Supporting Information-OL

An Effective Strategy to Tune Supramolecular Interaction *via* Spiro-bridged Spacer in Oligothiophene-*S*,*S*-dioxides and Their Anomalous Photoluminescent (PL) Behavior

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Chemicals. Magnesium turnings, *N*-bromosuccinimide (NBS), 3-bromothiophene, fluorenone, $Me_2{}^tBuSiCl$, and *m*-chloroperbenzoic acid (*m*-CPBA) were obtained from Aldrich Chemical Co. and were used without further purification. Spiro[cyclopenta[1,2-b:4,3-b']dithiophene-7,9'-fluorene] (SDTF) was prepared as previously reported. THF and diethyl ether were dried over sodium benzophenone ketyl anion radical and distilled under a dry nitrogen atmosphere immediately prior to use.

Procedures. ^{1}H- and ^{13}C-NMR in $CDCl_3$ were recorded at 400 MHz using a Varian Mercury 400 plus spectrometer. Mass spectra were recorded on a Shimadzu GCMS-QP2010 plus equipped with DB-5 ms column or a Shimadzu AXIMA-CFR *plus* spectrometer. The MALDI-TOF MS spectra were recorded in reflective mode, no substrates were used. Elemental analyses were carried out on an Elementar Analysensysteme GmbH Vario EL *III* Instrument. Absorption spectra (1 μM in CH_2Cl_2) were measured with a Shimadzu UV-3150 spectrometer at 25 °C, and emission spectra (1 μM in CH_2Cl_2) were recorded on a Shimadzu RF-530XPC luminescence spectrometer. Photoluminescence quantum yields (PLQY) were

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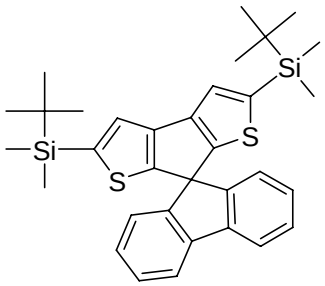
determined in dilute solutions (10^{-5} M) of $CHCl_3$ and cyclohexane, using quinine sulfate as reference, while for measurements on the solid state, samples were spin cast on a quartz substrate from $CHCl_3$ solution (5 mg mL^{-1}). The solid samples were placed into a 8 inch diameter integrating sphere and excited with a He–Cd CW laser (λ = 325 nm). Differential scanning calorimetry (DSC) analyses were performed on a Shimadzu DSC-60A Instrument. Thermogravimetric analyses (TGA) were conducted on a Shimadzu DTG-60H thermogravimetric Analyzer under a heating rate of 10 ^oC/min and a nitrogen flow rate of 20 cm^3/min. Cyclic voltammetric (CV) studies were conducted using an Eco Chemie B. V. AUTOLAB potentiostat in a typical three-electrode cell with a platinum sheet working electrode, a platinum wire counter electrode, and a silver/silver nitrate (Ag/Ag^+) reference electrode. All electrochemical experiments were carried out under a nitrogen atmosphere at room temperature in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF_6^-$) in CH_2Cl_2 at a sweeping rate of 0.1V/s. According to the redox onset potentials of the CV measurements, the HOMO/LUMO energy levels of the materials are estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum): HOMO/LUMO = $-(E_{onset} - 0.0468\ V) - 4.8$ eV, where the value 0.0468 V is for FOC vs Ag/Ag^+.

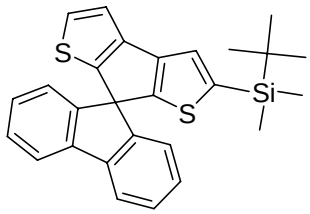
Data for X-ray structure analysis were collected at room temperature on a Bruker SMART 1K CCD area detector with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. Structures were solved by direct methods and refined against F^2 with the full-matrix, least-squares methods using SHELXS-97 and SHELXL-97, respectively. Crystal data for BSiSDTF: $C_{33}H_{40}S_2Si_2$, M = 556.95, colorless cuboid 0.35 × 0.20 × 0.20 mm, monoclinic, $P2_1/c$, Z= 8, a = 25.681(11) Å, b = 12.073(5) Å, c = 23.725 (10) Å, α = 90°, β = 117.111° (5), γ = 90°, V = 6547 (5) $Å^3$, F(000) = 2384, D_c = 1.130 Mg m^{-3}, μ (Mo K_α) = 0.255 mm^{-1}. Crystal data for BSiSDTFO: $C_{33}H_{40}O_2S_2Si_2$, M = 588.95, green needle 0.15 × 0.10 × 0.02 mm, triclinic, $P\bar{1}$, Z = 4, a = 12.45(4), b = 12.94(4), c = 22.63(7) (3) Å, α = 80.74°(5), β = 86.74°(5), γ = 79.99° (6), V = 3543 (18) $Å^3$, F(000) = 1256, D_c = 1.104 Mg m^{-3}, μ (Mo K_α) = 0.243 mm^{-1}.

