Development of Organic Semiconductors for Molecular Thin-Film Devices

Organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs) based on π-conjugated oligomers have been extensively studied as molecular thin-film devices. Organic semiconductors with low injection barriers and high mobilities are required for highly efficient OLEDs and OFETs. Radical cations or anions of an organic semiconductor have to be generated easily at the interface with an electrode (or a dielectric), and holes or electrons must move fast in the semiconducting layer. Compared with organic p-type semiconductors, organic n-type semiconductors for practical use are few and rather difficult to develop. Recently, we found that perfluorinated aromatic compounds are efficient n-type semiconductors for OLEDs and OFETs.

1. Synthesis, Structure, and Transport Property of Perfluorinated Oligofluorenes

We report the synthesis, structure, and properties of perfluorinated oligo(9,9-dimethylfluorene)s (PF-nFs). The cyclic voltammetry of PF-3F and PF-4F showed two reversible couples in THF. The reduction potentials are much more positive than those of conventional electron transport materials. PF-3F and PF-4F exhibited high glass transition temperatures ($T_g = 133$ and 163 °C, respectively), indicating that they are highly stable amorphous solids. The X-ray crystallography of PF-2F showed that a single crystal contained a 1:1 mixture of cis and trans conformers. The electron mobilities were measured by the time-of-flight technique. PF-3F and PF-4F displayed weak field dependence and high electron mobilities as amorphous n-type semiconductors ($2.1 \times 10^{-4}$ and $2.0 \times 10^{-4}$ cm² V⁻¹ s⁻¹ at $6 \times 10^5$ V cm⁻¹, respectively).

Figure 1. Structures of perfluorinated oligo(9,9-dimethylfluorene)s.

Figure 2. X-ray structures of trans-PF-2F (top) and cis-PF-2F (bottom).
2. Optical Properties of Pentacene and Perfluoropentacene Thin Films

The optical properties of pentacene (PEN) and perfluoropentacene (PFP) thin films on various SiO$_2$ substrates were studied using variable angle spectroscopic ellipsometry. Structural characterization was performed using x-ray reflectivity and atomic force microscopy. A uniaxial model with the optic axis normal to the sample surface was used to analyze the ellipsometry data. A strong optical anisotropy was observed, and enabled the direction of the transition dipole of the absorption bands to be determined. Furthermore, comparison of the optical constants of PEN and PFP thin films with the absorption spectra of the monomers in solution shows significant changes due to the crystalline environment. Relative to the monomer spectrum, the highest occupied molecular orbital to lowest unoccupied molecular orbital transition observed in PEN (PFP) thin film is reduced by 210 meV (280 meV). A second absorption band in the PFP thin film shows a slight blueshift (40 meV) compared to the spectrum of the monomer with its transition dipole perpendicular to that of the first absorption band.

Figure 3. Structures of pentacene (PEN) and perfluoropentacene (PFP).

3. Adsorption-Induced Intramolecular Dipole: Correlating Molecular Conformation and Interface Electronic Structure

The interfaces formed between pentacene (PEN) and perfluoropentacene (PFP) molecules and Cu(111) were studied using photoelectron spectroscopy, X-ray standing wave (XSW), and scanning tunneling microscopy measurements, in conjunction with theoretical modeling. The average carbon bonding distances for PEN and PFP differ strongly, that is, 2.34 Å for PEN versus 2.98 Å for PFP. An adsorption-induced nonplanar conformation of PFP is suggested by XSW (F atoms 0.1 Å above the carbon plane), which causes an intramolecular dipole of ~0.5 D. These observations explain why the hole injection barriers at both molecule/metal interfaces are comparable (1.10 eV for PEN and 1.35 eV for PFP) whereas the molecular ionization energies differ significantly (5.00 eV for PEN and 5.85 eV for PFP). Our results show that the hypothesis of charge injection barrier tuning at organic/metal interfaces by adjusting the ionization energy of molecules is not always readily applicable.

4. Structural Order in Perfluoropentacene Thin Films and Heterostructures with Pentacene

Synchrotron X-ray diffraction reciprocal space mapping was performed on perfluoropentacene (PFP) thin films on SiO$_2$ in order to determine the crystal structure of a novel, substrate-induced thin film phase to be monoclinic with unit cell parameters of $a = 15.76 \pm 0.02$ Å, $b = 4.51 \pm 0.02$ Å, $c = 11.48 \pm 0.02$ Å, and $\beta = 90.4 \pm 0.1^\circ$. Moreover, layered and co-deposited heterostructures of PFP and pentacene (PEN) were investigated by specular and grazing-incidence X-ray diffraction, atomic force microscopy, and Fourier-transform infrared spectroscopy. For a ca. three-monolayers-thick PFP film grown on a PEN underlayer, slightly increased lattice spacing was found. In contrast, co-deposited PEN/PFP films form a new mixed-crystal structure with no detectable degree of phase separation. These results highlight the structural complexity of these technically relevant molecular heterojunctions for use in organic electronics.

References