

The Ring-Opening Reaction of 7,7'-Dimethyl-2,5-bis(trimethylsilyl)-dithieno[2,3-*b*:3',2'-*d*]silole in the Presence of NXS (X = Cl, Br, I)

Caiyun Zhao¹, Li Xu², Jianwu Shi¹, Chunli Li¹, Zhihua Wang^{1,2}, Hua Wang^{1,2*}

¹Key Lab for Special Functional Materials of Ministry of Education, Henan University, Kaifeng, China

²College of Chemistry and Chemical Engineering, Henan University, Kaifeng, China

E-mail: *hwang@henu.edu.cn

Received September 23, 2011; revised October 25, 2011; accepted November 6, 2011

Abstract

In this paper, the synthetic method for making 7,7'-dimethyl-2,5-bis(trimethylsilyl)-dithieno[2,3-*b*:3',2'-*d*]silole (**1**) was developed by using 2,2'-dibromo-5,5'-bis(trimethylsilyl)-[3,3']bithiophenyl as starting material in one pot reaction. In the presence of NXS (X = Cl, Br, I), a novel ring-opening reaction was occurred on the silole ring of **1** in DMF or THF. By using such kind of reaction, two types of ring opened products, (2'-halo-5,5'-bis(trimethylsilyl)-[3,3']bithiophenyl-2-yl)-dimethylsilanols and 2,2'-dihalo-5,5'-bis(trimethylsilyl)-[3,3']bithiophenyl were obtained efficiently.

Keywords: Dithieno[2,3-*b*:3',2'-*d*]silole, Halogenation, Ring-Opening, Silanol

1. Introduction

The compound with silole unit as building block has low reduction potential and low-lying lowest unoccupied molecular orbital (LUMO) energy level [1,2] arising from the σ^* - π^* conjugation between the σ^* orbital of the silicon atom and the π^* -orbital of the butadiene moiety. The unique electronic structure make silole-based π -conjugated compounds, such as dithieno[3,2-*b*:2',3'-*d*]silole (DTS-1, **Figure 1**) based compounds can be used as functional materials in organic field effect transistor (OFET) [3], light-emitting diodes (LEDs) [4], hole transport in double-layer EL devices [5-7], photovoltaic devices [8,9] and dye-sensitized solar cells (DSSCs) [10,11].

The typical method for formation of DTS-1 has been reported by many research groups [4,6,8,9,12-17] in recent years, in which DTS-1 is formed in two steps. First one is the Br/Li exchange on 3,3'-dibromo-2,2'-bi-

thiophene and the second one is followed by reaction with dihalosilane to generate DTS-1 in good yield. However, few examples are reported about the formation of the isomer, DTS-2. Iyoda *et al.* [18] reported the synthesis of DTS-2 by the palladium catalyzed cyclization of bis-(3-bromo-thiophen-2-yl)-dimethylsilane in presence of Me₃SnSnMe₃ (0.9 equiv) with high loading (20%) of palladium catalyst.

The bromination of fused aromatic compound is an important step in the synthesis of functional materials. The bromination for derivatives of DTS-1, such as 4,4'-di-*n*-hexylsilylene-dithieno[3,2-*b*:2',3'-*d*]silole and 2,6-bis-(trimethylsilyl)-4,4'-di-*n*-hexylsilylene-dithieno[3,2-*b*:2',3'-*d*]silole in presence of NBS [8,9,12,13,19] or bromine [4,20,21] has been reported to generate dibromo-DTS-1s efficiently. In which, TMS group could be replaced by Br group and structure of silole ring in DTS-1 is stable. Different from the case of DTS-1, in our work, we found the ring opening phenomena occurred to DTS-2, 7,7'-dimethyl-2,5-bis-(trimethylsilyl)-dithieno[2,3-*b*:3',2'-*d*]silole (**1**) in the presence of NXS (X = Cl, Br, I) in DMF or THF at ambient temperature. To the best of our knowledge, few of ring opening reactions about silole compounds were reported. Braddock-Wilking [22] *et al.* gave an interesting example of bromination of 1,1-dimethoxy-2,5-bis(trimethylsilyl)-3,4-diphenylsilole tr-

