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Thermal and microwave assisted reactions of 2,5-disubstituted thienosultines with [60]fullerene: non-Kekulé biradicals and self-sensitized oxygenation of the cycloadduct

Chih-Chin Chi, I-Feng Pai and Wen-Sheng Chung*

Department of Applied Chemistry, National Chiao Tung University, 1001 Ta-Hseuh Rd., Hsinchu 30050, Taiwan, ROC

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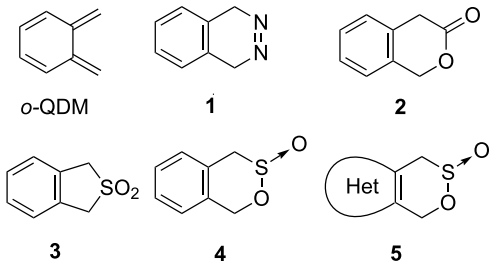
Abstract—Refluxing an *o*-dichlorobenzene solution of 2,5-disubstituted thienosultines **10a–f** with [60]fullerene for 2–24 h gave both 1:1 and 2:1 cycloadducts in 37–79% isolated yields. The reaction was highly accelerated by microwave irradiation giving comparable yields of cycloadducts. Sultines **10a–f** underwent cheletropic extrusion of SO_2 to form the corresponding non-Kekulé biradical intermediates **11a–f**, which were subsequently trapped by [60]fullerene to form corresponding cycloadducts. The activation energy barriers ($\Delta G_c^{\neq}$) determined for the boat-to-boat inversion of these 4′,5′,6′,7′-tetrahydrobenzo[*c*]thieno-[5′,6′:1,2][60]fullerene adducts **12a–f** were found to be in the range of 13.5–14.8 kcal/mol. Unexpectedly, one of the monoadduct **12a** was found to be labile when kept in air under ambient light. Two new products **15** (a sulfine-enone) and **16** (an endione) were isolated from the decomposed **12a** and were found to derive from self-sensitized singlet oxygen reaction on the 2,5-dimethylthieno moiety of **12a**.

1. Introduction

Functionalization of [60]fullerene is fascinating and promising for new ferromagnetic materials and biological application because of its unique spherical structure, photochemistry, and radical quenching properties.[1] The Diels–Alder reaction of [60]fullerene with *ortho*-quinodimethanes (*o*-QDMs)[2] has been developed extensively and represents one of the most powerful methods for synthesizing a large variety of functionalized fullerenes.[1,2] *o*-QDM is usually obtained from thermal or photochemical elimination of a small molecule from various precursors shown in Scheme 1.[2]

The diazene **1** can form *o*-QDM cleanly, but its five-membered ring heterocyclic analogues are usually unstable at room temperature.[3] Isochromanone **2** will undergo thermal decarboxylation only under harsh conditions (such as flash vacuum pyrolysis at 500 °C) unless it is substituted with electron-donating groups on the aromatic moiety.[4] Among the precursors for *o*-QDM, sulfolene[5] **3** and sultine[6] **4** are good choices because they undergo pyrolysis at reasonably low temperatures and yet they are usually stable indefinitely at room temperature.

Despite many reports of using hetero-*o*-QDM to functionalize [60]fullerene,[1,7] relatively little is known about whether the non-Kekulé biradicals[8] such as trimethylenemethane (TMM) or tetramethyleneethane (TME) will add to [60]fullerene efficiently. A pioneering work on the cycloaddition of TMM with C_{60} has been reported by Wudl,[9a] where the TMM biradical was generated from a 7-alkylidene-2,3-diazabicycloheptene, but the cycloadduct of the TMM-C_{60} was not isolated due to its similar polarity with C_{60}.[9a] Palladium-mediated addition of TMM to C_{60} has also been successfully carried out by Luh.[9b] Meanwhile, Ohno et al. reported[9c] the first success in using TME biradical to functionalize C_{60}, where 3,4-fused pyrrolo-3-sulfolenes were used as TME precursors. As our continuous interests in the research of



Scheme 1.

Keywords: Non-Kekulé biradical; TME biradical; Microwave; Cycloaddition; [60]Fullerene; Singlet oxygen reaction.
* Corresponding author. Tel.: +88 635131517; fax: +88 635723764; e-mail: wschung@cc.nctu.edu.tw

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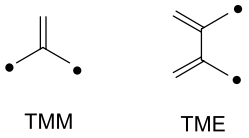
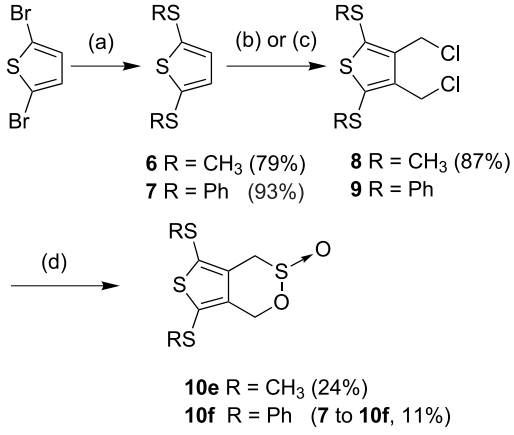
heteroaromatic-fused sultines **5** and their use in the generation of TME biradicals[10a,e] or hetero-*o*-QDMs,[10b–d] we report here the reaction of C_{60} with 2,5-disubstituted-thienosultines **10a–f** and an interesting self-sensitized singlet oxygen reaction of one of the fullerene adducts.



