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Electronegative Oligothiophenes for n-Type Semiconductors: Difluoromethylene-Bridged Bithiophene and Its Oligomers

Yutaka Ie,[†] Masashi Nitani,[†] Motomi Ishikawa,[‡] Ken-ichi Nakayama,[‡]
Hirokazu Tada,[§] Takahiro Kaneda,[†] and Yoshio Aso*,[†,‖]

The Institute of Scientific and Industrial Research, Osaka University, 8-1, Mihogaoka,
Ibaraki, Osaka 567-0047, Japan, CREST, Japan Science and Technology Agency
(JST), Japan, Department of Material and Life Science, Graduate School of
Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka, 565-0871, Japan, and
Graduate School of Engineering Science, Osaka University, Toyonaka,
Osaka 560-8531, Japan

aso@sanken.osaka-u.ac.jp

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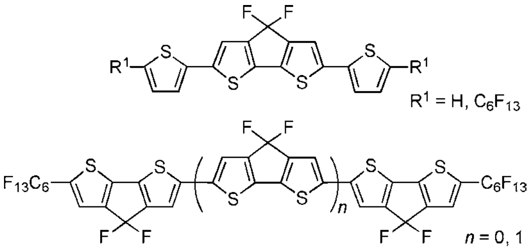
ABSTRACT



The synthesis of difluoromethylene-bridged bithiophene and its oligothiophenes are reported. The spectroscopic and electrochemical measurement as well as X-ray analyses unambiguously revealed that the difluoromethylene bridge largely contributes to keeping planarity between the thiophene rings and lowering the LUMO level. The perfluorohexyl-substituted quaterthiophene derivatives showed n-type semiconducting behavior with field-effect electron mobilities up to 0.018 cm^2 V^{-1} s^{-1}.

Thiophene-based oligomers and polymers have been attracting a great deal of attention because of their applicability to active electronic materials for organic field-effect transistors (OFETs), light-emitting diodes (OLEDs), and photovoltaic devices (solar cells).[1] Among them, OFETs have been the most actively investigated and seem to reach the practical stage.[2] However, the study of oligothiophenes with electron-transporting (n-type) ability is still limited as compared with that of hole-transporting (p-type) oligothiophenes. Recently, it has been systematically unveiled that π-conjugated systems incorporated with electron-withdrawing groups,[3,4] especially

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[†] The Institute of Scientific and Industrial Research.
[‡] Graduate School of Engineering.
[§] Graduate School of Engineering Science.
[‖] JST-CREST.

(1) For recent reviews on functional oligothiophenes, see: (a) Roncali, J. *J. Mater. Chem.* **1999**, *9*, 1875−1893. (b) *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, Germany, 1999. (c) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Rev.* **2001**, *34*, 359−369. (d) Otsubo, T.; Aso, Y.; Takimiya, K. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1789−1801. (e) Otsubo, T.; Aso, Y.; Takimiya, K. *J. Mater. Chem.* **2002**, *12*, 2565−2574.

(2) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; Macdonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabinyc, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. *Nat. Mater.* **2006**, *5*, 328−333.

(3) (a) Newman, C. R.; Frisbie, C. D.; da Silva Filho, D. A.; Brédas, J.-L.; Ewbank, P. C.; Mann, K. R. *Chem. Mater.* **2004**, *16*, 4436−4451. (b) Facchetti, A.; Yoon, M.-H.; Marks, T. J. *Adv. Mater.* **2005**, *17*, 1705−1725.

(4) Sakamoto, Y.; Komatsu, S.; Suzuki, T. *J. Am. Chem. Soc.* **2001**, *123*, 4643−4644.

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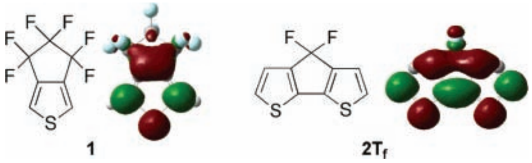
perfluoroalkyl groups, dramatically increase n-type character.[5−7] In addition, we have reported the synthesis of the hexafluorocyclopenta[*c*]thiophene unit **1** and its oligomers.[8] The spectroscopic measurements and X-ray analyses of these oligomers revealed that this unit effectively induces electronegative character without disturbing effective conjugation of the backbone π-systems. The calculated frontier orbitals of **1** at the B3LYP/6-31G(d,p) level[9] indicated that the antibonding σ^* C−F orbitals at the benzylic positions participate in the LUMO as shown in Figure 1 (left) and thus lower its orbital energy. On the basis of these findings, we anticipated that 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 (Figure 1, right). Here, we report on the synthesis and properties of newly designed electronegative difluoromethylene-bridged bithiophene $\mathbf{2T_f}$ and its oligothiophenes for n-type OFET materials.



