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Perfluoroalkyl-annelated conjugated systems toward n-type organic semiconductors*

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Abstract: The syntheses of perfluoroalkyl-annelated conjugated units: hexafluorocyclopenta[*c*]thiophene, 4,4-difluoro-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophene, and 6,6,12,12tetrafluoroindeno[3,2-*b*]fluorine, and these-containing oligomers have been accomplished. The annelation of the perfluoroalkyl groups effectively lowers the lowest unoccupied molecular orbitral (LUMO) energy levels without disrupting the effective conjugation of the backbones, which was unambiguously clarified by spectroscopic and electrochemical measurements as well as X-ray analysis. The perfluoroalkyl-annelated oligothiophenes exhibited n-type semiconducting behavior with field-effect electron mobility up to 0.018 cm² V⁻¹ s⁻¹.

Keywords: conjugated oligomer; n-type semiconductors; OFET devices; HOMO; LUMO; field-effect mobility.

INTRODUCTION

Structurally well-defined π -conjugated systems have been intensively investigated as advanced organic electronic materials such as organic field-effect transistors (OFETs), light-emitting diodes (OLEDs), and photovoltaic devices (solar cells) [1]. Especially, much attention has been focused on the development of active materials for OFETs [2]. However, the studies of π -conjugated systems with electron-transporting ability for n-type semiconductors are still limited as compared with those of hole-transporting systems. It has been well known that the introduction of electron-withdrawing groups into π -conjugated systems stabilizes the lowest unoccupied molecular orbitral (LUMO) energy and increases electron-transporting ability [3]. In this context, a perfluoroalkyl group has become a good leading candidate of electron-withdrawing groups owing to its stability, strong electron-withdrawing nature, and solubilizing effect [4–6]. We have recently developed newly designed perfluoroalkyl-annelated conjugated systems. Here, we present our research on the development of hexafluorocyclopenta[*c*]thiophene, 4,4-difluoro-4H-cyclopenta[2,1-*b*:3,4-*b*']dithiophene, and 6,6,12,12-tetrafluoroindeno[3,2-*b*]fluorine units and these-containing oligomers and on the evaluation of their potential as n-type OFETs.

RESULTS

Hexafluorocyclopenta[c]thiophene and its oligothiophenes

The introduction of perfluoroalkyl groups to both β -positions of the thiophene ring is expected to increase the electronegativity of oligothiophenes. However, such chemical modification might cause se-

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vere inhibition of the degree of conjugation, because it was speculated that β -perfluoroalkyl groups have significantly greater steric constraints than the corresponding alkyl substituents (Fig. 1, A) [5]. Previously, we have reported on the synthesis and properties of oligothiophenes **B** and revealed that the effective conjugation is maintained by fastening alkyl groups at every β -position as the cyclopentene ring annelations [7]. In this regard, we anticipated that the ring fusion of hexafluorocyclopentene to both β -sites of the thiophene ring (**C**) contributes to not only lowering the LUMO level but also keeping the conjugation between consecutive thiophene rings in its based oligomers. Actually, the calculated highest occupied molecular orbital (HOMO) and LUMO energy levels and dihedral angles of bithiophenes **D** and **E** are consistent with our predictions (Fig. 1) [8].



Fig. 1 Perfluoroalkyl-substituted bithiophene (**A**), cyclopenta[*c*]thiophene oligomers (**B**), hexafluorocyclopenta[*c*]thiophene (**C**), and calculated HOMO and LUMO energies of bithiophenes **D** and **E**.

We have recently succeeded in constructing a unique synthetic route based on a combination of two fluorination reactions to form 3 and in synthesizing conjugated oligomers from 3 (Scheme 1) [9].



Scheme 1 Synthetic route of hexafluorocyclopenta[c]thiophene and its based oligomers.

The UV–vis absorption and cyclic voltammetry (CV) data of 4, 3T, and $3T(\beta \cdot R_f)$ were summarized in Table 1 [9]. Compared with that of $3T(\beta \cdot R_f)$, the absorption maximum of 4 is largely redshifted. On CV measurement, 4 showed both irreversible oxidation and reduction peaks, and their potentials are much higher than those of 3T. It is important to note that the reduction potential of 4 is positively shifted compared with that of $3T(\beta \cdot R_f)$. These results clearly indicate that the introduction of the hexafluorocyclopentene unit does not break the conjugation between thiophene units but does effectively enhance the electronegativity of the oligothiophenes.

