

# Perfluoro-1,3,5-tris(*p*-oligophenyl)benzenes: Amorphous Electron-Transport Materials with High-Glass-Transition Temperature and High Electron Mobility

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Perfluoro-1,3,5-tris(*p*-quaterphenyl)benzene (PF-13Y) and perfluoro-1,3,5-tris(*p*-quinquephenyl)benzene (PF-16Y) have been synthesized and characterized. They showed higher glass transition temperatures compared with perfluoro-1,3,5-tris(*p*-terphenyl)benzene (PF-10Y). Organic light-emitting diodes were fabricated using these materials as the electron-transport layers. PF-13Y and -16Y are better electron transporters than PF-10Y. The electron mobilities of PF-10Y and Alq<sub>3</sub> were measured by the time-of-flight technique. PF-10Y showed higher electron mobilities (10<sup>-4</sup> cm<sup>2</sup>/V s) and weaker electric field dependence compared with Alq<sub>3</sub>. © 2002 Elsevier Science (USA)

**Key Words:** perfluorinated phenylene; amorphous; electron-transport material; glass-transition temperature; electron mobility; organic light-emitting diode; time-of-flight.

## INTRODUCTION

Recently,  $\pi$ -conjugated oligomers such as oligophenylenes and oligothiophenes have attained considerable attention as organic electronic materials (1). Thin films of these compounds can be obtained by sublimation under high vacuum and used for organic field-effect transistors and organic light-emitting diodes (OLEDs) (2). For OLEDs, each organic layer (hole-transport, emission, and electron-transport layers) is amorphous, and crystallization during the device operation results in shorter lifetime. We have been interested in developing new electron-transport materials for OLEDs and reported perfluorinated phenylene dendrimers (3) and linear oligomers (4). We found that branched oligomers, such as perfluoro-1,3,5-tris(*p*-terphenyl)benzene (PF-10Y), form stable amorphous solids with high-glass-transition temperatures. Linear oligomers, such as perfluoro-*p*-sexiphenyl (PF-6P), are crystalline solids

and showed excellent electron-transport properties. Therefore, it is interesting to extend the  $\pi$ -conjugation of PF-10Y by adding perfluoro-*p*-phenylene units. We report herein the synthesis, characterization, and electron-transport properties of perfluoro-1,3,5-tris(*p*-oligophenyl)benzenes (Chart 1).

## EXPERIMENTAL

### Synthesis

<sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on a JEOL JNM-LA 500 at 500 and 470.4 MHz, respectively. Chemical shifts were reported as  $\delta$  values (ppm) relative to internal tetramethylsilane (<sup>1</sup>H NMR) or hexafluorobenzene (<sup>19</sup>F NMR). MALDI-TOF mass spectra were collected on a Perseptive Biosystems Voyager NESTR with *trans*-3-indoleacrylic acid matrix in negative ion mode. EI mass spectra were obtained on a Shimadzu GCMS-QP5050A at 70 eV. The calorimetric data were obtained on a TA Instruments DSC 2920 at a scanning rate 15°C/min under a flow (50 mL/min) of argon. Cyclic voltammetry was recorded on a BAS-100B/W electrochemical analyzer (Chart 2).

**1.** A 300-mL, three-necked, round-bottomed flask fitted with a reflux condenser, Ar inlet, and rubber septum was charged with magnesium turnings (598 mg, 24.6 mmol). After 30 mL of THF was introduced into the flask with a syringe, 1-bromo-2,3,5,6-tetrafluorobenzene (5.61 g, 24.6 mmol) was added dropwise at a rate that maintained a gentle reflux. The mixture was stirred at room temperature for 2 h. To the resulting dark brown solution was added anhydrous copper (I) bromide (7.05 g, 49.2 mmol). The brown suspension was stirred at room temperature for 2 h, 30 mL of dioxane was added, and the resulting gray suspension was stirred at room temperature for 2 h. To the suspension was added a solution of

