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Development of Air-Stable n-Channel Organic Field-Effect Transistors

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A Dissertation Submitted to Tokyo Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Engineering

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Thesis outline

In this thesis, several kinds of organic semiconductors for n-channel organic transistors have been prepared. Transistor properties of these compounds are studied together with the single crystal structures, electrochemical properties, molecular orbital calculations, and thin-film analyses.

In chapter II, diphenyl-isodiketopyrrolopyrrole (**isoDPP**) and diphenyl-diketopyrrolopyrrole (**DPP**) have been prepared. Although **DPP** shows ambipolar transport, **isoDPP** shows dominantly electron transport. The difference is attributed to the deep HOMO level of **isoDPP**. This can be understood easily by replacing **isoDPP** and **DPP** with 2,6-naphthoquinone and 1,5-naphthoquinone or by reducing **isoDPP** and **DPP** to 2,3-diaminobutadiene and 1,4-diaminobutadiene. **isoDPP** shows smaller stabilization, larger bond alternation, and a larger HOMO-LUMO gap

In chapter III, a series of sulfur-rich electron acceptors, 3,3'-dialkyl-5,5'-bithiazolidinylidene-2,2'-dione-4,4'-dithiones (**OS-*R***)(*R* = Me, Et, Pr, Bu), 3,3'-diethyl-5,5'-bithiazolidinylidene-4,4'-dione-2,2'-dithione (**SO-Et**), 3,3'-dialkyl- 5,5'-bithiazolidinylidene-2,4,2',4'-tetrathiones (**SS-*R***)(*R* = Me, Pr, Bu) and 2,2'-(3,3'- diethyl-4,4'-dithioxo-5,5'-bithiazolylidene-2,2'-diylidene)dimalononitrile (**S(CN)$_2$-Et**), have been prepared. **S(CN)$_2$-Et** shows normally-on transistor characteristics, which are unusual in n-type organic transistors, because **S(CN)$_2$-Et** has very strong electron acceptor ability. **SS-Pr** exhibits the best transistor performance and stability among these acceptors. The result comes from the good crystallinity and the propyl group, which may be the most suitable alkyl chain in **SS-*R*** for thin-film transistors. **SS-*R*** compounds have stacking

structures with several intermolecular short S–S contacts. **OS-*R*** and **SO-Et** have herringbone structures with S–π interactions. The structures seem to be attributed to the weakened intermolecular S–S interactions. **OS-*R*** and **SO-Et** show degradation of the mobility and an increase of the threshold voltage and the off current under ambient atmosphere because of the shallow LUMO levels located above −4.0 eV.

In chapter IV, bulky alkylphenyl groups, benzyl (Bn) and 2-phenylethyl (EtPh), have been introduced to **OS-*R*** and **SS-*R***. **OS-Bn** shows relatively low mobility, and transistors based on **SS-Bn** does not work even under vacuum. **OS-Bn** and **SS-Bn** have similar staking structures with one-dimensional carrier pathway because of large torsion angles between the core part and the phenyl ring. This seems to make **OS-Bn** and **SS-Bn** to show poor transistor performance. **OS-EtPh** has a herringbone structure and shows the mobility of the same order of magnitude as the previous **OS-*R***. **OS-Bn** and **OS-EtPh** show air-sensitive n-type transistor characteristics, but maintains mobility in atmospheric conditions. **SS-EtPh** achieves the highest mobility of 0.27 $cm^2\ V^{-1}\ s^{-1}$ in this study and excellent ambient and long-term stability. The bulky 2-phenyl ethyl group blocks the intermolecular S–S contacts in the crystal and **SS-EtPh** forms a herringbone structure. **SS-EtPh** forms highly crystalline thin films and makes less tilted packing, which is favorable to thin-film transistors. Bulky substituents improve transistor performance and stability of **OS-*R*** and **SS-*R***.

In chapter V, charge transfer (CT) complexes of ditheno[2,3-*d*;2'3'-*d*'] benzo[1,2-*b*;4,5-*b*']dithiophene (DTBDT) and F_nTCNQ (n = 0, 2, 4) have been prepared and the single-crystal transistors have been fabricated. All the CT complexes show only electron transport and (DTBDT)(TCNQ) shows the highest mobility of 0.1 $cm^2\ V^{-1}\ s^{-1}$. Effective transfer integrals t^{eff} are estimated from the level splitting of the triads, where

t_e^{eff} is much larger than t_h^{eff}. These values are consistent with the carrier polarity. Carrier charge polarity can be explained by the bridge orbital. DTBDT HOMO−1 mainly contributes to the electron transport and results in the asymmetrical transport in the CT complexes.

The present work demonstrates that slight modifications of organic semiconductors, such as isoelectronic isomerization, introduction of alkyl chains and bulky substituents, can improve transistor characteristics significantly. The results contribute to the development of air-stable n-channel organic field-effect transistors.