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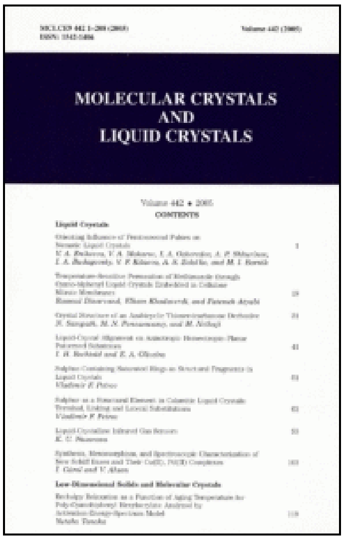

# Molecular Crystals and Liquid Crystals

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# Synthesis and Chromic Behaviors of Dithienosiloles with Push-Pull Substituents Toward VOC Detection

Joji Ohshita[a]; Daiki Tanaka[a]; Kwang-Hoi Lee[a]; Yasunori Kurushima[a]; Shotaro Kajiwara[a]; Yousuke Ooyama[a]; Yutaka Harima[a]; Atsutaka Kunai[a]; Yoshihito Kunugi[b]
[a] Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima, Japan [b] Department of Applied Chemistry, Faculty of Engineering, Tokai University, Hiratsuka, Japan

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# Synthesis and Chromic Behaviors of Dithienosiloles with Push-Pull Substituents Toward VOC Detection

JOJI OHSHITA,[1] DAIKI TANAKA,[1]
KWANG-HOI LEE,[1] YASUNORI KURUSHIMA,[1]
SHOTARO KAJIWARA,[1] YOUSUKE OOYAMA,[1]
YUTAKA HARIMA,[1] ATSUTAKA KUNAI,[1]
AND YOSHIHITO KUNUGI[2]

[1]Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima, Japan
[2]Department of Applied Chemistry, Faculty of Engineering, Tokai University, Hiratsuka, Japan

*2-Methylthio- and 2-n-hexylthienyl-6-(tricyanoethenyl)-4,4-diphenyldithienosilole were prepared as novel push-pull type compounds. These compounds exhibit solvatochromic behaviors with respect to their UV-vis absorption and emission spectra. Clear vapor chromism is also observed for their thin solid films and the color changed clearly on exposure of the films to organic solvent vapors, indicating the potential applications to VOC sensors.*

**Keywords** Chromic material; push-pull compound; sensor material; silole

## Introduction

Push-pull type compounds bearing electron-accepting and donating units linked by a $\pi$-conjugated system have been extensively studied and their utilities as functional materials, such as chromic and nonlinear optical materials have been demonstrated [1]. In those studies, oligothiophenes are often employed as the $\pi$-conjugated linkers, because of their efficient conjugation along the chain and the stability. Recently, we demonstrated that the introduction of an intramolecular bridge at the $\beta,\beta'$-position of bithiophene derivatives, forming a dithienosilole (DTS) ring, enhances the conjugation in these systems [2–4]. This is due not only to the coplanarity of two thiophene rings linked by the bridge, but also to bonding interaction between the silicon $\sigma^*$-orbital and the bithiophene $\pi^*$-orbital, which lowers the LUMO energy level.

In this article, we report the synthesis of DTSs featuring tricyanoethenyl, and methylthio or hexylthienyl groups as the electron-accepting and donating units,

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Address correspondence to Joji Ohshita, Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan. E-mail: jo@hiroshima-u.ac.jp