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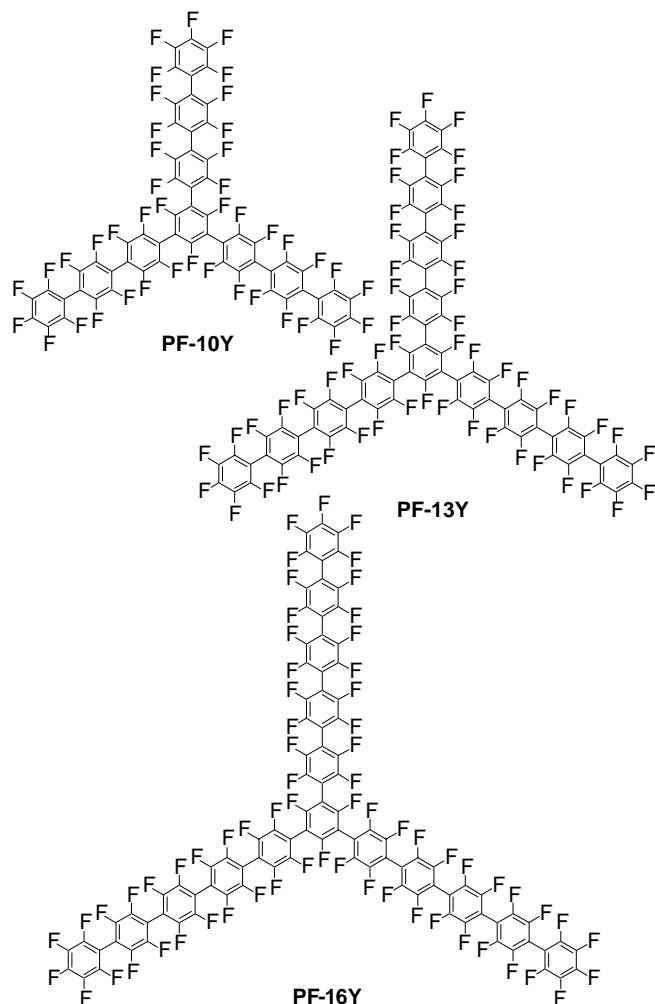


CHART 1

perfluoro-1,3,5-tris(4-bromophenyl)benzene (**3**) (1.00 g, 1.23 mmol) in 120 mL of toluene. The mixture was stirred at 80°C for 2 days and filtered through Celite. The solvent was removed on a rotary evaporator. The residue was dissolved in toluene, and the solution was washed with 6 M HCl and brine. The toluene solution was dried with MgSO<sub>4</sub> and filtered, and the filtrate was evaporated to dryness under reduced pressure. The residue was chromatographed

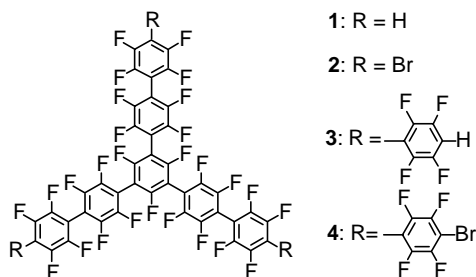


CHART 2

- 1: R = H
- 2: R = Br
- 3: R =
- 4: R =

over silica gel with *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> (5:1) to give **1** (930 mg, 74%): <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ 60.69 (s, 3F), 24.00–25.10 (m, 24F); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.27–7.34 (m, 3H); MS *m/z* 1020, 1021, 1022, 1023 (M<sup>+</sup>, 100, 45.5, 10.1, 1.46). Anal. Calcd for C<sub>42</sub>H<sub>3</sub>F<sub>27</sub>: C, 49.43; H, 0.30. Found: C, 49.36; H, 0.28.

**2.** A mixture of **1** (2.67 g, 2.61 mmol), bromine (8.34 g, 52.2 mmol), 60% fuming sulfuric acid (5 mL), and aluminum bromide (1.39 g, 5.22 mmol) was stirred at 60°C for 3 days. The reaction mixture was carefully poured into crushed ice. The resulting solid was filtered and washed with sodium carbonate, sodium bisulfite, and H<sub>2</sub>O. Flash chromatography over silica gel with CH<sub>2</sub>Cl<sub>2</sub> gave **2** (2.31 g, 70%): <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ 30.26–30.33 (m, 6F), 25.05–25.14 (m, 6F), 24.49–24.55 (m, 6F), 12.13 (t, *J* = 21.6 Hz, 3F), 1.43–1.56 (m, 6F); MS *m/z* 1254, 1255, 1256, 1257, 1258 (M<sup>+</sup>, 31.9, 14.5, 96.3, 42.8, 100). Anal. Calcd for C<sub>42</sub>Br<sub>3</sub>F<sub>27</sub>: C, 40.13. Found: C, 39.92.