1 $\mathbf{2T_f}$

Figure 1. Calculated LUMOs of **1** (left) and $\mathbf{2T_f}$ (right).

We focused on a desulfurative fluorination reaction as a key step for the preparation of difluoromethylene-bridged bithiophene $\mathbf{2T_f}$ as shown in Scheme 1. Thioketalization of 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophen-4-one (**2**)[10] with 1,2-ethanedithiol in the presence of $AlCl_3$ gave 1,3-dithiolane **3** in 89% yield,[11] which was then converted to the corresponding difluoromethylene-bridged dibromo compound **4** by treatment with HF•pyridine and NBS (57%).[12] Subsequent debromination of **4** with $LiAlH_4$ (LAH) gave $\mathbf{2T_f}$ in 95% yield. The structure of $\mathbf{2T_f}$ was unambiguously verified by GC−MS, ^1H, ^{13}C, and ^{19}F NMR spectroscopy, and elemental analysis.

Scheme 1. Synthesis of Difluoromethylene-Bridged Bithiophenes

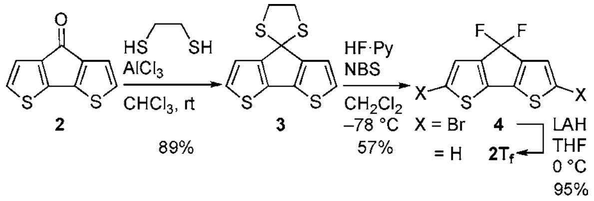


Table 1 shows the electronic absorption and cyclic voltammetry (CV) data of $\mathbf{2T_f}$ together with those of 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene ($\mathbf{2T_h}$).[13] The substitution of fluorine atoms for the hydrogens at the bridging position in $\mathbf{2T_h}$ results in a bathochromic shift of absorption maximum by 38 nm and shifts to more positive potentials for both the oxidation and reduction processes. Theoretical calculations for difluoromethylene-bridged $\mathbf{2T_f}$ and methylene-bridged $\mathbf{2T_h}$ at the B3LYP/6-31G(d,p) level[9] indicated almost flat conformations of both the bithiophene π-sytems; the dihedral angles between the thiophene rings are 0.1°. The calculated LUMO energy of $\mathbf{2T_f}$ is 0.73 eV lower than that of $\mathbf{2T_h}$, whereas a decrease in HOMO energy from $\mathbf{2T_h}$ to $\mathbf{2T_f}$ is 0.41 eV as shown in the Supporting Information (Figure S1). The above-mentioned bathochromic shift of absorption and the positive shifts of both the oxidation and reduction potentials are consistent with these theoretical predictions.

Table 1. Spectroscopic and CV Data for the Bithiophenes

compd	abs_{max}/nm^a	E_{pa}/V^b	E_{pc}/V^b
$\mathbf{2T_f}$	348	+0.99^c	−2.42^c
$\mathbf{2T_h}$	310	+0.68^c	−2.88^c

^{a} In THF. ^{b} In C_6H_5F, 0.1 M *n*-Bu_4NPF_6, V vs Fc/Fc^+. ^{c} Irreversible.

The promising electronegativity and coplanarity of the $\mathbf{2T_f}$ unit as well as its expected chemical stability by the substitution of fluorine atoms at the bridging position in $\mathbf{2T_h}$[14] have convinced us that it is a viable building unit for

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(5) (a) Facchetti, A.; Deng, Y.; Wang, A.; Koide, Y.; Sirringhaus, H.; Marks, T. J.; Friend, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 4547−4551. (b) Facchetti, A.; Mushrush, M.; Katz, H. E.; Marks, T. J. *Adv. Mater.* **2003**, *15*, 33−38. (c) Li, L.; Counts, K. E.; Kurosawa, S.; Teja, A. S.; Collard, D. M. *Adv. Mater.* **2004**, *16*, 180−183.

(6) (a) Facchetti, A.; Yoon, M.-H.; Stern, C. L.; Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 13480−13501. (b) Facchetti, A.; Mushrush, M.; Yoon, M.-H.; Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 13859−13874.

(7) (a) Ando, S.; Nishida, J.; Fujiwara, E.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *Chem. Mater.* **2005**, *17*, 1261−1264. (b) Ando, S.; Nishida, J.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *J. Am. Chem. Soc.* **2005**, *127*, 5336−5337. (c) Ando, S.; Murakami, R.; Nishida, J.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *J. Am. Chem. Soc.* **2005**, *127*, 14996−14997.