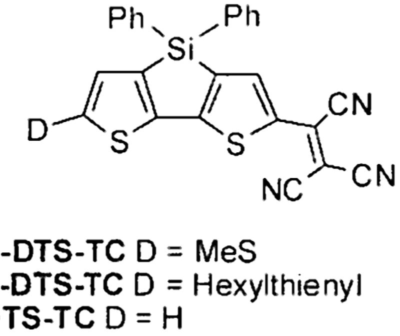
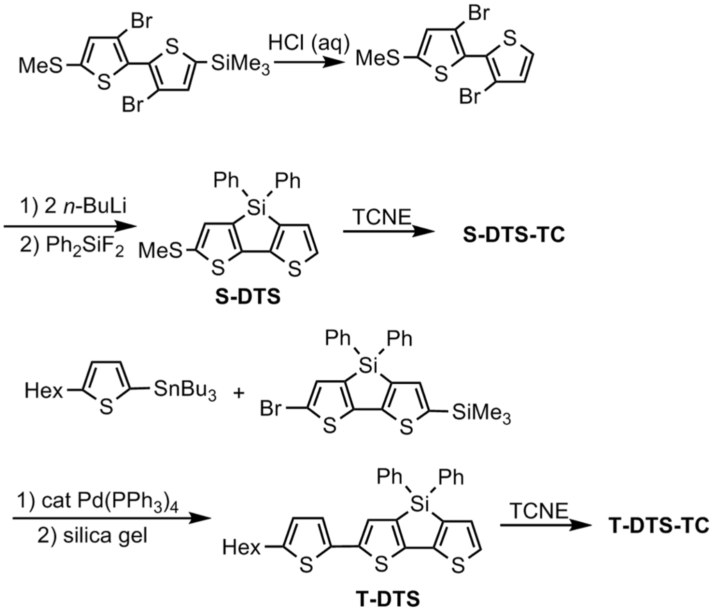


**Chart 1.** Tricyanoethenyl-substituted DTSs.

respectively (**S-DTS-TC** and **T-DTS-TC** in Chart 1). The tricyanoethenyl group that can be readily introduced to a thiophene ring, has been proven useful as an acceptor unit of push-pull type compounds [5]. We previously prepared a tricyanoethenyl-substituted DTS (**DTS-TC** in Chart 1) and found that **DTS-TC** showed spectral and color changes in response to organic solvent vapors in the films [6]. Sensing materials that detect volatile organic compounds (VOC) are of growing interest, because of their environmental concern [7]. The present **S-DTS-TC** and **T-DTS-TC** showed solvato- and vapor chromic behaviors in the solution phase as well as in the solid state, to larger extents than **DTS-TC**, indicating their potential applications as VOC-sensor materials.

## Results and Discussion

Push-pull type compounds, **S-DTS-TC** and **T-DTS-TC** were obtained by the reactions of **S-DTS** and **T-DTS** with tetracyanoethylene (TCNE) in DMF in 44% and 78% yields, respectively (Scheme 1). They are metallic golden colored solids, suggesting strong intermolecular interaction in the solid state, as previously reported for similar tricyanoethenyl-substituted $\pi$-conjugated compounds [5f]. We prepared also silole-free methylthio(tricyanoethenyl)bithiophene (**S-BT-TC**) for comparison (see Chart 2). Table 1 summarizes optical properties of the presently prepared compounds, together with those of the related compounds, reported previously (Chart 2) [3,6]. The UV-vis absorption and emission maxima of **S-DTS-TC** are largely red-shifted from that of **DTS-TC** [6]. Since introduction of a methylthio group on the DTS unit moves the absorption maxima by only 7 and 18 nm in a series of **DTS1** (Chart 2, $\lambda_{max} = 356$ nm) [2b], **S-DTS** (363 nm), and **S-DTS-S** (Chart 2, 381 nm) [3], respectively, the large shift of 34 nm from **DTS-TC** to **S-DTS-TC** indicates a considerable "push" effect of the methylthio group in this system. A similar red shift is observed for **S-BT-TC** relative to **BT-TC** [6]. Effects of tricyanoethenyl-substitution on the optical properties are clear, which leads to large red shifts for **S-DTS-TC** and **T-DTS-TC** from **S-DTS** and **T-DTS** ($\lambda_{max} = 395$ nm). The silicon bridge in **S-DTS-TC** also affects the optical properties, moving the $\lambda_{max}$ to longer wavelength by about 30 nm from that of **S-BT-TC**. A similar red shift was already reported for **DTS-TC** from **BT-TC** [6]. However, the $\lambda_{edge}$ values are not evidently affected by the existence of the silicon bridge. Presumably, in these compounds, it is mainly responsible for the red shifts of the absorption maxima that the silicon



**Scheme 1.** Synthesis of push-pull type DTSs.

bridge retains the high planarity of the bithiophene unit, while no significant electronic effects of the silicon bridge such as $\sigma^*$-$\pi^*$ interaction is involved, which should affect the $\lambda_{edge}$ if present.

