10240 *J. Am. Chem. Soc.* **2000,** *122,* 10240−10241

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

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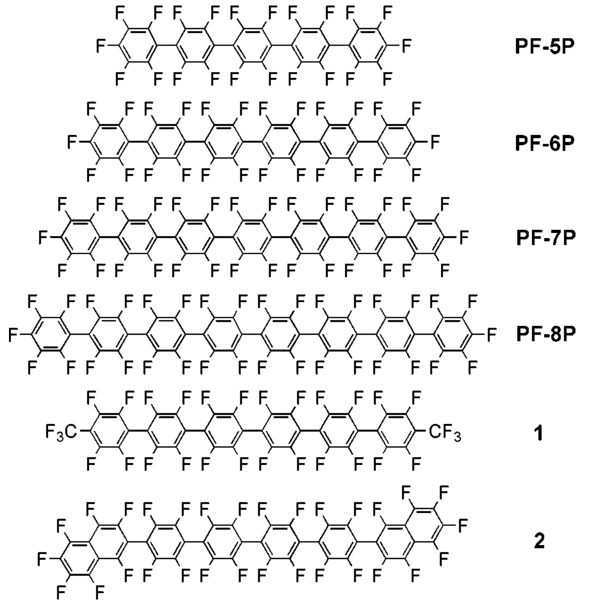
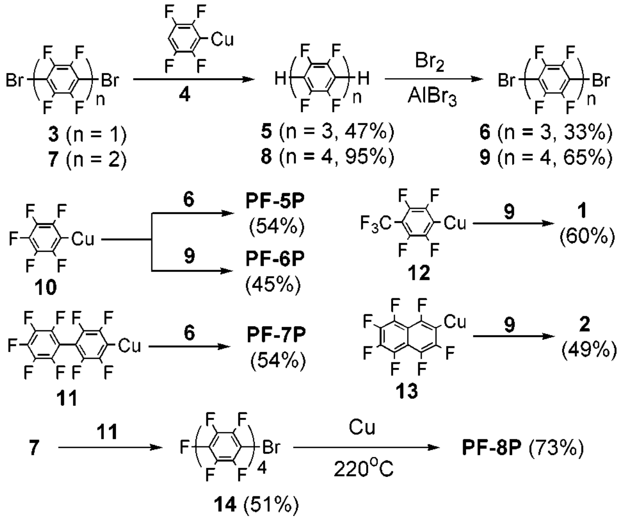
Received June 27, 2000

Organic light-emitting diodes (OLEDs) and field-effect transistors (FETs) based on π-conjugated oligomers have been extensively studied as molecular thin-film devices.[1] Organic n-type semiconductors (electron-transport materials) with low electron-injection barriers and high electron mobilities are required for highly efficient OLEDs[2] and n-type FETs.[3] 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. In the last paper, we reported that perfluorinated phenylene dendrimers ($C_{60}F_{42}$ and $C_{132}F_{90}$) function as the electron-transport layer of OLEDs.[4] A perfluorinated phenylene with longer para-conjugation and higher electron affinity exhibited better electron-transport capability. Perfluoro-1,3,5-tris(*p*-terphenyl)benzene, which can be viewed as a perfluoro-*p*-quaterphenyl derivative, showed the maximum luminance of 2860 cd/m^2 at 24.4 V. To develop efficient organic n-type semiconductors and improve the device performance, we decided to prepare perfluorinated phenylene oligomers with even longer para-conjugation. In this work, we report the synthesis of perfluorinated oligo(*p*-phenylene)s (**PF-*n*P**s: $n = 5-8$)[5] and the application for the electron-transport layer of OLEDs.[6] The use of higher **PF-*n*P**s dramatically improved the electron injection into the emission layer. Two **PF-6P** derivatives containing trifluoromethyl and perfluoro-2-naphthyl groups were also prepared, and the latter is a better electron transporter than conventional electron-transport materials such as tris(8-quinolinolato)aluminum (Alq$_3$).

