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[2]Pseudorotaxanes

Cooperative Ion–Ion Interactions in the Formation of Interpenetrated Molecules**

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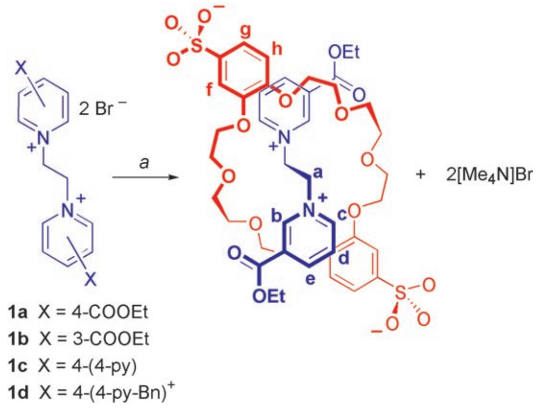
The importance of interlocked molecules in nanoscience has grown dramatically in recent years as inventive applications have been developed for these systems.[1] However, the synthesis of interlocked molecules can be challenging, as it almost always relies on the supramolecular assistance[2] provided by weak interactions such as hydrogen bonding,[3] π stacking,[4] ion–dipole,[5] or labile metal–ligand bonds.[6] Interestingly, one of the strongest noncovalent interactions possible, the electrostatic attraction between oppositely charged ions, has essentially been ignored as a driving force to form interpenetrated species and eventually interlocked molecules such as rotaxanes, catenanes, or related molecular machines. This is surprising, as it is known that a) the incorporation of pendant anionic functionalities into lariat crown ethers increases their ability to bind cations,[7] b) the addition of positively charged groups increases anion receptor abilities,[8] and c) supramolecular capsules can be readily assembled using oppositely charged components.[9]

We have devised a pseudorotaxane system in which the recognition event between an axle and a wheel is driven not only by the interplay of hydrogen bonds, ion–dipole interactions, and π stacking, but also by significant electrostatic ion–ion attractions. This concept should be applicable to other interpenetrated systems and has the benefit of eliminating the need for multiple counterions, which often complicate the study of noncovalent interactions in solution[10] and can dictate surface interactions[11] and solid-state structures.[12]

Herein we present the preparation of [2]pseudorotaxanes which utilize positively charged 1,2-bis(pyridinium)ethane axles and a negatively charged dibenzo[24]crown-8 ether wheel containing two pendant sulfonate (SO_3^-) functionalities (DSDB24C8^{2-}; see Scheme 1). The addition of two sulfonate groups to DB24C8 was accomplished by heating a solution of DB24C8 in CH_3CN with a slight excess of sulfuric acid for 16 hours.[13] The resulting diacid was converted into the Me_4N^+ salt by treatment with Me_4NOH in MeOH to give $[Me_4N]_2$[DSDB24C8] as a mixture of *syn* and *anti* isomers in excellent yield (>95%). Multiple recrystallizations from MeOH allowed isolation of the *anti* isomer in 44% overall yield;[14] this material was used for all the subsequent [2]pseudorotaxane studies.[15]



Scheme 1. Formation of [2]pseudorotaxane [**1b**⊂DSDB24C8]. Reaction conditions: a) one equivalent of $[Me_4N]_2$[DSDB24C8] (2.0×10^{-3} M) in either D_2O, CD_3CN, or CD_3OD. Bn = benzyl. Blue pyridinium-based axle **1**, red crown-ether wheel DSDB24C8^{2-}. The labeling scheme a–h shown for the product is used for the NMR spectra shown in Figure 1.

In our previous study on the formation of [2]pseudorotaxanes from 1,2-bis(pyridinium)ethane axles and neutral DB24C8 wheels, it was observed that axles such as **1a–d** containing an electron-withdrawing group exhibited the largest association constants, which range from 0.9×10^3 to 4.7×10^3 M^{-1} in CD_3CN at 298 K.[16] Attempts to measure association constants in less polar solvents were complicated by ion-pairing effects, and in more competitive solvents, noncovalent interactions were greatly reduced, often to the point of negating [2]pseudorotaxane formation altogether.

In Table 1, previously determined association constant measurements in CD_3CN are compared for [2]pseudorotaxanes involving bis(pyridinium)ethane axles and DB24C8 wheels[16] with those measured for the same axles with DSDB24C8^{2-} in competitive polar solvents such as CD_3OD, D_2O, and a mixture containing $(CD_3)_2SO$.

