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

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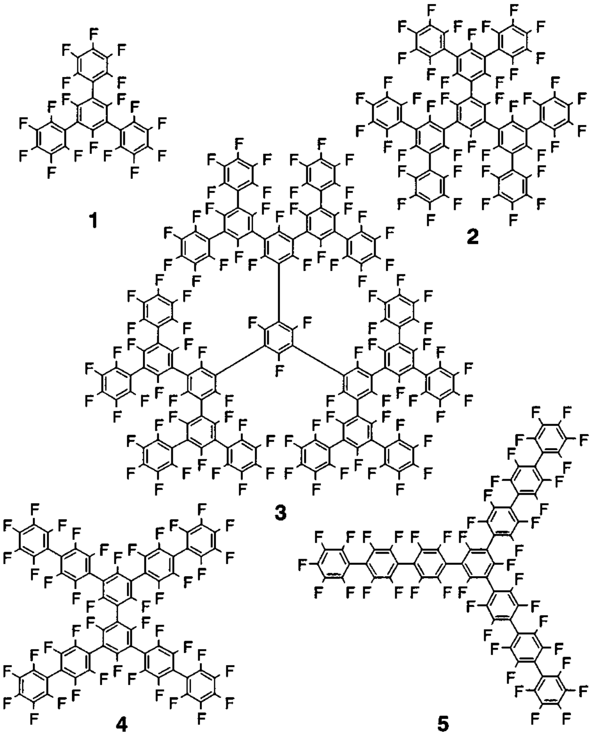
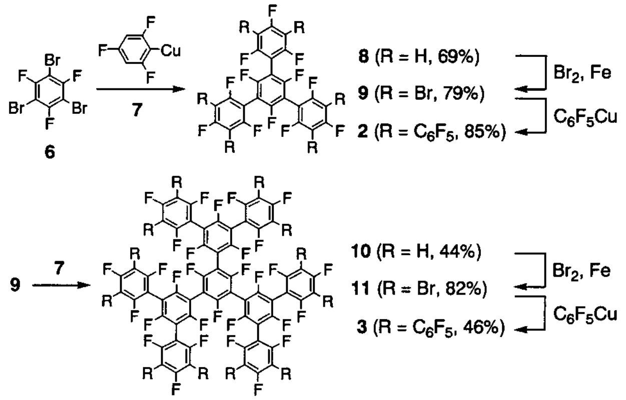
Recently, π-conjugated oligomers such as oligophenylenes and oligothiophenes have received considerable attention as electronic materials.[1] Thin films of these low molecular weight compounds can be obtained by sublimation under high vacuum and used for electronic devices such as organic field-effect transistors and organic light-emitting diodes (OLEDs).[2] For OLEDs, each organic layer (hole-transport, emission, and electron-transport layers) has to be amorphous, and crystallization during the device operation results in shorter lifetime. Unlike linear oligomers, dendrimers have a branched structure and are expected to favor an amorphous morphology.[3] We have been interested in developing new electron-transport materials[4] for OLEDs and designed perfluorinated phenylene dendrimers[5] because of (1) their low-lying LUMOs and HOMOs, which are important for electron injection and hole blocking, respectively, (2) relatively low sublimation temperature, which makes it possible to deposit high molecular weight compounds with high glass transition temperatures, and (3) thermal and chemical stability due to strong C−F bonds.[6] However, there have been few perfluorinated phenylene compounds,[7] and their general synthetic methods have not been developed. We report herein the repetitive synthesis of perfluorinated phenylene dendrimers and their thermal properties. OLEDs have been fabricated to investigate electron-transport properties of these new materials.

