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Novel electron donors containing multi-TTF units: synthesis and electrochemical properties

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Received 12th February 2003, Accepted 6th May 2003
First published as an Advance Article on the web 16th May 2003

The synthesis and electrochemical properties of five novel organosulfur electron donors containing two to four TTF nuclei are reported. The structures have been assigned by ^{1}H NMR spectroscopy, infrared spectrometry and mass spectra. Cyclic voltammetry (CV) studies show that the multi-TTFs display nearly ideal redox behavior for the TTF system with no distinct interaction between the TTF units.

Introduction

Tetrathiafulvalene (TTF) is the most famous redox unit known for the studies of organic conductors and superconductors.[1] During the past three decades, more than forty organic superconductors have been obtained, most of which are complexes of derivatives or analogues of TTF. In the past few years, the TTF moiety has been extensively used as a building block in macromolecular and supermolecular structures, as well as in the intramolecular donor–acceptor (D–σ-A) system in nonlinear optical (NLO) materials and molecular electronics.[2] Recently, the TTF unit has also been introduced into the construction of dendrimers and oligomers for the studies of multi-electron processes.[3] In such multi-TTF derivatives, the TTF units can be oxidized sequentially to the radical cation and dication, offering the prospect of controlled generation of multi(radical cation) and multi(dication) species. It seems to be of great interest to study the intramolecular and intermolecular interactions among such cations, which may provide the opportunity to study multi-electron redox switches or molecular magnets.[4] Here, we would like to report the synthesis and electrochemical properties of one TTF dimer (**1**) and two novel TTF trimers (**2a**,**b**) as well as two TTF tetramers (**3a**,**b**).

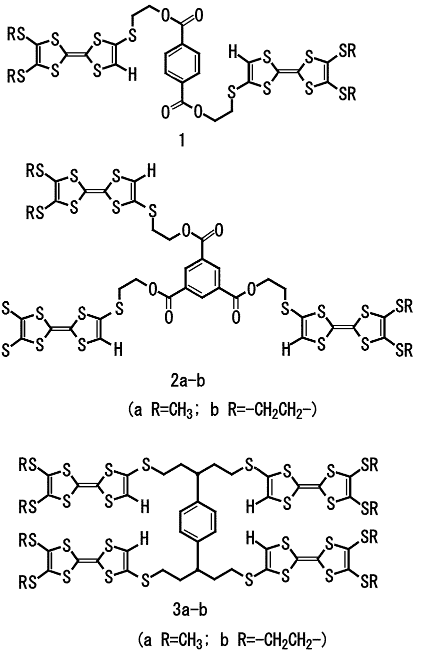
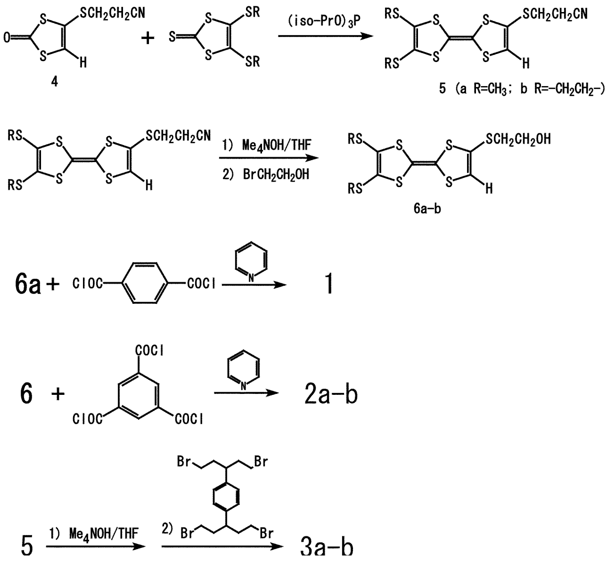


Chart 1 Molecular structure of the target compounds.

