Tetrathiafulvalene (TTF)-Bridged Resorcin[4]arene Cavitands: Towards New Electrochemical Molecular Switches

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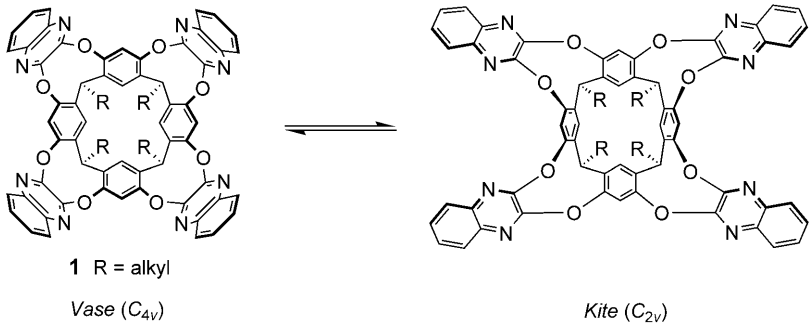
We report the synthesis of novel resorcin[4]arene-based cavitands featuring two extended bridges consisting of quinoxaline-fused TTF (tetrathiafulvalene) moieties. In the neutral form, these cavitands were expected to adopt the *vase* form, whereas, upon oxidation, the open *kite* geometry should be preferred due to *Coulombic* repulsion between the two TTF radical cations (*Scheme 2*). The key step in the preparation of these novel molecular switches was the $P(OEt)_3$-mediated coupling between a macrocyclic bis(1,3-dithiol-2-thione) and 2 equiv. of a suitable 1,3-dithiol-2-one. Following the successful application of this strategy to the preparation of mono-TTF-cavitand **3** (*Scheme 3*), the synthesis of the bis-TTF derivatives **2** (*Scheme 4*) and **19** (*Scheme 5*) was pursued; however, the target compounds could not be isolated due to their insolubility. Upon decorating both the octol bowl and the TTF cavity rims with long alkyl chains, the soluble bis-TTF cavitand **23** was finally obtained, besides a minor amount of the novel cage compound **25a** featuring a highly distorted TTF bridge (*Scheme 6*). In contrast to **25a**, the deep cavitand **23** undergoes reversible *vase* → *kite* switching upon lowering the temperature from 293 to 193 K (*Fig. 1*). Electrochemical studies by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) provided preliminary evidence for successful *vase* → *kite* switching of **23** induced by the oxidation of the TTF cavity walls.

1. Introduction. – Quinoxaline-bridged resorcin[4]arene-based cavitands such as **1** [1] can be reversibly switched, under the influence of various external *stimuli*, between a closed *vase* form, capable of guest inclusion [2][3], and an open *kite* form, featuring an extended flattened surface [1] (*Scheme 1*). The *vase* conformer is prevalent at room temperature at neutral pH, whereas the *kite* geometry is predominant at low temperatures ($\leq$213 K) [1], upon protonation with acids such as CF_3COOH (TFA) [4], or in the presence of Zn^{II} ions [5]. At low temperature, solvation of the more extended surface stabilizes the *kite* geometry, whereas, at higher temperature, the entropic term $T\Delta S_{solv}$ becomes unfavorable, and the *vase* conformation is dominant [1]. More recent investigations also showed that suitably sized solvent molecules (such as small benzene derivatives) favorably solvate (stabilize) the *vase* form and reduce the propensity for *vase* → *kite* transition [6]. On the other hand, the *kite* conformation is additionally stabilized by solvents with substantial H-bonding acidity: weak H-bonding interactions between the mildly basic quinoxaline N-atoms, and solvent molecules are more efficient in the open *kite* than in the closed *vase* form [6b]. Acid-induced switching from the *vase* to the *kite*

form is attributed to protonation of the mildly basic quinoxaline N-atoms in **1**, resulting in electrostatic repulsion between the cationic cavitand walls in the *vase* form [4]. This switching is reversed upon addition of base. Noticeably, both partially and differentially bridged resorcin[4]arene cavitands have been shown to undergo *vase* → *kite* conformational switching [7] (for a review, see [8]).

Scheme 1. *Temperature- or pH-Triggered Conformational* vase ⇌ kite *Equilibration of Quinoxaline-Bridged Resorcin[4]arene* **1**

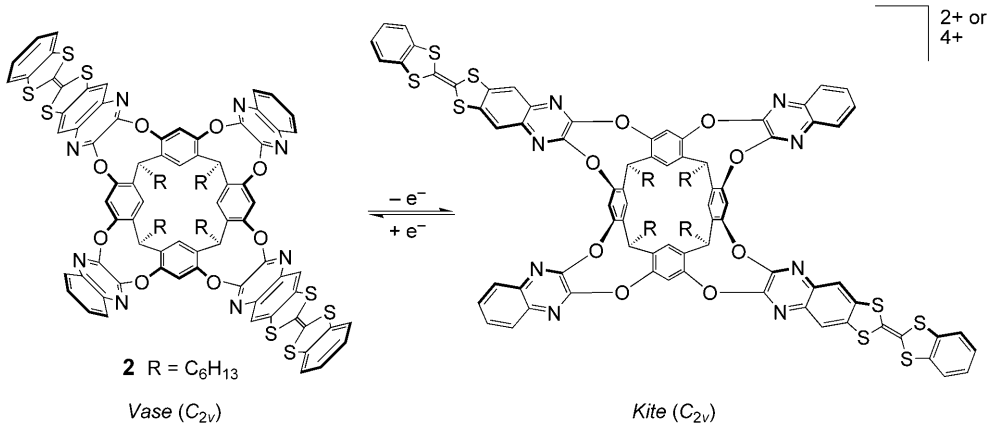


Here, we report the synthesis and conformational switching properties of novel resorcin[4]arene-based cavitands featuring two extended bridges consisting of quinoxaline-fused TTF (= tetrathiafulvalene) moieties, such as in **2** (*Scheme 2*) [9]. Our aim was to realize for the first time *vase* ⇌ *kite* interconversion under the stimulus of electrochemical electron-transfer processes (for examples of TTF-based electrochemical switches see [10]). In the neutral form, cavitand **2** was expected to adopt the *vase* form (for another deep cavitand with expanded cavity walls, see [11]), whereas, upon oxidation to the bis(TTF radical cation) or the bis(TTF dication), the open *kite* geometry should be preferred due to *Coulombic* repulsion between the two cationic wall flaps in the *vase* form. Upon electrochemical reduction, the initial *vase* form should be regained (for molecular switches, see [12]).

2. Results and Discussion. – 2.1. *Synthesis of Mono-TTF Cavitand* **3**. We first approached the synthesis of mono-TTF-cavitand **3** (*Scheme 3*) to develop the synthetic strategy that would subsequently enable the preparation of the desired bis-TTF derivative **2**. The most common protocol for the synthesis of 'asymmetric' TTF derivatives is the coupling of two 1,3-dithiol-2-thiones or 1,3-dithiol-2-ones [13] in the presence of trialkyl or triaryl phosphites or phosphines [14] (for a mechanistic proposal, see [15]). Hence, our route towards mono-TTF-cavitand **3** involved the macrocyclic 1,3-dithiol-2-thione **4** as an intermediate, which we intended to couple with 1,3-benzodithiol-2-one (**5**) [16] (*Scheme 3*). The preparation of **4** was envisaged by bridging the two free phenolic OH groups of cavitand **6** [2b][7b] with dichloroquinoxaline-fused 1,3-dithiol-2-thione **7**.

The synthesis of the key building block **7** started from bis-thiocyanate **8**, which was obtained in 57% yield from benzene-1,2-diamine by oxidative thiocyanation using Br_2 and KSCN in MeOH [17] (*Scheme 3*). Reductive cleavage of the thiocyanate substitu-

Scheme 2. *Electrochemically Induced* vase → kite *Switching of Bis-TTF Cavitand* **2**. TTF = tetrathiafulvalene.