To know the electronic states of the present systems, we carried out DFT calculations at the B3LYP/6-31G level (Table 1). For the calculations of the DTS derivatives, simplified model compounds that have hydrogen atoms in place of phenyls on the silicon atoms were employed. As shown in Table 1, the HOMOs and LUMOs lie at almost the same energies independent of the existence/absence of the silicon bridge, in agreement with the experimental observations described above.

Presently prepared compounds, **S-DTS-TC**, **S-BT-TC**, and **T-DTS-TC**, exhibit solvatochromic behaviors as shown in Table 2 and Figure 1. Although similar

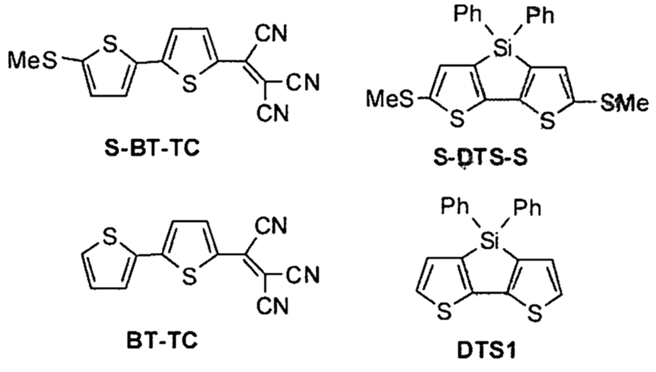


**Chart 2.** DTS and bithiophene derivatives.

**Table 1.** Optical properties of DTS- and bithiophene-based compounds

| | UV in THF | | DFT calculations[a] | |
|---|---|---|---|---|
| Compd | $\lambda_{max}$/nm | $\lambda_{edge}$/eV | HOMO/eV | LUMO/eV |
| **S-DTS-TC** | 546 | 1.8 | −6.34 | −3.77 |
| **T-DTS-TC** | 591 | 1.6 | −5.96 | −3.60 |
| **S-BT-TC** | 518 | 1.8 | −6.31 | −3.76 |
| **DTS-TC** | 512 | 2.1 | −6.40 | −3.72 |
| **BT-TC** | 484 | 2.2 | −6.45 | −3.75 |

[a] At the level of B3LYP/6-31G. For dithienosiloles, simplified model compounds were employed, in which phenyl groups on the silicon atom were replaced by hydrogen atoms.

**Table 2.** Absorption and emission maxima [nm] of **S-DTS-TC**, **S-BT-TC**, and **T-DTS-TC** in different solvents

| | S-DTS-TC | | S-BT-TC | | T-DTS-TC | |
|---|---|---|---|---|---|---|
| Solvt | abs | Emission | abs | Emission | abs | Emission |
| $CCl_4$ | 532 | 619 | 508 | 602 | 603 | 643 |
| Ether | 533 | 633 | 510 | 643 | 590 | 670 |
| AcOEt | 539 | 669 | 513 | 670 | – | – |
| THF | 546 | 660 | 518 | 659 | 591 | 713 |
| $CHCl_3$ | 564 | 666 | 540 | 660 | 621 | 711 |

solvatochromic behaviors were already reported for compounds **DTS-TC** and **BT-TC** [6], the chromic shifts for **DTS-TC** and **BT-TC** were only 22 nm and 20 nm at most, respectively, on changing the solvent from ether to chloroform, which were smaller than those of **S-DTS-TC**, **S-BT-TC**, and **T-DTS-TC**. Emission spectra also change in response to the solvents as shown in Table 2. Figure 2 represents the HOMO and LUMO profiles of the model of compound **S-DTS-TC**, derived from the DFT calculations. The HOMO is rather localized on the methylthio-DTS unit, while the LUMO mainly lies on the tricyanoethenyl unit, indicating a polarized

