VIII-H Development of Organic n-Type Semiconductors for Molecular Thin-Film Devices

Organic light-emitting diodes (OLEDs) and field-effect transistors (FETs) based on π-conjugated oligomers have been extensively studied as molecular thin-film devices. Organic n-type semiconductors (electron-transport materials) with low electron-injection barriers and high electron mobilities are required for highly efficient OLEDs and n-type FETs. Radical anions of an n-type semiconductor have to be generated easily at the interface with a metal electrode (electron injection), and electrons must move fast in the layer (electron mobility). Compared with organic p-type semiconductors (hole-transport materials), organic n-type semiconductors for practical use are few and rather difficult to develop. Recently, we found that perfluorinated phenylene dendrimers and oligomers are efficient electron-transport materials for OLEDs.

VIII-H-1 Synthesis, Characterization, and Electron-Transport Property of Perfluorinated Phenylene Dendrimers

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Two perfluorinated phenylene dendrimers, $C_{60}F_{42}$ (MW = 1518) and $C_{132}F_{90}$ (MW = 3295), have been synthesized via a sequence of brominations and cross-couplings using organocopper chemistry. Two other $C_{60}F_{42}$ isomers containing *p*-terphenyl and *p*-quaterphenyl groups were also prepared to see structure-property relationships. Three $C_{60}F_{42}$s showed glass transitions at 125–135 °C. Dendrimer $C_{132}F_{90}$ melts at 426 °C and did not show a glass transition. Organic light-emitting diodes have been fabricated on indium-tin-oxide coated glass substrates by high-vacuum thermal evaporation of TPTE (a tetramer of triphenylamine) as the hole-transport layer, tris(8-quinolinolato)-aluminum as the emission layer, perfluorinated phenylenes as the electron-transport layer, LiF, and Aluminum. The maximum luminance of the device is 2860 cd/m^2 at 24.4 V. The electrochemical measurements indicated that the performance of the devices is improved with increasing electron affinities of the compounds. This is probably because the electron-injection barriers between the metal layers and the electron-transport layers are reduced by increased electron affinities.

VIII-H-2 Perfluorinated Oligo(*p*-Phenylene)s: Efficient n-Type Semiconductors for Organic Light-Emitting Diodes

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Perfluorinated oligo(*p*-phenylene)s including perfluoro-*p*-quinquephenyl to -octiphenyl (**PF–5P** to **–8P**) have been synthesized by the organocopper cross-coupling method. Two **PF–6P** derivatives containing trifluoromethyl and perfluoro-2-naphtyl groups were also prepared. All compounds are colorless solids and insoluble in common organic solvents. The differential scanning calorimetry measurements indicated that they are highly crystalline solids without glass transitions. Organic light-emitting diodes have been fabricated on indium-tin-oxide coated glass substrates by high-vacuum thermal evaporation of TPTE (a tetramer of triphenylamine) as the hole-transport layer, tris(8-quinolinolato)aluminum as the emission layer, a perfluorinated oligomer as the electron-transport layer, LiF, and aluminum. The electron-transport capabilities of perfluorinated oligo(*p*-phenylene)s are excellent compared with perfluorinated phenylene dendrimers. The maximum luminance of the naphtyl derivative is 19970 cd/m^2 at 10.0 V. The luminance-voltage and current-voltage characteristics of **PF–7P** and **–8P** are almost identical to those of **PF–6P**. We speculate that the electron mobility in the layer rather than the electron injection at the interface is responsible for determining the current density of **PF–6P** to **–8P**.

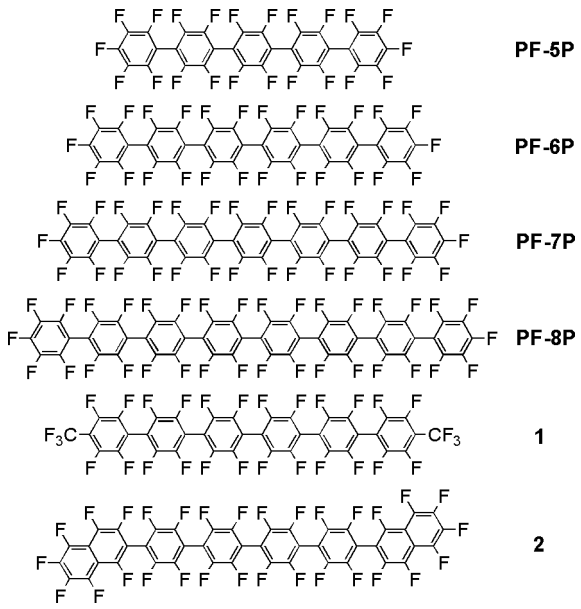

Figure 1. Perfluorinated phenylene oligomers.