(8) Ie, Y.; Umemoto, Y.; Kaneda, T.; Aso, Y. *Org. Lett.* **2006**, *8*, 5381−5384.

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; *Gaussian 03*, Revision B.04; Gaussian, Inc.: Wallingford, CT.

(10) Brzeziński, J. Z.; Reynolds, J. R. *Synthesis* **2002**, 1053−1056.

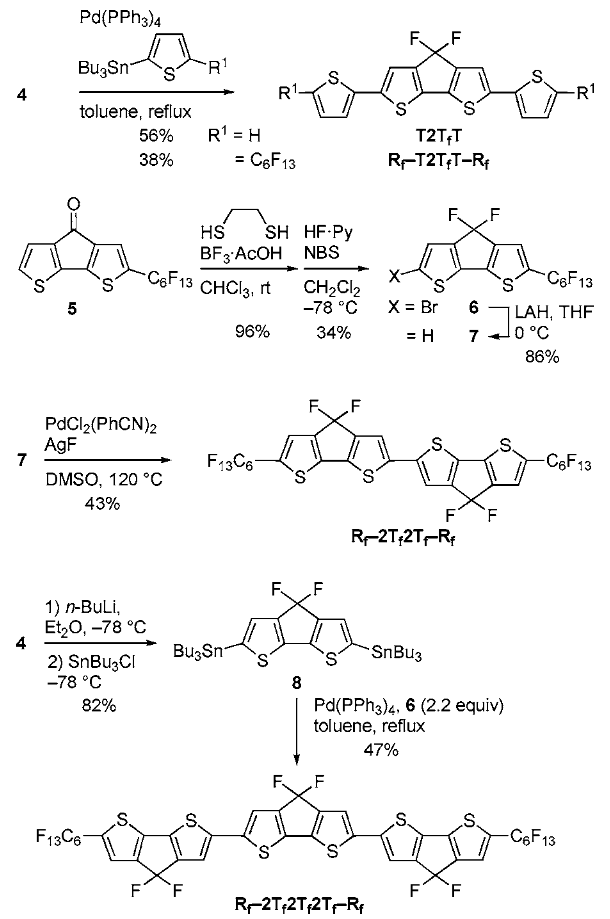
(11) Ong, B. S. *Tetrahedron Lett.* **1980**, *21*, 4225−4228.

(12) (a) Sondej, S. C.; Katzenellenbogen, J. A. *J. Org. Chem.* **1986**, *51*, 3508−3513. (b) Kuroboshi, M.; Hiyama, T. *J. Fluorine Chem.* **1994**, *69*, 127−128.

(13) Coppo, P.; Cupertino, D. C.; Yeates, S. G.; Turner, M. L. *Macromolecules* **2003**, *36*, 2705−2711.

electronegative oligomeric materials. Thus, a series of quaterthiophenes and sexithiophene were synthesized as shown in Scheme 2.[15]

Scheme 2. Synthesis of Difluoromethylene-Bridged Oligothiophenes



Taking account of the application for n-type OFETs, we have installed perfluorohexyl groups at the terminal α,ω-positions.[5] Palladium-catalyzed Stille coupling of **4** with 2-tributylstannylthiophene or 2-perfluorohexyl-5-tributylstannylthiophene yielded the quaterthiophenes **T2T$_f$T** or **R$_f$−T2T$_f$T−R$_f$**, respectively, in moderate yields. The key starting material **5** for the synthesis of homogeneous oligomers was facilely prepared from known spiro[4*H*-cyclopenta-[2,1-*b*:3,4-*b*′]dithiophene-4,2′-[1,3]dioxolane][16] by a two-step reaction (see the Supporting Information). In a similar manner to the preparation of **2T$_f$**, except for the use of a BF_3·AcOH catalyst instead of $AlCl_3$ to avoid chlorination of the benzylic C−F bonds,[17] the ketone **5** was transformed into **7**. Palladium-catalyzed oxidative homocoupling of **7** in the presence of AgF gave the quaterthiophene **R$_f$−2T$_f$2T$_f$−R$_f$** in 43% yield.[18] The sexithiophene **R$_f$−2T$_f$2T$_f$2T$_f$−R$_f$** was synthesized by Stille coupling of **8** with 2.2 equiv of **6** and subsequently sublimed twice under a high vacuum to produce the pure product in a yield of 47%.