Results and discussion

Synthesis

We have recently developed a facile method for the synthesis of 4-(2-cyanoethylthio)-1,3-dithole-2-one (**4**) from the zinc complex of 1,3-dithole-2-thione-4,5-dithiolate.[5] This compound can serve as a useful intermediate for the synthesis of TTF derivatives, due to the fact that cyanoethyl acts as an ideal protecting group for thiolate and can be deprotected under mild conditions. Here it was applied as the starting material for the synthesis of the target molecules **1**–**3** (Scheme 1), following the reported procedure.[5] First, cross coupling of **4** with 4,5-di(methylthio)-1,3-dithiole-2-thione or 4,5-ethylenedithio-1,3-dithiole-2-thione in the presence of triisopropylphosphite affords the TTF derivatives **5a** and **5b** bearing one cyanoethylthio group in 70% and 56% yield, respectively. Then the cyano groups of **5a**,**b** were transformed into hydroxy groups by the reaction of 2-bromoethanol with the thiolate anion of **5**, which was generated by Me$_4$NOH. The 2-hydroxyethyl substituted TTF derivatives **6a** and **6b** were obtained in 94.8% and 93% yield, respectively.



Scheme 1

DOI: 10.1039/b301587d

Table 1 Oxidation potentials (*vs.* SCE) of **1**, **2a**, **2b**, **3a** and **3b**[a]

Compound	$E_{\frac{1}{2}}^{1}$ (V)	$E_{\frac{1}{2}}^{2}$ (V)
1	0.51	0.90
2a	0.52	0.88
2b	0.51	0.89
3a	0.47	0.84
3b	0.46	0.85
BEDT-TTF	0.48	0.89

[a] 10^{-4} M in solvent, Bu_4NPF_6 (10^{-1} M), scan rate 50 mV s^{-1}.

Two strategies were employed for the synthesis of multi TTF systems: 1) esterification of TTF bearing hydroxy group to afford a multi-ester core; 2) nucleophilic substitution reaction of a multi-bromoalkane with the thiolate anion of TTF derivatives. The bis(TTF) **1** was synthesized in 42.3% yield by the reaction of terephthaloyl dichloride with compound **6a** in the presence of pyridine. The analogous reaction of **6a** and **6b** with trimesic acid trichloride gave the tris(TTF) derivatives **2a** and **2b** in yields of 24.1% and 28.1%, respectively. Finally, the electron donors **3a** and **3b** containing four TTF units were obtained by the reaction of **5a** and **5b** with 1,4-bis[3-bromo-1-(2-bromoethyl)propyl]benzene using Me_4NOH as a deprotection reagent in THF at room temperature. Since the bromide was sensitive to base, and the thiolate anion was generated *in situ*, in order to reduce the side reactions, the use of excess Me_4NOH should be avoided.

Electrochemical studies

An important aspect of this work was to evaluate the solution redox properties of the molecules synthesized. The oxidation potentials of **1**, **2a**, **2b**, **3a** and **3b** were determined with cyclic voltammetry in dichloromethane and the results are summarized in Table 1. For comparison, the oxidation potentials of BEDT-TTF measured under the same conditions are also included in Table 1. All these new compounds exhibited two redox couples which is typical for the TTF system and for the alkyl linked multi-TTF system, indicating that the TTF units (electron granting groups) have negligible effect on the redox behaviors of each other. This can be understood by the fact that an aryl or alkyl unit was inserted between the TTF cores, and thus there is no conjugation between the TTF cores. The half wave potentials are almost identical for compound **1**, **2a** and **2b** ($E_1^{\frac{1}{2}} \approx 0.51$ V and $E_2^{\frac{1}{2}} \approx 0.89$ V, *vs.* SCE). Compared with BEDT-TTF, the first redox potentials of these new donors are shifted anodically by 30 mV. This may be due to the electron withdrawing effect of the center ester group. The half wave potentials of compounds **3a** and **3b** are slightly lower than that of compounds **1** and **2a**,**b** and BEDT-TTF ($E_1^{\frac{1}{2}} \approx 0.46$ V and $E_2^{\frac{1}{2}} \approx 0.84$ V). This should be attributable to the electron donating properties of the center phenylalkyl group. The first waves of these five electron donors are reversible, and the second waves are quasi-reversible (for example, cyclic voltammograms of **1** and **2a** are shown in Fig. 1). The reductive peak for the second redox couple is obviously larger than that of the first wave. This could be accounted for by the deposition and accumulation of the electrochemically generated dication salt on the electrode surface, due to low solubility.

