(10 mL, distilled) was refluxed for 3 d. After removal of volatile fractions from the reaction mixture the residue was subjected to dialysis against pure water for 3 d and freeze-dried to give the iodide salt of 32[+]DPZn (17.3 mg, 79.0 %). This salt was then dialyzed for 2 d against saturated NaCl solution and an additional 2 d against pure water, after which it was freeze-dried. ^{1}H NMR (270 MHz, [D$_6$]DMSO, 80 °C): $\delta = 8.97$ (s, 8H, pyrrole-β), 8.73 (s, 32H, amide-NH), 7.84, 7.43 (d, $^3J = 7.42$ Hz, 128H, Ar-o-H, Ar-m-H), 7.51 (s, 8H, Ar-o-H), 7.23 (br s, 4H, Ar-p-H), 6.87 (s, 16H, Ar-o-H), 6.72 (s, 32H, Ar-o-H), 6.66 (s, 8H, Ar-p-H), 6.57 (s, 16H, Ar-p-H), 5.27 (s, 16H, OCH$_2$), 5.07 (s, 64H, OCH$_2$), 5.01 (s, 32H, OCH$_2$), 3.68, (br q, 64H, CH$_2$), 3.54 (br t, 64H, CH$_2$), 3.14 (s, 288H, NCH$_3$); ^{13}C NMR (68 MHz, [D$_6$]DMSO, 20 °C): $\delta = 166.02$ (CONH), 159.30, 159.10, 140.25, 139.18, 132.82, 127.20, 106.68, 100.95 (aromatic C), 68.68 (CH$_2$O), 63.68 (CH$_2$N), 52.57 (CH$_3$N), 33.75 (NHCH$_2$); UV/Vis (KOH/MeOH): λ_{max} (lgε) = 436.5 (5.49), 563, 608 nm; fluorescence (KOH/MeOH): $\lambda = 613$, 664 nm.

Electronic absorption spectra were recorded with a Jasco Model V-560 UV/Vis spectrometer. Fluorescence-polarization and energy-transfer experiments were performed at 20 °C with a Jasco Model FP-777 fluorescence spectrometer. In the energy-transfer experiments with 32[−]DPH$_2$ as acceptor, undesirable contamination of the fluorescence bands as a result of direct excitation of the acceptor was evaluated by a control experiment without donor under otherwise identical conditions. The spectrum that resulted was subtracted from the overall fluorescence spectrum for the donor/acceptor systems. The spectral profile of 32[−]DPH$_2$ in the control experiment was shown to obey the Lambert–Beer law.

Fluorescence lifetimes were measured in deoxygenated 0.1 M methanolic KOH at 20 °C with a Hamamatsu Model C4780 picosecond fluorescence lifetime measuring system equipped with a Model C4334 streak scope and a N$_2$ laser pumped coumarin 440 dye laser as excitation source. The N$_2$ laser was an LN120C2 device (15 Hz, peak width (FWHM) 350 ps, 10 mJ per pulse), and the excitation wavelength was 430 nm. Fluorescence bands were isolated from scattered laser light by a 600 nm glass cutoff filter. Emission was collected in the wavelength range 600–680 nm and analyzed with the program Photolumi version 2.4.4 after deconvolution of the instrument-response function (time resolution 50 ps).

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A Synthetic Cation-Transporting Calix[4]arene Derivative Active in Phospholipid Bilayers**

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The transport of cations through bilayer barrier membranes is a ubiquitous biological process, and one of the most critical for sustaining life. Cation transport in vivo is usually mediated by proteins having one or more transmembrane helices that organize into pores. Increasing evidence suggests that channel function may also be achieved by compounds such as the remarkable C peptide.[1] Although a vast amount is known about the biophysics of membrane transport, much of this information is descriptive and does not reveal mechanistic details;[2, 3] how transport occurs is simply not understood at the molecular level. Thus, several model ion transporters have been devised, including short-chain or "minimalist" peptides[4] and a variety of synthetic organic compounds such as tubelike structures, "half-channel" elements, single-strand compounds,[5, 6] and the tris(macrocyclic) channel model **4** that we devised.[7] Compound **4** has proved to be an effective conductor of Na$^+$ ions.[7] The two distal diaza[18]crown-6 macrocycles serve as headgroups in the amphiphilic sense, and as entry and exit points for cations traversing the bilayer.[8] Passage of the transient cation through the medial macrocycle, however, is not necessary.[7]

We describe herein two new channel compounds **1** and **2** having a calix[4]arene central unit in a 1,3-*alternate* conformation. Passage of cations through the center of such a rigid

