

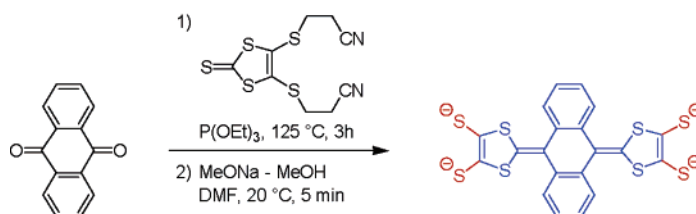
## Thiolated $\pi$ -Extended Tetrathiafulvalenes: Versatile Multifunctional $\pi$ -Systems

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Derivatives of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (ex-TTF) have been synthesized by a new synthetic methodology, viz., direct phosphite-mediated cross-couplings of anthraquinone with 1,3-dithiole-2-thione derivatives. These ex-TTFs bear one, two, or four cyanoethyl-protected thiol groups on the dithiole rings. Deprotection (NaOMe, MeOH, DMF, 20 °C) and trapping of the transient thiolates with electrophiles have afforded the new ex-TTF trimer **19**, dimeric cyclophanes **22** and **25**, the tetrakis-(hydroxyethylthio) derivative **23**, and the strained cyclophane **24**. Solution redox properties have been studied by cyclic voltammetry. For compounds **19**, **22**, and **25** each ex-TTF unit behaves as an independent 2-electron redox system giving rise to a single, quasi-reversible 6-, 4-, and 4-electron wave, respectively. The  $E_{\text{ox}}$  value for **24** ( $0 \rightarrow 2+$  wave) is positively shifted by 290 mV compared to that of its precursor **15** due to the short bridge in **24** obstructing the conformational change which accompanies oxidation. X-ray crystal structures of **23**·2.5MeOH, **23**·1.5MeCN, **24**·CH<sub>2</sub>Cl<sub>2</sub>, and **24**·1.5CH<sub>2</sub>Cl<sub>2</sub> show the saddle-shape folding (typical of ex-TTF derivatives), which in **24** is enhanced by the pentamethylene chain bridging the dithiole units. Both solvates of **23** show an unprecedented crystal packing motif due to hydrogen bonding.

### Introduction

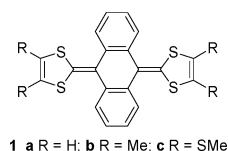
Tetrathiafulvalene (TTF) derivatives which possess extended  $\pi$ -electron conjugation between the two dithiole rings are important as building blocks for supramolecular and organic materials chemistry.<sup>1</sup> The incorporation of a central vinylogous<sup>2</sup> or *p*-quinodimethane spacer<sup>3</sup> leads to reduced on-site Coulombic repulsion and stabilization of the oxidized states, compared to those of the parent TTF. As an example of the latter family, 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (**1a**) (herein abbreviated as “ex-TTF”) provides a unique combination of redox, charge delocalization, and structural properties. Whereas TTF undergoes two, reversible, 1-electron oxidation waves in

solution electrochemical experiments, the ex-TTF system **1** (Chart 1) displays inverted potentials ( $E_{1^{\text{ox}}} > E_{2^{\text{ox}}}$ )<sup>4</sup> manifested as a single, 2-electron oxidation process,<sup>5</sup>  $\text{D}^0 \rightarrow \text{D}^{2+}$ , with  $E^{\text{ox}} = 0.30\text{--}0.60$  V vs Ag/AgCl, depending upon the solvent and the substituent R.<sup>6</sup> This redox process, which is electrochemically quasi-reversible and chemically reversible, triggers a dramatic conformational change in the molecule.<sup>7</sup> X-ray crystallographic studies established that the neutral molecule **1b** is

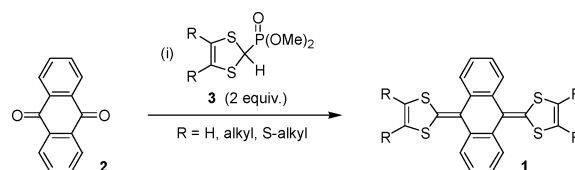
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## CHART 1



butterfly shaped with the anthracenediylidene unit strongly folded as a result of *peri*-interactions between the sulfur atoms and the hydrogen atoms on the benzoannulated quinoid moiety. In contrast, the dication (**1b**<sup>2+</sup>) possesses a planar and aromatic anthracene unit, with the heteroaromatic 1,3-dithiolium cations almost orthogonal to this plane.<sup>8</sup> These unusual redox and structural properties have been explained by theoretical studies of the minimum energy conformations and charge distribution in the neutral, radical cation, and dication states of **1**.<sup>9</sup> The transient radical cation of system **1** has been detected in flash photolysis<sup>10</sup> and pulse radiolysis<sup>11</sup> experiments. This remarkable interplay of electron donor properties and conformational change has led to derivatives of **1** being used as building blocks for charge-transfer salts,<sup>12</sup> nonlinear optical materials,<sup>13</sup> multistage redox assemblies,<sup>14</sup> dimeric ex-TTFs,<sup>15</sup> dendrimers,<sup>16</sup> cyclo-

SCHEME 1<sup>a</sup>

<sup>a</sup> Reagents and conditions: (i) **3**, LDA or BuLi, THF,  $-78\text{ }^{\circ}\text{C}$ .

phanes,<sup>17</sup> cation sensors,<sup>18</sup> self-assembled monolayers,<sup>19</sup> and donor–acceptor arrays, some of which possess long-lived charge-separated excited states.<sup>20</sup>

