

interferences. First, a calibration curve was obtained with standard solutions, which were prepared from the stock solution. It showed a good linearity for the range of interests. However, when concentrations were determined from the calibration curve, the result disagreed from the true values more than 20%. This was probably due to the interferences from the matrix of SRM. Thus, standard addition method was chosen and the results showed good agreement with the reference values (Table 4).

To increase the enrichment factor, sample volume should be increased. Currently, 1.0 mL of sample loop is used and the enrichment factor is 8 with the sampling speed of 15/hr. If it is increased to 10.0 mL, it could be increased more than 80 times. However, the sampling speed is reduced to 2/hr.

In conclusion, on-line precipitation preconcentration is a very simple and accurate technique to enhance the analytical capability of the existing instrument. Enrichment of 8 fold with accurate result could be done very comfortably. If time is sacrificed, further enrichment is possible and can be extended to various other elements.

Acknowledgement. The authors thank for the financial support from Korea Science and Engineering Foundation (81510-677) and the donation of Flame AA from Sun-il Inc.

References

- Mizuike, A.; Hiralde, M. *Pure and Appl. Chemistry* **1982**, *54*, 8, 1555.
- Hiraide, M.; Ito, T.; Mizuno, K. *Analytica Chim. Acta* **1983**, *148*, 305.
- Kim, Y. S.; Jung, Y. J.; Choi, H. S. *Bull. of the Korean Chem. Soc.* **1998**, *19*, 50.
- Porta, V.; Sarzanini, C.; Abollino, O.; Mentasti, E.; Carlami, E. *J. of Anal. Atom. Spectrom.* **1992**, *7*, 19.
- Reimer, R. A.; Mizaki, A. *J. of Anal. Atom. Spectrom.* **1992**, *7*, 1239.
- Posta, J.; Berndt, H.; Luo, S. K.; Schaldach, G. *Anal. Chem.* **1993**, *65*, 2590.
- Welz, B.; Xu, S.; Sperling, M. *Appl. Spectrosc.* **1991**, *45*(9), 1433.
- Fang, A.; Dong, L. *J. of Anal. Atom. Spectrom.* **1992**, *7*, 439.
- Santelli, R. E.; Gallego, M.; Valcarcel, M. *Anal. Chem.* **1989**, *61*, 1427.
- Cho, Y. M.; Pak, Y-N. *Anal. Sci.* **1997**, *13*, 41.
- Yeon, P. H.; Huh, G.; Pak, Y. N. *Bull. Korean Chem. Soc.* **1998**, *19*, 766.
- Park, K.; Pak, Y. N., *Bull. Korean Chem. Soc.* **1995**, *16*, 422.

Thiophene-Fused Tetrathiafulvalenes as a New Molecular Donor

Ha-Jin Lee, Young-Youn Kim, and Dong-Youn Noh*

Department of Chemistry, Seoul Women's University, Seoul 139-774, Korea

Received April 15, 1998

As a potential π -electron donor, tetrathiafulvalene (TTF) and its derivatives have been intensively studied and synthesized by coupling and noncoupling methods.¹⁻⁶ Recent examples include new TTF derivatives fused with some heterocycles such as pyrrole, pyrazine, selenophene and thiophene.⁴ These heterocycle-fused TTFs exhibit either lower or higher oxidation potentials than those of TTF depending on the electron withdrawing ability of heterocycles. As the precursors of recently developed TTF derivatives, a number of 2-thioxo-1,3-dithiole derivatives were developed by utilizing dmit moiety.¹⁻³ One of the useful synthetic routes is to use Lawesson's reagent (LR), in

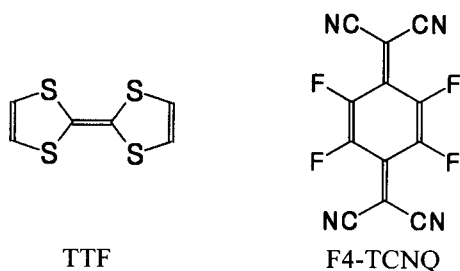
which heterocycles such as dithiin or thiophene are made by the unusual cyclization.⁵

Here, we report unexpected desulfurization of dicarbonyl dmit **4** accompanied with *in situ* cyclization to give thiophene-fused 2-thioxo-1,3-dithiole **1** along with the synthesis and electrochemical properties of its coupled products, bis(diphenylthiophene)-TTF **3** and diphenylthiophene-fused bis(methylthio)TTF **7**. The synthesis and the electrical property of charge-transfer salt of **7** with F4-TCNQ (tetrafluorotetracyano-*p*-quinodimethane) are also described.