Synthesis of 2,5-bis(dimethyl-*t*-butylsilyl)-spiro[cyclopenta[1,2-b:4,3-b'] dithiophene-7,9'-fluorene] (BSiSDTF)



To a solution of SDTF (1.0 g, 3.05 mmol, 1 equiv) in dry THF (10 mL) was added dropwise *n*-butyllithium (1.6 M in hexane, 3.8 mL, 6.1 mmol, 2 equiv) at room temperature. After 1 h, a solution of dimethyl-*tert*-butylsilyl chloride (0.921 g, 6.1 mmol, 2 equiv.) in THF (20 mL) was added dropwise. The reaction mixture was allowed to stir at room temperature overnight. Then water was added, the aqueous layer was extracted twice with ether, and the combined organic phases were dried over $MgSO_4$ and evaporated. After vacuum distillation, the solid residues were purified by column chromatography on silica gel with CH_2Cl_2/hexane to afford BSiSDTF as colorless solids (0.848 g, 50%). MALDI-TOF-MS (*m*/*z*): [M^+] calcd. For $C_{33}H_{40}S_2Si_2$, 556.2; Found: 556.1. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.796-7.777 (d, *J* = 8.0 Hz, 2 H), 7.397-7.359 (d, *J* = 7.6 Hz, 2 H), 7.306 (s, 2 H), 7.196-7.158 (t, *J* = 7.6 Hz, 2 H), 6.935-6.916 (d, *J* = 7.6 Hz, 2 H), 0.906 (s, 18 H), 0.256 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 156.818, 147.633, 145.403, 142.081, 141.209, 128.398, 128.214, 125.597, 124.148, 120.347, 62.785, 26.61, 17.193, -4.715.Anal. Calcd for $C_{33}H_{40}S_2Si_2$: C, 71.16; H, 7.24; S, 11.51; Si, 10.09. Found: C, 71.13; H, 7.23.

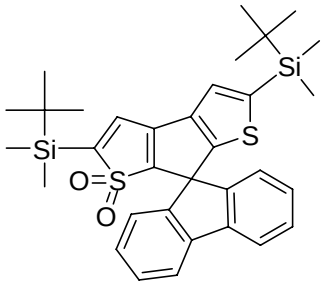
2-(Dimethyl-*t*-butylsilyl)-spiro[cyclopenta[1,2-b:4,3-b']dithiophene-7,9'-fluorene]



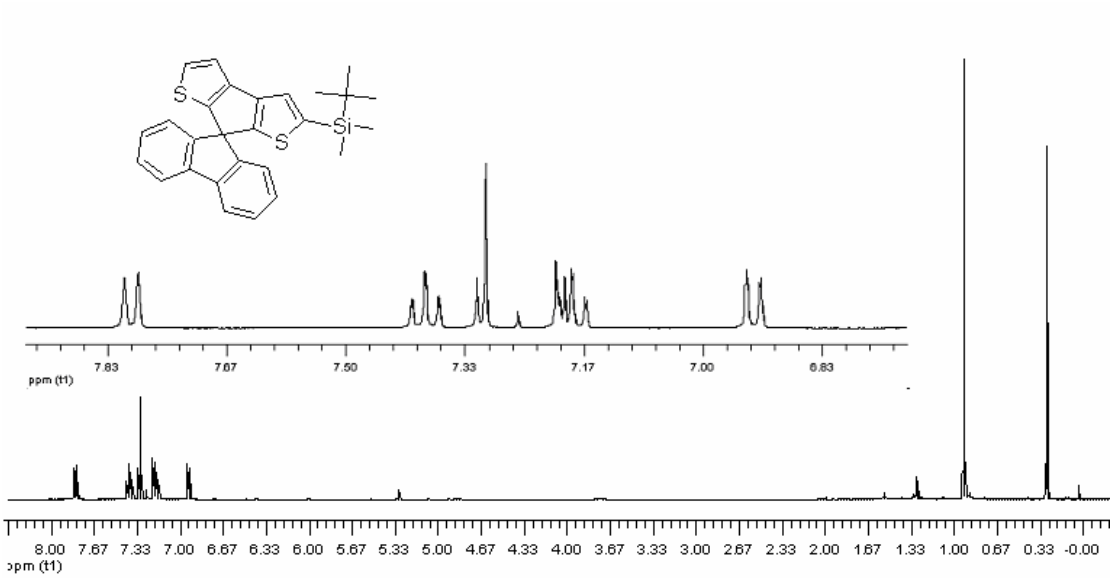
To afford byproduct 2-(dimethyl-*t*-butylsilyl)-spiro[cyclopenta [1,2-b:4,3-b']dithiophene-7,9'-fluorene] as colorless solids (0.405 g, 30%). GCMS

(*m*/*e*): 442. (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.809-7.79 (d, *J* = 7.6 Hz, 2 H), 7.408-7.368 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 2 H), 7.316-7.304 (d, s, *J* = 4.8 Hz, 2 H), 7.206-7.163 (t, d, *J* = 7.6 Hz, *J* = 4.8 Hz, 3 H), 6.938-6.919 (d, *J* = 7.6 Hz, 2 H), 0.922 (s, 9 H), 0.274 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 156.628, 150.74, 147.457, 145.572, 143.722, 142.22, 141.217, 128.959, 128.491, 128.258, 125.535, 124.088, 120.42, 118.384, 62.813, 26.63, 17.2, -4.684. Anal. Calcd for $C_{27}H_{26}S_2Si$: C, 73.25; H, 5.92; S, 14.49; Si, 6.34. Found: C, 73.21; H, 5.90.

