Functionalized and Partially or Differentially Bridged Resorcin[4]arene Cavitands: Synthesis and Solid-State Structures

by **Vladimir A. Azov**[a]), **Philip J. Skinner**[a]), **Yoko Yamakoshi**[a]), **Paul Seiler**[a]), **Volker Gramlich**[b]), and **François Diederich***[a])

[a]) Laboratorium für Organische Chemie, ETH-Hönggerberg, CH-8093 Zürich (phone: (0)1 632 2992; fax: (0)1 632 11 09; e-mail: diederich@org.chem.ethz.ch)
[b]) Laboratorium für Kristallographie, ETH-Zentrum, Sonneggstrasse 5, CH-8092 Zürich

Dedicated to Professor *Duilio Arigoni* on the occasion of his 75th birthday

We report the synthesis and structural characterization of modified *Cram*-type, resorcin[4]arene-based cavitands. Two main *loci* on the cavitand backbone were selected for structural modification: the upper part (wall domain) and the lower part (legs). Synthesis of unsymmetrically bridged cavitands with different wall components (*i.e.*, **7**, **8**, and **14**–**18**) was performed by stepwise bridging of the four couples of neighboring, H-bonded OH-groups of octol **1a** (*Schemes 1*, *2*, *4*, and *5*). Cavitands with modified legs (*i.e.*, **20**, **24**, **27**, and **28**), targeted for surface immobilization, were synthesized by short routes starting from suitable aldehyde starting materials incorporating either the fully preformed leg moieties or functional precursors to the final legs (*Schemes 7–10*). The new cavitand substitution patterns described in this paper should enable the construction of a wide variety of functional architectures in the future. X-Ray crystallography afforded the characterization of cavitands **2c** (*Fig. 3*) and **24** (*Fig. 7*) in the *vase* conformation, with **2c** featuring a well-ordered CH_2Cl_2 guest molecule in its cavity. A particular highlight is the X-ray crystal-structure determination of octanitro derivative **19** (*Scheme 6*), which, for the first time, shows a cavitand, lacking substituents in the *ortho*-position to the two O-atoms of the four resorcinol moieties, in the *kite*-conformation (*Fig. 5*).

1. Introduction. – One of the most fascinating classes of receptors for chemical molecular-recognition studies comprises the resorcin[4]arene cavitands initially introduced and studied by *Cram* and co-workers [1] (*Fig. 1*). A particularly interesting property of these systems is the reversible switching between a closed *vase* conformation with a deep cavity for guest encapsulation [2] (for supramolecular

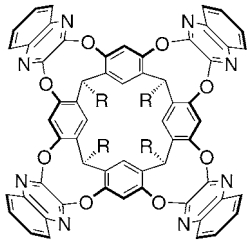


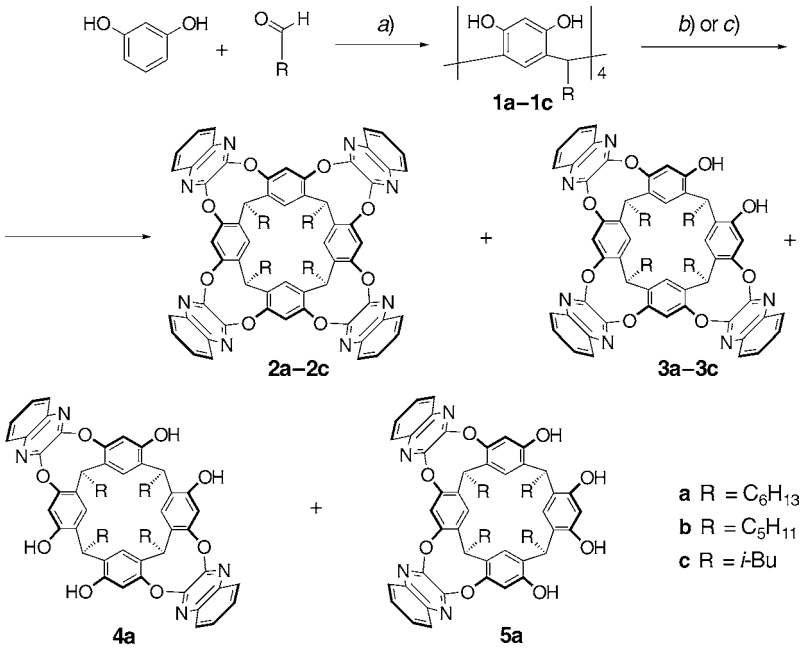
Fig. 1. *Original resorcin[4]arene cavitand reported by* Cram *and co-workers* [1]

capsules formed by resorcinarene cavitands, see [3]) and an open *kite* conformation with a flat, extended surface. This *vase* ⇌ *kite* equilibrium is controllable by both temperature [1] or p*H* variation [4], and resembles the movement of a molecular gripper. We became interested in exploring the potential of these switchable resorcin[4]arenes for single-molecule molecular manipulation (for a first scanning/tunnelling microscopy (STM) study, imaging the *vase* conformation at molecular resolution, see [5]). Integrated into suitable devices such as scanning-probe-microscopy tips, these cavitands should be able to capture (by complexation) a single molecule in the *vase* form and hold it during translocation, while releasing it upon switching to the nonbonding *kite* conformation. To reach this objective, much diverse groundwork is required. Here, we describe the synthesis of switchable resorcin[4]arene-derived cavitands bearing legs at the lower rim for attachment to solid surfaces [5]. Partial and unsymmetrical bridging of the resorcin[4]arene bowl (for a review on resorcin[4]arenes, see [6]) greatly expands the range of dynamic cavitands. A series of derivatives bearing fluorescent 'borondipyrromethene'(BODIPY) dyes [7] attached to the upper rim of the cavitand walls were prepared for mechanistic investigations of the switching dynamics by polarization-resolved single-molecule microscopy [8] (for a preliminary report on parts of this work, see [9]). The solid-state structures of cavitands in both *vase* and *kite* conformations are also described. In a following paper [10], we will report comprehensive investigations defining the experimental conditions under which the *vase* ⇌ *kite* equilibrium of fully and partially bridged resorcin[4]arenes can be precisely addressed and studied by ^{1}H-NMR and optical spectroscopy.

2. Results and Discussion. – 2.1. *Modification of the Cavity Walls.* A variety of modifications of the cavity walls to tune the size and the inner properties of the cavitands have been reported by *Rebek* and co-workers [3][11]. Whereas most of their work involved the 'symmetric'replacement of all four quinoxaline moieties (*Fig. 1*) by four new, identical wall components, some 'unsymmetric'systems with one flap differing from the residual three have also been reported [3c,e][12]. For our planned mechanistic studies of the *vase*–*kite* switching process by means of single-molecule confocal fluorescence microscopy in collaboration with *B. Hecht* (University of Basel), we were interested in preparing cavitands with one or two diazaphthalimide wall flaps bearing fluorescent BODIPY dyes. Deep cavitands with the latter array of wall components had not been previously described.

On the way to the targeted cavitands, three octols **1a**–**1c** with different, solubility-providing alkyl legs were prepared from resorcinol and the appropriate aliphatic aldehydes according to a standard protocol [13] (*Scheme 1*). X-Ray-quality crystals of a solvate of the isobutyl-legged octol **1c** with two MeOH and one EtOH molecules were obtained by slow cooling of a MeOH/EtOH 4:1 solution (*Fig. 2*; for previous X-ray crystal structures of differently legged octols, see [14]). It was actually possible to grow large transparent highly solvated rhombic crystals up to several millimeters in size, they readily lost solvent upon exposure to air and disintegrated. The bowl-shaped conformation of the octol is stabilized by very short (2.64–2.77 Å) intramolecular O–H···O H-bonds (*Fig. 2*,*a*). Each macrocycle forms a network of intermolecular O–H···O H-bonds to a neighboring octol and to the solvent molecules included in the crystal (*Fig. 2*,*b*).

Scheme 1. *Synthesis of Resorcin[4]arenes* **2**–**5**



a) Conc. HCl, EtOH, 90°, 14 h. *b*) 2,3-Dichloroquinoxaline (3 equiv.), K_2CO_3, Me_2SO, 20° (8 h), then 50° (18 h); 28% (**2a**), 35% (**3a**). *c*) 2,3-Dichloroquinoxaline (2 equiv.), K_2CO_3, Me_2SO, 20° (18 h), then 50° (6 h); 2.7% (**2a**), 16.6% (**3a**), 3.2% (**4a**), 19.6% (**5a**).

The partial bridging of octol **1a** with 3 equiv. of 2,3-dichloroquinoxaline was subsequently investigated and found to be quite sensitive to the applied experimental conditions. All reactions in DMF with K_2CO_3, Cs_2CO_3, or Et_3N as a base were unsuccessful. They afforded only the fully bridged cavitand **2a** together with some tarry product; additionally, the reaction in the presence of Et_3N was very slow. In Me_2SO [2b][15], triply bridged **3a** was obtained in 30–35% yield with K_2CO_3 as base; with Cs_2CO_3, only fully bridged **2a** was formed. Starting from octols **1b** and **1c**, lower yields of the triply bridged derivatives **3b** and **3c**, respectively, were obtained besides fully bridged **2b**,**c**; therefore, octol **1a** was selected for all future bridging experiments.

Crystals of pentyl-legged **2b** as solvate with one CH_2Cl_2 and two MeCN molecules were obtained by slow evaporation from MeCN/CH_2Cl_2. The X-ray crystal structure shows the cavitand in the *vase* conformation (*Fig. 3*,*a*) with a C_2 axis passing through the cavity (*Fig. 3*,*b*). The CH_2Cl_2 molecule is positioned deeply within the cavity at the level of the quinoxaline N-atoms. Each Cl-atom is located above the centers of two adjacent pyrazine rings, with atom-to-ring-center distances of 3.7–3.8 Å. The disordered MeCN molecules are located one atop the cavity and the second one in the space between the four pentyl legs. In the crystal lattice, the cavitand molecules stack in a head-to-tail arrangement, forming infinite, alternating antiparallel columns (see *Fig. 6* below).

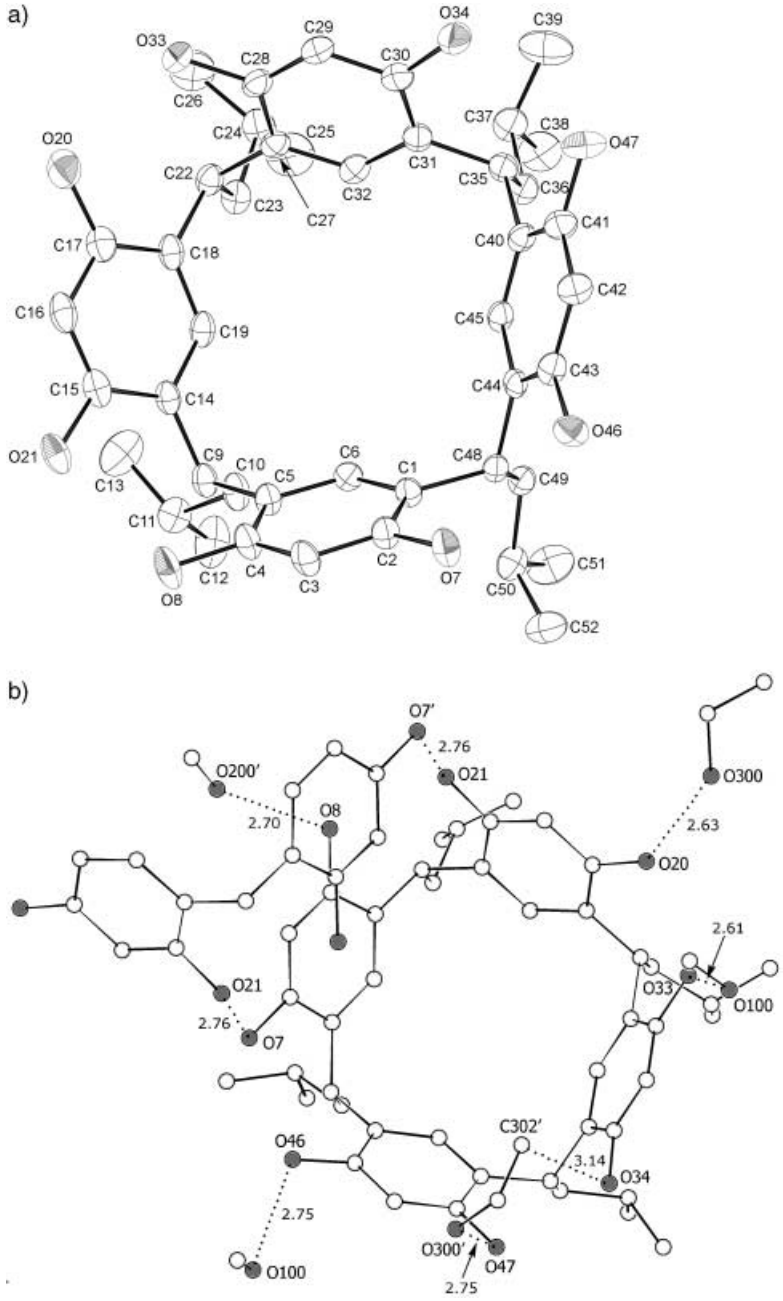


Fig. 2. a) *X-Ray crystal structure of the solvated octol* **1c** *with two MeOH and one EtOH molecules* (not shown). Arbitrary numbering. Atomic displacement parameters obtained at 233 K are drawn at the 30% probability level. Intramolecular O···O contacts [Å]: O(8)···O(21), 2.70; O(20)···O(33), 2.64; O(34)···O(47) 2.77; O(7)···O(46), 2.77. The subunit C(10)–C(13) is disordered over two orientations, here only one is shown for clarity. b) *Short intermolecular O···O contacts in the crystal packing of* **1c** *including solvent molecules and two O-atoms of the neighboring octol.* A short C–H···O interaction C(302′)···O(34) is also shown. The position of O(200′) is disordered over two orientations.