Summary

Five new multi-TTF derivatives have been synthesized and characterized during the course of this work. The oxidation potentials were determined by cyclic voltammetry. The key intermediates possessing reactive alcohol substituents, *e.g.* **5a** and **5b** are available in synthetically useful quantities and should be suitable for other synthetic transformations for the incorporation of TTF units into new compounds.

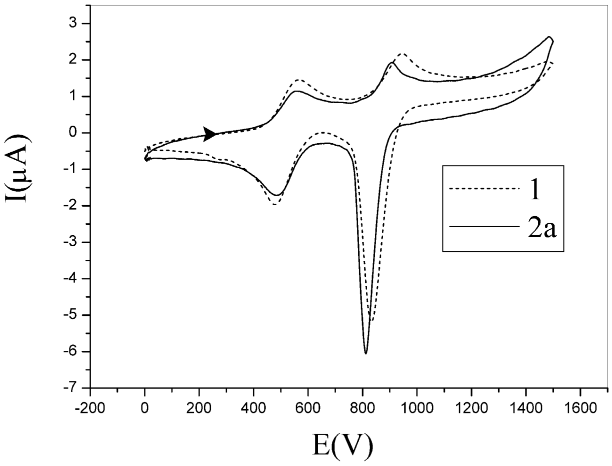


Fig. 1 Cyclic voltammograms of **1** and **2a** measured in CH_2Cl_2 solution (electrolyte Bu_4NPF_6, Pt disc electrode, *vs.* SCE, scan rate 50 mV s^{-1}).

Experimental

Melting points were measured with an XT_4-100_X microscope apparatus and uncorrected. ^1H NMR spectra were recorded on a dmx300, ARX400 or dmx500 machine, using $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard, and measured in ppm downfield from TMS. Coupling constants (*J*) are given in Hz. IR spectra were recorded on a PEKIN-ELMER SYSTERM 2000 FT-IR spectrometer. Mass spectra were determined with AEI-MS50 for EI-MS, BEFLEX III for MALDI-TOF-MS and BRUKER APEX II for high resolution positive-second ion mass spectra (P-SIMS) and high resolution MALDI mass spectra. Elemental analysis was performed on a Carlo-Erba-1106 instrument. Cyclic voltammetric measurements were conducted on an EG&G 328 System (10^{-4} M in CH_2Cl_2, Bu_4NPF_6 as supporting electrolyte, Pt electrode as working electrode, scan rate 50 mV s^{-1}, reported voltage *vs.* SCE).

4-(2-Cyanoethylthio)-4′,5′-bis(methylthio)tetrathiafulvalene, 5a

4,5-Di(methylthio)-1,3-dithiole-2-thione (3.33 g, 14.7 mmol) and 4-cyanoethylsulfanyl-1,3-dithiole-2-one (1.00 g, 4.92 mmol) were sequentially added to triisopropyl phosphite (25 cm^3) under a N_2 atmosphere. The resulting mixture was heated over an oil bath up to 110 °C and stirred for a further 4 h. The solvent was then removed under reduced pressure. Compound **5a** was obtained by column chromatography of the residue (silica gel, eluting with dichloromethane and petroleum ether (2 : 1)) as a yellow solid (1.31 g, 70.0%), mp 95 °C (dec.); δ_H ($CDCl_3$): 2.43 (6 H, s), 2.68–2.70 (2H, t, *J* 7.1), 2.95–2.97 (2 H, t, *J* 7.0), 6.56 (1 H, s); ν_{max} (KBr disc): 3065 (s), 1509 (s), 1421 (s), 1406 (s) cm $^{-1}$; HRMS (P-SIMS): 380.8926580, $C_{11}H_{11}NS_7$ requires 380.8930852.