Given this wide range of applications, the development of methodology leading to new derivatives of **1** is clearly important. To date two complementary routes to derivatives of **1** functionalized at the dithiole units have been reported: (1) Horner–Wadsworth–Emmons olefination of anthraquinone **2** with prefunctionalized (1,3-dithiol-2-yl)phosphonate ester reagents **3** (Scheme 1)<sup>21</sup> or (2) lithiation of ex-TTF derivatives bearing a hydrogen on one, or both, of the dithiole rings and trapping with electrophiles, e.g., reactions of **7** to yield **8** (Scheme 2).<sup>22</sup>

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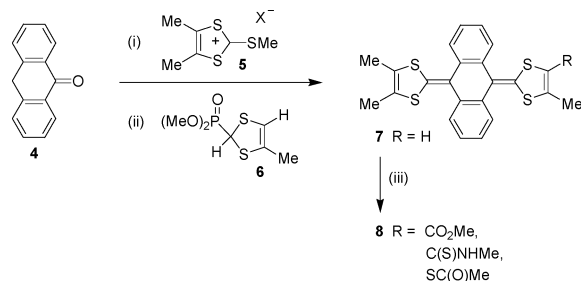
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SCHEME 2<sup>a</sup>

<sup>a</sup> Reagents and conditions: (i) **5**, pyridine, MeCO<sub>2</sub>H, reflux; (ii) **6**, LDA or BuLi, THF, -78 °C; (iii) LDA, THF, -78 °C, then electrophile<sup>+</sup>.

(Note that the preparation of compound **7** required a phosphonate reagent, **6**, for the second step, like route 1.)

We now report alternative methodology which is both labor- and cost-effective, avoiding the multistep syntheses of the phosphonate ester reagents **3** and **6**. We have found that the direct phosphite-mediated cross-coupling of readily available 1,3-dithiole-2-thione units with anthraquinone is an efficient route to symmetrical ex-TTF derivatives (i.e., 2-fold reaction with both dithiole units the same) and unsymmetrical systems (stepwise attachment of different dithiole units). Moreover, this new protocol allows the formation of products bearing protected thiol functionality, which will not survive the basic conditions of either route 1 or 2 above. The value of these thiolated ex-TTF derivatives has been established in a series of further transformations.

## Results and Discussion

**Synthesis.** The self-coupling and cross-coupling of 1,3-dithiole-2-one/thione/selenone units in refluxing triethyl phosphite is a well-established route to symmetrical and unsymmetrical TTF derivatives, respectively, and a good alternative to the functionalization of TTF by lithiation and trapping with electrophiles.<sup>23</sup> Generally the phosphite coupling proceeds efficiently with dithioles bearing electron-withdrawing groups, and oxones and selenones tend to give higher yields than the corresponding thiones.<sup>24</sup> To extend this methodology to cross-couplings with the less reactive anthraquinone, it was necessary to limit the formation of the self-coupled TTF derivative. An initial experiment established that heating a mixture of anthraquinone and 4,5-bis(methylthio)-1,3-dithiol-2-thione (**9**) (2 equiv) in neat triethyl phosphite at 125 °C for 3 h gave only tetrakis(methylthio)-TTF (56% yield), unreacted anthraquinone, and decomposed starting material. No cross-coupled product was detected (TLC evidence). However, slow addition of thione **9** to an excess of anthraquinone (**2**) in triethyl phosphite-chlorobenzene afforded the ketone **10** in 52% yield. This is

comparable to the literature yield of **10** from anthrone and the corresponding dithiolium salt.<sup>25</sup> In the second cross-coupling reaction 3.3 equiv of Becher's reagent **11**<sup>26</sup> was slowly added to **10** in neat P(OEt)<sub>3</sub> at 130 °C. The slow addition minimized self-coupling of **11**, and the ex-TTF system **12** was obtained in 73% yield (Scheme 3).

Following this protocol, 2-fold reactions of anthraquinone (**2**) and the thione reagents **11** and **14** gave the protected tetrathiolated and dithiolated ex-TTF derivatives **13** and **15** in 60% and 47% yields, respectively (Scheme 4). The lower yield for the latter compound was due to a recrystallization needed to separate **15** from the self-coupled TTF derivative. The synthetic versatility of these protected thiolate derivatives **12**, **13**, and **15** has been established in the series of reactions shown in Schemes 5–7.

Following the precedents of TTF chemistry,<sup>26</sup> the mono-deprotection of **12** was readily achieved by using 1 equiv of sodium methoxide: trapping of the intermediate thiolate anion **16** with methyl iodide gave compound **17** in 96% yield. The analogous deprotection of **17** and trapping with the trifunctional alkylating reagent **18** gave the ex-TTF trimer **19** in 97% yield.

Compound **12** served as the precursor to a new dimeric ex-TTF cyclophane, **22**, by using the difunctional alkylating reagent **20**, which was chosen because of its very reactive iodides and the *tert*-butyl groups, which should enhance the solubility of the products (Scheme 5). (The dibromo analogue of **20** has been used previously in the synthesis of TTF cyclophanes.<sup>27</sup>) Two, stepwise deprotections and alkylations afforded **22** in 77% yield from **12**: the probable intermediate **21** was neither isolated nor characterized. Although cyclophane **22** contains four *tert*-butyl groups, it was only sparingly soluble in many solvents. Elemental analysis and mass spectroscopy were consistent with structure **22**, but the <sup>1</sup>H NMR spectrum was hard to assign as the signals were weak and were broadened or split due to two different conformations of **22** in which the ex-TTF moieties were flipped up or down [i.e., conformation 1, (up, up) ≡ (down, down); conformation 2, (up, down) ≡ (down, up)]. To circumvent this problem, **22** was oxidized with iodine to give the tetracation **22**<sup>4+</sup>, which was soluble in DMSO-*d*<sub>6</sub>. The <sup>1</sup>H NMR spectrum (Figure S1 in the Supporting Information) reflected the high symmetry of **22**<sup>4+</sup>, which comprises planar symmetric moieties: none of the peaks are broadened or split. These data further secured the structure of **22**.