2,5-Bis(dimethyl-*t*-butylsilyl)-spiro[cyclopenta[1,2-b:4,3-b']dithiophene-mono-S, S-dioxides -7,9'-fluorene] (**BSiSDTFO**)



To a solution of BSiSDTF (1.0 g, 1.8 mmol) in 30 mL of methylene chloride was added stepwise *m*-CPBA (70%) (1.864 g, 7.54 mmol, 4.2 equiv) at room temperature. The solution was stirred for about 48 h at room temperature. Then the mixture was quenched with a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2, and the organic phase was separated, dried over $MgSO_2$, and evaporated. The crude product was chromatographed on silica gel using cyclohexane:ethyl acetate (6:1) as the eluent to provide green monosulfone BSiSTDFO (0.424 g, 40% yield). MALDI-TOF-MS (*m*/*z*): [M^+] calcd. For $C_{33}H_{40}O_2S_2Si_2$, 588.2; Found: 588.3. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.79-7.772 (d, *J* = 7.6 Hz, 2 H), 7.42-7.38 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 2 H), 7.286 (s, 1 H), 7.26 (s, 1 H), 7.247-7.206 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 2 H), 7.048-7.029 (d, *J* = 7.6 Hz, 2 H), 1.002 (s, 9 H), 0.897 (s, 9 H), 0.297 (s, 6 H), 0.256 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.181, 155.217, 147.705, 144.887, 144.754, 141.896, 141.524, 141.446, 132.388, 129.15, 128.323, 125.675, 124.049, 120.809, 63.375, 26.6, 26.514, 17.474, 17.11, -4.783, -5.716. Anal. Calcd for $C_{33}H_{40}O_2S_2Si_2$: C, 67.30; H, 6.85; O, 5.43; S, 10.89; Si, 9.54. Found: C, 67.28; H, 6.88.