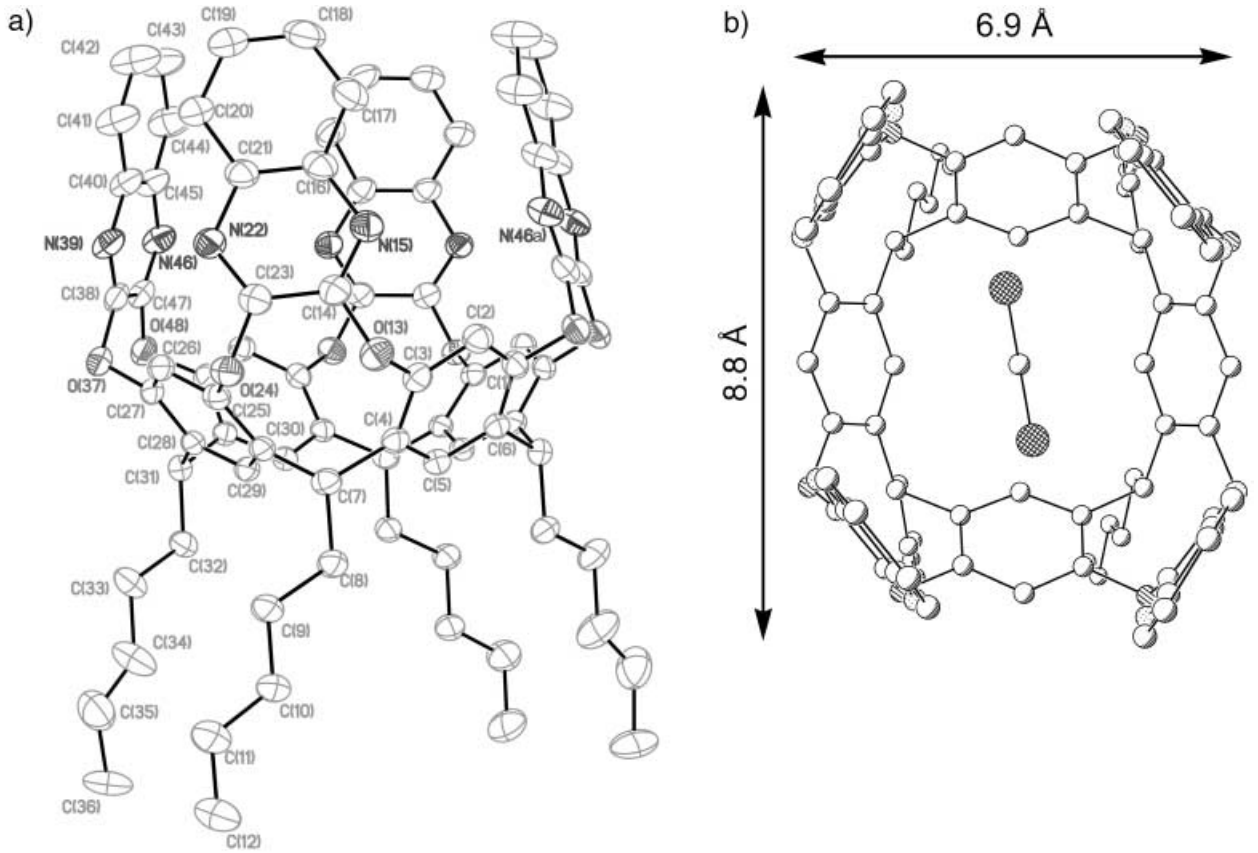


Fig. 3. a) *ORTEP Representation of the cavitand* **2b**. Arbitrary numbering. Atomic displacement parameters obtained at 295 K are drawn at the 50% probability level. Intramolecular N···N distances [Å]: N(15)···N(46a), 4.42; N(22)···N(39), 4.24. The subunit C(35)–C(36) is disordered over two orientations, here only one is shown for clarity. The CH_2Cl_2 molecule located within the cavity and two disordered MeCN molecules outside the cavity are not shown. b) *View down the* C_2 *axis into the cavity filled by the solvent.* N···Cl Distances between the Cl- and N-atoms of adjacent quinoxaline moieties range from 3.64 to 4.02 Å.

The reaction of octol **1a** with 2 equiv. of 2,3-dichloroquinoxaline (Me_2SO, K_2CO_3), followed by repeated chromatographic purification (SiO_2; CH_2Cl_2/AcOEt mixtures), afforded *anti* doubly bridged tetrol **4a** in up to 3.2% yield together with the *syn*-isomer **5a** as the major product (up to 20% yield). *Cram et al.* had previously also observed a preference for the formation of the *syn*-isomer during double bridging of an octol with methylene bridges; in fact, only the *syn*-product was isolated [16]. The chromatographic purification of the *anti*-isomer **4a** was particularly challenging due to the presence of a side product with a nearly similar retention time.

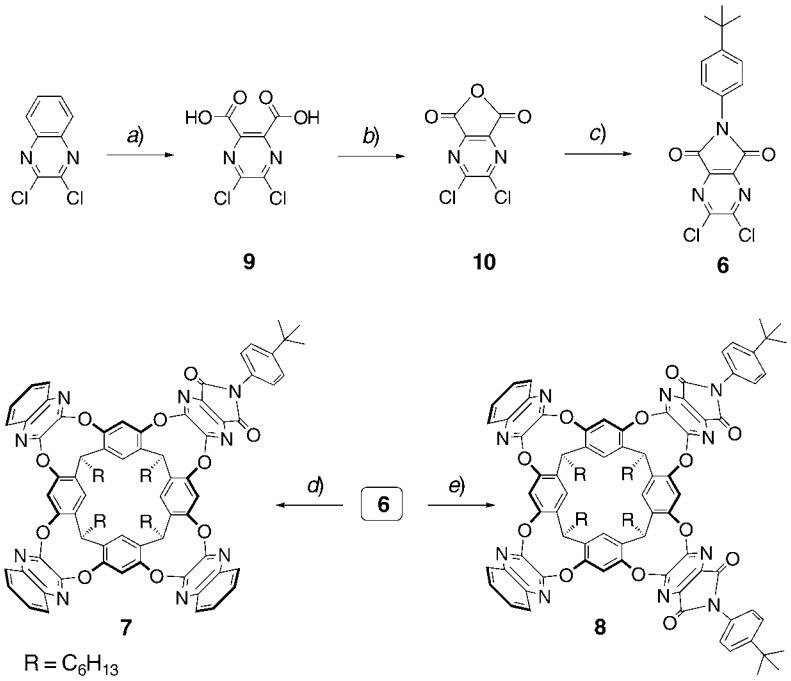
Side-products comprised structures with quinoxaline moieties attached to the octol by one ether linkage only (the structures of these colorless substances with complex NMR spectra were tentatively assigned by means of mass spectrometry (MS)) as well as colored material with a low R_f value. The latter presumably consists of products resulting from ring opening of the octol macrocycle, followed by oxidation under formation of xanthene dye-type structures [17]. Yields of the desired products increase and those of side products decrease when *i*) the starting material is freshly recrystallized and thoroughly dried under high vacuum (10^{-6} Torr) over P_2O_5, *ii*) the mixture is degassed before initiating the reaction by freeze-pump cycles, and *iii*) the reaction temperature is kept below 50°.

In a model reaction, the doubly and triply bridged octols **3a** and **5a** were transformed with dichlorodiazaphthalimide **6** into the unsymmetrically bridged cavitands **7** and **8** (*Scheme 2*). For the preparation of the bridging reagent **6**, 2,3-dichloroquinoxaline was oxidized ($KMnO_4$) to dicarboxylic acid **9** and subsequently transformed into anhydride **10** [1c]; oxalyl chloride was used instead of previously reported $SOCl_2$ as the ring-closure reagent. Heating **10** with 4-(*tert*-butyl)aniline in a small amount of Ac_2O, as reported [1c], did not prove to be very efficient, providing dichlorodiazaphthalimide **6** in only *ca.* 20% yield. On the other hand, milder conditions, with pyridine and oxalyl chloride as activation agents, afforded **6** in 86% yield. The reaction of **6** with diol **3a** and tetrol **5a** with K_2CO_3 in Me_2SO provided the fully bridged cavitands **7** and **8** in 66 and 50% yield, respectively. Neither macrocycle crystallized well; they eventually precipitated from $CHCl_3$ or THF solutions as very fine slightly yellowish powders.

For the planned single-molecule fluorescence studies, BODIPY dyes were selected as luminescent labels for their favorable electronic absorption and emission properties, and their low sensitivity to pH (which is important in proton-induced switching experiments) and environmental polarity [7]. Thus, 4-nitrobenzaldehyde was condensed with 2,4-dimethyl-3-ethylpyrrole under acidic conditions in CH_2Cl_2 to form the corresponding dipyrromethane, which was oxidized with chloranil and subsequently treated with $BF_3 \cdot OEt_2$ in the presence of Et_3N to form dye **11** in 38% yield (over the 3 steps; *Scheme 3*). Reduction of **11** (H_2, Pd/C) afforded amine **12**, which was coupled with anhydride **10** to give dichlorodiazaphthalimide **13**.

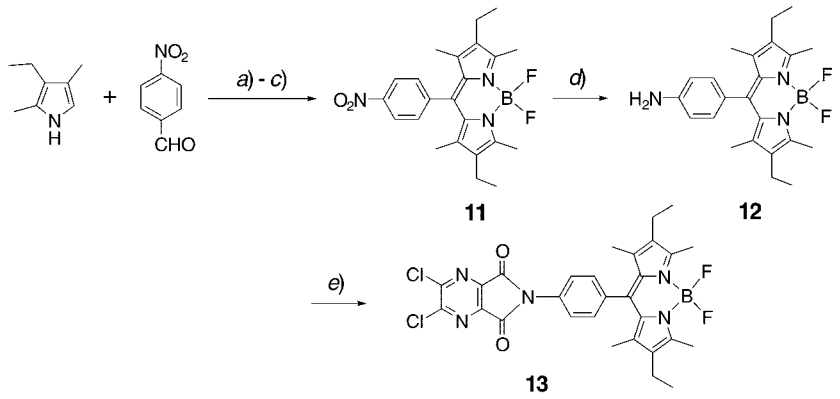
Compound **11** afforded dark-purple crystals upon slow diffusion of hexane into a $CHCl_3$ solution. The X-ray crystal structure contains three symmetry-independent molecules in the asymmetric unit with the plane of the BODIPY dye nearly orthogonal (75–87°) to the plane of the attached phenyl ring (*Fig. 4*). This should also be the case in the corresponding dye-labeled cavitands **14**–**16** (*Scheme 4*). This electronic decoupling of the π-systems ensures a very small influence of changes in the

Scheme 2. *Synthesis of the Unsymmetrically Bridged Cavitands* **7** *and* **8**



a) $KMnO_4$, H_2O, 95–97°, 2 h; 49%. *b*) $(COCl)_2$, Py (cat.), THF, 50°, 20 min; 61%. *c*) 4-(*tert*-butyl)aniline, THF, 1 h, then $(COCl)_2$, Py, 50°, 12 h; 89%. *d*) **3a** (1 equiv.), **6** (1 equiv.), K_2CO_3 (1 equiv.), Me_2SO, 20°, 24 h; 66%. *e*) **3a** (1 equiv.), **6** (2 equiv.), K_2CO_3 (2 equiv.), Me_2SO, 20°, 24 h; 50%. Py = pyridine.

Scheme 3. *Synthesis of Dichlorodiazaphthalimide* **13**



a) TFA, CH_2Cl_2, 20°, 2 h. *b*) DDQ, toluene, 1 h. *c*) NEt_3, 20° (10 min), then $BF_3 \cdot OEt_2$, 20° (30 min), then 50° (1 h); 38% (for steps *a*–*c*). *d*) H_2 (1 atm), Pd/C (10%), $CHCl_3$/EtOH 1:1, 20°, 12 h; 67%. *e*) **6**, THF, 1 h, then $(COCl)_2$, Py, 50°, 12 h; 72%. TFA = CF_3COOH, DDQ = 2,3-dichloro-5,6-dicyano-*p*-benzoquinone.

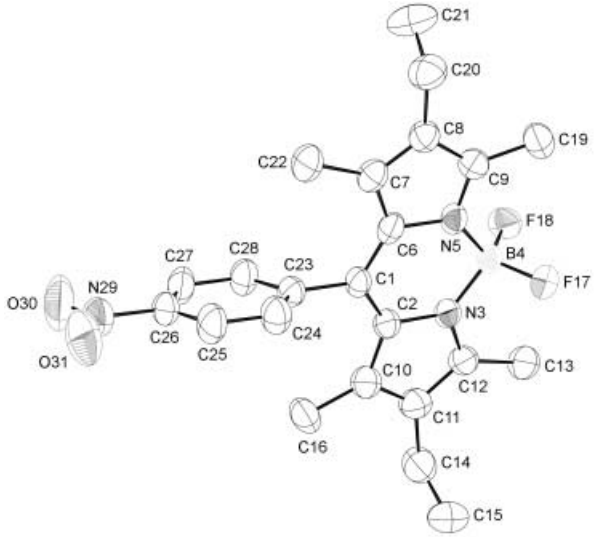


Fig. 4. *X-Ray crystal structure of BODIPY dye* **11**. Atomic displacement parameters obtained at 295 K are drawn at the 30% probability level. Only one of the three nonequivalent conformers in the elementary cell is shown.

protonation and conformation of the macrocycles on the position of the absorption and emission bands of the dye.

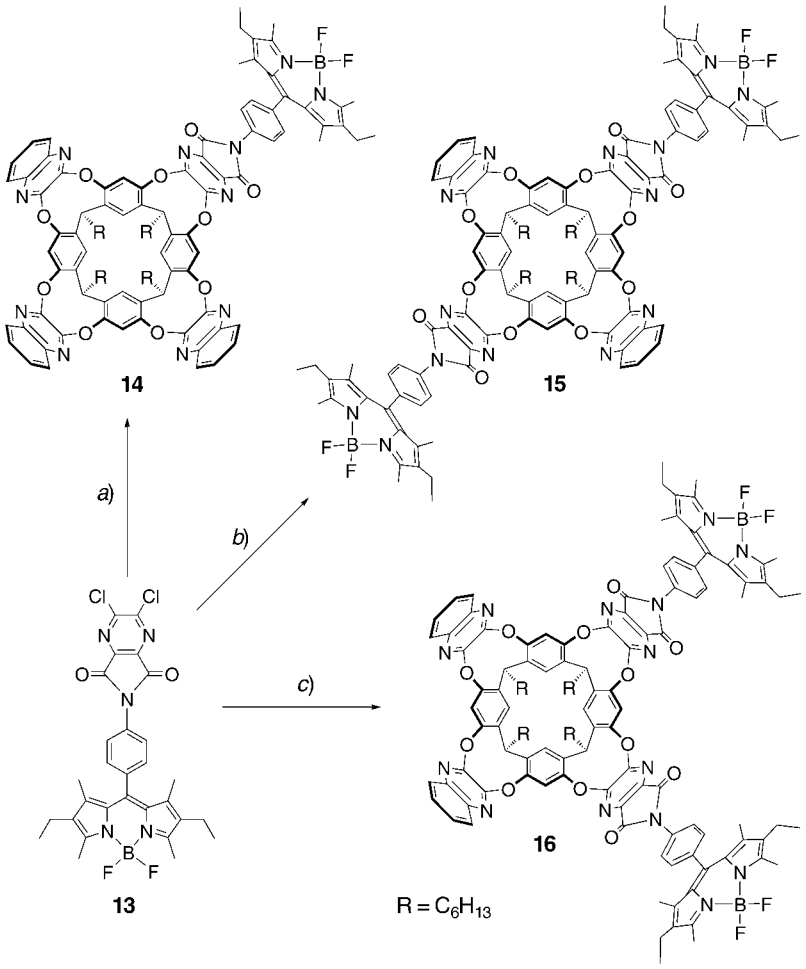
The BODIPY-substituted cavitands **14**–**16** were prepared from diol **3a**, and tetrols **4a** and **5a**, respectively, in 54–73% yield (*Scheme 4*). All three cavitands are brightly red-colored, featuring sharp optical absorption (530 nm) and emission (540 nm) maxima in $CHCl_3$ [9].

We also explored the introduction of different bridges into diol **3a** and tetrol **5a** by preparing the CH_2-bridged cavitands **17** and **18** (CH_2BrCl, K_2CO_3, Me_2SO; *Scheme 5*). The moderate yields (**17**: 55%; **18**: 48%) can be explained by the steric hindrance between neighboring quinoxalines, which is enhanced by the short, conformationally enforcing C_1-bridges in the cavitands. Interestingly, cavitand **18** could not be prepared starting with the corresponding *syn*-CH_2-bridged tetrol [16] and 2,3-dichloroquinoxaline.