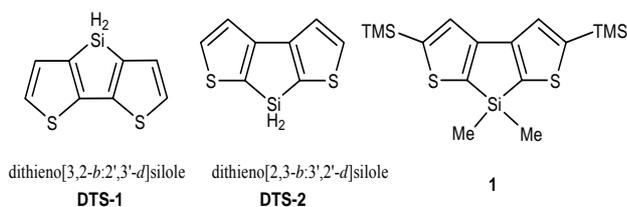


Figure 1. Chemical structures of DTS and **1**.

eated with Br₂, and the ring-opened product, 1-bromo-4-bromodi(methoxy)silyl-1,4-bis(trimethylsilyl)-2,3-diphenyl-1,3-butadiene was obtained. Recently, Xi [23] *et al.* showed an efficient and specific cleavage of the endo-C(sp²)-Si bond of silole rings by using an AcOH/ROH system. Different from the above cases of substituted silole, DTS-2 is a type of fused heterocyclic compound, its chemical stability is more important issue in both theory of organic chemistry and synthesis of materials.

2. Results and Discussion

2.1. Ring-Opening Reaction of **1**

1 could be prepared with 2,2'-dibromo-5,5'-bistrimethylsilyl[3,3']bithiophenyl (**3**) [24] as starting material in one pot reaction (step a, Scheme 1). Double Br/Li-exchange on **3** by *n*-BuLi at -78°C for 2 h, followed by reaction with dichlorodimethylsilane, **1** was obtained in 81.0% as white solid. With two TMS groups, **3** has a very good solubility and there is no solubility problem in both Br/Li-exchange step and subsequent silole formation step. On the other hand, TMS-protected **3** also prevented possible side reactions occurred on the acidic α positions. Compared with the method reported by Iyoda [18], our method offers a practical route without expensive palladium catalyst and poisonous Me₃SnSnMe₃ to offer **1** in 81% yield.

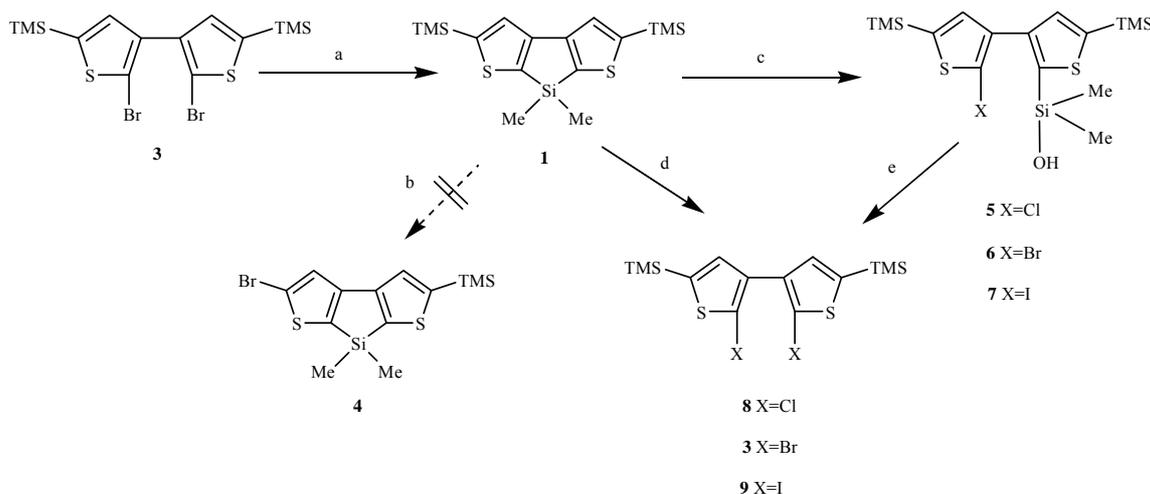
Bromination of DTS-2 is interested to us, because mono- and di-bromo-DTS-2 should be same important intermediates as dibromo-DTS-1 in synthesis of organic functional materials [3-11]. Different from the case of bromination of DTS-1, however, in bromination of **1** with NBS,

