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SYNTHESIS OF NEW π-DONORS USING THE REACTION OF EDT-TTF WITH LITHIUM DIISOPROPYLAMIDE[1]

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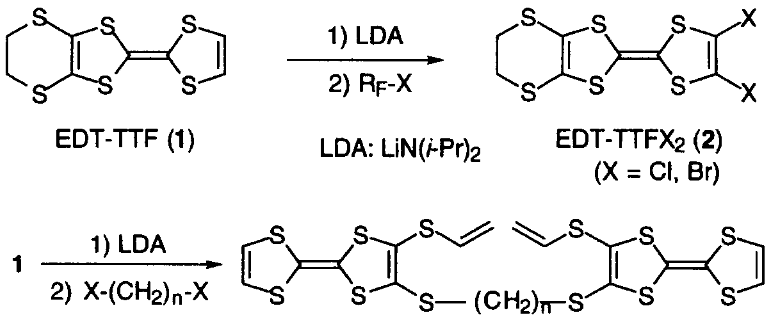
Abstract New bridged tetrathiafulvalene derivatives have been synthesized from ethylenedithiotetrathiafulvalene (EDT-TTF) in moderate to good yields using the lithiation-alkylation procedure. The X-ray analysis of the bridged molecule shows a spider-like structure.

Keywords: EDT-TTF, bridged π-donor, lithiation, alkylation, X-ray analysis

INTRODUCTION

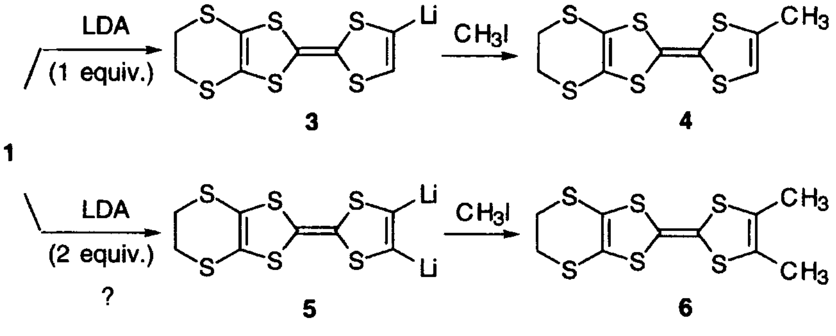
There is considerable current interest in macrocyclic and supramolecular chemistry incorporating tetrathiafulvalene (TTF) as a functional substituent. Although many methods have been reported for the preparation of TTF and its derivatives, only a few routes have been employed for the synthesis of bridged or cyclophane-type TTF derivatives.[2,3] The lithiation of TTF derivatives with lithium diisopropylamide (LDA) produces the corresponding anions which are known to be very useful intermediates.[4,5] We have recently reported the synthesis of dihalogenated ethylenedithiotetrathiafulvalene (EDT-TTFX_2) **2** by using lithiation of EDT-TTF (**1**) with LDA, followed by quenching with fluoroalkylated halides.[6] In the course of our study, we developed a new synthetic method of a bridged TTF system, and the results were reported in our previous paper.[7] We report here a new synthetic methodology of the novel bridged TTF system by using lithiation of EDT-TTF (**1**) with LDA, followed by alkylation with α,ω-dihalides (Scheme 1).