Finally, octanitrocavitand **19** was synthesized [11a] (*Scheme 6*) to study its conformational properties. It is the first resorcin[4]arene cavitand without substituents in *ortho*-position to the two O-atoms of the four resorcinol moieties that prefers the *kite*-conformation both in solution [10] and in the solid state.

Crystals of **19** were obtained by slow evaporation from acetone solution. They quickly disintegrated in the air due to the evaporation of solvent enclathrated in the crystal lattice. Also, they shattered at temperatures below *ca*. 230 K, probably due to a phase transition. The X-ray crystal structure obtained at 253 K is remarkable. First, the cavitand is present in the *kite*-conformation (*Fig. 5,a*), which had not previously been observed for this type of resorcin[4]arene-based cavitands. Second, the cavitands do not form *face*-to-*face* dimers, as reported before by *Cram et al.* [1c,d] for velcraplexes,

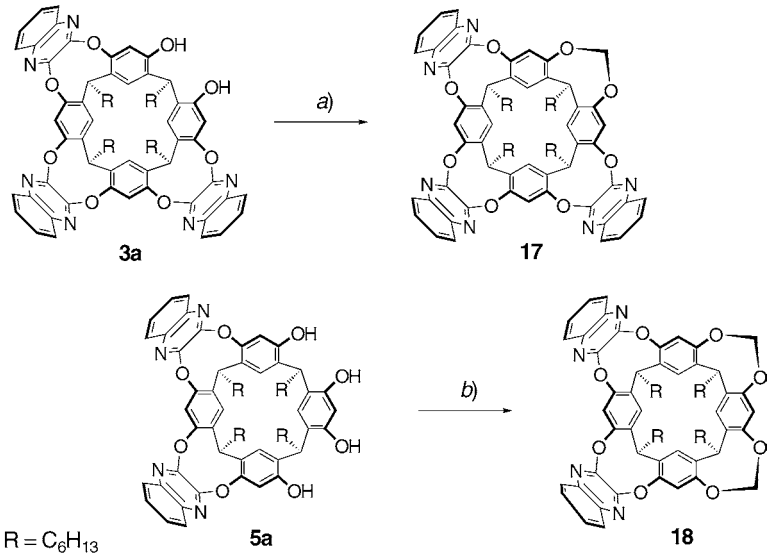
Scheme 4. *Synthesis of the Dye-Labeled Cavitands* **14**–**16**



a) **3a** (1 equiv.), **13** (1 equiv.), K_2CO_3 (1 equiv.), Me_2SO, 20°, 24 h; 73%. *b*) **4a** (1 equiv.), **13** (2.2 equiv.), K_2CO_3, (2.2 equiv.), Me_2SO, 20°, 4 h, then K_2CO_3, (2.2 equiv.), 30 min; 54%. *c*) **5a** (1 equiv.), **13** (2 equiv.), K_2CO_3 (2 equiv.), Me_2SO, 20°, 24 h; 66%.

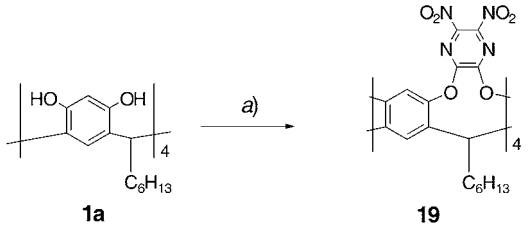
dimers of the velcrands, *i.e.*, resorcine[4]arene-based cavitands similar to those reported here but featuring Me-substituents in *ortho*-position to the two O-atoms of the four resorcinol moieties. Rather, the crystal lattice of **19** shows infinite 'head-to-tail'columns with voids filled by Me_2CO molecules (*Fig. 5*,*b*). We explain the preference of **19** for the *kite*-conformation with repulsive local dipole–dipole interactions between the eight NO_2 groups that approach each other closely in the *vase*-conformation. Dipolar repulsion between the NO_2 groups presumably also prevents the formation of *face*-to-*face* velcraplex-type dimers.

Scheme 5. *Synthesis of Cavitands* **17** *and* **18**



a) **3a** (1 equiv.), CH_2BrCl (4 equiv.), K_2CO_3 (2.5 equiv.), Me_2SO, 55°, 48 h; 55%. *b*) **5a** (1 equiv.), CH_2BrCl (10 equiv.), K_2CO_3 (4 equiv.), Me_2SO, 55°, 48 h; 47%.

Scheme 6. *Synthesis of the Octanitrocavitand* **19**



a) 1,2-Difluoro-3,4-dinitrobenzene, NEt_3, DMF, 70°, 20 h; 51%.

2.2. *Leg-Modified Cavitands.* The visualization of single cavitand molecules and the construction of practical devices require immobilization on various types of solid supports. Therefore, a substantial effort in our research program is aimed at the synthesis of cavitands suitable for surface immobilization. Previously reported modifications include the introduction of HO- [18] or NH_2-terminated legs for *i*) enhancing the solubility in aqueous media [3d], *ii*) covalent bonding to surfaces [19], and *iii*) coordination studies [20].

Cavitand **20** with four 3,5-di(*tert*-butyl)phenyl legs was prepared, since these legs had previously been shown to provide good adsorption of large molecules, such as porphyrins, on Cu surfaces for STM imaging [21]. The preparation of **20** started from 3,5-di(*tert*-butyl)phenylacetonitrile [22] that was converted *via* ester **21** into aldehyde **22** (*Scheme 7*). Acid-catalyzed condensation of **22** with resorcinol provided octol **23** in

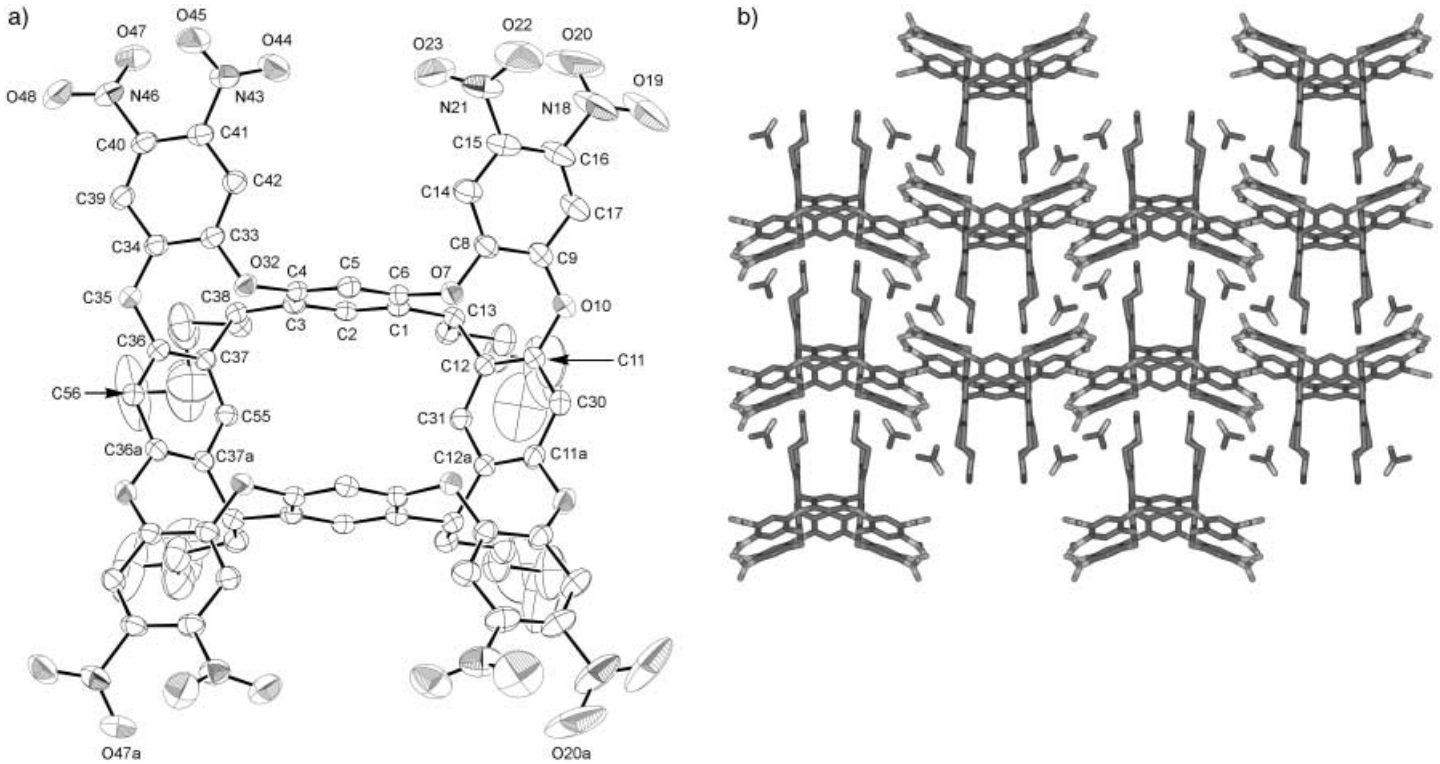
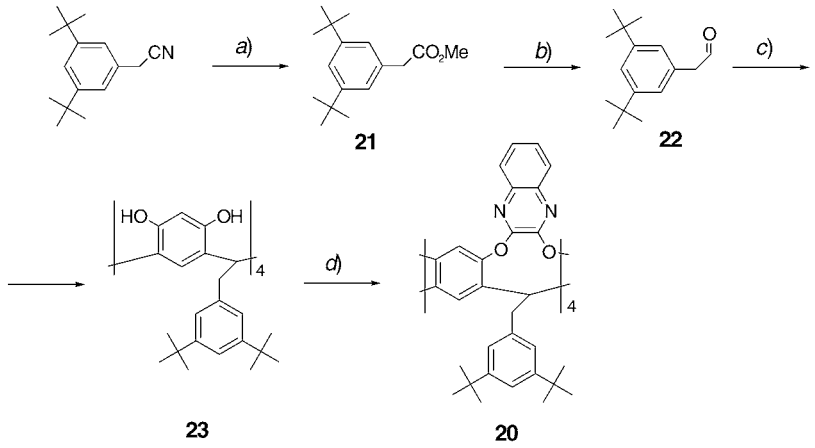


Fig. 5. a) *X-Ray crystal structure of octanitrocavitand* **19** *in a view onto the large* kite *surface*. Atomic displacement parameters obtained at 253 K are drawn at the 30% probability level. Intramolecular O ··· O distances [Å]: O(20) ··· O(20a), 15.65; O(47) ··· O(47a), 15.91; O(19) ··· O(48), 13.63. Enclathrated acetone molecules are not shown. b) *Packing diagram of* **19** *featuring columnar* head-*to*-tail *stacking.*

Scheme 7. *Synthesis of Cavitand* **20**



a) HCl/MeOH, reflux, 3 d; 99%. *b*) DIBAL-H, hexane, – 78°, 3 h; 58%. *c*) Conc. HCl, EtOH, 60°, 5 d; 35%. *d*) 2,3-Dichloroquinoxaline, Cs_2CO_3, DMF, 60°, 3 d; 68%. DIBAL-H = diisobutylaluminum hydride.

35% yield, and subsequent bridging with 2,3-dichloroquinoxaline afforded cavitand **20** in 68% yield [4]. The molecular structure of **20** in the crystal has been previously reported [4]; *Fig. 6* depicts the *head*-to-*tail* arrangements of the cavitand *vases* in the crystal lattice, leading to infinite columns, as already described for cavitands **2b** (in the *vase*-form) and **19** (in the *kite*-form). A view into these infinite columns reveals narrow channels spanning the crystal lattice.

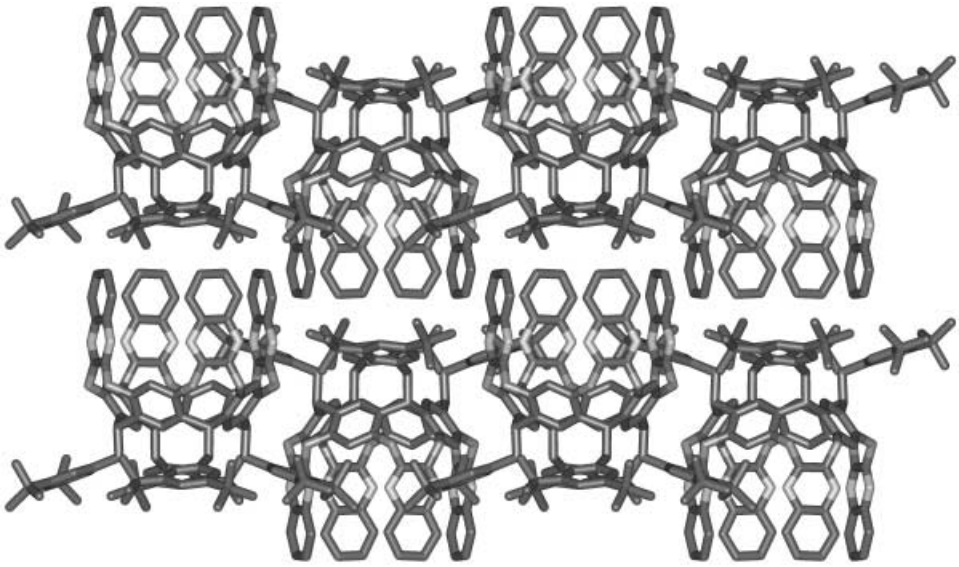
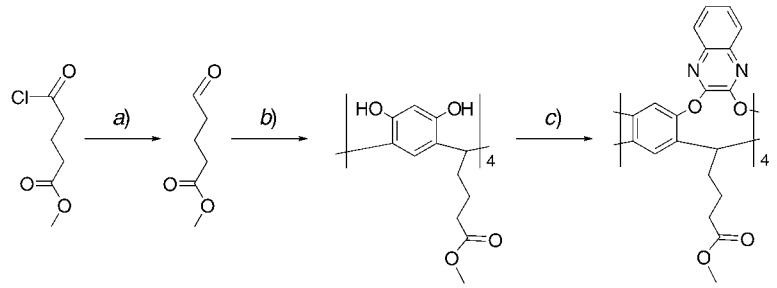


Fig. 6. *Packing diagram of cavitand* **20**

Cavitand **24**, with carboxylate legs, was prepared for *Langmuir* monolayer formation on an aqueous subphase. *Rosenmund* reduction of the acyl chloride of monomethyl glutarate gave aldehyde **25** that was condensed with resorcinol to afford octol **26** in 44% yield. Subsequent bridging with 2,3-dichloroquinoxaline provided **24** in 13% yield (*Scheme 8*). Attempts to hydrolyze the methyl ester legs proved to be fruitless; they either led to decomposition of the cavitand or left the ester intact (K_2CO_3, Li_2CO_3, or LiOH in H_2O/THF 1:3).

Scheme 8. *Synthesis of Cavitand* **24**



a) Pd/C, H_2, 2,6-dimethylpyridine, THF, 20°, 24 h. *b*) Resorcinol, conc. HCl, MeOH, 60°, 2 d; 44% (steps *a* and *b*). *c*) 2,3-Dichloroquinoxaline, Cs_2CO_3, DMF, 60°, 2 d; 13%.

Crystals of **24** were obtained by slow evaporation of a MeCN/$CHCl_3$ solution. The X-ray crystal-structure analysis at 293 K showed the cavitand in the *vase*-conformation with an asymmetric cavity (*Fig. 7*). The unit-cell contains pairs of perpendicularly aligned cavitands making *tail*-to-*tail* contacts. Disordered solvent (MeCN and, probably, H_2O) is localized within the cavity and among the ester legs.