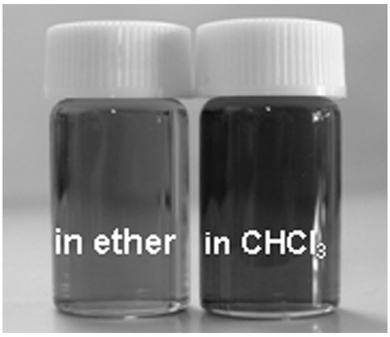


**Figure 1.** Solutions of **S-DTS-TC**.

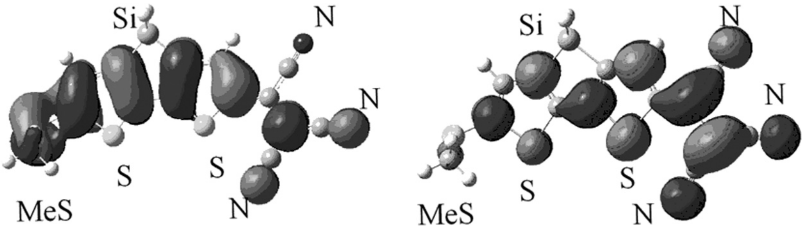
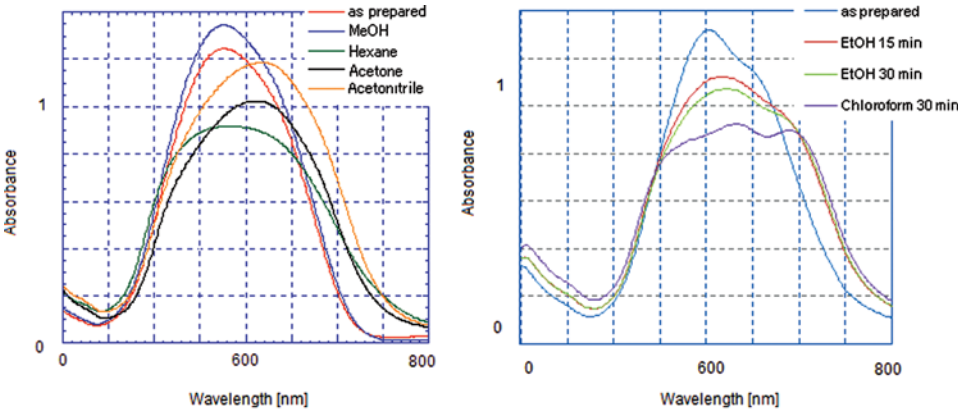


**Figure 2.** HOMO (left) and LUMO (right) profiles for a model of **S-DTS-TC**, derived from DFT calculations at the level of B3LYP/6-31G.

structure in the excited state. This seems to be responsible for the larger solvatochromic shifts in the emission spectra than those in the absorption spectra. No solvatochromic shifts larger than 2 nm are observed for **S-DTS** and **T-DTS** having no tricyanoethenyl acceptor unit.

Compounds **S-DTS-TC** and **T-DTS-TC** are vapor chromic in the solid state. Figure 3(a) depicts the spectral changes for **S-DTS-TC** with respect to the UV-vis absorption, on exposure of the vapor deposited films to organic solvent vapors for a few seconds. The largest vapor chromic shift of 45 nm is observed for **S-DTS-TC**, accompanied with a color change from ultramarine to blue (Fig. 4), when the film is exposed to an acetonitrile vapor. Spin coated films of **T-DTS-TC** also show vapor chromism (Fig. 3(b)), but spectral changes of **T-DTS-TC** occur relatively slowly with the time scale of minute, as compared with that of **S-DTS-TC**. No clear vapor chromism is observed for **S-BT-TC**, in contrast to its sensitive solvatochromism.

In conclusion, we prepared novel push-pull type compounds bearing a DTS system as the linker, which exhibit remarkable solvato and vapor chromic behaviors, potentially useful for VOC sensing. Both the experimental and theoretical studies suggest that electronic effect of the silicon bridge is not significantly operative in the present system. However, its steric effect making two thiophene rings coplanar



(A) (B)

**Figure 3.** Spectral changes of vacuum deposited films of **S-DTS-TC** (A) and spin coated films of **T-DTS-TC** (B) on exposure of the films to various solvent vapors.

