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A Facile Route to Aromatic Ring-Annelated Bis(ethylenedithio)tetrathiafulvalene Derivatives

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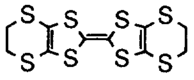
Abstract: The synthesis of bis(benzo)- and bis(naphtho)-fused derivatives of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) is easily achieved by employing the (4+2) cycloaddition reaction of oligo(1,3-dithiole-2,4,5-trithione) with appropriate olefins as the key step.

A substantial number of cation radical salts derived from the donor molecule, bis(ethylenedithio)tetrathiafulvalene[1] (BEDT-TTF or ET) **1**, display superconductivity with transition temperatures (T_c) as high as 12.8 K.[2] The conduction behavior, to a large measure, is due to the remarkable ability of ET molecules in the salts to engage in intermolecular inter-stack and intra-stack S····S interactions leading to quasi-two-dimensional band electronic structures.[2,3] Enlargement of the unit cell of isostructural ET salts, employing large charge-compensating anions, has been the most successful guiding principle to achieve higher superconducting transition temperatures (T_c).[3,4] Alternatively, lengthening the ET donor molecule skeleton could also lead to a larger unit cell volume, and in salts with desired packing motifs and quasi-two-dimensionality, higher T_cs might be realized. Replacement of the terminal 1,2-ethanediyl groups in the ET molecule with fused aromatic rings is expected to enlarge the unit cell volume, in addition to the attendant possibility of aromatic π-π interactions leading to new molecular packing motifs. To this end, we undertook the synthesis of two ET derivatives, dibenzo-ET **2** and dinaphtho-ET **3**. Furthermore, the conducting cation radical salts obtained from ET and the bis(areno)-fused derivatives **2** and **3** with gradually increasing and well-defined molecular dimensions could also find application as "molecular ruler" calibration standards in STM-based micro-machining.[5] The synthesis of **2** was reported recently by use of an elaborate procedure starting from 1,2-dimercaptobenzene in five steps, involving a low-yielding cyclization step, with an overall yield of less than 4%.[6] A convenient synthetic methodology was thus needed for the preparation of **2** and the hitherto unknown dinaphtho-ET **3** as potential new donor molecules for superconducting salts, and for their possible utility in the design of "molecular rulers".[5]



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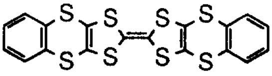

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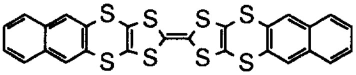
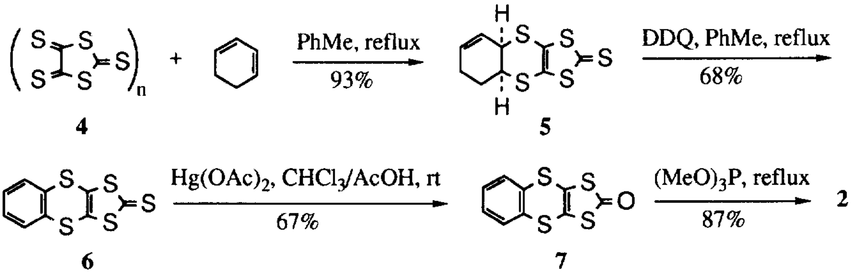


3

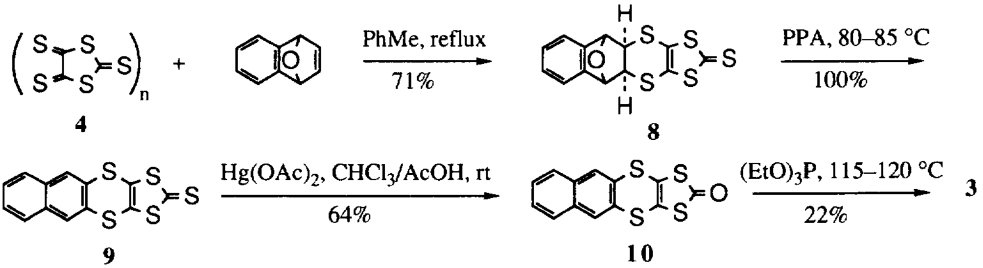
The synthesis of the target molecules **2** and **3** was achieved by use of the trithione oligomer, oligo(1,3-dithiole-2,4,5-trithione)[7] **4**, as the common starting material. Oligomer **4**, obtained by the oxidation of bis(tetraethylammonium) bis(1,3-dithiole-2-thione-4,5-dithiolato)zincate,[8] is known to undergo thermal depolymerization at *ca.* 100 °C and presents itself as an effective 4π component in pericyclic Diels-Alder type reactions.[7,9] Scheme 1 outlines the synthesis of the dibenzo-ET derivative **2** wherein the key step is the [4+2] cycloaddition of 1,3-cyclohexadiene with the trithione derived from oligomer **4**. Dehydrogenation of the resulting adduct **5** with DDQ in boiling toluene yielded the aromatized thione derivative **6**. Oxidation of thione **6** to the carbonyl derivative **7**,[6] employing mercuric acetate in chloroform/acetic acid at room temperature, followed by phosphite coupling afforded **2**. The cycloaddition route to the preparation of dibenzo-ET is a far more convenient and efficient method (overall yield of *ca.* 37%) than the previously reported synthesis.[6]

Scheme 1



The Diels-Alder reaction of the oligo(trithione) **4** was further exploited in the synthesis of the higher homolog, viz. the dinaphtho-ET **3** (Scheme 2).

