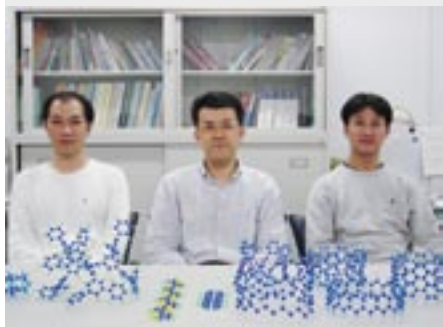


Development of Organic Semiconductors for Molecular Thin-Film Devices

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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.

1. Perfluoropentacene and Perfluorotetracene: Syntheses, Crystal Structures, and FET Characteristics¹⁾

We have synthesized perfluoropentacene and perfluorotetracene as potential n-type semiconductors for organic field-effect transistors (OFETs). Perfluoropentacene and perfluorotetracene are dark blue and reddish-orange crystalline solids, respectively. The HOMO-LUMO gaps of perfluorinated acenes are smaller than those of the corresponding acenes. The reduction potential of perfluoropentacene is almost the same as that of C₆₀, which is known as an excellent n-type semiconductor for FETs. Perfluoropentacene and perfluorotetracene are planar molecules that adopt herringbone structures with the angles of 91.2° and 91.1°, respectively. The short C–C contacts less than the sum of van der Waals radii were observed for both perfluorinated acenes. The interplanar distances are shorter than the layer separation of graphite, which may lead to high electron mobility along the stacking directions.

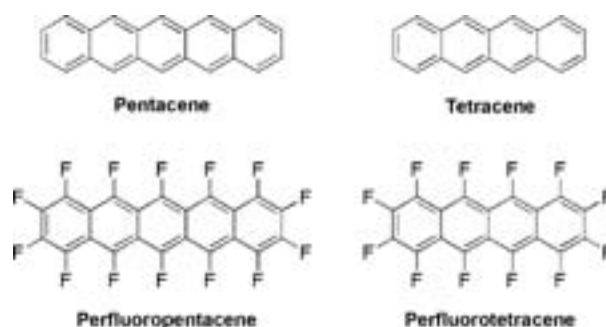
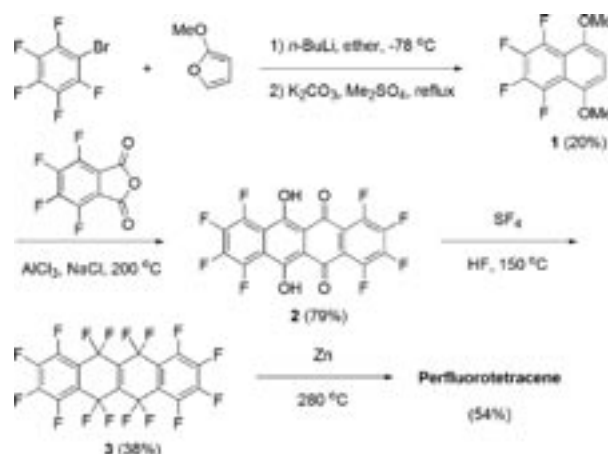


Figure 1. Structures of pentacene, tetracene, and their perfluorinated derivatives.



Scheme 1. Synthesis of perfluorotetracene.

2. Perfluorination of Tetracene: Effects on the Optical Gap and Electron-Acceptor Properties. An Electrochemical, Theoretical DFT, and Raman Spectroscopic Study

We report the synthesis and characterization of perfluorinated tetracene; a material with potential applications in organic electronics. The electrochemical behavior of the compound is analyzed by differential pulse voltammetry, and compared with that of tetracene. The structure of perfluorotetracene is planar as observed for pentacene. We also report a comparative Raman spectroscopic study of tetracene and perfluorotetracene in relation to their π -conjugational properties. Density functional theory calculations have been also performed, at the B3LYP/6-31G** level, to assess information regarding the topologies and energies of the frontier molecular orbitals around the gap, and about the vibrational normal modes associated with the Raman features selectively enhanced by the π -conjugation.

3. Optical Properties of Pentacene and Perfluoropentacene Thin Films

The optical properties of pentacene (PEN) and perfluoropentacene (PFP) thin films on various SiO₂ 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. Strong 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 HOMO-LUMO transition observed in PEN (PFP) thin film is reduced by 210 meV (280 meV). Surprisingly, 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.

4. The Effect of Fluorination on Pentacene/Gold Interface Energetics and Charge Reorganization Energy²⁾

The energy level alignment at interfaces between conjugated organic semiconductors and metals is recognized as a

key factor determining the performance of organic-based (opto-) electronic devices. Experimentally, the hole injection barriers (HIBs) at organic/metal interfaces can be directly determined by ultraviolet photoelectron spectroscopy (UPS). In addition, angle-resolved UPS (AR-UPS) allows to assess important aspects of surface molecular orientation. In the present work, we used this method to investigate interfaces between two prototypical organic semiconductors pentacene (PEN) and perfluoropentacene (PFP) and Au. PEN can successfully be used as active material in organic field-effect transistors (OFETs) with high hole mobility of up to 5.5 cm²/Vs. The fabrication of integrated circuits requires also high electron mobility OFETs, which turns out to be difficult to achieve with pentacene, with reported electron mobilities up to 0.04 cm²/Vs. One approach to improve *n*-type performance of OFETs was to use perfluoropentacene, resulting in high electron mobilities of more than 0.2 cm²/Vs. Commonly, Au is used as source and drain contact metal in OFETs. Therefore, the interface energetics between organic semiconductors and Au are of interest, since charges have to be transported across these interfaces and minimized contact resistance is sought for.

PEN and PFP monolayers on Au(111) exhibited very similar HIBs (0.60 eV vs. 0.65 eV), despite the significantly higher IE of the perfluorinated PEN analog. ϕ of Au(111) decreased upon PEN adsorption by 0.95 eV, while the decrease was only 0.5 eV for PFP. In the simple model of the “push-back” effect of surface metal electrons due to adsorption of molecules, our findings imply a larger bonding distance of PFP on Au compared to PEN. For PFP, four different layers away from Au were identified by significantly different HOMO binding energies, spreading by 0.8 eV. This spread was only 0.4 eV for PEN, and two layers could be resolved. PEN and PFP monolayers on Au(111) exhibited large charge reorganization energies, pointing towards strong charge localization at the interface.

References

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