*Perfluoro-1,3,5-tris(p-quaterphenyl)benzene (PF-13Y).* The procedure for **1** described above was followed using magnesium turnings (39 mg, 1.60 mmol) in 30 mL of THF, 4-bromononafluorobiphenyl (**3**) (632 mg, 1.60 mmol), anhydrous copper(I) bromide (459 mg, 3.20 mmol), 10 mL of dioxane, and **2** (100 mg, 0.08 mmol) in 20 mL of toluene. The mixture was stirred at 80°C for 3 days. Train sublimation afforded pure PF-13Y (80 mg, 51%): <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ 61.08 (s, 3F), 24.91–25.68 (m, 42F), 12.62–12.71 (m, 3F), 1.75–1.83 (m, 6F); MS *m/z* 1962, 1963, 1964, 1965 (M<sup>+</sup>, 100, 84.4, 35.1, 9.63). Anal. Calcd for C<sub>78</sub>F<sub>54</sub>: C, 47.73. Found: C, 47.40.

**3.** The procedure for **1** described above was followed using magnesium turnings (580 mg, 23.9 mmol) in 30 mL of THF, 1-bromo-2,3,5,6-tetrafluorobenzene (5.44 g, 23.9 mmol), anhydrous copper(I) bromide (6.85 g, 47.7 mmol), 15 mL of dioxane, and **2** (1.50 g, 1.19 mmol) in 50 mL of toluene. The mixture was stirred at 80°C for 3 days. Sublimation afforded pure **3** (1.59 g, 91%): <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ 61.12 (s, 3F), 23.45–25.43 (m, 36F); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.27–7.29 (m, 3H); MS *m/z* 1464, 1465, 1466, 1467 (M<sup>+</sup>, 100, 64.9, 20.7, 4.34). Anal. Calcd for C<sub>60</sub>H<sub>3</sub>F<sub>39</sub>: C, 49.20; H, 0.21. Found: C, 49.24; H, 0.41.

**4.** A mixture of **3** (1.59 g, 1.08 mmol), bromine (3.80 g, 23.8 mmol), 60% fuming sulfuric acid (5 mL), and aluminum bromide (635 mg, 2.38 mmol) was stirred at 60°C for 3 days. The reaction mixture was carefully poured into crushed ice. The resulting solid was filtered and washed with sodium carbonate, sodium bisulfite, and H<sub>2</sub>O. Flash chromatography over silica gel with *n*-hexane/CHCl<sub>3</sub> (1:3) gave **4** (750 mg, 41%): <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ 61.03 (m, 3F), 30.51–30.58 (m, 6F), 25.38–25.60 (m, 30F); MS *m/z* 1698, 1699, 1700, 1701, 1702 (M<sup>+</sup>, 29.0, 18.8, 90.6, 56.2, 100.00). Anal. Calcd for C<sub>60</sub>Br<sub>3</sub>F<sub>39</sub>: C, 42.36. Found: C, 42.53.

*Perfluoro-1,3,5-tris(p-quinquephenyl)benzene (PF-16Y)*. The procedure for **1** described above was followed using magnesium turnings (120 mg, 4.94 mmol) in 20 mL of THF, 4-bromononafluorobiphenyl (1.95 g, 4.94 mmol), anhydrous copper(I) bromide (1.42 g, 9.87 mmol), 10 mL of dioxane, and **4** (700 mg, 0.41 mmol) in 20 mL of toluene. The mixture was stirred at 80°C for 3 days. Train sublimation afforded pure PF-16Y (110 mg, 11%);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  61.20 (s, 3F), 24.92–25.74 (m, 54F), 12.68 (s, 6F), 1.76 (t, 3F); MS  $m/z$  2406, 2407, 2408, 2409 ( $\text{M}^+$ , 96.31, 100.00, 51.37, 17.41). Anal. Calcd for  $\text{C}_{96}\text{F}_{66}$ : C, 47.90. Found: C, 47.74.

### Fabrication of OLEDs

The devices were fabricated by vacuum deposition on ITO-coated glass substrates. First, the ITO surface was treated in rf plasma of argon/oxygen gas for 30 s at a pressure of  $7 \times 10^{-2}$  Torr for cleaning. The applied rf power was 10 W, and the power density was about  $100 \text{ mW/cm}^2$ . Then, a hole-transport layer of TPTE (5) (60 nm), an emission layer of tris(8-quinolinolato)aluminum ( $\text{Alq}_3$ , 40 nm), and an electron-transport layer of PF-*n*Y (20 nm) were formed on the ITO. Finally, a 0.5 nm-thick LiF layer was deposited as an electron-injection layer, followed by a 160 nm-thick Al layer as a cathode. All layers were continuously deposited under a vacuum of  $5 \times 10^{-7}$  Torr without vacuum break. After the cathode deposition, the devices were encapsulated with a glass plate and a UV epoxy resin in a dry nitrogen chamber. The emission area of the OLEDs was  $0.09 \text{ cm}^2$ . The luminance–voltage characteristics were measured using a current source (TAKEDA RIKEN TR-6150) connected to a Minolta photometer (LS-100) and a microcomputer.

