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Ultra-high pressure synthesis of a tetrathiafulvalene–diquat cyclophane

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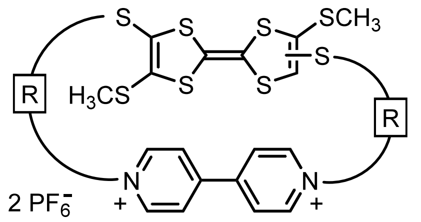
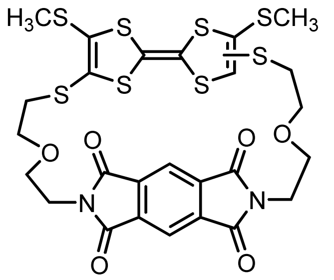
Abstract—Quaternization of a tetrathiafulvalene (TTF)/2,2′-bipyridine cyclophane under 10 kbar of pressure yields a TTF–diquat donor–acceptor cyclophane revealing distinct charge-transfer interactions. © 2003 Elsevier Science Ltd. All rights reserved.

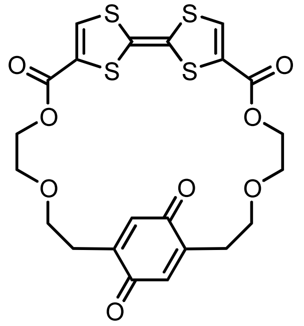
The pioneering work of Staab and co-workers[1] on donor–acceptor cyclophanes[2] has shown that such molecules provide fundamental knowledge about charge-transfer (CT) and π–π interactions, which are interactions that govern the self-assembly of a variety of supramolecular complexes and interlocked molecular compounds.[3] It has been of particular interest to incorporate tetrathiafulvalene (TTF) into such cyclophanes owing to its strong electron donating ability. Indeed, this donor molecule has found wide-spread applications in both materials and supramolecular chemistry.[4] Becher and co-workers have demonstrated the facile preparation of macrocyclic donor–acceptor systems based on tetramercapto-substituted TTFs and different electron acceptors, such as paraquat and pyromellitic diimide.[5,6] The cyclophanes **1a**–**c** and *cis*/*trans*-**2** represent such model compounds for studying CT interactions involving TTF. A quinone acceptor unit was successfully incorporated in the cyclophane *cis*-**3** by Moriarty et al.[7] Whereas no intramolecular CT transition seemed operative in the neutral cyclophane *cis*-**3**, the cyclophanes *cis*/*trans*-**2** experienced a small intramolecular CT band at λ_{max} 590 nm in CH_2Cl_2, mainly originating from the *trans*-isomer. The CT absorption was more significant for the charged viologen cyclophanes **1a**–**c**, with absorption maxima in the range 650–673 nm in MeCN, the strongest extinction experienced by the highly strained *trans*-**1a** (ε 650 M^{-1}



R = $(CH_2)_4$: *trans*-**1a**
R = $(CH_2)_5$: *cis/trans*-**1b**
R = $(CH_2)_2O(CH_2)_2$: *cis/trans*-**1c**



cis/trans-**2**



cis-**3**

Keywords: cyclophane; charge-transfer; diquat; high pressure; tetrathiafulvalene.