Alkyl-thioether legs were selected due to their well-known affinity for gold surfaces under formation of stable self-assembled monolayers (SAMs) [23][24]. Cavitands **27** and **28** with alkyl-thioether legs [5] of different length were constructed employing slightly different synthetic strategies. Cavitand **27** was synthesized by acid-catalyzed condensation of resorcinol with the unsaturated aldehyde **29**, followed by bridging the resulting octol **30** to give **31** featuring legs with terminal double bonds (*Scheme 9*). The thioether moiety was introduced in the last step by 9-BBN-catalyzed radical addition of decane-1-thiol to the olefinic legs. Cavitand **28** with shorter legs was prepared by direct condensation of the thioether-containing aldehyde **32,** obtained by oxidation of alcohol **33**, with resorcinol, followed by bridging the resulting octol **34** (*Scheme 10*). SAMs formed by **31** on Au(111) were successfully prepared and imaged by UHV-STM at the molecular level showing a well-ordered monolayer [5]. On the other hand, cavitand **28**, with shorter legs, afforded only poorly ordered SAMs.

3. Conclusions. A series of *Cram*-type resorcin[4]arene-derived cavitands with modified cavity walls and legs were prepared with the aim to investigate in detail the conformational *vase*–*kite* switching in bulk solution as well as at the level of single molecules immobilized on surfaces. Initial STM studies of monolayers on gold surfaces

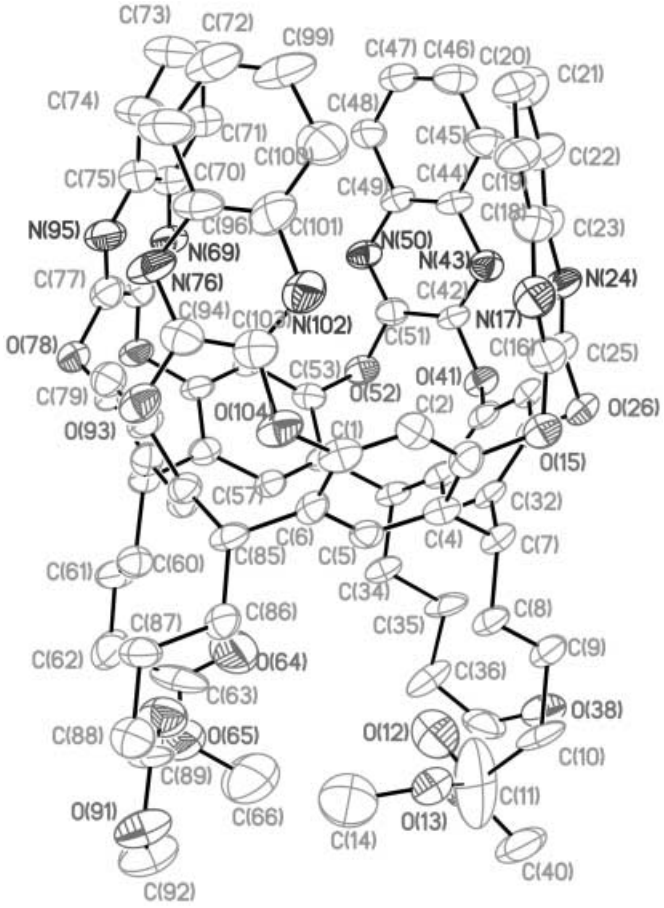
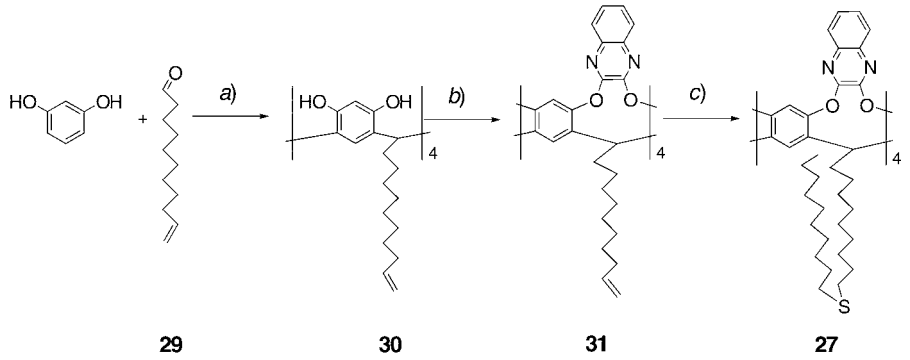


Fig. 7. *ORTEP Representation of cavitand* **24** *with atomic displacement parameters shown at the 30% probability level* (293 K). MeCN included within the cavity and solvent present among the ester tails are removed for clarity. Intramolecular N ··· N distances [Å]: N(17) ··· N(102), 4.18; N(24) ··· N(43), 4.30; N(50) ··· N(69), 4.22; N(76) ··· N(95), 4.47.

have already been reported [5], and a subsequent paper will present a detailed spectroscopic analysis of the scope and limitations of *vase–kite* switching in solution [10]. The novel substitution patterns of cavitands **15** and **16** with differential wall components open multiple opportunities for future functionalization. As an example, additional recognition sites could be attached (instead of the dye labels in **15** and **16**) for enhancing the selectivity for specific guests encapsulated in the deep cavitand cavity. Modification of the legs provided cavitands for surface immobilization and *Langmuir–Blodgett* film formation; *vase–kite* switching on surfaces and in monolayers is currently investigated in collaborative work by a variety of physical methods. This paper reports the first X-ray structural analysis of a resorcin[4]arene-based cavitand (**19**) in the *kite*-conformation. Consequently, the two different conformational

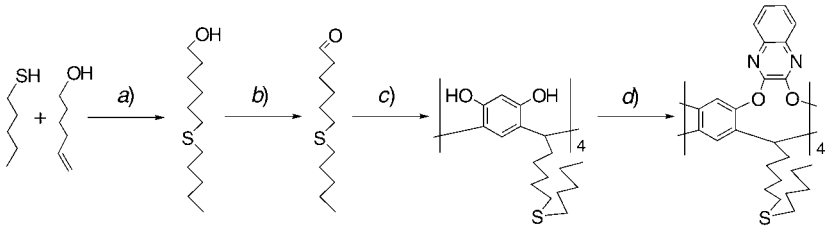
Scheme 9. *Synthesis of Cavitand* **17**



29 **30** **31** **27**

a) Conc. HCl, EtOH, 20°, 25 h; 93%. *b*) 2,3-Dichloroquinoxaline, Cs_2CO_3, Me_2SO, 20°, 2 d; 44%. *c*) Decane-1-thiol, 9-BBN, THF, 20°, 2 d; 74%. 9-BBN = *9*-Borabicyclo[3.3.1]nonane.

Scheme 10. *Synthesis of Cavitand* **28**



33 **32** **34** **28**

a) 9-BBN, THF, 20°, 3 h; 99%. *b*) PCC, CH_2Cl_2, 20°, 5 h; 31%. *c*) Conc. HCl, EtOH, 60°, 24 h; 99%. *d*) 2,3-Dichloroquinoxaline, Cs_2CO_3, Me_2SO, 20°, 4 d; 52%. PCC = pyridinium chlorochromate.

states are now structurally well-characterized in the solid state, which also provides a sound basis for the interpretation of the results of switching studies in solution [10] and at the single-molecule level.

Support by the *Swiss National Science Foundation*, *via* the *NFP 'Supramolecular Functional Materials'* and the *NCCR 'Nanoscience'* is gratefully acknowledged. *Y. Y.* thanks the *Japan Science Technology Corporation Overseas Fellowship Program* for a postdoctoral fellowship.

Experimental Part

General. Reagent-grade solvents and reagents were purchased and used without further purification (except for 2,3-dichloroquinoxaline that was recrystallized from EtOH or MeOH). Octols **1a**–**1c** were prepared according to [13]; they were purified by recrystallization (2×) from MeOH (**1a** and **1b)** or MeOH/EtOH 4:1 (**1c**; for X-ray, see *Fig. 2*) and dried under high vacuum over P_2O_5 to afford the products as slightly pinkish powders. Diol **3a** was prepared according to [2b], and pyrazine derivatives **9** and **10** according to [1c]. Cavitands **2a** [2b], and **2b** and **2c** [1b] have been previously reported (for the X-Ray crystal structure of **2b**, see *Fig. 3*). All reactions were carried out under Ar or N_2 atmosphere. Flash chromatography (FC): SiO_2 from *Fluka* or *Merck* 230–400 mesh (particle size 40–63 μm). Anal. TLC: precoated SiO_2 glass plates with *F-254* fluorescent indicator; visualization with UVlight at 254 or 366 nm. M.p.: *Büchi Melting Point B-540*; uncorrected. The m.p.

of the highly colored BODIPY dyes could not be accurately determined. UV/VIS [nm]: *Varian Cary-500 Scan* spectrophotometer; λ_{max} in nm (ε in M^{-1} cm^{-1}). Fluorescence: *Instruments S. A. Fluorolog-3* spectrofluorometer. IR [cm^{-1}]: *Perkin-Elmer 1600-FTIR*; in CCl_4 or in KBr pellets. ^1H-, ^{13}C-, and ^{19}F-NMR spectra [ppm]: *Varian Mercury-300* spectrometers at r.t.; internal references [ppm]: $CDCl_3$: 7.26 (^1H), 77.23 (^{13}C); CD_2Cl_2: 5.32 (^1H), 53.80 (^{13}C); $(CD_3)_2CO$: 2.05 (^1H), 29.80 (^{13}C); CD_3OD: 3.31 (^1H), 49.15 (^{13}C); (D_8)THF (C_4D_8O): 1.73 (^1H), 25.20 (^{13}C); $CFCl_3$ was used as a reference for ^{19}F-NMR (0.00 ppm). FT-ICR-MALDI-MS: *Ion Spec Ultima FT-ICR-MS* (337-nm N_2-laser system); matrix: DHB (2,3-hydroxybenzoic acid) or DCTB ({(2*E*)-3-[4-(*tert*-butyl)phenyl]-2-methylprop-2-enylidene}malonitrile). EI-MS: *VG Analytical Tribrid, USA*. FAB-MS: *VG Analytical ZAB2-SEQ, USA*. Elemental analyses were performed by the *Mikrolabor* at the Laboratorium für Organische Chemie, ETH Zürich.

r-*11*,c-*13*,c-*29*,c-*36-Tetrahexyl-7,10:12,15:24,27:29,32-tetraethano-8,31:14,25-dimethano-11*H,*28*H-*[1,4,14,17]-tetraoxacyclohexacosino[2,3*-b*:15,16-b′]diquinoxaline-36,38,42,43-tetrol* (**4a**) *and* r-*11*,c-*13*,c-*29*,c-*36-Tetrahexyl-9,15-(methano[1,3]benzenomethano)-11*H,*13*H-*benzo[1″,2″:5,6;-5″,4″:5′,6′]bis[1,4]benzodioxonino[2,3*-b*:2′,3′-b′]diquinoxaline-8,16,33,35-tetrol* (**5a**). To a degassed (freeze-pump) soln. of **1a** (2.48 g, 3.01 mmol) in Me_2SO (40 ml), K_2CO_3 (0.416 g, 3.01 mmol) and 2,3-dichloroquinoxaline (1.20 g, 6.02 mmol) were added, and the mixture was stirred for 1 h. More K_2CO_3 (0.832 g, 6.02 mmol) was added, and stirring under Ar was continued for 18 h at r.t. and 6 h at 50°. After cooling, the brown soln. was added to H_2O (50 ml), and the pH was adjusted to 6–7 by addition of 1M HCl. The pink precipitate formed was isolated by filtration, washed with H_2O (50 ml), and dried under high vacuum over P_2O_5. FC (SiO_2; CH_2Cl_2/AcOEt 95:5 → 85:5) afforded **2a** (107 mg, 2.7%) **3a** (603 mg, 16.6%), **4a** (103 mg, 3.2%), and **5a** (637 mg, 19.6%). *Data of* **4a**: R_f (SiO_2; CH_2Cl_2/AcOEt 90:10) 0.3. M.p. > 285° (dec.). IR (KBr): 3404 (br.), 2927, 2857, 1616, 1584, 1490, 1466, 1412, 1335, 1281, 1224, 1169, 1073, 894, 858, 760, 606. ^1H-NMR ($(CD_3)_2CO$, 300 MHz): 0.88–0.94 (*m*, 12 H); 1.25–1.48 (*m*, 32 H); 2.36-2.45 (*m*, 8 H); 4.56 (*t*, *J* = 7.8, 2 H); 5.51 (*t*, *J* = 7.8, 2 H); 7.15 (*s*, 4 H); 7.27–7.32 (*m*, 4 H); 7.55–7.60 (*m*, 4 H); 7.75 (*s*, 4 H); 9.04 (*s*, 4 H). ^{13}C-NMR ($(CD_3)_2CO$, 75 MHz): 14.36; 23.35; 28.88; 28.97; 32.69; 32.73; 33.99; 34.79; 34.96; 110.93; 125.33; 127.99; 129.62; 130.11; 131.69; 139.92; 152.70; 152.93; 153.08. HR-MALDI-MS (DHB): 1099.5568 ($[M + Na]^+$, $C_{68}H_{76}N_4O_8Na^+$; calc.: 1099.5555). *Data of* **5a**: R_f (SiO_2; CH_2Cl_2/AcOEt 85:15) 0.3. M.p. > 270° (dec.). IR (KBr): 3416 (br.), 2927, 2857, 1619, 1585, 1491, 1414, 1336, 1285, 1235, 1153, 1119, 1078, 899, 852, 759, 607. ^1H-NMR ($(CD_3)_2CO$, 300 MHz): 0.86–0.95 (*m*, 12 H); 1.24–1.50 (*m*, 32 H); 2.21–2.39 (*m*, 4 H); 2.41–2.51 (*m*, 4 H); 4.30 (*t*, *J* = 8.1, 2 H); 5.51 (*t*, *J* = 8.1, 2 H); 6.18 (*s*, 1 H); 7.13 (*s*, 2 H); 7.50 (*s*, 1 H); 7.62–7.81 (*m*, 8 H); 7.95 (*s*, 1 H); 8.08–8.11 (*m*, 2 H); 8.36 (*s*, 1 H); 8.72 (*s*, 4 H). ^{13}C-NMR ($(CD_3)_2CO$, 75 MHz): 14.34; 14.38; 23.33; 23.36; 28.87; 28.97; 32.60; 32.71; 34.08; 34.52; 35.15; 103.49; 110.73; 118.70; 124.39; 125.107; 125.62; 125.75; 128.37; 128.72; 130.09; 130.19; 130.47; 130.98; 137.88; 140.33; 140.38; 152.08; 152.80; 153.29; 153.37. HR-MALDI-MS (DHB): 1099.5563 ($[M + Na]^+$, $C_{68}H_{76}N_4O_8Na^+$; calc.: 1099.5555).