Scheme 1

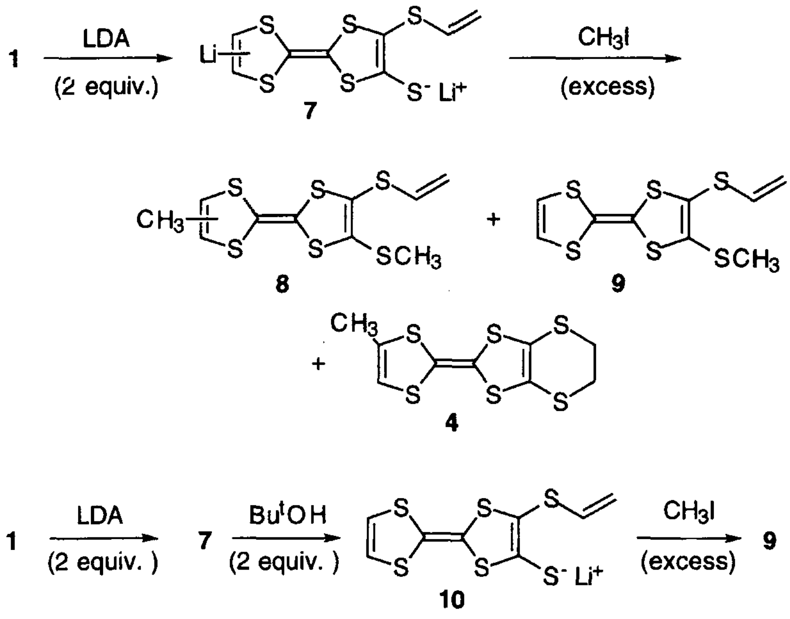
SYNTHESIS OF NEW BRIDGED π-DONORS

Ethylenedithiotetrathiafulvalene (EDT-TTF) **1** produces the corresponding lithiated EDT-TTF (**3**) by treatment with 1 equiv. of LDA.[5,6] Methylation of **3** with methyl iodide (excess) leads to the methylated EDT-TTF (**4**) shown in Scheme 2. We tried to produce the dilithiated EDT-TTF (**5**) which could yield the dimethylated EDT-TTF (**6**) (Scheme 2). However, the reaction of **1** with 2 equiv. of LDA, followed by quenching with methyl iodide (excess) afforded different results.



Scheme 2

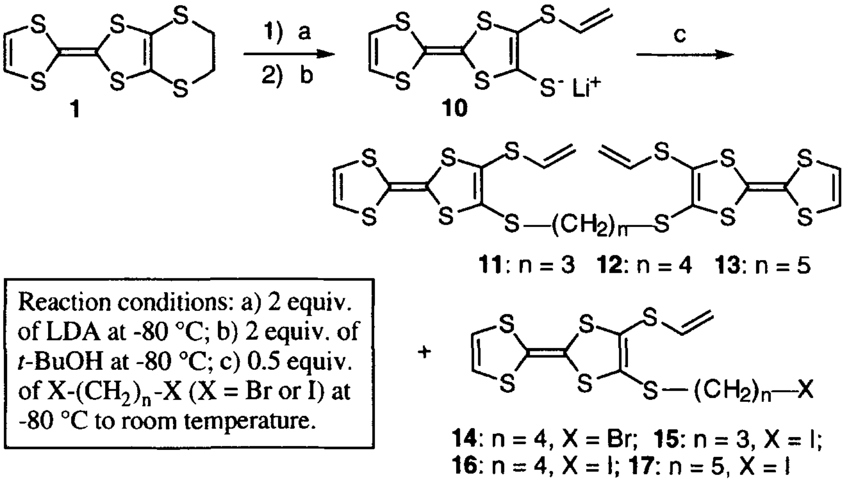
Treatment of EDT-TTF **1** with 2 equiv. of LDA in THF at -80 °C, followed by the reaction with methyl iodide (10 equiv.) produced the dimethylated **8** (42%), together with **9** (10%) and **4** (18%). It is thus speculated that the dianionic species **7** is formed by lithiation of **1** with 2 equiv. of LDA. As the dianion **7** can be converted into the thiolate anion **10** by treatment with *t*-butyl alcohol, successive treatments of **1** with LDA (2 equiv.), *t*-BuOH (2 equiv.), and methyl iodide (10 equiv.) resulted in the formation of the monomethylated **9** in 84% yield (Scheme 3).



Scheme 3

As shown in Scheme 3, the ring cleavage of the dithiacyclohexene ring occur-red when **1** was treated with 2 equiv. of LDA.[8] On the basis of these observations, we planned to synthesize new bridged TTFs **11-13**. As summarized in Table 1, the reaction of **10**, derived from **1**, with 1,4-dibromobutane (0.5 equiv.) at -80 °C to room temperature produced the bridged TTF **12** (22%) with the monoalkylated **14** (31%) (entry 1). The yields of the bridged TTFs were markedly improved by using α,ω-diiodoalkanes for the quenching of **10**. Thus, the reaction of **10** with 1,3-diiodopropane (0.5 equiv.) at -80 °C to room temperature gave the bridged TTF **11** (64%) with the monoalkylated **15** (11%) (entry 2). In a similar manner, the alkylation of **10** with 1,4-diiodobutane afforded the corresponding **12** (58%) and **16** (22%) (entry 3), whereas the reaction of **10** with 1,5-diiodopentane produced **13** (66%) and **17** (10%), respectively (entry 4). The bridged TTFs **11** and **12** are stable crystalline compounds, and **13** is a viscous orange oil.

Table 1. Conversion of EDT-TTF **1** to bridged TTF derivatives **11**, **12**, and **13**.