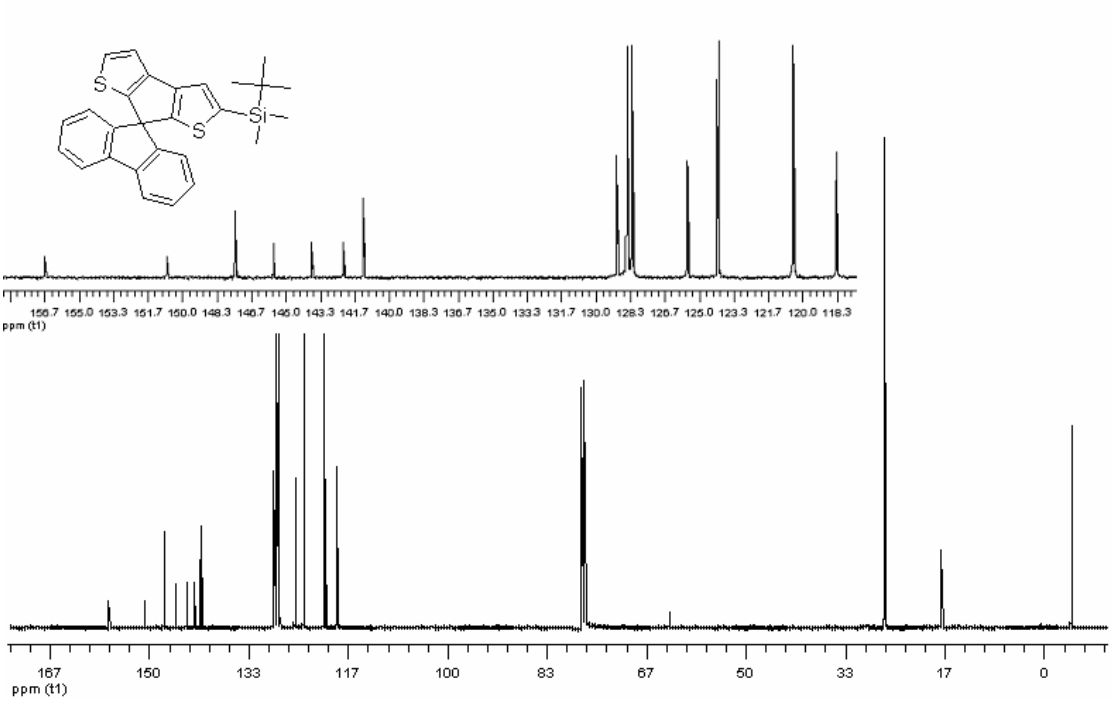
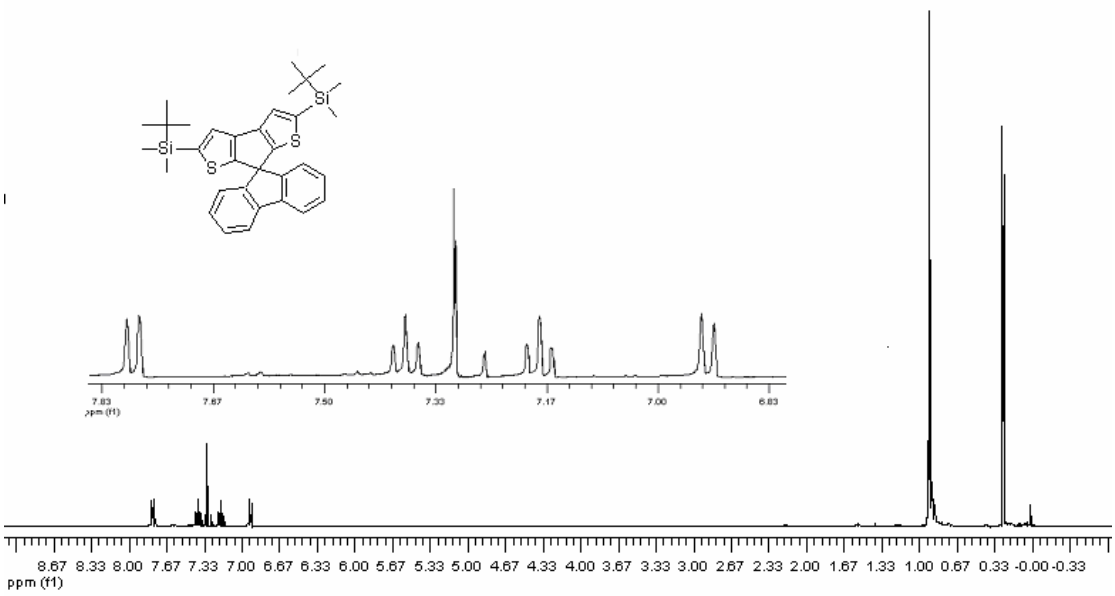


Figure SI-1. The ^{1}H-NMR and ^{13}C-NMR spectra of

2-(dimethyl-*t*-butylsilyl)-spiro[cyclopenta[1,2-b:4,3-b']dithiophene-7,9'-fluorene].



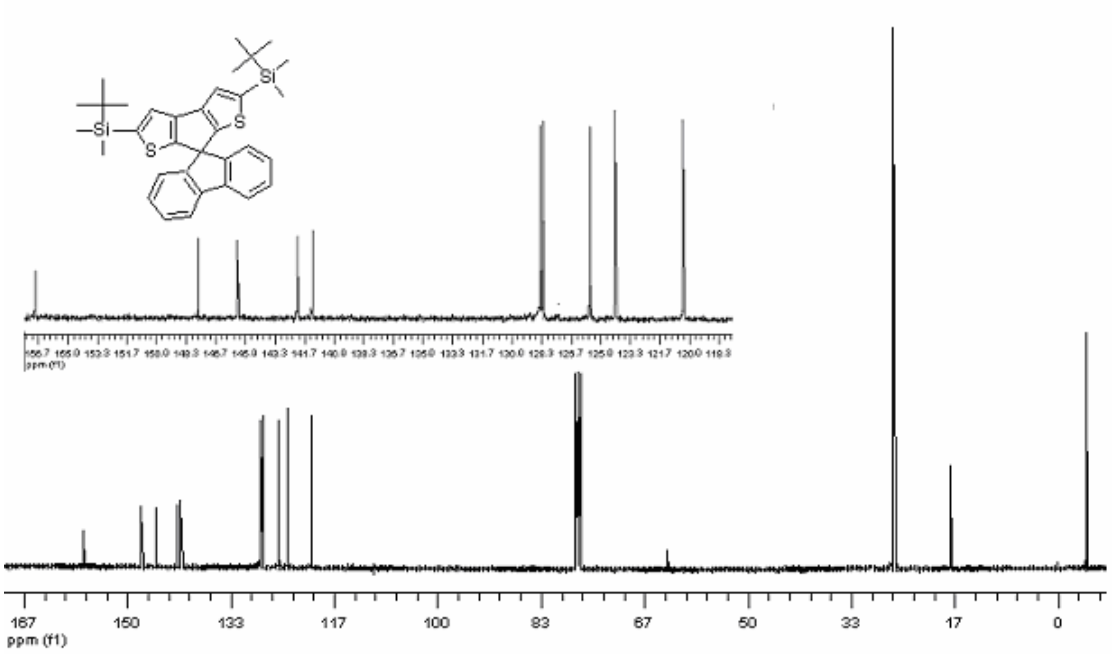


Figure SI-2. The ^{1}H-NMR and ^{13}C-NMR spectra of 2,5-bis(dimethyl-*t*-butylsilyl)-spiro[cyclopenta[1,2-b:4,3-b']dithiophene-7,9'-fluorene]