Experimental

Instrumentations such as NMR, FT-IR, UV, Mass spectrometer were described in the previous publication.⁷ Elemental analysis was carried out at Korea Basic Science Institute (KBSI).

1,8-diketone (4). To a purple ethanol solution (40 mL) of disodium salt **6** (10 mmol) was added two mole ratio of desylchloride **5** (20 mmol, 4.61 g) dissolved in ethanol (100 mL). After stirring for 1h, the yellow precipitate was collected from filtrate and washed with ethanol. yield ~100 %; mp. 157-158 °C; ¹H NMR (250 MHz, CDCl₃)



δ 7.8 (20H, m) 6.1 (H, s) 5.9 (H, s); FT-IR (KBr, cm^{-1}) 1674.3, 1595.2, 1579.8, 1448.6, 1275.0, 1207.5, 1188.2, 1060.9, 993.4, 694.4, 640.4, 553.6, 513.1; UV (CH_3CN , nm) 214 (m) 248 (st) 376 (w).

4,5-diphenylthieno[2,3-d]-1,3-dithiol-2-thione (1).

A toluene solution (100 mL) containing LR (10 mmol, 4.04 g) and **4** (10 mmol, 5.88 g) was refluxed for 24 h. After filtration at room temperature, the filtrate was decolorized with activated charcoal. Concentrated under reduced pressure, the red oily product was purified by column chromatography on silica gel eluting with chloroform/n-hexane (1:1). The second band (orange colour) was collected and crystallized as yellow needle. yield 41%; mp. 156-157 °C; ^1H NMR (250 MHz, CDCl_3) δ 7.3 (10H, m); ^{13}C NMR (62.9 MHz, CDCl_3) δ 128.500, 128.596, 128.735, 128.853, 129.043, 129.102, 132.633, 133.895, 140.747, 143.917, 213.663; FT-IR (KBr, cm^{-1}) 1593.8, 1528.0, 1495.5, 1477.7, 1442.1, 1081.3, 1052.0, 1038.0, 1029.0, 973.4, 917.8, 900.2, 858.4, 801.8, 771.8, 757.5, 712.9, 692.1, 603.3, 497.8, 481.9; UV (CH_3CN , nm) 214 (st) 230 (sh) 398 (st); EIMS (m/z) 342 (M^+); FABMS (m/z) 343 ($M+H$) $^+$.

4,5-diphenylthieno[2,3-d]-1,3-dithiol-2-one (2).

Compound **1** was transformed to its oxo form **2** following the standard method.³⁶ yield 68.5%; mp. 162-163 °C; ^1H NMR (250 MHz, CDCl_3) δ 7.3 (10H, m); ^{13}C NMR (62.9 MHz, CDCl_3) δ 121.148, 128.313, 128.773, 128.851, 129.012, 129.104, 129.643, 132.591, 134.682, 140.554; FT-IR (KBr, cm^{-1}) 1754.9, 1704.1, 1669.8, 1643.7, 1595.2, 1572.3, 1532.4, 1494.2, 1478.1, 1441.7, 1409.6, 1361.1, 1261.1, 1178.3, 1155.5, 1070.3, 1030.9, 917.9, 902.0, 852.6, 795.5, 772.0, 751.6, 712.4, 691.8, 601.5, 559.2, 535.9, 498.2, 483.7, 460.4, 402.5; UV (CH_3CN , nm) 216 (st) 226 (st) 284 (m); EIMS (m/z) 326 (M^+); FABMS (m/z) 326 (M^+).

