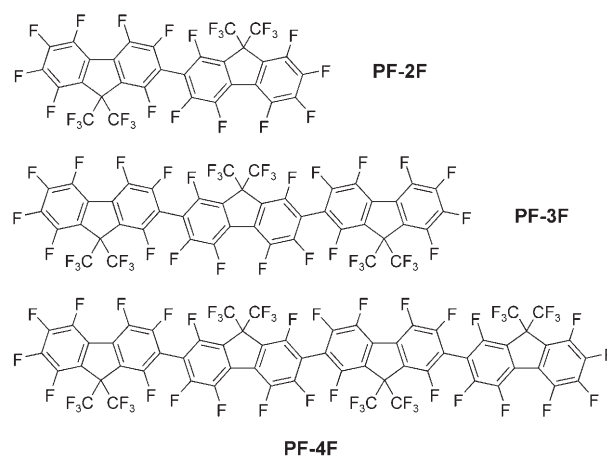


Synthesis, Structure, and Transport Property of Perfluorinated Oligofluorenes

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A perfluorinated aromatic compound is typically an electron acceptor and considered as an important n-type semiconductor for organic electronics.^[1] We have reported the synthesis and electron-transport properties of perfluorinated phenylene oligomers. Branched oligomers^[2] such as perfluoro-1,3,5-tris(*p*-terphenyl)benzene (C₆₀F₄₂) displayed the excellent ability to block excitons and holes in organic light-emitting diodes (OLEDs) with phosphorescent dopants. Linear oligomers^[3] such as perfluoro-*p*-sexiphenyl (C₃₆F₂₆) exhibited good electron injection and transport, but they were not practically useful for OLEDs because of their high crystallinity.^[4] The purpose of this research is to produce a new n-type semiconductor with 1) a high electron affinity, 2) a high electron mobility, and 3) a stable amorphous state. After theoretical calculations on several different structures, we recognized that perfluorinated oligofluorenes could be good candidates: The conversion of perfluorinated oligophenylenes to perfluorinated oligofluorenes significantly lowers the LUMO energy levels.^[5] Oligo- and polyfluorenes have been known as amorphous blue emitters with high carrier mobilities.^[6–8] We report here the synthesis, characterization, and properties of perfluorinated oligo(9,9-dimethylfluorene)s (PF-*n*Fs, Scheme 1).

Octafluorofluorene **3** was first reported by Filler et al. in 1980.^[9] Our improved synthesis starts with 1,2-dibromo-3,4,5,6-tetrafluorobenzene, and the total yield is 52% as shown in Scheme 2. The substitution reaction of **3** with hydrazine took place at the 2-position to provide **4**. Bromina-



Scheme 1. Structures of perfluorinated oligo(9,9-dimethylfluorene)s.

tion of **4** afforded 2-bromoheptafluorofluorene **5** in 47% yield. The reaction of **5** with the trifluoromethylating agent **6** in the presence of NaH and [15]crown-5 gave **7** in 53% yield. The dimer **PF-2F** was synthesized by the Ullmann coupling of **7** in 72% yield.

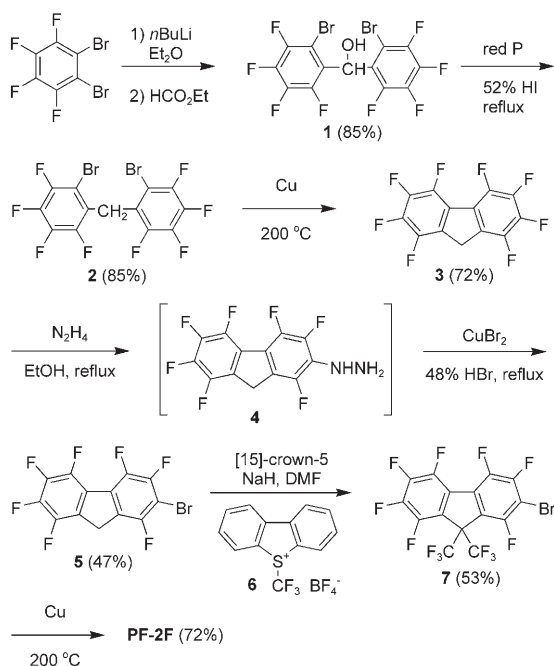
Further bromination of **5**, which was followed by trifluoromethylation, provided the dibromide **9** (Scheme 3). The copper derivative **10** was prepared from the Grignard reagent of **7** and copper(I) bromide without isolation. The reaction of **10** with **9** gave the trimer **PF-3F** (C₄₅F₃₈) in 52% yield. Similarly, the dimeric dibromide **11**,^[5] prepared from **5**, was allowed to react with **10** to afford the tetramer **PF-4F** (C₆₀F₅₀) in 46% yield.