4-(2-Cyanoethylthio)-4′,5′-(ethylenedithio)tetrathiafulvalene, 5b

Compound **5b** was synthesized by the coupling of 4,5-ethylenedithio-1,3-dithiole-2-thione with 4-cyanoethylsulfanyl-1,3-dithiole-2-one as described for **5a**. Yield 56%; mp 135 °C (dec.); δ_H ($CDCl_3$): 2.67–2.69 (2 H, t, *J* 7.0), 2.94–2.97 (2 H, t, *J* 7.0), 3.30 (4 H, s), 6.56 (1 H, s); ν_{max} (KBr disc): 3065 (s), 1421 (s), 1406 (s) cm $^{-1}$; HRMS (P-SIMS): 378.8773230, $C_{11}H_9NS_7$ requires 378.8774360.

4-(2-Hydroxyethylthio)-4′,5′-bis(methylthio)tetrathiafulvalene, 6a

Me_4NOH (0.107 cm^3 in a solution of methanol) was added to a solution of compound **5a** (0.100 g, 0.26 mmol) in tetrahydrofuran (15 cm^3) under a N_2 atmosphere and stirred for a further 0.5 h at room temperature. Then, a solution of 2-bromoethanol (0.038 g, 0.30 mmol) in tetrahydrofuran (3 cm^3) was added to the mixture in one portion. The reaction mixture was stirred at room temperature for 3 h. After removal of the solvent under reduced pressure, compound **6a** was obtained by column chromatography of the residue (silica gel, eluting with dichloromethane and petroleum ether (3 : 1)) as a red–brown oil (92 mg, 94.8%). δ_H ($CDCl_3$): 2.0 (1 H, s, br), 2.42 (6 H, s), 2.92–2.94 (2 H, t, *J* 5.9), 3.78–3.81 (2 H, t, *J* 5.9), 6.44 (1 H, s); ν_{max} (KBr disc): 3069 (s), 1489 (s), 1459 (s), 1423 (s) cm^{-1}; HRMS (P-SIMS): 371.8927490, $C_{10}H_{12}OS_7$ requires 371.8927507.

4-(2-Hydroxyethylthio)-4′,5′-(ethylenedithio)tetrathiafulvalene, 6b

Compound **6b** was synthesized from **5b** according to the method described for **6a**. Yield 91%; mp 93.7 °C; δ_H ($CDCl_3$): 1.64 (1 H, s, br), 2.93–2.95 (2 H, m), 3.29 (4 H, s), 3.78–3.80 (2 H, t, *J* 5.9), 6.44 (1 H, s); ν_{max} (KBr disc): 3078 (s), 1621 (m), 1453 (s), 1408 (m) cm^{-1}; HRMS (P-SIMS): 369.8769420, $C_{10}H_{10}OS_7$ requires 369.8771015.

The bis(TTF), 1

To a solution of compound **6a** (0.421 g, 1.13 mmol) and pyridine (89 mg, 1.13 mmol) in dried CH_2Cl_2 (5 cm^3) was added terephthaloyl dichloride (0.110 g, 0.54 mmol) under a N_2 atmosphere. The reaction mixture was heated under reflux for 3 h. The solvent was removed under reduced pressure. Column chromatography of the residue (silica gel, eluting with dichloromethane and petroleum ether (1 : 1)) afforded the bis(TTF) compound **1** as a yellow solid (0.200 g, 42.3%), mp 166.3 °C (dec.); δ_H ($CDCl_3$): 2.42 (12 H, s), 3.13 (4 H, s), 4.56 (4 H, s), 6.47 (2 H, s), 8.08 (4 H, s); ν_{max} (KBr disc): 3429 (s), 1630 (s), 1450 (s), 1428 (s), 1411 (m) cm^{-1}; HRMS (P-SIMS): 873.7920850, $C_{28}H_{26}O_4S_{14}$ requires 873.7915274.

