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A Pyrrolo-Tetrathiafulvalene Belt and Its TCNQ Complex: Syntheses and X-ray Crystal Structures

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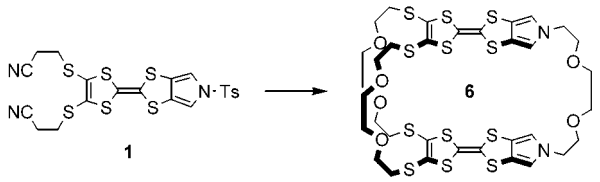
ABSTRACT



A general and efficient four-step synthesis of a tetrathiafulvalene-belt 6, starting from the monopyrrolo-tetrathiafulvalene building block 1, is described, together with its 7,7,8,8-tetracyano-*p*-quinodimethane charge transfer complex. The complexation of the electron acceptor 7,7,8,8-tetracyano-*p*-quinodimethane by the tetrathiafulvalene-belt 6 was investigated both in solution and in the solid state.

Since the discovery of the first metallic charge transfer (CT) complex[1] of tetrathiafulvalene (TTF) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), the chemistry[1b] of TTF and its derivatives has been intensively studied with the ultimate goal of preparing superconducting CT complexes and radical cation salts.[2] Furthermore, there has recently been an increasing interest in incorporating TTF into molecular, macrocyclic, and supramolecular systems capable of acting as, for example, sensors, catalysts, or switches at the molecular level.[3] Dimeric TTF molecules[4] and TTF-belts[5] in which two TTF units are linked by one or more spacer groups have received particular attention, due to the possibility of affecting the formation, structure, and physical properties of their CT complexes and ion radical salts.[4] Versatile TTF building blocks have been developed in recent years, and many problems concerning the selective functionalization of TTF have been solved.[3a,c,6] However, the four attachment sites of TTF usually result in a mixture of two inseparable isomers, a cis and a trans isomer. This problem can be circumvented using the newly described bis-cyanoethyl thiolate protected monopyrrolo-TTF building block[6] **1** (Scheme 1), which only possesses three attachment sites and thereby is devoid of cis/trans problems.

In this letter, we describe a general and efficient method for the preparation of TTF-belts employing the TTF building block **1**, together with a crystal structure analysis of the neutral TTF-belt **6**. Furthermore, we describe our preliminary complexation studies between the TTF-belt **6** and TCNQ,

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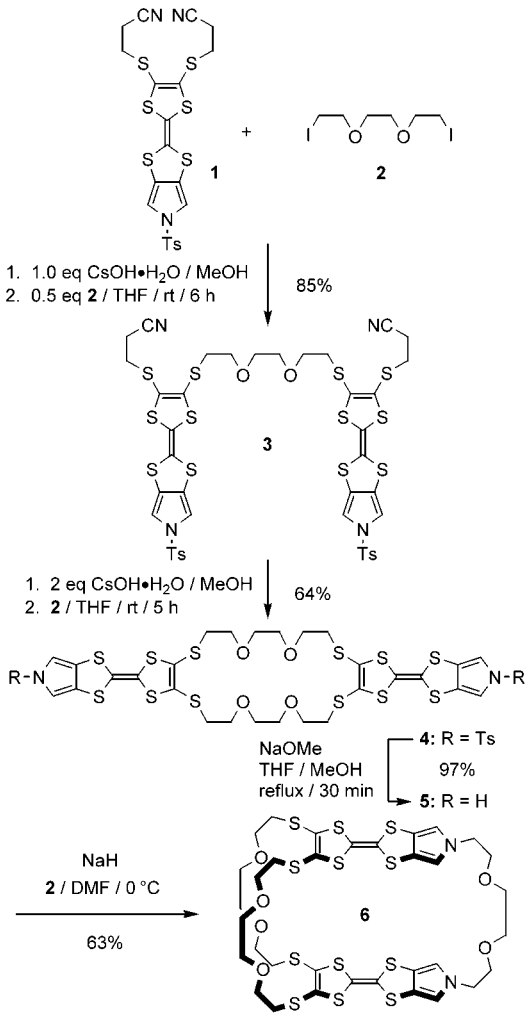
Scheme 1. Synthesis of the TTF-Belt **6**, Starting from the Monopyrrolo-TTF Building Block **1**



which have been carried out in solution using ^{1}H NMR, UV−vis, and ESR spectroscopies and in the solid state using IR spectroscopy and X-ray crystallography.[7]