2. Results and discussion

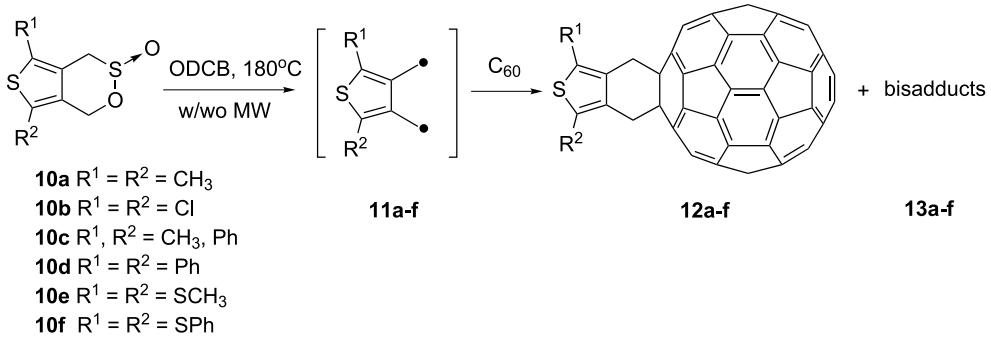
The syntheses of heterocyclic sultines **10a–d** through the reaction of corresponding bis(chloromethyl)thiophenes with Rongalite (sodium formaldehyde sulfoxylate) have been reported elsewhere.[10a,e] Sultines **10e** and **10f** were synthesized from **8** and **9** by a similar method, where the dialkylthio **8** and diarylthio **9** were obtained from lithium exchange of 2,5-dibromothiophene,[11] followed by thiolation, and then chloromethylation[3a,12] (Scheme 2). When refluxed in *o*-dichlorobenzene (ODCB) with C_{60} as a limiting reagent for different duration (2 h for **10a**,**c–f** and 24 h for **10b**), sultines **10a–f** underwent extrusion of SO_2, and the resulting non-Kekulé biradicals **11a–f** were intercepted as a mixture of 1:1 cycloadducts **12a–f** and 2:1 bisadducts **13a–f** in ca. 2–3:1 ratio (Scheme 3 and Table 1). When solutions of sultines **10a–f** with C_{60} were irradiated with microwave (900 W) under 180 °C for only 4 min, comparable yields of cycloadducts were obtained in all cases except **10b**; where sultine **10b** was almost completely converted to sulfolene instead of reacting with the C_{60}, therefore, only trace of adduct **12b** was observed. The isolated yields for these cycloadducts **12** and **13** were in the range of 37–79% (58–96% based on consumed C_{60}, Table 1). It is remarkable that microwave assisted synthesis dramatically shortened the reaction time needed compared to those by conventional heating.[13d] Furthermore, the ratio of monoadduct **12** vs. bisadduct **13** also increased from 2–3:1 to 3.5–6:1 when microwave was applied.



Scheme 2. Reagents and conditions: (a) 2.1 equiv *n*BuLi, THF, −78 °C, 30 min; 2.1 equiv RSSR, −78 °C, 1 h; (b) 37% HCHO, conc. HCl, rt, 8 h (for **8**); (c) $ClCH_2OCH_3$, $ZnCl_2$, $CHCl_3$, rt, 3 h (for **9**); (d) Rongalite, TBAB, DMF, rt, 10–24 h.

All fullerene adducts were separated by column chromatography on silica gel using cyclohexane/toluene as eluents. The low product yield for sultine **10b** was mainly due to its poor reactivity because there was no solubility problem. The bisadducts **13a–f** are mixtures of regioisomers and are usually difficult to be separated; therefore, their characterizations were only done by FAB-MS and ^{1}H NMR spectroscopy. The UV–vis spectra of compounds **12a–f** revealed a typical weak absorption band around 435 nm, which is characteristic of a dihydrofullerene structure for monoadduct.[1] Further support of the monoadducts **12a–f** came from FAB-MS by detecting their molecular ion peaks ($M+H^+$) at following *m*/*z* ratios: 859 for **12a**, 899 for **12b**, 921 for **12c**, 983 for **12d**, 921 for **12e**, and 1047 for **12f**.

^{1}H NMR spectra for **12a** showed that the methylene protons bridging C_{60} and thiophene displayed a singlet (δ 4.43) at 25 °C and the singlet became a well-resolved AB quartet below 5 °C. Variable-temperature NMR experiments revealed that these cycloadducts were in their boat forms and the boat-to-boat inversion rates can be determined. The coalescence temperature T_c of the two methylene doublets and their coupling constants were used to determine the activation energy barriers $\Delta G_c^{\neq}$.[10c,13,14] For **12a**, the two doublets coalesced to a broadened singlet at 291 K (T_c) and an activation energy, $\Delta G_c^{\neq}$, of 14.0±0.2 kcal/mol was calculated (Fig. 1a). Although different T_c values are expected for the two diastereotopic methylenes of **12c** due to molecular asymmetry, they happen to have same T_c values (290 K) and therefore have same activation energy barriers $\Delta G_c^{\neq}$ (Fig. 1b). Furthermore, despite the large variation in 2,5-disubstituents of **12a–f** (such as dimethyl, dichloro, diphenyl, bis(methylthio), and bis(phenylthio) groups), their $\Delta G_c^{\neq}$ are all within 13.5–14.8 kcal/mol



Scheme 3.

Table 1. Results of the cycloaddition reactions of sultines **10a–f** with C_{60} under microwave irradiation or conventional heating

Sultine	Microwave[a], yield (%)			Conventional heating[b], yield (%)		
	Time (min)	Monoadduct **12**	Bisadduct **13**	Time (h)	Monoadduct **12**	Bisadduct **13**
10a	4	47 (64)[c]	11 (15)[c]	2	38 (73)[c]	12 (23)[c]
10b	4	—[d]	—[d]	24	28 (44)[c]	9 (14)[c]
10c	4	39 (64)[c]	—[e]	2	47 (62)[c]	16 (20)[c]
10d	4	53 (81)[c]	9 (14)[c]	2	52 (65)[c]	20 (25)[c]
10e	4	41 (52)[c]	10 (13)[c]	2	52 (62)[c]	27 (32)[c]
10f	4	51 (76)[c]	15 (22)[c]	2	51 (63)[c]	27 (33)[c]

[a] Power 900 W, ODCB, 180 °C.
[b] ODCB, reflux.
[c] Based on consumed C_{60}.
[d] Sultine **10b** was completely converted to sulfolene without reacting with C_{60}.
[e] Trace.

(Table 2 and Figs. S1–S4). Compared to other 4,7-dihydrobenzo[*d*]thiophene-[5,6-*f*]-fullerene adducts such as **14a** and **14b**,[13b] these 4,7-dihydrobenzo[*c*]thiophene-[5,6-*e*]-fullerene adducts **12a–f** have larger $\Delta G_c^{\neq}$ by 2.8 kcal/mol on average.

