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The Self-Assembly of Catenated Calix[4]arenes

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Abstract: Two [2]catenanes, in which one calix[4]arene subunit is incorporated into the tetracationic ring, have been synthesized, the calix[4]arene moieties influence remarkably the conformation and solubility of the resulting catenanes.

Keywords: calixarene; catenanes; hydrogen bonding; conformation

The π-π stacking between the electronically complementary bipyridinium and hydroquinone units offers one efficient method to assemble the interlocked molecular compounds, catenanes[1]. By modifying the donor and/or acceptor units, a variety of more sophisticated catenanes with defined structures or functions have been constructed[2-7]. Calixarenes represent a class of macrocyclic compounds whose sizes and shapes have been exploited mainly for the recognition of metal ions and polar organic molecules[8,9]. In recent years, calixarenes, in particular calix[4]arenes with a versatile platform of well-defined shape, have been utilized extensively as molecular frameworks for construction of highly preorganized supramolecular systems[10,11]. Given their unique structural features and well-established modifications at both the lower and upper rims, it would be interesting to incorporate the calix[4]arene moiety into catenane molecules. The introduction of the calix[4]arene moiety will not only create a new class of supramolecular structures, but may also influence the solubility and dynamic processes of the resulting catenanes. Furthermore calix[4]arenes-containing catenanes may be utilized as model compounds to investigate further the effects of hydrogen bonding and steric and conformational factors on self-assembly processes of this type of interlocked molecular systems. Such an investigation should be of importance for future design of "informed" supramolecular system[12]. Herein , we wish to describe the self-assembly of two calix[4]arene-incorporating [2]catenanes. Although the calix[4]arene moieties do not act as donors or acceptors during the self-assembling process, they influence remarkably

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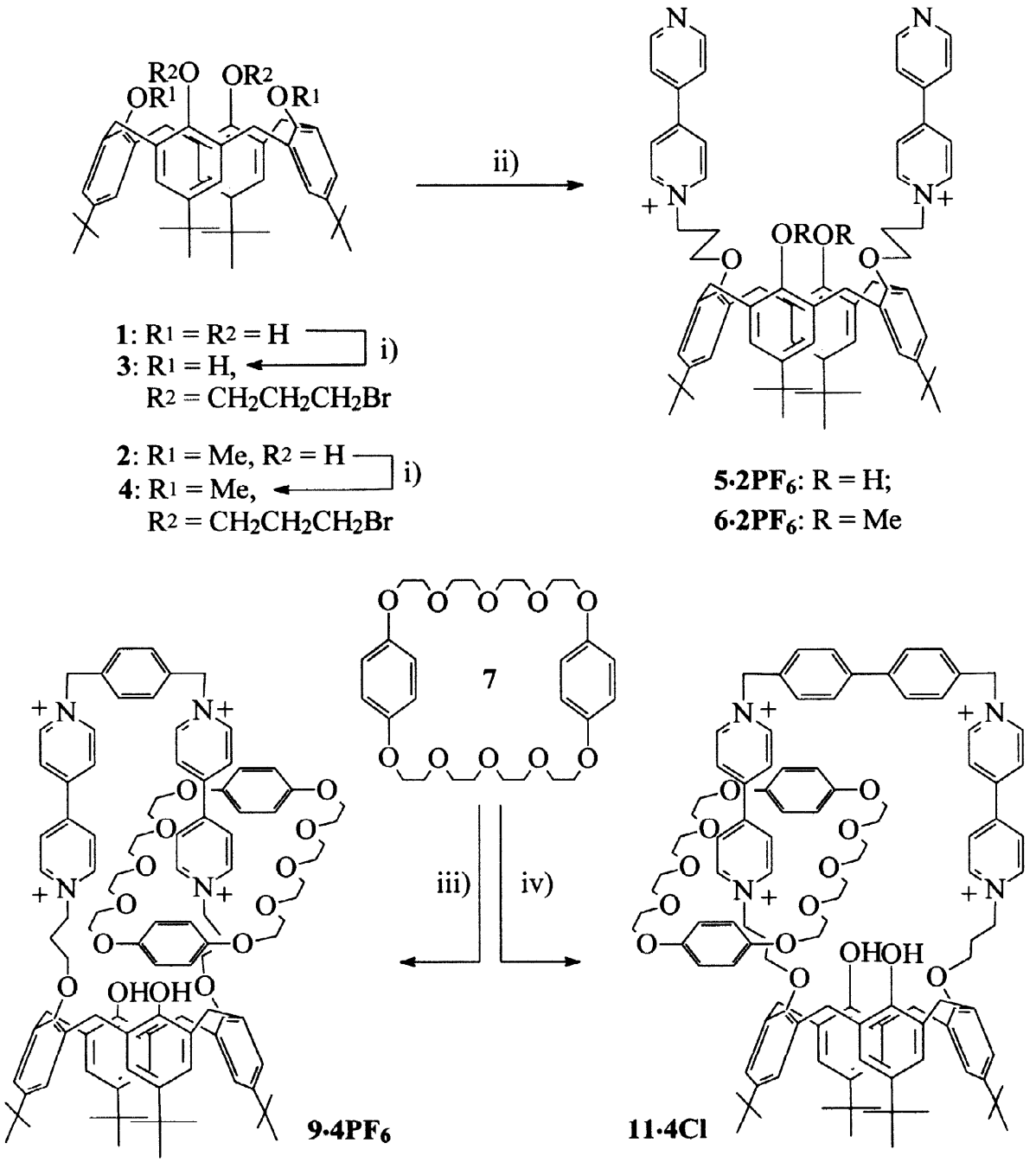
the conformation and solubility of the resulting catenanes.