There is continued interest in supramolecular assemblies which are ordered by hydrogen bonding.<sup>28</sup> For example, in the

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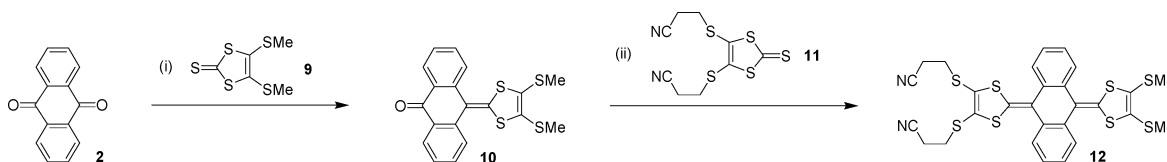
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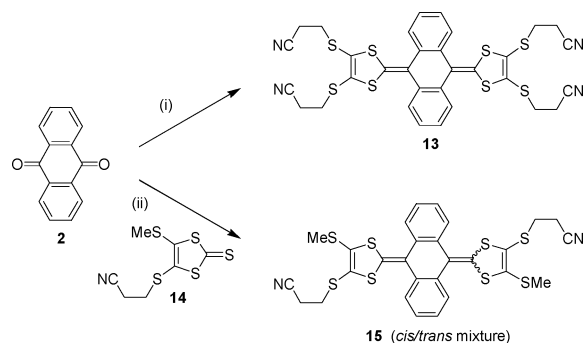
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SCHEME 3<sup>a</sup>

<sup>a</sup> Reagents and conditions: (i) **9**, P(OEt)<sub>3</sub>, PhCl, 135 °C, 3 h (52% yield); (ii) **11**, P(OEt)<sub>3</sub>, 130 °C, 3.5 h (73% yield).

SCHEME 4<sup>a</sup>

<sup>a</sup> Reagents and conditions: (i) **11**, P(OEt)<sub>3</sub>, 125 °C, 3 h (60% yield); (ii) **14**, P(OEt)<sub>3</sub>, 125 °C, 3 h (47% yield).

TTF series the crystal structure of tetrakis[(2-hydroxyethyl)-thio]-TTF shows the coexistence of uniform  $\pi$ - $\pi$  stacking and hydrogen-bonded O $\cdots$ H $\cdots$ O networks.<sup>29</sup> There are, however, very few examples of ex-TTF derivatives bearing hydroxyalkyl substituents.<sup>30</sup> As stated by Martín et al.,<sup>30b</sup> this is due to a lack of available procedures for their synthesis. We recognized the potential of compound **13** in this regard. Deprotection of **13** using sodium methoxide (5 equiv), followed by addition of bromoethanol (5 equiv), gave the tetrakis[(hydroxyethyl)thio] derivative **23** in 65% yield (Scheme 6), characterized by X-ray crystallography (vide infra). The structure is organized by a system of intra- and intermolecular hydrogen bonds in the absence of effective  $\pi$ - $\pi$  stacking.

To develop further the reactivity of these thiolated ex-TTF reagents, the diprotected derivative **15** was used to synthesize the ex-TTF cyclophanes **24** and **25**. A solution of **15** and 1,5-diiodopentane (1 equiv) was mixed with sodium methoxide (3 equiv) under high-dilution conditions to afford compounds **24** and **25** in 47% and 16% yield, respectively (Scheme 7).

The major compound was very soluble and analyzed correctly for the bridged cyclophane (<sup>1</sup>H NMR spectra showed that it was not a *cis/trans* mixture). An X-ray crystal structure (vide infra) established that the structure was the *cis* isomer **24**. This route to **24** is considerably more efficient than the previous synthesis of the dimethyl analogue **26** (Chart 2), which was obtained in 10% yield by a 2-fold Horner–Wadsworth–Emmons reaction of the corresponding bis[(1,3-dithiol-2-yl)-phosphonate ester] reagent with anthraquinone.<sup>17a</sup> The minor product (Scheme 7) was only sparingly soluble in a range of solvents, including carbon disulfide, toluene, chloroform, and dimethyl sulfoxide. Detailed <sup>1</sup>H NMR analysis was, therefore, very difficult. Mass spectra showed that it was a 2 + 2 product,

and the cyclic voltammogram was consistent with a nonstrained ex-TTF derivative (see below). The structure is confidently assigned as the macrocycle **25**, presumably as a mixture of isomers.