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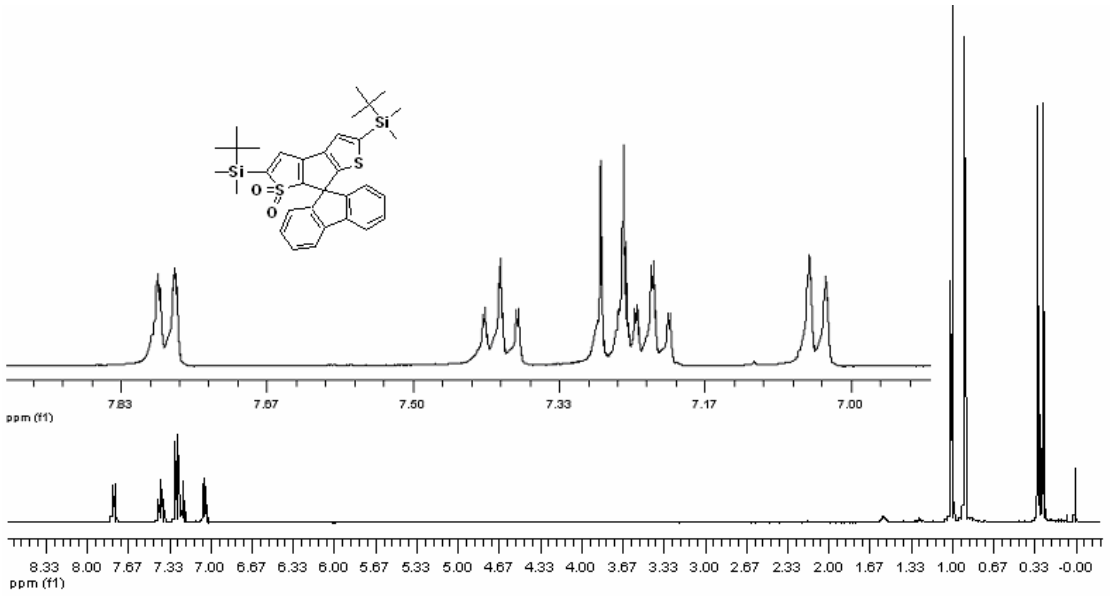


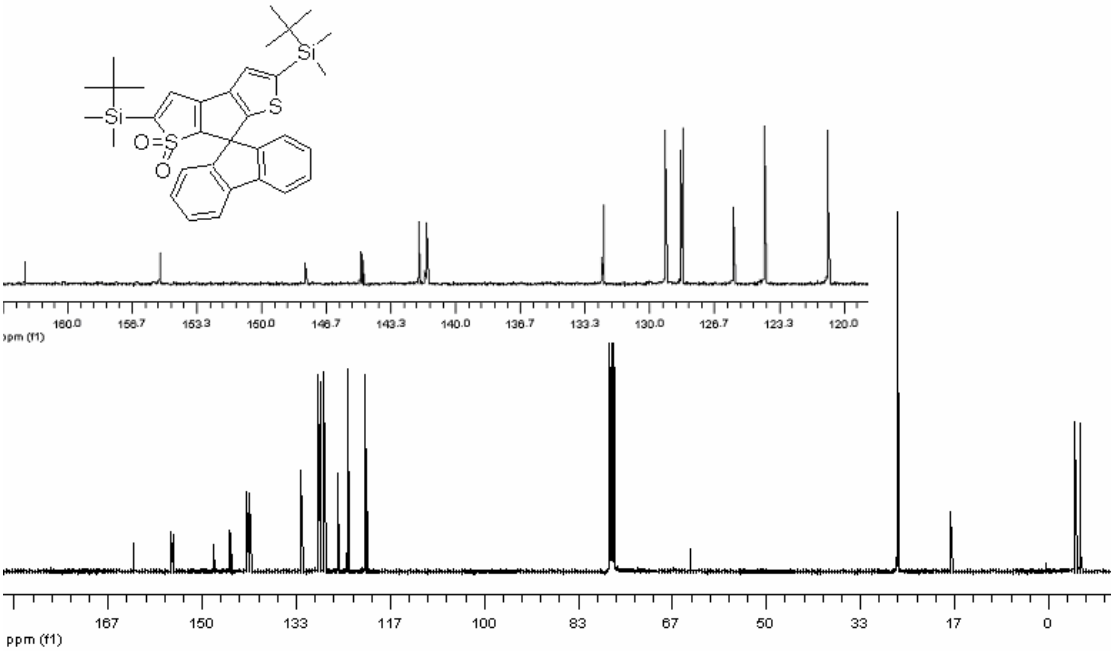


Figure SI-3. The ^{1}H-NMR and ^{13}C-NMR spectra of 2,5-bis(dimethyl-*t*-butylsilyl)-spiro[cyclopenta[1,2-b:4,3-b']dithiophene-S,S-dioxides -7,9'-fluorene].

