Synthesis and Conformational Switching of Partially and Differentially Bridged Resorcin[4]arenes Bearing Fluorescent Dye Labels

Preliminary Communication

by **Vladimir A. Azov**[a]), **François Diederich***[a]), **Yoriko Lill**[b]), and **Bert Hecht***[b])

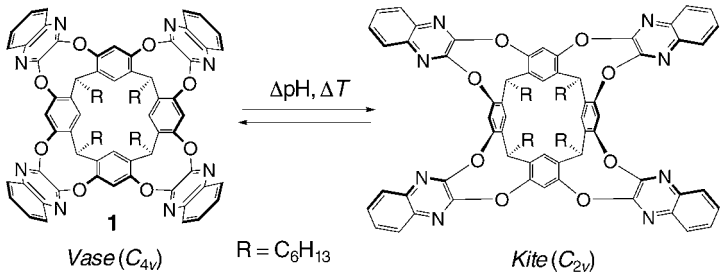
[a]) Laboratorium für Organische Chemie, ETH-Hönggerberg, CH-8093 Zürich
(e-mail: diederich@org.chem.ethz.ch)
[b]) Nano-optics group, Institut für Physik, Uni Basel, Klingelbergstrasse 82, CH-4056 Basel
(e-mail: bert.hecht@unibas.ch)

We report the synthesis of modified *Cram*-type cavitands bearing one or two fluorescent labels for single-molecule spectroscopic studies of *vase*–*kite* conformational switching (*Scheme 3*). Syntheses were performed by stepwise bridging of the four couples of neighboring H-bonded OH groups of resorcin[4]arene bowls (*Schemes 2* and *3*). The new substitution patterns enable the construction of a large variety of future functional architectures. ^{1}H-NMR Investigations showed that the new partially and differentially bridged cavitands feature temperature- and pH-triggered *vase*–*kite* conformational isomerism similar to symmetrical cavitands with four identical quinoxaline bridges (*Table*). It was discovered that *vase*–*kite* switching of cavitands is strongly solvent-dependent.

Cavitands, which consist of a resorcin[4]arene bowl bridged by four quinoxaline (**1**) or pyrazine moieties, were introduced by *Cram* and co-workers [1] as a family of macrocycles capable of adopting two preferred conformations with profound geometry and property differences (*Scheme 1*). The *vase* conformation, with a deep cavity for guest inclusion, is preferred at elevated temperatures (>318 K), whereas the *kite* conformation, with a large flat surface, dominates at low temperatures (<213 K). Conformational switching can also be reversibly induced at ambient temperature by pH changes, with the *kite* conformation being preferred at low pH [2]. The *vase*–*kite* isomerization is conveniently monitored by ^{1}H-NMR spectroscopy [1] as well as by optical absorption and emission spectroscopy [2]. The molecular-recognition properties of the cavitands in the *vase* form, as well as of supramolecular capsules formed by self-assembly of two cavitands with H-bonding rims, have been elegantly exploited by *Rebek* and co-workers [3].

We are interested in the mechanistic understanding of the temperature- and pH-triggered *vase*–*kite* conformational isomerism [2] as well as in the potential utilization of resorcin[4]arene cavitands as miniaturized mechanical grippers for molecular construction at the single-molecule level. Within this context, we recently reported the STM-imaging at molecular resolution of highly ordered self-assembled monolayers formed by alkylthiol-legged quinoxaline-bridged resorcin[4]arene cavitands on gold [4]. Investigations of the switching dynamics by polarization-resolved single-molecule microscopy [5] now required the formation of differentially bridged resorcin[4]arenes bearing suitable fluorescent dyes. We chose 'borondipyrrylmethane' (BODIPY) dyes

Scheme 1. *Temperature- or pH-Triggered Conformational* vase–kite *Equilibrium in Bridged Resorcin[4]arene* **1**