PF-2F to **PF-4F** were purified by train sublimation and used for characterization. The structures were determined by ¹⁹F NMR spectroscopy, mass spectrometry, and elemental analyses. They are colorless solids and soluble in CHCl₃, THF, and aromatic solvents such as toluene. The UV/Vis absorption and photoluminescence spectra^[5] of **PF-3F** were very similar to those of the parent compound (**3F**: C₄₅H₃₈)^[10] in shape but shifted by 40 nm to the higher energy. This is consistent with the DFT calculations on **3F**

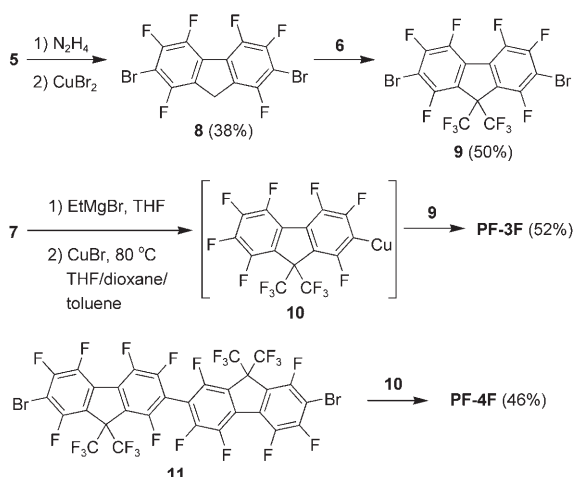
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Scheme 2. Synthesis of octafluorofluorene **3** and **PF-2F**.



Scheme 3. Synthesis of **PF-3F** and **PF-4F**.

and **PF-3F**: The HOMO–LUMO gaps are 3.81 and 4.03 eV, respectively. The wider HOMO–LUMO gap of **PF-3F** is probably because of its larger dihedral angles (**3F**: 37.2°; **PF-3F**: 55.2° by the DFT calculations). Contrary to oligo- and polyfluorenes, **PF-2F** to **PF-4F** showed only weak emissions with the peaks around 350 nm.^[5]

To estimate the LUMO energy levels, we measured the cyclic voltammetry (CV). Although **PF-2F** showed only one reversible couple at −1.80 V (versus the ferrocene/ferrocenium couple (Fc/Fc⁺)), **PF-3F** and **PF-4F** exhibited two reversible couples in THF (Figure 1). The reduction potentials shifted positively from **PF-3F** (−1.65 and −1.96 V) to **PF-4F** (−1.60 and −1.80 V). This is consistent with the LUMO energy levels obtained by the DFT calculations (**PF-2F**:

−2.64; **PF-3F**: −2.82; **PF-4F**: −2.91 eV). The potential difference between the first and second reductions (**PF-3F**: 0.31; **PF-4F**: 0.20 V) is smaller in **PF-4F** because of less electron–electron repulsion in its longer π -conjugation. The observed reduction potentials are more positive than those of conventional electron-transport materials such as Alq₃ (−2.36 V under the same conditions).^[11]

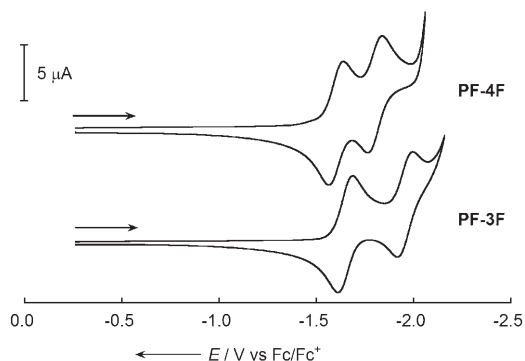


Figure 1. Cyclic voltammograms of **PF-3F** and **PF-4F** at 100 mV s^{−1} containing 0.1 M (nBu)₄NPF₆ in THF.

We performed the X-ray crystallography of **PF-2F** to see the molecular conformation and packing.^[12] Interestingly, a single crystal of **PF-2F** contains a 1:1 mixture of *cis* and *trans* conformers in the unit cell (Figure 2), and each conformer forms the separated layer.^[5] The dihedral angle is slightly larger in the *cis* conformer (*cis*: 57.7°; *trans*: 53.2°). These values are typical for perfluorinated oligo(*p*-phenylene)s. For example, the dihedral angles of perfluoro-*p*-quaterphenyl (C₂₄F₁₈) and -quinquephenyl (C₃₀F₂₂) are 59.5° and 53.5°, respectively.^[13]

The differential scanning calorimetry (DSC) measurements of **PF-3F** and **PF-4F** showed high glass transition temperatures (*T*_g = 133 and 163 °C, respectively).^[5] No peaks due to melting or crystallization were observed after the first cycle, indicating that they are stable amorphous solids.

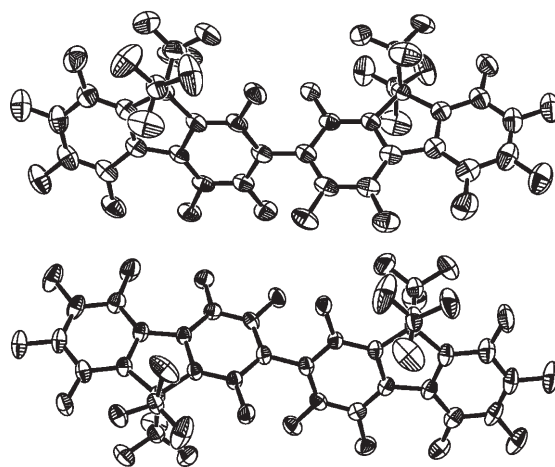


Figure 2. ORTEP drawing of *cis*-**PF-2F** (top) and *trans*-**PF-2F** (bottom). Thermal ellipsoids are shown at 50% probability.