The activation energy barriers of compounds **12a–f** are close to those of pyrazines[10c] and other carbocyclic fused [60]fullerenes.[14] Factors that may affect the activation energy barriers are dependent on the nature of the heterocyclic systems, such as bond lengths and angles,[7k,13b] tortional and angular constraints,[13b] electronic and steric effects.[10c] Bond order may have played an important role here on the magnitude of $\Delta G_c^{\neq}$, because **12a–f** which contain two *exocyclic* double bonds in the bridged cyclohexene ring have larger values in $\Delta G_c^{\neq}$, whereas compounds **14a**,**b** with an *endo* double bond character in the cyclohexene rings have smaller ones.[7f,13b,c] This observation is consistent with that reported by Illescas et al.[7f] where a correlation was found between the activation energies $\Delta G_c^{\neq}$ and the bond lengths of the cyclohexene double bond across the fullerene junction; that is, as the bond length increases the barrier also increases.

The ^{13}C NMR spectrum of **12a** showed only 20 peaks (with two peaks superimposed) when measured at 70 °C (well above T_c), where rapid ring inversion is expected and the symmetry of the molecule is simplified from C_s to C_{2v}, therefore, an overall of 21 peaks are expected. The ^{13}C NMR spectrum for **12a** showed the characteristic quaternary sp^3-carbon atoms of the 6,6-ring junction on the C_{60} cage at δ 66.9, the α-methyls of thiophene at δ 13.3, and the methylene bridges between thiophene and C_{60} at δ 41.4. There are 17 other peaks of quaternary sp^2 carbons between 134 and 158 ppm for compound **12a**. All spectroscopic features of **12a–f** are consistent with the monoadducts of thienobiradicals **11a–f** that add to C_{60} on its 6,6-ring junction. Complete spectroscopic data of **12a–f** are summarized in Section 3.

Research on the oxygenation[15–19] of fullerene derivatives has attracted considerable attention because it provides an excellent method for ring-opening of the fullerene cage.[1,19] Many oxidizing reagents, such as ozone,[15] iodosobenzene,[16] and *m*-CPBA,[18] have been employed to prepare fullerene oxides. Above all, photo-induced ring opening of [60]fullerene cage by reaction with singlet oxygen ($^1O_2$) seems to have drawn the most attention.[19] We were surprised to find that, short exposure of a non-degassed solution of **12a** in CS_2 to ambient light led to its quick decomposition, where two new products **15** and **16** (in about 1:2 ratio) could be isolated from this solution in 50–73% yields. Compound

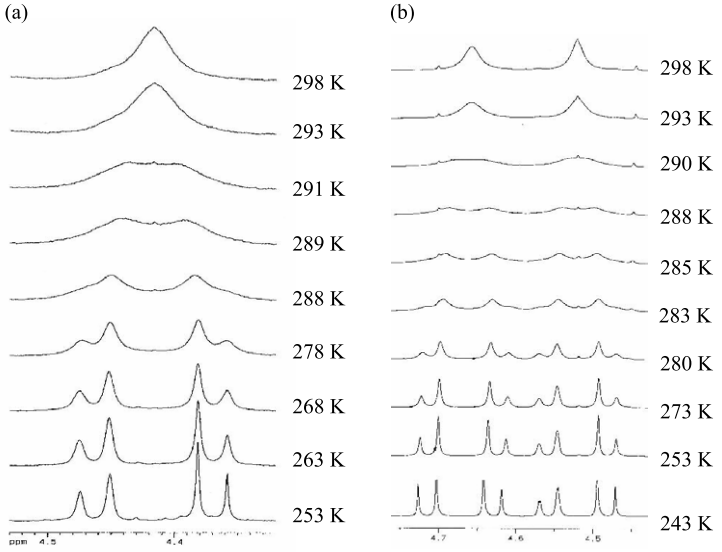
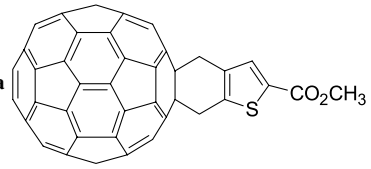
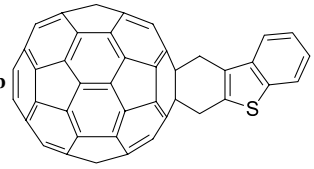


Figure 1. Various temperature ^1H NMR spectra (600 MHz, $CDCl_3/CS_2=1:2$) of cycloadducts: (a) **12a**, for which T_c is 291 K; and (b) **12c**, for which both the two T_c values are 290 K.

Table 2. Activation free energies ($\Delta G_c^{\neq}$) of [60]fullerene adducts **12a–f** from dynamic ^{1}H NMR[a] studies

Thienoadduct (substituents)	T_c (K)	$\Delta\nu$ (Hz)[b]	J_{AB} (Hz)[b]	$\Delta G_c^{\neq}$ (kcal/mol)	Reference
12a[c] (2,5-Dimethyl)	291	53.8	14.0	14.0±0.2	This work
12b[d] (2,5-Dichloro)	286	95.6	14.1	13.5±0.2	This work
12c[c] (2-Methyl-5-phenyl)	290	48.7	14.1	14.2±0.2	This work
	290	42.6	14.0	14.2±0.2	This work
12d[c] (2,5-Diphenyl)	304	59.1	14.1	14.8±0.2	This work
12e[c] (2,5-Bis(methlthio))	298	120.9	14.5	14.6±0.2	This work
12f[c] (2,5-Bis(phenylthio))	298	152.3	14.4	14.0±0.2	This work
14a 	245	26.2	14.7	12.0±0.2	13b
	241	14.8	13.9	11.9±0.2	13b
14b 	223	51.0	15.4	10.7±0.2	13b
	231	86.7	15.4	11.0±0.2	13b