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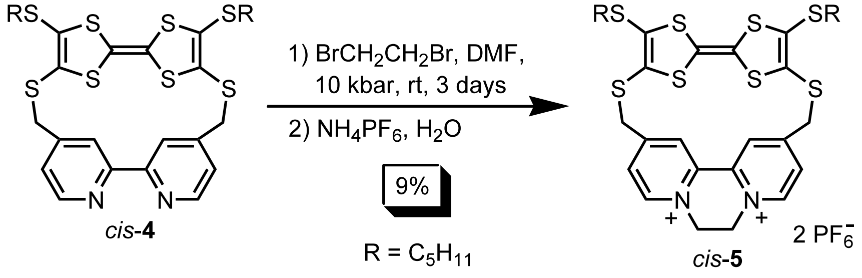
cm^{-1}). Although these CT bands are very strong, they are about one order of magnitude smaller than those observed for related catenane structures with cyclobis(paraquat-*p*-phenylene).[8] Recently, Nielsen et al.[9] demonstrated the strong influence of the donor oxidation potential and π-surface area on pseudorotaxane formation between differently derivatized TTFs and this same cyclic acceptor. Surprisingly however, the strong association displayed by a π-extended bis(pyrrolo)-TTF was, for reasons not understood, not paralleled by a stronger CT interaction in the corresponding donor–acceptor cyclophane with paraquat.[5] The question is, conversely, how a stronger viologen acceptor, such as diquat, will affect the properties,[10] that is, changing the 4,4′-bipyridinium unit for a 2,2′-bipyridinium and hereby enhancing the acceptor strength by about +0.05 V.[11]

Recently, the TTF/2,2′-bipyridine-cyclophane *cis*-**4** (Scheme 1) was synthesized, together with its *trans*-isomer, and employed for construction of trinuclear Ru(II) complexes.[12] Whereas the *trans*-isomer according to X-ray crystallography adopts a conformation in which the two nitrogens are in a *transoid* conformation, the *cis*-TTF isomer has to adopt a *cisoid* bipyridyl conformation in the ruthenium complexes. In order to shed more light on its preferred conformations, we performed semi-empirical PM3 geometry optimizations on the related cyclophane with $R=CH_3$, employing the Gaussian 98 program package.[13] This cyclophane was optimized from different initial geometries. Optimization of different *cisoid* bipyridyl initial geometries gave *cisoid* conformers with varying bipyridyl twist angles, but of about equal energies (differences <1 kcal mol^{-1}). The structures **I** and **II** depicted in Figure 1 represent two such minima with twist angles of 8 and 40°, respectively. In contrast, a *transoid* conformer was rotated during optimization into a *cisoid* one, such as **II**, or alternatively into an almost orthogonal bipyridyl conformer (**III**, 93.5° twist). The conformer **III** was slightly lower in energy than **I** by 0.9 kcal mol^{-1}. Pair-wise identical pyridyl protons of *cis*-**4**, as measured by ^{1}H NMR spectroscopy, indicates that conversion between these *cisoid*/*orthogonal* conformers is fast on the NMR timescale (300 MHz). In other words, the two nitrogens are more or less pre-organized for being bridged by an ethylene unit.

Nevertheless, attempts of quaternization upon reacting *cis*-**4** with 1,2-dibromoethane in refluxing MeCN/DMF caused decomposition of the cyclophane precursor. An alternative procedure for enabling Menschutkin reactions is the use of high pressure owing to the negative volume of activation associated with the quaternization.[14] Thus, high pressure has successfully been applied in the synthesis of cryptands and diazacoronands[15] as well as 4,4′-bipyridinium cyclophanes.[16] Gratifyingly, subjecting a mixture of *cis*-**4** and 1,2-dibromoethane (large excess) in DMF to a pressure of 10 kbar at room temperature for three days resulted in formation of TTF-diquat cyclophane *cis*-**5** (Scheme 1). After column chromatography (MeOH/2M NH_4Cl (aq.)/$MeNO_2$, 5:1:1) followed by ion exchange (NH_4PF_6), *cis*-**5** was isolated as a green solid in a yield of 9%.[17] The starting material *cis*-**4** was recovered in a yield of 65%, which gives a yield of quaternization based on recovered starting material of 26%. Although the yield of *cis*-**5** is very small, the exchange of strong heating for ultra-high pressure prevents formation of a complicated reaction mixture and degradation of starting material.

The pyridyl proton resonances of *cis*-**5** are significantly down-field shifted relative to those of *cis*-**4** at the 3,3′ ($\Delta\delta=+0.78$ ppm) and 5,5′ ($\Delta\delta=+0.94$ ppm) positions.



Scheme 1.

