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Organic Transistors Using Charge-Transfer Complexes

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Outline

In this thesis, various donor-acceptor (DA) complexes are prepared, and the crystal structures and transistor properties are investigated. In order to extract the rule determining the carrier charge polarity of the DA complexes and to design ambipolar complexes, the carrier charge polarity is analyzed from the viewpoint of the molecular orbitals.

In Chapter II, we have investigated transistor properties of tetraphenylpentacene derivatives. Halogen-substituted tetraphenylpentacenes (**4*X*4Ph**, *X* = F, Cl, and Br) have similar dimer-stack structures with similar HOMO/LUMO levels. However, while **4Cl4Ph** shows ambipolar characteristics, **4F4Ph** and **4Br4Ph** show only p-type characteristics. The molecular orbital of pentacene has nodes on each benzene ring, but the intermolecular overlap of HOMO and LUMO shows different periodicity with respect to the molecular long-axis displacement. As a result, depending on the slight difference of the stacking structures, intra- and interdimer LUMO transfer integrals are reduced in **4F4Ph** and **4Br4Ph**, in consistent with the observed p-type properties.

In chapter III, crystal structures and transistor properties of (BTBT)(F_nTCNQ) and (BSBS)(F_2TCNQ) (BTBT: benzothienobenzothiophene, BSBS: benzoselenobenzoselenophene, and F_nTCNQ: fluorinated tetracyanoquinodimethanes, n = 0, 2, and 4) are investigated. These complexes make n-type transistors with long-term air stability. All these complexes are regarded as practically neutral. (BTBT)(F_4TCNQ) shows the highest mobility of 0.19 $cm^2\ V^{-1}\ s^{-1}$ (maximum).

In chapter IV, crystal structures and transistor properties of (3T)(TCNQ) and (4T)(F_nTCNQ) (3T: terthiophene and 4T: quarterthiophene, n = 0, 2, and 4) are investigated. (4T)(TCNQ) shows a very rare case showing hole-dominant transport among TCNQ complexes. This is because 4T HOMO and TCNQ LUMO have the same stripe symmetries.

In chapter V, it is demonstrated that the symmetry of the molecular orbitals determines carrier charge polarity for DA complexes. Transfers from the A LUMO to the D HOMO−1 are dominant due to the orbital symmetry. This rule applies to many acenes, phenes, and thienoacenes; electron transport is generally expected in the TCNQ complexes of these donors. However, this rule is violated by the reduced symmetry due to the largely tilted molecular packing or by the use of low symmetry molecules such as 2,5-dimethyl-*N*,*N*'-dicyano-*p*-quinonediimine. By investigating other combinations of frontier orbital symmetry, DA complexes seem to be classified to two categories, electron transport and ambipolar transport.

In chapter VI, the crystal structures and transistor characteristics of (Perylene)(CyHex-PDI)$_2$ and (Coronene)(CyHex-PDI)$_2$ (CyHex-PDI: dicyclohexyl-perylene diimide) are investigated. The perylene HOMO/LUMO have the same symmetry as the CyHex-PDI HOMO/LUMO, respectively. Therefore, these DA complexes exhibit ambipolar characteristics. Coronene has a larger p-electron system than perylene, and not only the hole transport but also the electron transport increase. Although large π-electron systems have an excellent charge bridging ability, the charge transport properties increase in the combination of small and large molecules than the combination of large and large molecules.

In Chapter VII, transistor properties of 1,5-dibromo-2,6-naphthoquinhydrone are investigated. Quinhydrone is a DA complex with hydroquinone as a donor and quinone as an acceptor, and the HOMO of hydroquinone and the LUMO of quinone have the same symmetry. Although ambipolar property is expected, only n-type characteristics are observed. The transfer integrals between the donor HOMO and both the acceptor LUMO and HOMO–1 are large. These two contributions are canceled out and no hole conduction appears.

The present work has demonstrated that the carrier charge polarity of DA complexes is determined by the molecular orbitals of the donors and acceptors. The present study makes the conduction mechanism of the DA complexes clear.