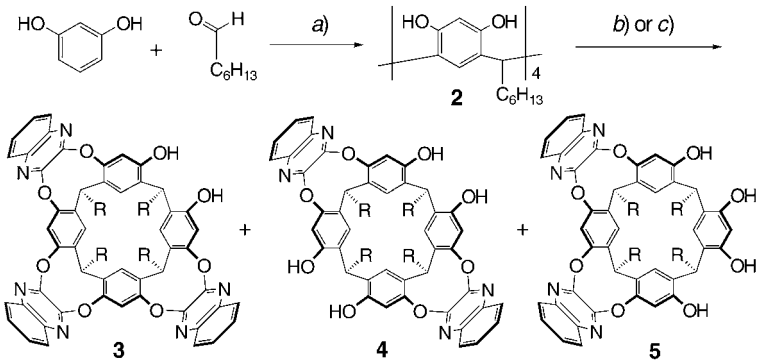
for their favorable electronic absorption and emission properties, and their low sensitivity to pH (important in proton-induced switching experiments) and environmental polarity [6]. Here, we report the synthesis of the first dye-labeled resorcin[4]arenes and demonstrate that these differentially bridged cavitands – as well as their partially bridged precursors – undergo efficient pH- or temperature-triggered *vase–kite* conformational switching. Besides, solvent-dependency of the *vase–kite* equilibrium was discovered and studied for the first time.

Starting resorcin[4]arene **2** was obtained by condensation [7] of resorcinol with heptanal, recrystalliation several times from MeOH, and drying over P_2O_5 (*Scheme 2*). Selective bridging of three of the four couples of neighboring, H-bonded OH groups was achieved as described in [8] in a reaction of tetrakis[benzene-diol] **2** with 3 equiv. of 2,3-dichloroquinoxaline, providing triply-bridged cavitand **3** in up to 35% yield. For the synthesis of doubly-bridged resorcin[4]arenes, 2 equiv. of 2,3-dichloroquinoxaline were used. The latter conversion yielded a mixture of several products, from which the desired bowls **4** and **5**, with the novel double bridging patterns, could be isolated by column chromatography (SiO_2; CH_2Cl_2/AcOEt 95 :5 → 85 :15) together with **3** (up to 20%) and fully bridged **1** (3–5%). Anhydrous conditions and purity of the starting tetrakis[benzene-diol] **2** proved to be critical for the partial bridging reactions; otherwise excessive tar formation was observed.

Dichloropyrazinedicarboximide **6** (*Scheme 3*) was selected for the introduction of the dyes into cavitands **7**–**9**. In **6** as well as in the corresponding cavitands **7**–**9** (*cf. Scheme 4*), the plane of the phenyl ring is nearly orthogonal to the plane of the BODIPY dye, and their π-systems are electronically decoupled; this ensures a very small influence of changes in the residual molecule (*e.g.*, from protonation) on the position of the absorption/emission bands of the dye. In the synthesis of **6**, anhydride **10** was prepared in two steps from 2,3-dichloroquinoxaline [1c]. The BODIPY fragment **11** was obtained in several steps starting from 2,4-dimethyl-3-ethyl-1*H*-pyrrole and 4-nitrobenzaldehyde (*Scheme 3*). Subsequent reaction of anhydride **10** with **11** under activation with oxalyl chloride provided imide **6**.

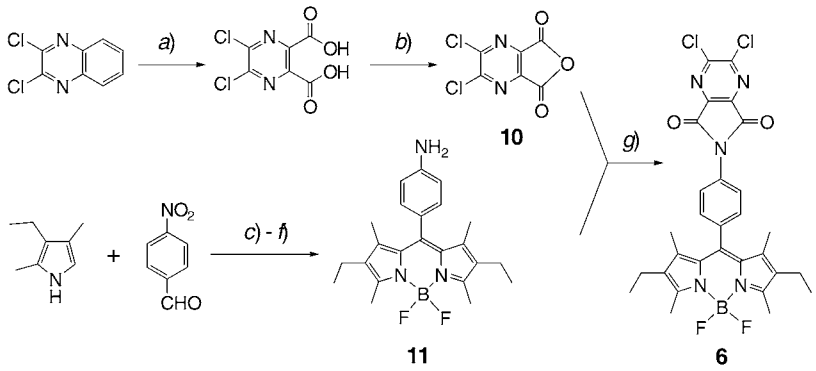
Finally, the BODIPY-substituted cavitands **7**–**9** were prepared from diol **3** and tetraols **4** and **5**, respectively, as shown in *Scheme 4*. All three cavitands are brightly red-colored, featuring sharp optical absorption/emission bands in $CHCl_3$ with maxima at 530/540 nm, respectively (*Fig.*). The substitution patterns of cavitands **8** and **9** are entirely novel and open multiple opportunities for future functionalization. For