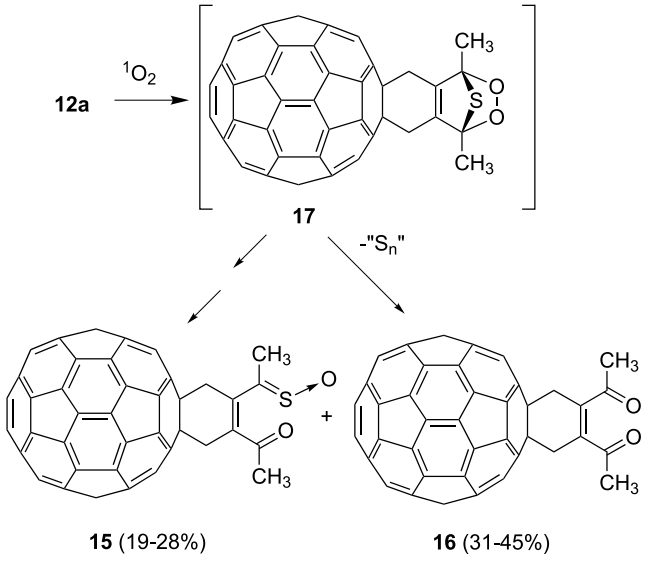
[a] Various temperature measurements were taken in a 600 MHz NMR (**12e** in a 500 MHz NMR). The activation free energies were obtained using equation: $k_c=2.22\ (\Delta\nu_{AB}^2+6J_{AB}^2)^{1/2}$, $\Delta G_c^{\neq}=4.58\ T_c\ (10.32+\log\ (T_c/k_c))\times10^{-3}$ kcal/mol.
[b] Data are reported at the highest temperature that affords well-separated quartet: −10 °C for **12a**, −15 °C for **12b**, 7 °C for **12c**, 20 °C for **12d**, −5 °C for **12e**, and 0 °C for **12f**.
[c] In $CDCl_3/CS_2=1:2$.
[d] In d_4-*ortho*-dichlorobenzene.

12a was found to be stable if either oxygen or light was kept from the system.

The new product **15** shows a molecular ion peak ($M+H^+$) at $m/z=891$, which is 32 units more than the cycloadduct **12a**. Furthermore, FT-IR spectrum of **15** shows medium signals at 1700 and 1529 cm^{-1}. Compound **16** shows strong vibrations at 1685, 1636 and 1617 cm^{-1} (Fig. S5, Supporting Information), but its molecular ion peak is the same with **12a** ($m/z=859$). The ^{13}C NMR of compound **15** shows the characteristic absorption of two carbonyl carbons at 197.7 (C=O) and 193.0 ppm (C=S→O) as well as two quaternary carbons of C_{60} moiety at 65.8 and 65.5 ppm. Compound **16** shows the characteristic absorption of only one carbonyl carbon at 200.6 ppm and one quaternary carbon of C_{60} moiety at 65.3 ppm.

Based on all structural information available for **15** and **16** and literature precedents,[19–21] we speculated that singlet oxygen reaction must have occurred on the thiophene moiety first and forming an endoperoxide **17**. Subsequent rearrangement of the endoperoxide **17** should lead to two fullerene products: one, an asymmetrical sulfine-enone **15**, and the other, a symmetrical endione **16** (see Scheme 4). Similar reactions have been reported in the methylene blue sensitized singlet oxygen reactions of cyclohexenone-fused thiophenes[20b,c] and 2,5-dimethylthiophene.[21] All spectroscopic data for **15** and **16** are consistent with the proposed structures.

It should be noted that other thienoadducts, such as 2,5-dichloro-, diphenyl-, bis(methylthio)-, bis(phenylthio)-, and 2-methyl-5-phenylthienofullerenes **12b–f**, are free from the singlet oxygen induced reaction and can be stored for several months in air with ambient light. There are two possibilities from the experimental results: (a) singlet oxygen was not formed in the solution of **12b–f**; therefore, they are stable in air and ambient light, or (b) singlet oxygen did form, however, the other cycloadducts **12b–f**, with different 2.5-substituents, simply did not react with it. We thus carried out two series of experiments to clarify possible reasons for the big differences in singlet oxygen reactivity towards **12a** and **12b–f**. In the first series of experiments, we found that adding 2,5-dimethylthiophene to the solution of other fullerene derivatives (e.g., **12d**) did result in the photoinduced oxygenation of 2,5-dimethylthiophene (entry



Scheme 4.

3 in Table 3 of Supporting Information). The results suggest that singlet oxygen is formed in all solutions of fullerene adducts **12a–f** and yet it reacts with them in very different rates.[22] In the second series of experiments, we prepared *d*-chloroform solutions of various 2,5-disubstituted thiophenes (**A–F**) with C_{60} (1.5 mol %) as a singlet oxygen sensitizer and irradiated them simultaneously with tungsten lamp to make sure that they were exposed to the same doses of light. The relative reactivity of singlet oxygen towards these 2,5-disubstituted thiophenes are: 2,5-dimethylthiophene **A** (37%), 2,5-bis(methylthio)thiophene **E** (26%), 2-methyl-5-phenylthiophene **C** (<6%) (Table 3, Supporting Information).[21c] The rest of the other 2,5-disubstituted-thiophenes (**B**, **D**, and **F**) did not show any observable reactivity toward singlet oxygen (namely <1% conversion) even after 42 h irradiation by tungsten lamp.

In summary, we report here the syntheses of a series of thieno-fused fullerenes which represents one of the rare examples in the derivatization of [60]fullerene through TME non-Kekulé biradicals.[9] When ODCB solutions of sultines **10a–f** and C_{60} were refluxed for 2–24 h or under microwave irradiation (900 W, <180 °C) for only 4 min, moderate to good yields (37–79%) of cycloadducts **12a–f** were obtained in all cases except **10b**. To our surprise, of the six thieno-[60]fullerene adducts **12a–f**, only **12a** was unstable in the presence of oxygen and ambient light. The decomposed products from **12a** were characterized and found to derive from singlet oxygen reaction on the 2,5-dimethylthiophene moiety of **12a**. Why some of the fullerene derivatives attract oxygen on standing, while others resist oxidation, deserves further photophysical and theoretical calculation study.