5,6-Dichloropyrazine-2,3-dicarboxylic Acid 4-(tert-*Butyl*)*phenylimide* **(6)**. To **10** (0.197 g, 0.90 mmol) in THF (3 ml), 4-(*tert*-butyl)aniline (0.144 ml, 0.90 mmol) was added, and the mixture was stirred for 2 h at r.t. under Ar. Oxalyl chloride (0.085 ml, 0.99 mmol) and pyridine (0.160 ml, 1.98 mmol) were added, and the mixture was heated to 50° for 12 h. After filtration, the mixture was evaporated to dryness, and the residue was co-evaporated with heptane (3×) to remove traces of pyridine. FC (SiO_2; CH_2Cl_2/cyclohexane 3:1) gave **6** (279 mg, 89%). Pale-yellow crystals. M.p. 268–268.5°. R_f (SiO_2; CH_2Cl_2/cyclohexane 3:1) 0.25. ^1H-NMR ($CDCl_3$, 300 MHz): 1.36 (*s*, 9 H); 7.33–7.38 (*m*, 2 H); 7.53–7.58 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 31.54; 35.15; 125.94; 126.60; 127.53; 143.24; 152.48; 154.09; 161.34.

7-[4-(tert-*Butyl)phenyl]-60-*endo,*64-*endo,*68-*endo,*72-*endo-*tetrahexyl-2,12,16,27,31,42,46,57-octaoxa-4,7,10,18,25,33,40,48,55-nonaazaheptadecacyclo[56.15.1.1*^{59,73}*.0*^{3,11}*.0*^{5,9}*.0*^{13,71}*.0*^{15,69}*.0*^{17,26}*.0*$^{1\ 9,24}$*.0*^{28,67}*.0*^{30,65}*.0*^{32,41}*.0*^{34,39}*.0*^{43,63}*.0*^{45,61}*.0*^{47,56}*.0*^{49,54}*]pentaheptaconta-1(73),3,5(9),10,13,15(69),17,19(24),20,22,25,28,30(65),32,34(39),35,37,40,43,45(61),47,49(54),50,52,55,58(74),59(75),62,66,70-triacontaene-6,8-dione* (**7**). To **3a** (0.081 g, 0.067 mmol) and **6** (0.024 g, 0.067 mmol) in degassed Me_2SO (2.5 ml), K_2CO_3 (0.012 g, 0.084 mmol) was added, and the mixture was stirred under Ar at r.t. for 40 h. After addition of H_2O, the precipitate formed was isolated by filtration, washed with H_2O (5 ml), and dried under vacuum over P_2O_5. FC (SiO_2; CH_2Cl_2/AcOEt 100:0 → 98:2) afforded **7** (65 mg, 66%). Yellowish powder. R_f (SiO_2; CH_2Cl_2/AcOEt 98:2) 0.43. M.p. > 340° (dec.). IR (KBr): 3070, 2955, 2927, 2858, 1795, 1742, 1606, 1570, 1516, 1482, 1414, 1362, 1333, 1265, 1223, 1159, 1118, 1091, 1066, 913, 898, 761, 604. ^1H-NMR ($CDCl_3$, 300 MHz): 0.90–0.96 (*m*, 12 H); 1.27–1.53 (*m*, 32 H); 1.43 (*s*, 9 H); 2.20–2.32 (br. *m*, 8 H); 5.46 (*t*, *J* = 7.8, 1 H); 5.50–5.59 (*m*, 3 H); 7.11–7.15 (*m*, 2 H); 7.20 (*s*, 2 H); 7.23 (*s*, 2 H); 7.33–7.60 (*m*, 8 H); 7.81–7.93 (*m*, 6 H); 8.13 (*s*, 2 H); 8.16 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.42; 22.99; 28.21; 29.67; 31.65; 32.16; 32.57; 32.75; 34.66; 35.18; 118.53; 118.96; 123.50; 123.80; 125.92; 126.35; 127.58; 127.87; 128.08; 128.70; 129.23; 129.46; 135.41; 135.55; 135.81; 136.85; 139.62; 139.76; 141.14; 152.05; 152.16; 152.24;

152.37; 152.63; 152.79; 152.87; 158.44; 161.77. HR-MALDI-MS (DHB): 1480.6805 (MH^+, $C_{92}H_{90}N_9O_{10}^+$; calc.: 1480.6805).

*7,21-Bis[4-(*tert*-butyl)phenyl]-59-*endo*,63-*endo*,67-*endo*,71-*endo*-tetrahexyl-2,12,16,26,30,41,45,56-octaoxa-4,7,10,18,21,24,32,39,47,54-decaazaheptadecacyclo[55.15.1.1^{58,72}.0^{3,11}.0^{5,9}.0^{13,70}.0^{15,68}.0^{17,25}.0^{19,23}.0^{27,66}.0^{29,64}.0^{31,40}.0^{33,38}.0^{42,62}.0^{44,60}.0^{46,55}.0^{48,53}]tetraheptaconta-1(72),3,5(9),10,13,15(68),17,19(23),24,27,29(64),31,33(38),34,36,39,42,44(60),46,48(53),49,51,54,57(73),58(74),61,65,69-octacosaene-6,8,20,22-tetrone* (**8**). To **5a** (0.060 g, 0.056 mmol) and **6** (0.039 g, 0.11 mmol) in degassed Me_2SO (2 ml), K_2CO_3 (0.019 g, 0.139 mmol) was added, and the mixture was stirred under Ar at r.t. for 24 h. H_2O (5 ml) was added, and the formed precipitate was isolated by filtration. Washing with H_2O (5 ml), drying under vacuum over P_2O_5, and FC (SiO_2; CH_2Cl_2/AcOEt 100:0 → 97:3) afforded **8** (46 mg, 50%). Yellowish powder. R_f = (SiO_2; CH_2Cl_2/AcOEt 98:2) 0.45. M.p. > 350° (dec.). IR (KBr): 3073, 2956, 2927, 2859, 1797, 1741, 1696, 1579, 1517, 1483, 1413, 1369, 1333, 1265, 1223, 1202, 1160, 1090, 1065, 914, 900, 817, 764; 603. ^{1}H-NMR ((D$_8$)THF, 300 MHz): 0.93–0.97 (*m*, 12 H); 1.36–1.54 (*m*, 32 H); 1.43 (*s*, 18 H); 2.36–2.47 (*m*, 8 H); 5.67 (*t*, *J* = 8.1, 2 H); 5.78 (*t*, *J* = 8.1, 2 H); 7.04–7.09 (*m*, 4 H); 7.32–7.60 (*m*, 12 H); 7.96–7.99 (*m*, 5 H); 8.24–8.25 (*m*, 3 H). ^{13}C-NMR ((D$_8$)THF, 75 MHz): 14.34; 23.47; 28.81; 28.85; 30.06; 30.11; 31.72; 32.77; 32.92; 34.93; 35.04; 35.29; 119.61; 119.99; 124.18; 124.63; 125.28; 125.95; 127.11; 128.38; 129.38; 129.64; 129.86; 130.17; 136.57; 136.72; 137.21; 137.76; 140.15; 140.27; 142.62; 142.96; 151.39; 152.66; 152.92; 153.07; 153.47; 153.57; 157.60; 157.85; 161.57; 162.27. HR-MALDI-MS (DHB): 1631.7306 (MH^+, $C_{100}H_{99}N_{10}O_{12}^+$; calc.: 1631.7444).

*2,8-Diethyl-5,5-difluoro-1,3,7,9-tetramethyl-10-(4-nitrophenyl)-dipyrrolo[1,2-*c*:2,1-*f*][1,3,2]diazaborinin-4-ium-5-uide* (**11**). A soln. of 2,4-dimethyl-3-ethyl-1*H*-pyrrole (3.21 g, 26.1 mmol) and 4-nitrobenzylaldehyde (1.97 g, 13.0 mmol) in CH_2Cl_2 (500 ml) was degassed (bubbling N_2 for 1 h), and TFA (0.10 ml, 1.3 mmol) was added. After stirring for 2 h at r.t., the mixture was washed with sat. aq. $NaHCO_3$ soln., H_2O, and sat. aq. NaCl soln., dried (Na_2SO_4), and evaporated to yield the intermediate dipyrromethane (4.98 g). This compound (4.01 g, 10.6 mmol) was dissolved in PhMe (50 ml), and DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone, 2.41 g, 10.6 mmol) was added as a suspension in PhMe (100 ml). After stirring for 1 h at r.t., Et_3N (4.4 ml, 32 mmol) was added to the black mixture, and, 10 min later, $BF_3 \cdot OEt_2$ (6.7 ml, 53 mmol) was added. The mixture was stirred at r.t. for 30 min, then heated to 50° for 1 h. After cooling, the mixture was filtered through a short plug (SiO_2; toluene), and the soln. was evaporated to dryness. FC (SiO_2; PhMe CH_2Cl_2/cyclohexane 3:2) gave **11** (1.71 g, 38%). Dark-red powder; purple soln. in $CHCl_3$. M.p. 193.5–196°. R_f (SiO_2; CH_2Cl_2/cyclohexane 3:2) 0.4. UV/VIS ($CHCl_3$): 533 (70000). Fluorescence ($CHCl_3$): 540. IR (CCl_4): 2966, 2930, 2873, 2853, 1600, 1543, 1530, 1475, 1411, 1388, 1346, 1320, 1192, 1161, 1114, 1083, 1054, 980, 856. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.98 (*t*, *J* = 7.5, 6 H); 1.26 (*s*, 6 H); 2.32 (*q*, *J* = 7.5, 4 H); 2.54 (*s*, 6 H); 7.51–7.55 (*m*, 2 H); 8.35–8.40 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 12.32; 12.91; 14.88; 17.36; 77.43; 124.36; 129.99; 133.57; 136.88; 137.76; 142.92; 148.25; 154.99. ^{19}F-NMR ($CDCl_3$, 282.5 MHz): −145.96 (*q*, *J* = 35). HR-MALDI-MS (DHB): 425.2083 (M^+, $C_{23}H_{26}BF_2N_3O_2^+$; calc.: 425.20807). X-Ray: see *Fig. 4*.

*10-[4-Aminophenyl]-2,8-diethyl-5,5-difluoro-1,3,7,9-tetramethyldipyrrolo[1,2-*c*:2,1-*f*][1,3,2]diazaborinin-4-ium-5-uide* (**12**). To **11** (485 mg, 1.14 mmol) in CH_2Cl_2/EtOH 1:1 (30 ml), Pd/C 10% (62 mg) was added, and the mixture was stirred under H_2 for 12 h. Filtration through *Celite*, evaporation to dryness, and FC (SiO_2; CH_2Cl_2) afforded **12** (301 mg, 67%). Orange powder; bright-orange soln. in $CHCl_3$. M.p. 280-285° (dec.). R_f (SiO_2; CH_2Cl_2) 0.47. UV/VIS ($CHCl_3$): 526 (71000). Fluorescence ($CHCl_3$): 536. IR (KBr): 3507, 3415, 2962, 2925, 2869, 1620, 1529, 1474, 1402, 1318, 1276, 1193, 1161, 1114, 1083, 1055, 1016, 976, 867, 831, 798, 761, 707, 659, 612, 534. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.98 (*t*, *J* = 7.5, 6 H); 1.40 (*s*, 6 H); 2.31 (*q*, *J* = 7.5, 4 H); 2.52 (*s*, 6 H); 3.82 (br. *s*, 2 H); 6.75–6.80 (*m*, 2 H); 6.99–7.03 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 12.26; 12.80; 14.99; 17.41; 115.55; 125.71; 129.33; 131.47; 132.58; 138.62; 141.13; 146.90; 153.26. ^{19}F-NMR ($CDCl_3$, 282.5 MHz): −145.29 (*q*, *J* = 35). HR-MALDI-MS (DHB): 395.2341 (M^+, $C_{23}H_{28}BF_2N_3^+$; calc.: 395.23389). Anal. calc. for $C_{23}H_{28}BF_2N_3$ (395.296): C 69.88, H 7.14, B 2.73, F 9.61, N 10.63; found: C 69.71, H 6.91, N 10.47.

*10-[4-(2,3-Dichloro-5,7-dioxo-6,7-dihydro-5*H*-pyrrolo[3,4-*b*]pyrazin-6-yl)phenyl]-2,8-diethyl-5,5-difluoro-1,3,7,9-tetramethyldipyrrolo[1,2-*c*:2,1-*f*][1,3,2]diazaborinin-4-ium-5-uide* (**13**). To **7** (0.109 g, 0.497 mmol) in THF (4 ml), **12** (0.187 g, 0.473 mmol)) was added, and the soln. was stirred for 1 h at r.t. under Ar. Oxalyl chloride (0.048 ml, 0.57 mmol) and pyridine (0.115 ml, 1.42 mmol) were added, and the mixture was heated to 50° for 12 h. The soln. obtained after filtration was evaporated to dryness, and the residue co-evaporated with heptane (3 ×) to remove traces of pyridine. FC (SiO_2; CH_2Cl_2) afforded **13** (212 mg, 72%). Red powder; bright-purple soln. in $CHCl_3$. M.p. 285–295° (dec.). R_f = (SiO_2; CH_2Cl_2) 0.55. UV/VIS ($CHCl_3$): 530 (73000). Fluorescence ($CHCl_3$): 537. IR (KBr): 2965, 2930, 2871, 1803, 1740, 1541, 1518, 1477, 1388, 1373, 1320, 1272, 1234, 1194, 1161, 1116, 1067, 979, 803, 760, 702, 536. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.99 (*t*, *J* = 7.5, 6 H); 1.35 (*s*, 6 H); 2.31 (*q*, *J* = 7.5, 4 H); 2.52 (*s*, 6 H); 7.48–7.52 (*m*, 2 H); 7.62–7.66 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 12.34;

12.87; 14.94; 17.42; 77.43; 126.70; 129.56; 130.67; 131.03; 133.26; 136.62; 138.35; 143.01; 154.34; 160.92. ^{19}F-NMR ($CDCl_3$, 282.5 MHz): −145.14 (*q*, *J* = 35). HR-MALDI-MS (DHB): 595.1523 (M^+, $C_{29}H_{26}BCl_2F_2N_5O_2^+$; calc. 595.15192).

Compound **14** (for nomenclature and full characterization, see [9]). Preparation as described for **7** from **3a** (0.060 g, 0.050 mmol), **13** (0.030 g, 0.050 mmol), and K_2CO_3 (0.0086 g, 0.062 mmol) in Me_2SO (2.5 ml). CC (SiO_2; CH_2Cl_2/AcOEt 100 : 0 → 98 : 2) afforded **14** (63 mg, 73%). Bright-red solid.

Compound **15** (for nomenclature and full characterization, see [9]). To a degassed soln. of **4a** (0.018 g, 0.0167 mmol) and **13** (0.022 g, 0.0367 mmol) in Me_2SO (1 ml), K_2CO_3 (0.0051 g, 0.0367 mmol) was added. After stirring under Ar at r.t. for 4 h, additional K_2CO_3 (0.0051 g, 0.0367 mmol) was added. A dark-red precipitate formed within 30 min, H_2O (5 ml) was added, and the precipitate was isolated by filtration, washed with H_2O (5 ml), and dried under vacuum over P_2O_5. FC (SiO_2; CH_2Cl_2/AcOEt 100 : 0 → 97 : 3) provided **15** (19 mg, 54%). Bright-red solid.

Compound **16** (for nomenclature and full characterization, see [9]). Preparation as described for **8** from **5a** (0.035 g, 0.032 mmol), **13** (0.038 g, 0.064 mmol), and K_2CO_3 (0.009 g, 0.064 mmol) in Me_2SO (1.5 ml). FC (SiO_2; CH_2Cl_2/AcOEt 100 : 0 → 97 : 3) gave **16** (45 mg, 66%). Bright-red solid.