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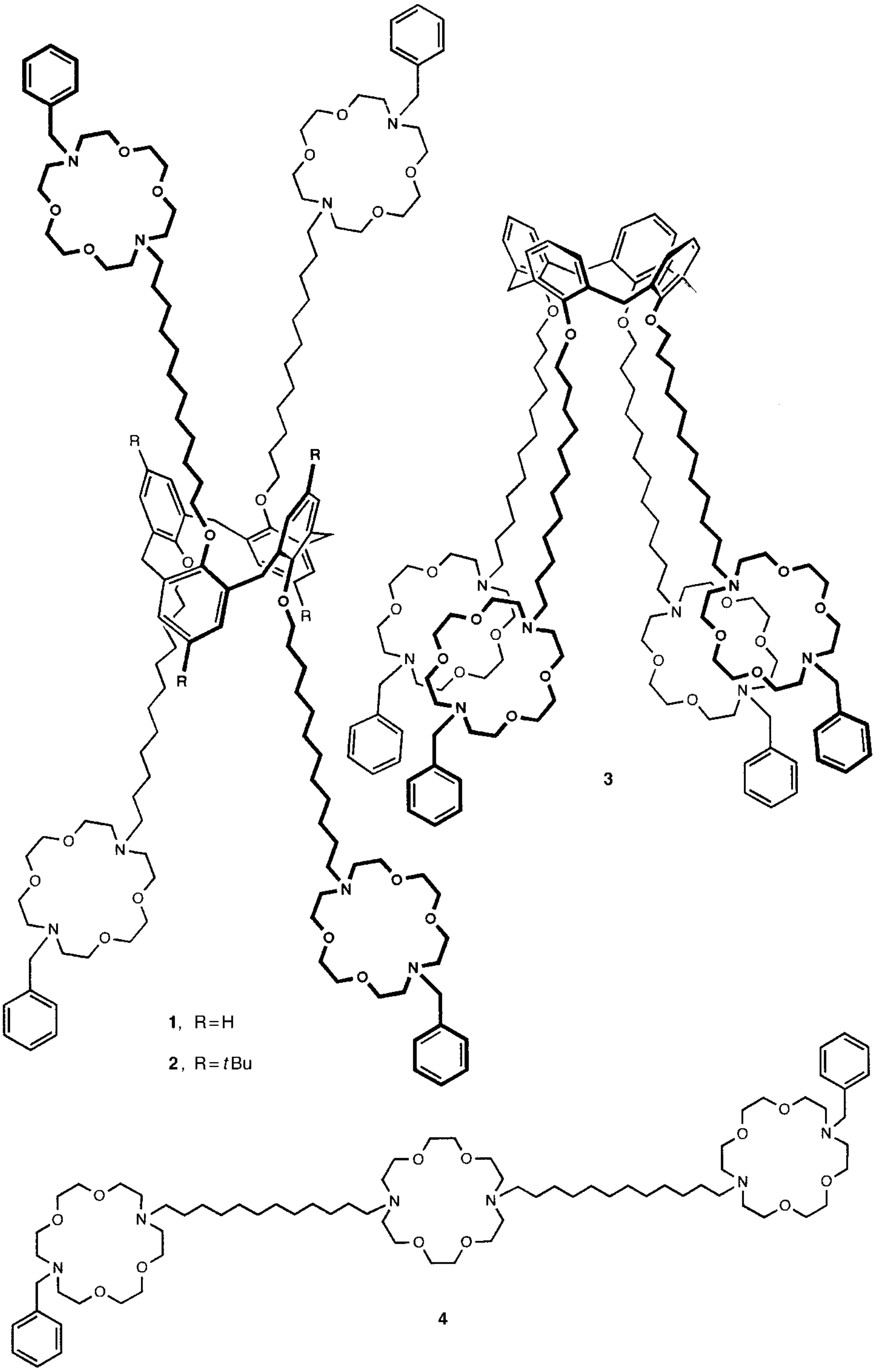

1, R=H

2, R=*t*Bu

3

4

framework has recently been demonstrated.[9] If successful, the movement of the cation through the calix would constitute a useful strategy for the design of synthetic channels.[10] In compound **2** the calix[4]arene is substituted by bulky *tert*-butyl groups. For comparison, the cone derivative of **1** (i.e., **3**) was also prepared and studied. In all cases, dodecyl chains terminated in 10-benzyl-1,10-diaza[18]crown-6 units were attached to each of the calixarene phenol groups to allow direct comparison with the already studied tris(macrocycle) channel compound **4**.