instead of formation of bromo-DTS-2 (**4**) (step b, Scheme 1), a ring opening product, (2'-bromo-5,5'-bistrimethylsilyl[3,3']bithiophenyl-2-yl)-dimethylsilanol (**6**) was obtained in 78.5% yields when 1.05 equiv NBS was employed in DMF (Step c, Scheme 1). None of **4** could be observed.

With 1.05 equiv of NCS and NIS instead of NBS, the corresponding ring opening products, **5** and **7** were attained in 39.3% and 71.2% yields, respectively (Step c, Scheme 1). In addition, when the solvent was changed to THF, the yield of **5** could be increased to 55.3%, but the yields of **6** (78.3%) and **7** (61.2%) have a little changed.

With 2.05 equiv of NXS employed in THF, 2,2'-dihalo-5,5'-bis(trimethylsilyl)-[3,3']bithiophenyls (**8**, **3** and **9**) were obtained in 83.4%, 94.7% (isolated yields) and 43.5% (GC-MS analysis), respectively (Step d, Scheme 1). In which, iodination of **1** showed low selectivity, the crude product gave weak polarity with one spot (R_f = 0.70) on TLC (eluent: hexane). We failed in separation of **9** by column chromatography on silica gel or recrystallization. From the GC-MS analysis for the crude product, 43.5% of **9** was observed. The main of other possible side-products were ring opened compounds with one TMS group or one to three iodine groups.

In order to understand the possible reaction process worked by two steps: monohalogenation and dihalogenation, we tried step d in Scheme 1. 1.05 equiv of NXS (X = Cl, Br and I) was used to react with **5**, **6**, **7** in THF (Step e, Scheme 1), **8**, **3** and **9** could be obtained smoothly in 86.2%, 92.6% and 44.7%, respectively. The results show that the dihalogenation of **1** could be occurred step by step.



Scheme 1. Synthetic route to **1**, **3**, **5-9**. Reagents and conditions: (a) (i) 2.1 equiv *n*-BuLi in THF, -78°C/2 h (ii) 1.1 equiv Me₂SiCl₂, **1**, 81.0%; (b) 1.05 equiv NBS in DMF; (c) 1.05 equiv NXS (X = Cl, Br, I) in DMF, **5**, 39.3%; **6**, 78.5%; **7**, 71.2%; (d) 2.05 equiv NXS (X = Cl, Br, I) in THF, **8**, 83.4%; **3**, 94.7%; **9**, 43.5% (GC-MS); (e) 1.05 equiv NXS (X = Cl, Br, I) in THF, **8**, 86.2%; **3**, 92.6%; **9**, 44.7%.

2.2. X-Ray Structural Analysis of 7

The structure of **7** was confirmed by single crystal X-ray analysis¹. There are two enantiomers of **7** packing in the crystal, and only one of two enantiomer molecules is shown in **Figure 2** (All hydrogen atoms are omitted for clarity). The two linked thiophene rings are non-coplanar with the torsion angle (C4-C1-C8-C9) is 108.60° and the dihedral angle between them is 75.28°. Iodine atom and silicon atom point away from each other with a distance of 5.173 Å (I1...Si2). There are short contacts including hydrogen bondings in the crystal packing. The distances of O1...H1, Si2...H1, H2A...H1, S2...H28C and O1...O2 are 2.035, 3.208, 2.274, 2.961 and 2.788 Å, respectively.