52-endo,*56*-endo,*60*-endo,*64*-endo-*Tetrahexyl-2,4,8,19,23,34,38,49-octaoxa-10,17,25,32,40,47-hexaazapentadecacyclo[48.15.1.1^{51,65}.0^{5,63}.0^{7,61}.0^{9,18}. 0^{11,16}.0^{20,59}.0^{22,57}.0^{24,33}.0^{26,31}.0^{35,55}.0^{37,53}.0^{39,48}.0^{41,46}]heptahexaconta-1(65),5,7(61),9,11(16),12,14,17,20,22(57),24,26(31),27,29,32,35,37 (53),39,41(46),42,44,47,50(66),51(67),54,58,62-heptacosaene* (**17**). To a degassed soln. of **3a** (0.088 g, 0.073 mmol) in Me_2SO (4 ml), K_2CO_3 (0.015 g, 0.109 mmol) and CH_2BrCl (0.019 ml, 0.29 mmol) were added, and the mixture was stirred for 12 h at 45° under Ar. Additional K_2CO_3 (0.10 g, 0.073 mmol) and CH_2BrCl (0.019 ml, 0.29 mmol) were added, and the mixture was stirred at 55° for 30 h. After addition of cold H_2O (10 ml), the precipitate formed was isolated by filtration and dried (P_2O_5). FC (SiO_2; CH_2Cl_2/AcOEt 100 : 0 → 97 : 3) provided **17** (49 mg, 55%). Colorless amorphous solid. R_f (SiO_2; CH_2Cl_2/cyclohexane 3 : 1) 0.37. M.p. 335° (dec.). IR (KBr): 3067, 2954, 2927, 2857, 1607, 1579, 1570, 1485, 1415, 1334, 1276, 1222, 1162, 1118, 1068, 972, 913, 896, 759, 606. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.91 – 0.98 (*m*, 12 H); 1.32 – 1.55 (*m*, 32 H); 2.22 – 2.37 (*m*, 8 H); 4.10 (*d*, *J* = 7.2, 1 H); 4.71 (*t*, *J* = 8.1, 1 H); 5.66 (*d*, *J* = 7.2, 1 H); 5.71 (*m*, 3 H); 7.22 (*s*, 2 H); 7.23 (*s*, 2 H); 7.24 (*s*, 2 H); 7.44 – 7.59 (*m*, 6 H); 7.68 – 7.72 (*m*, 2 H); 7.86 – 7.93 (*m*, 4 H); 8.29 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.30; 22.89; 28.07; 28.18; 29.62; 29.70; 30.62; 32.09; 32.34; 32.55; 34.30; 34.46; 36.55; 99.63; 117.38; 118.92; 121.88; 123.94; 128.02; 129.28; 129.36; 129.49; 135.42; 136.12; 136.53; 138.66; 139.90; 139.94; 152.18; 152.67; 152.88; 152.92; 153.09; 155.44. HR-MALDI-MS (DHB): 1215.5966 (MH^+, $C_{77}H_{79}N_4O_8^+$; calc.: 1215.59602).

43-endo,*47*-endo,*51*-endo,*55*-endo-*Tetrahexyl-2,4,8,10,14,25,29,40-octaoxa-16,23,31,38-tetraazatridecacyclo-[39.15.1.1^{42,56}.0^{5,54}.0^{7,52}.0^{11,50}.0^{13,46}.0^{15,24}.0^{17,22}.0^{26,46}.0^{28,44}.0^{30,39}.0^{32,37}]octapentaconta-1(56),5,7(52),11,13(48),15,17(22),18,20,23,26,28(44),30,32(37),33,35,38,41(57),42(58),45,49,53-docosaene* (**18**). To a degassed soln. of **5a** (0.070 g, 0.066 mmol) in Me_2SO (3 ml), K_2CO_3 (0.036 g, 0.26 mmol) and CH_2BrCl (0.042 ml, 0.65 mmol) were added, and the mixture was stirred under Ar for 12 h at 55°. Additional K_2CO_3 (0.018 g, 0.13 mmol) and CH_2BrCl (0.021 ml, 0.325 mmol) were added, and the mixture was stirred for 24 h. After addition of cold H_2O (10 ml), the precipitate formed was isolated by filtration and dried (P_2O_5). FC (SiO_2; CH_2Cl_2/AcOEt 100 : 0 → 99.5 : 0.5) afforded **18** (34 mg, 47%). Colorless powder. R_f (SiO_2; CH_2Cl_2/cyclohexane 3 : 1) 0.42. M.p. 295° (dec.). IR (KBr): 3068, 2954, 2927, 2857, 1607, 1579, 1486, 1414, 1333, 1284, 1261, 1222, 1118, 1073, 973, 914, 896, 760, 719, 606. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.89 – 0.97 (*m*, 12 H); 1.30 – 1.57 (*m*, 32 H); 2.19 – 2.35 (*m*, 8 H); 4.16 (*d*, *J* = 7.2, 2 H); 4.71 (*t*, *J* = 8.1, 2 H); 5.65 (*d*, *J* = 7.2, 2 H); 5.73 (*t*, *J* = 8.1, 2 H); 6.33 (*s*, 1 H); 7.14 (*s*, 1 H); 7.19 (*s*, 1 H); 7.21 (*s*, 2 H); 7.32 (*s*, 2 H); 7.55 – 7.67 (*m*, 4 H); 7.83 (br. *d*, *J* = 7.8, 2 H); 8.01 (br. *d*, *J* = 7.8, 2 H); 8.34 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.41; 22.98; 23.01; 28.14; 28.30; 29.73; 29.79; 30.51; 32.18; 32.21; 32.28; 34.54; 36.60; 99.54; 116.61; 117.15; 118.72; 120.28; 121.97; 124.33; 128.03; 129.38; 129.65; 135.34; 136.25; 137.86; 139.01; 139.88; 151.95; 152.46; 152.76; 153.08; 154.80; 155.39. HR-MALDI-MS (DHB): 1101.5748 (MH^+, $C_{70}H_{77}N_4O_8^+$; calc.: 1101.57423).

2,3 : 2′,3′ : 2″,3″ : 2‴,3‴-{2-endo,*8*-endo,*14*-endo,*20*-endo-*Tetrahexylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,24:6,10 : 12,16 : 18,22-octayloctaoxy}tetrakis(5,6-dinitropyrazine)* (**19**). To **1a** (0.890 g, 1.08 mmol) and 1,2-difluoro-3,4-dinitrobenzene (0.969 g, 4.75 mmol) in DMF (30 ml), Et_3N (2.41 ml, 17.3 mmol) was added dropwise, and the mixture was heated to 70° for 12 h. After cooling, the mixture was poured into 1M HCl (200 ml), and the precipitate formed was isolated by filtration, washed with 1M HCl (200 ml), H_2O (200 ml), and dried (P_2O_5). FC (SiO_2; CH_2Cl_2) afforded **19** (814 mg, 51%). Slightly yellowish powder. M.p. 295 – 315° (dec.). R_f (SiO_2; CH_2Cl_2) 0.65; R_f = (SiO_2; CH_2Cl_2/cyclohexane 3 : 1) 0.13. IR (KBr): 3056, 2930, 2858, 1594, 1542, 1486, 1362, 1326, 1287, 1192, 1142, 1078, 899, 851, 823, 752, 653. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.84 – 0.89 (*m*, 12 H); 1.09-1.19 (*m*, 32 H); 1.96 – 2.08 (*m*, 8 H); 3.90 – 3.96 (*m*,

4 H); 6.21 (br. *s*, 2 H); 7.01 (*s*, 2 H); 7.02 (*s*, 2 H); 7.22 (br. *s*, 2 H); 7.63 (*s*, 4 H); 7.66 (*s*, 4 H). ^{13}C-NMR ($(CD_3)_2CO$, 75 MHz): 14.24; 23.28; 27.81; 31.85; 32.52; 37.14; 153.72 (other peaks not resolved due to conformational equilibration). HR-MALDI-MS (DHB): 1503.4538 ($[M+Na]^+$, $C_{76}H_{72}N_8O_{24}Na^+$; calc.: 1503.45569). X-Ray: see *Fig. 5*.

*Methyl 2-[3,5-Di(*tert*-butyl)phenyl]acetate* (**21**) [25]. HCl Gas was bubbled for 20 min through a soln. of 2-[3,5-di-(*tert*-butyl)phenyl]acetonitrile [22] (38.8 g, 169 mmol) in anh. MeOH (350 ml), and the mixture was heated to reflux for 3 d under Ar. Evaporation under reduced pressure gave a residue that was dissolved in CH_2Cl_2 (1000 ml). The soln. was washed with 1M HCl (400 ml), dried ($MgSO_4$), and evaporated. Filtration of the resulting oil through a short column (5 cm SiO_2; CH_2Cl_2) gave **21** (43.8 g, 99%). Pale-yellow oil. R_f (SiO_2; hexane/CH_2Cl_2 1:1) 0.42. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.33 (*s*, 18 H); 3.66 (*s*, 2 H); 3.70 (*s*, 3 H); 7.13 (*d*, $J=1.9$, 2 H); 7.34 (*t*, $J=1.9$, 1 H). ^{13}C-NMR (75 MHz, CD_3OD): 30.5; 34.2; 40.8; 51.0; 120.7; 123.2; 133.4; 150.8; 173.2. EI-MS: 262 (M^+), 247 ($[M-Me]^+$).

*2-[3,5-Di(*tert*-butyl)phenyl]acetaldehyde* (**22**) [26]. To a soln. of **21** (43.8 g, 167 mmol) in hexane (350 ml), cooled to $-78°$, DIBAL-H (1M in hexane, 200 ml) was added *via* cannula under N_2, and the mixture was stirred at $-78°$ for 3 h. After cautious addition of MeOH (30 ml), the mixture was poured into sat. aq. Na/K tartrate soln. (400 ml). AcOEt (400 ml) was added, and the mixture was stirred for 12 h. The org. layer was separated, and the aq. layer was washed with AcOEt (2×300 ml). The combined org. layers were dried (K_2CO_3) and evaporated under reduced pressure. Distillation (114–116° 0.8 Torr) gave **22** (22.4 g, 58%). Yellow oil. R_f (SiO_2; CH_2Cl_2) 0.58. UV/VIS (MeOH): 256 (1120). IR (CH_2Cl_2): 2964, 1718, 1595, 1472, 1395, 1364, 1262, 1190, 1159, 1097, 1000, 892, 867, 815, 697. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.35 (*s*, 18 H); 3.68 (*d*, $J=2.4$, 2 H); 7.08 (*d*, $J=1.8$, 2 H); 7.40 (*t*, $J=1.8$, 1 H); 9.77 (*t*, $J=2.4$, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 31.5; 34.9; 51.3; 121.7; 124.0; 124.4; 131.2; 151.9; 200.3. EI-MS: 232.2 (M^+), 217.2 ($[M-Me]^+$), 203.2 ($[M-CHO]^+$).

Compound **23** (for nomenclature and full characterization, see [4]). To resorcinol (2.47 g, 22.5 mmol) and **22** (5.20 g, 22.4 mmol) in EtOH (50 ml) at 0° under N_2, conc. HCl (40 ml) was added dropwise over 30 min. The soln. was stirred at 60° for 5 d, then poured into H_2O (1500 ml). After stirring for 2 h at r.t, the precipitate formed was collected by filtration and recrystallized (MeCN) to give **23** (2.57 g, 35%). Pale-brown solid.

Compound **20** (for nomenclature and full characterization including X-ray structure analysis (*Fig. 6*), see [4]). A soln. of **22** (0.56 g, 0.43 mmol), 2,3-dichloroquinoxaline (0.39 g, 1.96 mmol), and Cs_2CO_3 (1.18 g, 3.62 mmol) in anh. DMF (60 ml) was stirred under N_2 for 2 d at 60°. After cooling, CH_2Cl_2 (400 ml) was added. Washing with H_2O, drying (Na_2SO_4), and evaporation provided a solid that was purified by FC (SiO_2; CH_2Cl_2/MeOH 99.5:0.5) to give **20** (0.53 g, 68%). Off-white solid.

Tetramethyl 4,4′,4″,4‴-(4,6,10,12,16,18,22,24-Octahydroxypentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-2,8,14,20-tetrayl)tetrabutanoate (**26**). Pd/C (10%) (2.9 g) was flushed with H_2, freshly distilled THF (900 ml) was added, and the soln. was reflushed with H_2. 2,6-Dimethylpyridine (21.2 g, 198 mmol) and glutaric acid monomethyl ester chloride (29.8 g, 181 mmol) were added, and the soln. was stirred at r.t. under H_2 for 24 h. Filtration through *Celite* and evaporation under reduced pressure left a residue that was taken up in CH_2Cl_2 (500 ml). Washing with H_2O (300 ml), 1M HCl (300 ml), and H_2O (300 ml) and evaporation under reduced pressure provided **25** (25.3 g). Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.80–2.30 (*m*, 2 H); 2.38 (*t*, $J=7.5$, 2 H); 2.49–2.60 (*m*, 2 H); 3.68 (*s*, 3 H); 9.79 (*t*, $J=1.2$, 1 H). To **25** (25.3 g) and resorcinol (19.9 g, 181 mmol) in MeOH (300 ml) at 0°, conc. HCl (5 ml) was added over 30 min, and the soln. was stirred under Ar at r.t. for 2 h, then at 60° for 2 d. The soln. was poured into H_2O (1500 ml), and the resulting cream-colored precipitate was collected by filtration and recrystallized (MeCN) to give **26** (17.59 g, 44%). White solid. M.p. 205–210°. UV/VIS (MeOH): 286 (17300). ^{1}H-NMR (300 MHz, CD_3OD): 1.58 (*quint.*, $J=7.5$, 8 H); 2.25 (*q*, $J=7.8$, 8 H); 2.42 (*t*, $J=7.4$, 8 H); 3.66 (*s*, 12 H); 4.31 (*t*, $J=7.9$, 4 H); 6.23 (*s*, 4 H); 7.24 (*s*, 4 H). ^{13}C-NMR (75 MHz, CD_3OD): 24.7; 34.1; 34.6; 34.8; 52.1; 104.1; 125.3; 153.2; 176.0. HR-MALDI-MS (DHB): 911.3460 ($[M+Na]^+$, $C_{48}H_{56}NaO_{16}^+$; calc.: 911.3461). Anal. calc. for $(C_{48}H_{56}O_{16})_2\cdot H_2O\cdot MeCN$ (1836.965): C 64.08, H 6.42 N 0.76; found: C 63.7, H 6.35, N 0.74.

*2,3:2′,3′:2″,3‴:2‴,3‴′-{2-*endo*,8-*endo*,14-*endo*,20-*endo*-Tetrakis[3-(methoxycarbonyl)propyl]pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,24:6,10:12,16:18,22-octayloctaoxy}tetraquinoxaline* (**24**). A soln. of 2,3-dichloroquinoxaline (1.51 g, 7.57 mmol), **26** (1.50 g, 1.69 mmol), and Cs_2CO_3 (4.50 g, 13.8 mmol) in anh. DMF (250 ml) was stirred under Ar at 60° for 2 d. The mixture was poured into dilute aq. AcOH soln., and the resulting precipitate was collected by filtration. Recrystallization (MeCN) gave **24** (0.305 g, 13%). Colorless solid. M.p. > 250°. UV/VIS ($CHCl_3$): 315 (36500), 328 (32000). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.68–1.82 (*m*, 8 H); 2.34–2.46 (*m*, 8 H); 2.54 (*t*, $J=7.3$, 8 H); 3.74 (*s*, 12 H); 5.65 (*t*, $J=8.0$, 4 H); 7.34 (*s*, 4 H); 7.44–7.51 (*m*, 8 H); 7.77–7.83 (*m*, 8 H); 8.19 (*s*, 4 H). ^{13}C-NMR

(75 MHz, $CDCl_3$): 23.5; 31.7; 33.7; 34.4; 51.7; 119.0; 123.8; 127.9; 129.1; 135.7; 139.8; 152.6; 152.7; 174.1. HR-MALDI-MS (DHB): 1415.4494 ($[M+Na]^+$, $C_{80}H_{64}N_8NaO_{16}^+$; calc.: 1415.4338). X-Ray: see *Fig. 7*.