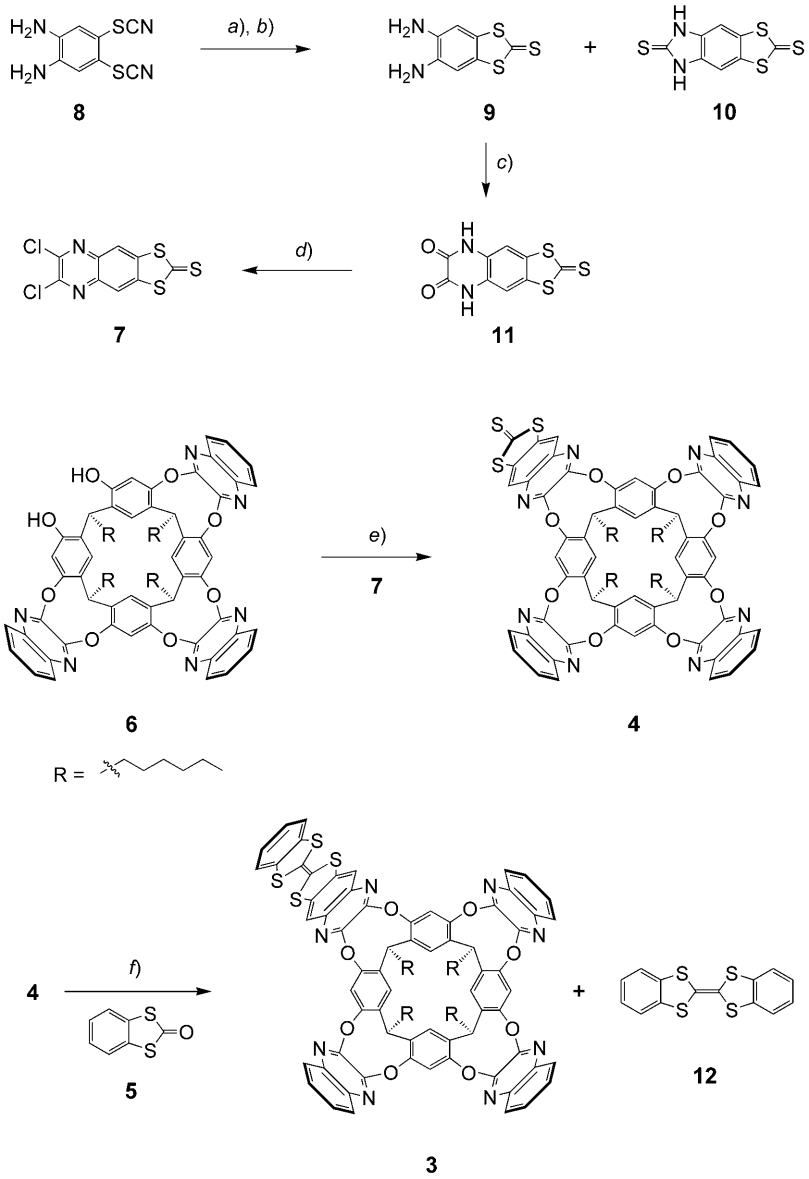


ents [18], followed by condensation with CS_2, afforded the desired 1,3-dithiol-2-thione **9** (52%) together with thiourea side product **10** (16%). Subsequent bridging of the 1,2-diamino groups in **9** with diethyl oxalate [19] provided the dihydroquinoxaline-dione **11** in 90% yield. Halogenation under aromatization to **7** with $SOCl_2$ at 75° [20] proceeded in only 25% yield. The yield was substantially improved (56%) by using phosgene at room temperature.

Cavitand **6** was subsequently bridged under standard conditions (Cs_2CO_3, Me_2SO)[1][6][7] with dichloroquinoxaline **7** to afford the macrocyclic bis(1,3-dithiol-2-thione) **4** in 74% yield. Subsequent coupling of **4** with dithiolone **5** (fourfold excess) in the presence of $P(OEt)_3$ led to the targeted TTF cavitand **3**, which was isolated as a red solid in 9% yield besides dibenzo-fused TTF **12** as the major product (42% yield). Products from homo-coupling of **4** were not observed in the conversion, which required addition of toluene to enhance the solubility of the macrocyclic dithiolone. The structure of **3** was established by ^{1}H- and ^{13}C-NMR spectroscopy as well as by high-resolution matrix-assisted laser-desorption-ionization mass spectrometry (HR-MALDI-MS; matrix: 3-hydroxypicolinic acid (3-HPA)), which showed the protonated molecular ion as base peak at *m*/*z* 1555.5180 ($[M+H]^+$, $C_{92}H_{83}N_8O_8S_4^+$; calc. 1555.5211).

2.2. *Synthesis of Bis-TTF Cavitands.* In analogy to the preparation of **3**, the *anti*-bis(quinoxaline)-bridged resorcin[4]arene **13** [7][21a] was reacted with 2 equiv. of **7** to give cavitand **14** (56%; *Scheme 4*). The coupling of **14** with benzo-1,3-dithiol-2-one (**5**; 6 equiv.) produced the desired target molecule **2** as revealed by HR-MALDI-MS (matrix: 3-HPA) after workup. The parent peak in the spectrum was the protonated molecular ion at *m*/*z* 1782.422 ($[M+H]^+$, $C_{100}H_{85}N_8O_8S_8$; calc. 1782.429). However, the solubility of **2** in all common organic solvents was extremely low, and isolation in pure form could not be accomplished. While the viability of the synthetic strategy towards bis-TTF cavitands was unambiguously established with the mass-spectrometric detection of **2**, changes in functionalization were clearly required to obtain a system with sufficient solubility for isolation and subsequent physical study.

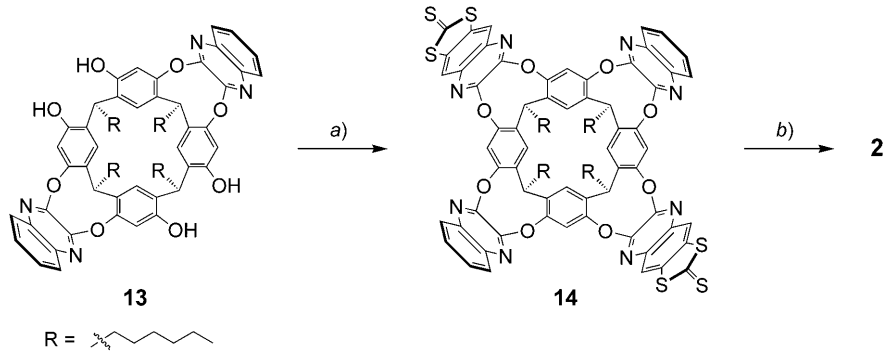
Scheme 3. *Synthesis of the Mono-TTF Cavitand* **3**



a) $Na_2S \cdot 9\ H_2O$, H_2O, 70°, 1 h. *b*) CS_2, 50°, 2 h; 52% (**9**), 16% (**10**). *c*) $(COOEt)_2$, 165°, 16 h; 90%. *d*) $COCl_2$, DMF, toluene, 20°, 3 d; 56%. *e*) Cs_2CO_3, Me_2SO, 50°, 2 d; 74%. *f*) $P(OEt)_3$, toluene, 130°, 6 h; 9% (**3**), 42% (**12**).

A first approach to enhance the solubility consisted in enlarging the size of the alkyl legs of the cavitand from C_6 to C_{11} chains. For this purpose, octol **15** was prepared (71%) by acid-catalyzed condensation (HCl/EtOH) of resorcinol with dodecanal, as previ-

Scheme 4. *Synthesis of the Insoluble Bis-TTF Cavitand* **2**



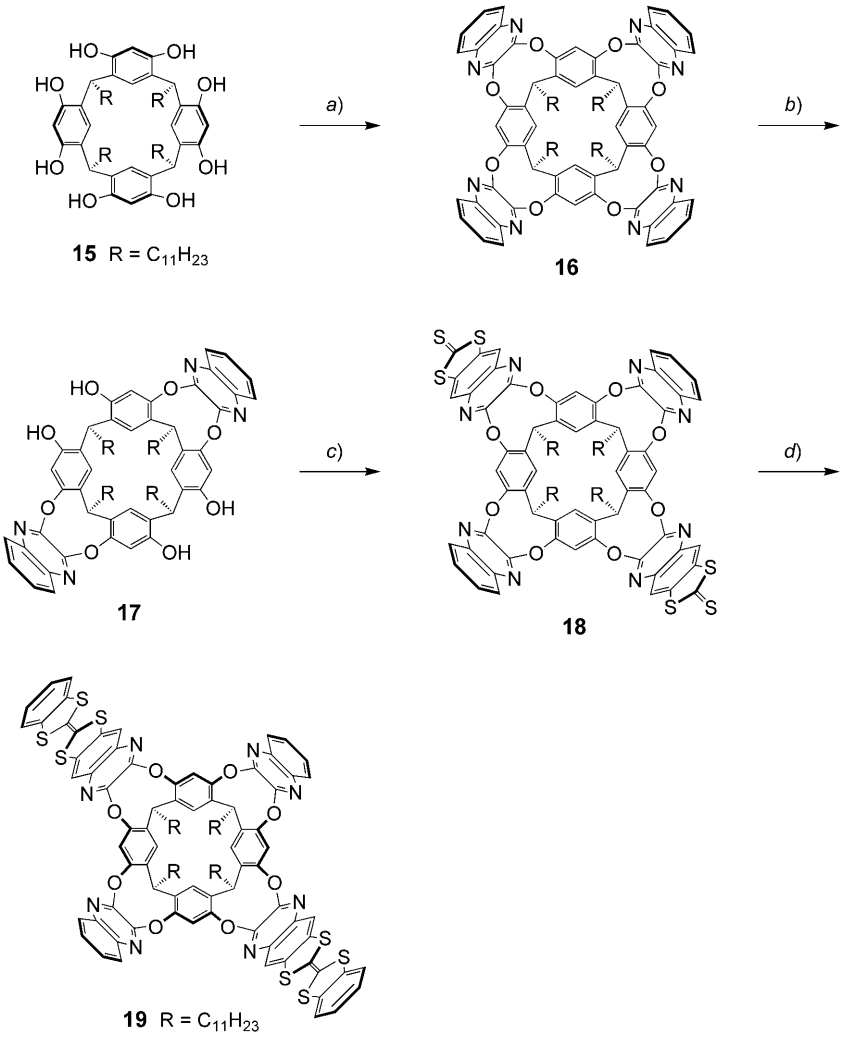
a) **7**, K_2CO_3, Me_2SO, 60°, 16 h; 56%. *b*) **5**, $P(OEt)_3$, toluene, 130°, 16 h.

ously reported by *Aoyama et al.* [22] (*Scheme 5*). Bridging with 2,3-dichloroquinoxaline afforded cavitand **16** (73%). Selective removal of the two quinoxaline flaps in the *anti*-position by reaction with catechol (CsF/DMF) [21a] provided tetrol **17** in 58% yield. Subsequent bridging with 2 equiv. of **7** led to bis-dithiolthione **18** in 72% yield. $P(OEt)_3$-mediated coupling of **18** with dithiolone **5** produced bis-TTF derivative **19** (HR-MALDI-MS). However, similar to the attempted preparation of **2**, isolation of **19** was not successful due to low solubility. It, therefore, became apparent that functionalization of the upper rim of the cavitand was additionally required to provide sufficient solubility to the targeted bis-TTF cavitand.

