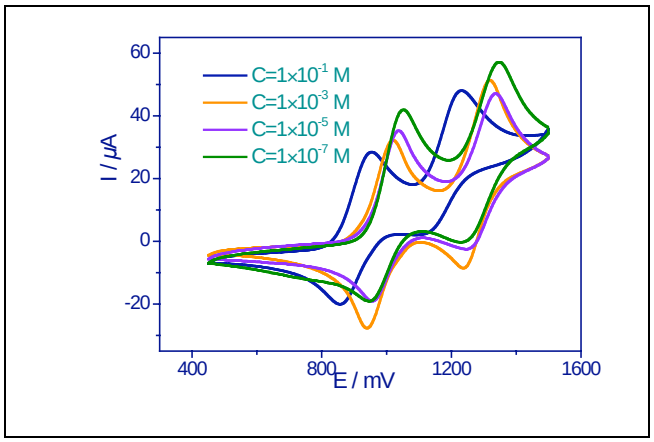
Syntheses, Electrochemical studies and Crystal Structures of New Unsymmetrical Tetrathiafulvalene Carboxylate Derivatives

Wei Liu,[a] Yun-Jun Guo,[a] Xi-Rui Zeng,[b] Jing-Lin Zuo,[a,*] and Xiao-Zeng You[a]

[a]Coordination Chemistry Institute and the State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China
E-mail: zuojl@nju.edu.cn
[b] Department of Chemistry, JingGangShan Normal College, Jian 343009, China

Received July 28, 2006



A series of new unsymmetrical tetrathiafulvalene carboxylate derivatives (**7**-**11**) were synthesized and characterized by NMR, MS, electrochemical studies and X-ray crystal structural determination. Compound **8** showed obvious changes in redox peak potentials as the concentration of *p*-toluenesulfonic acid changes.

J. Heterocyclic Chem., **44**, 831 (2007).

INTRODUCTION

Tetrathiafulvalene (TTF) and its derivatives have attracted increasing attention for their versatile applications not only in new materials exhibiting high conductivity, but also in LB films, molecular switches, magnets, non-linear optics and LC materials [1]. Many good examples have revealed that TTF moiety serves as an ideal redox-active unit because of its unique π-electron donating properties [2]. Recently, TTF-based molecular systems are explored and developed for application in cation [3-6] and anion [7] recognition and even in supramolecular devices [2b]. However, as we know, proton-sensitive TTF compounds are little exploited [8], while proton-assisted redox reactions are very important in biosystem [9].

Over the years, unsymmetrical TTF derivatives are found to be the most frequently involved in the above progress and the synthesis and studies on unsymmetrical TTF analogues have aroused much interest [10], since they are good precursors to a multitude of supramolecular structures and materials [11]. But they are far less studied compared to the symmetric analogues, which is due to the difficulty and troublesome work in separation and purification of unsymmetrical TTF.

The unsymmetrical TTF carboxylate derivatives are a kind of important starting material to prepare unsymmetrical TTF. Furthermore, they can be hydrolyzed to form soluble TTF-dicarboxylic salt which exhibits different oxidation / reduction potentials, as the concentration of proton changes. As we know, the dissociated H^+ of *p*-toluenesulfonic acid will exist bonding with the solvent used; therefore, *p*-toluenesulfonic acid can be used as proton resource in organic solvents. In current work, we have adopted the cross-coupling method for the preparation of a series of new unsymmetrical TTF carboxylate derivatives, Dimethyl benzotetrathiafulavalene-1,2-dicarboxylate (**7**), Ethylenedithio-4',5'-dimethyltetrathiafulavalene-4,5-dicarboxylate (**10**), Propylene dithio-4',5'-dimethyltetrathiafulavalene-4,5-dicarboxylate (**11**). One of the TTF-dicarboxylic salt derivated from compound **7**, $K_2[C_{12}H_4O_4S_4]$ (**8**), shows proton-sensitive redox properties and it may be explored as chemical sensors.

RESULTS AND DISCUSSION

The synthetic procedures of our new unsymmetrical TTF carboxylate derivatives (**7**-**11**) are shown in Scheme 1. The products were prepared by coupling two electronically distinct 1,3-dithiole heterocycles at first. The homo- coupling products have been observed and removed through column chromatography. In consideration of less reactive thione, we optimized this

reaction by coupling the 1,3-dithiole-2-thione and 1,3-dithiole-2-one to obtain TTF framework.