2,8,14,20-Tetrakis(dec-9-enyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol (**30**). To resorcinol (11.2 g, 0.1 mol) and **29** (17.7 g, 0.1 mol) in EtOH (100 ml), conc. HCl (16 ml) was added dropwise over 30 min at 0° under Ar. After stirring for 25 h at r.t., the mixture was poured into H_2O (300 ml). The precipitate formed was isolated by filtration, triturated with H_2O, and dried under vacuum at 70° for 20 h to give **30** (24.3 g, 93%). Orange-colored solid. R_f = (SiO_2; $CHCl_3$/MeOH 5:1) 0.60; R_f (SiO_2; CH_2Cl_2/MeOH 10:1) 0.42. M.p. > 250° (EtOH). IR (KBr): 3316, 2924, 2866, 1639, 1617, 1504, 1461, 1436, 1367, 1344, 1300, 1267, 1194, 1166, 1150, 1083, 989, 907, 848, 828, 722, 628, 611, 556, 512. ^{1}H-NMR ($(CD_3)_2CO$, 200 MHz): 1.20–1.70 (*m*, 56 H); 2.28 (*m*, 8 H); 4.30 (*t*, *J* = 7.9, 4 H), 4.93 (*m*, 8 H); 5.82 (*m*, 4 H); 6.25 (*s*, 4 H); 7.55 (*s*, 4 H); 8.50 (br. *s*, 8 H). FAB-MS: 1040.6 (M^+). HR-MALDI-MS: 1063.6995 ($[M+Na]^+$, $C_{68}H_{96}NaO_8^+$; calc.: 1063.7003).

2,3:2′,3′:2″,3″:2‴,3‴-[2-endo,*8*-endo,*14*-endo,*20*-endo-*Tetrakis(dec-9-enyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,24:6,10:12,16:18,22-octayloctaoxy}tetraquinoxaline* (**31**). A soln of **30** (2.08 g, 2.0 mmol), 2,3-dichloroquinoxaline (1.66 g, 8.0 mmol), and Cs_2CO_3 (2.90 g, 8.8 mmol) in dry Me_2SO (70 ml) was stirred under Ar at r.t. for 2 d. The mixture was poured into ice-water, and the brownish precipitate formed was isolated by filtration. The filtrate was extracted with CH_2Cl_2, and the org. layer was washed with H_2O and evaporated to provide additional solid crude product that was combined with the first precipitate. FC (SiO_2 (150 g); CH_2Cl_2/AcOEt 98:2 → 90:10) afforded **31** (1.285 g, 44%). Colorless flakes. R_f (SiO_2; CH_2Cl_2) 0.23; R_f = (SiO_2; CH_2Cl_2/AcOEt 20:1) 0.66. M.p. > 250° (CH_2Cl_2/Me_2CO). IR (KBr): 3066, 2925, 2852, 1711, 1639, 1606, 1570, 1482, 1416, 1400, 1361, 1265, 1222, 1160, 1117, 1061, 1017, 994, 950, 911, 896, 759, 722, 606, 583, 522, 461. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.20–1.50 (*m*, 48 H); 1.99–2.09 (*m*, 8 H); 2.24 (*m*, 8 H); 4.95 (*m*, 8 H); 5.53 (*t*, *J* = 8.2, 4 H); 5.81 (*m*, 4 H); 7.18 (*s*, 4 H); 7.40–7.49 (*m*, 8 H); 7.72–7.81 (*m*, 8 H); 8.12 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 27.8; 28.9; 29.0; 29.4; 29.5; 32.3; 33.7; 34.1; 114.2; 118.7; 123.4; 127.8; 129.8; 135.8; 139.3; 139.7; 152.5; 152.6. FAB-MS: 1546 (MH^+). HR-MALDI-MS: 1567.7950 ($[M+Na]^+$, $C_{100}H_{104}N_8NaO_8^+$; calc.: 1567.7875), 1545.8168 (MH^+, $C_{100}H_{105}N_8O_8^+$; calc.: 1545.8055). Anal. calc. for $C_{100}H_{104}N_8O_8 \cdot$ AcOEt (1634.05): C 76.44, H 6.91, N 6.86; found: C 76.15, H 6.82, N 6.78.

2,3:2′,3′:2″,3″:2‴,3‴-[2-endo,*8*-endo,*14*-endo,*20*-endo-*Tetrakis[10-(decylsulfanyl)delcyl]pentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,24:6,10:12,16:18,22-octayloctaoxy}tetraquinoxaline* (**27**). To **27** (474 mg, 0.33 mmol) in freshly distilled THF (20 ml), decane-1-thiol (0.7 ml, 3.3 mmol) was added, and the mixture was stirred under Ar at 0° for 1 h. After addition of 9-BBN (0.5M in THF, 33 ml, 16.5 mmol), the mixture was stirred under Ar for 2 d at r.t., then poured into H_2O (200 ml), and extracted with CH_2Cl_2 (200 ml). Washing with H_2O (2 × 200 ml), drying ($MgSO_4$), evaporation, and FC (SiO_2 (50 g); CH_2Cl_2/AcOEt 99:1 → 50:50) gave **27** (543 mg, 0.242 mmol, 74%). Colorless powder. R_f (SiO_2; CH_2Cl_2) 0.25. M.p. 53–55° (CH_2Cl_2/Me_2CO). IR (KBr): 2924, 2851, 1482, 1417, 1336, 1266, 1160, 897, 758, 607. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.86 (*t*, *J* = 6.6, 12 H); 1.20–1.70 (*m*, 128 H); 2.22 (*m*, 8 H); 2.48 (*m*, 16 H); 5.54 (*t*, *J* = 8.2, 4 H); 7.18 (*s*, 4 H); 7.40–7.49 (*m*, 8 H); 7.73–7.81 (*m*, 8 H); 8.13 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.0; 22.6; 27.8; 28.9–29.7 (15 ×); 31.8; 32.1; 34.1; 118.8; 123.4; 127.8; 129.0; 135.8; 139.7; 152.5; 152.6. MALDI-MS: 2242.5 (MH^+, $C_{140}H_{193}N_8O_8S_4^+$; calc.: 2242.3823), 2264.5 ($[M+Na]^+$, $C_{140}H_{192}N_8NaO_8S_4^+$; calc.: 2264.3643); 2281.4 ($[M+K]^+$, $C_{140}H_{192}KN_8O_8S_4^+$; calc.: 2280.3382). Anal. calc. for $C_{140}H_{192}N_8O_8S_4$ (2243.34): C 74.96, H 8.63, N 4.99; found: C 74.85, H 8.41, N 5.01.

6-(Pentylsulfanyl)hexan-1-ol (**33**). To hex-6-en-1-ol (1.22 ml, 1.0 g, 10 mmol) in freshly distilled THF (20 ml), 9-BBN (0.5M in THF, 100 ml, 50 mmol) was added at 0° under N_2. Pentane-1-thiol (1.28 ml, 1.24 g, 10 mmol) was added at 0°, and the mixture was stirred for 3 h at r.t. The mixture was poured into sat. aq. NaCl soln. (100 ml) and extracted with CH_2Cl_2 (3 × 100 ml). Drying ($MgSO_4$), evaporation, and FC (SiO_2; CH_2Cl_2/AcOEt 5:2) provided **33** (2.2 g, 99%). Colorless oil. R_f = (SiO_2; hexane/AcOEt 2:1) 0.35–0.38. IR (neat): 3356, 2922, 2856, 1461, 1378, 1300, 1267, 1217, 1056, 895, 728. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.87 (*t*, *J* = 7.2, 3 H); 1.20–1.64 (*m*, 14 H); 2.47 (*t*, *J* = 7.5, 2 H); 2.49 (*t*, *J* = 7.5, 2 H); 3.62 (br. *m*, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.8; 22.2; 25.3; 28.6; 29.3; 29.5; 31.0; 32.0; 32.1; 32.5; 62.9. EI-MS: 204 (M^+), 157 ($[M-MeS]^+$), 143 ($[M-EtS]^+$), 131 ($[M-BuO]^+$), 115 ($[M-BuS]^+$). Anal. calc. for $C_{11}H_{24}OS$ (204.3737): C 64.65, H 11.84; found: C 64.59, H 11.83.

6-(Pentylsulfanyl)hexanal (**32**). To a suspension of PCC (1.6 g, 7.5 mmol) and *Celite* (1.6 g) in freshly distilled CH_2Cl_2 (20 ml), a soln. of **33** (1.02 g, 5 mmol) in freshly distilled CH_2Cl_2 (5 ml) was added dropwise under Ar at r.t. After stirring for 5 h under Ar at r.t., the mixture was filtered through a pad of SiO_2, which was subsequently washed with CH_2Cl_2. The combined filtrates were concentrated to yield **32** (313 mg, 31%). Colorless oil. R_f (SiO_2; CH_2Cl_2)0.59. IR (neat): 2929, 2856, 2711, 2357, 2333, 1722, 1458, 1300, 1272, 1217, 1156,

1078. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.87 (*t*, *J* = 7.2, 3 H); 1.24–1.47 (*m*, 6 H); 1.50–1.69 (*m*, 6 H); 2.37–2.45 (*m*, 2 H); 2.47 (*t*, *J* = 7.2, 2 H); 2.49 (*t*, *J* = 7.2, 2 H); 9.75 (*t*, *J* = 1.7, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.8; 21.6; 22.2; 28.3; 29.3 (2×); 31.0; 31.8; 32.1; 43.7; 202.7. EI-MS: 202 (M^+), 174 ($[M-CO]^+$). Anal. calc. for $C_{11}H_{22}OS$ (202.3578): C 65.29, H 10.96; found: C 65.28, H 10.77.

2,8,14,20-Tetrakis[5-(pentylsulfanyl)pentyl]pentacyclo[19.3.1.1^{3,7}*.1*^{9,13}*.1*^{15,19}*]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol* (**34**). To **32** (282 mg, 1.39 mmol) and resorcinol (156 mg, 1.39 mmol) in EtOH (1.4 ml), conc. HCl (0.22 ml) was added dropwise over 30 min at 0° under N_2. The mixture was stirred at r.t. for 1 h and at 60° for 24 h, then it was poured into ice-water. The formed precipitate was isolated by filtration and dried under vacuum for 2 d to give **34** (412 mg, 99%). Colorless powder. M.p. > 250° (EtOH). IR (KBr): 3254, 2927, 2856, 1618, 1500, 1450, 1367, 1328, 1294, 1256, 1211, 1167, 1089, 900, 833. ^{1}H-NMR ($(CD_3)_2CO$, 300 MHz): 0.89 (*t*, *J* = 7.1, 12 H); 1.22–1.42 (*m*, 24 H); 1.42–1.64 (*m*, 24 H); 2.27–2.35 (*m*, 8 H); 2.50 (*t*, *J* = 7.3, 16 H); 4.30 (*t*, *J* = 7.8, 4 H); 6.24 (*s*, 4 H); 7.55 (*s*, 4 H); 8.48 (*s*, 8 H). ^{13}C-NMR ($(CD_3)_2CO$, 50 MHz): 14.3; 22.9; 29.6; 30.1; 30.4; 30.8; 31.8; 32.5; 32.6; 34.2; 34.3; 103.7; 125.3; 125.5; 152.8. HR-MALDI-MS: 1199.6497 ($[M+Na]^+$, $C_{68}H_{104}NaO_8S_4^+$; calc.: 1199.6512).

*2,3:2′,3′:2″,3″:2‴,3‴-{2-*endo*,8-*endo*,14-*endo*,20-*endo*-tetrakis[5-(pentylthio)pentyl]pentacyclo[19.3.1.1*^{3,7}*.1*^{9,13}*.1*^{15,19}*]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,24:6,10:12,16:18,22-octayloctaoxy}tetraquinoxaline* (**28**). A soln. of **34** (133 mg, 0.113 mmol), 2,3-dichloroquinoxaline (94 mg, 0.45 mmol), and Cs_2CO_3 (163 mg, 0.50 mmol) in dry Me_2SO (5 ml) was stirred at r.t. under Ar for 4 d. The mixture was poured into ice-water, and the precipitate formed was isolated by filtration, triturated with H_2O, and then dissolved in Me_2CO/CH_2Cl_2. The soln. was dried ($MgSO_4$) and concentrated to give a dark-brown solid that was purified by FC (SiO_2; CH_2Cl_2/AcOEt 98:2 → 80:20) to give **28** (99 mg, 52%). Colorless flakes. M.p. 227–230° (EtOH). IR (KBr): 3067, 2926, 2856, 1606, 1572, 1483, 1467, 1417, 1400, 1361, 1336, 1265, 1233, 1222, 1160, 1117, 1072, 1044, 1011, 950, 906, 896, 867, 757, 722, 606, 583. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (*t*, *J* = 7.1, 12 H); 1.28–1.50 (*m*, 24 H); 1.50–1.75 (*m*, 24 H); 2.27 (*m*, 8 H); 2.52 (*t*, *J* = 7.3, 8 H); 2.55 (*m*, 8 H); 5.59 (*t*, *J* = 8.1, 4 H); 7.18 (*s*, 4 H); 7.41–7.50 (*m*, 8 H); 7.71–7.80 (*m*, 8 H); 8.16 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 13.9; 22.2; 27.5; 28.7; 29.4; 29.6; 31.1; 32.1; 32.2 (2×); 34.0; 118.9; 123.3; 127.8; 129.0; 135.7; 139.7; 152.5; 152.6. HR-MALDI-MS: 1703.7388 ($[M+Na]^+$, $C_{100}H_{112}N_8NaO_8S_4^+$; calc.: 1703.7384), 1681.7578 (MH^+, $C_{100}H_{113}N_8O_8S_4^+$; calc.: 1681.7656). Anal. calc. for $C_{100}H_{112}N_8O_8S_4$ (1682.2724): C 71.40, H 6.71, N 6.66; found: C 71.50, H 7.02, N 6.86.

X-Ray Crystal Structure of **1c**. Crystal data at 233 K for $C_{44}H_{56}O_8 \cdot 2(MeOH) \cdot MeCH_2OH$ (M_r823.04): monoclinic, space group *C*2/*c* (No. 15), $D_c = 1.207$ g/cm^3, $Z = 8$, $a = 36.049(7)$, $b = 11.564(2)$, $c = 21.773(5)$ Å, $\beta = 93.71(2)°$, $V = 9058(3)$ Å^3, *Nonius CAD4* diffractometer, CuK_α radiation, $\lambda = 1.5418$ Å. A crystal, obtained by slow cooling of a MeOH/EtOH soln. (linear dimensions *ca.* 0.2 × 0.18 × 0.16 mm) was mounted at low temp. to prevent evaporation of enclosed solvent. The structure was solved by direct methods (*SIR97*) [27] and refined by full-matrix least-squares analysis (SHELXL-97) [28], by using an isotropic extinction correction, and $w = 1/[\sigma 2(F_o^2) + (0.0933P)^2 + 49.1608P]$, where $P = (F_o^2 + 2F_c^2)/3$. The subunit C(10)–C(13) and one MeOH are disordered over two orientations. For C(11), C(12), C(13), and O(200), two sets of atomic parameters were refined with population parameters of 0.7 and 0.3, resp. In *Fig. 2*, only one orientation is shown for clarity. All heavy atoms were refined anisotropically (H-atoms of the ordered structure isotropically, whereby H-positions are based on stereochemical considerations). Final $R(F) = 0.084$, $wR(F^2) = 0.241$ for 626 parameters and 5047 reflections with $I > 2\sigma(I)$ and $2.46 < \theta < 56.96°$ (corresponding *R* values based on all 6098 reflections are 0.098 and 0.252 resp.). CCDC-214738.