Chart 1



Scheme 1



We synthesized **PF-5P** to **-7P** by the organocopper cross-coupling method, which has been successfully applied to perfluorinated phenylene dendrimers.[4] As shown in Scheme 1, 1,4-dibromotetrafluorobenzene (**3**) was allowed to react with excess 2,3,5,6-tetrafluorophenylcopper (**4**) in a THF/dioxane/toluene mixture at 80 °C for 48 h to give **5** in 47%.[7] Bromination of **5** yielded perfluoro-4,4″-dibromo-*p*-terphenyl (**6**) in 33%. A similar reaction of 4,4′-dibromooctafluorobiphenyl (**7**) with **4** followed by bromination afforded perfluoro-4,4‴-dibromo-*p*-quaterphenyl (**9**). Treatment of excess pentafluorophenylcopper (**10**) with **6** and **9** produced perfluoro-*p*-quinquephenyl (**PF-5P**: $C_{30}F_{22}$; MW = 778) and perfluoro-*p*-sexiphenyl (**PF-6P**: $C_{36}F_{26}$; MW = 926) in 54 and 45%, respectively. Perfluoro-*p*-septiphenyl (**PF-7P**: $C_{42}F_{30}$; MW = 1074) was obtained in 54% by using nonafluoro-4-biphenylcopper (**11**) and **6**. Two **PF-6P** derivatives **1** ($C_{38}F_{30}$; MW = 1026) and **2** ($C_{44}F_{30}$; MW = 1098) were prepared by the reactions of **9** with 4-trifluoromethyltetrafluorophenylcopper (**12**)

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(1) *Electronic Materials: The Oligomer Approach;* Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998.

(2) For a recent review, see: Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121−128.

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(4) Sakamoto, Y.; Suzuki, T.; Miura, A.; Fujikawa, H.; Tokito, S.; Taga, Y. *J. Am. Chem. Soc.* **2000**, *122*, 1832−1833.

(5) (a) The reaction of decafluorobiphenyl with excess C_6F_5MgBr in THF gave a mixture of **PF-*n*P**s. **PF-3P** and **-4P** have been isolated and characterized. Maruo, K.; Wada, Y.; Yanagida, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3439−3449. (b) Treatment of $Cp_2Zr(C_6F_5)_2$ with excess C_6F_6 in THF provided a mixture containing up to **PF-13P**, which was determined by LC-TOF mass spectrometry: Edelbach, B. L.; Kraft, B. M.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 10327−10331.

(6) Partially fluorinated oligo(*p*-phenylene)s such as 2′,2″,3′,3″,4,4‴,5′,5″,6′,6″-decafluoro-*p*-quaterphenyl ($C_{24}H_8F_{10}$) for OLEDs: Winkler, B.; Meghdadi, F.; Tasch, S.; Müllner, R.; Resel, R.; Saf, R.; Leising, G.; Stelzer, F. *Opt. Mater.* **1998**, *9*, 159−162.

(7) See Supporting Information for the experimental details.

10.1021/ja002309o CCC: $19.00

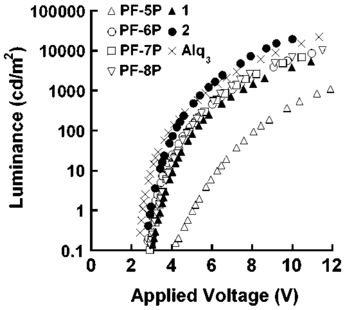

Figure 1. Luminance−voltage characteristics of the OLEDs as a function of the electron-transport layer.

and heptafluoro-2-naphthylcopper (**13**) in 60 and 49%, respectively. The Ullmann coupling of perfluoro-4-bromo-*p*-quaterphenyl (**14**), which was obtained by the reaction of **7** with **11** in 51%, gave perfluoro-*p*-octiphenyl (**PF-8P**: $C_{48}F_{34}$; MW = 1222) in 73%.[8]

Perfluorinated oligomers were purified by train sublimation[9] and used for characterization. They are colorless solids and insoluble in common organic solvents.[10] The structures were determined by MALDI-TOF mass spectrometries and elemental analyses.[7] The differential scanning calorimetry (DSC) measurements indicated that the samples purified by train sublimation are highly crystalline solids: The melting endotherm of each oligomer (**PF-5P**, 306; **PF-6P**, 352; **PF-7P**, 383; **PF-8P**, 410; **1**, 350; **2**, 352 °C) is accompanied by a broad peak due to sublimation, which occurs simultaneously. No glass transitions were observed on the second heating.

