Synthesis, Properties, and Structures of Difluoromethylene-bridged Coplanar *p*-Terphenyl and Its Aryl-capped Derivatives for Electron-transporting Materials

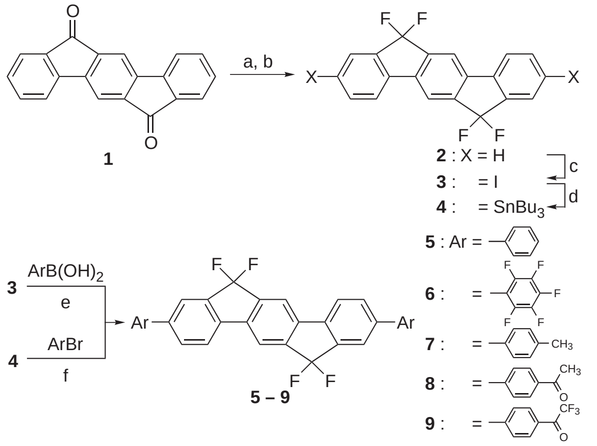
Yutaka Ie, Masashi Nitani, and Yoshio Aso*
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047

(Received August 16, 2007; CL-070873; E-mail: aso@sanken.osaka-u.ac.jp)

A series of oligophenylene derivatives consisting of 6,6,12,12-tetrafluoroindenofluorene moieties were synthesized. Photophysical properties and X-ray analyses clearly showed that these conjugated molecules have potentials for electron-transporting materials.

There has been a great interest in developing novel conjugated oligomers for advanced functional materials such as organic light emitting diodes (OLEDs), organic field-effect transistors (OFETs), and photovoltaic devices (solar cells).[1] One of recent trends in these fields is to develop electronegative conjugated systems, which is basically accomplished by lowering the LUMO energy level, for n-type organic semiconductors.[2] In this regard, it has been demonstrated that the incorporation of strongly electron-withdrawing groups, especially perfluoroalkyl groups, into oligothiophenes dramatically increases their n-type performance.[3] Recently, we have reported the synthesis of perfluoroalkyl-annelated oligothiophenes and revealed the effectiveness of the perfluoroalkyl annelation in both keeping the effective conjugation and increasing the electron affinity.[4] In continuation of our work in the field of the perfluoroalkyl-annelated conjugated systems, we have newly designed bis(difluoromethylene)-bridged *p*-terphenyl, 6,6,12,12-tetrafluoroindeno[3,2-*b*]fluorene, as a new electron-transporting unit. Although indenofluorene derivatives are known to behave as p-type semiconductors in OLEDs and OFETs,[5,6] the indenofluorene derivative bearing geminal trifluoromethyl substituents at 6,6,12,12-positions has been known as only one candidate for electronegative materials.[7] Therefore, exploring new indenofluorene units with electronegative character remains still of great interest. Herein, we describe the synthesis of 6,6,12,12-tetrafluoroindeno[3,2-*b*]fluorene (**2**) and its 2,8-diaryl derivatives **5**–**9** and the investigation of their electronic properties and X-ray crystallographic structures. The modification of the terminal aryl groups is attractive because of the possibility of further tuning the electronic structure as well as inducing desirable stacking structure for carrier transport in organic thin films.

Indeno[3,2-*b*]fluorene-6,12-dione (**1**)[8] was converted to the difluoromethylene-bridged terphenyl **2** according to the procedure described in Scheme 1.[9] The Pd-catalyzed Suzuki coupling reaction of **3** with the corresponding aryl boronic acids gave **5**–**8** in moderate yields.[10] Compound **9** was synthesized by the Stille coupling reaction of **4** with the aryl bromide. These indenofluorene derivatives were further purified by sublimation under a high vacuum and unambiguously characterized by GC-MS, ^{1}H NMR spectroscopy, and elemental analysis.[11]



Scheme 1. Reagents and conditions: (a) 1,2-ethanedithiol, $BF_3 \cdot AcOH$, $CHCl_3$, 70 °C, 99%; (b) HF•Py, NIS, CH_2Cl_2, −78 °C, 95%; (c) $PhI \cdot (OCOCF_3)_2$, I_2, $CHCl_3$, rt, quant.; (d) *n*-BuLi, $SnBu_3Cl$, THF, −78 °C, 55%; (e) **5**: $Pd(PPh_3)_4$, $NaHCO_3$, DME/H_2O, 90 °C, 33%; **6**: $Pd(PPh_3)_4$, Ag_2O, CsF, DME, 70 °C, 62%; **7**: $Pd(PPh_3)_4$, $NaHCO_3$, THF/H_2O, 90 °C, 74%; **8**: $Pd(PPh_3)_4$, $NaHCO_3$, THF/H_2O, 90 °C, 35%; (f) **9**: $Pd(PPh_3)_4$, toluene, reflux, 60%.