Scheme 1 Synthetic procedures

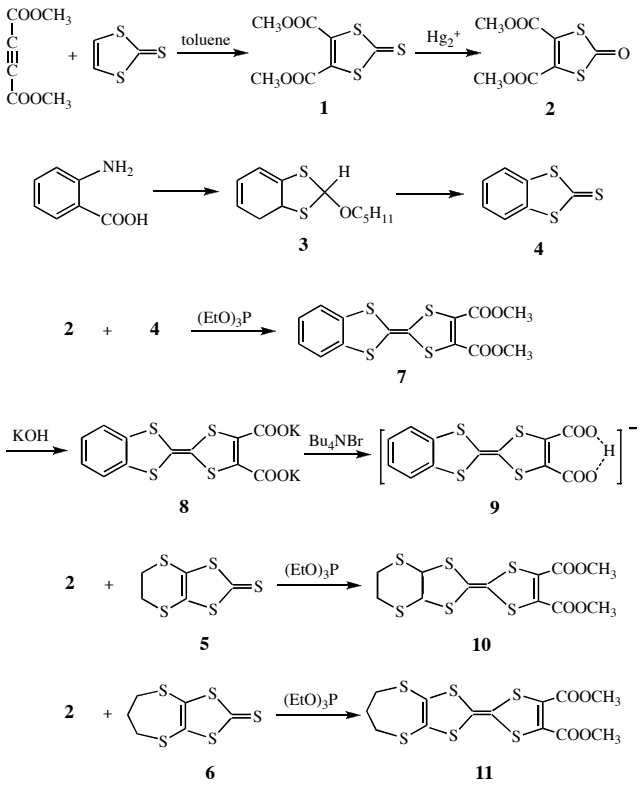


Table 1

The half-wave potentials (E/V) for compounds **7**, **9**-**11**

Compound	**7**	**9**	**10**	**11**
$E^1_{1/2}$	0.721	0.660	0.707	0.715
$E^2_{1/2}$	0.988	0.989	0.986	0.982

Electrochemical Studies. The redox potentials of compounds **7**-**11** were measured in CH_3CN solution by cyclic voltammetry. All compounds studied show two separate one-electron oxidation waves. Couples of stable and well-defined redox peaks appear in the potential range 0.4-1.4 V. It should be noted that, although the synthesis and redox potentials of compound **10** have been reported [9b], the crystal structure has not yet been presented previously. The half-wave potentials are collected and listed in Table 1 for comparison.

Table 2

The half-wave potentials (E/V) for compounds **8** at different concentration of *p*-toluenesulfonic acid.

C	1×10^{-1} M	1×10^{-3} M	1×10^{-5} M	1×10^{-7} M
$E^1_{1/2}$	0.905	0.980	0.997	1.000
$E^2_{1/2}$	1.161	1.278	1.291	1.289

For compound **7**, the first single-electron redox potential ($E^1_{1/2}$ = 0.721V) is assigned to **7**/**7**$^+$, and the second redox potential ($E^2_{1/2}$ = 0.988V) is assigned to

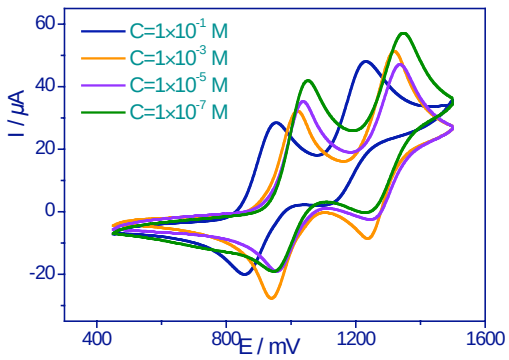


Figure 1. Cyclic voltammetry of **8** with the concentration of $1x10^{-3}$ *M*, measured in CH_3CN solution at different concentration of *p*-toluenesulfonic acid (C), *n*-Bu_4NClO_4 (0.1 *M*) as the supporting electrolyte, platinum as the working and counter electrodes, Ag/AgCl as the reference electrode, at scanning rate 50 mV/s.