Figure 1 shows the sequential addition of DSDB24C8^{2-} to a solution of $\mathbf{1b}^{2+}$ in CD_3OD. Formation of the pseudorotaxane is slow on the NMR spectroscopy timescale, and the forces stabilizing the interpenetrated geometry are significant; so much so, that the free dianionic wheel is never observed in the presence of up to one equivalent of dicationic axle. The apparent association constants K_a of $>10^5$ for the

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Table 1: A comparison of association constants[a] $K_a/10^3\,\text{M}^{-1}$ for the formation of [2]pseudorotaxanes in various solvents at 298 K.

	CD_3CN[b]	CD_3OD[c]	D_2O[c]	$CD_3OD/D_2O/(CD_3)_2SO$[d]
DB24C8				
$\mathbf{1a}^{2+}$	1.9	5.4	[e]	0.1
$\mathbf{1b}^{2+}$	4.7	12.9	[e]	0.7
$\mathbf{1c}^{2+}$	0.9	2.2	[e]	0.1
$\mathbf{1d}^{4+}$	1.0	[e]	[e]	0.2
$DSDB24C8^{2-}$				
$\mathbf{1a}^{2+}$	[e]	> 100	0.2	0.5
$\mathbf{1b}^{2+}$	[e]	> 100	0.3	3.7
$\mathbf{1c}^{2+}$	[e]	> 100	0.1	0.5
$\mathbf{1d}^{4+}$	[e]	> 100	2.3	7.7

[a] Determined by the single-point method utilizing the equation $K_a = [\text{pseudorotaxane}]/[\text{axle}]^2$ and using equal initial concentrations of axle and wheel (2.0×10^{-3} M) and the integral values of the NCH_2 resonances (^1H NMR spectroscopy) for complexed and uncomplexed axles. Errors are estimated to be 10% or less. [b] Values in CD_3CN are for BF_4^- salts; Ref. [16]. [c] Axles are employed as Br^- salts. [d] a mixture of 50% CD_3OD, 40% D_2O, and 10% $(CD_3)_2SO$. [e] One or more components are insoluble in this solvent.

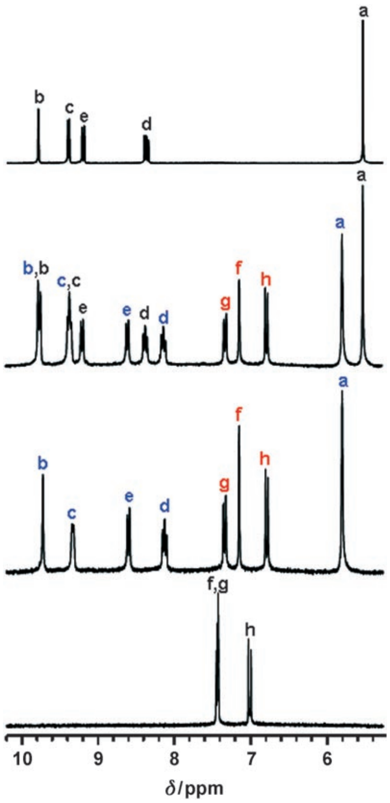

Figure 1. Downfield region of the ^1H NMR spectra of a solution (2.0×10^{-3} M) of $\mathbf{1b}^{2+}$ (270 MHz, CD_3OD) showing positions of the aromatic and ethylene proton signals in the presence of increasing amounts of $[Me_4N]_2DSDB24C8$; from top to bottom: 0.0, 0.5, and 1.0 equivalents. For comparison, the spectrum of the uncomplexed crown ether $DSDB24C8^{2-}$ is shown at the bottom. Red and blue labels: components of the [2]pseudorotaxane, black labels: uncomplexed axle $\mathbf{1b}^{2+}$ and free $DSDB24C8^{2-}$. For labeling key, see Scheme 1.

formation of [2]pseudorotaxanes with $DSDB24C8^{2-}$ in methanol are significantly greater than those observed for DB24C8.