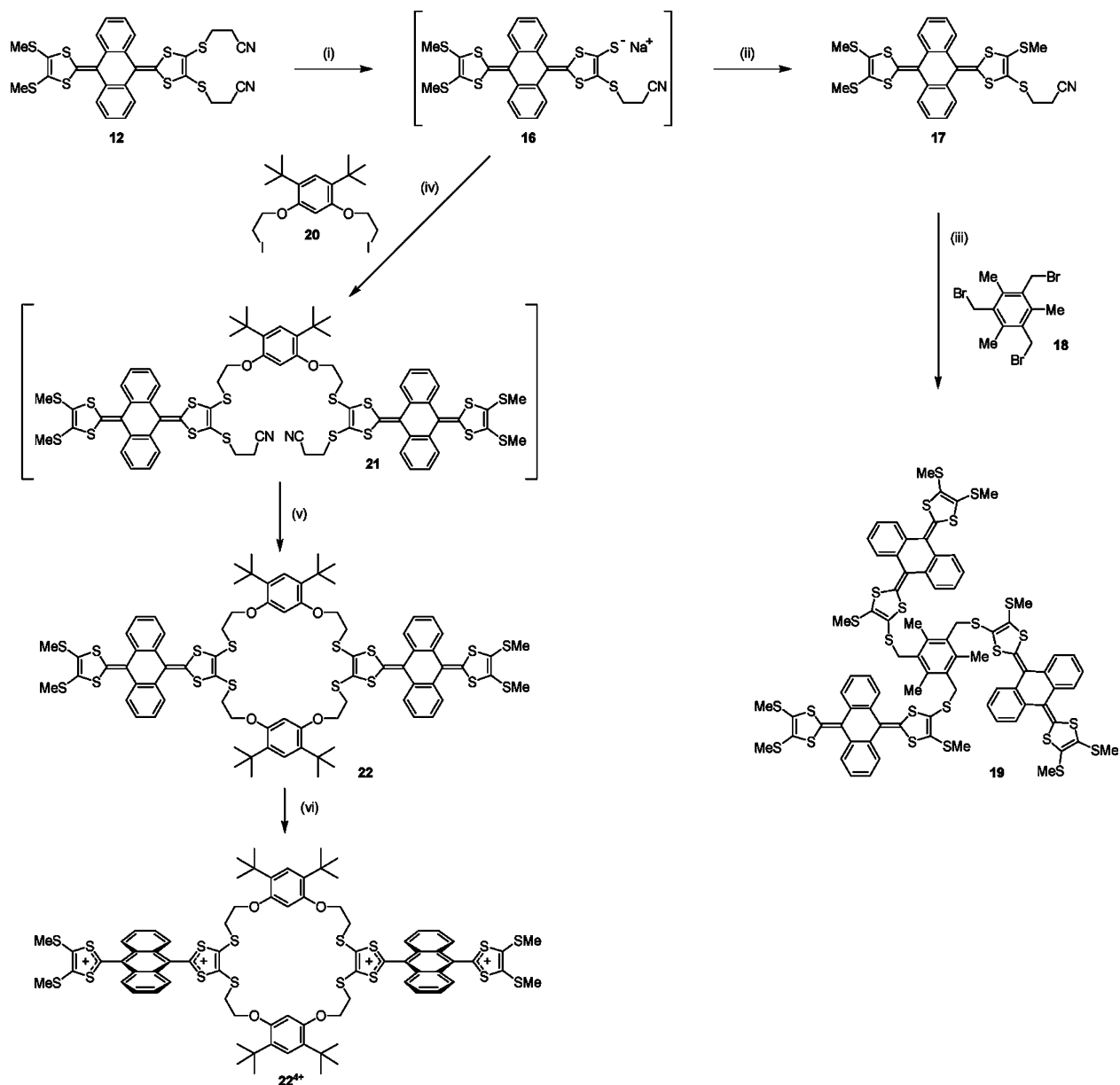
**X-ray Crystal Structures of 23 and 24.** Compound **23** crystallized from methanol and acetonitrile as two different solvates (pseudopolymorphs). Both contain one molecule of **23** per asymmetric unit together with nonstoichiometric amounts of solvent, tentatively **23**·2.5MeOH (**23a**) and **23**·1.5MeCN (**23b**). The ex-TTF core of **23** adopts the usual saddle conformation<sup>8,22b,25</sup> (Table 1 and Figure 1). The dihydroanthracene system is folded along the C(9) $\cdots$ C(10) vector, as shown by the angle ( $\varphi$ ) between the planar benzene rings. Both dithiole rings are folded inward along the S(1) $\cdots$ S(2) and S(5) $\cdots$ S(6) vectors (folding angles  $\delta_1$  and  $\delta_2$ , respectively), so that the planar S(1)C(16)C(17)S(2) and S(5)C(19)C(20)S(6) moieties are tilted inward, toward one another. The angle ( $\theta$ ) between these two planes and the transannular distances between exocyclic sulfur atoms, S(3) $\cdots$ S(7) and S(4) $\cdots$ S(8), or the adjacent dithiole carbons, C(16) $\cdots$ C(19) and C(17) $\cdots$ C(20), give a measure of the overall U-bending of the ex-TTF. The bending of **23** is comparable with that of other nonbridged ex-TTFs (where  $\theta$  varies from 73° to 101° and  $\varphi$  from 139° to 145°) and somewhat weaker than in compound **1c**<sup>25</sup> (see Table 1).

The usual packing motif of ex-TTFs is a pair of “mutually engulfing” molecules, so that one dithiole end of each molecule fills the intramolecular cavity of the other.<sup>8,22b</sup> Neither pseudopolymorph of **23** shows such packing: in **23a** the intramolecular cavity is occupied by a guest methanol molecule (Figure 2), in **23b** by a benzene ring of an adjacent (host) molecule. The remaining methanol in **23a** and (all) acetonitrile in **23b** are chaotically disordered along the infinite channels, which run between the host molecules (see ESI). In both phases the host molecule is also disordered. In **23a** the entire bis[(2-hydroxyethyl)thio]dithiolyldiene substituent at C(10) is distributed between two positions in a 84:16 ratio. This can be interpreted as a libration of the entire molecule **23** around the opposite dithiole end, the alternative positions of other atoms being too close to resolve. In **23b**, the ex-TTF core is ordered, but all four (hydroxyethyl)thio chains are intensely disordered. Nevertheless, the major conformation in each case suggests the existence of intramolecular hydrogen bonds between *adjacent* (hydroxyethyl)thio substituents.