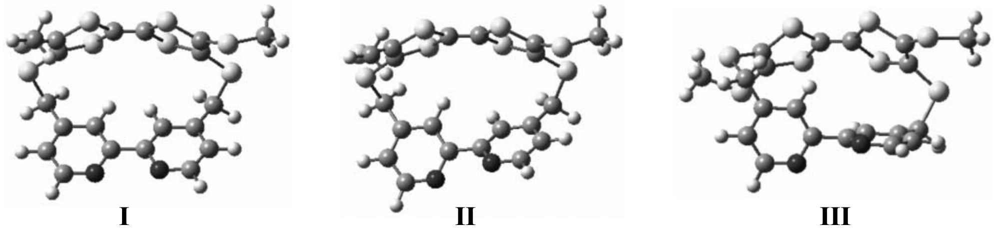


Figure 1. Three PM3-optimized energy minima conformations of *cis*-**4** (with $R=CH_3$), representing different degrees of twisting in the bipyridyl unit, but of about equal energies.

The non-cyclic SCH_2 protons experience a down-field shift of +0.17 ppm, which is similar to the shift observed upon encirclement of related TTFs with cyclobis(paraquat-*p*-phenylene).[8]

The UV–vis absorption spectrum (Fig. 2) of *cis*-**5** revealed a strong CT absorption band in MeCN with a λ_{max} of 540 nm (ε 1930 M^{-1} cm^{-1}). The CT band of *cis*-**5** is hypsochromically shifted relative to that of *trans*-**1a** (λ_{max} 673 nm in MeCN[5]), but is almost three times as intense in MeCN. The CT absorption band was considerably diminished in $MeNO_2$, albeit this solvent is of comparable polarity to MeCN. In the more polar mixture H_2O/MeCN (19:1), the CT transition appeared as a broad band intermediate between those observed in MeCN and $MeNO_2$.

Half-wave redox potentials versus Ag/AgCl of the new cyclophane *cis*-**5** were obtained by cyclic voltammetry (scan rate: 100 mV s^{-1}, supporting electrolyte: *n*-Bu_4NPF_6, working electrode: Pt; counter electrode: Pt). Cyclophane *cis*-**5** was oxidized in two steps at $E^1_{1/2}=0.79$ V and $E^2_{1/2}=1.01$ V in MeCN/CH_2Cl_2 10:1, whereas the neutral cyclophane *cis*-**4**[12] underwent oxidations at 0.64 and 1.05 V in CH_2Cl_2. Thus, *cis*-**5** experiences a huge anodic shift (+150 mV) in the first oxidation potential; limited solubilities did unfortunately not allow the measurements to be carried out in the same solvent, but the reluctance of *cis*-**5** towards oxidation should become even stronger in CH_2Cl_2. For comparison, the anodic shift in the first oxidation of *trans*-**1a** ($E^1_{1/2}=0.58$ V in MeCN) was 'only' +70 mV relative to a neutral TTF reference compound.[5] Tetramercapto-substituted TTFs encircled by the tetracationic acceptor cyclobis(paraquat-*p*-phenylene) were found to be oxidized at about $E^1_{1/2}=0.6$ V in MeCN.[8,18] The much higher first oxidation potential experienced by the dicationic cyclophane *cis*-**5** reflects both the closer approach to the central TTF core of the two positive charge centers in the 2,2′-bipyridinium entity as compared to a 4,4′-bipyridinium entity, an electrostatic interaction that occurs in a rigidified and hence more or less fixed cyclophane conformation, as well as strong CT interactions as ascertained by UV–vis spectroscopy. In accordance hereto, it has been inferred from crown-ether annelated TTF–macrocycles that complexation of metal ions induces the largest anodic shift when the metal ion is brought close to the central TTF fulvene bond.[19] The largest positive shift reached by such an arrangement is +140 mV, experienced by a bis(pyrrolo)-TTF macrocycle upon complexation of Pb^{2+}.[20]