3. Experimental

3.1. General

3.1.1. 2,5-Bis(methylthio)thiophene 6. The preparation of **6** followed a literature[11] procedure. To a solution of 2,5-dibromothiophene (5.00 g, 20.7 mmol) in diethyl ether (100 mL) at −78 °C was added *n*-butyllithium (2.5 M in hexane, 43.4 mmol) via syringe under nitrogen. After the solution was stirred for 30 min, dimethyl disulfide (4.28 g, 45.5 mmol) in ether (20 mL) was added dropwise with vigorous stirring. The mixture was stirred at −78 °C for 1 h and then slowly warmed to room temperature. An ice-cold saturated ammonium chloride solution (50 mL) was added. The two layers were separated, and the aqueous layer was extracted with ether (3×30 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. The residue was subjected to silica gel chromatography using hexane as the eluent to yield 2.89 g (16.4 mmol, 79%) of **6** as a colorless oil: R_f=0.68 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.90 (2H, s), 2.48 (6H, s); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 139.1 (Cq), 131.0 (CH), 21.9 (CH_3); MS (EI) *m/z* 178/177/176 (M^+, 9/5/95), 161 (M^+-CH_3, 100), 114 ($M^+-CH_3-SCH_3$, 42), 69 (42); HRMS *m/z* calcd for $C_6H_8^{32}S_3$ 175.9789, found 175.9788.

3.1.2. 2,5-Bis(phenylthio)thiophene 7. Follow the same procedures as in the preparation of **6**. 2,5-Dibromothiophene (5.00 g, 20.7 mmol) was allowed to react with *n*-butyllithium (2.5 M in hexane, 43.4 mmol), and then with diphenyl disulfide (9.48 g, 43.4 mmol). The crude product was purified by column chromatography (hexane) to give 5.79 g (19.3 mmol, 93%) of **7** as a colorless solid: mp 42–43 °C (hexane); R_f=0.33 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.18 (10H, m), 7.16 (2H, s); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 137.4 (Cq), 136.9 (Cq), 135.5 (CH), 129.1 (CH), 128.1 (CH), 126.7 (CH); MS (EI) *m/z* 303/302/301/300 (M^+, 3/16/24/100), 299 (M^+-1, 23), 190 (78); HRMS *m/z* calcd for $C_{16}H_{12}S_3$ 300.0103, found 300.0096; Anal. Calcd for $C_{16}H_{12}S_3$: C, 63.96; H, 4.03. Found: C, 63.73; H, 4.17.

3.1.3. 3,4-Bis(chloromethyl)-2,5-bis(methyl)thiophene 8.[12] Concentrate hydrochloric acid (12 M, 20 mL) was added to the mixture of **6** (2.00 g, 11.3 mmol) and 37% formaldehyde aqueous solution (1.70 g, 56.7 mmol). The mixture was stirred at room temperature for 8 h, then poured into water (30 mL), and extracted with CH_2Cl_2 (3×20 mL). The organic layers were combined, washed with water (2×30 mL), brine, dried over $MgSO_4$, filtered, and concentrated in vacuum to yield 2.71 g (9.92 mmol, 87%) of **8** as a pale green solid. Product **8** decomposed after chromatography on silica gel; therefore, crude product was used without further purification. Mp 75.5–77 °C (a colorless solid after recrystallization from hexane). (lit.[23] 78–78.5 °C); R_f=0.75 (hexane/ethyl acetate=4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.77 (4H, s), 2.47 (6H, s); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 139.2 (Cq), 138.9 (Cq), 37.2 (CH_2), 21.7 (CH_3); MS (EI) *m/z* 276/275/274/273 (M^+, 7/6/30/15), 272 (M^+-1, 61), 239 (30), 237 (M^+-Cl, 100), 186 (38), 69 (57); HRMS *m/z* calcd for $C_8H_{10}^{35}Cl_2S_3$ 271.9324, found 271.9318.

3.1.4. 5,7-Bis(methylthio)-1,4-dihydro-1*H*−3λ^4-thieno[3,4-*d*][2,3]oxathiin-3-oxide, sultine 10e. A solution of **8** (2.86 g, 10.5 mmol), Rongalite (3.33 g, 20.9 mmol), and TBAB (1.71 g, 5.24 mmol) in DMF (50 mL) was stirred at room temperature for 24 h. The mixture was diluted with H_2O (40 mL) and extracted with CH_2Cl_2 (3×20 mL). The organic layer was dried over $MgSO_4$, concentrated, and purified by column chromatography (6:1 hexane/ethyl acetate) to give 0.68 g (2.55 mmol, 24%) of **10e**, as a white solid after recrystallization from a solvent of CH_2Cl_2 and hexane: mp 71–73 °C (CH_2Cl_2/hexane); R_f=0.45 (hexane/ethyl acetate=4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.19, 5.10 (2H, ABq, J=14.7 Hz), 3.91, 3.81 (2H, A′B′q, J=15.9 Hz), 2.44 (3H, s), 2.42 (3H, s); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 137.1 (Cq), 132.8 (Cq), 132.0 (Cq), 126.8 (Cq), 58.8 (CH_2), 51.1 (CH_2), 21.3 (CH_3), 21.3 (CH_3); MS (EI) *m/z* 268/267/266 (M^+, 3/5/13), 265 (M^+-1, 22), 202 (M^+-SO_2, 32), 201 (40), 187 (100); HRMS *m/z* calcd for $C_8H_{10}O_2S_4$ 265.9565, found 265.9577; Anal. Calcd for $C_8H_{10}O_2S_4$: C, 36.07; H, 3.78. Found: C, 36.42; H, 4.20.