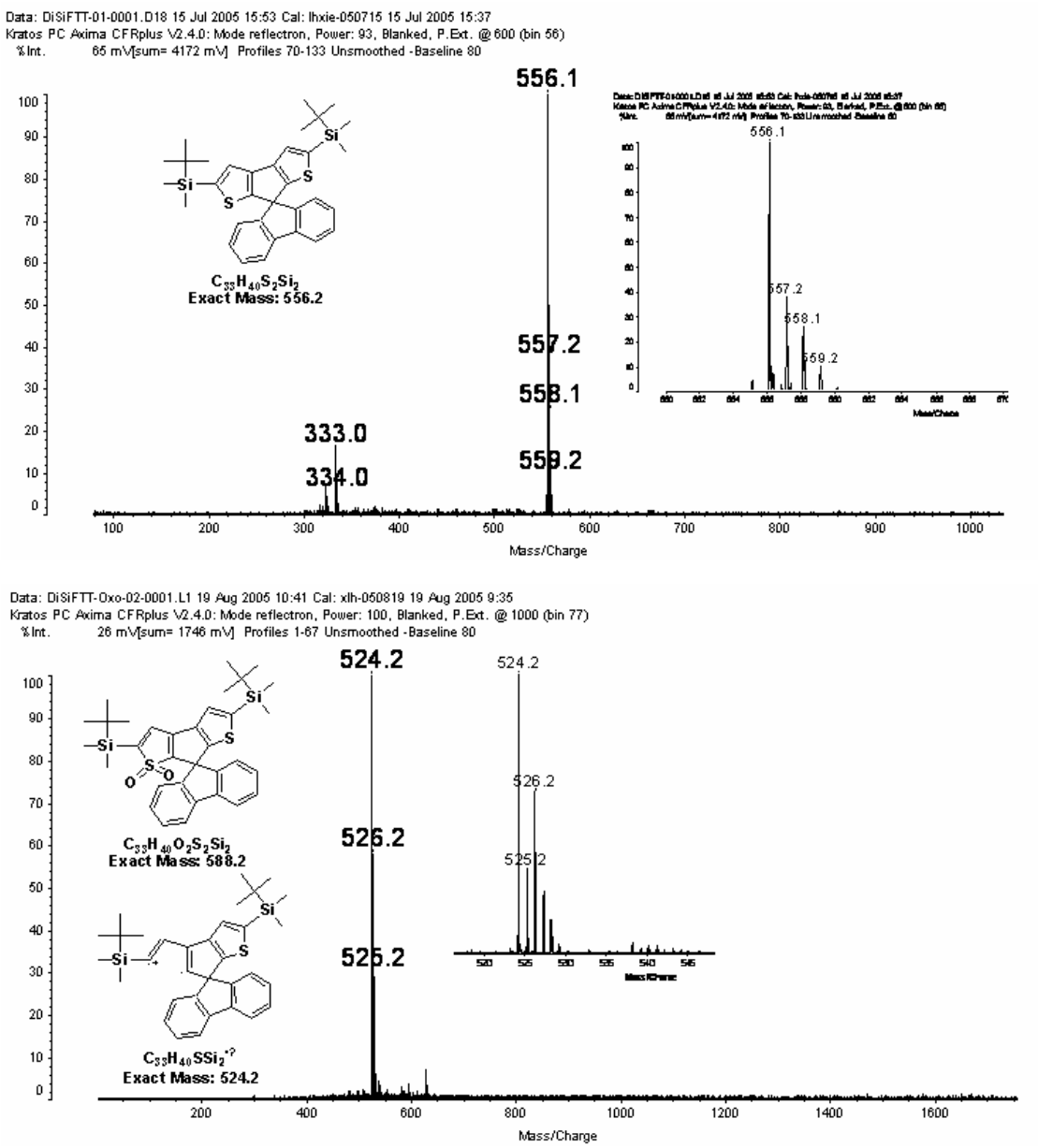
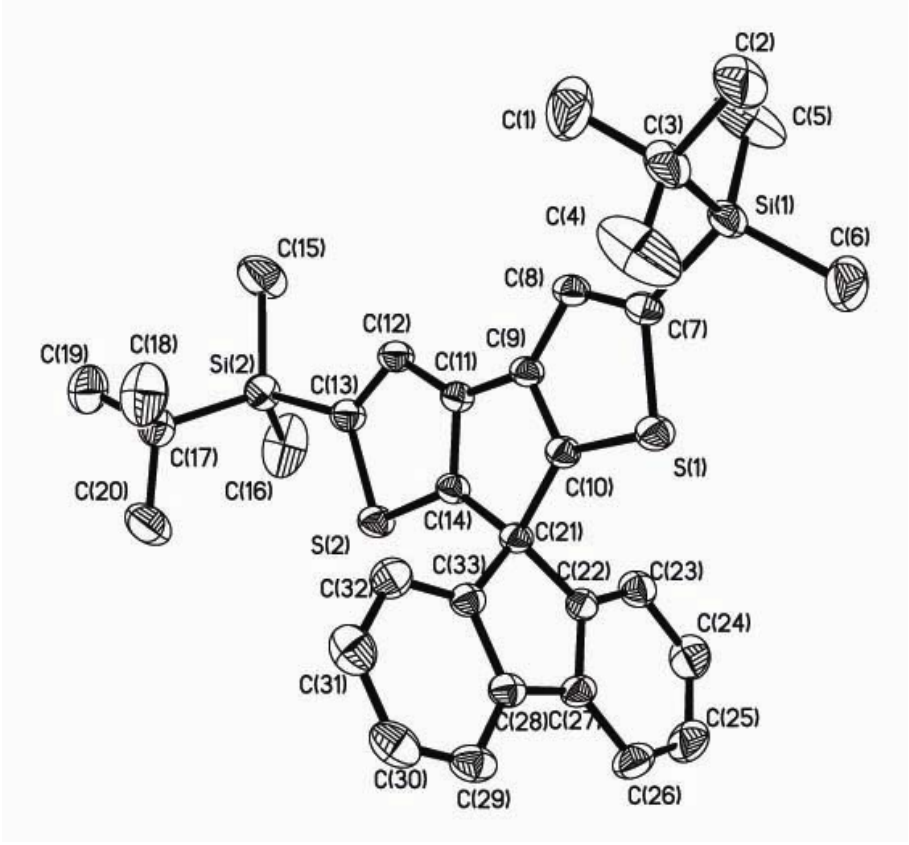