The TTF-belt **6** was designed to participate in host−guest chemistry,[8] where the belt incorporating two identical TTF electron donors could be expected to act as a host molecule for electron-deficient guests such as TCNQ. The optimal distance between two TTF moieties for CT and/or $\pi-\pi$ interaction with the purpose of stabilizing inclusion of a guest is approximately 7 Å.[9] A Cory−Pauling−Koltun (CPK) model inspection revealed that 1,2-bis(2-iodoethoxy)ethane spacers between two TTF moieties would allow the distance between the two TTF moieties to be longer/or equal to 7 Å.

The TTF-belt **6** was synthesized as illustrated in Scheme 1. A solution of the monopyrrolo-TTF building block[6] **1** was treated with 1 equiv of $CsOH·H_2O$. This procedure generated the TTF-monothiolate, which was alkylated with 0.5 equiv of 1,2-bis(2-iodoethoxy)ethane (**2**) to afford the bis-TTF **3** in 85% yield. Subsequently, the two remaining cyanoethyl protecting groups in **3** were deprotected using 2 equiv of $CsOH·H_2O$ followed by addition of 1 equiv of 1,2-bis(2-iodoethoxy)ethane (**2**), which effected the second deprotection/alkylation sequence, affording **4** in 64% yield. Deprotection of the tosyl groups were carried out in near quantitative yield by refluxing **4** in a 1:1 mixture of THF and MeOH in the presence of an excess of NaOMe. Employing high-dilution conditions allowed a 63% yield of the TTF-belt[10] **6** to be obtained following N-alkylation of the pyrrole units in **5** with 1,2-bis(2-iodoethoxy)ethane (**2**).

The redox behavior of the TTF-belt **6** was investigated in solution by cyclic voltammetry (CV). The CV of **6** exhibited two well-defined two-electron reversible redox waves at $E_{1/2}^1 = 0.37$ V and $E_{1/2}^2 = 0.91$ V corresponding to the simultaneous formation of two radical cations followed by formation of two dications at a higher potential.[11]

Single crystals of **6** were obtained by crystallization from CH_2Cl_2−MeOH, and its structure was solved by X-ray crystallography[12] (Figure 1). The TTF-belt is rather elongated

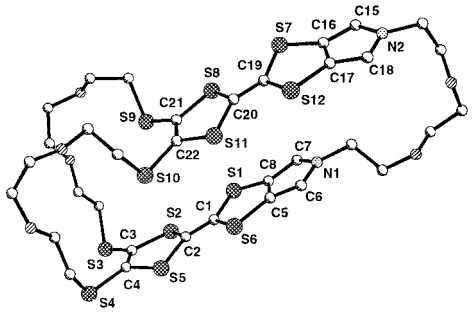


Figure 1. Crystal structure of the TTF-belt **6**. Hydrogen atoms are omitted for clarity.

with the two TTF parts having there longer axes parallel. The interplanar distance is not well-defined but on the order of 5.5 Å, and one TTF part is rotated approximately 15°

(7) For examples of TTF·TCNQ complexes, see: (a) Batsanov, A. S.; Bryce, M. R.; Chesney, A.; Howard, J. A. K.; John, D. E.; Moore, A. J.; Wood, C. L.; Gershtenman, H.; Becker, J. Y.; Khodorkovsky, V. Y.; Ellern, A.; Bernstein, J.; Perepichka, I. F.; Rotello, V.; Gray, M.; Cuello, A. O. *J. Mater. Chem.* **2001**, *11*, 2181−2191. (b) Legros, J.-P.; Dahan, F.; Binet, L.; Carcel, C.; Fabre, J.-M. *J. Mater. Chem.* **2000**, *10*, 2685−2691.

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(10) **Data for TTF-belt 6:** ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 3.00 (t, $J = 6.1$ Hz, 8H), 3.50 (s, 4H), 3.53 (t, $J = 5.2$ Hz, 4H), 3.62 (s, 8H), 3.72 (t, $J = 6.1$ Hz, 8H), 3.89 (t, $J = 5.2$ Hz, 4H), 6.47 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 36.0, 50.8, 70.5, 70.6, 70.7, 70.9, 110.8, 113.0, 118.6, 121.0, 128.2; MS(EI) *m/z* 956 (M^+); mp 162−163 °C. Anal. Calcd for $C_{34}H_{40}N_2O_6S_{12}$ (957.5): C, 42.51; H, 4.29; N, 2.90; S, 40.03. Found: C, 42.65; H, 4.21; N, 2.93; S, 40.18.