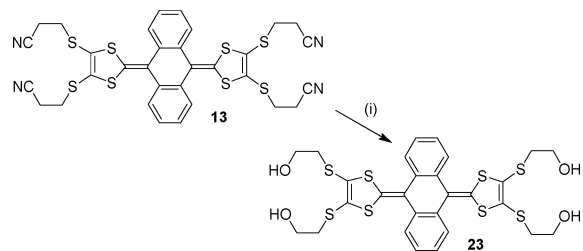
Different crystallizations of **24** from DCM/hexane also yielded two pseudopolymorphs, **24**·CH<sub>2</sub>Cl<sub>2</sub> (**24a**) and **24**·1.5CH<sub>2</sub>Cl<sub>2</sub> (**24b**). The asymmetric unit of **24a** comprises one molecule of **24** with a partially disordered DCM molecule inside the cavity (Figure 3). In **24b** there are two independent host molecules, each with a similarly disordered DCM in the cavity, and two symmetrically nonequivalent extraannular DCM molecules, each of them disordered between two overlapping positions related by an inversion center (which gives two additional half-molecules per asymmetric unit and one per

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SCHEME 5<sup>a</sup>

<sup>a</sup> Reagents and conditions: (i) MeONa–MeOH (1 equiv), DMF, 20 °C, 1.5 h; (ii) MeI (excess), 20 °C, 30 min (96% yield from **12**); (iii) MeONa–MeOH (1 equiv), DMF, 20 °C, 30 min, then **18** (0.3 equiv), DMF, 20 °C, 18 h (97% yield from **18**); (iv) **20** (0.5 equiv), DMF, 20 °C, 12 h; (v) **20** (1 equiv), MeONa–MeOH (2.7 equiv), DMF, 20 °C, 20 h, high dilution (77% yield from **12**); (vi) I<sub>2</sub>, DMSO-*d*<sub>6</sub>, 20 °C, 1 h (100% yield by NMR).

SCHEME 6<sup>a</sup>

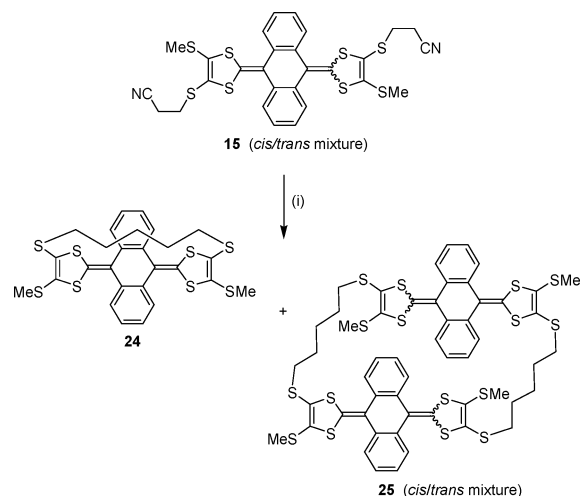
<sup>a</sup> Reagents and conditions: (i) MeONa–MeOH (5 equiv), DMF, 20 °C, 5 min, then BrCH<sub>2</sub>CH<sub>2</sub>OH (5 equiv), DMF, 20 °C, 16 h (65% yield).

formula unit). The pentamethylenedithio bridge of **24** adopts a nearly planar *all-trans* conformation, with S–C–C–C and C–C–C–C torsion angles in the range 160–180°, and drasti-

cally enhances the U-bend of the ex-TTF core, as indicated by the increase of both  $\delta$  angles and a decrease of the  $\theta$  angle (Table 1 and Figure 1), whereas the  $\varphi$  angle is little affected. Interestingly, the  $\theta$  angle in **24** is ca. 10° wider than in molecule **26** containing the same bridge. The difference is probably due to a wedging effect of the intramolecular solvent molecule (not present in the crystal of **26**). Note that the transannular distances in **26** are symmetrical, whereas in **24** they are longer on the solvent side than on the bridge side.

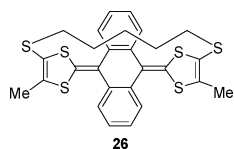
**Solution Electrochemical and Optical Absorption Properties.** Solution electrochemical data, obtained by cyclic voltammetry (CV), are collated in Table 2. Data for compound **1c** are included for comparison.

With the exception of the strained cyclophane **24**, which is discussed below, all the oxidation potentials fall in the range expected for tetrakis(alkylthio)-substituted ex-TTF derivatives.<sup>6</sup>

SCHEME 7<sup>a</sup>

<sup>a</sup> Reagents and conditions: (i) MeONa–MeOH (3 equiv), DMF, 20 °C, 16 h, 1,5-diiodopentane, high dilution (**24**, 47% yield; **25**, 16% yield).

## CHART 2

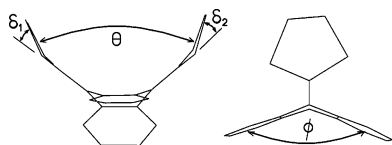


**TABLE 1.** Transannular Distances (Å) and Interplanar Angles (deg) in ex-TTF Derivatives

	<b>23a</b>	<b>23b</b>	<b>24a</b>	<b>24b<sup>a</sup></b>	<b>24b<sup>a</sup></b>	<b>26<sup>b</sup></b>	<b>1c<sup>c</sup></b>
C(16)···C(19)/Å	8.81	8.83	7.27	7.27	7.32	7.06	8.45
C(17)···C(20)/Å	8.83	8.76	7.60	7.59	7.63	7.01	8.59
S(3)···S(7)/Å	10.99	10.92	8.13	8.13	8.16	8.09	10.24
S(4)···S(8)/Å	11.08	10.86	9.24	9.33	9.32		10.60
$\delta_1$ /deg	11.4	16.0	23.3	22.0	26.2	29.4	17.4
$\delta_2$ /deg	14.3	11.1	28.6	27.2	23.8	22.6	8.0
$\theta$ /deg	86.0	83.8	44.1	45.4	45.2	34.7	77.4
180- $\varphi$ /deg	38.8	38.2	41.7	40.3	39.8	43.4	37.8

<sup>a</sup> Two independent molecules. <sup>b</sup> Reference 17a (the ordered molecule).