3. Experimental Section

Synthesis of 1: To a solution of **3** (1.00 g, 2.13 mmol) in anhyd Et₂O (25 mL), *n*-BuLi (2.43 M, 1.85 mL, 2.1 equiv) was added dropwise at -78°C. After keeping at -78°C for 2 h, Me₂SiCl₂ (0.31 mL, 2.56 mmol, 1.2 equiv) was added, the reaction mixture was warmed slowly to ambient temperature, then 25 mL anhyd THF was added and refluxed at 70°C - 80°C overnight. The reaction mixture was quenched with H₂O (40 mL), extracted with Et₂O (3 × 40 mL) and then washed with sat. NaHCO₃ (50 mL) and

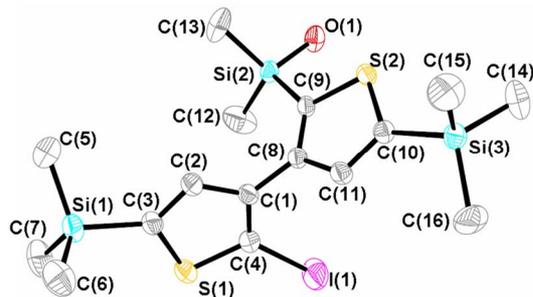


Figure 2. Crystallographic structure of **7**. All hydrogen atoms are omitted for clarity.

¹Crystal Data for **7**: M = 1021.33, C₃₂H₅₄I₂O₂S₄Si₆ (two enantiomers) triclinic, space group P⁻¹, a = 11.8196(11) Å, b = 15.3056(14) Å, c = 15.5471(15) Å, α = 71.4980(10)°, β = 88.2930(10)°, γ = 68.2770(10)°, V = 2465.5(4) Å³, Z = 2, d_{calcd} = 1.376 g/cm³. A colorless crystal of dimensions 0.41 × 0.39 × 0.37 mm was used for measurement at 296 (2 K with the ω scan mode on a Bruker Smart APEX diffractometer with CCD detector using Mo-Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects and absorption corrections were performed using SADABS program. The crystal structures were solved using the SHELXTL program and refined using full matrix least squares. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons. The final cycle of fullmatrix least-squares refinement was based on 9111 independent reflections [I > 2σ(I)] and 431 variable parameters with R1 = 0.0379, wR2 = 0.1027. G. M. Sheldrick, SADABS; University of Göttingen: Germany, 1996. G. M. Sheldrick, SHELXTL Version 5.1; Bruker Analytical X-ray Systems, Inc., Madison/WI, 1997.

H₂O (2 × 50 mL). After drying over MgSO₄, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with PE (60°C - 90°C) as eluent to yield **1** (0.63 g, 81.0%) as a white solid. mp 143°C - 145°C. ¹H NMR (400 MHz, CDCl₃): δ 7.39 (s, 2 H), 0.49 (s, 6 H), 0.35 (s, 18 H). ¹³C NMR (100 MHz, CDCl₃): δ 153.6, 151.2, 141.7, 127.9, 0.0, -1.9. HRMS (TOF MS EI⁺) m/z calcd for [C₁₆H₂₆S₂Si₃] 366.0784, found 366.0788. IR (KBr): 3211 (C-H) cm⁻¹.

Synthesis of 6 from 1: To a solution of **1** (75.5 mg, 0.20 mmol) in DMF (10 mL), NBS (36.6 mg, 0.20 mmol) was added at ambient temperature for 1 h, the reaction mixture was quenched with H₂O (15 mL), extracted with Et₂O (3 × 20 mL), and then washed with H₂O (3 × 30 mL). After drying over MgSO₄, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with CHCl₃ as eluent to yield **6** (74.7 mg, 78.5%) as a white solid. From another one reaction on 56.3-mg scale of **1** in THF, 44.1 mg (78.3%) of **6** was obtained. mp 102°C - 103°C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.33 (s, 1 H), 7.24 (s, 1 H), 6.13 (s, 1 H), 0.31 (s, 9 H), 0.28 (s, 9 H), 0.04 (s, 6 H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 144.2, 143.4, 142.8, 140.0, 139.9, 137.9, 137.3, 114.1, 1.4, -0.0, -0.5; HRMS (TOF MS EI⁺) m/z calcd for [C₁₆H₂₇BrOS₂Si₃] 461.9994, found 461.9995. IR (KBr): 3273 (O-H), 2956 (C-H), 839 (Si-O) cm⁻¹.