Bis(diphenylthiophene)-tetrathiafulvalene (3). A mixture of **2** (1 mmol, 326 mg) and triethyl phosphite (23.3 mmol, 4 mL) was refluxed for 2 h with stirring. The orange precipitate was filtered and washed with ethanol and chloroform at room temperature. yield 58%; mp. 235 °C (dec.); FT-IR (KBr, cm^{-1}) 3061.2, 3026.5, 1674.3, 1595.2, 1496.9, 1481.4, 1442.8, 1068.6, 1030.1, 1001.1, 916.2, 889.2, 842.9, 769.6, 756.1, 715.6, 694.4, 603.8, 507.3; UV (CH_3CN , nm) 234 (st); FABMS (m/z) 619.99 (M^+); HR-FABMS calc. for $\text{C}_{34}\text{H}_{20}\text{S}_6$ 619.9889 found 619.9869.

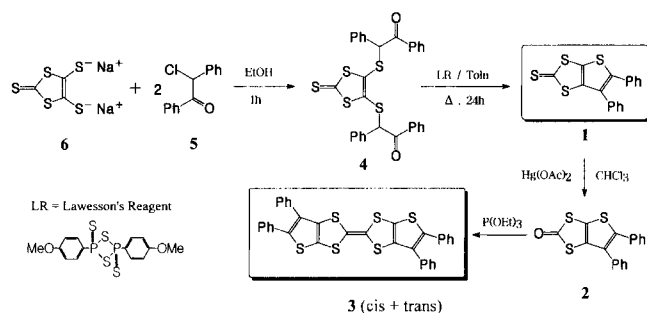
Diphenylthiophene-fused bis(methylthio)tetrathiafulvalene (7). A mixture of **2** (1 mmol, 326 mg), **9** (1 mmol, 226 mg) and triethyl phosphite (23.3 mmol, 4 mL) was refluxed for 40 min. with stirring. Cooling down to room temperature, the orange precipitate was filtered and confirmed as a self-coupled product **3**. Second precipitate was obtained by adding methanol to a residue solution and keeping in freezer. Product **7** obtained thereby was purified by column chromatography on silica gel eluting with chloroform. yield 31%; mp. 198-200 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.3 (10H, m) 2.4 (6H, d); ^{13}C NMR (62.9 MHz, CDCl_3) δ 19.197, 19.251, 127.061, 127.813, 127.920, 128.256, 128.558, 128.760, 134.856; FT-IR (KBr, cm^{-1}) 3055.4, 3022.6, 2916.6, 1595.2, 1481.4, 1442.8, 1419.7, 1365.7, 1311.7, 1265.4, 1072.5, 1028.1, 966.4, 889.2, 758.1, 711.8, 694.4, 603.8, 495.7; UV (CH_3CN , nm) 214 (st) 228 (sh) 304 (st) 332 (sh) 384 (w); FABMS (m/z) 503.91 (M^+); HR-FABMS calc. for $\text{C}_{22}\text{H}_{16}\text{S}_7$ 503.9297 found 503.9310.

Electrochemical Synthesis of 7 · (F4-TCNQ) Charge-transfer Complex. Polycrystalline **7** · (F4-TCNQ) charge-transfer complex was obtained by the conventional electrochemical crystallization method² with **7** (9.13×10^{-5} mol, 46 mg) and F4-TCNQ (9.05×10^{-5} mol, 25 mg) in dried trichloroethane (15 mL each) using H-type cell. Black plate-like polycrystals were collected from the anodic chamber after applying 1 μA for ca. 13 days. Anal. Calcd. for $\text{C}_{34}\text{H}_{16}\text{N}_4\text{S}_7\text{F}_4$: C 52.29 N 7.17 S 28.74, Found: C 51.32 N 7.05 S 30.38; FT-IR (KBr, cm^{-1}) 2193.2, 2170.1, 1637.7, 1535, 1496.9, 1425.5, 1388.8, 1317.5, 1197.9, 1143.9, 1072.5, 968.3, 887.3, 808.2, 760, 711.8, 696.3, 603.8, 470.7, 443.7; UV (CH_3CN , nm) 206 (st) 280 (w) 308 (w) 344 (w) 366 (w) 388 (st) 410 (st) 478 (w) 686 (w) 754 (m).