Scheme 2



Cycloaddition reaction of **4** with 1,4-dihydronaphthalene-1,4-endoxide[10] (as a 2π component) in refluxing toluene resulted in the formation of the endoxide adduct **8**. Subsequent aromatization of **8** with polyphosphoric acid at 80–85 °C afforded the thione **9**. Conversion of thione **9** to the carbonyl derivative **10**, employing mercuric acetate in chloroform/acetic acid, followed by triethylphosphite-mediated coupling of **10** at 115–120 °C yielded the dinaphtho-ET **3**. The overall yield of **3** from the above four steps was *ca.* 10%.

All the new intermediates and the final target molecules were characterized spectroscopically, and by elemental analyses.[11] The redox behavior of the donor molecules was studied by cyclic voltammetry. The half-wave potentials vs $Ag/AgNO_3$ reference are listed in Table 1.

Table 1: Electrochemical Half-Wave Potentials[a] of the ET Derivatives.

Donor Molecule	Half-Wave Potentials (mV) vs $Ag/AgNO_3$	
	$E_{1/2}^1$	$E_{1/2}^2$
ET **1**[b]	86	505
Dibenzo-ET **2**[b]	242	610
Dinaphtho-ET **3**[c]	268	572

[a] Potentials recorded using a Pt disk working electrode, Pt wire as counter electrode, and $Ag/AgNO_3$ as a reference electrode, scan rates 100mV/s, 200mV/s. [b] in dichloromethane containing 0.1M $n\text{-}Bu_4NPF_6$. [c] in warm chlorobenzene (72°C) containing 0.1M $n\text{-}Bu_4NPF_6$.

Cyclic voltammogram of dibenzo-ET **2** exhibits two distinct one-electron redox waves in dichloromethane at room temperature. Both the first and the second half-wave potentials of **2** are shifted anodically in comparison to the parent ET molecule by 156 mV and 105 mV, respectively. These results are consistent with that reported by Müller et al.[6] Both the redox processes are fully reversible under our experimental conditions. The ferrocene/ferrocenium couple, used as an internal standard in the voltammetric experiment with **2**, has a half-wave potential value of 32 mV vs $Ag/AgNO_3$. Due to the insolubility of dinaphtho-ET **3** in dichloromethane, no redox waves were observed. Employing warm chlorobenzene (72 °C) as the solvent for the electrochemical experiments, two reversible redox waves could be observed for **3** with half-wave potential values of 268 mV and 572 mV, respectively. Preparation and evaluation of the electrical properties of the cation radical salts of the aromatic ring-annelated ET derivatives are in progress.

In conclusion, the synthesis of two examples of bis(areno)-fused ET derivatives, viz. dibenzo-ET **2** and dinaphtho-ET **3** has been accomplished by a general and convenient method taking advantage of the facile [4+2] cycloaddition reaction of the known oligo(1,3-dithiole-2,4,5-trithione) **4** with appropriate dienophiles.

Acknowledgement

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11. Analytical data of the annelated ET derivatives:
    Dibenzo-ET **2**: yellow microcrystals; mp. 289–290 °C with decomposition (lit.[6] mp. 286–287 °C, dec.). IR (KBr, cm^{-1}): 3050, 1560, 1447, 1424, 1252, 1109, 1028, 914, 772, 737, 656, 459. ^{1}H-NMR (300 MHz, CS_2 : C_6D_6 containing 1%TMS, 0.4mL : 10 drops) δ(ppm): 7.23 (AB q, 4H, J = 3.09 Hz), 7.09 (AB q, 4H, J = 3.09 Hz). Time-of-flight laser desorption MS: 480 (M^+). Anal. Calcd for $C_{18}H_8S_8$: C, 44.97; H, 1.68; S, 53.36. Found: C, 44.85; H, 1.81; S, 53.34.
    Dinaphtho-ET **3**: golden yellow fluffy crystals; mp. > 350 °C. IR (KBr, cm^{-1}): 3050, 1576, 1487, 1425, 1308, 1264, 1223, 1196, 1107, 1021, 916, 868, 804, 772, 733, 656, 605, 467, 455. ^{1}H-NMR (300 MHz, CS_2 : C_6D_6 containing 1%TMS, 0.4mL : 10 drops) δ(ppm): 7.71 (s, 4H), 7.59 (AB q, 4H, J = 3.09 Hz), 7.36 (AB q, 4H, J = 3.09 Hz). Time-of-flight laser desorption MS: 580 (M^+). Anal. Calcd for $C_{26}H_{12}S_8$: C, 53.76; H, 2.08; S, 44.16. Found: C, 53.34; H, 1.92; S, 44.50.

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