We finally succeeded in producing a soluble target compound by adding two additional hexylthio chains to each of the two TTF moieties in the cavitand. The required starting dithiolone intermediate **20** was prepared by reduction of CS_2 with Na [23] to give the unstable intermediate dianionic 1,3-dithiol-2-one-4,5-thiolate [24], which was immediately converted into the Zn^{II} complex **21** (60% yield; *Scheme 6*). Subsequent alkylation with hexyl bromide [25] afforded dithiolthione **22**, which was transformed with $Hg(OAc)_2$ into the desired dithiolone **20**. $P(OEt)_3$-Mediated coupling of macrocyclic dithiolthione **18** with **20** (6 equiv.) provided the red-colored bis-TTF cavitand **23** (9%), besides the corresponding TTF derivative **24** as the major product (45%) and a third macrocyclic TTF derivative **25a** (<1% yield), whose proposed structure will be further discussed below. Separation and purification of the three products required affinity chromatography on SiO_2 (CH_2Cl_2), followed by gel permeation chromatography (GPC, *BioBeads S-X1*; CH_2Cl_2).

The structure assigned to the targeted cavitand **23** was fully supported by spectroscopic analysis. The HR-MALDI-MS (3-HPA) depicted the molecular ion as the parent ion at *m*/*z* 2424.9562 (M^+, $C_{136}H_{168}N_8O_8S_{12}^+$; calc. 2424.9633), with the notable absence of major fragment ions, confirming the stability of the macrocycle. The UV/VIS spectrum (CH_2Cl_2, 293 K) featured absorption bands at λ_{max} 269 ($\varepsilon = 24200$ l mol^{-1} cm^{-1}), 320 (17500), and 463 nm (4400). The weak band at 463 nm is characteristic for TTF derivatives in the neutral (reduced) form [26] and confers the red color to **23**. The ^{13}C-NMR spectra (75 MHz, $CDCl_3$) confirmed the C_{2v} symmetry, with 17 (expected) resonances appearing in the aromatic and olefinic spectral region between 107.9 and

Scheme 5. *Synthesis of the Insoluble Bis-TTF Cavitand* **19**

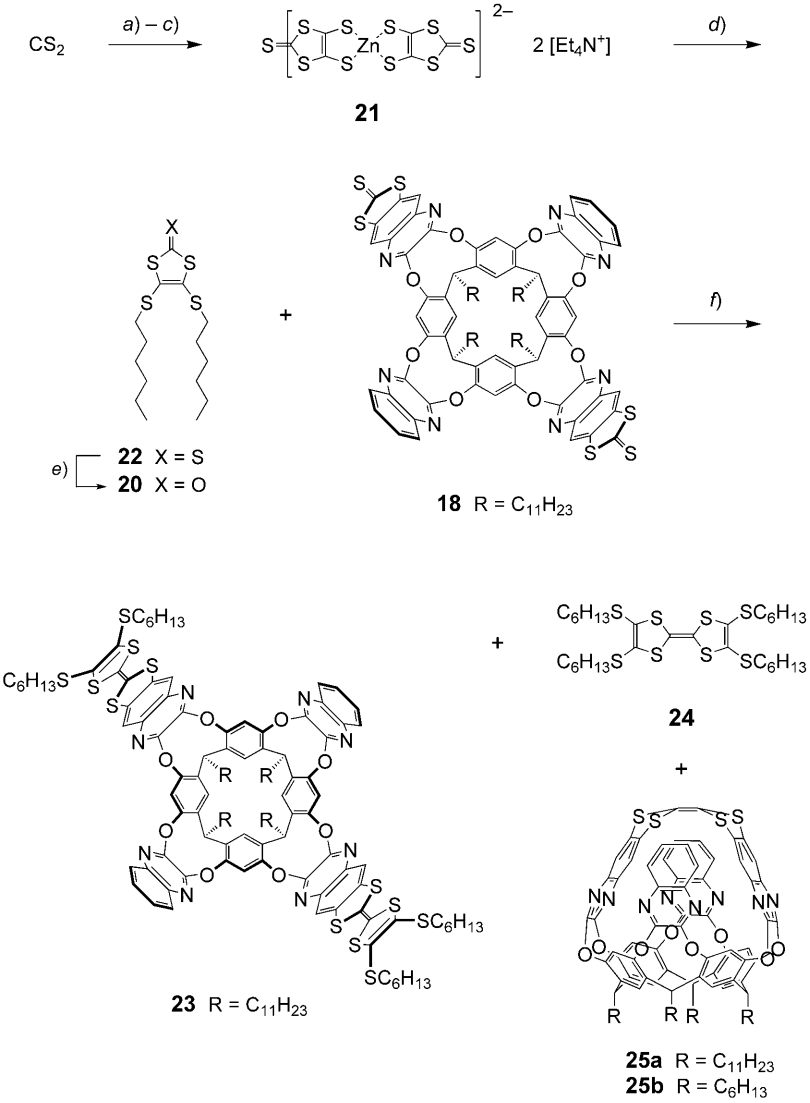


a) 2,3-Dichloroquinoxaline, K_2CO_3, Me_2SO, 60°, 16 h; 73%. *b*) Catechol, CsF, DMF, 80°, 45 min; 58%. *c*) **7**, K_2CO_3, Me_2SO, 60°, 16 h; 72%. *d*) **5**, $P(OEt)_3$, toluene, 130°, 16 h.

152.5 ppm. In the ^{1}H-NMR spectrum (300 MHz, $CDCl_3/CS_2$ 1:1) at 298 K, all aromatic resonances could be unambiguously assigned (*Fig. 1*, *a*). Moreover, the presence of two overlapping '*triplets*' at 5.57 and 5.51 ppm, respectively, for the methine H-atoms H^a and H^b in the octol bowl clearly demonstrates the preference of the *vase* conformation at or above the room temperature [1].

Gratifyingly, the deep cavitand **23** undergoes *vase* → *kite* switching upon cooling: at 193 K, the methine protons H^a and H^b appear strongly upfield-shifted, as a broad signal around 3.67 ppm (*Fig. 1*, *b*). This position is highly characteristic for the *kite* conformer

Scheme 6. *Synthesis of the Soluble Bis-TTF Cavitand* **23**



a) Na, DMF, 20°,16 h. *b*) $ZnCl_2$, NH_3/MeOH. *c*) Et_4NBr, H_2O, 20°, 16 h; 60% (steps *a*–*c*). *d*) Hexyl bromide, MeCN, 80°, 24 h; 81%. *e*) $Hg(OAc)_2$, CH_2Cl_2, 20°, 1 h; 81%. *f*) $P(OEt)_3$, toluene, 130°, 16 h; 9% (**23**), 45% (**24**), <1% (**25a**).

[1]. Acid (TFA)-induced switching of **23** is not advised in view of the instability of the TTF moieties in acidic environments. In contrast, both 1,3-dithiol-2-thione-fused cavitands **14** and **18** could be reversibly switched in $CDCl_3$ or CH_2Cl_2 from the *vase* to the *kite* form either by lowering the temperature or by addition of TFA [4].