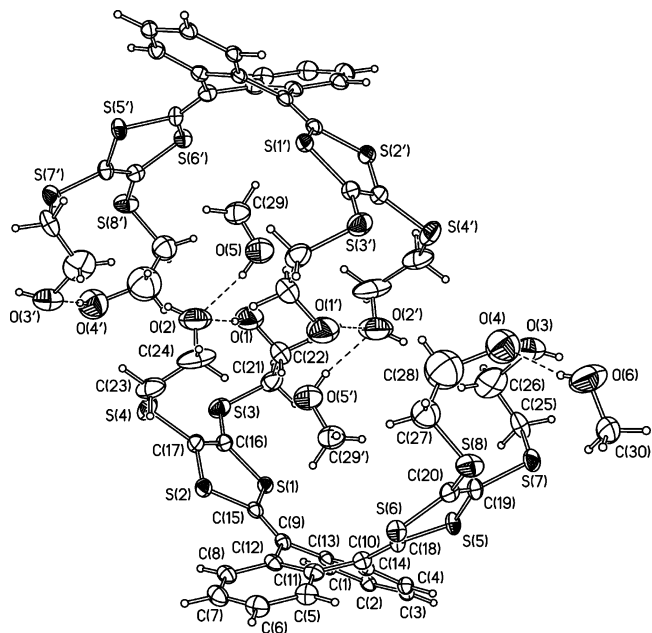
<sup>c</sup> Reference 25.



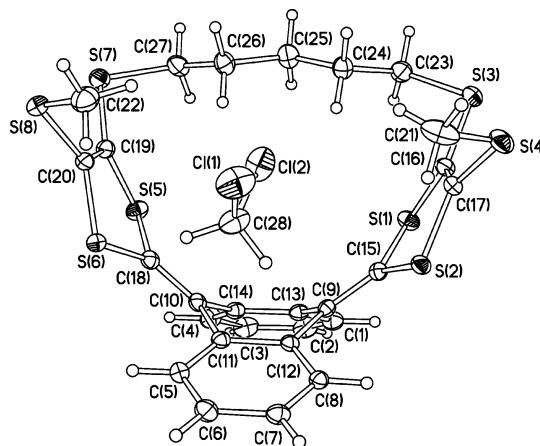
**FIGURE 1.** Diagram of the ex-TTF framework, defining the angles used in Table 1.

Each cyanoethyl group raises  $E^{\text{ox}}$  by ca. 30 mV, and this effect is additive. Thus, there is an incremental increase along the series **1c** → **17** → **12/15** → **13**, with the value for **13** raised by 110 mV compared to that for **1c**.

The CV of **24** showed the 2-electron oxidation wave to be positively shifted by 290 mV compared to that of its precursor **15** (Figure 4). This is a shift similar to that observed for other ex-TTF cyclophanes which possess a single short bridge between the two dithiole rings.<sup>17a,b</sup> An explanation is that the bridge obstructs the marked conformational change which accompanies oxidation, and thereby the dication is destabilized. Consistent with this,  $\Delta E$  for **24** is reduced from the typical value for nonbridged derivatives of >100 mV to only 60 mV. This



**FIGURE 2.** X-ray structure of **23**·2.5MeOH (**23a**), showing 30% thermal ellipsoids and probable hydrogen bonds. Minor positions of disordered atoms are omitted, and inversion-related atoms are primed.



**FIGURE 3.** X-ray molecular structure of **24**·CH<sub>2</sub>Cl<sub>2</sub> (**24a**), showing 50% thermal ellipsoids and the major (89%) orientation of the disordered DCM molecule.

increased reversibility of the oxidation process is consistent with the dication **24<sup>2+</sup>** adopting a conformation closer to the neutral saddle shape than is the case for nonbridged dicationic derivatives.

The CV of the dimeric cyclophane **25** was similar to those of nonbridged tetrakis(alkylthio)-ex-TTFs, e.g., its precursor **12**, as expected for a system where the bridges are too long to impose any strain on the  $\pi$ -system. The dimer **22** and the trimer **19** also showed a single, quasi-reversible, oxidation wave at typical oxidation potentials. No intramolecular electronic interaction was observed in the CVs of the multi-ex-TTFs **19**, **22**, and **25**: each ex-TTF unit behaves independently, and the oxidation waves represent 6-, 4-, and 4-electron processes, respectively.