Scheme 2. *Synthesis of Resorcin[4]arenes* **3**–**5**



a) Conc. HCl, EtOH, 90°, 14 h; 51%. *b*) 2,3-Dichloroquinoxaline (2 equiv.), K_2CO_3, Me_2SO, 20° (8 h), then 50° (18 h); 35% (**3**). *c*) 2,3-Dichloroquinoxaline (3 equiv.), K_2CO_3, Me_2SO, 20° (18 h), then 50° (6 h); 16% (**3**), 3.5% (**4**), 20% (**5**).

Scheme 3. *Synthesis of Dichlorodiazaphthalimide* **6**

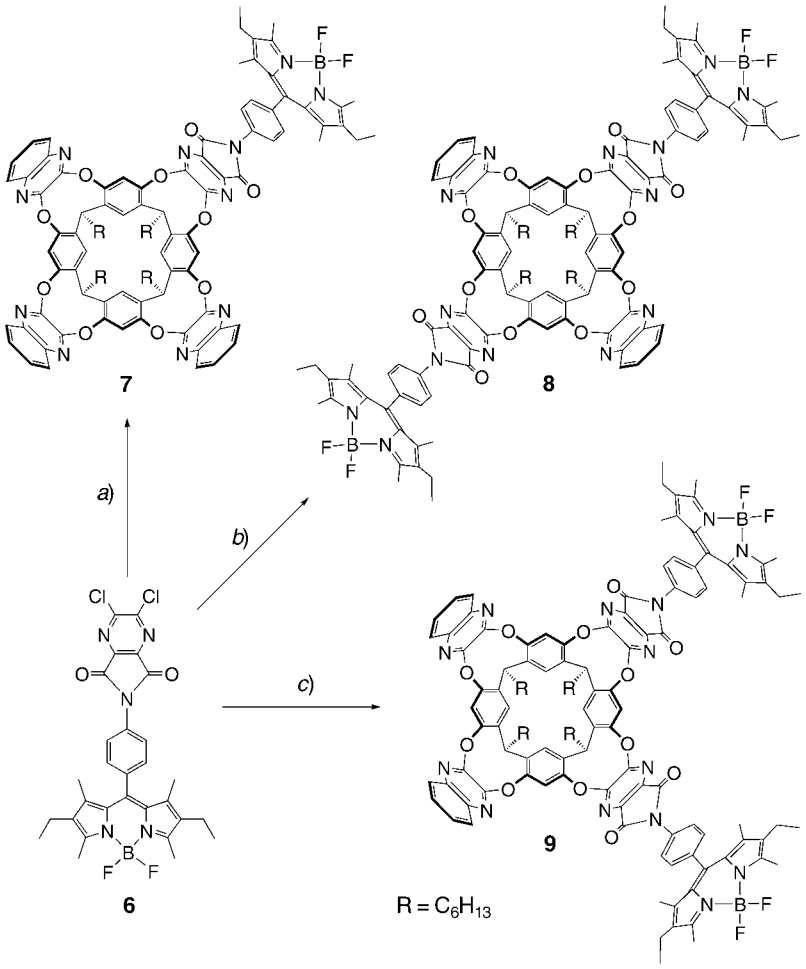


a) $KMnO_4$, H_2O, 95–97°, 2 h; 49%. *b*) $(COCl)_2$, Py (cat.), THF, 50°, 20 min; 49%. *c*) TFA, CH_2Cl_2, 20°, 2 h. *d*) DDQ, toluene, 1 h. *e*) Et_3N, 20° (10 min), then $BF_3 \cdot Et_2O$, 20° (30 min), then 50° (1 h); 31% for *c* – *e*. *f*) H_2 (1 atm), Pd/C (10%), $CHCl_3$/EtOH (1:1), 20°, 12 h; 67%. *g*) THF, 1 h, then $(COCl)_2$, Py, 50°, 12 h; 72%. Py = pyridine, TFA = CF_3COOH, DDQ = 2,3-dichloro-5,6-dicyano-*p*-benzoquinone.

example, receptor sites can be attached instead of the dye moieties for specific guest binding.

Before starting polarization-resolved single-molecule fluorescence-microscopic investigations, it was important to demonstrate that the substantial structural modification of cavitands **7**–**9** – as compared to parent **1** – was not interfering with reversible temperature- or pH-induced *vase*–*kite* switching. This conformational isomerism is conveniently monitored by measuring the ^{1}H-NMR chemical shift of the methine H-atom in the skeleton of the octol bowl. In **1**, this resonance appears at $\delta \approx$ 5.5 ppm in the *vase* and at $\delta \approx 3.7$ ppm in the *kite* conformation (*Table*). Acid-triggered

