Development of Organic Semiconductors for Molecular Thin-Film Devices

Research Center for Molecular Scale Nanoscience
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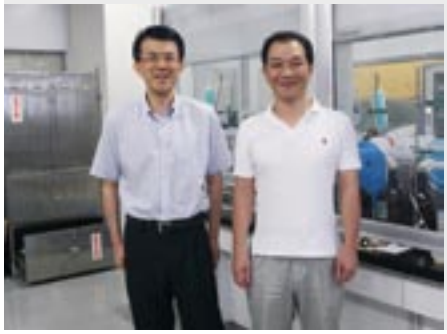

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Organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs) based on π-conjugated oligomers have been extensively studied as molecular thin-film devices. Organic semiconductors with low injection barriers and high mobilities 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.

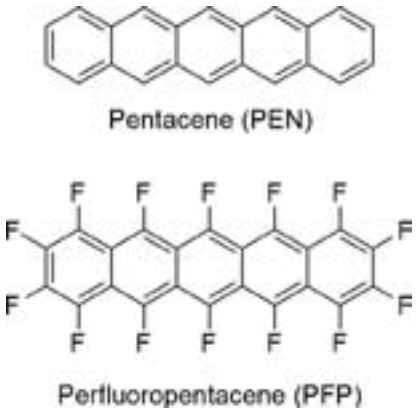

Figure 1. Molecular structures of pentacene (PEN) and perfluoropentacene (PFP).

1. Effect of Fluorination on the Molecular Packing of Perfluoropentacene and Pentacene Ultrathin Films on Ag (111)[1)]

The growth of perfluoropentacene (PFP) and pentacene (PEN) ultrathin films on Ag(111) has been investigated using low-temperature scanning tunneling microscopy. To understand the influence that perfluorination of the parent molecule has on its resultant packing structure, the results are compared against each other in the framework of morphological differences. Perfluorination leads to a different packing structure in the first monolayer. We observed only one closely packed arrangement with periodic dislocation lines for PFP molecules, while for PEN molecules, there are two coexisting arrangements in the first monolayer. Monolayers of each molecule are commensurate with the underlying substrate with long axes of both molecules aligned in the [110] direction along the silver surface. The disparity in arrangements is attributed to the difference in peripheral atoms of the two molecules. Additional photoemission spectroscopy studies reveal that PFP physisorbs on Ag (111).

2. Synthesis, Structure, and Property of Fluorinated Rubrenes

Rubrene is the tetraphenyl-substituted tetracene and has a nonplanar structure unlike pentacene. The single-crystal field-effect transistors (FETs) with rubrene have shown the highest hole mobilities up to 40 $cm^2V^{-1}s^{-1}$. We synthesized partially and fully fluorinated rubrenes for single-crystal FETs with high electron mobilities. Tetradecafluororubrene (**F14-RB**) and perfluororubrene (**PF-RB**) are red crystalline solids similar to rubrene. The electrochemical measurements showed that the first reduction potentials shifted positively in the order of rubrene, **F14-RB**, and **PF-RB** (–2.06, –1.48, and –0.92 V *vs* Fc/Fc^+, respectively). The single-crystal X-ray analyses indicated that **F14-RB** adopted the 2-D π-stacking interactions with face-to-face distances as short as 3.54 Å. In the case of **PF-RB**, no face-to-face interactions were found probably because the fluorine atoms resulted in larger molecular distances compared to the hydrogen atoms. The thin-film tran-

sistors (TFTs) with **F14-RB** and **PF-RB** have been fabricated, and they showed the n-type behaviors with the mobilities of 10^{-6} to 10^{-5} $cm^2V^{-1}s^{-1}$. These values are similar to that of the rubrene TFT. The fabrications of the single-crystal transistors are underway.