11: n = 3 **12**: n = 4 **13**: n = 5

Reaction conditions: a) 2 equiv. of LDA at -80 °C; b) 2 equiv. of *t*-BuOH at -80 °C; c) 0.5 equiv. of X-$(CH_2)_n$-X (X = Br or I) at -80 °C to room temperature.

14: n = 4, X = Br; **15**: n = 3, X = I;
16: n = 4, X = I; **17**: n = 5, X = I

Entry	α,ω-Dihaloalkane[a]	Products (Yield)[b]	
1	Br-$(CH_2)_4$-Br	**12** (22%)	**14** (31%)
2	I-$(CH_2)_3$-I	**11** (64%)	**15** (11%)
3	I-$(CH_2)_4$-I	**12** (58%)	**16** (22%)
4	I-$(CH_2)_5$-I	**13** (66%)	**17** (10%)

[a]0.5 equiv of α,ω-dihaloalkane was used. [b]Isolated yields.

REDOX POTENTIALS MEASURED BY CYCLIC VOLTAMMETRY

In order to estimate the donor ability of the TTF derivatives reported here, the oxidation potentials of **9** and **11-13** were measured by a cyclic voltammetric analysis. As shown in Table 2, all compounds reported here show only two oxidation waves. Therefore, **11**, **12**, and **13** are oxidized by two two-electron steps. The first oxidation potentials ($E^{1}_{1/2}$) of **11-13** are similar to that of EDT-TTF.[9] The $E^{1}_{1/2}$-value of **9** shows that the ring cleavage of the dithiacyclohexene ring in EDT-TTF causes an increase of the $E^{1}_{1/2}$-value compared with EDT-TTF. However, the $E^{1}_{1/2}$-values of the bridged derivatives **11-13** decrease by 0.05 V compared to **9** through the through-space interaction of two TTF moieties.[10] The almost same oxidation potentials in **11-13** reflect the nearly same through-space interactions of the TTF parts in the bridged system, although their molecular models show some conformational mobilities.

Table 2. Redox potentials[a] of TTF, EDT-TTF, BEDT-TTF, **9**, and **11-13**.

Compound	$E^1_{1/2}$/V	$E^2_{1/2}$/V	ΔE/V
TTF	0.37	0.78	0.41
EDT-TTF	0.45	0.81	0.36
BEDT-TTF	0.52	0.83	0.31
9	0.53	0.81	0.28
11	0.48	0.79	0.31
12	0.48	0.80	0.32
13	0.48	0.81	0.33

[a] Conditions: n-Bu_4NClO_4, benzonitrile, room temperature, Pt working and counter electrodes. Potentials were measured against an Ag/Ag^+ electrode and converted to the value vs SCE (Fc/Fc^+ = 0.31 V).

CRYSTAL STRUCTURE OF RECEPTOR-TYPE NEW DONOR

The molecular structure and packing diagram of **11** were determined by an X-ray analysis (Figures 1 and 2).[11] As shown in Figure 1, **11** has a crystallographic C_2 symmetry and the two-fold axis passes through the C(10) atom. Interestingly, this molecule has a π-receptor structure with TTF-arms, and two vinylthio groups settle the conformation of **11** into a spider-like form. Two TTF moieties are located almost parallel and the interatomic distance between C(6) and C(5*) is 10.64 Å which is enough to incorporate C_{60}-like molecules.