Scheme 4. *Synthesis of the Dye-Labeled Cavitands* **7**–**9**



a) **3** (1 equiv.), **6** (1 equiv.), K_2CO_3 (1 equiv.), Me_2SO, 20°, 24 h; 73%. *b*) **4** (1 equiv.), **6** (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*) **5** (1 equiv.), **6** (2 equiv.), K_2CO_3 (2 equiv.), Me_2SO, 20°, 24 h; 66%.

vase → *kite* isomerization is readily reversed upon addition of base (K_2CO_3 plus catalytic Et_3N). The following results were obtained.

i) *vase*–*kite* Switching is strongly solvent-dependent and was observed only in the apolar, nonaromatic solvents $CDCl_3/CS_2$ 1:1, CD_2Cl_2, and $C_2D_2Cl_4$. In (D_8)toluene or (D_6)benzene, addition of TFA led to minor changes in the ^{1}H-NMR spectrum that cannot be ascribed to *vase*–*kite* equilibration; no temperature variations in (D_8)toluene (except for line broadening) were detected. In the polar solvents ((D_6)acetone and (D_8)THF), no spectral changes upon TFA addition or temperature variation were observed. This supports the explanation advaned by *Cram* and co-workers that

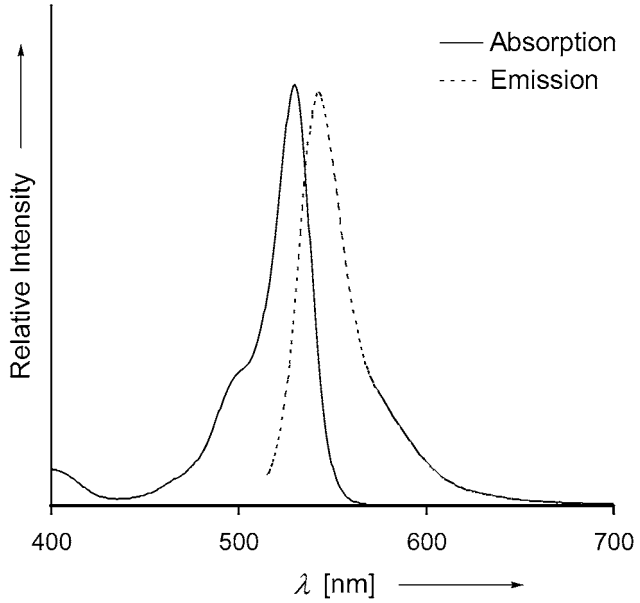


Figure. *Electronic absorption and emission spectra of cavitand* **7**. Intensity not to scale. Cavitands **8** and **9** feature similar spectra.