7$^+$/**7**$^{2+}$. Compound **10** shows these peak potentials at 0.707 V and 0.986 V; for **11**, these potentials are 0.715 V and 0.982 V, respectively. The close redox potential for **7**, **10**, and **11** indicates that all the substitutions show similar electron effect on the TTF core. The relatively lower potentials in compounds **10** and **11** suggest that more sulfur atoms which are incorporated into TTF system will increase the electron delocallization in this system.

Electrochemical behavior of one of the potassium salt of the TTF carboxylate derivatives, K_2 [$C_{12}H_4O_4S_4$] (**8**), was also investigated. It is obvious that the peaks of redox potential are strongly influenced by the concentration of *p*-toluenesulfonic acid. A decrease of the concentration of *p*-toluenesulfonic acid caused a significant negative shift in both the oxidation and reduction peak potentials, and thus the half-wave potentials moved markedly to negative direction. Table 2 summarizes the result and Figure 1 depicts the cyclic

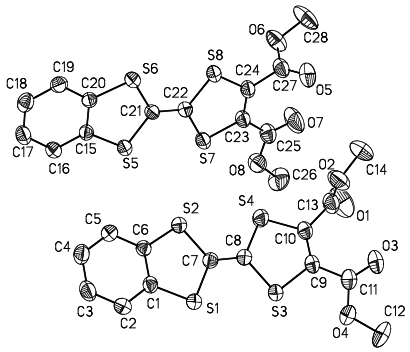


Figure 2. ORTEP view of compound **7** with atom numbering scheme: Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

voltammetry curves at different concentration of *p*-toluenesulfonic acid. The mechanism of proton-sensitive phenomenon may be ascribed to the proton

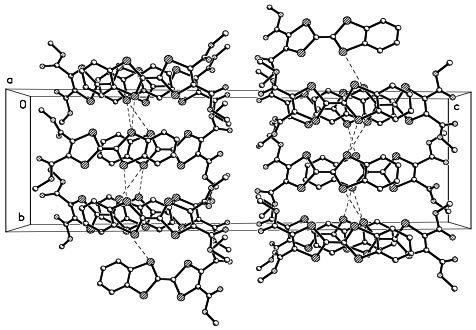


Figure 3. The packing diagram of compound **7** view along the *a* axis (the dotted line representing S···S non-bonded contacts less than 3.7 Å).

association/dissociation and two separate one-electron transfer redox process [8]. This proton sensitive TTF-system shows a character of redox-coupled proton transfer, which is remarkable in potential application for electrochemically influenced molecular-scale information processing such as proton-activated redox-switchable supramolecular fluorescent probe or sensors [11a].

Crystal structures. The selected bond lengths and angles for compounds **7**, **9-11** are given in Table 3. Parameters for data collection and refinement of **7**, **9-11** are summarized in Table 4. The atom-labeling scheme of the neutral compound **7** is shown in Figure 2, showing the planarity of the molecule. The bond lengths and angles of **7** are all in normal range and the packing diagram for molecules is shown in Figure 3. The shortest intermolecular S···S contact is 3.6193(9) Å, corresponding to the transverse S···S short contact with the neighboring chain.

The molecular structure of the anion of **9** is shown in Figure 4, together with the atomic numbering scheme. The anion shows a boat conformation, folding along C(11)-C(12) and S(3)-S(4) vectors by 1.1 and 10.1°. The central C(7)-C(8) bond distance in the monoanion of **9** is 1.350 Å, which is longer than that of C=C bond length in neutral molecule **7** [1.343 Å]. The two carboxyl- groups are equivalent in nature and have one proton in common to form a seven-membered ring.