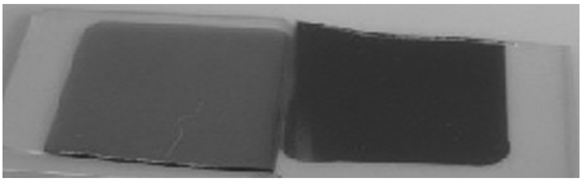


**Figure 4.** Films of **S-DTS-TC** as prepared by vacuum deposition (left) and exposed to an acetonitrile vapor (right).

significantly enhances the conjugation. Studies on applications of DTS based push-pull compounds as organic device materials are underway.

## Experimental

### *General Procedure*

3,3′-Dibromo-5-methylthio-5′-trimethylsilyl-2,2′-bithiophene was prepared as reported in the literature [4]. THF and ether were dried over sodium-benzophenone and distilled immediately before use. Toluene and DMF were distilled from sodium and calcium hydride, respectively, and were stored over activated molecular sieves until use. All reactions were carried out in dry nitrogen. Usual workup described below involves hydrolysis of the reaction mixture with water, separation of the organic layer, extraction of the aqueous layer with chloroform, drying the combined organic layer and extracts over anhydrous magnesium sulfate, and evaporation of the solvent, in that order.

### *Preparation of 3,3′-Dibromo-5-methylthio-2,2′-bithiophene*

A mixture of 2.14 g (4.85 mmol) of 3,3′-dibromo-5-methylthio-5′-trimethylsilyl-2,2′-bithiophene, 40 mL of THF, and 15 mL of 35% HCl (aq) was heated to reflux for 3 days. To the resulting mixture was added 50 mL of ether. The organic layer was separated and washed with water, then dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on a silica gel column eluting with hexane to give 1.71 g (95% yield) of the title compound: viscous pale yellow oil; MS $m/z$ 370 [$M^+$];$^1$H NMR ($\delta$ in $CDCl_3$) 2.54 (s, 3H, SMe), 6.99 (s, 1H, ring H), 7.06 (d, 1H, $J = 5.4$ Hz, ring H), 7.38 (d, 1H, $J = 5.4$ Hz, ring H); $^{13}$C NMR ($\delta$ in $CDCl_3$) 20.94, 111.68, 112.44, 127.46, 128.61, 129.76, 130.78, 132.18, 140.18.

### *Preparation of S-DTS*

To a solution of 1.69 g (4.56 mmol) of 3,3′-dibromo-5-methylthio-2,2′-bithiophene in 50 mL of ether and 25 mL of THF was added drop wise 5.77 mL (9.12 mmol) of a 1.58 M $n$-butyllithium/hexane solution at −80°C and the mixture was stirred at room temperature for 1 h. The mixture was again cooled at −80°C and 1.30 g (5.90 mmol) of difluorodiphenylsilane was added slowly to the mixture, then the mixture was heated to reflux for 15 h. After the usual workup, the residue was chromatographed on a silica gel column eluting with hexane/ethyl acetate = 40/1 to give a crude solid. Recrystallization of the crude solid from hexane/ethyl acetate afforded 0.638 g (36% yield) of compound **S-DTS** as a yellow needle-like solid: mp 113.8–141.2°C; MS *m*/*z* 392 [M$^+$]; $^1$H NMR ($\delta$ in $CDCl_3$) 2.49 (s, 3H, SMe), 7.20 (s, 1H, thiophene), 7.21 (d, 1H, $J = 4.8$ Hz, thiophene), 7.27 (d, 1H, $J = 4.8$ Hz, thiophene), 7.33–7.44 (m, 6H, *m*- and *p*-Ph), 7.61 (dd, 4H, $J = 8.0$ and 1.5 Hz, *o*-Ph); $^{13}$C NMR ($\delta$ in $CDCl_3$) 22.87, 126.31, 128.19, 129.62, 130.39, 131.47, 134.66, 135.35, 137.86, 139.30, 140.13, 150.31, 152.50; $^{29}$Si NMR ($\delta$ in $CDCl_3$) −20.23. Anal. Calcd for $C_{21}H_{16}S_3Si$: C, 64.24; H, 4.11. Found: C, 64.26; H, 4.20.