Table. *^{1}H-NMR Investigation of the Temperature- or pH-Triggered* vase–kite *Isomerization, with Monitoring of the Methine Resonance of the Octol Bowl*

Cavitand	Solvent	δ_H [ppm]/T [K][a])	δ_H [ppm]/T [K][b])[c])	δ_H [ppm] at [TFA] = 0.5M[b])
1	CD_2Cl_2	5.51/293	3.65/203	3.76
3	CD_2Cl_2	5.61, 5.51 (2 H), 4.29/308	3.65(3 H), 4.40/193	4.37, 3.96 (2 H), 3.85
4	CD_2Cl_2	5.39 (2 H), 4.36 (2 H)/293	–	4.43 (2 H), 3.74 (2 H)
5	CD_2Cl_2	5.52 (2 H), 4.22 (2 H)/293	–	4.35 (2 H), 3.79 (2 H)
7	CD_2Cl_2	5.52 (3 H), 5.40/308	3.65/193	3.80
8	$CDCl_3/CS_2$ (1:1)	5.56 (2 H), 5.37 (2 H)/333	3.71/193	3.89 (2 H), 3.83 (2 H)
9	$CDCl_3/CS_2$ (1:1)	5.56 (2 H), 5.35 (2 H)/333	3.71/193	3.97 (2 H), 3.91 (2 H)

[a]) Corresponds to *vase* conformation. [b]) Corresponds to *kite* conformation. [c]) *Multiplet* is not resolved.

solvent–cavitand interactions represent a key factor in controlling the switching process [1a,b].

ii) All BODIPY-dye-substituted cavitands undergo reversible *vase–kite* switching both upon temperature change and upon TFA addition. The differences in temperature at which the *vase* conformer is present exclusively, were, however, noticeable: in the ^{1}H-NMR spectrum of cavitand **7** with a single pyrazinedicarboximide wall component, all signals of the *vase* conformation became resolved at 308 K (CD_2Cl_2), as compared to 293 K for **1**. In the spectra of cavitands **8** and **9** with two pyrazinedicarboximide wall components, signals of the *vase* conformer became resolved only at 323 K ($CDCl_3$).

iii) Interestingly and unexpectedly, even the partially bridged resorcin[4]arenes **3**, **4**, and **5** undergo switching. For diol **3**, low-temperature experiments revealed that the switching was not complete, *i.e.*, both *kite* and *vase* conformers were present at 193 K (CD_2Cl_2). On the other hand, complete switching from *vase* to *kite* occurred upon addition of TFA. For tetrols **4** and **5**, low-temperature scans could not be performed, since they started to precipitate from a solution at temperatures below 273 K; addition of TFA at room temperature, on the other hand, led to complete transition from *vase* to *kite*. These experiments clearly underline the power of the pH-switching protocol recently introduced by us [2].

In summary, the BODIPY-dye-labeled cavitands **7**–**9** were prepared and shown in solution to undergo reversible *vase*–*kite* switching triggered either by temperature or pH changes. Samples immobilized at the solid–liquid interface support are now being investigated by polarization-resolved single-molecule microscopy in real time. The optical spectra in solution, as well as preliminary fluorescence-microscopy studies on **6** and **7** in spin-coated films in poly(methyl methacrylate) (PMMA) or neat on glass microscope cover slips, clearly confirmed the stability of the BODIPY dye labels and their compatibility with methods of single-molecule microscopy. Monitoring the switching at the level of single molecules should allow assessment of important parameters such as switching time and orientational distribution under various conditions, and these investigations are currently being pursued.

Support by the *Swiss National Science Foundation*, *via* the *NFP 'Supramolecular Functional Materials'*, the *NCCR 'Nanoscience'*, and a *SNF Förderprofessur* (*B. H.*) is gratefully acknowledged.