The conjugated structure ensures the stability of the mono-proton compound. Except for the hydrogen bonding

Table 3

Selected bond lengths (Å) and angles (°) for **7, 9-11**

				7			
O(1)-C(13)	1.184(2)	O(2)-C(13)	1.305(2)	O(2)-C(14)	1.460(2)	O(4)-C(12)	1.446(2)
O(3)-C(11)	1.194(2)	O(4)-C(11)	1.329(2)	C(1)-C(6)	1.393(2)	C(7)-C(8)	1.343(2)
C(9)-C(10)	1.333(2)	C(2)-C(3)	1.382(2)	C(3)-C(4)	1.378(2)	C(4)-C(5)	1.382(2)
C(7)-S(1) -C(1)	95.36(8)	C(7)-S(2)-C(6)	95.32(8)	C(9)-S(3)-C(8)	93.65(8)	C(10)-S(4)-C(8)	93.96(9)
C(2)-C(1)-S(1)	123.21(1)	C(5)-C(6)-C(1)	119.86(1)	C(11)-C(9)-S(3)	118.66(1)	C(13)-C(10)-S(4)	115.46(1)
				9			
O(1)-C(11)	1.280(4)	O(3)-C(12)	1.224(4)	O(1)-H(100)	1.28(5)	C(1)-C(2)	1.375(5)
O(2)-C(11)	1.214(4)	O(4)-C(12)	1.268(4)	O(4)-H(100)	1.14(5)	C(4)-C(5)	1.401(4)
C(7)-C(8)	1.350(4)	C(9)-C(10)	1.344(4)				
C(10)-S(1)-C(8)	94.71(1)	C(9)-S(2)-C(8)	95.05(1)	C(7)-S(3)-C(5)	94.24(1)	C(7)-S(4)-C(4)	95.03(1)
C(3)-C(4)-S(4)	123.8(3)	C(6)-C(5)-S(3)	123.4(2)	C(2)-C(3)-C(4)	119.1(3)	C(1)-C(6)-C(5)	118.5(3)
				10			
O(1)-C(9)	1.091(12)	O(2)-C(9)	1.255(11)	O(3)-C(11)	1.186(12)	O(4)-C(11)	1.292(12)
C(1)-C(2)	1.388(16)	C(4)-C(3)	1.328(12)	C(6)-C(5)	1.346(12)	C(8)-C(7)	1.319(11)
C(1)-S(1)-C(3)	101.6(6)	C(4)-S(2)-C(2)	101.6(6)	C(7)-S(5)-C(6)	94.9(4)	C(6)-S(6)-C(8)	95.8(4)
				11			
C(1)-C(2)	1.523(3)	C(2)-C(3)	1.506(3)	C(4)-C(5)	1.344(2)	C(6)-C(7)	1.340(3)
C(8)-C(9)	1.340(3)	O(1)-C(11)	1.326(2)	O(2)-C(11)	1.196(2)	O(3)-C(10)	1.303(3)
O(1)-C(12)	1.449(3)	O(3)-C(13)	1.451(2)				
C(2)-C(1)-S(1)	116.5(0)	C(3)-C(2)-C(1)	115.5(6)	C(2)-C(3)-S(2)	116.6(3)	S(1)-C(5)-S(3)	116.4(1)
C(5)-S(1)-C(1)	102.9(7)	C(4)-S(2)-C(3)	102.9(6)	C(8)-S(5)-C(7)	94.66(9)	C(9)-S(6)-C(7)	94.75(9)

Table 4

Crystal Data, Data Collection and Structure Refinement for **7, 9**-**11**

	7	**9**	**10**	**11**
Empirical formula	$C_{28}H_{20}O_8S_8$	$C_{28}H_{41}NO_4S_4$	$C_{12}H_{10}O_4S_6$	$C_{13}H_{12}O_4S_6$
Formula weight	740.92	583.86	410.56	424.59
Crystal system	Monoclinic	Tetragonal	Monoclinic	Monoclinic
Space group	P 2_1/c	P 4(3)	P 2_1/c	P 2_1/c
a (Å)	8.4290(13)	9.8923(3)	7.4237(18)	12.2263(6)
b (Å)	10.8742(16)	9.8923(3)	16.442(4)	6.7776(4)
c (Å)	34.291(5)	31.830(2)	14.086(4)	21.9714(12)
α (°)	90	90	90	90
β (°)	98.593(4)	90	105.279(11)	100.9930(10)
γ (°)	90	90	90	90
Volume (Å^3)	3128.7(8)	3114.9(3)	1658.6(7)	1787.25(17)
Z	4	4	4	4
D_{calc} (g/cm^3)	1.573	1.245	1.644	1.578
μ (mm^{-1})	0.620	0.337	0.836	0.779
F (000)	1520	1248	840	872
θ range for data collection (°)	2.39–28.27	2.98–28.28	1.94–24.99	3.15–28.28
Index ranges	−10 ≤ h ≤ 11	−12 ≤ h ≤12	−8 ≤ h ≤ 8	−16 ≤ h ≤ 16
	−14 ≤ k ≤ 13	−13 ≤ k ≤ 10	−19 ≤ k ≤19	−9 ≤ k ≤9
	−45 ≤ l ≤ 45	−28 ≤ l ≤ 42	−16 ≤ l ≤ 8	−28 ≤ l ≤ 29
No. reflections collected	23301	7709	8127	13444
No. independent reflections	7715	5010	2925	4387
R(int)	0.0343	0.0236	0.0878	0.0234
Data/restraints/parameters	7715 / 0 / 417	5010 / 1 / 342	2925 / 0 / 209	4387 / 0 / 210
Goodness-of-fit on F^2	1.020	0.998	1.037	1.148
R1[a]/*w*R2[b](I>2σ)	0.0319 / 0.0574	0.0393 / 0.0864	0.0988/0.2527	0.0336/0.0954
Largest difference peak and hole (e· Å^{-3})	0.317 / –0.261	0.165/ –0.135	0.472/ –0.510	0.296/ –0.279