3.1.5. 3,4-Bis(chloromethyl)-2,5-bis(phenylthio)thiophene 9 and 5,7-bis(phenylthio)-1,4-dihydro-1*H*-3λ^4-thieno[3,4-*d*][2,3]oxathiin-3-oxide, sultine 10f. Adapted from a literature method.[4b] To a stirred solution of **7** (2.00 g, 6.66 mmol) and zinc chloride (1.4 g, 10 mmol) in dry chloroform (20 mL) was added dropwise chloromethyl-methyl ether (1.6 g, 20 mmol) via syringe. The mixture

turned dark green upon addition. The reaction mixture was stirred at room temperature under nitrogen for 3 h, and then poured into ice–water (20 mL), and CH_2Cl_2 (40 mL) was added. After stirring for 10 min, the layers were separated and the organic layer was washed with water (20 mL) and dried over $MgSO_4$. The solvent distilled off in vacuum to yield 2.67 g of crude product as viscous orange oil. Without purification, the crude product was dissolved in DMF (50 mL), and added Rongalite (5.16 g, 33.5 mmol) and TBAB (1.08 g, 3.45 mmol). The reaction mixture was stirred at room temperature for 10 h. The mixture diluted with H_2O (40 mL) and extracted with CH_2Cl_2 (3×20 mL). The organic layer was dried over $MgSO_4$, concentrated, and purified by column chromatography (10:1 hexane/ethyl acetate) to give 0.29 g (0.47 mmol, 11% overall yield from **7** in two steps) of **10f**.

3.1.6. Data of compound 9. a colorless liquid; $R_f=0.3$ (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.20 (10H, m), 4.85 (4H, s); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 141.5 (Cq), 136.6 (Cq), 135.7 (Cq), 129.3 (CH), 128.9 (CH), 127.3 (CH), 37.1 (CH_2); MS (EI) *m/z* 398/399/400 (M^+, 87/76/13), 396 (M^+-1, 100), 348 (37), 231 (51), 216 (69), 215 (81), 203 (61), 184 (43), 171 (40), 51 (50), 50 (74), 38 (55); HRMS *m/z* calcd for $C_{18}H_{14}^{35}Cl_2S_3$ 395.9637, found 395.9625.

3.1.7. Data of compound 10f. A white solid after recrystallization from a solvent of CH_2Cl_2 and hexane; mp 71–72 °C (CH_2Cl_2/hexane); $R_f=0.65$ (hexane/ethyl acetate=4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.18 (10H, m), 5.17, 5.10 (2H, ABq, $J=15.0$ Hz), 3.87, 3.81 (2H, A′B′q, $J=16.4$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 136.0 (Cq), 135.7 (Cq), 135.5 (Cq), 134.2 (Cq), 130.6 (Cq), 129.5 (CH), 129.4 (CH), 128.0 (CH); MS (EI) *m/z* 390/391 (M^+, 2/14), 326 (M^+-SO_2, 80), 325 (M^+-1-SO_2, 100), 216 (38), 215 (41), 184 (67), 77 (40), 51 (71); HRMS *m/z* for $C_{18}H_{14}O_2S_4$ 389.9878, found 389.9885; Anal. Calcd for $C_{18}H_{14}O_2S_4$: C, 55.36; H, 3.61. Found: C, 55.19; H, 3.73.

3.1.8. Cycloaddition reactions of thienosultines 10a–f with C_{60}. General procedure. A solution of C_{60} (50 mg, 0.069 mmol) and thienosultine (1.5 equiv. for **10a–f**) in ODCB (20 mL) was refluxed under nitrogen or irradiated with microwave (900 W, $\leq$180 °C). The resulting brown reaction mixture was evaporated to dryness under reduced pressure. The residue was subjected to silica gel chromatography with cyclohexane/toluene (4/1) as the eluent. The reaction conditions and yields after purification are shown in Table 1.

3.1.9. 1′,3′-Dimethyl-4′,5′,6′,7′-tetrahydrobenzo[*c*]-thieno-[5′,6′:1,2][60]fullerene (12a). A brown solid; mp>495 °C; $R_f=0.75$ (cyclohexane); ^{1}H NMR (25 °C, 600 MHz, *o*-$C_6D_4Cl_2$) δ 4.43 (4H, s), 2.56 (6H, s); ^{1}H NMR (5 °C, 600 MHz, *o*-$C_6D_4Cl_2$) δ 4.43, 4.38 (4H, ABq, $J=$ 13.5 Hz), (2H, ABq, $J=13.3$ Hz), 2.55 (6H, s); ^{13}C NMR (70 °C, 150 MHz, *o*-$C_6D_4Cl_2$) δ 159.9, 148.5, 147.3, 147.0, 146.6, 146.3, 146.2, 146.1, 145.5, 143.9, 143.4, 143.1, 142.9, 142.4, 141.1, 136.4, 135.8, 134.7, 66.9 (sp^3 C of C_{60}), 41.4 (CH_2), 13.3 (CH_3); FAB-MS (MNB) *m/z* 859 ($M+H^+$, 4), 858 (M^+, 4), 721 (90), 461 (100), 460 (95); UV ($CHCl_3$) λ_{max}, nm (log ε) 434 (3.33), 308 (4.47), 256 (4.97); HRMS (FAB+) calcd for $C_{68}H_{10}S$ 858.0504, found 858.0523.

3.1.10. Adduct 13a. A brown solid; $R_f=0.45$ (cyclohexane); FAB-MS (MNB) *m/z* 997/998 ($M+H^+$, 5/3), 857/858 (4/3), 721 (100); HRMS (FAB+) calcd for $C_{76}H_{20}S_2$ 996.1006, found 996.1751.

3.1.11. 1′,3′-Dichloro-4′,5′,6′,7′-tetrahydrobenzo[*c*]-thieno-[5′,6′:1,2][60]fullerene (12b). A brown solid; mp>495 °C; $R_f=0.75$ (cyclohexane); ^{1}H NMR (25 °C, 600 MHz, *o*-$C_6D_4Cl_2$) δ 4.49 (4H, s); ^{1}H NMR (−15 °C, 600 MHz, *o*-$C_6D_4Cl_2$) δ 4.54, 4.38 (4H, ABq, $J=14.1$ Hz); ^{13}C NMR (70 °C, 150 MHz, *o*-$C_6D_4Cl_2$) δ 156.5, 148.5, 147.3, 147.1, 146.5, 146.3, 146.2, 145.8, 145.4, 143.8, 143.4, 142.9, 142.4, 141.1, 136.2, 135.8, 122.7, 65.8 (sp^3 C of C_{60}), 40.6 (CH_2); FAB-MS (MNB) *m/z* 899 ($M+H^+$, 3), 898 (M^+, 3), 720 (8), 460 (100); UV ($CHCl_3$) λ_{max}, nm (log ε) 434 (3.57), 310 (4.37), 257 (4.89); HRMS (FAB+) calcd for $C_{66}H_4Cl_2S$ 897.9712, found 897.9510.