With the exception of cyclophane **24**, the solution UV–vis absorption spectra of the new ex-TTF derivatives displayed strong bands at  $\lambda_{\text{max}}$  ca. 435 and 365 nm which are characteristic of the tetrakis(alkylthio)-substituted ex-TTF framework.<sup>10</sup> For **24** there is a blue shift of the longer wavelength band to  $\lambda_{\text{max}}$

TABLE 2. Cyclic Voltammetric Data<sup>a</sup>

compd	$E^{\text{ox}}_{\text{pa}}/\text{V}$	$E^{\text{ox}}_{\text{pc}}/\text{V}$	$\Delta E^b/\text{V}$
1c	0.55	0.43	0.12
12	0.60	0.50	0.10
13	0.66	0.54	0.12
15	0.61	0.45	0.16
17	0.57	0.44	0.13
19	0.55	0.45	0.10
22	0.60	0.42	0.18
23	0.54	0.43	0.11
24	0.90	0.84	0.06
25	0.59	0.41	0.18

<sup>a</sup> Data were obtained using a one-compartment cell with a Pt disk working electrode and a Pt counter electrode vs Ag/AgCl. Conditions: compound ca.  $1 \times 10^{-3}$  M, electrolyte 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in dichloromethane, 20 °C, scan rate 100 mV s<sup>-1</sup>. <sup>b</sup>  $\Delta E = E^{\text{ox}}_{\text{pa}} - E^{\text{ox}}_{\text{pc}}$  ( $E^{\text{ox}}_{\text{pa}}$  is the oxidation peak potential on the first anodic scan;  $E^{\text{ox}}_{\text{pc}}$  is the coupled reduction peak potential on the cathodic scan).

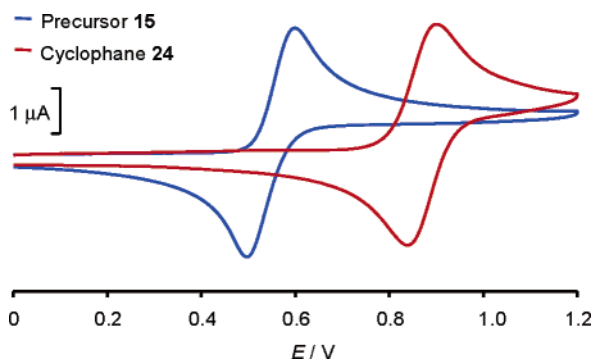


FIGURE 4. Cyclic voltammograms of **24** and its precursor **15**. Experimental conditions are given in Table 2.

421 nm and a decrease of the extinction coefficient, indicating loss of  $\pi$ -conjugation. We have noted recently that this trend is consistent with increased folding of the ex-TTF moieties.<sup>17c</sup> Qualitatively similar behavior is observed for strained TTF cyclophanes.<sup>31</sup>

## Conclusions

The availability of ex-TTF derivatives with protected thiolate functionality (compounds **12**, **13**, and **15**) is a significant milestone in the synthetic chemistry of this redox system. The phosphite-mediated cross-coupling methodology by which they have been obtained avoids the multistep synthesis of (1,3-dithiol-2-yl)phosphonate ester reagents. The versatility of these new ex-TTF building blocks has been demonstrated in the efficient syntheses of a trimer, two dimeric cyclophanes, a hydrogen-bonded self-assembly, and a strained cyclophane. In the trimer **19** and the dimers **22** and **25**, each ex-TTF unit behaves independently and the oxidation waves represent 6-, 4-, and 4-electron processes, respectively. For the cyclophane **24** the conformational changes and gain in aromaticity which drive the second oxidation process in ex-TTFs have been restricted by the conformational constraints of the pentamethylene chain bridging the dithiole units. This results in a positive shift of the oxidation potential and increased reversibility of this 2-electron wave. In

both solvates of **23** the usual packing motif of ex-TTFs was overruled by an unprecedented hydrogen-bonded self-assembly.

This methodology opens the way to a wide range of derivatives of this fascinating redox system, with chemical and physical functionality tailored for new applications in supramolecular and materials chemistry, especially processes involving inter- and intramolecular electron transfer.

## Experimental Section

**10**-[4,5-Bis(methylthio)-1,3-dithiol-2-ylidene]anthracene-9(10H)-one (**10**). A degassed mixture of triethyl phosphite (50 mL) and chlorobenzene (150 mL) was stirred under argon and heated to 135 °C whereupon anthraquinone (**2**) (8.00 g, 38.4 mmol) was added in one portion. Over the next 1.5 h thione **9**<sup>26c</sup> (4.53 g, 20.0 mmol) was added as a solid in small portions, against a positive pressure of argon, affording a dark red solution. A second batch of **2** (4.00 g, 19.2 mmol) was added in one portion, and addition of more thione **9** (4.53 g, 20.0 mmol) in small portions was continued over the next 1.5 h. The reaction mixture was cooled to room temperature. The excess anthraquinone which crystallized was removed by filtration, and the remaining reaction mixture was concentrated under reduced pressure to a volume of 50 mL, whereupon methanol (300 mL) was added to give a red precipitate. The precipitate was filtered, washed with methanol (3  $\times$  15 mL), dried in vacuo, and column chromatographed (silica gel, dichloromethane) to give **10** as an orange powder (7.97 g, 52%). Mp: 204–205 °C (lit.<sup>25</sup> 185 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.27 (2H, d,  $J = 7.8$  Hz), 7.76 (2H, d,  $J = 7.8$  Hz), 7.66 (2H, t,  $J = 7.8$  Hz), 7.44 (2H, t,  $J = 7.8$  Hz), 2.42 (6H, s).

