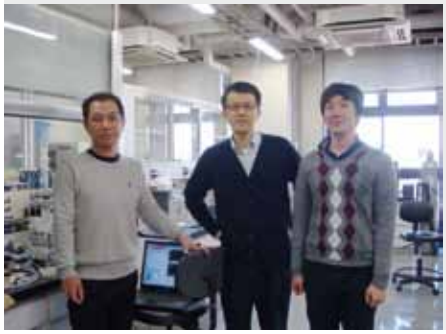
Development of Organic Semiconductors for Molecular Thin-Film Devices

Research Center for Molecular Scale Nanoscience
Division of Molecular Nanoscience



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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 Synthesis and Crystal Structure of [10]Cycloparaphenylene[1)]

[10]Cycloparaphenylene ([10]CPP) was selectively synthesized in four steps in 13% overall yield from commercially available 4,4'-diiodobiphenyl by using mono-I–Sn exchange, Sn–Pt transmetalation, I–Pd exchange, and subsequent oxidative coupling reactions. The structure of [10]CPP was determined by using single-crystal X-ray analysis. Suitable crystals were obtained by slow vapor diffusion of *n*-hexane into a solution of [10]CPP in CH_2Cl_2 at room temperature. In the solid state, [10]CPP is slightly distorted to an ellipsoidal structure with major and minor axes of 13.9 and 13.5 Å, respectively. The cavity of [10]CPP is occupied by a hexane molecule, which was highly disordered. Although the D_{5h} structure with a dihedral angle between two paraphenylene units of 32°–33° was calculated to be the most stable conformer, the structure is closer to a D_{2h} conformer with alternating triphenylene and biphenylene units. The dihedral angles between two paraphenylene units were approximately 20° and 45°, respectively. The average C_{ipso}–C_{ipso}, C_{ipso}–C_{ortho}, and C_{ortho}–C_{ortho} bond lengths are 1.484(1), 1.399(2), and 1.385(9) Å, respectively. [10]CPP molecules pack in a herringbone manner, and there are no significant π–π interactions among [10]CPP molecules. A tilted tubular channel structure was observed along the *b* axis. The crystal packing is similar to [9]- and [12]CPPs but different from [6]CPP. The size of the CPP may be important for determining the packing arrangement.

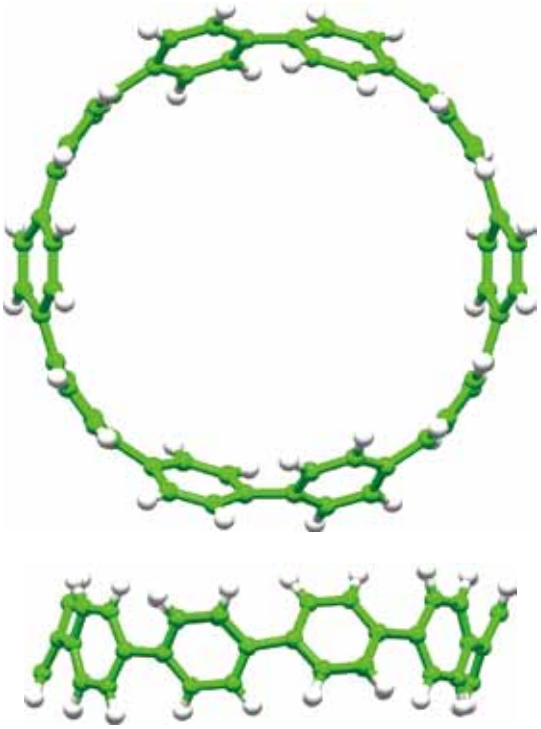

Figure 1. X-ray structure of [10]CPP.

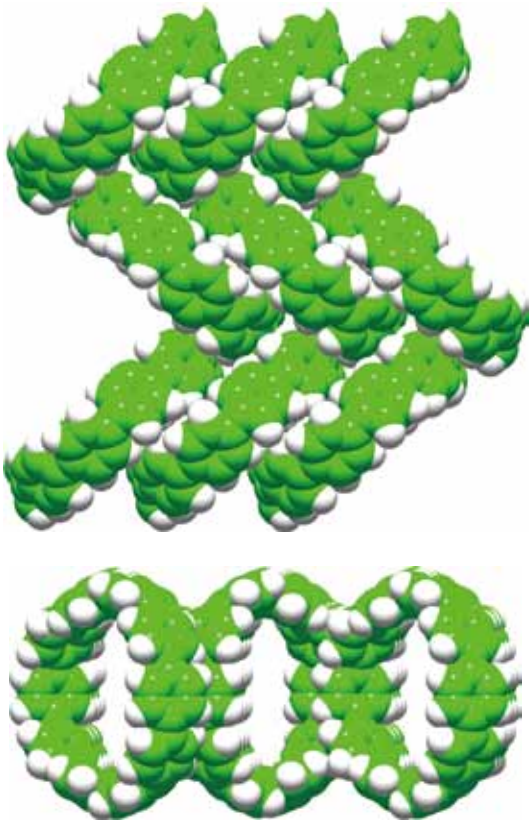

Figure 2. Packing structure of [10]CPP.

Reference

1) E. Kayahara, Y. Sakamoto, T. Suzuki and S. Yamago, *Org. Lett.* **14**, 3284–3287 (2012).