Synthesis of 5 from 1: **5** was prepared from **1** according to the same method used for **6**. The reaction was taken on 47.4 mg scale of **1** in DMF, 22.2 mg (39.3%) of **5** was obtained. From another one reaction on 201.3 mg scale of **1** in THF, 127.3 mg (55.3%) of **5** were obtained, respectively. mp 93°C - 95°C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.35 (s, 1 H), 7.28 (s, 1 H), 6.16 (s, 1 H), 0.30 (s, 9 H), 0.28 (s, 9 H), 0.06 (s, 6 H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 144.4, 143.5, 141.6, 137.4, 137.2, 137.1, 136.9, 128.8, 1.3, -0.1, -0.5. HRMS (TOF MS EI⁺) m/z calcd for [C₁₆H₂₇ClOS₂Si₃] 418.0500, found 418.0505. IR (KBr): 3273 (O-H), 2958 (C-H), 841 (Si-O) cm⁻¹.

Synthesis of 7 from 1: **7** was prepared from **1** according to the same method used for **6**. The reaction was taken on 50.0 mg scale of **1** in DMF, 50.1 mg (71.2%) of **7** was obtained. From another one reaction on 27.0-mg scale of **1** in THF, 23.0-mg (61.2%) of **7** was obtained. mp 108°C - 109°C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.31 (s, 1 H), 7.13 (s, 1 H), 6.10(s, 1 H), 0.31 (s, 9 H), 0.27 (s, 9 H), 0.01(s, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ 146.5, 145.9, 145.7, 145.6, 141.6, 137.7, 136.6, 81.0, 1.2, 0.0, -0.3. HRMS (TOF MS EI⁺) m/z calcd for [C₁₆H₂₇IOS₂Si₃] 509.9862, found 509.9856. IR (KBr): 3292 (O-H), 2954 (C-H), 843 (Si-O) cm⁻¹.

Synthesis of 8 from 1: To a solution of **1** (55.2 mg, 0.15 mmol) in THF (8 mL), NCS (40.2 mg, 0.31 mmol)

was added at ambient temperature and stirred overnight. The reaction mixture was quenched with H₂O (15 mL), extracted with Et₂O (3 × 20 mL), and then washed with H₂O (3 × 30 mL). After drying over MgSO₄, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with PE (60°C - 90°C) as eluent to yield **8** (47.6 mg, 83.4%) as a white solid. mp 60°C - 61°C. ¹H NMR (400 MHz, CDCl₃): δ 7.18 (s, 2 H), 0.32 (s, 18 H). ¹³C NMR (100 MHz, CDCl₃): δ 138.2, 134.9, 132.8, 131.4, -0.3. HRMS (TOF MS EI⁺) m/z calcd for [C₁₄H₂₀C₁₂S₂Si₂] 377.9922, found 377.9926. IR (KBr): 2956 (C-H) cm⁻¹.

Synthesis of 3 from 1: The preparation of **3** from **1** was made according to the same method used for making **8** from **1**. From two reactions on a 51.5-mg and 46.7-mg scale of **1** in THF, 62.3 mg (94.7%) and 55.7 mg (93.4 %) of **3** were obtained, respectively. mp 79°C - 80°C (lit. mp 79°C - 81°C [13]).