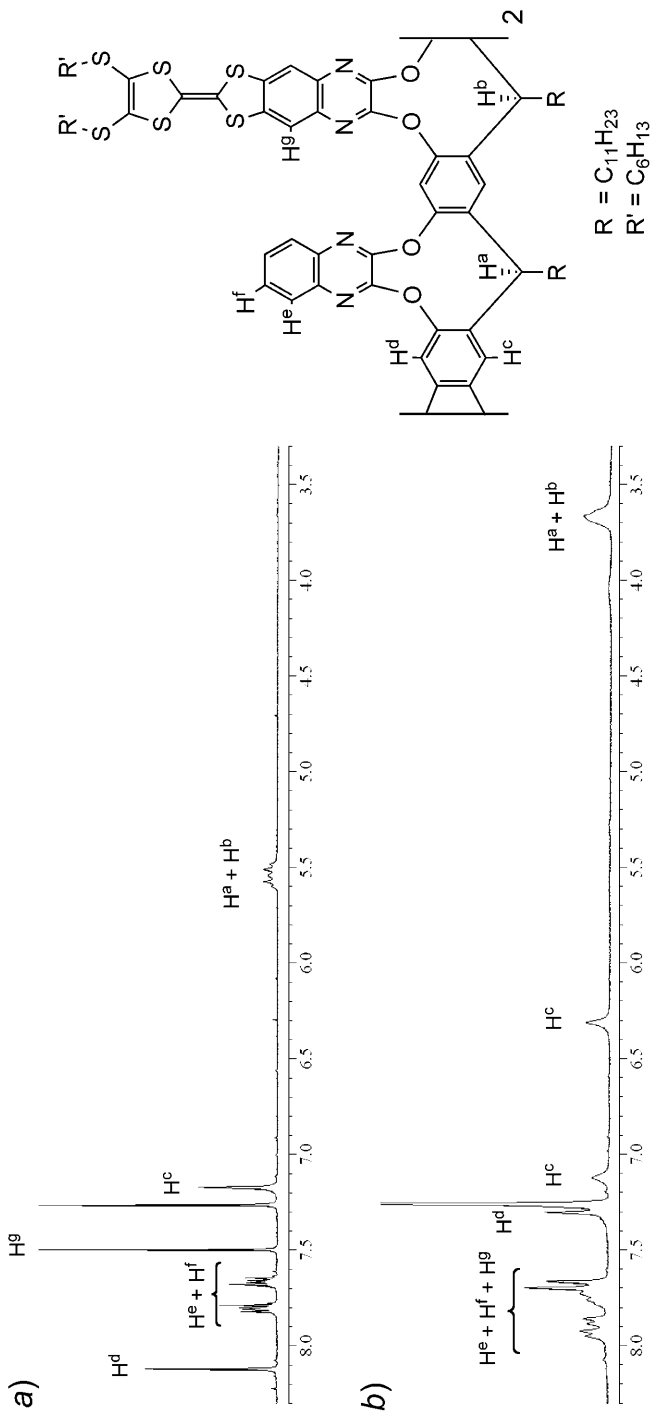


Fig. 1. *300-MHz ^{1}H-NMR Spectra of bis-TTF cavitand* **23** *recorded in $CDCl_3/CS_2$ 1:1 with peak assignments.* Spectrum *a*) at 298 K depicts the *vase* and spectrum *b*) at 193 K the *kite* conformer.

With less than 1% yield, a second macrocyclic TTF derivative was isolated during the preparation of **23** (*Scheme 6*), and HR-MALDI-MS (3-HPA) suggested the formation of structure **25a** (*m/z* 1757.790 ($[M+H]^+$, $C_{106}H_{117}N_8O_8S_4^+$; calc. 1757.787), formed by intramolecular homo-coupling of bis(1,3-dithiol-2-thione) **18**. This structural assignment was also supported by ^{1}H-NMR spectroscopy (not shown). Consequently, pure **14** (the analog of **18** with hexyl instead of undecyl legs) was subjected to $P(OEt)_3$-mediated coupling in toluene (130°, 16 h), and chromatographic workup (SiO_2; CH_2Cl_2 followed by *BioBeads S-X1*, CH_2Cl_2) afforded pure **25b** in 8% yield. Computer modeling, using PM3 implemented in Spartan 02, suggested that the TTF moiety in **25a**/**25b** would be highly strained [27] (*Fig. 2*, *a*). The bent angle between the plane through the central TTF C=C bond, and each of the two planes encompassing the two S-atoms and the C=C bond fused to the adjacent quinoxaline amounts to *ca.* 51°. However, such a distortion is not without precedence and *Müllen* and co-workers reported in 1988 cage compound **26** with a similarly bent TTF moiety [28] (for another strained cage compound, see [29]). X-Ray crystallography revealed a similar bent angle (as defined above) of 50° for this stable compound (*Fig. 2*, *b*).

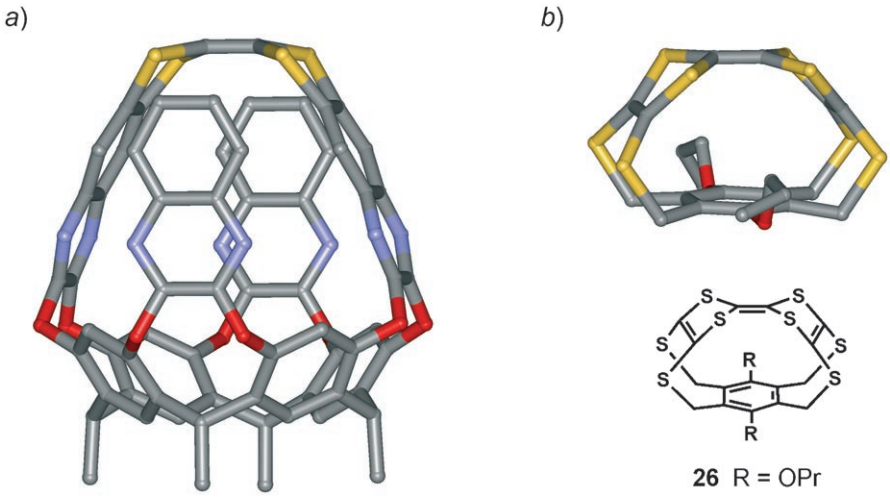


Fig. 2. a) *Energy-minimized structure* (PM3, Spartan 02) *of the strained TFF cage* **25**. Alkyl legs are omitted for clarity. *b*) *X-Ray crystal structure* (CSD code 53228) *of cage compound* **26** [28a]. Color coding: C-atoms: grey; O-atoms: red; N-atoms: blue; S-atoms: yellow.

The ^{1}H-NMR spectrum ($CDCl_3$) confirms the C_{2v}-symmetric structure of **25b** (*Fig. 3*). All aromatic resonances are fully assignable, and their positions further support the close proximity between quinoxaline flaps and bridging TTF moiety, suggested by the modeling. The signals of the resorcin[4]arene H-atoms at C(1) and C(5) (see *Fig. 3* for arbitrary numbering) appear only slightly shifted upon changing from **23** (8.19 and 7.17 ppm) to **25b** (8.22 and 7.11 ppm). The resonance of the TTF-fused quinoxaline (H–C(4)) moves slightly upfield, from 7.49 (**23**) to 7.25 (**25b**) ppm. A remarkable downfield shift is seen for the resonances of H–C(2) and H–C(3) in the free quinoxa-

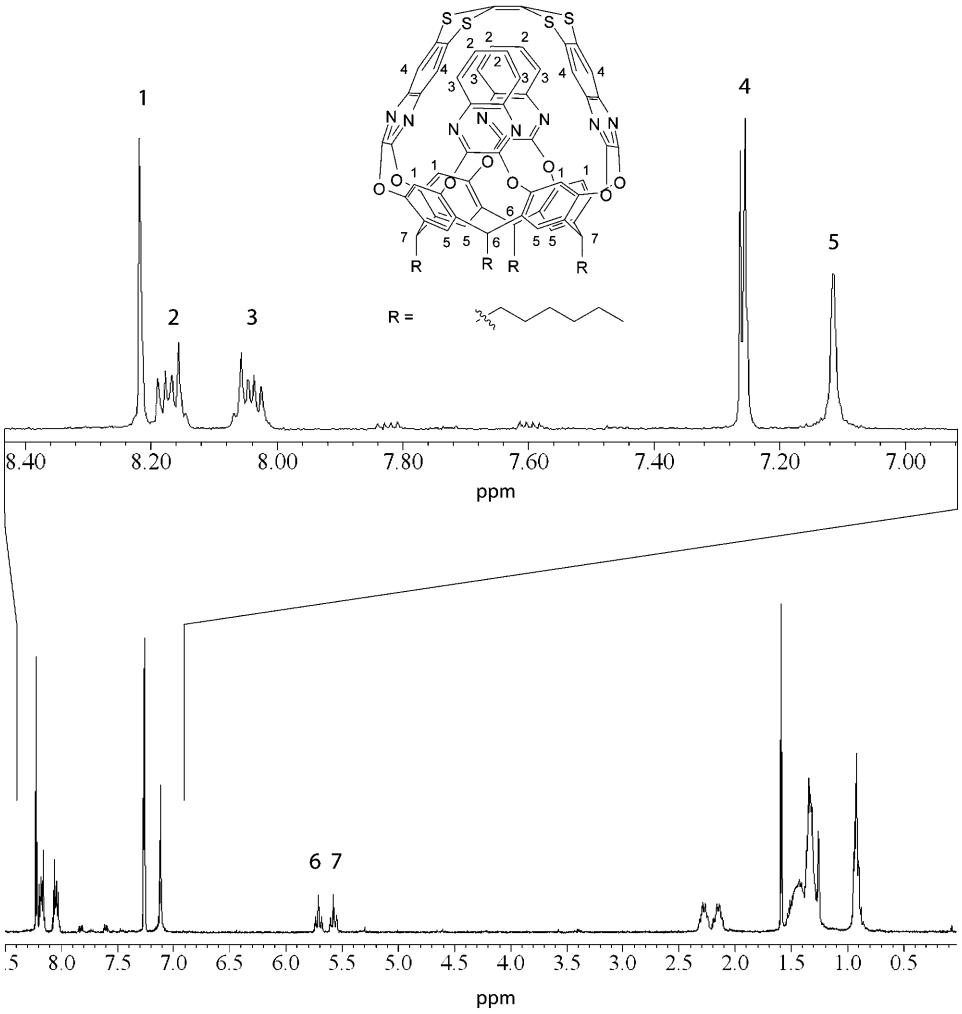


Fig. 3. *^{1}H-NMR Spectra* (300 MHz) *of* **25b** *in $CDCl_3$ at 298 K.* The aromatic resonances are enlarged and assigned. The weak peaks around 7.8 and 7.6 ppm belong to a non-identified impurity, which, according to MALDI-MS, is not the 'dimer' from intermolecular homo-coupling of two molecules of **14**.

