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. We found that perfluorinated aromatic compounds are efficient n-type semiconductors for OLEDs and OFETs.

1. Optical Properties of Fully and Partially Fluorinated Rubrene in Films and Solution[1)]

We present the optical properties of fully ($C_{42}F_{28}$, **PF-RUB**) and half-fluorinated ($C_{42}F_{14}H_{14}$, **F14–RUB**) rubrene, both in thin films and as monomers in solution and compare them to hydrogenated rubrene ($C_{42}H_{28}$, **RUB**). All three compounds show similar optical absorption bands and photoluminescence line shapes. The results are interpreted with density functional calculations of the orbital energies and time-dependent density functional theory for the HOMO–LUMO transition. Red shifts induced by the surrounding solvent or organic thin films remain much smaller than for polyacenes, in keeping with previous observations for rubrene and existing models for the solvatochromic shifts.

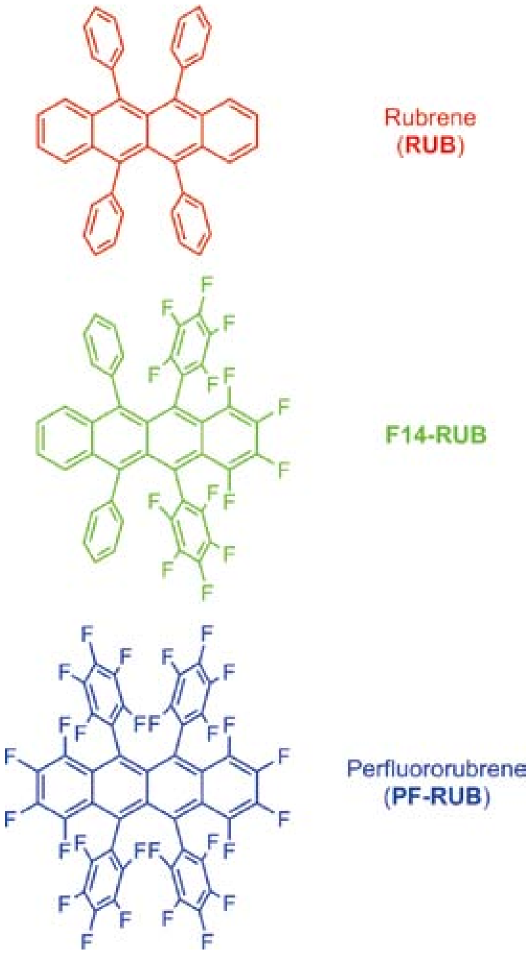

Figure 1. Structures of **RUB**, **F14-RUB**, and **PF-RUB**.

2. Selective Synthesis of [6]-, [8]-, and [10] Cycloparaphenylenes2)

The selective synthesis of [6]-, [8]-, and [10]cycloparaphenylenes (CPPs) was achieved by a new synthetic route involving Ni(0)-mediated coupling of bis(*para*-haloaryl)dinuclear arylplatinum complexes and the reductive elimination of the complexes. Importantly, the highly strained [6]CPP was prepared in good overall yield.

3. Experimental Reorganization Energies of Pentacene and Perfluoropentacene: Effects of Perfluorination3)

Electron–phonon coupling of the highest occupied molecular orbital (HOMO) state is studied by high-resolution ultraviolet photoelectron spectroscopy (UPS) for pentacene (PEN) and perfluoropentacene (PFP) monolayers on graphite. The reorganization energy and related coupling constants associated with the interaction between holes and molecular vibrations are obtained experimentally using a single mode analysis (SMA) of the observed vibronic-satellite intensities of the monolayers. The results are compared with those estimated by multimode analyses of UPS spectra and those derived by means of theoretical approaches, indicating that the purely experimental method with SMA is useful for studying the reorganization energy and the hopping mobility of organic systems. Furthermore, we found that the reorganization energy of PFP is significantly greater than that of PEN, which is ascribed to the extended HOMO distribution of PFP by perfluorination of PEN. The comparison with the results derived from gas-phase UPS measurements is also discussed.

References

1) F. Anger, R. Scholz, E. Adamski, K. Broch, A. Gerlach, Y. Sakamoto, T. Suzuki and F. Schreiber, *Appl. Phys. Lett.* **102**, 013308 (2013).

2) E. Kayahara, T. Iwamoto, T. Suzuki and S. Yamago, *Chem. Lett.* **42**, 621–623 (2013).

3) S. Kera, S. Hosoumi, K. Sato, H. Fukagawa, S. Nagamatsu, Y. Sakamoto, T. Suzuki, H. Huang, W. Chen, A. T. S. Wee, V. Coropceanu and N. Ueno, *J. Phys. Chem. C* **117**, 22428–22437 (2013).