Single crystals of **T2T$_f$T** and **R$_f$−T2T$_f$T−R$_f$** suitable for X-ray crystallographic analyses were grown from $CHCl_3$ and hexane−EtOAc solutions, respectively, by slow evaporation.[19] As shown in Figure 2, the crystallographic structures definitely confirm the expected nearly coplanar geometries owing to the difluoromethylene bridging. In contrast to an anti-syn-anti conformation of **T2T$_f$T**, **R$_f$−T2T$_f$T−R$_f$** adopts a syn-syn-syn conformation, which might be due to their packing force in the crystal.[20]

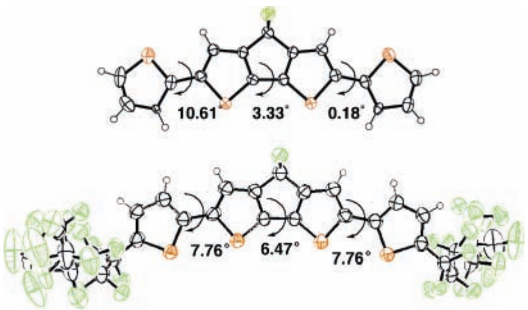


Figure 2. Molecular structures of **T2T$_f$T** (top) and **R$_f$−T2T$_f$T−R$_f$** (bottom).

The packing diagram of **R$_f$−T2T$_f$T−R$_f$**, as shown in Figure 3, exhibits a favorable π-stacking pattern with regular intervals, whereas that of **T2T$_f$T** is elusive and no π-stacking interaction is observed. Apparently, this difference is attributable to the presence of the terminal perfluorohexyl groups in **R$_f$−T2T$_f$T−R$_f$**.[6b] 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). On the other hand, the shortest intermolecular nonbonding distances for C−F and S−F are 3.07 and 3.27 Å, respectively, and these contacts are almost equal to the sum of their van der Waals radii (C−F: 3.17 Å; and S−F: 3.27 Å).[21]

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[14] (a) Pasini, M.; Destri, S.; Botta, C.; Porzio, W. *Tetrahedron* **1999**, *55*, 14985−14994. (b) Zotti, G.; Destri, S.; Porzio, W.; Pasini, M.; Rizzo, S.; Benincori, T. *Macromol. Chem. Phys.* **2001**, *202*, 3049−3056.

[15] All new compounds were fully characterized by spectroscopic measurements and elemental analyses; see the Supporting Information.

[16] Lucas, P.; Mehdi, N. E.; Ho, H. A.; Bélanger, D.; Breau, L. *Synthesis* **2000**, 1253−1258.

[17] Riera, J.; Castañer, J.; Carilla, J.; Robert, A. *Tetrahedron Lett.* **1989**, *30*, 3825−3828.

[18] Masui, K.; Ikegami, H.; Mori, A. *J. Am. Chem. Soc.* **2004**, *126*, 5074−5075.

[19] Crystal Data for **T2T$_f$T**: $C_{17}H_8F_2S_4$, $M = 378.49$, orthorhombic, space group *Pbca* (No. 61), $a = 10.5780(1)$ Å, $b = 7.9399(1)$ Å, $c = 37.4367(4)$ Å, $V = 3144.2(1)$ Å^3, $Z = 8$, $D_{calc} = 1.599$ g cm^{-3}, $F_{(000)} = 792.00$, $\mu = 0.618$ cm^{-1} (Mo Kα; $\lambda = 0.71069$ Å), 38070 reflections measured, 3543 unique, $R = 0.0857$ for $I > 2\sigma(I)$, $wR = 0.1674$ for all data. Crystal data for **R$_f$−T2T$_f$T−R$_f$**: $C_{29}H_6F_{28}S_4$, $M = 1014.58$, monoclinic, space group *C*2/*c* (No. 15), $a = 53.0849(14)$ Å, $b = 6.5227(2)$ Å, $c = 9.6315(5)$ Å, $\beta = 95.9290(14)°$, $V = 3317.1(2)$ Å^3, $Z = 4$, $D_{calc} = 2.032$ g cm^{-3}, $F_{(000)} = 1984$, $\mu = 4.394$ cm^{-1} (Cu Kα; $\lambda = 1.54187$ Å), 18235 reflections measured, 3018 unique, $R = 0.0809$ for $I > 2\sigma(I)$, $wR = 0.2449$ for all data.

[20] The energy difference between the anti-syn-anti conformer and the syn-syn-syn conformer for both **T2T$_f$T** and **R$_f$−T2T$_f$T−R$_f$** is calculated to be less than 1.0 kcal/mol.