### Electron-Mobility Measurement

The electron mobilities were measured by the conventional time-of-flight technique (6). The samples were prepared by vacuum deposition on ITO-coated glass substrates. A thinner layer of  $\text{Alq}_3$  (0.2  $\mu\text{m}$ ) was deposited on the ITO for photocarrier generation and a thicker layer (about 3  $\mu\text{m}$ ) of a compound was deposited on the  $\text{Alq}_3$  layer. An aluminum electrode was then deposited on the compound layer. The transient photocurrent due to the electron transit through the compound layer was observed by an irradiation of  $\text{N}_2$  pulse laser (wavelength: 337 nm). The photocurrent was characterized by a sharp pulse at  $t = 0$ , a plateau, and a dispersive tail. The transit time was defined at the demarcation point between the plateau and the dispersive tail. The electron mobility was calculated from the transit time.

## RESULTS AND DISCUSSION

PF-13Y ( $\text{C}_{78}\text{F}_{54}$ ; MW=1963) and PF-16Y ( $\text{C}_{96}\text{F}_{66}$ ; MW=2407) have been synthesized by applying the procedure for PF-10Y ( $\text{C}_{60}\text{F}_{42}$ ; MW=1518). The structures were confirmed by  $^{19}\text{F}$  NMR, MALDI-TOF-MS, and elemental analyses. They are colorless solids and soluble in  $\text{CHCl}_3$ , THF, and aromatic solvents such as toluene. Figure 1 shows the differential scanning calorimetry (DSC) curves of PF-10Y, -13Y, and -16Y. As expected, PF-13Y and -16Y exhibited higher glass transition temperatures ( $T_g = 161^\circ\text{C}$  and  $176^\circ\text{C}$ , respectively) compared with PF-10Y ( $T_g = 135^\circ\text{C}$ ). No peaks due to melting or crystallization were observed even after several cycles, indicating that they are highly stable amorphous solids.

To estimate the LUMO energy levels, we measured the cyclic voltammetry (CV). In THF, these compounds showed irreversible reductions. The reduction peaks shift positively in the order PF-10Y ( $-2.24 \text{ V}$ ), PF-13Y ( $-2.20 \text{ V}$ ), and PF-16Y ( $-2.18 \text{ V}$  vs  $\text{Fc}/\text{Fc}^+$ ). This order is consistent with the number of para-conjugated benzene rings: PF-10Y (*p*-quaterphenyl) < PF-13Y (*p*-quinquephenyl) < PF-16Y (*p*-sexiphenyl). This is reasonable because the higher para-conjugation, the lower LUMO energy level is expected. The reduction peak of  $\text{Alq}_3$  is  $-2.36 \text{ V}$  under the same conditions.

OLEDs were made on indium-tin-oxide (ITO)-coated glass substrates by high-vacuum thermal evaporation ( $5 \times 10^{-7}$  Torr) of TPTE as the hole-transport layer (60 nm),  $\text{Alq}_3$  as the emission layer (40 nm), PF-*n*Y as the electron-transport layer (20 nm), LiF as the electron-injection layer (0.5 nm), and aluminum as the cathode (160 nm). For comparison, the device with  $\text{Alq}_3$  as both the emission and electron-transport layers (60 nm) was also fabricated. When a negative voltage was applied to Al, a green emission due to  $\text{Alq}_3$  was observed. Figure 2 shows the luminance–voltage characteristics for these OLEDs. All the OLEDs showed the performance of luminance with

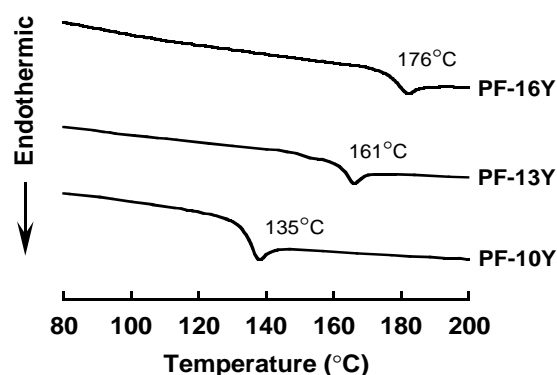


FIG. 1. DSC curves of compounds PF-10Y, -13Y, and -16Y. The heating rate is  $15^\circ\text{C}/\text{min}$ .