Quite reasonable K_a values were obtained in pure water when the sulfonated crown ether $DSDB24C8^{2-}$ was employed. It is very unlikely that the array of C–H···O hydrogen bonds and $N^+\cdots O^{\delta-}$ ion–dipole and π-stacking interactions normally identified as important in stabilizing a [2]pseudorotaxane geometry between a 1,2-bis(pyridinium)ethane axle and DB24C8 could sustain an interpenetrated geometry in a very polar solvent such as water.

A solvent mixture of 50% CD_3OD, 40% D_2O, and 10% $(CD_3)_2SO$ was identified as a medium in which the K_a values for DB24C8 and $DSDB24C8^{2-}$ could be compared directly without significant solubility problems. It can be seen from Table 1 that on going from DB24C8 to $DSDB24C8^{2-}$ for the dicationic axles ($\mathbf{1a}^{2+}$, $\mathbf{1b}^{2+}$, and $\mathbf{1c}^{2+}$), the increase in K_a is approximately fivefold, but for the tetracationic axle $\mathbf{1d}^{4+}$, the increase in K_a is by a factor of almost fifty. This means there is actually a reversal in the trend for K_a values; for DB24C8, $\mathbf{1}^{2+} \geq \mathbf{1}^{4+}$ but for $DSDB24C8^{2-}$, $\mathbf{1}^{4+} > \mathbf{1}^{2+}$. This is undoubtedly a qualitative measure of the increased importance of the newly added electrostatic $N^+\cdots SO_3^-$ interaction in this solvent. An ion–ion interaction would be greater for a system with an increased total charge (+4 versus +2) but it should be noted that the additional pyridinium groups on $\mathbf{1d}^{4+}$ are also in closer proximity to the sulfonate groups, which would also greatly enhance the coulombic attraction.

Regardless of which axle and wheel were employed, the ratio of the two components, the solvent used, or their concentrations, a 1:1 complexation stoichiometry was founded by direct integration of ^1H NMR resonances for complexed axle and complexed wheel.

To determine a quantitative measurement of this new electrostatic interaction on the formation of [2]pseudorotaxanes, we applied Hunter's strategy[17] for extracting non-covalent interactions from some of the mixed solvent data from Table 1. The double-mutant cycle for the four adducts $[\mathbf{1c}\subset DB24C8]^{2+}$, $[\mathbf{1c}\subset DSDB24C8]$, $[\mathbf{1d}\subset DB24C8]^{4+}$ and $[\mathbf{1d}\subset DSDB24C8)]^{2+}$ is shown in Figure 2. From this cycle, the ion–ion interactions and any accompanying cooperative effects are estimated to be $\Delta(\Delta G) = -5.1\ \text{kJ}\,\text{mol}^{-1}$. This is quite significant, accounting for approximately one quarter of the interaction for $[\mathbf{1d}\subset DSDB24C8]^{2+}$ in this polar solvent mixture.

The effect of adding the sulfonate groups can also be seen in the solid state. Figure 3 shows the X-ray structures of the charge-neutral species $[\mathbf{1a}\subset DSDB24C8]$ and $[\mathbf{1b}\subset DSDB24C)]$.[18] In both cases the overall geometry of the structure is very similar to that found for $[\mathbf{1a}\subset DB24C8]^{2+}$.[19] The long axis of the bis(pyridinium) axle and the crown ether are essentially parallel, and the axle adopts a stepped *anti* conformation at the central ethane fragment and the crown ether the familiar S-shaped conformation.[20] This packing allows the aromatic rings on both components to lie parallel and be suitably separated for significant π-stacking interactions.

Although the inclusion of the sulfonate group leads to stronger interactions between axle and wheel, and this increase must be in large part due to an electrostatic attraction, there does not appear to be a strong correlation with the distance between the oppositely charged units within

