An oligooxamacrocycle containing a π-donor tetrathiafulvalene and a π-acceptor quinone. Molecular and supramolecular structure

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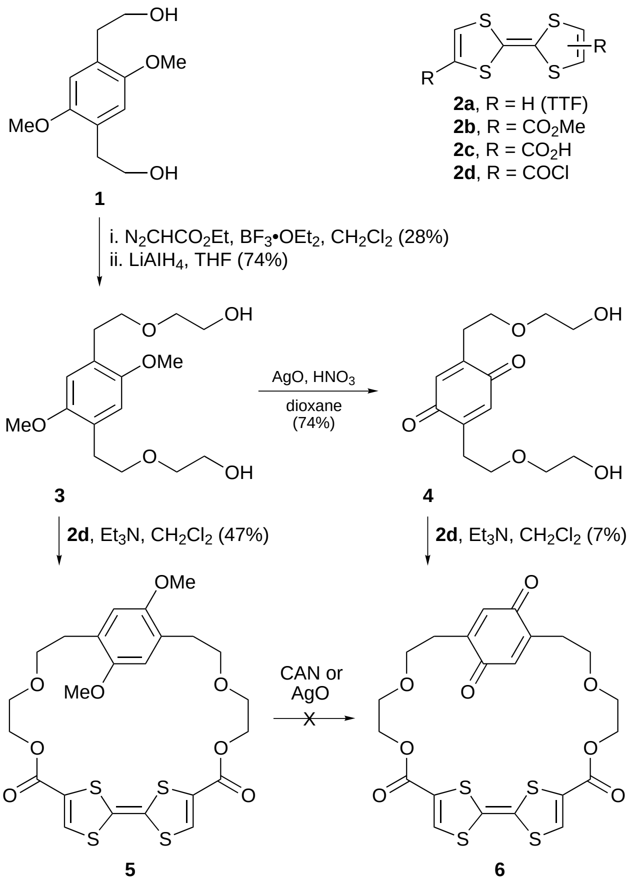
Tetrathiafulvalenedicarbonyl chloride reacts with 2,5-bis[(2-hydroxyethoxy)ethyl]-1,4-benzoquinone to afford a novel charge-transfer oligooxamacrocycle whose molecular and supramolecular structure are reported.

The π-donor charge transfer role of tetrathiafulvalene (TTF) (**2a**) as a molecular redox component is a key feature of organo-electrochemical devices such as conducting and superconducting materials, sensors, molecular shuttles, NLO materials, organic ferromagnets and C_{60}-complexes.[1] An important structural feature in these materials is the spatial arrangement of the TTF with respect to the π-acceptor unit, either a non-covalent self-assembled array, or a covalently bonded system in which the position of the interacting (charge transfer groups) is fixed by synthetic design. Structures of increasingly evolved synthetic design have been reported, notably, the synthesis of tetrathiafulvalenoparacyclophanes and tetrathiafulvalenophanes by Staab *et al.*,[2] the joining of TTF-thiols by Hg^{2+} or Ni^{2+},[3] the incorporation of TTF into crown ethers,[4] cages[5] and [3]-pseudocatenanes,[6] the coupling of TTF to a ferrocenyl unit,[7] and the incorporation of TTF into a dimacrocycle with a catenated cyclobis(paraquat-*p*-phenylene).[8] Incorporation of TCNQ into a [2.2]paracyclophane has been accomplished; however, the π-donor was not TTF but the essentially irrelevant phenyl[9] and 1,4-dimethoxyphenyl groups.[10]

These molecules and others[11] represent only partial solution to the synthetic problem of fixing both the π-donor TTF and π-acceptor within the same molecule. We now report the synthesis of such a molecule as embodied in the oligooxamacrocycle **6** (Scheme 1).