Table 1. Spectroscopic data for compounds **5**–**9** in THF

Compd	Abs_{max}/nm	Abs_{sh}/nm	Flu_{max}/nm	Φ_{flu}
5	347	389	430	0.61
6	336	372	410	0.57
7	350	392	436	0.64
8	352	393	429	0.61
9	358, 375	393	434	0.87

The UV–vis absorption spectrum of **2** showed characteristic bands at 255 and 325 nm with vibronic structures and a shoulder at a longer wavelength around 350 nm (Figure S1).[11] On the basis of TD-DFT calculation at the B3LYP/6-31G(d,p) level, the shoulder can be assigned to π–π^* transition, which is red-shifted compared to that of 6,12-dihydroindeno[3,2-*b*]fluorene (**10**). The cyclic voltammogram (CV) of **2** in fluorobenzene showed reduction peak potential at −2.46 V vs. Fc/Fc$^+$, while that of **10** lies at −2.79 V. This positive shift of **2** clearly indicates that the electron affinity increases upon the substitution of fluorine atoms for hydrogens at the two bridging positions in the indenofluorene. The determined electrochemical HOMO–LUMO gap of 3.43 eV correlates well with the optical gap of 3.28 eV estimated from the onset of the absorption spectrum.

The UV–vis absorption and photoluminescence (PL) spectra of the quinquephenylene compounds are summarized in Table 1 and Figure S2.[11] They exhibit red-shifted absorptions relative to that of the parent compound **2**. The introduction of pentafluorophenyl groups leads to a blue-shift of absorption compared with that of **5**, which matches well the tendency of pentafluorophen-

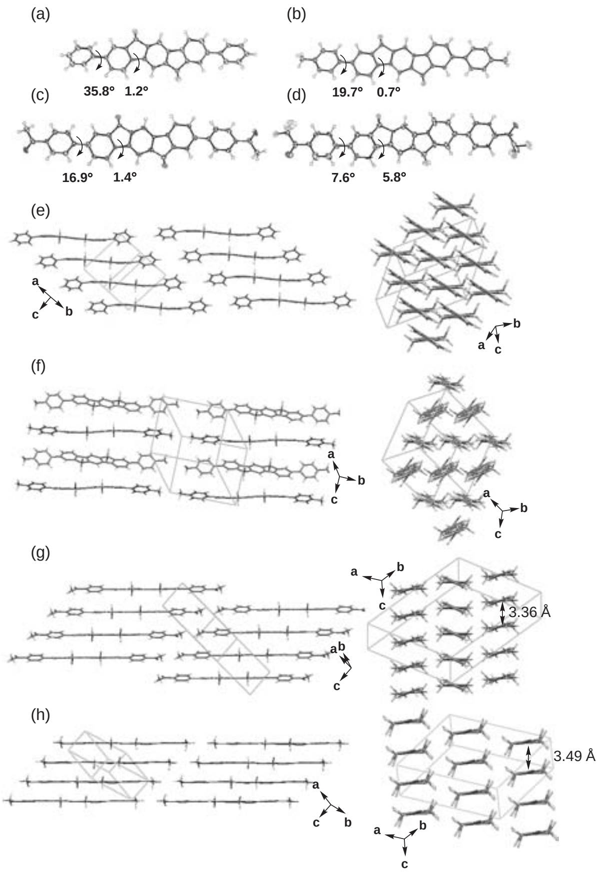


Figure 1. Molecular structures of **5** (a), **7** (b), **8** (c), and **9** (d) and packing diagrams of **5** (e), **7** (f), **8** (g), and **9** (h).

yl–thiophene-conjugated system.[12] All of these compounds show blue emission with good quantum yields of 0.57–0.87. Their low solubility in organic solvents prevented us from measuring their CVs.

