducting behavior with a small activation energy. [AuEt] exhibits large negative thermoelectric power of –900 μV K^{-1} at room temperature, so a highly correlated system is expected. Because of the half-filled one-dimensional band, [AuEt] is regarded as a Mott insulator.

In Chapter V, binaphthosemiquinone (BNQ) derivatives are proved to show ambipolar transistor properties. These compounds have one-dimensional stacks, and because the charge transport is restricted in the stacking direction, the hole and electron mobilities are in the order of 10^{-3} cm^2 V^{-1} s^{-1}. In general, there is a tendency that a

bulky alkyl group reduces the intermolecular overlap and charge transport properties. The ambipolar properties are obviously associated with the small HOMO-LUMO gaps and the characteristic blue colors. Such a property comes from the semiquinone structure. The quinone parts work as an electron acceptor and the alkoxy groups act as an electron donor, and these molecules contain donor and acceptor parts in a molecule.

In Chapter VI, dicyanomethylene terthiophene (DCMT) exhibits excellent ambipolar properties on tetratetracontane (TTC). In principle, the key parameters, electron and hole threshold voltages (V_T and V_T'), are estimated from four different ways. These estimations afford approximately the same values, and depending on the applied gate voltage V_G and drain voltage V_D, the operation modes are classified to saturated, linear, ambipolar, and off regions. To analyze the temperature dependence, Lang's method is not naively applicable to the ambipolar region, because drain current I_D is given by the sum of the electron and hole currents containing different trap parameters. However, the actual transistors are operated mostly in the unipolar saturated region. Therefore, similarly to the usual unipolar transistors, the temperature dependence of the transfer characteristics is analyzed according to Lang's method, and the result proves that the DCMT/TTC transistor has a comparatively small number of traps. It is considered that the quantitative analysis shown here is useful for understanding the operation of ambipolar transistors and for evaluating organic semiconductors.

The present work demonstrates that molecular modification in organic conductors and semiconductors is a versatile tool to control the structural and physical properties, and furthermore it is an important tool to investigate the device physics in organic transistors. The present study is expected to contribute to progress in molecular design in organic conductors and transistors.