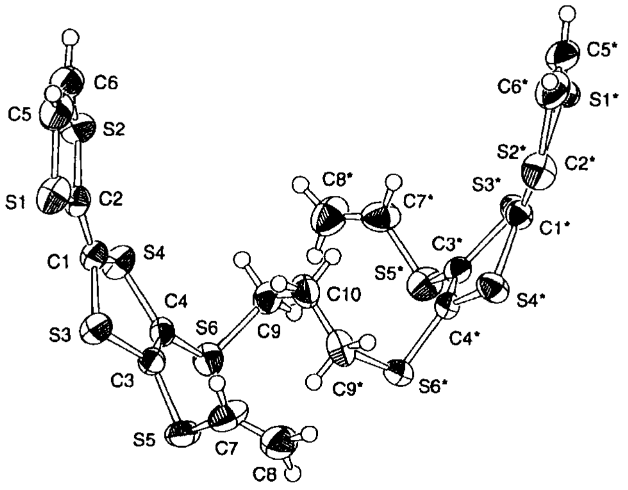
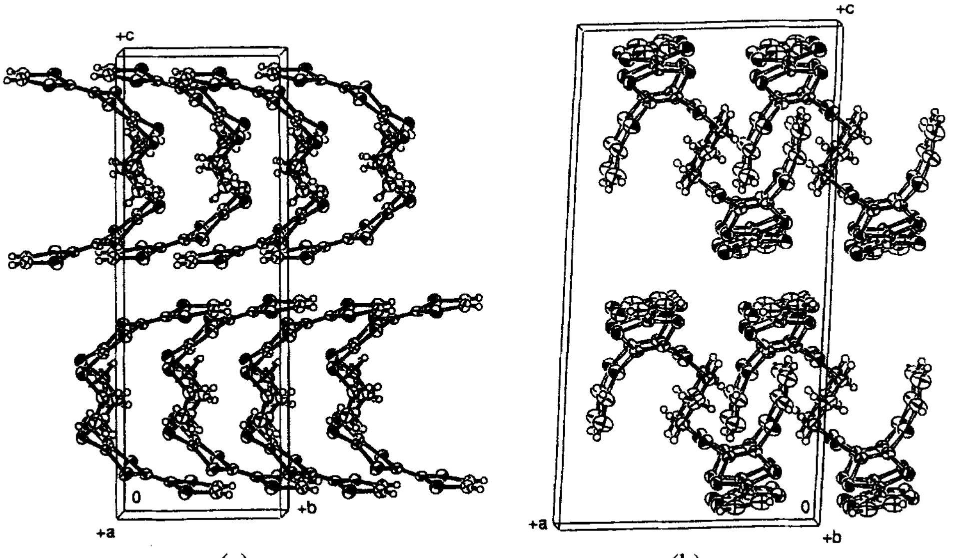


Figure 1. Crystal structure of **11**.

As shown in Figure 2, the packing diagram of **11** shows a unique feature. In the eight molecules in Figure 2a, the molecules stand side by side but the upper and lower columns are directed to the opposite direction. The first and third molecules from the left side are situated on the front side and the other four on the back side. Figure 2b shows that the TTF moieties in the upper and lower columns are located in a dimeric mode. However, the C(2)•••C(2) and C(4)•••(6) distances are 3.416(7) and 3.582(6) Å, respectively, which are longer than the sum of the van der Waals radii. There is only one intermolecular S•••S distance shorter than the sum of the van der Waals radii [S(1)•••S(4) = 3.588(2) Å].



(a) (b)

Figure 2. (a) Packing diagram of **11** viewed down the *a* direction and (b) viewed down the *b* direction.

CONCLUSION

We developed a new methodology to prepare the bridged TTF system starting from the readily obtainable EDT-TTF. Our method has a synthetic utility because a series of the bridged TTF derivatives can be synthesized very easily by one-pot lithiation-alkylation procedure.

The molecular structure of the bridged TTF molecule **11** determined by X-ray analysis revealed its receptor-type structure with a spider-like arms. Therefore, the bridged TTF molecule **11** can act as a large π-receptor. Similarly, the molecular structures of **12** and **13** can be expected to possess spider-like forms as **11**, because the redox properties of **11-13** indicate similar interactions between the two TTF moieties in **11-13**. Preparation and characterization of the CT-complexes and radical salts are now under investigation.

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EXPERIMENTAL

PREPARATION OF **4**. A solution of LDA, generated at -80 °C with diisopropylamine (0.28 ml. 2 mmol) and 1.55 M *n*-BuLi in hexane (1.29 ml, 2 mmol) in THF (10 ml), was dropwise added over 20 min to a solution of EDT-TTF (**1**)[12] (589 mg, 2 mmol) in THF (50 ml) at -80 °C under nitrogen. A yellowish solution was formed and stirred at -80 °C for 1 h. To the mixture was added dropwise a solution of methyl iodide (0.62 ml, 10 mmol) in THF (5 ml). The resulting mixture was stirred at -80 °C for 1 h, and then LDA, prepared from $HN(iPr)_2$ (0.14 ml, 1 mmol) and 1.55 M *n*-BuLi (0.64 ml, 1 mmol) in THF (5 ml), was added dropwise to the mixture.[13] After being stirred at -80 °C for 1 h, the mixture was allowed to warm to room temperature. Saturated aq. NH_4Cl solution (20 ml) was added and the solvent was removed by evaporation. The residue was extracted with CS (50 ml x 3), and the extracts were passed through a short column of silica gel (eluted with CS_2). The product was further purified by gel permeation chromatography (JAI model LC-908 liquid chromatography) to give **4** (0.416 g, 67%).