### *Preparation of 5-Methylthio-2,2′-bithiophene*

To a solution of 3.00 g (18.0 mmol) of bithiophene was added 11.4 mL (18.0 mmol) of a 1.58 M *n*-butyllithium/hexane solution at −80°C and the mixture was allowed to warm to room temperature. A small portion of the reaction mixture was sampled and quenched with chlorotrimethylsilane, which was then analyzed by GC indicating the formation of a mixture consisting of bithiophene, monolithiobithiophene, and dilithiobithiophene in an approximate ratio of 1:7:2. The mixture was again cooled to −80°C and 1.55 mL (18.0 mmol) of dimethyl disulfide was added slowly to the mixture. The mixture was then stirred at room temperature for 3 h. After the usual workup, the residue was chromatographed on a silica gel column eluting with hexane to give 1.94 g (51% yield) of the title compound as yellow oil: MS *m*/*z*, 212 [M$^+$]; $^1$H NMR ($\delta$ in $CDCl_3$) 2.51 (s, 3H, SMe), 6.97–7.02 (m, 3H, thiophene H), 7.13 (d, 1H, $J = 3.6$ Hz, thiophene H), 7.20 (d, 1H, $J = 5.3$ Hz, thiophene H); $^{13}$C NMR ($\delta$ in $CDCl_3$) 20.95, 111.23, 113.24, 130.26, 132.41, 133.29, 136.94, 139.85, 143.20.

### *Preparation of T-DTS*

A mixture of 6.41 g (14.0 mmol) of 5-hexyl-2-tributylstannylthiophene, 6.99 g (14.0 mmol) of 2-bromo-6-trimethylsilyl-4,4-diphenyldithienosilole, 0.81 g (0.70 mmol) of $Pd(PPh_3)_4$, 0.013 g (0.70 mmol) of CuI, and 30 mL of toluene was heated to reflux for 72 h. After the usual workup, the residue was chromatographed on a silica gel column eluting with hexane/toluene = 3/1 to give a crude solid. Recrystallization of the crude product from hexane gave 4.46 g (62% yield) of **T-DTS** as a yellow solid: mp 134.7–136.9°C; MS *m*/*z* 512 [M$^+$]; $^1$H NMR ($\delta$ in $CDCl_3$) 0.88 (t, 3H, Hex), 1.40–1.24 (m, 6H, Hex), 1.69–1.62 (m, 2H, Hex), 2.77 (t, 2H, $J = 7.2$ Hz, Hex), 6.66 (d, 1H, $J = 2.9$ Hz, thiophene), 6.96 (d, 1H, $J = 3.9$ Hz, thiophene), 7.20 (br d, 2H, $J = 5.8$ Hz, thiophene), 7.24 (d, 1H, $J = 3.9$ Hz, thiophene), 7.33–7.44 (m, 6H, *m*- and *p*-Ph), 7.64 (dd, 4H, J = 7.8 and 1.7 Hz, *o*-Ph); $^{13}$C NMR ($\delta$ in $CDCl_3$) 14.08, 22.56, 28.71, 28.72, 30.16, 31.55, 123.13, 124.77, 125.43, 126.00, 128.19, 129.67, 130.35, 131.56, 134.70, 135.40, 139.27, 139.34, 140.98, 145.25, 148.20, 150.36. Exact MS Calcd for $C_{30}H_{28}S_3Si$ [M$^+$]: 512.1122. Found: 512.1125.

### *Preparation of S-DTS-TC, S-BT-TC, and T-DTS-TC*

A solution of 0.300 g (0.764 mmol) of **S-DTS** and 0.196 g (1.53 mmol) of TCNE in 2 mL of DMF was stirred at room temperature for 12 h. To this were added 5 mL of water and 3 mL of ethyl acetate. After the usual workup, the residue was chromatographed on a silica gel column eluting with hexane to give 0.167 g (44% yield) of **S-DTS-TC** as a metallic green needle-like solid: mp 268.5–269.2°C; MS *m*/*z*, 493