Compounds **1**–**3** was synthesized by attachment of four THP-protected (THP = 2-tetrahydropyranyl) 12-bromododecanol chains to the lower rim of the corresponding calix[4]arene (Cs_2CO_3/DMF for the 1,3-*alternate* conformation, NaH for the cone conformation).[11] The chains were deprotected and brominated (CBr_4/PPh_3), and the resulting tetrabromo derivatives were allowed to react with 10-benzyl-1,10-diaza[18]crown-6 to afford channels **1** and **2** as waxy solids in 42 % yield. Cone compound **3** was obtained similarly in 26 % yield.[12]

Since the ring does not invert at room temperature, two arms must radiate from either side of the central platform. The diazacrown units are presumed to be headgroups that stabilize the sidearms in an extended arrangement at the membrane boundaries, but whether the crowns are perpendicular or parallel to the lipid axis is unknown.[13] Thus, the overall length of the channel lies between 34 and 60 Å and is enough to span the lipid portion of a typical bilayer membrane (normally about 30 Å thick).

The ability of calix[4]arene compounds **1**–**3** to conduct cations was assessed by using the planar bilayer conductance (PBC) technique.[14] In this method, a pinhole in a Teflon disk is covered by a phospholipid mixture[15] to create a planar bilayer membrane (black lipid). Addition of **1** or **2** (1 μL of a 1 μM solution, i.e., 1 pmol of substance) in the bilayer dramatically increased either the Na^+ or K^+ permeability of the previously nonpermeable membrane. Data on sodium transport obtained for **1** and **2** at +100 mV are shown in Figure 1. Doubling the amount of **1** or **2** added increased the intensities and frequencies of the observed transitions. Both compounds exhibited "burst" events of nearly 300 pS. These intense ion fluxes normally persisted less than a second, but the presumed overlap of several conductance events resulted in occasional episodes of longer than 3 s.

Compound **3**, the "control" structure having the cone conformation, did not conduct cations when added to the bilayer in concentrations as high as 100 pmol (2 μL of a 50 μM solution) under otherwise identical conditions. Inspection of CPK models showed that **3** is too short to span the

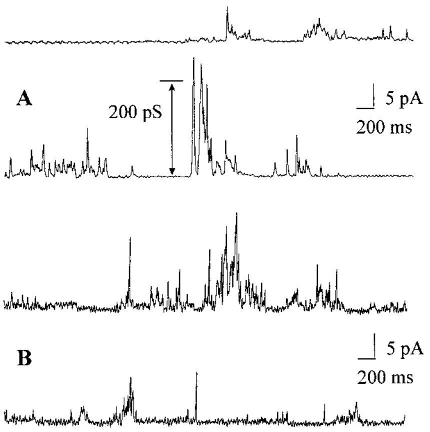

Figure 1. Planar bilayer conductance data for **1** (A) and **2** (B; 1 pmol of each in THF); [NaCl] = 0.5 M, +100 mV applied potential.

phospholipid bilayer. On the other hand, when amounts of **1**–**3** approaching 1 nmol were added, the membranes apparently lost their well-defined structure and exhibited erratic permeability behavior.

The bursts shown in Figure 1 are reminiscent of the behavior seen in bilayers in the absence of any channel former when very high voltages (≥200 mV) are applied across the membrane (electroporation experiments).[16] To discount this possibility, additional data were collected in separate runs conducted at ±40, ±60, ±80, and ±100 mV (data for **1** at +40 mV are shown in Figure 2). The observed pattern of current amplitudes was proportional to that recorded at 100 mV, showing that the channels behave generally as expected for a symmetrical ion transporter.

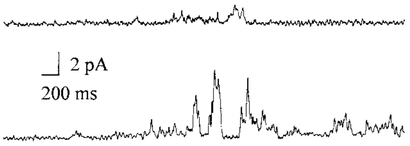

Figure 2. Planar bilayer conductance data for **1** (1 pmol in THF); [NaCl] = 0.5 M, +40 mV applied potential.

Compound **4**, the tris(macrocycle), typically shows single open–close transitions in the PBC experiment.[7] The amplitudes of these transitions are normally integral and range between 10 and 20 pS, a value typical for gramicidin and many natural sodium-transporting proteins. The behavior of novel channels **1** and **2** is dramatically different in two senses. Not only are the amplitudes much higher (spiking to levels of hundreds of pS), but bursts rather than flat-topped integral transitions are observed. Similar behavior has recently been observed for an oligo-THF channel model system.[6j]

The unusual behavior of **1** and **2** can be rationalized by considering their overall structures. In the tris(macrocyclic) channel model **4**, a single crown ether group is thought to reside at each membrane surface to form a cation-conducting nanotube. In contrast, in **1** and **2** the two crown ether groups on each side may rapidly exchange positions; this leads, on average, to a much larger opening in the membrane. If the sidearms sweep out a conical surface in each direction from the bilayer midplane, conductance should be quite high, and the great flexibility of the system would lead to the observed spikes.