 Table 1 Electronic absorption and CV data for the oligomers.

Comp.	Abs _{max} /nm ^a	$E_{\rm pa}/{\rm V^b}$	$E_{\rm pc}/{\rm V^b}$
4	373	+1.63 ^c	-1.72 ^c
$\frac{\mathbf{3T}}{\mathbf{3T}(\boldsymbol{\beta}\mathbf{-R_f})^d}$	354 304	+1.15 ^c +2.01	nd (<-2.00) -2.23

3T C₆F₁₃ F₁₃C₆ S 3T(β-R_f)

^aIn CH₂Cl₂. ^bIn C₆H₅F 0.1 M TBAPF₆, V vs Fc/Fc⁺. ^cIrreversible. ^dIn THF, see ref. 5a.

The X-ray crystallographic analysis of newly synthesized oligomer **5** was performed [10,11]. As shown in Fig. 2, the dihedral angles between the adjacent thiophene rings are 22.8 and 16.3°, which are consistent with the estimation of the above-mentioned theoretical calculation. Oligomer **5** exhibited a π -overlapped arrangement with minimum interplanar distance of 3.49 Å, being a good packing diagram for OFET materials. A bottom-contact FET device fabricated by the vacuum-deposition film of **5** on a SiO₂/Si substrate exhibited a typical n-type FET response, and its drain-source current (I_{ds}) characteristics with different gate voltage (V_g) were presented in Fig. 3. The estimated field-effect electron mobility is 1.8×10^{-4} cm² V⁻¹ s⁻¹.



Fig. 2 Molecular structure and crystal packing of 5.



Fig. 3 Output characteristics of the FET device using 5.

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Difluoromethylene-bridged bithiophene and its oligothiophenes

The calculated frontier orbitals of hexafluorocyclopenta[*c*]thiophene (**C**) indicated that the antibonding σ^* C–F orbitals at the benzylic positions effectively participate with the LUMO as shown in Fig. 4 and thus lower its orbital energy [8]. Based on this finding, we anticipated that the bridging of a bithiophene unit with a difluoromethylene group contributes to not only keeping the conjugation between the thiophene rings by fixing the conformation but also lowering the LUMO energy by rather effective orientation of the C–F bonds against the bithiophene π -orbital (Fig. 4). As we expected, theoretical calculations indicate that difluoromethylene-bridged **6** has an almost flat conformation of the bithiophene π -system like methylene-bridged **7**: the dihedral angles between the thiophene rings are 0.1°, and the LUMO energy of **6** is 0.73 eV lower than that of **7**, whereas a decrease in HOMO energy from **7** to **6** is 0.41 eV [8].



Fig. 4 Calculated LUMOs of C and 6 and calculated HOMO and LUMO energies of 6 and 7.

The synthesis of **6** has been accomplished by the fluorination reaction of the corresponding carbonyl compound via thioketalization, and conjugated oligomers **8** and **9** (Fig. 5) were prepared by Stille coupling reactions [12]. The substitution of fluorine atoms for the hydrogens at the bridging position in **7** results in a bathochromic shift of absorption maximum of **6** by 38 nm and positive potential shifts of both oxidation and reduction peaks. These results are consistent with theoretical predictions.



Fig. 5 Structures of 4,4-difluoro-4H-cyclopenta[2,1-b:3,4-b']dithiophene (6), 8, and 9.

As shown in Fig. 6, the crystallographic structure of **8** definitely confirms the expected nearly coplanar geometry owing to the difluoromethylene bridging. The packing diagram exhibits a favorable π -stacking pattern with regular intervals: the intermolecular face-to-face distance between the π -backbones is 3.6 Å, the value of which is slightly larger than typical interactions of carbon-based conjugated systems (3.4 Å).



Fig. 6 Molecular structure and packing diagram of 8.