Chart 1



Scheme 1



The cross-coupling reaction between two different fluorinated phenyl groups is the most important step for preparing perfluorinated dendrimers. We found that organocopper chemistry gave the most satisfactory results: pentafluorophenylcopper (C_6F_5Cu)[8] was allowed to react with 1,3,5-tribromo-2,4,6-trifluorobenzene (**6**) to give **1**[9] in 81%.[10] Then, this procedure was applied to perfluorinated phenylene dendrimer **2** ($C_{60}F_{42}$; MW = 1518) as shown in Scheme 1. Trifluorophenylcopper **7**, prepared from the corresponding Grignard reagent ($C_6H_2F_3MgBr$) and copper(I) bromide without isolation, was allowed to react with **6** in a THF/dioxane/toluene mixture at 80 °C for 24 h to afford compound **8** in 69%. Bromination of **8** gave hexabromide **9** in 79%. Again, the coupling reaction of **9** and C_6F_5Cu yielded **2** in 85%.[11,12] Similarly, dendrimer **3** ($C_{132}F_{90}$; MW = 3295), the higher generation of dendrimer **2**, was prepared from compound **9** by repeating cross-coupling and bromination as depicted in Scheme 1. We also synthesized two $C_{60}F_{42}$ isomers **4** and **5** to see structure−property relationships. Compounds **2**−**5** were purified

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(4) (a) Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *Science* **1995,** *267,* 1969−1972. (b) Tamao, K.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996,** *118,* 11974−11975. (c) Noda, T.; Shirota, Y. *J. Am. Chem. Soc.* **1998,** *120*, 9714−9715 and references therein.

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(7) For example, perfluoro-3,3′,5,5′-tetrakis(phenyl)-1,1′-biphenyl: Kobrina, L. S.; Salenko, V. L.; Yakobson, G. G. *J. Fluorine Chem.* **1976**, *8*, 193−207.

(8) Cairncross, A.; Sheppard, W. A.; Wonchoba, E. *Organic Syntheses*; Wiley & Sons: New York, 1988; Collect. Vol. VI, pp 875−882.

(9) Pozdnyakovich, Yu. V.; Shteingarts, V. D. *Zh. Org. Khim.* **1977**, *13,* 1911−1917.

(10) Attempts to use the Stille reaction for the synthesis of perfluorinated phenylenes have been unsuccessful: the reaction of $C_6F_5SnMe_3$ and **6** in the presence of Pd(0) or Pd(II) catalysts gave **1** in 5%. (a) Farina, V.; Krishnamurthy, V.; Scott, W. J. *The Stille Reaction*; Wiley & Sons: New York, 1998. (b) Deacon, G. B.; Gatehouse B. M.; Nelson-Reed, K. T. *J. Organomet. Chem.* **1989,** *359,* 267−283.

(11) See Supporting Information for the experimental details.

(12) The reaction of perfluoro-3,5-bis(phenyl)phenylcopper and **6** gave a complex mixture.

10.1021/ja994083z CCC: $19.00

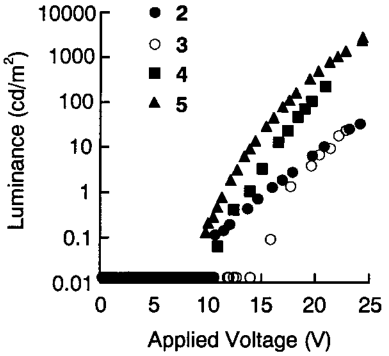

Figure 1. Luminance−voltage characteristics for the OLEDs, ITO/TPTE (60 nm)/Alq$_3$(40 nm)/**2**−**5**(20 nm)/LiF(0.5 nm)/Al(160 nm).

by train sublimation[13] and used for characterization. The structures of **2**−**5** were confirmed by ^{19}F NMR, EI-MS, and elemental analyses. All perfluorinated phenylenes are colorless solids and soluble in CHCl$_3$, THF, and aromatic solvents such as toluene.

The differential scanning calorimetry (DSC) measurements indicated that dendrimers **2** and **3** purified by train sublimation are highly crystalline solids (mp = 277 and 426 °C, respectively).[11] In the case of **2**, the melting endotherm shifted from 277 to 243 °C on the second heating, indicating the formation of a different crystalline phase. A glass transition was observed at 125 °C, only when the melt of **2** was rapidly cooled by liquid nitrogen. Compound **4** showed a melting endotherm at 313 °C on the first heating, and a glass transition at 133 °C was observed on the second heating. Although compound **5** is conformationally more rigid compared with **2** and **4**, it favors an amorphous phase: only a glass transition at 135 °C was observed.