3.1.12. Adduct 13b. A brown solid; $R_f=0.63$ (cyclohexane); FAB-MS (MNB) *m/z* 1074/1076/1077/1078/1079/1080 ($M+H^+$, 0.7/0.9/0.9/1/1/0.8), 720 (8), 307 (100); HRMS (FAB+) calcd for $C_{72}H_8Cl_4S_2$ 1075.8821, found 1075.8821.

3.1.13. 1′-Methyl-3′-phenyl-4′,5′,6′,7′-tetrahydrobenzo[*c*]thieno-[5′,6′:1,2][60]fullerene (12c). A brown solid; mp>495 °C; $R_f=0.6$ (cyclohexane); ^{1}H NMR (25 °C, 600 MHz, 1:2 $CDCl_3/CS_2$) δ 7.53–7.51 (2H, m), 7.38–7.36 (2H, m), 7.29–7.26 (1H, m), 4.66 (2H, br s), 4.52 (2H, br s), 2.67 (3H, s); ^{1}H NMR (−20 °C, 600 MHz, 1:2 $CDCl_3/CS_2$) δ 7.53–7.52 (2H, m), 7.40–7.38 (2H, m), 7.31–7.28 (1H, m), 4.72, 4.63 (2H, ABq, $J=14.1$ Hz), 4.56, 4.48 (2H, ABq, $J=14.0$ Hz), 2.69 (3H, s); ^{13}C NMR (25 °C, 150 MHz, 1:2 $CDCl_3/CS_2$) δ156.4 (br), 147.4, 146.2, 146.2, 146.0, 145.6, 145.2, 144.7, 144.5, 142.9, 142.4, 141.9, 141.8, 141.4 (br), 140.0, 134.6, 133.6, 133.1, 132.6, 128.8 (CH), 128.6 (CH), 127.4 (CH), 65.5 (sp^3 C of C_{60}), 65.4 (sp^3 C of C_{60}), 40.5 (CH_2), 34.0 (CH_2), 12.8 (CH_3); FAB-MS (MNB) *m/z* 921 ($M+H^+$, 5), 920 (M^+, 5), 720 (100); UV ($CHCl_3$) λ_{max}, nm (log ε) 487 (3.34), 432 (3.64), 257 (5.07); HRMS (FAB+) calcd for $C_{73}H_{12}S$ 920.0661, found 920.0663.

3.1.14. Adduct 13c. A brown solid; $R_f=0.3$ (cyclohexane); FAB-MS (MNB) *m/z* 1121 ($M+H^+$, 8), 721 (18), 392 (100); HRMS (FAB+) calcd for $C_{86}H_{24}S_2$ 1120.1321, found 1120.1461.

3.1.15. 1′,3′-Diphenyl-4′,5′,6′,7′-tetrahydrobenzo[*c*]thieno-[5′,6′:1,2][60]fullerene (12d). A brown solid; mp>495 °C; $R_f=0.54$ (cyclohexane); ^{1}H NMR (25 °C, 600 MHz, 1:2 $CDCl_3/CS_2$) δ 7.59–7.57 (4H, m), 7.42–7.39 (4H, m), 7.33–7.31 (2H, m), 4.76 (2H, br s), 4.69 (2H, br s); ^{1}H NMR (−20 °C, 600 MHz, 1:2 $CDCl_3/CS_2$) δ 7.59–7.58 (4H, m), 7.44–7.41 (4H, m), 7.34–7.32 (2H, m), 4.79, 4.69 (4H, ABq, $J=14.2$ Hz); ^{13}C NMR (−20 °C, 150 MHz, 1:2 $CDCl_3/CS_2$) δ 156.0, 155.9, 147.1, 145.98, 145.96, 145.8, 145.7, 145.32, 145.27, 145.1, 145.1, 144.95, 144.91, 144.88, 144.4, 144.2 (2C), 142.7, 142.6, 142.1, 142.1, 141.7, 141.6, 141.6, 141.5, 141.3, 141.1, 139.78, 139.76, 137.9, 135.7,

134.7, 133.9, 132.9, 128.8 (CH), 128.5 (CH), 127.7 (CH), 65.0 (sp^3 C of C_{60}), 40.1 (CH_2); FAB-MS (MNB) *m/z* 984/983 ($M+H^+$, 2/3), 982 (M^+, 3), 721 (24), 461 (67), 392 (100); UV ($CHCl_3$) λ_{max}, nm (log ε) 432 (3.55), 257 (5.10); HRMS (FAB+) calcd for $C_{78}H_{14}S$ 982.0817, found 982.0905.

3.1.16. Adduct 13d. A brown solid; R_f=0.2 (cyclohexane); FAB-MS (MNB) *m/z* 1246/1245 ($M+H^+$, 4/5), 721 (67), 461 (57), 392 (100); HRMS (FAB+) calcd for $C_{96}H_{28}S_2$ 1244.1634, found 1244.1669.

3.1.17. 1′,3′-Bis(methylthio)-4′,5′,6′,7′-tetrahydrobenzo[*c*]thieno-[5′,6′:1,2][60]fullerene (12e). A brown solid; mp>495 °C; R_f=0.45 (cyclohexane); ^{1}H NMR (25 °C, 500 MHz, 1:2 $CDCl_3/CS_2$) δ 4.62 (4H, br s), 2.46 (6H, s); ^{1}H NMR (−25 °C, 500 MHz, 1:2 $CDCl_3/CS_2$) δ 4.74, 4.49 (4H, ABq, J=14.5 Hz), 2.46 (6H, s); ^{13}C NMR (70 °C, 150 MHz, *o*-$C_6D_4Cl_2$) δ 157.3, 148.5, 147.3, 147.0, 146.5, 146.2, 146.2, 146.0, 145.5, 143.9, 143.4, 142.9, 142.4, 141.1, 136.2, 135.8, 135.0, 66.5 (sp^3 C of C_{60}), 41.8 (CH_2), 23.2 (CH_3); FAB-MS (MNB) *m/z*; 923 ($M+H^+$, 3), 614 (32), 462 (100), 444 (26); UV ($CHCl_3$) λ_{max}, nm (log ε) 435 (3.67), 310 (4.80), 256 (5.31); HRMS (FAB+) calcd for $C_{68}H_{10}S_3$ 921.9946, found 922.0023.