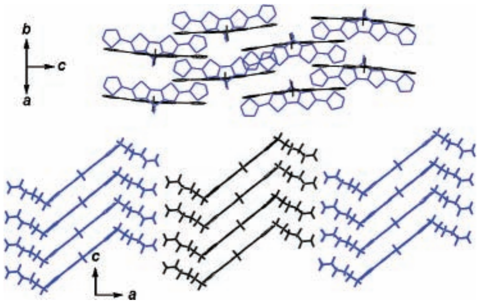
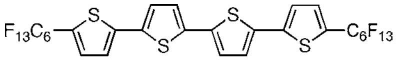


Figure 3. Packing diagrams of **T2T$_f$T** (top) and **R$_f$–T2T$_f$T–R$_f$** (bottom).

Table 2. Spectroscopic and CV Data for the Oligomers



R$_f$-4T-R$_f$

compd	abs$_{max}$/nm^a	flu$_{max}$/nm^a	E_{pa}/V^b	E_{pc}/V^b
T2T$_f$T	433	531	+0.57	−2.03
R$_f$–T2T$_f$T–R$_f$	433	519	+0.88	−1.95
R$_f$–2T$_f$2T$_f$–R$_f$	443	515	+0.98	−1.80
R$_f$–2T$_f$2T$_f$2T$_f$–R$_f$	490	576	*c*	
R$_f$–4T–R$_f$	396	458, 485	+0.82	−2.16

[a] In THF. [b] In C_6H_5F, 0.1 M *n*-Bu_4NPF_6, V vs Fc/Fc$^+$. [c] Not measured.

Table 2 summarizes the UV–vis absorption, fluorescence, and CV data of the oligomers together with the corresponding data of **R$_f$–4T–R$_f$**[5b] for comparison. The absorption maxima are red-shifted with increasing the number of **2T$_f$** units as seen for **R$_f$–T2T$_f$T–R$_f$** and **R$_f$–2T$_f$2T$_f$–R$_f$**, indicating effective conjugation between the **2T$_f$** units. Although the electronic spectra of **R$_f$–2T$_f$2T$_f$2T$_f$–R$_f$** were successfully measured, its low solubility precluded the investigation of electrochemical properties. The introduction of perfluorohexyl groups at the α,*ω*-positions has influence on both oxidation and reduction peaks as seen for **T2T$_f$T** and **R$_f$–T2T$_f$T–R**. As we expected, an increase in the number of **2T$_f$** units results in positive shifts to both the oxidation and reduction processes, with a slightly greater effect on the reduction potentials. This can be rationalized by the fact that the fluoromethylene bridging more effectively lowers the LUMO energy.

Finally, charge carrier mobilities were measured on OFET devices by using a top contact configuration.[22] The organic layers (15 nm) were fabricated by vacuum deposition with a stable rate of 2.0 Å/s. The transfer characteristics of **R$_f$–T2T$_f$T–R$_f$** and **R$_f$–2T$_f$2T$_f$–R$_f$** are presented in Figure 4. Both the devices showed n-type FET behavior with field-effect mobility of 1.8 × 10^{-2} cm^2 V^{-1} s^{-1} (I_{on}/I_{off}: 1.3 × 10^3) for **R$_f$–T2T$_f$T–R$_f$** and 1.4 × 10^{-3} cm^2 V^{-1} s^{-1} (I_{on}/I_{off}: 5.4 × 10^2) for **R$_f$–2T$_f$2T$_f$–R$_f$**.

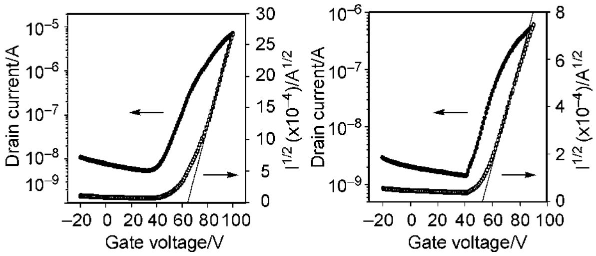


Figure 4. Transfer characteristics of **R$_f$–T2T$_f$T–R$_f$** (left) and **R$_f$–2T$_f$2T$_f$–R$_f$** (right) at 100 V of drain voltage.

In conclusion, we have achieved the synthesis of difluoromethylene-bridged bithiophene and its oligomers. The effectiveness of the bridging unit has been unambiguously revealed by the spectroscopic measurements and X-ray analyses, as well as by the OFET performance. Further work aimed at the optimization of OFET devices to obtain high charge–carrier mobility and at the elucidation of the structure–property–FET characteristic relationship will be reported in due course.

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Supporting Information Available: Synthesis and characterization of all compounds and crystallographic CIF files of **T2T$_f$T** and **R$_f$–T2T$_f$T–R$_f$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

(22) For details of FET devices as well as XRDs of **R$_f$–T2T$_f$T–R$_f$** and **R$_f$–2T$_f$2T$_f$–R$_f$** see the Supporting Information.