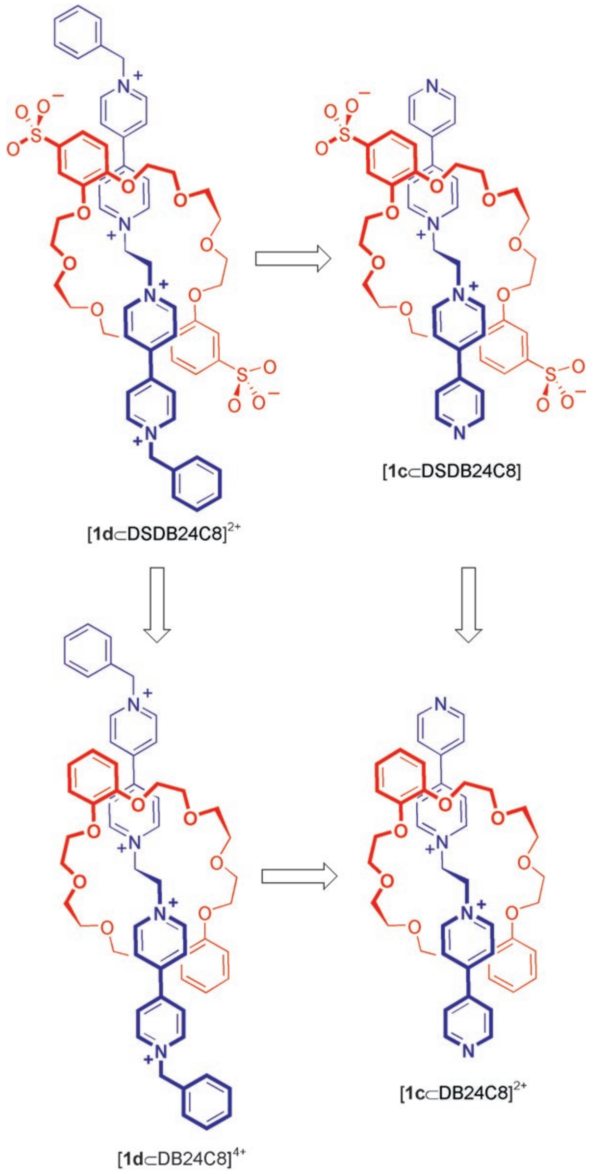

Figure 2. The double-mutant cycle used to determine the electrostatic contribution to the formation of [2]pseudorotaxane in a mixed solvent of 50% CD_3OD, 40% D_2O, and 10% $(CD_3)_2SO$. Arrows represent variation of an axle or of a wheel.

the interpenetrated structure. For example, the closest intramolecular approaches between a pyridinium nitrogen atom and a sulfonate oxygen atom within a pseudorotaxane are only 6.14 Å (N1···O4) for [**1a**⊂DSDB24C8] and 7.17 Å (N1···O5) for [**1b**⊂DSDB24C8]. At these distances there should not be a strong electrostatic attraction, thus it must be concluded that the charges are significantly distributed over the entire ring system and that this contributes significantly to the overall interaction between axle and wheel. On the other hand, in the solid state the pyridinium and sulfonate groups can attain quite close intermolecular interactions. The lack of counterions in the structures of [**1a**⊂DSDB24C8] and [(**1b**⊂DSDB24C8] leads to very tight packing between [2]pseudorotaxanes. The closest intermolecular approaches of a pyridinium nitrogen atom and sulfonate oxygen atom are

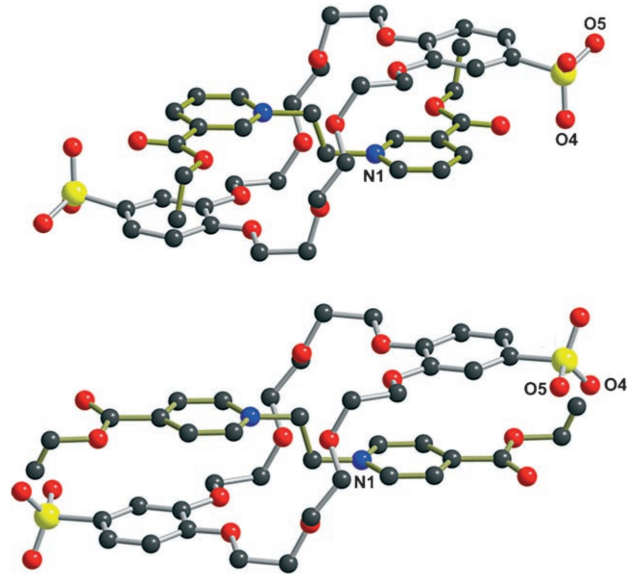

Figure 3. Ball-and-stick representations of the X-ray structures of [**1a**⊂DSDB24C8] (bottom) and [**1b**⊂DSDB24C8] (top). S yellow, O red, N blue, C black, axle = gold bonds, wheel = silver bonds; hydrogen atoms omitted for clarity.