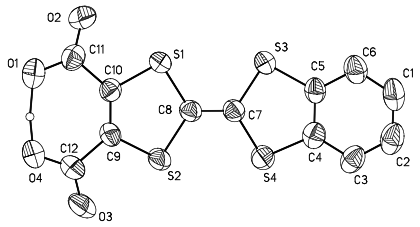


Figure 4. ORTEP view of compound **9** with atom numbering scheme: Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

interactions (Figure 5), there is no significant interaction between the molecules through shorter S···S contacts. The

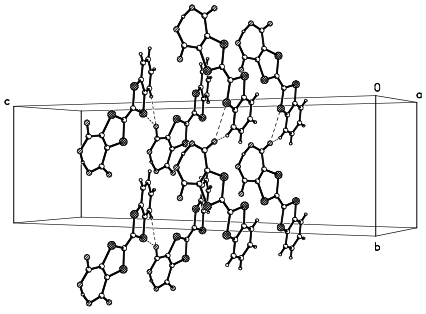


Figure 5. The packing diagram of compound **9** view along the *a* axis (the dotted line representing S···S non-bonded contacts less than 3.7 Å or hydrogen bonding).

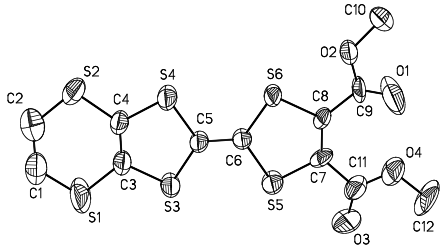


Figure 6. ORTEP view of compound **10** with atom numbering scheme: Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

reason is that the presence of the bulky tetrabutyl-ammonium cations prevents the compact overlap of the anions.

The ORTEP view of **10** with atom numbering scheme is shown in Figure 6. The C=C bond length of central TTF unit in **10** is similar to that in molecule **7** [1.343 Å]. Figure 7 shows that the molecules are stacked in two different oriented directions approximately along the *a* axis. The shortest inter-stack S···S contact is 3.243 Å. Figure 8 shows the molecular structure of **11**. Apparently, it adopts non-planar conformation. Atoms S(3), S(4), C(6), C(7), S(5), S(6), C(8), C(9), C(10) and C(11) lie in a plane, while atoms S(1), S(2), C(4), C(5), S(3) and S(4) including the tetrathiafulvalene group also form a plane. The dihedral angle of the above two planes is 18.0°. This seven-membered ring (C(1), C(2), C(3), C(4), C(5), S(1)

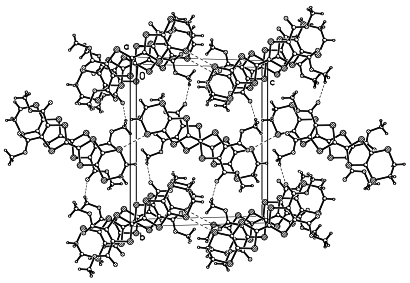


Figure 7. The packing diagram of compound **10** view along the *a* axis (the dotted line representing S···S non-bonded contacts less than 3.7 Å or hydrogen bonding).