The charge carrier mobilities for **PF-3F** and **PF-4F** were measured by the conventional time-of-flight (TOF) technique with a N_2 pulse laser. The samples were prepared on ITO-coated glass substrates by high-vacuum thermal evaporation of tris(8-quinolinolato)aluminum (Alq_3 , 30 nm) as the charge-generation layer, **PF-3F** (5.6 μm) or **PF-4F** (3.8 μm), and aluminum (100 nm). Relatively thick films of **PF-3F** and **PF-4F** were nicely transparent, and no crystallization was observed. A negative voltage was applied to the ITO electrode to examine the electron-transport properties. Figure 3a and b show the representative transient photocurrents for **PF-3F** and **PF-4F** films, respectively. **PF-3F** exhibited a current plateau followed by a tail in the double-linear plot (Figure 3a). This nondispersive transport in the solid film indicates that the density of electron traps due to energetic disorder is small. Carrier transit times (T_t) were obtained from the intersection point in the double-logarithmic plots (insets of Figure 3a and 3b). The electron mobilities can be calculated from the carrier transit times and are plotted against the square of the electric field as shown in Figure 4. **PF-3F** and **PF-4F** displayed weak field dependence and high electron mobilities (2.1×10^{-4} and $2.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $5.8 \times 10^5 \text{ V cm}^{-1}$, respectively) compared to Alq_3 ($2.7 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $1.2 \times 10^6 \text{ V cm}^{-1}$).

In conclusion, we have synthesized perfluorinated oligo(9,9-dimethylfluorene)s up to the tetramer. **PF-3F** and **PF-4F** are amorphous n-type semiconductors with high elec-

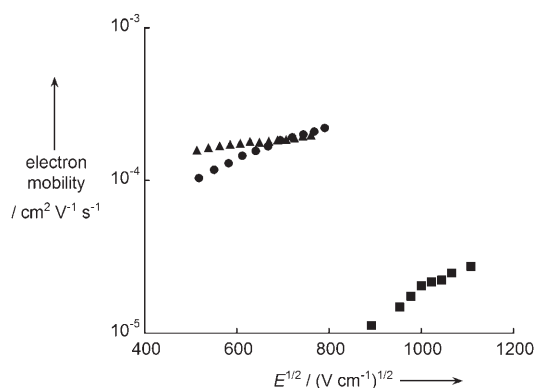


Figure 4. Electron mobilities of **PF-3F** (●), **PF-4F** (▲), and Alq_3 (■) by the time-of-flight technique.

tron affinity and mobility. The application to OLEDs is currently underway and will be reported elsewhere.

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Keywords: amorphous materials • electron transport • fluorine • oligomerization • semiconductors

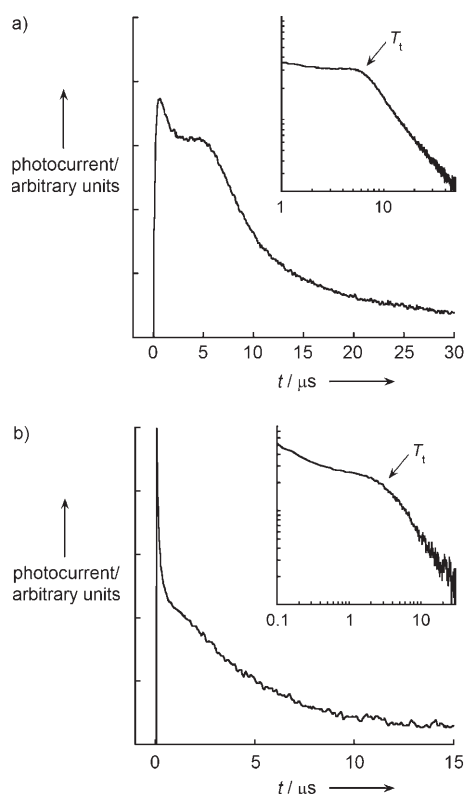


Figure 3. TOF current transients for a) **PF-3F** at $4.8 \times 10^5 \text{ V cm}^{-1}$ and b) **PF-4F** at $5.0 \times 10^5 \text{ V cm}^{-1}$. Insets of a) and b) are the double-logarithmic plots.

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- [12] Crystal data for **PF-2F**: $C_{60}F_{52}$, $M_r = 1708.58$, triclinic, space group $P\bar{1}$, $a = 10.027(5)$, $b = 12.407(6)$, $c = 23.003(11)$ Å, $\alpha = 92.961(7)$, $\beta = 93.513(9)$, $\gamma = 90.443(8)^\circ$, $V = 2852(2)$ Å³, $T = 173$ K, $Z = 2$, $R = 0.0819$, $GOF = 1.007$. CCDC 677181 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif
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