line flaps, from *ca*. 7.80 and 7.67 in **23** to *ca*. 8.15 and 8.04 ppm, respectively, in **25b**. This downfield shift presumably is a result of the anisotropic deshielding caused by the TTF bridge.

The ^{13}C-NMR spectrum ($CDCl_3$) depicts 15 resonances in the aromatic/olefinic range between 153.4 and 119.4 ppm, as expected for C_{2v}-symmetric **25b**. Particularly revealing is the position of the central C(sp^2) resonance in the bridging TTF moiety. In planar TTF derivatives such as **12** (110.8 ppm), **24** (110.4 ppm), or **23** (107.9 and 115.1 ppm), this signal appears around 110 ppm. In contrast, this resonance is substantially downfield shifted to 137.0 ppm in **25b**, as a result of the strong pyramidalization of

the sp^2-hybridized C-atom (similar to the curvature effects in fullerenes [30]). Notably, the corresponding signal in the strained TTF cage **26** (*Fig. 2,a*) also appears downfield shifted at 134.5 ppm [28a].

The bridging TTF moiety strongly enforces the *vase* conformation of **25b**. On the other hand, cooling from 298 down to 193 K induces an upfield shift of the H–C(6) resonance (numbering of *Fig. 3*) adjacent to the free quinoxaline flap from 5.71 to 5.42 ppm, while the signal of H–C(7) remains unchanged at 5.57 ppm. The specific upfield shift of H–C(6) suggests some degree of conformational change in the flexible, nonbridged parts of the molecule upon lowering the temperature, but not a transition towards an open *kite* geometry.

2.3. *Electrochemical Investigations.* Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies were conducted in CH_2Cl_2 in the presence of Bu_4NPF_6 (0.1 M). All potentials were referenced against the ferricinium/ferrocene (Fc^+/Fc) couple. The CV and DPV traces of bis-TTF-cavitand **23** are shown in *Fig. 4*.

Compound **23** expectedly undergoes two reversible $2e^-$ oxidation steps, the first one leading to the bis(TTF radical cation) and the second one to the bis(TTF dication). The first redox couple shows a broad oxidation and a broad reduction peak with a half-wave potential $E_1^{1/2} = +0.26$ V ($\Delta E = 99$ mV). In contrast, the oxidation and reduction peaks of the second redox couple are much narrower with $E_2^{1/2} = +0.58$ V and $\Delta E = 60$ mV. For comparison, the parent tetrathiafulvalene (TTF) undergoes the two oxidation steps at $E_1^{1/2} = 0.03$ and $E_2^{1/2} = 0.40$ V under the same conditions [31]. Both the electron-accepting effect of the hexylsulfanyl substituents [32] and the fused quinoxaline render the two oxidation steps in **23** more difficult than in the parent TTF.

If two TTF moieties in a molecule are in sufficiently close proximity to each other, the first oxidation to the bis(radical cation) is split into two steps [33]. In this case, the electronic stabilization of the first-formed radical cation by the π electrons of the second TTF moiety reduces the potential of the first $1e^-$ oxidation step. Furthermore, the second $1e^-$ oxidation step becomes more difficult as a result of the proximity of the first-formed radical cation. If the distance between the two TTF moieties is slightly increased, the two $1e^-$ oxidation peaks merge into a single, broadened peak. If the distance is further increased, thereby eliminating any electronic coupling between the two TTF chromophores, a single, narrow peak for both $1e^-$ oxidations to the bis(radical cation) is observed. Such influences of the interactions between two TTF moieties on the electrochemical properties have most recently been described by *Sallé* and co-workers in the study of a calix[4]arene–bis-TTF conjugate [34].

Based on this reasoning, we propose an explanation for the observed broadening of the first and the sharpening of the second oxidation peaks (*Fig. 4*). In the *vase* conformation, the two TTF moieties in **23** are sufficiently close to exhibit some degree of electronic coupling, which results in a broadened peak for the first $2e^-$ oxidation step to the bis(radical cation). Attempts to further resolve this broad peak by changing the experimental conditions (temperature, scan rate, nature of the working electrode (Pt, Au, glassy carbon)) were not successful.

On the other hand, the reversible second $2e^-$ oxidation step to the bis(TTF dication) suggests that the two chromophores are at larger distance and no longer in electronic communication. We take this as the first evidence for a possible electrochemically induced conformational switching from the *vase* to the *kite* form as a result of

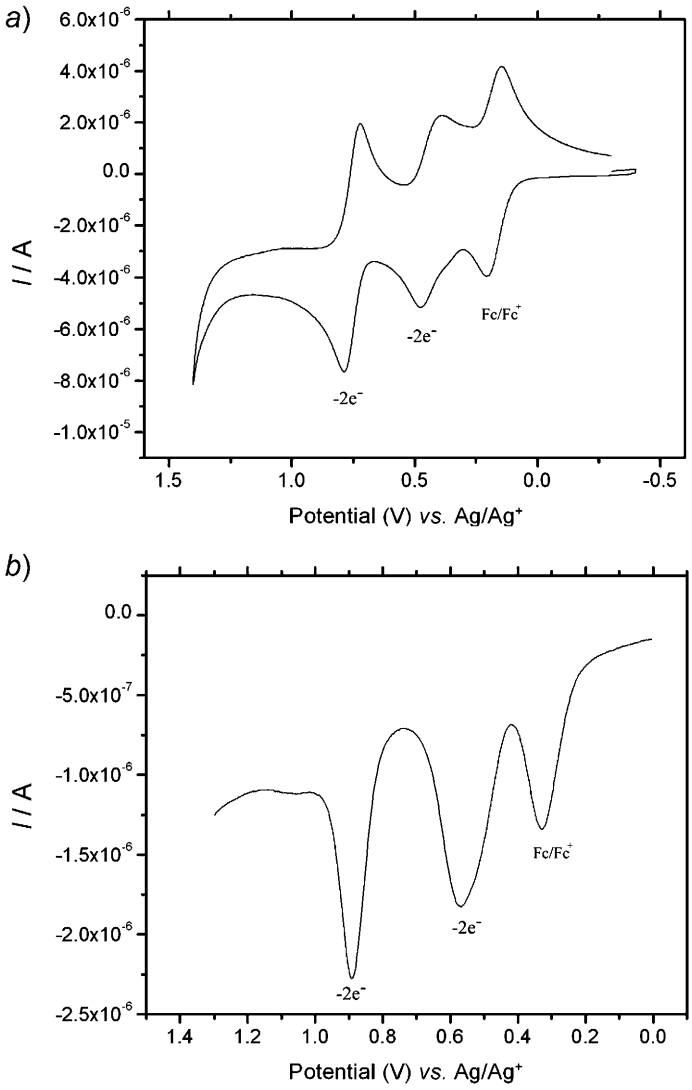


Fig. 4. a) *CV of* **23** (0.5 mM) *in* CH_2Cl_2 (+0.1M Bu_4NPF_6) *at 293 K*. Scan rate: 100 mV/s. b) *DPV of* **23** *under the same conditions.* Scan rate: 4 mV/s.

the *Coulombic* repulsion between the two TTF radical cations. Additional experiments to validate the electrochemical *vase* → *kite* conformational switching are under way.