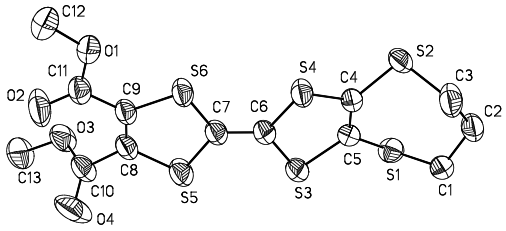


Figure 8. ORTEP view of compound **11** with atom numbering scheme: Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

and S(2)) adopts a chair conformation. The packing diagram is shown in Figure 9.

EXPERIMENTAL

General procedures. Reagent-grade $P(EtO)_3$ was distilled prior to use, other solvents and chemicals were purchased from commercial sources and used as received. Schlenk techniques were used in carrying out manipulation under nitrogen atmosphere. Melting points were determined with an X-4 digital micro melting point apparatus. Elemental analyses for C, H were performed on a Perkin-Elmer 240C analyzer. The IR spectra were taken on a Bruker Vector22 Spectrophotometer with KBr pellets in the 400-4000cm^{-1} regions. NMR spectra were measured on a Bruker AM 500 spectrometer. Absorption spectra were measured with Hitachi (model UV-3100) UV-Vis spectrophotometer. ESI-MS spectra were measured on a Varian MAT 311A instrument. The crystal structure was determined at room temperature using Bruker SMART CCD-based diffractometer. Cyclic voltammetry were recorded by an EG&G PAR Model 283 electrochemical analytical instrument. A series of solutions with different concentration of *p*-toluenesulfonic acid were prepared by dissolving *p*-toluensulfonic acid in CH_3CN, and then adjusted to the desired concentration.

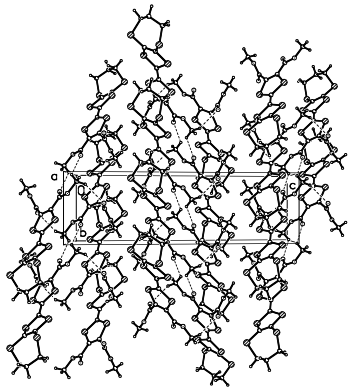


Figure 9. The packing diagram of compound **11** view along the a axis (the dotted line representing S···S non-bonded contacts less than 3.7 Å or hydrogen bonding).

Crystal Structure Determination. Single-crystal X-ray structure determination were made on crystal of molecule **7, 9**-**11**. Data collection for the block-shaped single crystals of **7, 9**-**11** was performed on a Bruker CCD system with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The sizes of the crystals used for data collection were 0.28×0.26×0.17 mm^3 for **7,** 0.31×0.26×0.19 mm^3 for **9**, 0.21×0.12×0.07 mm^3 for **10**, and 0.40×0.23×0.15 mm^3 for **11**. The structure was solved by direct methods and refined on F^2 using SHELXTL software. Anisotropic thermal parameters were applied for all the non-hydrogen atoms. All hydrogen atoms were positioned geometrically and refined as riding, with C-H distances of 0.97 Å and with U_{iso} (H) = 1.2*U*eq (C). Crystallographic parameters and agreement factors are contained in Table 4. CCDC-289204, 289205, 289206 and 289207 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

Synthesis. Compounds **1–6** were synthesized following the literature procedures [11].

Dimethyl benzotetrathiafulavalene-1,2-dicarboxylate $C_{14}H_{10}O_4S_4$ (**7**). Under a N_2 atmosphere, to the mixture of dimethyl 1,3-dithiole-2-one-dicarboxylate (**2)** (0.94 g, 4 mmol) and 2-thioxo-1, 3-benzodithiol (**4)** (1.1 g, 6 mmol) was added 20 ml of freshly distilled $P(OEt)_3$. The reaction mixture was heated at 110 ℃ for 1 h and then allowed to cool to room temperature. 20 mL of methanol was added to the above suspension; after standing for 4 hour, filtrated; the brown-red precipitate was collected and washed with methanol, which was then chromatographed on a silica gel column using dichloromethane/ petroleum ether (v/v, 4:1) as the eluent. Orange powder **7** was obtained. Yield: 0.78 g (53% based on **2**). mp: 174-175 ℃; ^{1}H NMR ($CDCl_3$, ppm) δ 3.81 (s, 3H), 7.08 (m, 2H), 7.22 (s, 2H); IR (KBr, cm^{-1}): 3418(w), 2958(w), 1749(m), 1738(s), 1716(s), 1580(m), 1565(m), 1535(w), 1433(m), 1250(s), 1120(w), 1089(m), 1019(m), 1004(w), 912(w), 846(w), 767(m), 738(m), 674(w); MS (ESI): M^+ = 369.9; Anal. Calcd. $C_{14}H_{10}O_4S_4$: C, 45.39; H, 2.72; Found: C, 45.28; H, 2.73.