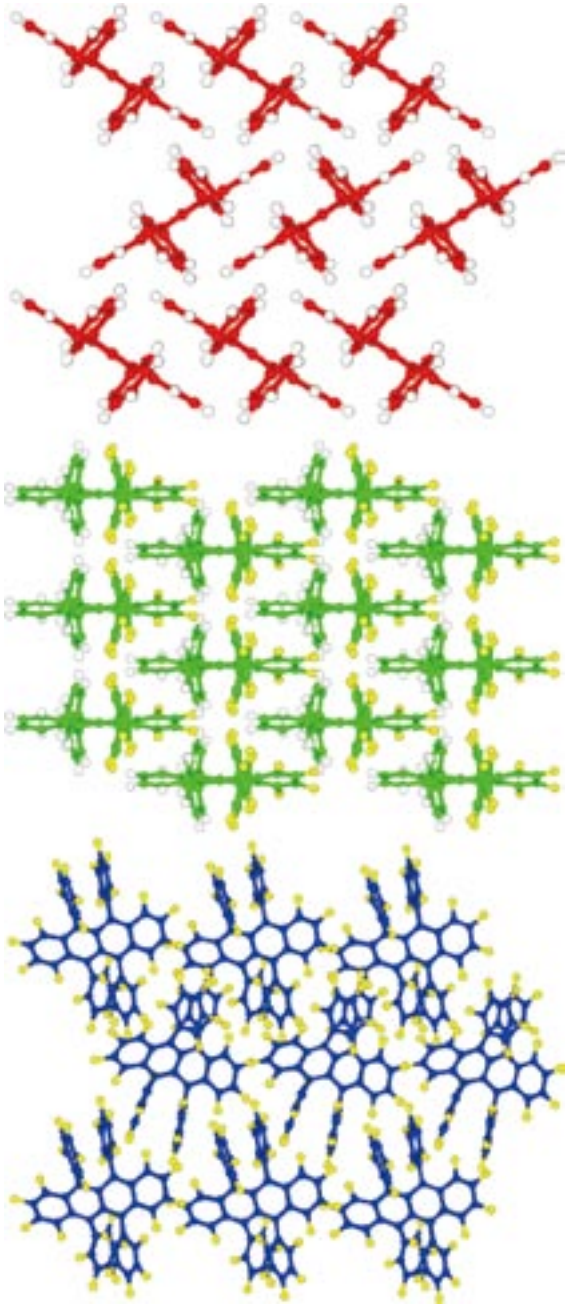

Figure 2. Crystal structures of rubrene (top), **F14-RB** (middle), and **PF-RB** (bottom).

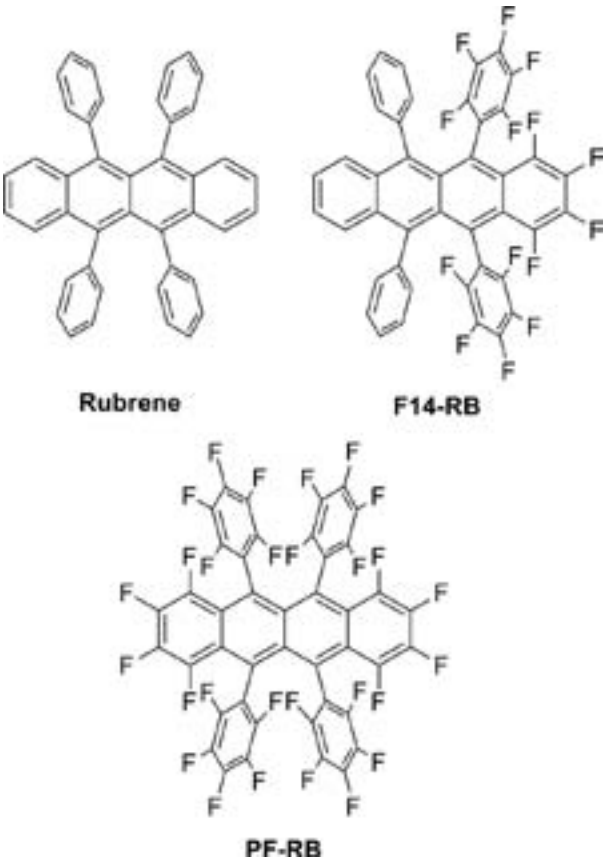

Figure 3. Molecular Structures of rubrene (top), **F14-RB** (middle), and **PF-RB** (bottom).

Reference

1) S. L. Wong, H. Huang, Y. L. Huang, Y. Z. Wang, X. Y. Gao, T. Suzuki, W. Chen and A. T. S. Wee, *J. Phys. Chem. C* **114**, 9356–9361 (2010).