(11) CV was performed using a 0.84 mM solution of **6** in anhydrous CH_2Cl_2 with *n*-Bu_4NPF_6 (0.10 M) as the supporting electrolyte and Ag/AgCl as the reference electrode at a scan rate of 100 mV/s.

(12) **Selected interatomic distances (Å) for 6:** S(1)−C(8) 1.746(2), S(1)−C(1) 1.762(2), S(2)−C(2) 1.757(2), S(2)−C(3) 1.766(2), S(3)−C(3) 1.746(2), S(4)−C(4) 1.745(3), S(5)−C(4) 1.756(2), S(5)−C(2) 1.758(3), S(6)−C(5) 1.738(2), S(6)−C(1) 1.770(2), N(1)−C(6) 1.361(3), N(1)−C(7) 1.364(2), C(1)−C(2) 1.342(3), C(3)−C(4) 1.344(4), C(5)−C(6) 1.371(3), C(5)−C(8) 1.411(3), C(7)−C(8) 1.362(3).

with respect to the other part. In addition to the rotation, there is a rather long translation in the longitudinal direction (4.4 Å), thus leading to a ring-over-bond arrangement. The central C_2S_4 systems and the pyrrole part of the TTF moieties are approximately planar. Derivations from planarity of the moieties can be described by the interplanar angles A−B 4.7°, A−C 17.1°, D−E 16.5°, and D−F 6.4°, where the planes are defined by the atoms: A(S1, S6, S5, S2, C1, C2), B(S1, S6, C5, C8), C(S2, S5, C3, C4), D(S7, S12, S8, S11, C19, C20), E(S7, S12, C16, C17), and F(S8, S11, C21, C22). Finally, a few shorter intermolecular S···S distances indicate some weak sidewise interactions between neighboring TTF-belts.

The complexation behavior between the TTF-belt **6** (host) and TCNQ (guest) was investigated in solution using UV−vis, ^{1}H NMR, and electron paramagnetic resonance (EPR) spectroscopies.

Addition of 1 equiv of TCNQ to a CH_2Cl_2 solution of **6** (2.5×10^{-4} M) resulted in an immediate color charge from orange to green and the appearance of two CT absorption bands, centered on λ_{max} 749 and 849 nm in the UV−vis spectrum (Figure 2). This might indicate two different forms

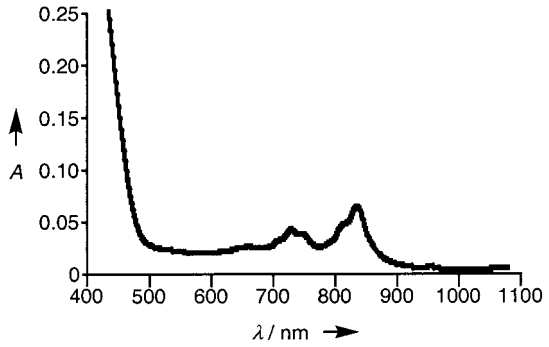

Figure 2. Absorption spectra (CH_2Cl_2, 25 °C) recorded on a 1:1 mixture of **6** and TCNQ.

of complexation in solution, an inside and an outside (alongside) form. The ^{1}H NMR spectrum (250 MHz) recorded at 25 °C in $CDCl_3$ revealed a weak upfield shift ($\Delta\delta$ = 0.02 ppm) of the resonances associated with the pyrrole protons. Furthermore, EPR spectroscopy of **6**·TCNQ recorded in CH_2Cl_2 revealed a radical signal[13] at g = 2.009. The line width and g-value are consistent with the presence of a TTF radical cation.[14] These results indicate that a CT interaction between the host and guest is taking place in solution. However, these results do not provide any information regarding the stoichiometry of the complexation or whether TCNQ is complexed inside the cavity of **6** or associated at the outside of **6**.