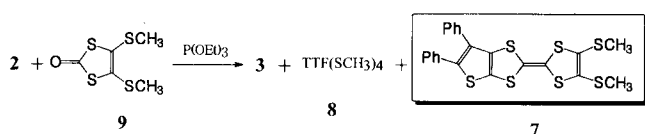
Results and Discussion

1,8-Dicarbonyl compound **4** was obtained from nucleophilic substitution reaction of desyl chloride **5** with Na_2dmf **6** in dry ethanol or THF. Solvent removal followed by chromatographic purification with chloroform produced orange-colored product **4**. Treatment of **4** with LR in toluene for 24 h afforded thiophene-fused 2-thioxo-1,3-dithiole **1** in 41% yield. (Scheme 1) The loss of sulfur and consecutive *in situ* cyclization were detected by several spectroscopic analyses; ^{13}C NMR (four peaks at 143.917, 140.747, 133.895 and 132.633 ppm for four unequivalent carbones in thiophene moiety), FT-IR (characteristic frequencies of thiophene at 692.1, 712.9, 757.5 and 771.8 cm^{-1}) and MS data ($m/z = 342$ for M^+). The electron withdrawing property of phenyl groups may play an important role in this reaction producing thiophene moiety in **1**, which is comparable to the previous result that six-membered ring (1,4-dithiin) instead of five-membered ring (thiophene) was formed when monophenyl analogue of **5** was used.⁵

In order to synthesize self-coupled product, thiophene-fused 2-thioxo-1,3-dithiole **1** was converted to its oxygen analogue **2** via a standard method using $\text{Hg}(\text{OAc})_2$ in chloroform.³ Reaction of **2** in freshly distilled $\text{P}(\text{OEt})_3$ yielded possible isomers of self-coupled compound **3** in which TTF was bi-fused with diphenyl-substituted thiophenes. This compound showed very low solubility in conventional solvents such as methanol, THF and chloroform. Conventional NMR spectra and cyclic voltammogram, therefore, could not be measured, but high-resolution FABMS technique was applied for identification. In order to obtain the other coupled product having improved solubility, **2** was coupled with **9** according to the



Scheme 1



Scheme 2

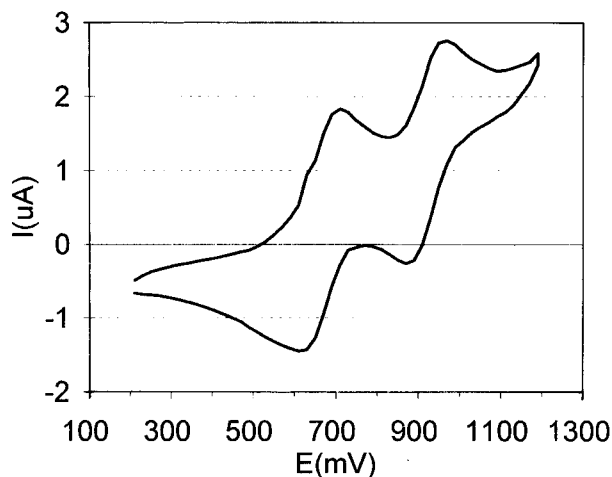


Figure 1. Cyclic Voltammogram of 7 (scan speed 50 mV/s, Pt-button working and Pt wire counter electrodes, Ag/AgNO₃ reference electrode in CH₃CN with 0.1 M tetra-n-butylammonium tetrafluoroborate as supporting electrolyte).

previous reaction conditions. Consequently, a mixture of coupled products was obtained (Scheme 2), from which 3 (5%) could be firstly isolated due to its insolubility and, 7 (31%) and 8 (trace amount) were successfully separated by silica column chromatography. 7 was recrystallized from benzene/methanol and analyzed.