OLEDs were made on indium−tin−oxide (ITO) coated glass substrates by high-vacuum thermal evaporation (5×10^{-7} Torr) of TPTE[14] (a tetramer of triphenylamine) as the hole-transport layer (60 nm), tris(8-quinolinolato)aluminum (Alq$_3$) as the emission layer (40 nm), **2**−**5** (20 nm), LiF[15] (0.5 nm) as the electron-injection layer, and Aluminum (160 nm) as the cathode.[11] When a negative voltage was applied to Al, a green emission due to Alq$_3$ was observed for each device. This indicates that perfluorinated phenylenes **2**−**5** work as the electron-transport layer. Figure 1 shows the luminance−voltage characteristics for these OLEDs. The performance of the devices is improved in the order **3** < **2** < **4** < **5**.[16] The maximum luminance of the device with **5** is 2860 cd/m^2 at 24.4 V.

To understand the above results, we performed the electrochemical measurements on compounds **2**−**5**.[11] In THF, all compounds showed irreversible electroreductions by cyclic voltammetry (CV). The reduction peaks shift more positive in the order **3** (−2.66 V), **2** (−2.56 V), **4** (−2.31 V), and **5** (−2.24 V vs Fc/Fc$^+$).[17] This order is consistent with the number of para-conjugated benzene rings in these compounds: **2** and **3** (biphenyl) < **4** (*p*-terphenyl) < **5** (*p*-quaterphenyl). When the LUMO energy level of the electron-transport material becomes lower (in this case, from **3** to **5**), the electron injection from the metal layer to the electron-transport layer should be easier. It has been pointed out that there are no correlations between reduction potentials and electron-transport capabilities: a good electron acceptor is not always a good electron-transport material.[4a] This indicates that chemical interactions between an organic molecule and a metal should be taken into account.[18] In our case, however, a F−Li$^+$ bond would be much weaker than an O−Li$^+$ bond or a N−Li$^+$ bond in the case of O- or N-containing electron-transport materials. Therefore, the reduction potentials correlate well with the electron-injection barriers and the performance of the devices.

In conclusion, we have shown the general synthetic method for perfluorinated phenylene compounds with relatively high molecular weights. Contrary to our expectation, perfluorinated phenylenes **4** and **5** gave more stable amorphous films and showed better electron-transport capabilities compared with dendrimers **2** and **3**. These findings should be useful in designing new amorphous materials for electronic devices. We are currently measuring electron mobilities[19] for compounds **2**−**5** to obtain further information about their electron-transport properties and preparing perfluorinated phenylenes with longer para-conjugated units.[20]

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Supporting Information Available: Experimental details for **2**−**5** and OLEDs, ^{19}F NMR and mass spectra of **2** and **3**, and DSC curves and CVs of **2**−**5** (PDF). This materials is available free of charge via the Internet at http://pubs.acs.org.

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(16) After a few days, a decrease of luminance was observed for the device with **3** because of crystallization.

(17) The reduction peak of Alq$_3$ is −2.36 V under the same conditions.

(18) For example, it was suggested that Alq$_3$ forms a stable anion radical salt with Li. In the facial isomer, Li$^+$ is strongly coordinated by the three oxygen atoms of Alq$_3$. Curioni, A.; Andreoni, W. *J. Am. Chem. Soc.* **1999**, *121*, 8216−8220 and references therein.

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(20) Very recently, we found that the use of perfluoro-*p*-sexiphenyl (C$_{36}$F$_{26}$) as an electron-transport layer dramatically improved the device performance. The maximum luminance reached 12200 cd/m^2 at 13.7 V. Further experiments are being carried out and will be reported elsewhere. Heidenhain, S.; Sakamoto, Y.; Miura, A.; Fujikawa, H. Unpublished work, 1999.