Scheme 1

Macrocycle **5** is a yellow crystalline material which could not be oxidized to **6** using ceric ammonium nitrate (CAN) or AgO. Charge transfer complex **6** is a black crystalline material.† The UV-VIS spectrum of **6** in chloroform shows absorptions at 252, 285, 302, 314 and 424 nm. There is no difference in the UV-VIS spectrum of **6** when measured as a film made by spin-coating from chloroform solution. In the VIS-NIR range no absorption appears between 600–2500 nm. The position of the ^1H NMR chemical shift for the TTF portion in **6** is at 7.44 ppm compared with 7.35 ppm for **2b**. Likewise, the quinone hydrogen is at 6.65 ppm in **4** and 6.79 ppm in **6**. The conductivity of a film of **6** (0.1 mm thick, 4 probe method) is $\sigma = 2.1 \times 10^{-5}$ S cm^{-1}, which reveals the material to be a semiconductor.

The X-ray structure‡ of **6** may be discussed in terms of the unit molecule **6** (Fig. 1), an arbitrary dimer and its stacking (Fig. 2), and the supramolecular crystalline architecture (Fig. 3). Fig. 1 shows the unit molecular structure. In agreement to expectation, the quinone and TTF do not lie directly above and below each other, although they do lie in parallel planes. The distance between the centres of the non-overlapping quinone and TTF is 6.869 Å. The quinone occupies a plane about 3.6 Å above the extended parallel plane of the TTF. Fig. 2 shows a stack of three pairs of 'dimers.' Each pair is composed of two almost parallel planes of quinone and TTF. Going from the left to the right of Fig. 2, the first two molecules of **6** nestle together to afford partial overlap of TTF and quinone. These two are related by a crystal inversion center [1.0 − *x*, 1.0 − *y*, *z*] in the cell. However, the relationship between the second and the third molecule is such that there are certain close atom contacts, but the quinone and TTF of adjacent molecules do not overlap. They are related by a different inversion centre [1.0 − *x*, 1.0 − *y*, 1.0 − *z*]. Repeats of these operations produce an oblique stack of pairs (dimers that possess quinone–TTF overlaps) culminating in the depicted array of six stacks (including solvent $CHCl_3$) as shown in Fig. 3.

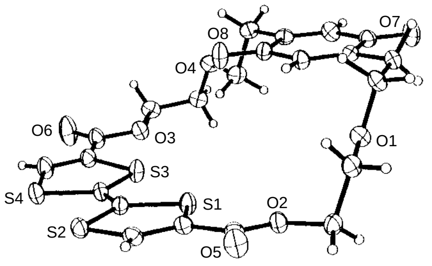


Fig. 1 X-Ray structure of the unit molecule **6**

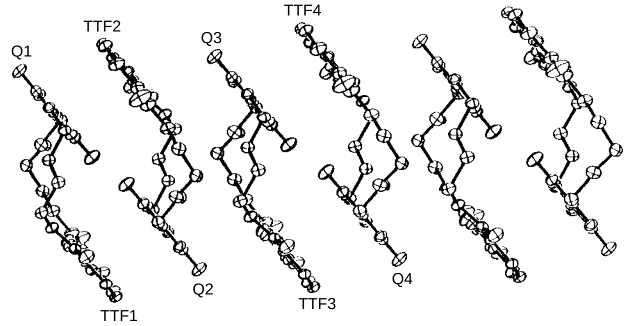


Fig. 2 Stack of three dimers. Hydrogens and solvent ($CHCl_3$) are removed for clarity

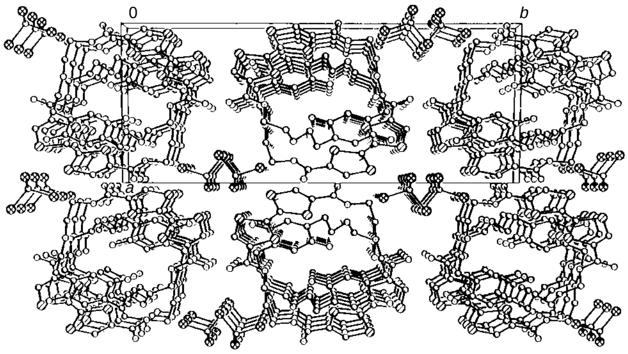


Fig. 3 Six stacks viewed down the *c* axis of the unit cell. Solvent chloroform is included in channels.