4: red crystals, mp 110-112 °C, MS (EI) 342 (M^+); ^1H NMR (400 MHz, $CDCl_3/CS_2$ 1:1) δ 5.825 (s, 1H), 3.266 (s, 4H), 2.073 (s, 3H).[14]

REACTION OF EDT-TTF (**1**) WITH 2 EQUIV. OF LDA, FOLLOWED BY QUENCHING WITH METHYL IODIDE. A solution of LDA, generated at -80 °C with diisopropylamine (0.14 ml. 1 mmol) and 1.55 M *n*-BuLi in hexane (0.7 ml, 1.1 mmol) in THF (5 ml), was dropwise added over 15 min to a solution of **1** (147 mg, 0.5 mmol) in THF (15 ml) at -80 °C under nitrogen. A yellowish solution was stirred at -80 °C for 5 h. To the resulting mixture was dropwise added over 15 min a solution of methyl iodide (0.31 ml, 5 mmol) in THF (5 ml). After being stirred at -80 °C for 1 h, the mixture was allowed to warm to room temperature. Saturated aq. NH_4Cl solution (20 ml) was added and the solvent was removed by evaporation. The residue was extracted with CS_2 (50 ml x 3), and the extracts were passed through a short column of silica gel (eluted with CS_2). The products were further purified by gel permeation chromatography (JAI model LC-908 liquid chromatography) to give **8** (68 mg, 42%), **9** (4.6 mg, 10%) and **4** (8.3 mg, 18%).

8: orange oil, MS (FAB) 323 (M+1); ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ 1:1) δ 6.339 (dd, J = 16.5 Hz, 9.5 Hz, 1H), 5.841 (s, 1H), 5.359 (d, J = 9.5, 1H), 5.350 (d, J = 16.5, 1H), 2.411 (s, 3H), 2.073 (s, 3H).

9: orange oil, MS (FAB) 308 (M^+); ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ 1:1) δ 6.344 (dd, J = 16.5, 9.5, 1H), 6.295 (s, 2H), 5.366 (d, J = 9.5, 1H), 5.357 (d, J = 16.5, 1H), 2.418 (s, 3H).

PREPARATION OF **9**. A solution of LDA, prepared from HN(*i*Pr)$_2$ (0.14 ml. 1 mmol) and 1.55 M *n*-BuLi (0.7 ml, 1.1 mmol) in THF (5 ml) at -80 °C, was dropwise added over 40 min to a solution of **1** (147 mg, 0.5 mmol) in THF (15 ml) at -80 °C under nitrogen. A yellowish solution was stirred at -80 °C for 1 h, and a solution of *t*-butyl alcohol (0.091 ml, 1 mmol) in THF (5 ml) was added over 10 min. After 2 h at -80 °C, a solution of methyl iodide (0.31 ml, 5 mmol) in THF (5 ml) was added dropwise. After being stirred at -80 °C for 1.5 h, the mixture was allowed to warm to room temperature. Saturated aq. NH_4Cl solution (20 ml) was added and the solvent was removed by evaporation. The residue was extracted with CS_2 (50 ml x 3), and the extracts were passed through a short column of silica gel (eluted with CS_2). The product was further purified by gel permeation chromatography (JAI model LC-908 liquid chromatography) to give **9** (129 mg, 84%).

PREPARATION OF THE BRIDGED TTF (**11**, **12** AND **13**). A solution of LDA, prepared from HN(*i*Pr)$_2$ (0.14 ml. 1 mmol) and 1.55 M *n*-BuLi (0.7 ml, 1.1 mmol) in THF (5 ml), was dropwise added over 40 min to a solution of **1** (147 mg, 0.5 mmol) in THF (15 ml) at -80 °C under nitrogen. The solution was stirred at -80 °C for 1 h, and a solution of *t*-butyl alcohol (0.091 ml, 1 mmol) in THF (5 ml) was added over 10 min. After 2 h at -80 °C, a solution of α,ω-diiodoalkane (0.25 mmol) in THF (5 ml) was added over 30 min. After being stirred at -80 °C for 1 h, the mixture was allowed to warm to room temperature. Saturated aq. NH_4Cl solution (20 ml) was added and the solvent was removed by evaporation. The residue was extracted with CS_2 (50 ml x 3), and the extracts were passed through a short column of silica gel (eluted with CS_2). The products were further purified by gel permeation chromatography (JAI model LC-908 liquid chromatography) to give the bridged TTFs (**11-13**) together with the monoalkylated products (**15-17**) (the yields of the products, see Table 1 in the text).