3. Conclusions. – In this paper, we report new fascinating functional molecular architectures, merging TTF redox chemistry with the unique *vase* → *kite* switching properties of bridged resorcin[4]arene cavitands. As in many projects targeting molecular nanoscale devices, solubility has been a serious issue and compound **23** required decoration both of the octol bowl and of the TTF cavity rims with long alkyl chains

to become soluble in common organic solvents. The formation and isolation of cage compounds **25a**/**25b** was quite unexpected, in view of their severely distorted TTF bridge. While their characterization and structural assignment are unambiguous, we became nevertheless more assured of the assigned structure when we found literature precedence by *Müllen* and co-workers for the similarly strained TTF cage **26** for which an X-ray crystal structure had been obtained [28]. Whereas the deep cavitand **23** undergoes reversible *vase* → *kite* isomerization upon passing from 293 to 193 K, the strained, rigid TTF bridge in **25a**/**25b** prevents such large conformational change. Preliminary evidence for the targeted *vase* → *kite* switching of **23** induced by oxidation of the TTF cavity walls was obtained by electrochemical studies. Whereas the first $2e^-$ oxidation wave in CV and DPV is broadened, as a result of electronic coupling between the two TTF chromophores in the *vase* form, the second $2e^-$ oxidation step leads to a sharp wave, which would be expected if the two TTF radical cations are located at substantially larger distance, as in the *kite* form. Obviously, more experiments will be required to fully validate this hypothesis. Furthermore, future investigations will address the host–guest binding properties of the bis-TTF cavitands, and how complexation affects the redox processes.

We thank the *Swiss National Science Foundation* for support of this work *via* the *National Research Program (NRP) 'Supramolecular Functional Materials'* and the *NCCR 'Nanoscale Science'*. Support from the *US National Science Foundation*, grant CHE-0408367, is also gratefully acknowledged. We thank Dr. *C. Thilgen* (ETH) for help with the nomenclature.

Experimental Part

General. Solvents and reagents were purchased reagent-grade and used without further purification (except for 2,3-dichloroquinoxaline, which was recrystallized from EtOH or MeOH). Solvents for extractions and chromatography were of technical grade and were distilled prior to use. All reactions were carried out under an Ar atmosphere unless otherwise stated. Toluene was distilled from sodium, CH_2Cl_2 from CaH_2. Anh. Me_2SO and DMF, stored over molecular sieves, were purchased from *Fluka*. All products were dried under high vacuum (10^{-2} Torr) before anal. characterization. The preparation of the following compounds has been reported in the literature: **5** [16], **6** [2b][7b], **8** [17], **12** [35], **13** [7], **15** [22], **16** [36], **17** [36], **21** [24]. Flash chromatography (FC): SiO_2 from *Fluka* or *Merck* 230–400 mesh. Prep. gravity gel permeation chromatography (GPC): *BIO-RAD Beads SX-1* (pore size 200–400 μm) as stationary phase at amb. pressure and temp.; eluent: CH_2Cl_2; 10–20 drops min^{-1}; fractions of 5–10 ml. Anal. TLC: precoated SiO_2 glass plates with *F-254* fluorescent indicator; visualization by UV light at 254 nm or by staining with a soln. of $(NH_4)_6Mo_7O_{24}\cdot 6\,H_2O$ (20 g) and $Ce(SO_4)_2$ (0.4 g) in 10% aq. H_2SO_4 (400 ml). M.p.: *Büchi Melting Point B-540*; uncorrected. UV/VIS Spectra [nm]: *Varian Cary 500 Scan* spectrophotometer. IR Spectra [cm^{-1}]: *Perkin-Elmer 1600-FT-IR* spectrometer or a *Perkin-Elmer Spectrum BX II*. NMR (^1H and ^{13}C) Spectra [ppm]: *Varian Gemini 300*, *Varian Mercury 300*, or *Bruker AMX-500* spectrometers; spectra were recorded at r.t. with the solvent peak as reference. FT-ICR-MALDI-MS: *Ion Spec Ultima FT-ICR-MS* (337 nm N_2 laser system); matrix: 3-HPA (3-hydroxypicolinic acid) or DCTB ({(2*E*)-3-[4-(*tert*-butyl)phenyl]-2-methylprop-2-enylidene}malonitrile). EI-MS: *VG Analytical Tribrid,* USA. Elemental analyses were performed by the *Mikrolabor* at the *Laboratorium für Organische Chemie, ETH-Zürich*. The names of compounds **3**, **4**, **14**, **18**, **23**, and **25** were generated using the cyclophane nomenclature [37].

Electrochemical Measurements. All electrochemical measurements were performed with the *CHI 440 Electrochemical Workstation* (*CH Instruments Inc*., Austin, Texas). 0.1M Bu_4NPF_6 (from *Fluka*) was used as the supporting electrolyte in redistilled CH_2Cl_2, degassed with Ar. Pt Wire was employed as the counter electrode. An aq. Ag/AgCl electrode, separated by a 0.1M Bu_4NPF_6 salt-bridge, was

used as the reference. Ferrocene (Fc) was added as an internal reference, and all potentials were referenced relative to the Fc/Fc^+ couple. A glassy C electrode (*CHI*, 3 mm in diameter), polished with 1.0–0.3 μm Al paste and ultrasonicated in deionized H_2O and a CH_2Cl_2 bath, was used as the working electrode. The scan rates for cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were 100 and 4 mV/s, resp. For the DPV measurements, the amplitude was 50 mV, and the pulse width was 0.05 s. All experiments were performed at 293 ± 2 K.

5,6-Diamino-1,3-benzodithiol-2-thione (**9**) *and 5*H*-[1,3]Dithiolo[4,5-*f*]benzimidazol-2,6(7*H*)-dithione* (**10**). Compound **8** (2.44 g, 11 mmol) was added as a solid to a soln. of $Na_2S \cdot 9\,H_2O$ (8.71 g, 96.3 mmol) in degassed H_2O (135 ml), and the mixture was stirred for 1 h at 70°. After cooling to 50°, CS_2 (1.4 ml, 23.2 mmol) was added dropwise, and stirring was continued for 2 h at 50° and 3 h at 20°. The yellow precipitate was isolated by filtration, washed with H_2O, and dried under high vacuum (10^{-2} Torr). FC (SiO_2; pentane/THF 1:1) afforded **9** (1.20 g, 52%) and **10** (0.46 g, 16%).

Data of **9**. Orange solid. M.p.: 213–215°. IR (neat): 3375, 3292, 3188, 1615, 1553, 1481, 1405, 1282, 1046, 1026. ^{1}H-NMR (300 MHz, $(CD_3)_2SO$): 6.81 (*s*, 2 H); 5.12 (*s*, 4 H). ^{13}C-NMR (75 MHz, $(CD_3)_2SO$): 209.8; 136.6; 127.7; 105.3. EI-HR-MS: 213.9687 (M^+, $C_7H_6N_2S_3^+$; calc. 213.9693).

Data of **10**. Yellow solid. M.p. > 300°. IR (neat): 3147, 3039, 2910, 2357, 1597, 1489, 1455, 1325, 1166, 1057, 1031, 1018. ^{1}H-NMR (300 MHz, $(CD_3)_2SO$): 12.88 (*s*, 2 H); 7.65 (*s*, 2 H). ^{13}C-NMR (75 MHz, $(CD_3)_2SO$): 212.5; 169.7; 133.9; 132.7; 103.1. HR-EI-MS: 255.9252 (M^+, $C_8H_4N_2S_4^+$; calc. 255.9257).

*2-Thioxo-5,8-dihydro[1,3]dithiolo[4,5-*g*]quinoxaline-6,7-dione* (**11**). A suspension of **9** (890 mg, 4.2 mmol) in diethyl oxalate (50 ml) was stirred for 16 h at 165°, then cooled to 20°, and filtered. The product was washed with EtOH and dried (10^{-2} Torr) to give **11** (1.00 g, 90%). M.p. > 300°. IR (neat): 3256, 3028, 2914, 1682, 1439, 1377, 1328, 1197, 1057. ^{1}H-NMR (300 MHz, $(CD_3)_2SO$): 12.22 (*s*, 2 H); 7.49 (*s*, 2 H). ^{13}C-NMR (75 MHz, $(CD_3)_2SO$): 212.2; 154.5; 134.2; 126.2; 108.1.

*6,7-Dichloro[1,3]dithiolo[4,5-*g*]quinoxaline-2-thione* (**7**). To a suspension of **11** (2.00 g, 7.5 mmol) in DMF (22 ml), $COCl_2$ (20% soln. in toluene, 12.6 ml, 24 mmol) was added. After stirring for 3 d, CH_2Cl_2 was added, and the mixture was filtered through SiO_2 and concentrated *in vacuo*. The residue was purified by FC (SiO_2; pentane/CH_2Cl_2 1:1) to give **11** (1.27 g, 56%). Yellow solid. M.p. 240°. IR (neat): 3059, 2920, 2852, 1651, 1587, 1437, 1328, 1259, 1145, 1091, 1060, 1005. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.02 (*s*, 2 H). ^{13}C-NMR (500 MHz, $CDCl_3$): 210.8; 146.7; 145.4; 139.1; 119.9. HR-MALDI-MS (DCTB): 303.8758 (M^+, $C_9H_2Cl_2N_2S_3^+$; calc. 303.8757). Anal. calc. for $C_9H_2N_2S_3Cl_2$ (305.21): C 35.42, H 0.66, N 9.18; found: C 35.55, H 0.72, N 9.19.