The synthesis of calix[4]arene-containing catenanes is shown in scheme 1. Thus, treatment of *p-tert*-butylcalix[4]arene **1** with an excess of 1,3-dibromopropane in the presence of potassium carbonate afforded 1,3-di(3-bromopropoxy)-*p-tert*-butylcalix[4]arene **3** in 70% yield. Similarly, reaction of 1,3-dimethoxy-*p-tert*-butylcalix[4]arene **2** with 1,3-dibromopropane with cesium carbonate as a base gave tetraalkoxy-*p-tert*-butylcalix[4]arene **4** in 46% yield. **5•2PF$_6$** and **6•2PF$_6$** were obtained from reactions of compounds **3** and **4** with an excess of 4,4'-bipyridine in 55% and 34% yields, respectively. As expected, di-*o*-substituted calix[4]arene derivatives **3** and **5•2PF$_6$** are in the *cone* conformation, whereas the tetra-*o*-substituted **4** and **6•2PF$_6$** are conformationally mobile. **5•2PF$_6$** reacted with 1,4-(dibromomethyl)benzene **8** in the presence of bisparaphenylene-34-crown-10 **7**, affording [2]catenane **9•4PF$_6$** in 35% yield after normal work-up and ion exchange, while [2]catenane **11•4Cl** was obtained from the reaction of **5•2PF$_6$**, **7**, and 4,4'-(dibromomethyl)biphenyl **10** in 22% yield. Purification of **11•4Cl** was simplified greatly as a result of the fact that this chloride was insoluble in water. Therefore it could be separated from ammonium chloride by simply washing thoroughly with water after column chromatography. No [3]catenane, in which two crown ether rings are threaded simultaneously through the tetracationic cyclophane, was obtained from the latter reaction[13]. It is worthy to note that the free tetracationic cyclophane could not be obtained from the reaction of **5•2PF$_6$** with dibromide **8** or **10**, regardless of whether templating threadlike molecules incorporating hydroquinone rings were present in the reaction mixture or not[14]. Under similar conditions, no catenanes were obtained from reaction of **6•2PF$_6$**, **7**, and **8** or **10**, which only gave insoluble residues. This observation seems to indicate that the two bipyridine cationic subunits in **6•2PF$_6$** prefer to stay away from each other as a result of the mobile conformation.

All new compounds were characterized by elemental analysis, mass spectra, and, if possible, by ^{1}H and ^{13}C NMR spectra[15]. The *cone* conformation of compounds **3**, **5•2PF$_6$** and **9•4PF$_6$** were inferred from their ^{1}H NMR spectra, since the Ar*CH$_2$*Ar protons of all these compounds exhibit an AX system, which is typical for a fixed *cone* conformation. The peaks in ^{1}H NMR spectrum of **9•4PF$_6$** are also assigned on the basis of 2D COSY spectra. The protons of hydroquinone rings of the crown ether do not exhibit two so-called "inside" and "alongside" signals of the "parent" [2]catenane at room temperature[1], a single broad resonance at δ5.60 is still observed for these protons even at low temperature of -25 °C, reflecting that the strength of the donor/acceptor recognition motif in **9•4PF$_6$** is reduced significantly as a result of introducing the calix[4]arene subunit into the acceptor cyclophane.