Synthesis of 8 from 5: To a solution of **5** (95.0 mg, 0.23 mmol) in THF (6 mL), NCS (36.3 mg, 0.27 mmol) was added at ambient temperature and stirred for 3 days. The reaction mixture was quenched with H₂O (10 mL), extracted with Et₂O (3 × 10 mL), and then washed with H₂O (3 × 30 mL). After drying over MgSO₄, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with PE (60-90°C) as eluent to yield **8** (74.1 mg, 86.2%) as a white solid.

Synthesis of 3 from 6: The preparation of **3** from **6** was made according to the same method used for making **8** from **5**. From two reactions on a 95.3 mg and 61.6 mg scale of **6** in THF, 89.5 mg (92.6%) and 56.3 mg (90.1%) of **3** were obtained, respectively.

Synthesis of 9 from 7: The preparation of **9** from **7** was made according to the same method used for making **8** from **5**. From two reactions on a 98.0-mg and 45.1-mg scale of **7** in THF, 48.3 mg (44.7%) and 21.6 mg (43.5%) of **9** were obtained, respectively. mp 105°C - 107°C. ¹H NMR (400 MHz, CDCl₃): δ 7.06 (s, 2 H), 0.32 (s, 18 H). ¹³C NMR (100 MHz, CDCl₃): δ 146.8, 143.9, 135.8, 131.4, -0.2. HRMS (ESI): m/z [M⁺ + H] calcd for C₁₄H₂₁I₂S₂Si₂: 562.87071; found: 562.86951. IR (KBr): 2957 (C-H) cm⁻¹.

4. Conclusions

In summary, we have developed the synthetic method for making **1**. In the presence of NXS (X = Cl, Br, I), a new type of ring opening reaction of DTS-2 is observed, which is important in theoretical understanding for the stability of π-conjugated systems containing silole rings. In addition, by using this ring opening reaction, two types of ring opened products, silanols (**5** - **7**) and dihalo[3,3']bithiophenyls (**8**, **3** and **9**) were obtained effi-

ciently. The new findings are useful for application in organic synthesis.

5. Acknowledgements

This work was supported by the NSFC (20972041, 50803015, 20672028), Program for Innovation Scientists and Technicians Troop Construction Projects of Henan Province (104100510011), Program for SBGJ090506.

6. References

- [1] A. P. Sadimenko, "Organometallic Compounds of Pyrrole, Indole, Carbazole, Phospholes, Siloles, and Boroles," *Advances in Heterocyclic Chemistry*, Vol. 79, 2001, pp. 115-197. doi:10.1016/S0065-2725(01)79023-X
- [2] B.-H. Kim and H.-G. Woo, "Dehydrocoupling of 1,1-Dihydrotetraphenylsilole to an Electroluminescent Polysilole," *Organometallics*, Vol. 21, No. 13, 2002, pp. 2796-2798. doi:10.1021/om0200151
- [3] P. M. Beaujuge, W. Pisula, H. N. Tsao, S. Ellinger, K. Müllen and J. R. Reynolds, "Tailoring Structure-Property Relationships in Dithienosilole-Benzothiadiazole Donor-Acceptor Copolymers," *Journal of the American Chemical Society*, Vol. 131, No. 22, 2009, pp. 7514-7515.
- [4] M. S. Liu, J. D. Luo and A. K.-Y. Jen, "Efficient Green-Light-Emitting Diodes from Silole-Containing Copolymers," *Chemistry of Materials*, Vol. 15, No.18, 2003, pp. 3496-3450. doi:10.1021/cm030063r
- [5] J. Ohshita, T. Sumida and A. Kunai, "Synthesis of Polymers Composed of Alternating Diphenylenedithienosilole and Diethynylenesilylene Units and Their Applications to Hole Transport in Double-Layer EL Devices," *Macromolecules*, Vol. 33, No. 23, 2000, pp. 8890-8893. doi:10.1021/ma0005062
- [6] K.-H. Lee, J. Ohshita, K. Kimura, Y. Kunugi and A. Kunai, "Synthesis of Oligomers Having a Pendant Dithienosilole Unit and Their Applications to EL Device Materials," *Journal of Organometallic Chemistry*, Vol. 690, No. 2, 2005, pp. 333-337. doi:10.1016/j.jorganchem.2004.09.039
- [7] J. Ohshita, K. Kimura, K.-H. Lee, A. Kunai, Y.-H. Kwak, E.-C. Son and Y. Kunugi, "Synthesis of Silicon-Bridged Polythiophene Derivatives and Their Applications to EL Device Materials," *Journal of Polymer Science Part A: Polymer Chemistry*, Vol. 45, No. 20, 2007, pp. 4588-4596. doi:10.1002/pola.22196
- [8] L. J. Huo, H.-Y. Chen, J. H. Hou, T. L. Chen and Y. Yang, "Low Band Gap Dithieno[3,2-b:2',3'-d]silole-Containing Polymers, Synthesis, Characterization and Photovoltaic Application," *Chemical Communications*, No. 37, 2009, pp. 5570-5572. doi:10.1039/b910443g
- [9] J. H. Hou, H.-Y. Chen, S. Q. Zhang, G. Li and Y. Yang, "Synthesis, Characterization, and Photovoltaic Properties of a Low Band Gap Polymer Based on Silole-Containing Polythiophenes and 2,1,3-Benzothiadiazole," *Journal of*