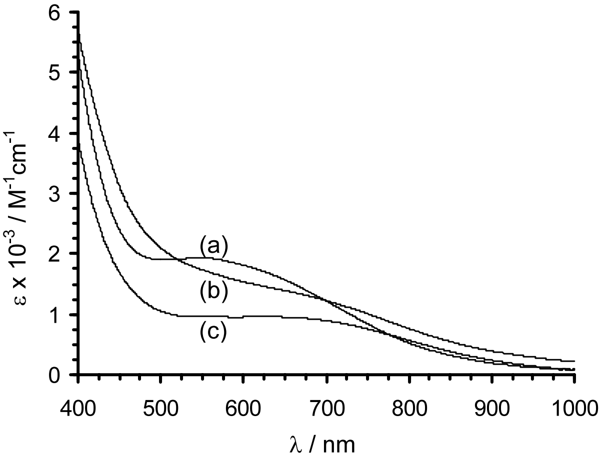


Figure 2. UV–vis absorption spectra of *cis*-**5** in (a) MeCN, (b) H_2O/MeCN 19:1, (c) $MeNO_2$.

In summary, we have prepared a new donor–acceptor cyclophane exhibiting strong electrostatic and CT interactions. Generation of the acceptor unit by quaternization of a preformed TTF–cyclophane differs from previous protocols, in which the acceptor unit is either formed during cyclization or already present in the one module. Whereas paraquat (4,4′-bipyridinium) has been incorporated into several donor-acceptor cyclophanes, *cis*-**5** is to our knowledge the first such diquat (2,2′-bipyridinium)-based one.

Acknowledgements

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17. Preparation of *cis*-**5**: *cis*-**4** (50.0 mg, 0.0766 mmol) was dissolved in dry, nitrogen-degassed DMF (6.0 mL) and 1,2-dibromoethane (6.0 mL) and transferred to a high-pressure reaction Teflon tube, which was then compressed at 10 kbar (PSIKA Pressure Systems Ltd.) at rt for 3 days. The resulting brownish mixture was concentrated in vacuo. The residues from two such reactions were combined and partly redissolved in $MeNO_2$ (20 mL). Unreacted starting material was filtered off, and the filtrate purified by column chromatography (SiO_2, MeOH/2 M NH_4Cl (aq)/$MeNO_2$ 5:1:1). The green band was collected, and the organic solvents were removed in vacuo. The remaining water phase containing a green precipitate was subjected to centrifugation, whereupon the water phase was decanted off. Water was added to the residue, and the mixture was then again subjected to centrifugation. The dark green water phase was collected by decantation; the residue was extracted with water again until no coloration occurred. The combined water fractions (ca. 35 mL) were treated with NH_4PF_6 until precipitation was complete. The product was filtered and washed with water, affording *cis*-**5** as a green solid (13.5 mg, 9%, resulting from two 50.0 mg portions of *cis*-**4**). δ_H (300 MHz, CD_3CN): 0.92 (6H, t, *J* 6.8, CH_2CH_3), 1.34 (8H, m, $(CH_2)_2CH_3$), 1.53 (4H, m, SCH_2CH_2), 2.76 (4H, t, *J* 7.1, $SCH_2C_4H_9$), 4.34 (4H, s, SCH_2Py), 5.05 (4H, s, $N(CH_2)_2N$), 8.28 (2H, dd, *J* 1.4, 6.3, Py*H*-5,5′), 8.77 (2H, d, *J* 1.4, Py*H*-3,3′), 8.80 (2H, d, *J* 6.3, Py*H*-6,6′); δ_C (75 MHz, CD_3CN): 14.7, 23.3, 30.5, 31.6, 38.0, 39.8, 53.2, 117.1, 124.6, 130.2, 132.4, 134.0, 140.0, 148.4, 162.6; *m*/*z* (ES): 825 ($[M-PF_6]^+$), 340 ($[M-2PF_6]^{2+}$); *m*/*z* (HR-MALDI): 679.0529 ($[M-2PF_6-H]^+$, $C_{30}H_{35}N_2S_8$ requires 679.0566).
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