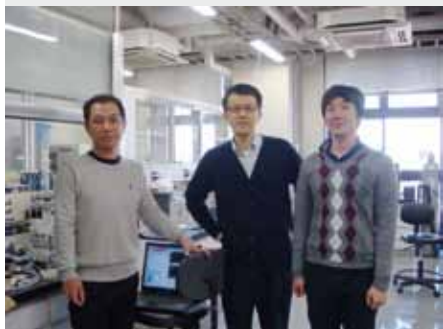


Development of Organic Semiconductors for Molecular Thin-Film Devices

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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. Selective and Random Syntheses of $[n]$ Cycloparaphenylenes ($n = 8-13$) and Size Dependence of Their Electronic Properties¹⁾

$[n]$ Cycloparaphenylenes ($n = 8-13$, CPPs) were synthesized, and their physical properties were systematically investigated. [8] and [12]CPPs were selectively prepared from the reaction of 4,4'-bis(trimethylstannyl)biphenyl and 4,4''-bis(trimethylstannyl)terphenyl, respectively, with Pt(cod)Cl₂ (cod = 1,5-cyclooctadiene) through square-shaped tetranuclear platinum intermediates. A mixture of [8]–[13]CPPs was prepared in good combined yields by mixing biphenyl and terphenyl precursors with platinum sources. Products were easily separated and purified by using gel permeation chromatography. In ¹H NMR spectra, the proton of the CPPs shifts to a lower field as n increased due to an anisotropic effect from the nearby PP moieties. Although the UV-vis spectra were rather insensitive to the size of the CPPs, the fluorescence spectra changed significantly in relation to their size. A larger Stokes shift was observed for the smaller CPPs. Redox properties of the CPPs were measured for the first time by using cyclic



Figure 1. [8], [10], and [12]CPPs.

voltammetry, and the smaller CPPs had lower oxidation potentials. The results are consistent with the HOMO energies of CPPs, of which the smaller CPPs had higher energies.

Reference

- 1) T. Iwamoto, Y. Watanabe, Y. Sakamoto, T. Suzuki and S. Yamago, *J. Am. Chem. Soc.* **133**, 8354–8361 (2011).

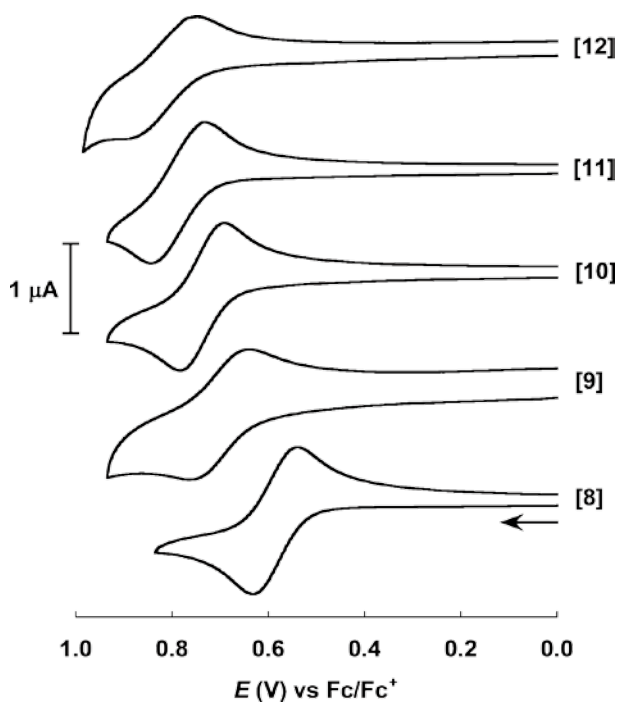


Figure 2. Cyclic voltammograms of [8] to [12]CPPs at 100 mV/s in 1,1,2,2-tetrachloroethane containing 0.1 M $(n\text{-Bu})_4\text{NPF}_6$.