The charge carrier mobilities of **8** and **9** were measured on top-contact OFET devices, in which the organic layers were fabricated by vacuum deposition. As shown in Fig. 7, both the devices showed n-type FET behavior with field-effect electron mobility of 1.8×10^{-2} cm² V⁻¹ s⁻¹ (I_{on}/I_{off} : 1.3×10^{3}) for **8** and 1.4×10^{-3} cm² V⁻¹ s⁻¹ (I_{on}/I_{off} : 5.4×10^{2}) for **9**.



Fig. 7 Transfer characteristics of 8 (left) and 9 (right) at 100 V of drain voltage.

Difluoromethylene-bridged terphenyl and its derivatives

We have extended our work of the perfluoroalkyl-annelated conjugated systems to phenylene oligomers and have designed 6,6,12,12-tetrafluoroindeno[3,2-*b*]fluorene as a new coplanar electron-transporting unit. Although some indenofluorene derivatives are known to behave as p-type semiconductors in OLEDs and OFETs [13,14], an indenofluorene derivative bearing geminal trifluoromethyl substituents at 6,6,12,12-positions has been known as only one candidate for electronegative materials [15]. Therefore, exploring new indenofluorene units with electronegative character still remains of great interest. The synthesis of 6,6,12,12-tetrafluoroindeno[3,2-*b*]fluorene (**10**) and its 2,8-diaryl derivatives **11–13** (Fig. 8) was accomplished by the two-step fluorination reaction of indeno[3,2-*b*]fluorine-6,12dione and subsequent Suzuki coupling reactions, respectively [16].



Fig. 8 Structures of 6,6,12,12-tetrafluoroindeno[3,2-b]fluorene (10) and its 2,8-diaryl derivatives.

The CV of **10** in fluorobenzene showed reduction peak potential at -2.46 V vs Fc/Fc⁺ together with oxidation potential at +0.97 V, while the reduction potential of 6,12-dihydroindeno[3,2-*b*]fluorene lies at -2.79 V. This positive reduction-potential shift of **10** clearly indicates that the electron affinity increases upon the substitution of fluorine atoms for hydrogens at the two bridging positions in indenofluorene. The electrochemically determined 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.

Although the low solubility of oligomers 11-13 in organic solvents prevented us from measuring their CVs, the LUMO energies of 11 and 12 were estimated to be -2.88 and -2.93 eV, respectively, based on their HOMO energy levels of -5.60 eV for 11 and -5.91 eV for 12 that were determined by an ambient photoelectron spectroscopy method using the vacuum-deposited films on glass substrates, and their optical HOMO–LUMO gaps obtained from the UV–vis absorption edge. The estimated LUMO energy of 11 exhibits a much lower value than that of the corresponding methylene-bridged oligomer (-2.0 eV) [14a], also highlighting the contribution of the difluoromethylene bridges to increasing the electronegativity.

Figure 9 shows the crystallographic molecular and packing structures of **11**, **12**, and **13**. As we expected, the indenofluorene unit displays nearly coplanar geometries. Torsion angles between the central indenofluorene and terminal aryl units are 35.8° , 16.9° , and 7.6° for **11**, **12**, and **13**, respectively. Interestingly, the introduction of carbonyl group at the terminal position has an improving effect on coplanarity of the whole molecular conjugation as well as face-to-face stacking, which are concomitant with the occurrence of CH–carbonyl interactions between the stacking columns. The nearly ideal



Fig. 9 Molecular structures of 11 (a), 12 (b), and 13 (c) and packing diagrams of 11 (d), 12 (e), and 13 (f).

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 π -stacked geometry of 13 will give fundamental insights into the design of n-type organic semiconductor materials.

CONCLUSION

In summary, we demonstrated the synthesis and properties of a series of perfluoroalkyl-annelated conjugated systems and revealed the influence of the perfluoroalkyl annelation on the electronegativity by spectroscopic measurements, X-ray analyses, and OFET performances. This molecular design enabled us to open a clue for the development of new materials for n-type OFETs. Further studies on the evaluation of the performances of electron mobilities in OFETs as well as the modification of the molecular structure to gain insight into structure–property–FET characteristic relationships are still in progress.

