VIII-F Development of Organic n-Type Semiconductors for Molecular Thin-Film Devices

Organic light-emitting diodes (OLEDs) and field-effect transistors (FETs) based on π-conjugated oligomers have been extensively studied as molecular thin-film devices. Organic n-type semiconductors with low electron-injection barriers and high electron mobilities are required for highly efficient OLEDs and n-type FETs. Radical anions of an n-type semiconductor have to be generated easily at the interface with a metal electrode (electron injection), and electrons must move fast in the layer (electron mobility). 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 oligomers are efficient electron-transport materials for OLEDs.

VIII-F-1 Tetradecafluorosexithiophene: The First Perfluorinated Oligothiophene

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[*J. Am. Chem. Soc.* **123**, 4643 (2001)]

Perfluoro-a-sexithiophene (**PF-6T**) was synthesized by the fluorination of thienyllithiums with *N*-fluoro-*N*-(phenylsulfonyl)benzenesulfonamide and the Stille and Ullmann couplings. **PF-6T** is an orange crystalline solid and slightly soluble in $CHCl_3$ and aromatic solvents such as toluene. Its structure was determined by EI-MS, elemental analysis, and X-ray crystallography. **PF-6T** exhibits bluish-green photoluminescence in solution and an orange emission in the solid state. A sharp melting endotherm was observed at 286 °C by DSC. The differential pulse voltammogram (DPV) in 1,2-dichlorobenzene showed that the redox potentials of **PF-6T** shifted positively relative to α-sexithiophene (**6T**). Single crystals of **PF-6T** were successfully grown by slow sublimation at 270 °C under a flow of 1 atm of argon. The structure of **PF-6T** is *all-trans* and planar as observed for **6T**. **PF-6T** adopts a π-stack structure with face-to-face molecules. This is quite different from the herringbone structure of **6T**, in which π-π interactions between neighboring molecules are minimized to reduce the repulsion between π-orbitals. High electron mobility is expected along the π-π stacking direction. Fabrication of n-type FETs with this new material is currently underway.

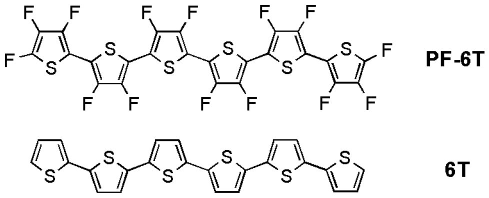

Figure 1. Perfluoro-α-sexithiophene and α-sexithiophene.

VIII-F-2 Highly Efficient Phosphorescence from Organic Light-Emitting Devices with an Exciton-Block Layer

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[*Appl. Phys. Lett.* **79**, 156 (2001)]

One of the keys to highly efficient phosphorescent emission in organic light-emitting devices is to confine triplet excitons generated within the emitting layer. We employ “starburst” perfluorinated phenylenes ($C_{60}F_{42}$) as a both hole- and exciton-block layer, and a hole-transport material 4,4’,4”-tri(*N*-carbazolyl) triphenylamine as a host for the phosphorescent dopant dye in the emitting layer. A maximum external quantum efficiency reaches to 19.2%, and keeps over 15% even at high current densities of 10–20 mA/cm^2, providing several times the brightness of fluorescent tubes for lighting. The onset voltage of the electroluminescence is as low as 2.4 V and the peak power efficiency is 70–72 lm/W, promising for low-power display devices.