K_2 [$C_{12}H_4O_4S_4$] (8) The potassium salt of Compound 7. To a solution of **7** (222 mg, 0.6 mmol) in 10 ml of THF was added 1 ml aqueous solution of KOH (100 mg). The color of the solution changed from red to light orange as the reaction proceeded. The mixture was stirred at room temperature for 1 hour, then 30 ml of THF (excess) was added and the solution was cooled to –20 ℃. The obtained yellow precipitate was washed with THF and Et_2O, and then dried *in vacuo*. Yield: 209mg (83.2% based on **7**). mp: >296 ℃ IR (KBr, cm^{-1}): 3395(m), 3289(m), 1670(s),

1588(s), 1533(m), 1376(s), 1349(s), 1263(w), 751(m), 676(w); ^{1}H NMR (D_2O, ppm) δ 7.21 (s, 2H), 7.39 (m, 2H).

$C_{28}H_{41}NO_4S_4$ (9) The tetrabutylammonium salt of compound 7. Aqueous of the yellow solid of **8** and *n*-Bu_4NBr gave red crystalline precipitate. mp: 137-138 ℃; Block-shaped orange crystals suitable for X-ray diffraction were recrystallized from CH_3CN/Et_2O.

By a similar procedure to that described for **7,** compounds **10** and **11** were prepared. $C_{12}H_{10}O_4S_6$ (**10**) Ethylenedithio-4',5'-dimethyltetrathiafulavalene-4,5-dicarboxylate.
Dichloromethane/petroleum ether (v/v, 1:1) as the eluent; Brown-red powder. Yield: 3.2 g (56% based on **2**). mp: 104-105 ℃; ^{1}H NMR ($CDCl_3$) δ 3.86 (s, -OCH_3, 6H), 3.32(t, CH_2, 4H); IR (KBr, cm^{-1}): 3447(m), 2947(w), 1750(s), 1570(w), 1541(w), 1431(m), 1294(m), 1208(s), 1085(w), 1011(m), 769(w), 725(w); MS (ESI) M^+ = 409.9; Anal. Calcd.: $C_{12}H_{10}O_4S_6$; C, 35.10, H, 2.45; Found: C, 35.11; H, 2.46.

Propylenedithio-4',5'-dimethyl-tetrathiafulavalene-4,5-dicarboxylate $C_{13}H_{12}O_4S_6$ (11). Dichloromethane/petroleum ether (v/v, 2:1) as eluent; Red powder. Yield: 3.2 g (40% based on **2**). mp: 167-168 ℃; ^{1}H NMR ($CDCl_3$) δ 3.85 (s, -OCH_3, 6H), 2.71(t, -CH_2-, 4H), 2.42(m, -CH_2-, 2H); IR (KBr, cm^{-1}): 3424(w), 2944(w), 2910(w), 2887(w), 1732(s), 1722(s), 1582(s), 1434(m), 1423(m), 1262(s), 1090(s), 1023(s), 891(m), 688(m); MS (EI) M^+ = 424.2; Anal. Calcd.: C, 36.77; H, 2.85; Found: C, 36.72; H, 2.84.

Single crystals of **7**, **10**, and **11** suitable for X-ray determination were obtained by slowly diffusing *n*-pentane into a chloroform solution of the respective compounds.

Acknowledgement. This work was supported by the National Natural Science Foundation of China (20531040 and 90501002), and the Major State Basic Research Development Program (Grant No. 2006CB806104). J. -L. Zuo thanks the Program for New Century Excellent Talents in University of China (NCET-04-0469).

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