EXPERIMENTAL

Experimental procedure for the synthesis of 5. Compound **4** (300 mg, 0.757 mmol) was placed in a 50-mL two-necked flask and dissolved with tetrahydrofuran (THF) (8 mL). To the solution was added TMEDA (528 mg, 4.55 mmol) and *n*-BuLi (1.58 M hexane solution, 1.9 mL, 3.03 mmol) at -78 °C under N₂ atmosphere. After being stirred for 0.5 h, Bu₃SnCl (0.82 mL, 3.03 mmol) was added. The mixture was gradually warmed up to room temperature, and then the reaction was quenched by addition of water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with H₂O, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on alumina (hexane) and then by gel permeation chromatography (GPC) (CHCl₃) to give the distannyl compound (559 mg, 76 %).

The distannyl compound (315 mg, 0.32 mmol), 4'-bromo-2,2,2-trifluoroacetophenone (205 mg, 0.81 mmol), and tetrakis(triphenylphosphine)palladium(0) (37 mg, 0.032 mmol) were placed in a test tube and dissolved with toluene (3 mL). The mixture was stirred at 120 °C for 12 h. After the mixture was cooled to room temperature, the resulting precipitate was collected, washed several times with hexane, then dried in vacuo to give **5** (103 mg, 43 %).

Red solid; mp 258–261 °C; ¹H NMR (CDCl₃) δ 8.13 (d, 4H, J = 8.0 Hz), 7.80 (d, 4H, J = 8.7 Hz), 7.50 (d, 2H, J = 3.9 Hz), 7.53 (d, 2H, J = 3.9 Hz); MS (EI) m/z 740 (M⁺); anal. calcd for C₃₁H₁₂F₁₂O₂S₃: C, 50.27; H, 1.63; found: C, 49.88; H, 1.25.

FET device fabrications. The field-effect mobility of **5** was measured using bottom-contact thinfilm field-effect transistor (FET) geometry. The n-doped silicon substrate functions as the gate electrode. A 300-nm-thick silicon oxide dielectric layer was thermally grown on the gate substrate. Interdigital source and drain electrodes were constructed with gold films (30 nm) that were formed on the SiO₂ layer. The channel width and length are 38 mm and 5 μ m, respectively. The silicon oxide surface was first washed with acetone and *i*-PrOH. The silicon oxide surface was then activated by ozone treatment and pretreated with HMDS. The semiconductor layer was vacuum-deposited on the Si/SiO₂ substrate maintained at 70 °C at a rate of 0.5 Å /s under a pressure of 4.0×10^{-6} Pa to a thickness of 35 nm determined by a quartz crystal monitor. The characteristics of the OFET devices were measured at room temperature under a pressure of 2.0×10^{-6} Pa. The field-effect mobility was calculated in the saturated region at the $V_{\rm DS}$ of 100 V. Current on/off ratio was determined from the $I_{\rm DS}$ at $V_{\rm g} = 0$ V ($I_{\rm off}$) and $V_{\rm g} = 120$ V ($I_{\rm on}$).

The field-effect mobility of the **8** and **9** was measured using top-contact thin-film FET geometry. The n-doped silicon substrate functions as the gate electrode. A 300-nm-thick silicon oxide dielectric layer with a capacitance of 11.8 nF cm⁻² was thermally grown on the gate substrate. The silicon oxide surface was first washed with acetone, toluene, methanol, and deionized water. The silicon oxide surface was then activated by ozone treatment and pretreated with HMDS at 50 °C for 10 h. The semi-

conductor layer was vacuum-deposited on the Si/SiO₂ substrate maintained at 90 °C at a rate of 2 Å/s under a pressure of 1.0×10^{-5} Torr to a thickness of 15 nm determined by a quartz crystal monitor. On the top of the semiconductor layer, gold films (30 nm) as source and drain electrodes were deposited by using shadow masks with a channel width (5.5 mm) and a channel length (100 µm). The characteristics of the OFET devices were measured at room temperature under a pressure of 3.0×10^{-4} Torr. The field-effect mobility was calculated in the saturated region at the $V_{\rm DS}$ of 100 V. Current on/off ratio was determined from the $I_{\rm DS}$ at $V_{\rm g} = 32$ V ($I_{\rm off}$) and $V_{\rm g} = 100$ V ($I_{\rm on}$) for **8** and from the $I_{\rm DS}$ at $V_{\rm g} = 41$ V ($I_{\rm off}$) and $V_{\rm g} = 100$ V ($I_{\rm on}$) for **9**.

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