3.1.18. Adduct 13e. A brown solid; R_f=0.41 (cyclohexane: toluene=9:1); FAB-MS (MNB) *m/z* 1124 ($M+H^+$, 3), 1123 (M^+, 3) 720 (18), 442 (25), 308 (100); HRMS (FAB+) calcd for $C_{76}H_{20}S_6$ 1123.9892, found 1123.9897.

3.1.19. 1′,3′-Bis(phenylthio)-4′,5′,6′,7′-tetrahydrobenzo[*c*]thieno-[5′,6′:1,2][60]fullerene (12f). A brown solid; mp> 495 °C; R_f=0.35 (cyclohexane); ^{1}H NMR (40 °C, 600 MHz, 1:2 $CDCl_3/CS_2$) δ 7.32–7.30 (4H, m), 7.17–7.15 (4H, m), 7.10–7.09 (2H, m), 4.66 (4H, br s); ^{1}H NMR (−30 °C, 600 MHz, 1:2 $CDCl_3/CS_2$) δ 7.28–7.24 (4H, m), 7.19–7.16 (4H, m), 7.11–7.10 (2H, m), 4.78, 4.52 (4H, ABq, J=14.4 Hz); ^{13}C NMR (40 °C, 150 MHz, 1:2 $CDCl_3/CS_2$) δ 156.0, 147.5, 146.3, 146.1, 145.6, 145.4, 145.3, 144.9, 144.5, 144.4, 143.0, 142.4, 141.9, 141.9, 141.4, 140.1, 136.8, 135.2, 131.2, 129.0 (CH), 128.3 (CH), 126.7 (CH), 65.0 (sp^3 C of C_{60}), 40.7 (CH_2); FAB-MS (MNB) *m/z* 1047 ($M+H^+$, 5), 1046 (M^+, 5), 766 (5), 720 (20), 613 (40), 460 (100); UV ($CHCl_3$) λ_{max}, nm (log ε) 435 (3.67), 310 (4.80), 256 (5.31); HRMS (FAB+) calcd for $C_{78}H_{14}S_3$ 1046.0259, found 1046.0404.

3.1.20. Adduct 13f. A brown solid; R_f=0.28 (cyclohexane/toluene=9:1); FAB-MS (MNB) *m/z* 1373 ($M+H^+$, 5), 1372 (M^+, 5), 721 (32), 442 (37), 308 (100); HRMS (FAB+) calcd for $C_{96}H_{28}S_6$ 1372.0518, found 1372.0522.

3.1.21. Synthesis of 15 and 16. An air-saturated solution of **12a** (25 mg, 0.029 mmol) in CS_2 (15 mL) was stirred at room temperature under the irradiation of room light and monitored by TLC chromatography until the starting compound disappeared which took about 3 days. After removal of the solvent, the residue was purified by silica gel chromatography (3–1:2 cyclohexane/$CHCl_3$) to give 7.3 mg of **15** (28%) and 11.6 mg of **16** (45%).

3.1.22. Data of 15. A brown solid, mp>495 °C; R_f=0.3 (cyclohexane: $CHCl_3$=1:1); FT-IR (KBr, cm^{-1}) 1700 (C=O), 1529 (C=C); ^{1}H NMR (25 °C, 600 MHz, $CDCl_3$) δ 4.56 (2H, br s), 4.45 (2H, br s), 2.71 (3H, s), 2.53 (3H, s); ^{13}C NMR (25 °C, 150 MHz, $CDCl_3$) δ 197.7 (C=O), 193.0 (C=S→O), 155.5, 155.4, 147.7 (2C), 146.6 (2C), 146.3 (2C), 145.8, 145.6 (3C), 145.5 (2C), 145.2, 144.7 (2C), 143.2, 142.7, 142.6, 142.3, 142.2, 142.1 (2C), 141.7 (2C), 140.2 (2C), 137.9, 135.8, 135.7, 65.8 (sp^3 C of C_{60}), 65.5 (sp^3 C of C_{60}), 49.1 (CH_2), 42.6 (CH_2), 30.9 (CH_3), 30.3 (CH_3); FAB-MS (MNB) *m/z* 891 ($M+H^+$, 2), 890 (M^+, 3), 889 (M^+-1, 2), 721 (100); HRMS (FAB+) calcd for $C_{68}H_{10}O_2S$ 890.0402, found 890.0382.

3.1.23. Data of 16. A brown solid; mp>495 °C; R_f=0.25 (cyclohexane/$CHCl_3$=2:3); FT-IR (KBr, cm^{-1}) 1685 (C=O); ^{1}H NMR (25 °C, 600 MHz, $CDCl_3$) δ 4.31 (4H, s), 2.63 (6H, s); ^{13}C NMR (25 °C, 150 MHz, $CDCl_3$) δ 200.6 (C=O), 155.2, 147.5, 146.6, 146.4, 145.7, 145.7, 145.6, 145.2, 144.9, 144.7, 143.2, 142.7, 142.3, 142.1, 141.7, 140.3, 135.7, 65.3 (sp^3 C of C_{60}), 41.7 (CH_2), 29.2 (CH_3); FAB-MS (NMB) 859 ($M+H^+$, 2), 858 (M^+, 2), 720 (100); HRMS (FAB+) calcd for $C_{68}H_{10}O_2$ 858.0681, found 858.0712.

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Supplementary data

Various temperature ^{1}H NMR spectra of compounds **12b**, **d–f**, ^{1}H NMR spectra of compounds **6**, **8**, **9**, and **10e**, ^{1}H and/or ^{13}C NMR spectra of compounds **12**, **13**, **15** and **16** and FTIR spectra of adducts **15** and **16**.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2004.09.040

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