The tris(TTF), 2a

Compound **2a** was synthesized as described for compound **1** by the reaction of **6a** and trimesic acid trichloride. Yield 24.1%, mp 60.5 °C (dec.); δ_H ($CDCl_3$): 2.40 (9 H, s), 2.42 (9 H, s), 3.13–3.17 (6 H, t, *J* 6.1), 4.59–4.63 (6 H, t, *J* 6.1), 6.50 (s, 3 H), 8.81 (s, 3 H); ν_{max} (KBr disc): 3069 (s), 1725 (s), 1422 (m) cm^{-1}; HRMS (MALDI): 1271.6651380, $C_{39}H_{36}O_6S_{21}$ requires 1271.6640916.

The tris(TTF), 2b

Compound **2b** was synthesized as described for compound **1** by the reaction of **6b** and trimesic acid trichloride. Yield 28.1%, mp 90.1 °C (dec.); δ_H ($CDCl_3$): 3.14–3.17 (6H, t, *J* 6.1), 3.26–3.36 (12 H, t, *J* 5.3), 4.60–4.63 (6 H, t, *J* 6.1), 6.52 (3 H, s), 8.78 (3 H, s); ν_{max} (KBr disc): 3071 (s), 1725 (s), 1632 (m), 1451 (s), 1412 (s) cm^{-1}; HRMS (MALDI): 1265.6151810, $C_{39}H_{30}O_6S_{21}$ requires 1265.6171440.

The tetrakis(TTF), 3a

A solution of Me_4NOH (0.107 cm^3, 25% wt) in MeOH was added to a solution of compound **5a** (0.100 g, 0.26 mmol) in tetrahydrofuran (15 cm^3) under a N_2 atmosphere and stirred for 0.5 h. Then, a solution of 1,4-bis[3-bromo-1-(2-bromoethyl)-propyl]benzene[6] (0.0339 g, 0.064 mmol) in THF (5 cm^3) was added to the above mixture. The reaction mixture was stirred for a further 4 h at room temperature. Evaporation of the solvent and column chromatography of the residue (silica gel) using CS_2–CH_2Cl_2 (5 : 1) as eluent afforded compound **3a** as a yellow solid (15 mg, 15.5%); mp 57.2 °C (dec.); δ_H ($CDCl_3$): 1.90–1.96 (8 H, m), 2.43 (24 H, s), 2.46–2.48 (2 H, m), 2.57–2.64 (8 H, m), 6.33 (4 H, s), 7.10 (4 H, s); ν_{max} (KBr disc): 3068 (s), 1639 (s), 1551 (s), 1507 (m), 1423 (s) cm^{-1}; *m*/*z* (MALDI-TOF): 1522.2 (M^+).

The tetrakis(TTF), 3b

Compound **3b** was synthesized as described for **3a** from **5b**. Yield 18 mg, 18.5%; mp 88.3 °C (dec.); δ_H ($CDCl_3$): 1.87–1.92 (8 H, m), 2.44–2.51 (4 H, m), 2.56–2.62 (4 H, m), 2.85–2.86 (2 H, m), 3.29–3.31 (16 H, t, *J* 4.7), 6.33–6.36 (4 H, s), 7.08 (4 H, s); ν_{max} (KBr disc): 3433 (br), 1635 (s), 1470 (s) cm^{-1}; *m*/*z* (MALDI-TOF): 1513.1 (M^+).

Acknowledgements

The present research work was financially supported by the Chinese Academy of Sciences, NSFC (Grant 20202012), and the State Basic Research Development Program (Grant G2000077505, G1999064601).

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