4.05 Å (N1···O5) for [**1a**⊂DSDB24C8] and 4.22 Å (N1···O5) for [**1b**⊂DSDB24C8]. These distances are very similar to those observed for cationic [2]pseudorotaxanes in which CF_3SO_3 ions are used as the counterion.[12b] Presumably, there would be a much closer intramolecular approach of sulfonate and pyridinium ions for the terminally alkylated axle **1d**$^{4+}$.

In conclusion, we have shown that anionic functionalities, such as sulfonate groups, can easily be added to DB24C8 to yield DSDB24C8^{2-}, and that this negatively charged crown ether can form [2]pseudorotaxanes with axles derived from 1,2-bis(pyridinium)ethane cations in highly competitive solvents such as methanol and water owing to significant electrostatic interactions between the axle and wheel. When the axle is a dication, this results in the formation of charge-neutral [2]pseudorotaxanes and the complete elimination of counterions. We are investigating the incorporation of DSDB24C8^{2-} and related anionic crown ether wheels in place of DB24C8 in a variety of previously prepared rotaxanes,[21] catenanes,[22] molecular machines,[23] and solid-state systems[24] involving 1,2-bis(pyridinium)ethane-type axles. It is very likely that this same methodology can be applied successfully to the many other interlocked systems that involve the interaction between neutral crown ether wheels and cationic axles.

Experimental Section

The 1,2-bis(pyridinium)ethane axles **1a**–**d** were prepared as described previously.[16] DSDB24C8^{2-} was prepared by a slight modification of the reported procedure.[13] All association constant measurements were recorded on a Bruker AMX 500 MHz NMR spectrometer at 298 K.

DSDB24C8^{2-}: DB24C8 (1.0 g, 2.2 mmol) was dissolved in MeCN (9.0 mL) and a solution of concentrated H_2SO_4 (0.49 g, 5.0 mmol) in MeCN (1.0 mL) was added dropwise with stirring to give a clear pale yellow solution. The solution was refluxed for 16 h and then the solvent removed to give a yellow oil. Preliminary ^{1}H NMR spectroscopy in D_2O clearly showed a mixture of two isomers. A 25 % solution of Me_4NOH in MeOH (0.45 g, 2.1 mL) and then ethyl acetate (15 mL) were added to the oil, and the reaction flask was placed in an ultrasonic bath for 40 min, which resulted in the formation of a white solid that was separated by filtration and washed with ethyl acetate (10 mL). The solid was determined to be a mixture of *syn* and *anti* $[Me_4N]_2$[DSDB24C8] by ^{1}H NMR spectroscopy. Yield, 1.68 g (99 %). After three recrystallizations from MeOH, only one isomer was observed in the ^{1}H NMR spectrum (44 % yield). This was identified as the *anti* isomer from subsequent X-ray structure determinations.