[M$^+$]; $^1$H NMR ($\delta$ in $CDCl_3$) 2.64 (s, 3H, SMe), 7.20 (s, 1H, thiophene), 7.41–7.51 (m, 6H, *m*- and *p*-Ph), 7.58 (d, 4H, $J = 6.8$ Hz, *o*-Ph), 8.09 (s, 1H, $J = 4.8$ Hz, thiophene); $^{13}$C NMR ($\delta$ in $CDCl_3$) 20.67, 112.66, 113.10, 113.16, 128.41, 128.71, 128.85, 135.32, 135.86, 142.42, 143.13, 146.88, 149.89, 150.87, 164.67 (three carbon signals may be overlapped); $^{29}$Si NMR ($\delta$ in $CDCl_3$) −19.96; IR 2216 cm$^{-1}$ (C≡N). Anal. Calcd for $C_{26}H_{15}N_3S_3Si$: C, 63.25; H, 3.06; N, 8.51. Found: C, 63.08; H, 3.11; N, 8.42.

Compound **S-BT-TC** was obtained in 47% yield by the reaction of 5-(methylthio)-2,2′-bithiophene and TCNE in DMF, in a fashion similar to that above, and was purified by silica gel column chromotography with hexane as eluent: dark green solid; mp 178.8–180.0°C; MS *m*/*z*, 313 [M$^+$]; $^1$H NMR ($\delta$ in $CDCl_3$) 2.60 (s, 3H, SMe), 6.98 (d, 1H, $J = 3.9$ Hz, thiophene), 7.26 (d, 1H, $J = 4.5$ Hz, thiophene), 7.38 (d, 1H, $J = 3.9$ Hz, thiophene), 7.96 (d, 1H, $J = 4.5$ Hz, thiophene); $^{13}$C NMR ($\delta$ in $CDCl_3$) 20.28, 112.16, 112.50, 112.67, 124.82, 129.26, 131.66, 131.71, 131.73, 134.08, 141.55, 146.28, 151.74 (one carbon signal may be overlapped); IR 2220 cm$^{-1}$ (C≡N). Anal. Calcd for $C_{14}H_7N_3S_3$: C, 53.65; H, 2.25; N, 13.41. Found: C, 53.67; H, 2.27; N, 13.30. Compound **T-DTS-TC** was obtained in 78% yield by the reaction of 5-(hexylthienyl)-4,4-diphenyldithienosilole and TCNE in DMF, in a fashion similar to that above, and purified by preparative GPC eluting with chloroform: metallic dark green solid; mp 252.58–254.9°C; MS *m*/*z* 613 [M$^+$]; $^1$H NMR ($\delta$ in $CDCl_3$) 0.89 (t, 3H, $J = 6.3$ Hz, Hex), 1.40–1.25 (m, 6H, Hex), 1.73–1.65 (m, 2H, Hex), 2.83 (t, 2H, $J = 7.2$ Hz), 6.76 (d, 1H, $J = 3.9$ Hz, thiophene), 7.13 (d, 1H, $J = 3.9$ Hz, thiophene), 7.35 (s, 1H, thiophene), 7.54–7.42 (m, 7H, thiophene, and *m*- and *p*-Ph), 7.62 (dd, 4H, $J = 7.7$ and 1.9 Hz, *o*-Ph), 8.08 (s, 1H, thiophene); $^{13}$C NMR ($\delta$ in $CDCl_3$) 14.05, 22.53, 28.67, 30.28, 31.43, 31.49, 112.82, 113.15, 113.30, 125.67, 125.88, 126.31, 126.32, 128.44, 128.70, 129.01, 130.87, 131.41, 133.27, 135.36, 136.07, 142.90, 144.96, 148.40, 148.76, 150.92, 165.21; IR 2216 cm$^{-1}$ (C≡N). Exact MS Calcd for $C_{35}H_{27}N_3S_3Si$ [M$^+$]: 613.1136. Found: 613.1129.

### *DFT Calculations*

All calculations were performed by the density functional theory (DFT) calculations. The Becke-three-parameter-Lee-Yang-Parr hybrid functional [8] and the 6-31G basis set was employed, which is implemented in Gaussian03 program package [9].

## Acknowledgments

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