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論　文　内　容　の　要　旨

Since the first report of the conductive polymers, a number of organic semiconductors have been created from polymer to small molecules. Because of their unique structural and optical properties, small molecule-based organic semiconductors are promising candidates for optoelectronic devices such as OFETs, OLEDs, and OSCs. For enhancement of these device performances, organic semiconductor requires some properties such as high charge carrier mobility and excellent absorption properties. In this thesis, the author has investigated structure-property relationship between a series of organic semiconductors and OSCs properties.

In this thesis, small-molecule organic semiconductors were developed and applied to OSCs. To control the nanostructure and the optical and electrochemical properties of the device, a series of organic semiconductors with different functional groups were synthesized, and the structure–property relationships of the synthesized products were investigated. Disk-shaped molecules such as pyrene, triphenylene, and hexabenzocoronene are promising building block for the organic semiconductors. A self-assembled 1D columnar structure of the disk-shaped molecules exhibited the high carrier mobilities. Pyrene consists of four fused aromatic rings, which can be chemically modified to tune the optical, electrochemical, and carrier transport properties. We have designed and synthesized pyrene-cored disk-shaped organic semiconductors for bulk-heterojunction (BHJ) solar cells (**chapter 2-4**). Metal-free organic dyes for dye-sensitized solar cells (DSSCs) have been attracted the attentions due to low-cost and tuning their energy levels easily. The π-bridge of the organic dyes is important for the charge carrier transportation after the photoexitation. Benzothiadiazole-fulorene unit was used as the carrier transportation unit in the polymeric semiconductors in OLEDs. We have designed and synthesized novel organic dyes having benzothidiazole-fluorene unit (**chapter 5**).

The results of this study are summarized below:

Chapter 2 deals with the synthesis and investigation of BHJ solar cell properties of the disk-shaped molecules having pyrene core and oligothiophene side chains. It was found that the lowest unoccupied molecular orbital (LUMO) energy levels of synthesized molecules were ideal for achieving efficient electron transfer to fullerene derivatives $PC_{61}BM$ and $PC_{71}BM$, and that

disk-shaped molecules can function as electron donor components in solution-processed BHJ solar cells. Disk-shaped molecules organized ordered structures through intermolecular π–π interactions as monitored by temperature-controlled polarized optical microscope (TPOM), differential scanning calorimetry (DSC), and powder X-ray diffraction (XRD). Solution-processed BHJ solar cells using disk-shaped donor and fullerene derivatives as acceptor materials were fabricated and investigated. The oligothiophene lengths were reflected in the performance characteristics of solar cell devices fabricated using disk-shaped donors. Power conversion efficiency (PCE) of 2.6% was achieved for small-molecule BHJ solar cells containing self-organized crystals of disk-shaped molecules in the active layer under one sun condition.

Chapter 3 described low band gap disk-shaped donors having acceptor terminal unit. Disk-shaped donors composed of a pyrene core, dithiophene linkers and rhodanine terminates were synthesized. The introduction of rhodanine terminal units into the pyrene-cored donors could effectively broaden the absorption spectrum and improve the molar absorption coefficient. The positions of dithiophene linkers in the pyrene core affected to their optical and electrochemical properties as well as the molecular ordering and carrier transport properties in solid state. In addition, length of peripheral alkyl chains in dithiophene linkers changed molecular ordering and carrier transport properties in solid state. The HOMO and LUMO energy levels of these materials were suitable for the donor component in BHJ solar cells with fullerene acceptor. The BHJ solar cells were fabricated by the solution process using mixed solutions of pyrene-cored donors with fullerene acceptors. The PCE values strongly depended on the structure of the donor. In addition, the shortening of the peripheral alkyl chain length in the dithiophene linkers improved the PCE due to its better hole-mobility in the film. A highest PCE was achieved an overall power conversion efficiency of 3.7% with a short-current density of 8.4mA/cm^2, open-circuit voltage of 1.09V, and fill factor of 41% under one sun condition.

In **chapter 4**, non-fullerene BHJ solar cells based on two disk-shaped molecules were fabricated and investigated their properties. Perylene diimide (PDI) derivatives were used as electron donor component in solution-processed BHJ solar cells. The introduction of the thiophene in the bay position of PDI can be tuned their optical and redox properties as well as molecular ordering in the solid state. The HOMO and LUMO energy level of the PDI derivatives are suitable for the energy transfer to the disk-shaped donor. The BHJ solar cells were fabricated by solution process using mixed solution of disk-shaped donor and PDI derivatives as acceptor. The performances of BHJ solar cells were influenced by the molecular structure of PDI derivatives. Optimizations of the nano-structure in blended film by adding 1,8-diiodeoctane have greatly improved the PCE of BHJ solar cells. The highest PCE of two disk-shaped donor and acceptor based BHJ solar cell was achieved 0.7% of PCE with V_{oc} of over 1V under one sun condition.

Chapter 5 described development of organic dyes containing fluorene-benzothiadiazole unit for DSSCs sensitizers. The introduction of different electron donating and electron accepting unit into the fluorene-benzothiadiazole bridge was achieved the tuning optical and electrochemical properties. DFT calculations of synthesized organic dyes showed completely separated the HOMO and LUMO electron density distributions. The DSSCs using synthesized dyes exhibited 4.0% of PCE with high V_{oc} and FF compared with those of rhuthenium sensitizer (N719).