X-Ray Crystal Structure of **2b**. Crystal data at 293 K for $C_{80}H_{72}N_8O_8 \cdot CH_2Cl_2 \cdot 2$ MeCN (M_r 1440.51): monoclinic, space group *C*2/*c* (No. 15), $D_c = 1.224$ g/cm^3, $Z = 4$, $a = 19.007(14)$, $b = 17.623(13)$, $c = 24.57(2)$ Å, $\beta = 109.63(6)°$, $V = 7752(11)$ Å^3; *Picker-Stoe* diffractometer, CuK_α radiation, $\lambda = 1.5418$ Å. Prismatic crystals (linear dimensions *ca.* 0.15 × 0.1 × 0.1 mm) were obtained by slow evaporation from $MeCN/CH_2Cl_2$. The structure was solved by direct methods (SHELXS-86) [29] and refined by full-matrix least-squares analysis (SHELXL-93) [30]. The subunit C(35)–C(36) and both MeCN molecules are disordered over two orientations. In *Fig. 3*, only one orientation is shown for clarity. All heavy atoms were refined anisotropically, H-atoms were fixed isotropically with atomic positions based on stereochemical considerations. Final $R(F) = 0.0602$, $wR(F^2) = 0.1681$ for 511 parameters and 3228 reflections with $I > 2\sigma(I)$ and $3.52 < \theta < 49.98°$. CCDC-214733.

X-Ray Crystal Structure of **11**. Crystal data at 295 *K* for $C_{23}H_{26}BF_2N_3O_2$ (M_r 425.28): triclinic, space group $P\bar{1}$ (No. 2), $D_c = 1.042$ g/cm^3, $Z = 6$, $a = 13.9886(4)$, $b = 17.0634(5)$, $c = 18.9111(6)$ Å, $\alpha = 71.360(2)°$, $\beta = 72.540(2)°$, $\gamma = 88.770(2)°$, $V = 4066.3(2)$ Å^3; *Bruker-Nonius Kappa-CCD* diffractometer, MoK_α radiation, $\lambda = 0.7107$ Å. A dark-red crystal (linear dimensions *ca.* 0.3 × 0.3 × 0.02 mm) was obtained by slow evaporation of a $CHCl_3$ soln. The structure was solved by direct methods (SIR97) [27] and refined by full-matrix least-

squares analysis (SHELXL-97) [28], by using an isotropic extinction correction and $w = 1/[\sigma 2(F_o^2) + (0.1974P)^2 + 1.6862P]$, where $P = (F_o^2 + 2F_c^2)/3$. All heavy atoms were refined anisotropically (H-atoms isotropically, whereby H-positions are based on stereochemical considerations). Final $R(F) = 0.087$, $wR(F^2) = 0.258$ for 839 parameters and 4959 reflections with $I > 2\sigma(I)$ and $3.13 < \theta < 20.03°$ (corresponding R values based on all 7142 reflections are 0.118 and 0.298 resp.). CCDC-214739.

X-Ray Crystal Structure of **19**. Crystal data at 253 K for $C_{76}H_{72}N_8O_{24} \cdot 2\ Me_2CO$ (M_r 1597.57): monoclinic, space group $P2_1/m$ (No. 11), $D_c = 1.234$ g/cm^3, $Z = 2$, $a = 12.3125(3)$, $b = 27.0211(7)$, $c = 13.1175(4)$ Å, $\beta = 99.780(1)°$, $V = 4300.7(2)$ Å^3; *Bruker-Nonius Kappa-CCD* diffractometer, MoK_α radiation, $\lambda = 0.7107$ Å. An orange crystal, obtained by evaporation of a Me_2CO soln. (linear dimensions *ca.* $0.3 \times 0.3 \times 0.28$ mm) was mounted at low temp. in epoxy resin to prevent evaporation of enclosed solvent. The crystals shatter below *ca.* 230 K. At 253 K, they desintegrate within a few hours. The structure was solved by direct methods (SIR97) [27] and refined by full-matrix least-squares analysis (SHELXL-97) [28], by using an isotropic extinction correction and $w = 1/[\sigma 2(F_o^2) + (0.1188P)^2 + 2.8782P]$, where $P = (F_o^2 + 2F_c^2)/3$. All heavy atoms were refined anisotropically (H-atoms isotropically, whereby H-positions are based on stereochemical considerations). Final $R(F) = 0.081$, $wR(F^2) = 0.209$ for 568 parameters and 4932 reflections with $I > 2\sigma(I)$ and $1.75 < \theta < 24.11°$ (corresponding R values based on all 6523 reflections are 0.104 and 0.231 resp.). CCDC-214740.

X-Ray Crystal Structure of **24**. Crystal data at 293 K for $C_{80}H_{64}N_8O_{16} \cdot MeCN$ (M_r 1434.46): monoclinic, space group $P2(1)/c$ (No. 14), $D_c = 1.311$ g/cm^3, $Z = 4$, $a = 21.08(2)$, $b = 17.07(2)$, $c = 20.99(3)$ Å, $\beta = 104.03(9)°$, $V = 7332(15)$ Å^3; *Picker-Stoe* diffractometer, CuK_α radiation, $\lambda = 1.5418$ Å. Prismatic crystals (linear dimensions *ca.* $0.1 \times 0.1 \times 0.07$ mm) were obtained by slow evaporation from $MeCN/CHCl_3$. The structure was solved by direct methods (SHELXS-86) [29] and refined by full-matrix least-squares analysis (SHELXL-93) [30]. All heavy atoms were refined anisotropically, H-atoms fixed isotropically with atomic positions based on stereochemical considerations. Final $R(F) = 0.1088$, $wR(F2) = 0.2957$ for 977 parameters and 3500 reflections with $I > 2\sigma(I)$ and $2.16 < \theta < 42.50°$. CCDC-214734.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* (*CCDC*). Copies of the data can be obtained, free of charge, on application to the *CCDC,* 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

REFERENCES

[1] a) J. R. Moran, S. Karbach, D. J. Cram, *J. Am. Chem. Soc.* **1982**, *104*, 5826; b) J. R. Moran, J. L. Ericson, E. Dalcanale, J. A. Bryant, C. B. Knobler, D. J. Cram, *J. Am. Chem. Soc.* **1991**, *113*, 5707; c) D. J. Cram, H.-J. Choi, J. A. Bryant, C. B. Knobler, *J. Am. Chem. Soc.* **1992**, *114*, 7748; d) D. J. Cram, J. M. Cram, 'Container Molecules and Their Guests', Royal Society of Chemistry, Cambridge, 1994, p. 107–130.

[2] a) E. Dalcanale, P. Soncini, G. Bacchilega, F. Ugozzoli, *J. Chem. Soc., Chem. Commun.* **1989**, 500; b) P. Soncini, S. Bonsignore, E. Dalcanale, F. Ugozzoli, *J. Org. Chem.* **1992**, *57*, 4608.

[3] a) F. Hof, S. L. Craig, C. Nuckolls, J. Rebek Jr., *Angew. Chem.* **2002**, *114*, 1556; *Angew. Chem., Int. Ed.* **2002**, *41*, 1488; b) D. M. Rudkevich, G. Hilmersson, J. Rebek Jr., *J. Am. Chem. Soc.* **1998**, *120*, 12216; c) A. R. Renslo, F. C. Tucci, D. M. Rudkevich, J. Rebek Jr., *J. Am. Chem. Soc.* **2000**, *122*, 4573; d) T. Haino, D. M. Rudkevich, A. Shivanyuk, K. Rissanen, J. Rebek Jr., *Chem. – Eur. J.* **2000**, *6*, 3797; e) S. D. Starnes, D. M. Rudkevich, J. Rebek Jr., *J. Am. Chem. Soc.* **2001**, *123*, 4659.

[4] P. J. Skinner, A. G. Cheetham, A. Beeby, V. Gramlich, F. Diederich, *Helv. Chim. Acta* **2001**, *84*, 2146.

[5] Y. Yamakoshi, R. R. Schlittler. J. K. Gimzewski, F. Diederich, *J. Mater. Chem.* **2001**, *11*, 2895.

[6] P. Timmerman, W. Verboom, D. N. Reinhoudt, *Tetrahedron* **1996**, *52*, 2663.

[7] J. Karolin, L. B.-Å. Johansson, L. Strandberg, T. Ny, *J. Am. Chem. Soc.* **1994**, *116*, 7801; R. W. Wagner, J. S. Lindsey, *Pure Appl. Chem.* **1996**, *68*, 1373; M. Kollmannsberger, T. Garies, S. Heinl, J. Breu, J. Daub, *Angew. Chem.* **1997**, *109* 1391; *Angew. Chem., Int. Ed.* **1997**, *36*, 1333; A. Burghart, H. Kim, M. B. Welch, L. H. Thoresen, J. Reibenspies, K. Burgess, F. Bergström, L. B.-Å. Johansson, *J. Org. Chem.* **1999**, *64*, 7813.

[8] S. Weiss, *Science* **1999**, *283*, 1676; B. Hecht, B. Sick, U. P. Wild, V. Deckert, R. Zenobi, O. J. F. Martin, D. W. Pohl, *J. Chem. Phys.* **2000**, *112*, 7761; W. Trabesinger, A. Renn, B. Hecht, U. P. Wild, A. Montali, P. Smith, C. Weder, *J. Phys. Chem. B* **2000**, *104*, 5221.

[9] V. A. Azov, F. Diederich, Y. Lill, B. Hecht, *Helv. Chim. Acta* **2003**, *86*, 2149.

[10] V. A. Azov, B. M. Jaun, F. Diederich, *Helv. Chim. Acta*, in press.

[11] a) F. C. Tucci, D. M. Rudkevich, J. Rebek Jr., *J. Org. Chem.* **1999**, *64*, 4555; b) A. Shivanyuk, K. Rissanen, S. K. Körner, D. M. Rudkevich, J. Rebek Jr., *Helv. Chim. Acta* **2000**, *83*, 1778; c) S. K. Körner, F. C. Tucci, D. M. Rudkevich, T. Heinz, J. Rebek Jr., *Chem. Eur. J.* **2000**, *6*, 187; d) S. L. Craig, S. Lin, J. Chen, J. Rebek Jr., *J. Am. Chem. Soc.* **2002**, *124*, 8780.
[12] F. C. Tucci, A. R. Renslo, D. M. Rudkevich, J. Rebek Jr., *Angew. Chem.* **2000**, *39*, 1118; *Angew. Chem., Int. Ed.* **2000**, *39*, 1076; U. Lücking, F. C. Tucci, D. M. Rudkevich, J. Rebek Jr., *J. Am. Chem. Soc.* **2000**, *122*, 8880; S. D. Starnes, D. M. Rudkevich, J. Rebek Jr., *Org. Lett.* **2000**, *2*, 1995; U. Lücking, J. Chen, D. M. Rudkevich, J. Rebek Jr., *J. Am. Chem. Soc.* **2001**, *123*, 9929.
[13] L. Abis, E. Dalcanale, A. Du Vosel, S. Spera, *J. Org. Chem.* **1988**, *53*, 5475.
[14] L. M. Tunstad, J. A. Tucker, E. Dalcanale, J. Weiser, J. A. Bryant, J. C. Sherman, R. C. Helgeson, C. B. Knobler, D. J. Cram, *J. Org. Chem.* **1989**, *54*, 1305; T. Lippmann, H. Wilde, M. Pink, A. Schäfer, M. Hesse, G. Mann, *Angew. Chem.* **1993**, *105*, 1258; *Angew. Chem., Int. Ed.* **1993**, *32*, 1195; D. E. Hibbs, M. B. Hursthouse, K. M. Abdul Malik, H. Adams, C. J. M. Stirling, F. Davis, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1998**, 987; K. Murayama, K. Aoki, *Chem. Commun.* **1998**, 607; L. R. MacGillivray, J. L. Atwood, *Chem. Commun.* **1999**, 181; H. Mansikkamäki, M. Nissinen, K. Rissanen, *Chem. Commun.* **2002**, 1902.
[15] M. Vincenti, E. Dalcanale, P. Soncini, G. Guglielmetti, *J. Am. Chem. Soc.* **1990**, *112*, 445.
[16] D. J. Cram, L. M. Tunstad, C. B. Knobler, *J. Org. Chem.* **1992**, *57*, 528.
[17] M. He, R. J. Johnson, J. O. Escobedo, P. A. Beck, K. K. Kim, N. N. St. Luce, C. J. Davis, P. T. Lewis, F. R. Fronczek, B. J. Melancon, A. A. Mrse, W. D. Treleaven, R. M. Strongin, *J. Am. Chem. Soc.* **2002**, *124*, 5000.
[18] B. C. Gibb, R. G. Chapman, J. C. Sherman, *J. Org. Chem.* **1996**, *61*, 1505.
[19] A. R. Far, Y. L. Cho, A. Rang, D. M. Rudkevich, J. Rebek Jr., *Tetrahedron* **2002**, *58*, 741.
[20] L. Pirondini, D. Bonifazi, E. Menozzi, E. Wegelius, K. Rissanen, C. Massera, E. Dalcanale, *Eur. J. Org. Chem.* **2001**, 2311.
[21] T. A. Jung, R. R. Schlittler, J. K. Gimzewski, H. Tang, C. Joachim, *Science* **1996**, *271*, 181; J. K. Gimzewski, C. Joachim, R. R. Schlittler, V. Langlais, H. Tang, I. Johannsen, *Science* **1998**, *281*, 531.
[22] M. Yoshifuji, K. Shimura, K. Toyota, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1980.
[23] A. Ulman, *Chem. Rev.* **1996**, *96*, 1533; C. D. Bain, E. B. Throughton, Y.-T. Tao, J. Evall, G. M. Whitesides, R. G. Nuzzo, *J. Am. Chem. Soc.* **1989**, *111*, 321.
[24] H. Schönherr, M. W. J. Beulen, J. Bügler, J. Huskens, F. C. J. M. van Veggel, D. N. Reinhoudt, G. J. Vansco, *J. Am. Chem. Soc.* **2000**, *122*, 4963, and refs cit. therein.
[25] H. G. Aurich, E. Deuschle *Liebigs Ann. Chem.* **1981**, 719.
[26] M. G. J. Beets, W. Meerburg, H. van Essen, *Recl. Trav. Chim. Pays-Bas* **1959**, 570.
[27] A. Altomare, M. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115.
[28] G. M. Sheldrick, 'SHELXL-97 Program for the Refinement of Crystal Structures', University of Göttingen, Germany, 1997.
[29] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
[30] G. M. Sheldrick, 'SHELXL-93 Program for the Refinement of Crystal Structures', University of Göttingen, Germany, 1993.

Received July 21, 2003