**9**-[4,5-Bis(2-cyanoethylthio)-1,3-dithiol-2-ylidene]-10-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-9,10-dihydroanthracene (**12**). Triethyl phosphite (10 mL) was degassed, heated to 130 °C, and stirred under argon, and then **10** (0.317 g, 0.82 mmol) was added in one portion. Over the next 3 h thione **11**<sup>26b</sup> (0.830 g, 2.73 mmol) was added as a solid in small portions against a positive pressure of argon. The reaction mixture turned dark red-brown, and the formation of **12** was monitored using TLC (silica, dichloromethane as eluent). After addition of one-third of **11** a yellow solid began to precipitate. The mixture was stirred for another 30 min at 130 °C and then cooled to 0 °C, and methanol (70 mL) was added. The precipitate was filtered, washed with methanol (3  $\times$  5 mL), dried in vacuo, and column chromatographed (silica gel, dichloromethane) to give **12** as a yellow foam (0.386 g, 73%). Yellow prisms grew by slow diffusion of hexane into a solution of **12** in dichloromethane. Mp: 236–237 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.62–7.60 (2H, m), 7.52–7.49 (2H, m), 7.37–7.31 (4H, m), 3.14–3.07 (2H, m), 3.03–2.95 (2H, m), 2.72–2.68 (4H, m), 2.40 (6H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  134.6, 134.1, 131.7, 128.3, 126.8, 126.4, 126.2, 125.5, 125.4, 125.2, 124.9, 122.9, 117.4, 31.1, 18.92, 18.90. UV–vis (CH<sub>2</sub>-Cl<sub>2</sub>):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 362 (4.21), 431 (4.44) nm. MS (EI):  $m/z$  (rel intens) 642 (93, M<sup>+</sup>), 264 (100). Anal. Calcd for C<sub>28</sub>H<sub>22</sub>N<sub>2</sub>S<sub>8</sub> (MW 643.02): C, 52.30; H, 3.45; N, 4.36. Found: C, 52.24; H, 3.42; N, 4.39.

**9**-[4-[(2-Cyanoethylthio)-5-(methylthio)-1,3-dithiol-2-ylidene]-10-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-9,10-dihydroanthracene (**17**). To a stirred solution of **12** (1.00 g, 1.56 mmol) in dry degassed *N,N*-dimethylformamide (100 mL) under argon at room temperature was added dropwise a solution of sodium methoxide (3.11 mL of a 0.5 M solution in methanol, 1.56 mmol) over 30 min. The color changed from yellow to red. The solution was stirred for a further 1 h, and then methyl iodide (1.0 mL, 2.28 g, 16.1 mmol) was added in one portion. The yellow reaction mixture was stirred for 30 min and concentrated in vacuo and the residue purified by column chromatography (silica gel, dichloromethane) to afford **17** as a yellow foam (0.907 g, 96%). Yellow crystals grew by slow diffusion of hexane into a solution of **17** in dichloromethane. Mp: 207–208 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.60–

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7.51 (4H, m), 7.34–7.31 (4H, m), 3.08–3.01 (1H, m), 2.96–2.88 (1H, m), 2.70–2.66 (2H, m), 2.43 (3H, s), 2.40 (3H, s), 2.39 (3H, s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  134.6, 134.5, 134.4, 134.3, 133.0, 131.3, 129.7, 126.5 (2C), 126.34, 126.33, 125.7, 125.5, 125.41, 125.36, 125.32, 125.28, 124.2, 123.2, 118.4, 117.6, 31.1, 19.00, 18.96, 18.93, 18.8. UV–vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 272 (4.34), 365 (4.20), 434 (4.44) nm. MS (EI):  $m/z$  (rel intens) 603 (100,  $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{26}\text{H}_{21}\text{NS}_8$  (MW 603.98): C, 51.70; H, 3.50; N, 2.32. Found: C, 51.63; H, 3.45; N, 2.34.

**Trimer 19.** To a stirred solution of **17** (0.199 g, 0.33 mmol) in dry degassed *N,N*-dimethylformamide (10 mL) under argon at room temperature was added a solution of sodium methoxide (0.66 mL of a 0.5 M solution in methanol, 0.33 mmol) in one portion. The color changed from yellow to red. The solution was stirred for 30 min, and then a solution of tris(bromomethyl)mesitylene (**18**)<sup>32</sup> (0.040 g, 0.10 mmol) in dry degassed *N,N*-dimethylformamide (2 mL) was added dropwise over 15 min. A yellow precipitate formed. The mixture was stirred overnight, and then excess methyl iodide (0.1 mL, 1.6 mmol) was added to quench the excess thiolate. The reaction mixture was concentrated in vacuo and the residue purified

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by column chromatography (silica gel, dichloromethane–carbon disulfide, 1:9, v/v) to give **19** as a yellow powder (0.175 g, 97%). Mp: 225 °C dec.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.59–7.55 (12H, m), 7.34–7.30 (12H, m), 4.19–4.16 (3H, m), 4.03–3.99 (3H, m), 2.53 (9H, s) 2.39–2.36 (27H, m). UV–vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 367 (4.68), 436 (4.91) nm. MS (MALDI):  $m/z$  1808.8 (calcd 1809.0). Anal. Calcd for  $\text{C}_{81}\text{H}_{66}\text{S}_{24}$  (MW 1808.97): C, 53.78; H, 3.68. Found: C, 53.90; H, 3.79.

**Acknowledgment.** We thank EPSRC and The Danish Research Academy for funding to C.A.C. We thank Professor J. A. K. Howard for the use of X-ray facilities and EPSRC for funding the improvement to the X-ray instrumentation.

**Supporting Information Available:** Synthetic details and characterization data for compounds **13**, **15**, **20**, **22**, **22**<sup>4+</sup>, and **23**–**25**,  $^1\text{H}$  NMR spectrum of **22**<sup>4+</sup>, X-ray crystallographic file for **23**·2.5MeOH, **23**·1.5MeCN, **24**· $\text{CH}_2\text{Cl}_2$ , and **24**·1.5 $\text{CH}_2\text{Cl}_2$  in CIF format, and diagrams of the crystal structures of **23a** and **24b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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