Does either Na^+ or K^+ pass through the hole of calix[4]arenes **1** and **2**? In the solid state, the mean distance between two aryl groups in a calix[4]arene in the 1,3-*alternate* conformation is about 5.9 Å (between the centers of the aryl ring).[17] This value is compatible with those from theoretical calculations on ideally sandwiched benzene-M^+-benzene arrangements, where $M^+ = Na^+$ (4.96 Å) or K^+(5.84 Å).[18] Shinkai and co-workers[9] have shown that cations can pass through a 1,3-*alternate* calix[4]arene. However, in the case of tetra-*tert*-butyl derivative **2**, CPK models show that the core is completely blocked at both sides of the 1,3-*alternate* conformation when the aryl rings are parallel to each other. Thus, to permit cations to penetrate the calix with any significant frequency the conformation must distort markedly in a sequential way: Two rings open slightly while the others close accordingly. The reverse process should then occur at the other end of the hole to allow the cations to exit. The essential similarity of the PBC traces for Na^+ and K^+ with *both* **1** and **2** suggests that cations cross the bilayer by similar mechanisms, and makes it highly unlikely that either Na^+ or K^+ cations pass through the calix. In other words, since passage through the calix is hampered in **2**, ions must pass outside the rings *also* in **1**. This does not prove that cations never penetrate the calix, but if the phenomenon were favored evidence for it would be expected from experiments such as this one.

In conclusion, a novel class of cation-conducting channels, with high conductance levels for both Na^+ and K^+ cations, has been developed. In these compounds, however, the core calix[4]arene in 1,3-*alternate* conformation behaves as a preorganized platform that organizes the tails at either side rather than acting as a tube for ions. Channels have been designed around other platforms—such as self-assembling cyclic peptides[6f] or cyclodextrins[6c]—and could utilize the wider, more flexible, calix[6]arenes. These higher oligomers of calixarenes are currently under investigation.

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X-Ray Structural Analysis of a Novel Lithium Hydride/Lithium *tert*-Butoxide Superaggregate: $Li_{33}H_{17}(OtBu)_{16}$**

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The high lattice energy of lithium hydride drastically reduces its reactivity and is responsible for its insolubility in organic solvents.[1, 2] Consequently, any form of lithium hydride, whether complexed by ligands or uncomplexed, is an amorphous solid. Crystal structures of lithium hydride or of mixed aggregates containing lithium hydride have not been reported. We have recently provided evidence that the photochemical and thermal decomposition[3] of *tert*-butyllithium/lithium *tert*-butoxide mixtures[4] (molar ratio 3:7) in cyclopentane leads to highly reactive, hydrocarbon-soluble LiH[5] in the form of mixed LiH/LiO*t*Bu aggregates.[6] Precipitation of amorphous lithium hydride from such mixtures is apparently prevented by the excess of lithium *tert*-butoxide, which assists in solubilizing the LiH by incorporating it in mixed aggregates.[7, 8] Previous NMR spectroscopic studies revealed that the photochemical decomposition product is the decamer $Li_{10}H(OtBu)_9$, while the thermal decomposition product is dodecameric $Li_{12}H(OtBu)_{11}$.[6] It is noteworthy that these mixed aggregates form only at high alcoholate:alkyllithium ratios (ROLi:RLi $\geq$ 7:3), that is, when a large excess of *tert*-butoxide ligands is present. At lower ROLi:RLi ratios, amorphous lithium hydride precipitates from solution.

X-ray structural analyses of crystals grown from photolyzed *t*BuOLi/*t*BuLi mixtures (ca. 7:3) showed the presence of the hydride-rich superaggregate $Li_{33}H_{17}(OtBu)_{16}$ (**1**, Figure 1).[9] The synthesis is reproducible and, under the conditions chosen, exclusively yields crystals of **1**. To our knowledge, this is the largest lithium-containing aggregate so far known. The structural framework consists of fused cubic subunits (Figure 2), whose arrangement to form an infinite lattice is disrupted by the incorporation of the sterically demanding *tert*-butoxide groups. The inner core of the aggregate is hydride-rich, while in the outer shell *tert*-butoxide ligands are

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