Single crystals for X-ray analyses were obtained by slow evaporation of the $CHCl_3$ solution for **5** and **7** and by sublimation for **8** and **9**. Figure 1 shows the crystallographic molecular and packing structures of **5**, **7**, **8**, and **9**.[13] As we expected, the indenofluorene unit displays nearly coplanar geometries. Torsion angles between the central and terminal aryl units are 35.8, 19.7, 16.9, and 7.6° for **5**, **7**, **8**, and **9**, respectively. Interestingly, the introduction of carbonyl group at the terminal position has improving effect on coplanarity of the whole molecular conjugation as well as face-to-face packing, which are concomitant with the occurrence of CH–carbonyl interactions between the columns.[14] Above all, the molecules **9** pack in nearly ideal π-stacked geometry with a minimum interplanar distance of 3.49 Å, while **5** and **7** pack in the slipped-stack and random arrangements, respectively.

Compared to the UV–vis spectra of **9** in solution, a red-shift of absorption maximum up to 35 nm was observed in its vacuum-deposited 40-nm-thick film on glass substrate (Figure S3).[11] Moreover, in the PL spectra of the film, we could observe a characteristic long-wavelength broad emission at 536 nm, assignable to the excimer emission. These phenomena clearly suggest that the presence of strong intermolecular interactions, as deduced from the packing diagram of **9**, impacts on the photophysical properties in the film state.

In summary, we have synthesized a series of 6,6,12,12-tetrafluoroindenofluorene derivatives and revealed the influence of the difluoromethylene bridges on the electronegativity. The photophysical properties of **9** in thin film are in line with packing analysis, which gave fundamental insights into the design of n-type organic semiconductor materials. Further studies on the evaluation of the performances of electron mobilities in OFETs are now in progress.

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References and Notes

1 For a recent review on organic electronics, see the special issue of Chemistry of Materials: S. A. Jenekhe, *Chem. Mater.* **2004**, *16*, 4381.

2 a) C. R. Newman, C. D. Frisbie, D. A. da Silva Filho, J.-L. Brédas, P. C. Ewbank, K. R. Mann, *Chem. Mater.* **2004**, *16*, 4436. b) A. Facchetti, M.-H. Yoon, T. J. Marks, *Adv. Mater.* **2005**, *17*, 1705.

3 a) A. Facchetti, Y. Deng, A. Wang, Y. Koide, H. Sirringhaus, T. J. Marks, R. H. Friend, *Angew. Chem., Int. Ed.* **2000**, *39*, 4547. b) A. Facchetti, M.-H. Yoon, C. L. Stern, G. R. Hutchison, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **2004**, *126*, 13480.

4 a) Y. Ie, Y. Umemoto, T. Kaneda, Y. Aso, *Org. Lett.* **2006**, *8*, 5381. b) Y. Ie, M. Nitani, M. Ishikawa, K.-i. Nakayama, H. Tada, T. Kaneda, Y. Aso, *Org. Lett.* **2007**, *9*, 2115.

5 T. Hadizad, J. Zhang, Z. Y. Wang, T. C. Gorjanc, C. Py, *Org. Lett.* **2005**, *7*, 795.

6 a) J. P. M. Serbena, I. A. Hümmelgen, T. Hadizad, Z. Y. Wang, *Small* **2006**, *2*, 372. b) C. Py, T. C. Gorjanc, T. Hadizad, J. Zhang, Z. Y. Wang, *J. Vac. Sci. Technol., A* **2006**, *24*, 654. c) T. Hadizad, J. Zhang, D. Yan, Z. Y. Wang, J. P. M. Serbena, M. S. Meruvia, I. A. Hümmelgen, *J. Mater. Sci.: Mater. Electron.* **2007**, *18*, 903.

7 The synthesis and only photophysical properties of the tetrakis(trifluoromethyl)indenofluorene have been reported: J. P. Amara, T. M. Swager, *Macromolecules* **2006**, *39*, 5753.

8 S. Merlet, M. Birau, Z. Y. Wang, *Org. Lett.* **2002**, *4*, 2157.

9 M. Kuroboshi, T. Hiyama, *J. Fluorine Chem.* **1994**, *69*, 127.

10 As pentafluorophenylboronic acid was inactive under normal reaction conditions, we applied the modified reaction condition to obtain **6**: T. Korenaga, T. Kosaki, R. Fukumura, T. Ema, T. Sakai, *Org. Lett.* **2005**, *7*, 4915.

11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

12 M.-H. Yoon, A. Facchetti, C. E. Stern, T. J. Marks, *J. Am. Chem. Soc.* **2006**, *128*, 5792.

13 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 658930–658933. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

14 Recently, carbonyl-functionalized oligothiophenes have been reported. However, their packing diagrams are unknown: M.-H. Yoon, S. A. DiBenedetto, A. Facchetti, T. J. Marks, *J. Am. Chem. Soc.* **2005**, *127*, 1348.

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