*(17*S*,18*R*,19*R*,20*S*)-17,18,19,20-Tetrahexyl-2,4,6,8,10,12,14,16-octaoxa-3(6,7)-([1,3]dithiolo[4,5-*g*]-quinoxalina)-7,11,15(2,3)-triquinoxalina-1,5,9,13(1,2,4,5)-tetrabenzenapentacyclo[11.3.1.1^{1,5}.1^{5,9}.1^{9,13}]icosaphane-3^2-thione* (**4**). A suspension of **6** (150 mg, 0.12 mmol), **7** (38 mg, 0.12 mmol), and Cs_2CO_3 (48 mg, 0.15 mmol) in dry Me_2SO (7 ml) was stirred for 48 h at 50°. After cooling to 20°, the mixture was poured into H_2O. The formed precipitate was isolated by filtration, air-dried, and purified by FC (SiO_2; CH_2Cl_2/AcOEt 97:3) to give **4** (127 mg, 74%). Yellow solid. M.p. > 300°. IR (neat): 3064, 2925, 2853, 1734, 1576, 1478, 1413, 1396, 1328, 1264, 1158, 1062. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.18 (*s*, 2 H); 8.11 (*s*, 2 H); 7.90–7.75 (*m*, 6 H); 7.73 (*s*, 2 H); 7.63–7.48 (*m*, 6 H); 7.23 (*s*, 2 H); 7.21 (*s*, 2 H); 5.66–5.56 (*m*, 3 H); 5.51 (*t*, *J* = 8.2, 1 H); 2.35–2.20 (*m*, 8 H); 1.58–1.30 (*m*, 32 H); 0.94 (*t*, *J* = 6.7, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.3; 153.2; 152.4; 152.3; 152.2; 152.1; 142.0; 139.5; 139.4; 139.3; 138.0; 135.9; 135.6; 135.6; 135.4; 129.2; 129.2; 128.9; 127.8; 127.6; 127.2; 123.4; 123.2; 119.2; 118.6; 118.6; 34.4; 32.7; 32.4; 32.0; 29.5; 28.0; 22.8; 14.2. HR-MALDI-MS (DCTB): 1434.5124 (M^+, $C_{85}H_{78}N_8O_8S_3^+$; calc. 1434.5105).

*(17*S*,18*R*,19*R*,20*S*)-3^2-(1,3-Benzodithiol-2-ylidene)-17,18,19,20-tetrahexyl-2,4,6,8,10,12,14,16-octaoxa-3(6,7)-([1,3]dithiolo[4,5-*g*]quinoxalina)-7,11,15(2,3)-triquinoxalina-1,5,9,13(1,2,4,5)-tetrabenzenapentacyclo[11.3.1.1^{1,5}.1^{5,9}.1^{9,13}]icosaphane* (**3**). To a stirred suspension of **4** (100 mg, 70 μmol) in $P(OEt)_3$ (0.7 ml) at 130°, a soln. of **5** (51 mg, 280 μmol) in toluene (1 ml) was added. After stirring for 6 h at 130°, the mixture was cooled to 20° and the solvent removed *in vacuo*. Purification by FC (SiO_2; CH_2Cl_2) afforded **3** (9 mg, 9%) and **12** (18 mg, 42%).

Data of **3**: Red solid. M.p. > 300°. IR (neat): 2924, 2853, 2289, 2050, 1979, 1700, 1602, 1570, 1481, 1414, 1398, 1363, 1328, 1263, 1221, 1186, 1158, 1118, 1097, 1062. ^{1}H-NMR (300 MHz, $CDCl_3$, 50°): 8.20 (*s*, 2 H); 8.13 (*s*, 2 H); 7.86–7.74 (*m*, 8 H); 7.66–7.44 (*m*, 10 H); 7.24 (*s*, 2 H); 7.23 (*s*, 2 H); 5.70–5.55 (*m*, 4 H); 2.35–2.20 (*m*, 8 H); 1.58–1.27 (*m*, 32 H); 0.94 (*t*, *J* = 6.6, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$,

50°): 152.5; 152.4; 152.3; 152.3; 140.0; 139.6; 139.6; 139.5; 138.2; 135.8; 135.8; 135.7; 135.7; 129.1; 129.1; 129.0; 128.9; 127.8; 127.6; 127.4; 123.3; 123.2; 118.9; 118.7; 118.7; 34.3; 32.5; 31.9; 29.7; 29.4; 28.0; 22.7; 14.0. HR-MALDI-MS (3-HPA): 1555.5180 ($[M+H]^+$, $C_{92}H_{83}N_8O_8S_4^+$; calc. 1555.5211).

*(17*S*,18*S*,19*S*,20*S*)-17,18,19,20-Tetrahexyl-2,4,6,8,10,12,14,16-octaoxa-3,11(6,7)-bis([1,3]dithiolo[4,5-g]-quinoxalina)-7,15(2,3)-diquinoxalina-1,5,9,13(1,2,4,5)-tetrabenzenapentacyclo[11.3.1.1^{1,5}.1^{5,9}.1^{9,13}]icosaphane-3^2,11^2-dithione* (**14**). A suspension of **13** (505 mg, 0.47 mmol), **7** (287 mg, 0.94 mmol), and K_2CO_3 (155 mg, 1.12 mmol) in dry Me_2SO (32 ml) was stirred for 16 h at 60°. After cooling to 20°, the mixture was poured into H_2O. The formed precipitate was isolated by filtration, washed with H_2O, air-dried, and purified by FC (SiO_2; CH_2Cl_2/AcOEt 99:1 → 98:2) to give **14** (400 mg, 56%). Yellow solid. M.p. >300°. IR (neat): 3070, 2920, 2848, 1576, 1478, 1414, 1396, 1328, 1261, 1197, 1155, 1065. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.07 (*s*, 4 H); 7.79 (*s*, 4 H); 7.80–7.75 (*m*, 4 H); 7.61–7.55 (*m*, 4 H); 7.19 (*s*, 4 H); 5.49 (*t*, *J* = 7.7, 2 H); 5.41 (*t*, *J* = 7.8, 2 H); 2.26–2.18 (*m*, 8 H); 1.58–1.24 (*m*, 32 H); 0.92 (*t*, *J* = 6.7, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 210.6; 153.2; 152.8; 152.5; 142.7; 139.7; 138.4; 136.1; 135.6; 129.6; 127.8; 123.7; 119.5; 118.7; 34.7; 34.7; 32.6; 32.6; 32.1; 29.5; 28.1; 22.9; 14.3. HR-MALDI-MS (3-HPA): 1541.4156 ($[M+H]^+$, $C_{86}H_{77}N_8O_8S_6^+$; calc. 1541.4183).

*(17*s*,18*s*,19*s*,20*s*)-17,18,19,20-Tetrahexyl-2,4,6,8,10,12,14,16-octaoxa-3,11(6,7)-bis([1,3]dithiolo[4,5-g]-quinoxalina)-7,15(2,3)-diquinoxalina-1,5,9,13(1,2,4,5)-tetrabenzenapentacyclo[11.3.1.1^{1,5}.1^{5,9}.1^{9,13}]icosaphane-3^2,11^2-dithione* (**18**). A suspension of **17** (360 mg, 0.27 mmol), **7** (162 mg, 0.53 mmol), and K_2CO_3 (88 mg, 0.63 mmol) in dry Me_2SO (20 ml) was stirred for 16 h at 60°. After cooling to 20°, the mixture was poured into H_2O. The formed precipitate was isolated by filtration, washed with H_2O, air-dried and purified by FC (SiO_2; CH_2Cl_2 → CH_2Cl_2/AcOEt 98:2) to give **18** (347 mg, 72%). Yellow solid. M.p. > 280°. IR (neat): 2921, 2850, 1647, 1559, 1415, 1399, 1368, 1330, 1259, 1160, 1115, 1066, 1014. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.07 (*s*, 4 H); 7.80 (*s*, 4 H); 7.81–7.75 (*m*, 4 H); 7.62–7.56 (*m*, 4 H); 7.18 (*s*, 4 H); 5.49 (*dd*, *J* = 8.2, 7.4, 2 H); 5.41 (*dd*, *J* = 8.2, 8.0, 2 H); 2.30–2.18 (*m*, 8 H); 1.50–1.20 (*m*, 72 H); 0.89 (*t*, *J* = 6.5, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 210.6; 153.2; 152.8; 152.5; 142.7; 139.7; 138.4; 136.0; 135.6; 129.6; 127.8; 123.7; 119.5; 118.7; 34.7; 32.6; 32.2; 30.0; 29.7; 28.1; 22.9; 14.4. HR-MALDI-MS (3-HPA): 1821.7279 ($[M+H]^+$, $C_{106}H_{117}N_8O_8S_6^+$; calc. 1821.7313). Anal. calc. for $C_{106}H_{116}N_8O_8S_6$ (1822.50): C 69.86, H 6.42, N 6.15; found: C 69.93, H 6.55, N 6.31.