Experimental Part

7-[4-(2,8-Diethyl-5,5-difluoro-1,3,7,9-tetramethyldipyrrolo[1,2-c:*2,1-f][1,3,2]diazaborinin-4-ium-5-uid-10-yl)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*^{19,24}*.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**). Bright-red solid. R_f (SiO_2; CH_2Cl_2/AcOEt, 98:2) 0.55. UV/VIS ($CHCl_3$): λ_{max} 530 (ε 71000 м$^{-1}$ cm^{-1}). Fluorescence ($CHCl_3$): λ_{max} 542. IR (CCl_4): 3075, 2962, 2930, 2859, 1744, 1543, 1481, 1415, 1400, 1363, 1335, 1265, 1192, 1161, 1118, 1087, 981, 898. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.90–0.96 (*m*, 12 H); 1.06 (*t*, *J* = 7.5, 6 H); 1.28–1.53 (*m*, 32 H); 1.45 (*s*, 6 H); 2.21–2.32 (br. *m*, 8 H); 2.39 (*q*, *J* = 7.5, 4 H); 2.59 (*s*, 6 H); 5.48 (*t*, *J* = 7.8, 1 H); 5.54–5.63 (*m*, 3 H); 7.21–7.31 (*m*, 8 H); 7.41–7.52 (*m*, 6 H); 7.79–7.85 (*m*, 4 H); 7.96–8.00 (*m*, 2 H); 8.16 (*s*, 2 H); 8.17 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 12.30; 12.94; 14.39; 15.01; 17.49; 22.97; 28.20; 29.66; 32.15; 32.70; 34.63; 118.56; 118.93; 123.47; 123.81; 126.74; 127.57; 127.90; 128.99; 129.30; 130.74; 131.40; 133.29; 135.42; 135.58; 135.83; 136.18; 136.91; 138.09; 138.51; 139.56; 139.64; 139.72; 141.05; 152.09; 152.24; 152.31; 152.41; 152.58; 152.63; 152.86; 154.46; 158.56; 161.15. ^{19}F-NMR ($CDCl_3$, 282.5 MHz): −145.12 (*q*, *J* = 35). HR-MALDI-MS (2,5-dihydroxybenzoic acid (DHB)): 1706.7853 ([*M* − F]$^+$, $C_{105}H_{102}BFN_{11}O_{10}^+$; calc. 1706.78882), 1726.7983 (*M*H$^+$, $C_{105}H_{103}BF_2N_{11}O_{10}^+$; calc. 1726.79505).

*7,36-Bis[4-(2,8-diethyl-5,5-difluoro-1,3,7,9-tetramethyldipyrrolo[1,2-*c*:2,1-f][1,3,2]diazaborinin-4-ium-5-uid-10-yl)phenyl]-59-*endo,*63-*endo,*67-*endo,*71-*endo-*tetrahexyl-2,12,16,27,31,41,45,56-octaoxa-4,7,10,18,25,33,-36,39,47,54-decaazaheptadecacyclo[55.15.1.1*^{58,72}*.0*^{3,11}*.0*^{5,9}*.0*^{13,70}*.0*^{15,68}*.0*^{17,26}*.0*^{19,24}*.0*^{28,66}*.0*^{30,64}*.0*^{32,40}*.0*^{34,38}*.0*^{42,62}*.0*^{44,60}*.-0*^{46,55}*.0*^{48,53}*]tetraheptaconta-1(72),3,5(9),10,13,15(68),17,19(24),20,22,25,28,30(64),32,34(38),39,42,44(60),-46,48(53),49,51,54,57(73),58(74),61,65,69-octacosaene-6,8,35,37-tetrone* (**8**). Bright-red solid. R_f (SiO_2; CH_2Cl_2/AcOEt, 97:3) 0.4. UV/VIS ($CHCl_3$): λ_{max} 529 (ε 122000 м$^{-1}$ cm^{-1}). Fluorescence ($CHCl_3$): λ_{max} 542. IR (CCl_4): 3080, 2963, 2930, 2859, 1746, 1544, 1481, 1412, 1363, 1322, 1264, 1192, 1160, 1088, 981, 900. ^{1}H-NMR ((D_8)THF, 300 MHz): 0.93–0.99 (*m*, 24 H); 1.44 (*s*, 12 H); 1.35–1.55 (*m*, 32 H); 2.27–2.49 (*m*, 16 H); 2.51 (*s*, 12 H); 5.71 (*t*, *J* = 8.1, 2 H); 5.80 (*t*, *J* = 8.1, 2 H); 7.32–7.36 (*m*, 4 H); 7.50 (*s*, 4 H); 7.51–7.59 (*m*, 8 H); 7.98–8.02 (*m*, 4 H); 8.26 (*s*, 4 H). ^{13}C-NMR ((D_8)THF, 125 MHz): 12.06; 12.63; 14.42; 14.96; 17.64; 23.59; 25.87; 28.94; 28.99; 30.18;