(13) The EPR spectrum also revealed a radical signal at g = 2.004, which is consistent with the presence of $TCNQ^{\bullet-}$; see: Bryce, M. R.; Moore, A. J.; Tanner, B. K.; Whitehead, R.; Clegg, W.; Gerson, F.; Lamprecht, A.; Pfenninger, S. *Chem. Mater*. **1996**, *8*, 1182−1188.

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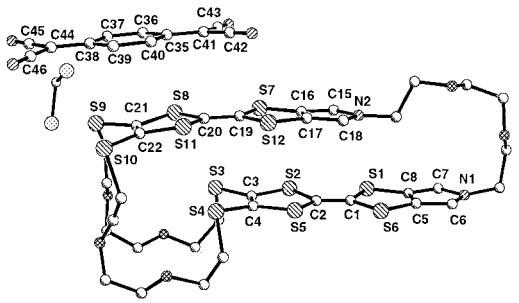

Figure 3. Crystal structure of the CT complex **6**·TCNQ. Hydrogen atoms are omitted for clarity.

Single crystals of **6**·TCNQ (Figure 3) suitable for X-ray diffraction analysis were grown by slow evaporation of a CH_2Cl_2 solution containing **6** and TCNQ in a 1:1 ratio.[15] The crystal structure determination[16] (Figure 3) surprisingly revealed that the TCNQ molecule is located between two different TTF-belts and not as expected within a molecular cavity. In this structure, the TTF-belt is more collapsed, leaving no cavity between the two TTF parts. The crystal structure of **6**·TCNQ comprises mixed stacks of an ··· ADDADD··· type (Figure 4) having almost parallel molec-

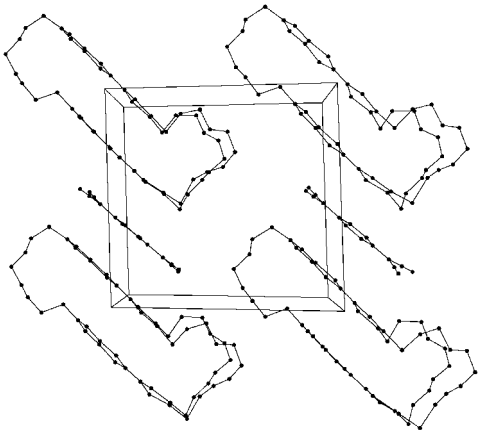

Figure 4. Crystal packing of **6**·TCNQ. CH_2Cl_2 groups are omitted for clarity.

ular planes,[17] where the interplanar distance between the two TTF parts have been reduced to ca. 3.5 Å. The structure

(15) **Selected interatomic distances (Å) for 6·TCNQ:** S(7)−C(16) 1.735(3), S(7)−C(9) 1.754(3), S(8)−C(10) 1.745(3), S(8)−C(11) 1.761-(3), S(9)−C(11) 1.748(3), S(10)−C(12) 1.754(3), S(11)−C(10) 1.741(3), S(11)−C(12) 1.747(3), S(12)−C(13) 1.729(3), S(12)−C(9) 1.755(3), N(2)−C(14) 1.366(4), N(2)−C(15) 1.370(4), C(9)−C(10) 1.358(4), C(11)−C(12) 1.345(4), C(13)−C(14) 1.371(4), C(13)−C(16) 1.414(4), C(15)−C(16) 1.380(4), C(35)−C(41) 1.383(4), C(35)−C(40) 1.430(4), C(35)−C(36) 1.437(4), C(36)−C(37) 1.345(5), C(37)−C(38) 1.431(5), C(38)−C(44) 1.394(5), C(38)−C(39) 1.434(4), C(39)−C(40) 1.352(4), C(41)−C(42) 1.421(4), C(41)−C(43) 1.427(4), C(44)−C(45) 1.428(5), C(44)−C(46) 1.429(5).

also reveals that the degrees of overlap between the TCNQ•••TTF (containing C1 and C2) and TCNQ•••TTF (containing C9 and C10) are not identical,[18] indicating that the charge transfer can be different for the two TTF parts in the same molecule. In a TCNQ moiety, bond lengths tend to change with an increase in the negative charge located on the acceptor.

It has been found that differences in the bond length of TCNQ (Figure 5) change practically linearly[19] from 0.069

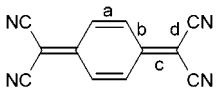

Figure 5. Structure of TCNQ.