OLEDs were made on indium−tin oxide (ITO)-coated glass substrates by high-vacuum thermal evaporation (5×10^{-7} Torr) of TPTE (a tetramer of triphenylamine) as the hole-transport layer (60 nm), Alq_3 as the emission layer (40 nm), a perfluorinated oligomer as the electron-transport layer (20 nm), LiF as the electron-injection layer (0.5 nm), and aluminum as the cathode (160 nm).[7,11] For comparison, the device with 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 Alq_3 was observed. Figures 1 and 2 show luminance−voltage and current−voltage characteristics of these OLEDs, respectively. We found that the electron-transport capabilities of perfluorinated oligo(*p*-phenylene)s are excellent compared with perfluorinated phenylene dendrimers.[4] The maximum luminance of **PF-5P** is 5540 cd/m^2 at 17.0 V, which is much better than that of perfluoro-1,3,5-tris(*p*-terphenyl)benzene. When **PF-5P** was replaced by **PF-6P**, the device performance was dramatically improved. The device with **PF-6P** showed the maximum luminance of 12150 cd/m^2 at 13.7 V. Interestingly, the luminance−voltage and current−voltage characteristics of **PF-7P** and **-8P** are almost identical to those of **PF-6P**. Substitution of a fluorine atom with a trifluoromethyl group would change solid-state morphology and electron-transport behavior. In the case of **1**, the luminance and current density decreased slightly compared to **PF-6P**. A perfluoro-2-naphthyl group turned out to be an excellent building block for constructing n-type semiconductors.[12] The luminance and current density of **2** are higher than those of Alq_3 above 4.5 V. The luminance at 10.0 V reached 19970 cd/m^2.

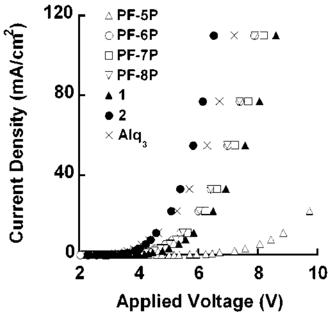

Figure 2. Current−voltage characteristics of the OLEDs as a function of the electron-transport layer.

The above results (**PF-5P** < **PF-6P** = **PF-7P** = **PF-8P**) are contrary to our expectation because the low LUMO energy of a higher **PF-*n*P** should facilitate the electron-injection from a cathode to an electron-transport layer (**PF-5P** < **PF-6P** < **PF-7P** < **PF-8P**).[13] This might indicate that the rate of electron injection is not affected by the LUMO energy any more if its level is low enough.[14] We assume that electron mobilities are not very different in these molecules because solid-state morphology is expected to be similar. Therefore, the electron mobility in the layer rather than the electron injection at the interface could be responsible for determining the current density of **PF-6P** to **-8P**.[15]

In conclusion, we have synthesized perfluorinated oligo(*p*-phenylene)s up to *p*-octiphenyl and shown that they are efficient n-type semiconductors. Because **PF-*n*P**s have high electron mobilities, n-type FETs with these materials are quite interesting. Fabrication of FETs is currently underway and will be reported elsewhere.[16]

Acknowledgment. We thank S. Makita for measuring MALDI-TOF mass spectra. This work was supported by Japan Society for the Promotion of Science (Grant-in-Aid for Scientific Research C-11640594 and B-12554027).

Supporting Information Available: Experimental details and MALDI-TOF mass spectra of **PF-5P** to **-8P** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Treatment of **9** with excess **11** produced only perfluoro-4-bromo-*p*-sexiphenyl, which is insoluble in a THF/dioxane/toluene mixture.

(9) Wagner, H. J.; Loutfy, R. O.; Hsiao, C.-K. *J. Mater. Sci.* **1982**, *17,* 2781−2791.

(10) **PF-5P** is slightly soluble in hot toluene.

(11) The thin films of the perfluorinated oligomers are transparent and probably amorphous.

(12) Naphthalene derivatives with high electron mobilities, see ref 3c.

(13) The PM3 molecular orbital calculations predict that the LUMO energy level of **PF-*n*P** would become lower in the order **PF-5P** (−2.36 eV) > **PF-6P** (−2.39 eV) > **PF-7P** (−2.41 eV) > **PF-8P** (−2.42 eV).

(14) This kind of saturation was also observed for perfluorinated oligo-(2,6-naphthalene)s. Trimer ($C_{30}F_{20}$) and tetramer ($C_{40}F_{26}$) showed the same luminance−voltage and current−voltage characteristics. Sakamoto, Y., unpublished work, 2000.

(15) The electron mobility of **PF-6P**, determined by the time-of-flight technique, is 2.0×10^{-3} cm^2 V^{-1} s^{-1} at 9.4×10^5 V cm^{-1}. This value is much higher than that of Alq_3 under the same conditions (1.3×10^{-5} cm^2 V^{-1} s^{-1} at 1.0×10^6 V cm^{-1}). Therefore, another possibility is that the low electron mobility of Alq_3 is responsible for the saturation of current density. Fujikawa, H., unpublished work, 2000.

(16) Takada, M.; Tada, H., unpublished work, 2000.