Development of Narrow-Bandgap π-Conjugated Small Molecules and Their Application in Solution-Processed Organic Solar Cells

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論 文 名　：Development of Narrow-Bandgap π-Conjugated Small Molecules and Their Application in Solution-Processed Organic Solar Cells
(狭バンドギャップ π 共役低分子化合物の開発と塗布型有機薄膜太陽電池への応用)

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論　文　内　容　の　要　旨

Energy conversion from renewable and ubiquitous solar energy to electricity using solar cell technology is one of the most critical project to dissolve the global energy demand problem. Current conventional solar cell technologies including silicon, CdTe, copper-indium-gallium-selenide (CIGS) solar cells have not successfully replaced existing electrical power supply due to the high production cost and related environmental issues. In recent years, solution-processed organic solar cell (OSC) technology has attracted great interest owing to their synthetic variability, low-temperature and less energy-consuming fabrication process, and the potentials of lightweight, flexibility, mass production, and inexpensive solar cells. These unique properties allow not only to expansion of OSCs onto grid-electricity but to generate new applications and commercial opportunities such as energy-harvesting power supply from surrounding environment for off-grid internet-of-thing (IoT) devices and wearable electronics.

The author has focused on solution-processable small molecules (SMs) for electron donor materials of OSCs as research subjects because of their well-defined molecular structures without molecular-weight distributions and thereby reliable analysis results in comparison with polymer donors with which outstanding photovoltaic performances have been reported. OSCs based on SM donors have lagged behind polymer counterpart in device performance with the power conversion efficiency (PCE) of up to 11%. For the further improvement in PCE of SM-based OSCs, deeper understanding of the structure–property relationships in SM donors and new molecular design strategies are needed, which should contribute to entire field of OSCs. This thesis describes three strategies to improve and to control the photovoltaic parameters in OSCs, i.e. short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF), through the development of a series of novel SM donors and systematic evaluation of solution-processable OSCs.

Chapter 1 is general introduction including current states of solar energy utilization, history of solar cells, operational principle of OSCs with representative loss mechanisms, state-of-the-art photovoltaic materials, and overview of this thesis.

Chapter 2 deals a strategy for precise control of the highest occupied molecular orbital (HOMO) energy levels of SMs by systematic fluoro-functionalization of the molecule to manipulate V_{oc} of resultant devices. The terminal phenyl groups of a donor molecule were substituted with fluoro and trifluoromethyl groups. Two or four substitution using each substituent led stepwise reduction of HOMO levels of the molecules over a range of −5.23 to −5.47 eV, while maintaining small bandgap energies of approximately 1.6 eV in their thin films. With such proper engineering of the HOMO levels, OSCs based on fluoro-factionalized

molecules as donors and [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) as an acceptor showed tunable open-circuit voltages of 0.76–0.94 V, which are found to correlate with the Hammett constants, empirical well-known parameters. Further investigation of film properties revealed that in comparison to SMs with trifluoromethyl end groups, SMs with fluoro end groups show superior charge transport and self-organization ability, contributing to higher PCEs of the OSCs.

In Chapter 3, four SM donors were newly designed, in which thienylene-vinylene-thienylene (TVT) was adopted as the central electron-rich core to couple with two terminal rhodanine or dicyanorhodanine-based electron-deficient units through different numbers of hexylthiophene rings. Because of high coplanarity in TVT unit, the introduction of the TVT core is expected to induce the self-organization capability and thereby high carrier mobility, as well as lowered bandgap energy. As expected, all SMs exhibited photoabsorption over the entire visible range with relatively low-lying HOMO energy levels. Besides, these coplanar π-conjugated molecules showed high crystallinity and crystalline coherence in the thin films upon solvent vapor annealing (SVA) treatment. This feature leads to significantly improved hole mobilities close to 0.1 $cm^2\ V^{-1}\ s^{-1}$, which are far higher than those of common SM and polymer donors. By simply optimizing the phase-segregated morphology and crystallinity in the active layers via proper duration of SVA, photovoltaic performances for the SM-OSCs were drastically improved and the resulting PCEs were increased by 4–6 times as a result of the enhanced FFs.

Chapter 4 describes effect of SM donor substitution with halogens varying from fluorine to iodine on photovoltaic performance as well as photophysical properties, charge transport characteristics, and miscibility with $PC_{71}BM$. A series of SMs consisting of a donor core coupled with terminal 1,3-indandione acceptor units, which are monosubstituted with various halogen groups including fluorine, chlorine, bromine, and iodine, were newly designed. The halogenated SMs showed one order of magnitude higher hole mobilities than that of the parent non-halogenated SM. Besides, substitution with heavy halogens was found to reduce domain size in the blend films with $PC_{71}BM$, which was ascribed to small interfacial free energy between donor and acceptor domains. Consequently, OSCs using halogenated all SMs exhibited superior photovoltaic performance with 1.5 time higher FFs in comparison with those using the non-halogenated compound, resulting in the best PCE of 9.2% for iodine-substituted compound without any processing additives and post-treatment process.

Chapter 5 summarizes this thesis and describes future perspectives.