11: yellow crystals, mp 125-126 °C, MS (FAB) 629 (M+1); ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ 1:1) δ 6.360 (dd, J = 16.5, 9.5, 2H), 6.289 (s, 4H), 5.380 (d, J = 9.5, 2H), 5.367 (d, J = 16.5, 2H), 2.930 (t, J = 6.8, 4H), 1.919 (quint, J = 6.8, 2H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$ 1:1) δ 129.63, 128.43, 125.99, 118.86, 116.26, 116.10, 105.47, 34.35, 28.92.

12: orange crystals, mp 103-104 °C, MS (FAB) 643 (M+1); ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ 1:1) δ 6.354 (dd, J = 16.5, 9.5, 2H), 6.288 (s, 4H), 5.370 (d, J = 9.5, 2H), 5.356 (d, J = 16.5, 2H), 2.802 (m, 4H), 1.744 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$ 1:1) δ 129.67, 129.16, 125.04, 118.84, 116.06, 115.88, 105.60, 35.69, 28.24.

13: orange oil, MS (FAB) 657 (M+1); ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ 1:1) δ 6.346 (dd, J = 16.5, 9.5, 2H), 6.228 (s, 4H), 5.366 (d, J = 9.5, 2H), 5.347 (d, J = 16.5, 2H), 2.787 (t, J = 6.8, 4H), 1.650-1.596 (m, 4H), 1.550-1.540 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$ 1:1) δ 129.67, 129.52, 124.46, 118.81, 115.92, 115.79, 105.62, 36.04, 29.12, 27.15.

15: orange oil, MS (FAB) 462 (M^+); ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ 1:1) δ 6.368 (dd, J = 16.5, 9.5, 1H), 6.294 (s, 2H), 5.391 (d, J = 9.5, 1H), 5.380 (d, J = 16.5, 1H), 3.293 (t, J = 6.5, 2H), 2.897 (t, J = 6.5, 2H), 2.081 (quint, J = 6.5, 2H).

16: orange oil, MS (FAB) 476 (M^+); ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ 1:1) δ 6.365 (dd, J = 16.5, 9.5, 1H), 6.297 (s, 2H), 5.380 (d, J = 9.5, 1H), 5.365 (d, J = 16.5, 1H), 3.163 (t, J = 7.0, 2H), 2.813 (t, J = 7.0, 2H), 1.988 (quint, J = 7.0, 2H), 1.771 (quint, J = 7.0, 2H).

17: orange oil, MS (FAB) 490 (M^+); ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ 1:1) δ 6.355 (dd, J = 16.6, 9.3, 1H), 6.293 (s, 2H), 5.370 (d, J = 9.3, 1H), 5.357 (d, J = 16.6, 1H), 3.159 (t, J = 7.0, 2H), 2.797 (t, J = 7.0, 2H), 1.874-1.802 (m, 2H), 1.665-1.611 (m, 2H), 1.557-1.499 (m, 2H).

ELECTROCHEMICAL MEASUREMENTS. Cyclic voltammetric measurements were made on a BAS CV-27 electrochemical analyzer. The working and counter electrodes were a platinum disk and a platinum wire, respectively. An Ag/Ag^+ electrode was used as a reference electrode. The measurements were carried out in PhCN with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte, and the scanning rate was 100 mVs^{-1}.

CRYSTAL STRUCTURE ANALYSIS. X-ray data were collected on a Rigaku AFC7R diffractometer using the graphite-monochromated Mo Kα radiation and the ω-2θ scan technique. Crystal data for **11** is as follows: $C_{19}H_{16}S_{12}$, FW = 629.06, monoclinic, space group C2/c; a = 12.569(7) Å, b = 8.570(6) Å, c = 24.062(4) Å, β = 93.60(2)°, V = 2586(1) Å^3, Z = 4, d_{calcd} = 1.616 g cm^{-1}. The structure was solved by a direct method using SHELXS86. Full matrix least-squares refinement yielded the final R value of 0.039 (R_W = 0.035) for 1908 independent reflections [$2\theta \leq 55.1°$, $I > 3.00\sigma(I)$].

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13. Without treatment of the additional LDA, the reaction produced **4** in 38% yield together with the recovered EDT-TTF (37%).
14. All the new crystalline compounds gave satisfactory elemental analyses.