4,5-Bis(hexylsulfanyl)-1,3-dithiol-2-thione (**22**). To a suspension of **21** (354 mg, 0.49 mmol) in MeCN (7 ml), 1-bromohexane (0.34 ml, 2.45 mmol) was added, and the mixture was heated to reflux for 24 h. After cooling to 20°, the mixture was filtered, and the filtrate was concentrated *in vacuo*. After addition of CH_2Cl_2 and washing with H_2O, the org. phase was dried ($MgSO_4$) and concentrated *in vacuo*. Purification by FC (SiO_2; pentane/CH_2Cl_2 1:1) afforded **22** (290 mg, 81%). Yellowish oil. IR (neat): 2955, 2922, 2854, 2359, 2127, 1759, 1671, 1459, 1375, 1288, 1244, 1062. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.85 (*t*, *J* = 7.3, 4 H); 1.63 (*quint.*, *J* = 7.3, 4 H); 1.45–1.20 (*m*, 12 H); 0.87 (*t*, *J* = 6.9, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 210.9; 136.1; 36.8; 31.4; 29.7; 28.3; 22.6; 14.2. EI-HR-MS: 366.0634 (M^+, $C_{15}H_{26}S_5^+$; calc. 366.0638).

4,5-Bis(hexylsulfanyl)-1,3-dithiol-2-one (**20**). To a soln. of **22** (1.80 g, 4.9 mmol) in CH_2Cl_2 (150 ml), $Hg(OAc)_2$ (4.64 g, 14.7 mmol) was added. The mixture was stirred for 1 h at 20°, then it was filtered and the filtrate concentrated *in vacuo*. Purification by FC (SiO_2; pentane/CH_2Cl_2 1:1) afforded **20** (1.39 g, 81%). Yellowish oil. IR (neat): 2924, 2854, 2360, 2217, 1752, 1668, 1605, 1455, 1293, 1101. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.83 (*t*, *J* = 7.4, 4 H); 1.70–1.58 (*m*, 4 H); 1.46–1.21 (*m*, 12 H); 0.88 (*t*, *J* = 6.9, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 190.4; 127.4; 36.9; 31.5; 29.8; 28.4; 22.7; 14.2. EI-HR-MS: 350.0859 (M^+, $C_{15}H_{26}OS_4^+$; calc. 350.0867).

*(17*S*,18*S*,19*S*,20*S*)-3^2,11^2-Bis[4,5-bis(hexylsulfanyl)-1,3-dithiol-2-ylidene]-17,18,19,20-tetraundecyl-2,4,6,8,10,12,14,16-octaoxa-3,11(6,7)-bis([1,3]dithiolo[4,5-g]quinoxalina)-7,15(2,3)-diquinoxalina-1,5,9,13-(1,2,4,5)-tetrabenzenapentacyclo[11.3.1.1^{1,5}.1^{5,9}.1^{9,13}]icosaphane* (**23**), *4,4′,5,5′-Tetrakis(hexylsulfanyl)-2,2′-bi-1,3-dithiol* (**24**), *and (17*S*,18*S*,19*S*,20*S*)-17,18,19,20-Tetraundecyl-2,4,6,8,10,12,14,16-octaoxa-3,11(6,7)-bis([1,3]dithiolo[4,5-g]quinoxalina)-7,15(2,3)-diquinoxalina-1,5,9,13(1,2,4,5)-tetrabenzenahexacyclo-[11.3.1.1^{1,5}.1^{5,9}.1^{9,13}.0^{3,11}]icosaphan-3^2(11^2)-ene* (**25a**). To a stirred suspension of **18** (100 mg, 55 μmol) in $P(OEt)_3$ (0.7 ml) at 130°, a soln. of **20** (115 mg, 330 μmol) in toluene (1 ml) was added. After stirring for 16 h at 130°, the mixture was cooled to 20°, and the solvent was removed *in vacuo*. Purification by FC (SiO_2; CH_2Cl_2) and GPC (CH_2Cl_2) afforded **23** (12 mg, 9%), **24** (99 mg, 45%), and **25a** (1 mg, <1%).

Data of **23**. Red solid. M.p. >280°. IR (neat): 3069, 2924, 2852, 2324, 2050, 1979, 1694, 1607, 1576, 1481, 1467, 1456, 1414, 1398, 1363, 1329, 1262, 1221, 1186, 1159, 1117, 1062, 1019. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.19 (*s*, 4 H); 7.82–7.78 (*m*, 4 H); 7.70–7.63 (*m*, 4 H); 7.49 (*s*, 4 H); 7.17 (*s*, 4 H); 5.57 (*t*, *J* = 8.4, 2 H); 5.51 (*t*, *J* = 7.9, 2 H); 2.97–2.77 (*m*, 8 H); 2.29–2.16 (*m*, 8 H); 1.73–1.62 (*m*, 8 H); 1.50–1.22 (*m*, 96 H); 0.94–0.86 (*m*, 24 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 152.5; 152.4; 152.3; 152.2; 140.4; 139.5; 138.2; 135.6; 135.5; 129.4; 127.8; 127.5; 123.3; 118.7; 118.6; 115.1; 107.9; 36.4; 34.1; 32.4; 32.2; 31.9; 31.2; 29.6; 29.3; 28.1; 27.8; 22.6; 22.5; 14.0; 14.0. HR-MALDI-MS (3-HPA): 2424.9562 (M^+, $C_{136}H_{168}N_8O_8S_{12}^+$; calc. 2424.9633).

Data of **24**. Orange solid. M.p. 26–28°. IR (neat): 2951, 2921, 2854, 2359, 1674, 1458, 1418, 1374, 1306, 1258, 1206, 1109. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.81 (*t*, *J* = 7.4, 8 H); 1.62 (*quint.*, *J* = 7.4, 8 H); 1.47–1.20 (*m*, 24 H); 0.87 (*t*, *J* = 6.9, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 128.0; 110.4; 36.5; 31.5; 29.9; 28.4; 22.8; 14.3. EI-HR-MS: 668.1830 (M^+, $C_{30}H_{52}S_8^+$; calc. 668.1836).

Data of **25a**. White solid. M.p. 239–242°. IR (neat): 2921, 2848, 2358, 2051, 1979, 1732, 1576, 1466, 1414, 1399, 1366, 1330, 1259, 1159, 1115, 1075. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.22 (*s*, 4 H); 8.20–8.12 (*m*, 4 H); 8.08–8.00 (*m*, 4 H); 7.25 (*s*, 4 H); 7.11 (*s*, 4 H); 5.71 (*t*, *J* = 8.4, 2 H); 5.57 (*t*, *J* = 8.1, 2 H); 2.34–2.08 (*m*, 8 H); 1.60–1.20 (*m*, 72 H); 0.92–0.80 (*m*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 153.2; 153.0; 152.9; 152.3; 139.8; 138.8; 137.8; 136.8; 136.0; 135.7; 130.6; 127.6; 123.2; 121.6; 119.2; 34.0; 33.7; 33.3; 31.9; 31.6; 29.8; 29.7; 29.4; 29.4; 27.9; 22.7; 14.1. HR-MALDI-MS (3-HPA): 1757.790 ($[M+H]^+$, $C_{106}H_{117}N_8O_8S_4^+$; calc. 1757.787).

*(17*s*,18*s*,19*s*,20*s*)-17,18,19,20-Tetrahexyl-2,4,6,8,10,12,14,16-octaoxa-3,11(6,7)-bis([1,3]dithiolo[4,5-*g*]-quinoxalina)-7,15(2,3)-diquinoxalina-1,5,9,13(1,2,4,5)-tetrabenzenahexacyclo[11.3.1.1^{1,5}.1^{5,9}.1^{9,13}.0^{3,11}]icosaphan-3^2(11^2)-ene* (**25b**). A suspension of **14** (100 mg, 65 μmol) in $P(OEt)_3$ was heated to 130°. Toluene (1 ml) was added, and heating at 130° was continued for 16 h. Evaporation *in vacuo* and FC (SiO_2; CH_2Cl_2), followed by GPC (CH_2Cl_2), provided **25b** (7 mg, 8%). White solid. M.p. 227°. IR (neat): 2920, 2851, 2358, 2051, 1979, 1734, 1580, 1479, 1466, 1443, 1414, 1396, 1361, 1329, 1262, 1222, 1186, 1154, 1116, 1075. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.22 (*s*, 4 H); 8.20–8.12 (*m*, 4 H); 8.08–8.00 (*m*, 4 H); 7.25 (*s*, 4 H); 7.11 (*s*, 4 H); 5.71 (*t*, *J* = 8.4, 2 H); 5.57 (*t*, *J* = 8.1, 2 H); 2.34–2.08 (*m*, 8 H); 1.56–1.24 (*m*, 32 H); 0.96–0.86 (*m*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 153.4; 153.3; 153.1; 152.5; 140.0; 139.0; 138.0; 137.0; 136.2; 135.9; 130.8; 127.9; 123.4; 121.8; 119.4; 33.9; 33.6; 31.9; 31.5; 29.6; 27.9; 22.6; 14.0. HR-MALDI-MS (3-HPA): 1477.4771 ($[M+H]^+$, $C_{86}H_{77}N_8O_8S_4^+$; calc. 1477.4747).

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