Figure SI-4. The MALDI-TOF-MS spectra of BSiSDTF and BSiSDTFO.



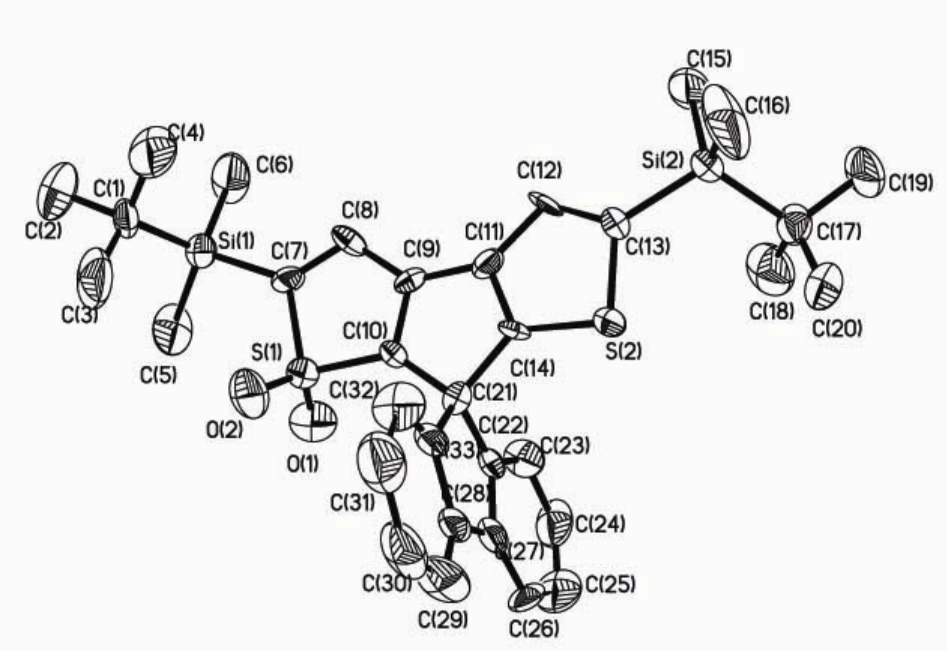


Figure SI-5. ORTEP drawing of BSiSDTF and BSiSDTFO. The ellipsoid probability is 30%.