Å ($b-c$) and 0.062 Å ($d-c$) in neutral TCNQ[20] to zero in the TCNQ radical anion.[21] In the case of **6**•TCNQ, the average bond lengths are $a = 1.349(5)$ Å, $b = 1.433(4)$ Å, $c = 1.389(4)$ Å, and $d = 1.426(5)$ Å, suggesting that the charge transfer is ca. 0.4 *e*. A similar model of linearly dependency[22] can be applied for the central C−S bonds of the TTF moiety, suggesting positive charges[23] of 0.2 and 0.0 *e*, respectively, for the two TTFs in the same belt. This inconsistency in balance between negative and positive charges can presumably be ascribed to a change in central C−S bond length between unsubstituted TTF[24] (1.757(2) Å) and substituted monopyrrolo-TTF[25] (1.761(2) Å). **6**•TCNQ exhibits a lower degree of intermolecular charge transfer than TTF•TCNQ,[26] which is not surprising, since the oxidation potential of **6** ($E_{1/2}^1 = 0.37$ V, vs Ag/AgCl in CH_2Cl_2) is slightly higher than that of TTF ($E_{1/2}^1 = 0.34$ V, vs Ag/AgCl in MeCN). The nitrile absorption frequency in the solid-state IR spectrum of **6**•TCNQ is shifted to a lower wavenumber[27] (2195 cm^{-1}) with respect to that of TCNQ (2222 cm^{-1}), which also suggests that a charge transfer occurs between the TTF part and TCNQ in the solid state.[28]

In summary, a general and efficient method for the preparation of TTF-belts has been developed. The TTF-belt **6** was designed to allow complexation of TCNQ inside its cavity. However, a solid-state X-ray crystal structure analysis of the CT complex **6**•TCNQ revealed that the TCNQ is associated outside (alongside) one of the electron donors, reflecting that the complicated and subtle balance between all the individual noncovalent forces acting in cooperation are difficult to predict. The efficient synthetic methodology described in this letter allows us, in a few steps, to make related TTF-belts in which the spacers can be varied in order to optimize the complexation properties of the macrocyclic host. Work is aimed in this direction, together with further functionalization generating also TTF-cages incorporating three or more monopyrrolo-TTF moieties.

Acknowledgment. We thank University of Southern Denmark for a Ph.D. Scholarship to K.N., Carlsbergfondet for financial support to J.O.J., and Lars Duelund for recording the EPR spectrum.

Supporting Information Available: Characterization data for **3**−**6**, together with crystallographic data for **6** and **6**•TCNQ. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) The crystal structure contains one solvent molecule per **6**•TCNQ, and one of the spacer chains is somewhat disordered, which was modeled by two slightly different conformations (only one of which is shown in Figure 3).

(17) Deviations from planarity can be described by the interplanar angles A−B 1.8°, A−C 3.5°, D−E 2.2°, and D−F 10.6° of **6**•TCNQ; translation of the two TTF parts in the longitudinal direction was 4.5 Å.

(18) The overlap between TCNQ•••TTF (containing C9 and C10) is largest.

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(23) The values 0.2 and 0.0 were determined from the equation $f = 1.757$ Å $- 0.0385(\rho^+)$, where f is the average bond length of the central C−S bonds in the CT complex, 1.757 Å is the average bond length of the central C−S bonds in neutral unsubstituted TTF, and ρ^+ is the degree of positive charge on the TTF unit in the CT complex.

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(25) The average bond length for the central C−S bonds in **6**. If the value 1.757 is changed to 1.761 Å in the equation described in ref 23, the positive charges on the two TTF units are ca. 0.3 and ca. 0.1 *e*, respectively.

(26) Kistenmacher, T. J.; Phillips, T. E.; Cowan, D. O. *Acta Cryst*. **1974**, *B30*, 763−768.

(27) The change in absorption frequencies measured by IR spectroscopy (2195 cm^{-1}) suggests a charge transfer of ca. 0.7 *e* according to the model proposed by Chappell and co-workers.[28] However, these results are inconsistent with the degree of charge transfer suggested by the crystal structure analysis (ca. 0.4 *e*). A similar inconsistency has been observed in CT complexes of BEDT−TTF•TCNQ; see: Wu, W.; Zhang, D.; Li, H.; Zhu, D. *J. Mater. Chem*. **1999**, *9*, 1245−1249.

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