Surprisingly, [2]catenane **11•4Cl** is a mixture of conformational isomers, as indicated by its ^{1}H NMR spectrum, which is composed of broad peaks in all regions. This result reveals that the



Scheme 1 *Reagents and Conditions:* i) $BrCH_2CH_2CH_2Br$ (10 equiv.), MeCN, 80 °C, 72 hrs; ii) (a) 4,4'-bipyridine, MeCN, 80 °C, 48 hrs; (b) ion exchange; iii) (a) 1,4-bis(bromomethyl)-benzene **8**, **5•2PF$_6$**, MeCN, r.t., 7 days; (b) ion exchange; iv) 4,4'-bis(bromomethyl)biphenylene **10**, **5•2PF$_6$**, MeCN, r.t., 5 days.

tension produced by the incorporation of the "extended" bisphenylene subunit into the tetracationic cyclophane is considerable, which is able to destroy the intramolecular hydrogen bonding between the two hydroxy hydrogens and the two substituted oxygens of the calix[4]arene moiety. This represents the first example that the fixed *cone* conformation of a calix[4]arene derivative can be broken by formation of a cyclophane. The difference in the solubility of

[2]catenanes **9•4PF$_6$** and **11•4Cl** are remarkably large. At room temperature, **9•4PF$_6$** is soluble in acetonitrile (2.0×10^{-2} M) and methanol (3.5×10^{-3} M), while **11•4Cl** is insoluble in most common organic solvents ($<1.0\times10^{-5}$ M).

In summary, we have established a convenient method to assemble calix[4]arene-containing [2]catenanes. The fact that conformationally mobile compound **6•2PF$_6$** did not afford the expected catenane product indicates that the *cone* calix[4]arene precursor is indispensable for the construction of calix[4]arene-derived catenanes. The results also demonstrate that introducing calixarene moieties into catenane molecules provides new approach to influence and/or control their properties.

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[15] Selected Analytical data: **9•4PF$_6$.** ^{1}H NMR (CD_3CN) 300MHz: 1.19 (s, 18 H), 1.33 (s, 18 H), 2.75 (m, 4 H), 3.47 (m, 8H), 3.56 (d, 4H), 3.78 (m, 8 H), 3.86 (m, 16 H), 4.10 (t, 4 H), 4.36 (d, 4 H), 4.66 (t, 4 H), 5.60 (br, 8 H), 5.87 (s, 4 H), 7.23 (s, 4 H), 7.32 (s, 4 H), 7.59 (s, 2 H), 7.83 (d, 8 H), 7.92 (s, 4 H), 8.85 (d, 4 H), and 9.02 (d, 4 H) ppm; ^{13}C NMR (CD_3CN) 300MHz: 20.3, 20.5, 20.8, 21.0, 21.3, 21.5, 30.4, 30.9, 33.7, 34.0, 58.2, 67.5, 69.6, 70.2, 70.5, 73.5, 114.5, 115.4, 117.6, 125.6, 126.1, 127.5, 130.9, 133.1, 145.7, 148.4, 149.6, 149.9, 151.7, and 173.4 ppm; ES-MS: 1972 $[M\text{-}2PF_6]^+$, 1826 $[M\text{-}3PF_6]^+$, 1365 $[2M\text{-}3PF_6]^{3+}$, 987 $[M\text{-}2PF_6]^{2+}$, 610 $[M\text{-}3PF_6]^{4+}$. **11•4Cl.** ^{1}H NMR (CD_3OD) 300MHz: 1.05-1.49 (m, 36 H), 2.56-4.53 (m, 52 H), 5.5-6.2 (m, 12 H), 7.1-9.2 (m, 34 H) ppm; ES-MS: 1826 $[M\text{-}2Cl]^+$, 1233 $[M\text{-}3Cl]^+$, 1233 $[2M\text{-}3Cl]^{3+}$, 916 $[M\text{-}2Cl]^{2+}$, and 597 $[M\text{-}3Cl]^{3+}$.