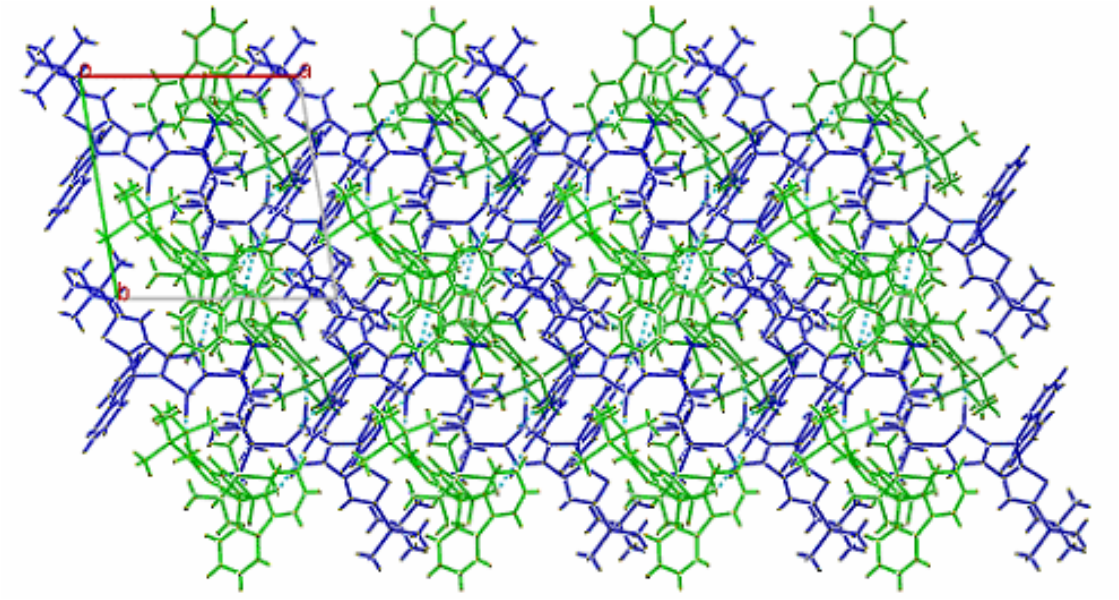


Figure SI-6. View along the *c* axis of the crystal structure of BSiSDTFO.

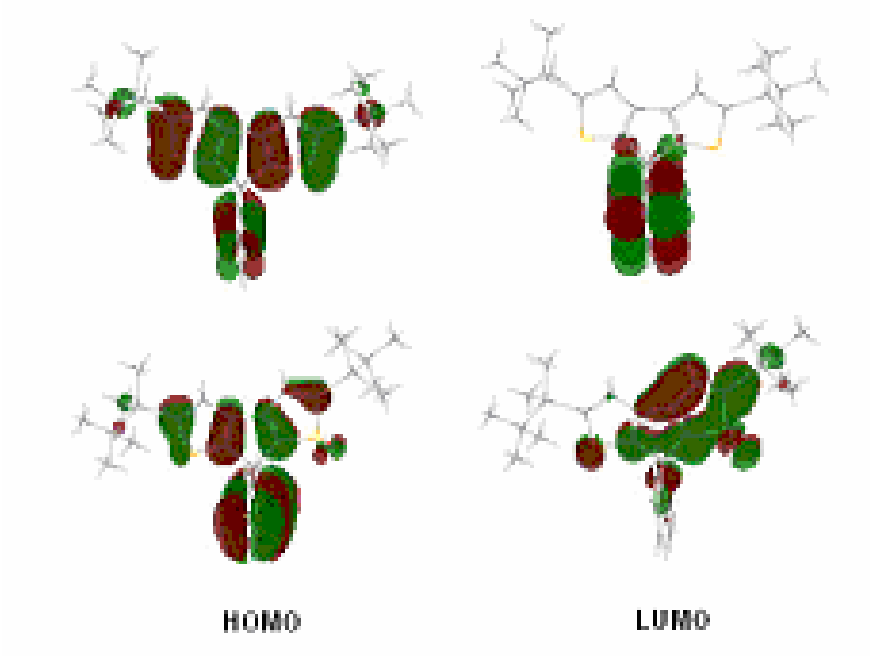


Figure SI-7. B3LYP/6-31G* electronic densities and energies of the frontier orbitals of BSiSDTF and BSiSDTFO.

Table SI-1. Hydrogen bonds for BSiSDTFO [Å and deg.].

D-H...A	d (D-H)	d (H...A)	d (D...A	<(DHA)
C(3)-H(3B)...O(2)	0.96	2.55	3.376(17)	143.8
C(8)-H(8A)...O(4)	0.93	2.87	3.643(14)	141.7
C(12)-H(12A)...O(4)	0.93	2.69	3.500(15)	146
C(20)-H(20B)...S(2)	0.96	2.82	3.607(12)	139.8
C(35)-H(35C)...O(4)	0.96	2.88	3.623(17)	134.7
C(26)-H(26A)...S(2)#1	0.93	2.94	3.835(15)	161.7
C(38)-H(38C)...O(2)#2	0.96	2.8	3.562(13)	137.3
C(41)-H(41A)...O(2)#2	0.93	2.41	3.234(15)	147.1
C(48)-H(48B)...O(1)#3	0.96	2.84	3.569(13)	133.1
C(53)-H(53B)...O(1)#3	0.96	2.91	3.850(15)	167.9
C(58)-H(58A)...O(1)#4	0.93	2.61	3.520(19)	167.2
C(62)-H(62A)...O(3)#5	0.93	2.59	3.383(14)	143.4