30.25; 30.63; 32.84; 32.89; 33.14; 35.09; 119.78; 124.84; 127.25; 129.50; 129.93; 130.17; 131.46; 132.96; 133.71; 136.84; 136.99; 137.97; 138.07; 139.72; 140.70; 142.73; 153.21; 153.29; 153.96; 155.08; 159.04; 156.32. ^{19}F-NMR ($CDCl_3$, 282.5 MHz): −143.99 (*q*, *J* = 35). HR-MALDI-MS (*trans*-2-{3-[4-(*tert*-butyl)phenyl]-2-methylprop-2-enylidene}malononitrile (DCTB)): 2103.9791 ($[M-F]^+$, $C_{126}H_{124}B_2F_3N_{14}O_{12}^+$; calc. 2103.96614), 2145.9598 ($[M+Na]^+$, $C_{126}H_{124}B_2F_4N_{14}O_{12}Na^+$; calc. 2145.95431).

*7,21-Bis[4-(2,8-diethyl-5,5-difluoro-1,3,7,9-tetramethyldipyrrolo[1,2-*c*:2,1-*f*][1,3,2]diazaborinin-4-ium-5-uid-10-yl)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* (**9**). Bright-red solid. R_f (SiO_2; CH_2Cl_2/EtOAc, 97:3) 0.44. UV/VIS ($CHCl_3$): λ_{max} 530 (ε 135000 M^{-1} cm^{-1}). Fluorescence ($CHCl_3$): λ_{max} 543. IR (CCl_4): 3075, 2963, 2930, 2860, 1744, 1543, 1481, 1414, 1364, 1322, 1264, 1192, 1162, 1116, 1085, 980, 899. ^{1}H NMR ((D_8)THF, 300 MHz): 0.93–0.99 (*m*, 24 H); 1.26 (*s*, 12 H); 1.36–1.54 (*m*, 32 H); 2.29–2.46 (*m*, 16 H); 2.50 (*s*, 12 H); 5.68 (*t*, *J* = 8.1, 2 H); 5.79 (*t*, *J* = 8.1, 2 H); 7.28–7.65 (*m*, 16 H); 7.89–8.08 (*m*, 5 H); 8.20–8.24 (*m*, 3 H). ^{13}C-NMR ((D_8)THF, 75 MHz): 12.17; 12.52; 14.34; 14.96; 17.51; 23.47; 28.80; 28.85; 30.05; 30.12; 32.77; 32.92; 34.96; 35.06; 119.46; 119.54; 119.81; 124.36; 124.79; 125.43; 127.86; 128.66; 129.08; 129.43; 129.93; 130.14; 131.19; 132.67; 133.43; 136.34; 136.67; 136.75; 137.30; 137.97; 138.38; 139.74; 140.16; 142.62; 142.94; 152.61; 153.05; 153.38; 153.53; 154.41; 157.81; 158.22; 161.62; 161.89. ^{19}F-NMR ($CDCl_3$, 282.5 MHz): −144.19 (*q*, *J* = 35). HR-MALDI-MS (DHB): 2103.9735 ($[M-F]^+$, $C_{126}H_{124}B_2F_3N_{14}O_{12}^+$; calc.: 2103.96614), 2145.9580 ($[M+Na]^+$, $C_{126}H_{124}B_2F_4N_{14}O_{12}Na^+$; calc. 2145.95431).

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