- the American Chemical Society*, Vol. 130, No. 48, 2008, pp. 16144-16145. [doi:10.1021/ja806687u](https://doi.org/10.1021/ja806687u)
- [10] S. Ko, H. Choi, M.-S. Kang, H. Hwang, H. Ji, J. Kim, J. Ko and Y. Kang, "Silole-Spaced Triarylamine Derivatives as Highly Efficient Organic Sensitizers in Dye-Sensitized Solar Cells (DSSCs)," *Journal of Material Chemistry*, Vol. 20, No. 12, 2010, pp. 2391-2399. [doi:10.1039/b926163j](https://doi.org/10.1039/b926163j)
- [11] W. D. Zeng, Y. M. Cao, Y. Bai, Y. H. Wang, Y. S. Shi, M. Zhang, F. F. Wang, C. Y. Pan and P. Wang, "Efficient Dye-Sensitized Solar Cells with an Organic Photosensitizer Featuring Orderly Conjugated Ethylenedioxythiophene and Dithienosilole Blocks," *Chemistry of Materials*, Vol. 22, No. 5, 2010, pp. 1915-1925. [doi:10.1021/cm9036988](https://doi.org/10.1021/cm9036988)
- [12] H. Usta, G. Lu, A. Facchetti and T. J. Marks, "Dithienosilole- and Dibenzosilole-Thiophene Copolymers as Semiconductors for Organic Thin-Film Transistors," *Journal of the American Chemical Society*, Vol. 128, No. 28, 2006, pp. 9034-9035. [doi:10.1021/ja062908g](https://doi.org/10.1021/ja062908g)
- [13] J. Ohshita, "Conjugated Oligomers and Polymers Containing Dithienosilole Units," *Macromolecular Chemistry and Physics*, Vol. 210, No. 17, 2009, pp. 1360-1370. [doi:10.1002/macp.200900180](https://doi.org/10.1002/macp.200900180)
- [14] J. W. Chen and Y. Cao, "Silole-Containing Polymers: Chemistry and Optoelectronic Properties," *Macromolecular Rapid Communications*, Vol. 28, No. 17, 2007, pp. 1714-1742. [doi:10.1002/marc.200700326](https://doi.org/10.1002/marc.200700326)
- [15] H. Jung, H. Hwang and K.-M. Park, "Palladium-Catalyzed Cross-Coupling Reactions of Dithienosilole with Indium Reagents: Synthesis and Characterization of Dithienosilole Derivatives and Their Application to Organic Light-Emitting Diodes," *Organometallics*, Vol. 29, No. 12, 2010, pp. 2715-2723. [doi:10.1021/om100222b](https://doi.org/10.1021/om100222b)
- [16] J. Ohshita, M. Nodono and T. Watanabe, "Synthesis and Properties of Dithienosiloles," *Journal of Organometallic Chemistry*, Vol. 553, No. 1-2, 1998, pp. 487-491. [doi:10.1016/S0022-328X\(97\)00643-8](https://doi.org/10.1016/S0022-328X(97)00643-8)
