IX-B 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.

IX-B-1 Synthesis and Characterization of Three Novel Perfluoro-Oligothiophenes Ranging in Length from the Trimer to the Pentamer

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[*J. Phys. Chem. B* **109**, 20737–20745 (2005)]

In this article, we report on the synthesis and full characterization of three perfluorinated oligothiophenes, ranging in length from the trimer to the pentamer (**PF-*n*T**, with *n* = 3, 4, or 5). The differential pulse voltammetry (DPV) analysis of the compounds showed that they can be both oxidized and reduced (*i.e.*, they display a dual or amphoteric electrochemical behavior), with the reduction peaks positively shifted relative to those of the corresponding unsubstituted oligothiophenes. The electrochemically determined energy gaps are in agreement with those measured from the UV-vis-NIR absorption spectra in solution. The conjugational properties have been investigated by means of FT-Raman spectroscopy, both as pure solids and as dilute solutes in CH_2Cl_2, revealing that: (i) π-conjugation does not still reach saturation with chain length for the longest oligomer, and (ii) conformational distortions from a nearly coplanar arrangement of the successive thiophene units upon solution are not too large. DFT and TDDFT quantum chemical calculations have been performed, at the B3LYP/6-31G** level, to assess information about the optimized molecular structure, equilibrium atomic charges distribution, energies and topologies of the frontier molecular orbitals (MO) around the gap, vibrational normal modes associated with the most outstanding Raman scatterings, and vertical one-electron excitations that give rise to the main optical absorptions.

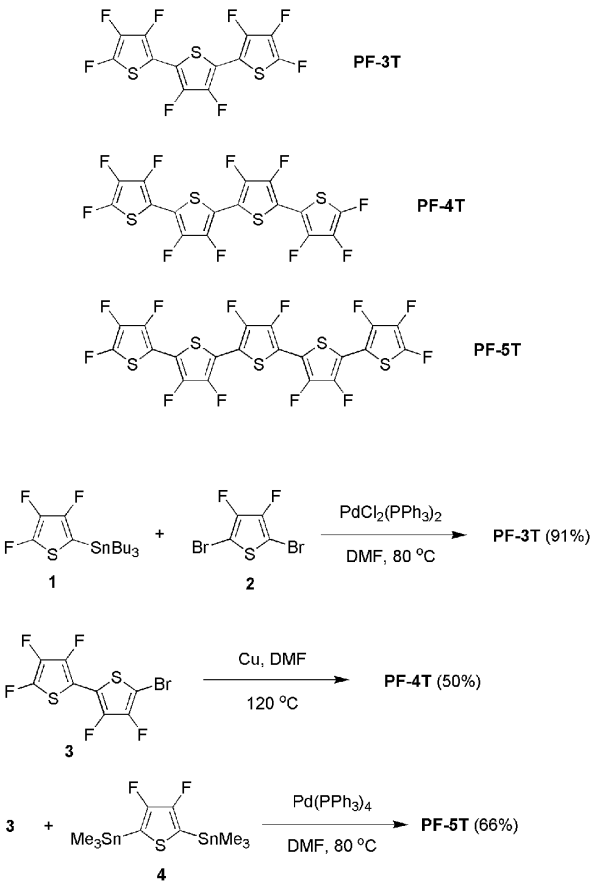

Figure 1. Structures and syntheses of perfluorooligothiophenes.