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Molecular Design of Organic Semiconductors Based on Extended Thienoisatins

Presented by

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Outline

This thesis covers several kinds of organic semiconductors based on extended thienoisatins. Because thienoisatin has two reaction sites, it was possible to selectively extend thienoisatin by using appropriate reagents. Thienoisoindigo, derived from the dimerization of β-position carbonyl groups of the nitrogen, shows relatively narrow energy gap implying possibility of ambipolar property. Bisthienoisatin, derived from the dimerization of α-position of the sulfur atom, is appropriate for n-type OFET because of the low-lying LUMO level. By dealing with these two fundamental molecules, various derivatives and analogs have been synthesized as small-molecule organic semiconductors to study structure-property relationships by investigating thin-film transistor properties together with the crystal structures, electrochemical properties, and thin-film properties.

N-unsubstituted thienoisoindigo (**TIIG**) and the α-substituted diphenyl derivative (**Dph-TIIG**) have been prepared in Chapter III. These molecules exhibit ambipolar transistor properties as expected from the narrow energy gaps. **Dph-TIIG** has shown much smaller energy gap owing to the extended π-skeleton, but range of the reduced energy gap is small owing to the tilted phenyl groups. This causes a hybrid of brickwork and herringbone structures, whereas **TIIG** forms a stacking structure. When compared to *N*-hexyl substituted molecules, dimensionality of conduction path in **TIIG** increases from zero to one and that of **Dph-TIIG** increases from one to two. Therefore, the transistor properties are improved, particularly more than 0.1 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$ in **Dph-TIIG**, and superiority as transistor materials is signified in the *N*-unsubstituted molecules.

Based on the results in Chapter III, in order to investigate a hybrid of isoindigo and

TIIG, **CS** (thieno-benzo-isoindigo) and **NS** (thieno-pyridine-isoindigo) have been prepared in Chapter IV. The energy levels deepen in the order of **TIIG** < **CS** < **NS** according to the order of electron withdrawing ability of the substituted rings. Even though many interactions are confirmed in the crystal structures of **CS** and **NS**, **CS** has a stacking structure and **NS** constructs a dimerized stacking structure due to the twisted molecular structures. Owing to the large transfer integrals of LUMO, these molecules exhibit moderate mobilities with n-dominant ambipolar properties similarly to **TIIG**. In addition, **Dth-TIIG** (α-thienyl-substituted **TIIG**), **Dfu-TIIG** (α-furyl-substituted **TIIG**), and **Bis(1-ph-5-py)-TIIG** (α-(1-phenyl-5-pyrazolyl)-substituted **TIIG**) have been prepared in Chapter IV to identify the π-skeleton extension effects. It is confirmed that crystal structures change according to the α-substituents. Because of the largely tilted substituents in **Bis(1-ph-5-py)-TIIG**, thin-films of this molecule constitute amorphous grains and the transistor property is obviously reduced. **Dfu-TIIG** forms a stacking structure, while **Dth-TIIG** forms a brickwork structure with flipping disorder. Therefore, these molecules show slightly degraded mobilities in comparison with **Dph-TIIG**, and molecular disorder observed in **Dth-TIIG** suggests possibility of the same kind of disorder in polymers with similar chemical structures.

In Chapter V, bisthienoisatins (**BTI-*R*** with *R* = *n*-propyl, *n*-hexyl, and 2-ethylhexyl) and the dicyanomethylene derivatives (**BTICN-*R*** with *R* = *n*-propyl, *n*-hexyl, and 2-ethylhexyl) have been prepared. The crystals have uniform stacking structures, but the packing pattern of the stacks varies depending on the alkyl chains. These materials show n-type transistor properties, and **BTICN**s exhibit greater performance than **BTI**s with remarkable long-term air stability. This is resulted from the quite low-lying LUMO levels about −4.3 eV of **BTICN**s, but this strong electron acceptor ability causes normally-on transistor characteristics, which are rare in n-type OFETs. In particular, **BTICN-EH** shows the maximum electron mobility exceeding 0.2 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ due to the large transfer integrals.

In Chapter VI, bulky substituents, benzyl (**Bn**) and 2-phenylethyl (**EtPh**), have been introduced to **BTI**, **TIIG**, and dibenzothienoisoindigo (**DBTII**). Uniform stacking structures are maintained in these molecules, but only in **EtPh-BTI**, a two-dimensional slipped herringbone structure is observed. The benzyl groups are largely distorted from the molecular core, but the 2-phenylethyl groups are slightly twisted owing to the ethylene spacer. Therefore, 2-phenylethyl substituted molecules show relatively fine thin-film qualities, while in the thin films of **Bn-TIIG** and **Bn-DBTII**, two kinds of molecular orientations coexist randomly resulting in poor thin-film qualities. This is reflected in much better performance of the transistor properties in the 2-phenylethyl substituted molecules. The **BTI** derivatives show only electron transport, but other compounds exhibit ambipolar transistor properties, which are the same carrier polarities in Chapter III and V. In particular, **EtPh-TIIG** and **EtPh-DBTII** show maximum hole mobilities of about 0.04 ~ 0.05 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ together with moderate electron mobilities.

The present work demonstrates molecular modifications of organic semiconductors such as atom substitutions, introduction of functional groups, introduction or removal of alkyl groups, and introduction of bulky substituents by using extended thienoisatins. From these kinds of molecular engineering, improved device performance as well as elucidation of structure-property relationships can be achieved. The author believes that these results contribute to the development of organic semiconductors.