- [17] K.-H. Lee, J. Ohshita and A. Kunai, "Synthesis and Properties of Bis(methylthio)dithieno-silole and Its Oxides," *Organometallics*, Vol. 23, No. 23, 2004, pp. 5481-5487. [doi:10.1021/om049642b](https://doi.org/10.1021/om049642b)
- [18] M. Iyoda, M. Miura, S. Sasaki, S. M. H. Kabir, Y. Kuwatani and M. Yoshida, "Synthesis of Dithienothiophenes, Cyclopentadithiophene and Silacyclopentadithiophenes Using Palladium-Catalyzed Cyclization," *Tetrahedron Letters*, Vol. 38, No. 26, 1997, pp. 4581-4582. [doi:10.1016/S0040-4039\(97\)00979-9](https://doi.org/10.1016/S0040-4039(97)00979-9)
- [19] G. Lu, H. Usta, C. Risko, L. Wang, A. Facchetti, M. A. Ratner and T. J. Marks, "Synthesis, Characterization, and Transistor Response of Semiconducting Silole Polymers with Substantial Hole Mobility and Air Stability. Experiment and Theory," *Journal of the American Chemical Society*, Vol. 130, No. 24, 2008, pp. 7670-7685. [doi:10.1021/ja800424m](https://doi.org/10.1021/ja800424m)
- [20] L. Liao, L. Dai, A. Smith, M. Durstock, J. Lu, J. Ding and Y. Tao, "Photovoltaic-Active Dithienosilole-Containing Polymers," *Macromolecules*, Vol. 40, No. 26, 2007, pp. 9406-9412. [doi:10.1021/ma071825x](https://doi.org/10.1021/ma071825x)
- [21] Y. He, G. Zhao, M. Zhang, J. Min and Y. F. Li, "Synthesis and Characterization of Low Bandgap Poly (Dithienosilole Vinylene) Derivatives," *Synthetic Metals*, Vol. 160, No. 9-10, 2010, pp. 1045-1049. [doi:10.1016/j.synthmet.2010.02.024](https://doi.org/10.1016/j.synthmet.2010.02.024)
- [22] J. Braddock-Wilking, Y. Zhang, J. Y. Corey and N. P. Rath, "Preparation of 1,1-Disubstituted Silacyclopentadienes," *Journal of Organometallic Chemistry*, Vol. 693, No. 7, 2008, pp. 1233-1242. [doi:10.1016/j.jorganchem.2008.01.017](https://doi.org/10.1016/j.jorganchem.2008.01.017)
- [23] Q. Luo, C. Wang, Y. X. Li, K. B. Ouyang, L. Gu, M. Uchiyama and Z. F. Xi, "Opening the Silole Ring: Efficient and Specific Cleavage of the *endo*-C(sp²)-Si Bond with AcOH/ROH System," *Chemical Science*, Vol. 2, No. 11, 2011, pp. 2271-2274. [doi:10.1039/c1sc00356a](https://doi.org/10.1039/c1sc00356a)
- [24] Y. G. Wang, Z. H. Wang, D. F. Zhao, Z. Wang, Y. X. Cheng and H. Wang, "Efficient Synthesis of Trimethylsilyl-Substituted Dithieno[2,3-*b*:3',2'-*d*]-thiophene, Tetra-[2,3-thienylene] and Hexa[2,3-thienylene] from Substituted [3,3']Bithiophenyl," *Synlett*, Vol. 15, 2007, pp. 2390-2394.