Cyclic voltammogram of 7 was measured in acetonitrile solution with tetra-n-butylammonium tetrafluoroborate as supporting electrolyte and plotted in Figure 1. Similar to TTF, 7 shows two pairs of reversible redox peaks. The oxidation potentials of 7 observed at $E_{ox}^1 = 0.71$ V and $E_{ox}^2 = 0.97$ V are higher than those of TTF ($E_{ox}^1 = 0.56$ V and $E_{ox}^2 = 0.93$ V) indicating that 7 has weaker electron donor ability than TTF itself but very close to TTF(SET)₄ ($E_{ox}^1 = 0.72$ V and $E_{ox}^2 = 0.97$ V).³ The potential difference (ΔE_{ox}) between the first and the second oxidation potentials of 7 is 0.26 V which is smaller than that of TTF ($\Delta E_{ox} = 0.37$ V) due to reduction of on-site Coulomb repulsion.

Attempts to obtain charge-transfer(CT) salt of 7 with TCNE (tetracyanoethylene), TCNQ (tetracyano-*p*-quinodimethane), DDQ (dichlorodicyano-*p*-benzoquinone) and TBA · I₃

(tetra-n-butylammonium triiodide) by both chemical and electrochemical methods were unsuccessful. However, extended efforts employing stronger acceptor molecule (F4-TCNQ) in H-type electrochemical cell were successful: Black plate-like polycrystals were collected from the anodic chamber and identified as an 1:1 charge-transfer complex, 7 · (F4-TCNQ), based on elemental analysis. C≡N stretching frequency of F4-TCNQ (2226 cm⁻¹) shifts to 2193.2 cm⁻¹ ($\Delta \nu_{C\equiv N} = 33$ cm⁻¹). The degree of charge transfer (Z) estimated from the correlation⁸ $\Delta \omega/Z = -44$ cm⁻¹ where $\Delta \omega$ is the C≡N frequency difference between F4-TCNQ and CT salt, is 0.8. In spite of high degree of charge transfer, electrical conductivity of CT salt on the pressed pellet was measured as 10⁻⁶ S/cm at room temperature. It means that this CT salt could be Mott insulator as other CT complexes of F4-TCNQ.⁹

Acknowledgement. The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program year of 1997.

References

- (a) Krief, A. *Tetrahedron* **1986**, 42, 1209. (b) Narita, M.; Pittman Jr., C. U. *Synthesis* **1976**, 489 and references therein.
- Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors (including Fullerenes)*; Prentice Hall: Englewood Cliffs, NJ, 1992.
- Noh, D.-Y.; Lee, H.-J.; Hong, J.; Underhill, A. E. *Tetrahedron Lett.* **1996**, 37, 7603.
- (a) Zong, K.; Cava, M. P. *J. Org. Chem.* **1997**, 62, 1903. (b) Lahlil, K.; Moradpour, A.; Merienne, C.; Bowlas, C. *J. Org. Chem.* **1994**, 59, 8030. (c) Rovira, C.; Veciana, J.; Santal, N.; Tarrs, J.; Cirujeda, J.; Molins, E.; Llorca, J.; Espinosa, E. *J. Org. Chem.* **1994**, 59, 3307. (d) Ketcham, R.; Hornfeldt, A.; Gronowitz, S. *J. Org. Chem.* **1984**, 49, 1117. (e) Engler, E. M.; Patel, V. V.; Andersen, J. R.; Schumaker, R. R.; Fukushima, A. A. *J. Am. Chem. Soc.* **1978**, 100, 3769.
- Ozturk, T. *Tetrahedron Lett.* **1996**, 37, 2821.
- Varma, K. S.; Bury, A.; Harris, N. J.; Underhill, A. E. *Synthesis* **1987**, 837.
- Lee, H.-J.; Noh, D.-Y. *Bull. Korean Chem. Soc.* **1998**, 19, 339.
- Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, 103, 2442.
- Bloch, A. N. *Bull. Am. Phys. Soc.* **1980**, 25, 255.