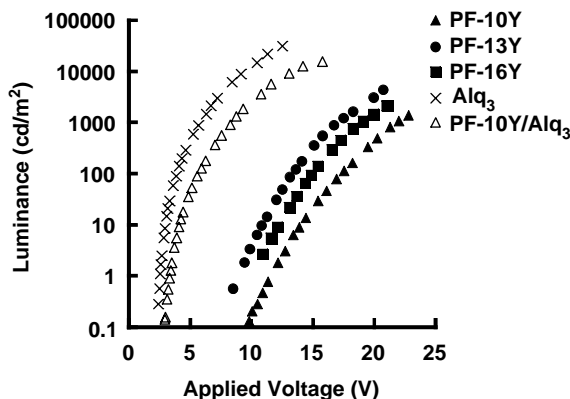


FIG. 2. Luminance–voltage characteristics of the OLEDs as a function of the electron-transport layer.

turn-on voltage less than 10 V. This indicates electron injection from the cathode to the PF-*n*Y layer and electron-transport ability of the PF-*n*Y layer. As expected from previous observations (3, 4), the device performance of PF-13Y was improved relative to the device with PF-10Y. This is probably due to the improvement of electron injection. The electron-transport capability of PF-16Y is higher than that of PF-10Y, but slightly lower than that of PF-13Y.<sup>2</sup> (7). The maximum luminance of the device with PF-13Y is 4380 cd/m<sup>2</sup> at 20.7 V.

The electron mobilities of PF-10Y and Alq<sub>3</sub> were measured by the time-of-flight technique. As shown in Fig. 3, PF-10Y showed much better electron mobilities and weaker electric-field dependence compared with Alq<sub>3</sub>. The electron mobilities of PF-10Y range from  $8.8 \times 10^{-5}$  cm<sup>2</sup>/Vs ( $1.3 \times 10^5$  V/cm) to  $2.3 \times 10^{-4}$  cm<sup>2</sup>/Vs ( $6.3 \times 10^5$  V/cm). These values are relatively high for amorphous n-type semiconductors (7, 8). The transient photocurrent exhibited a very clear plateau indicating a nondisersive transport, which is also different from that of Alq<sub>3</sub>. This is attributable to a less severe trapping problem or a narrow distribution of hopping sites.

The high electron mobility of PF-10Y was also confirmed by the following experiment: as shown in Fig. 2 (PF-10Y/Alq<sub>3</sub>), the device performance was dramatically improved by introducing Alq<sub>3</sub> as the electron-injection layer (TPTE/Alq<sub>3</sub>/PF-10Y/Alq<sub>3</sub>/LiF/Al). The maximum luminance reached 15,600 cd/m<sup>2</sup> at 15.8 V. This result indicates that PF-*n*Ys may be used as the hole-blocking layer because of their low HOMO energy levels. Recently, Ikai *et al.* reported that PF-10Y was so far the

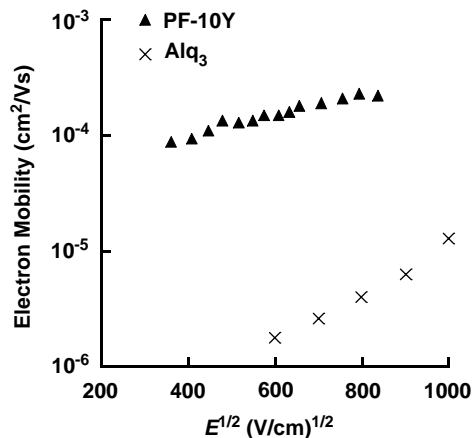


FIG. 3. Electron mobilities of PF-10Y and Alq<sub>3</sub> by the time-of-flight technique.

best hole- and exciton-blocking material for highly efficient phosphorescence OLEDs (9). The electron-mobility measurements for PF-13Y and -16Y would be useful to understand structure–property relationships and are in progress (10).

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<sup>2</sup>A similar result was obtained with long linear oligomers such as perfluoro-*p*-decaphenyl (PF-10P). Its OLED performance was poorer than that of perfluoro-*p*-octiphenyl (PF-8P). S. B. Heidenhain, unpublished work.