The basic molecule **6** and higher oligooxa homologue tethers of increasing –OCH_2CH_2O– units available by modification of the synthetic route offer the interesting possibility of complexation of alkali metal ions. Finally, the design of **6** owes much to the pioneering work of Staab and coworkers on oligooxaparacyclophane charge-transfer quinhydrones.[12]

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Footnotes and References

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† The starting material **1** was prepared from 2,5-dihydroxy-benzene-1,4-diacetic acid (J. H. Wood and R. E. Gibson, *J. Am. Chem. Soc.*, 1949, **71**, 393). **2d** was prepared from carbon disulfide and methyl propiolate *via* three steps (L. R. Melby, H. D. Hartzler and W. A. Sheppard, *J. Org. Chem.*, 1974, **39**, 2456). Compound **6** was isolated from the reaction mixture by filtration and purified by column chromatography.

‡ The crystalline compound **6** is monoclinic with space group $P2_1/c$. Parameters of the unit cell at 294 K: $a = 10.8785$, $b = 26.237$, $c = 10.5339$ Å, $\alpha = \gamma = 90$, $\beta = 108.530°$, $V = 2850.7$ Å^3, $Z = 4$. Refinement method: full-matrix least-squares on F^2. Final R indices [$I > 2\sigma(I)$]: $R = 0.0491$, $wR = 0.1080$; R indices for all data: $R = 0.1023$, $wR = 0.1284$. CCDC 182/671.

1 T. K. Hansen and J. Becher, *Adv. Mater.*, 1993, **5**, 288.
2 H. A. Staab, J. Ippen, C. Tao-pen, C. Krieger and B. Starker, *Angew. Chem. Int. Ed. Engl.*, 1980, **19**, 66; J. Ippen, C. Tao-pen, B. Starker, D. Schweitzer and H. A. Staab, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 67.
3 N. Le Narvor, N. Robertson, E. Wallace, J. D. Kilburn, A. E. Underhill, P. N. Bartlett and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1996, 823.
4 T. K. Hansen, T. Jørgensen, P. C. Stein and J. Becher, *J. Org. Chem.*, 1992, **57**, 6403.
5 F. Bertho-Thoroval, A. Robert, A. Souizi, K. Boubekeur and P. Batail, *J. Chem. Soc., Chem. Commun.*, 1991, 843.
6 Z.-T. Li, P. Stein, N. Svenstrup, K. H. Lund and J. Becher, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2524.
7 A. J. Moore, P. J. Skabara, M. R. Bryce, A. S. Batsanov, J. A. K. Howard and S. T. A. K Daley, *J. Chem. Soc., Chem. Commun.*, 1993, 417.
8 D. Philp, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 1584.
9 M. Yoshida, H. Tatemistu, Y. Sakata and S. Misumi, *Tetrahedron Lett.*, 1976, 3821.
10 H. A. Staab and H.-E. Henke, *Tetrahedron Lett.*, 1978, 1955.
11 K. Matsuo, K. Takimiya, Y. Aso, T. Otsubo and F. Ogura, *Chem. Lett.* 1995, 523; K. Takimiya, Y. Shibata, K. Imamura, A. Kashibara, Y. Aso and T. Otsubo, *Tetrahedron Lett.*, 1995, **36**, 5045.
12 H. A. Staab and W. Rebafka, *Chem. Ber.*, 1977, **110**, 3333; H. A. Staab, C. P. Herz, C. Krieger and M. Rentzea, *Chem. Ber.*, 1983, **116**, 3813; H. Bauer, V. Matz, M. Lang, C. Krieger and H. A. Staab, *Chem. Ber.*, 1994, **127**, 1993.

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