Crystals of [**1a**$\subset$DSDB24C8] and [**1b**$\subset$DSDB24C8] were frozen in paratone oil inside a cryoloop. Reflection data were integrated from frame data obtained from hemisphere scans on a Bruker APEX diffractometer with a CCD detector. Decay was monitored by 50 standard data frames measured at the beginning and end of data collection. Diffraction data and unit-cell parameters were consistent with assigned space groups. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data sets. The structures were solved by direct methods, completed by subsequent Fourier syntheses, and refined using full-matrix least-squares methods against $|F^2|$ data. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library (G. M. Sheldrick, Madison, WI). Crystal data for [**1a**$\subset$DSDB24C8]: $C_{48}H_{76}N_2O_{24}S_2$, $M_r = 1129.2$, yellow prisms ($0.26 \times 0.20 \times 0.18$ mm^3), monoclinic, $P2_1/n$, $a = 12.129(2)$, $b = 15.649(3)$, $c = 13.915(3)$ Å, $\beta = 93.748(2)°$, $U = 2635.5(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.322$ g cm^{-3}, $\mu = 0.188$ mm^{-1}, min/max transmission = 0.9053, $2\theta_{max} = 56.6°$, $Mo_{K\alpha} = 0.71073$ Å, $T = 173.0(2)$ K, 19789 total reflections ($R(int) = 0.0339$), $R1 = 0.0960$, $wR2 = 0.2622$ ($I > 2\sigma I$), $R1 = 0.1077$, $wR2 = 0.2743$ (all data), GoF(F^2) = 1.077, data/variables/restraints = 3438/346/0. Crystal data for [**1b**$\subset$DSDB24C8]: $C_{42}H_{70}N_2O_{23}S_2$, $M_r = 1099.2$, yellow prisms ($0.26 \times 0.26 \times 0.14$ mm^3), monoclinic, $P2_1/c$, $a = 12.455(3)$, $b = 15.977(2)$, $c = 13.972(3)$ Å, $\beta = 108.23(3)°$, $U = 2606.7(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.400$ g cm^{-3}, $\mu = 0.192$ mm^{-1}, min/max transmission = 0.9286, $2\theta_{max} = 56.6°$, $Mo_{K\alpha} = 0.71073$ Å, $T = 173.0(2)$ K, 4034 total reflections ($R(int) = 0.0375$), $R1 = 0.1142$, $wR2 = 0.3193$ ($I > 2\sigma I$), $R1 = 0.1407$, $wR2 = 0.3453$ (all data), GoF(F^2) = 1.459, data/variables/restraints = 2337/378/57. Restraints were required to model a twofold disorder of the SO_3 group and maintain chemically reasonable bonding parameters. CCDC-653058 (**1a**$\subset$DSDB24C8) and CCDC-653059 (**1b**$\subset$DSDB24C8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) J. E. Green, J. W. Choi, A. Boukai, Y. Bunimovich, E. Johnston-Halperin, E. Delonno, Y. Luo, B. A. Sheriff, K. Xu, Y. S. Shin, H.-R. Tseng, J. F. Stoddart, J. R. Heath, *Nature* **2007**, *445*, 414; b) J. Berná, D. A. Leigh, M. Lubomska, S. M. Mendoza, E. M. Pérez, P. Rudolf, G. Teobaldi, F. Zerbetto, *Nat. Mater.* **2005**, *4*, 704; c) J. D. Badjic, C. M. Ronconi, J. F. Stoddart, V. Balzani, S. Silvi, A. Credi, *J. Am. Chem. Soc.* **2006**, *128*, 1489; d) J. D. Badjic, V. Balzani, A. Credi, S. Silvi, J. F. Stoddart, *Science* **2004**, *303*, 1845; e) V. Serreli, C. F. Lee, E. R. Kay, D. A. Leigh, *Nature* **2007**, *445*, 523; f) J.-P. Sauvage, *Chem. Commun.* **2005**, 1507; g) N. Yui, T. Ooya, *Chem. Eur. J.* **2006**, *12*, 6730; h) Y. Inoue, P. Kuad, Y. Okumura, Y. Takashima, H. Yamaguchi, A. Harada, *J. Am. Chem. Soc.* **2007**, *129*, 6396.

[2] a) M. C. T. Fyfe, J. F. Stoddart, *Acc. Chem. Res.* **1997**, *30*, 393; b) A. R. Williams, B. H. Northrop, T. Chang, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem.* **2006**, *118*, 6817; *Angew. Chem. Int. Ed.* **2006**, *45*, 6665; c) B. H. Northrop, F. Aricó, N. Tangchiavang, J. D. Badjiæ, J. F. Stoddart, *Org. Lett.* **2006**, *8*, 3899; d) S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders, J. F. Stoddart, *Angew. Chem.* **2002**, *114*, 938; *Angew. Chem. Int. Ed.* **2002**, *41*, 898; e) W. G. Skene, V. Berl, H. Risler, R. Khoury, J.-M. Lehn, *Org. Biomol. Chem.* **2006**, *4*, 3652.

[3] See for example: a) B. A. Blight, K. A. Van Noortwyk, J. A. Wisner, M. C. Jennings, *Angew. Chem.* **2005**, *117*, 1523; *Angew. Chem. Int. Ed.* **2005**, *44*, 1499; b) M. Asakawa, C. L. Brown, S. Menzer, F. M. Raymo, J. F. Stoddart, D. J. Williams, *J. Am. Chem. Soc.* **1997**, *119*, 2614; c) F. Huang, C. Slebodnick, E. J. Mahan, H. W. Gibson, *Tetrahedron* **2007**, *63*, 2875; d) D. A. Leigh, A. Murphy, J. P. Smart, A. M. Z. Slawin, *Angew. Chem.* **1997**, *109*, 752; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 728; e) G. Kaiser, T. Jarrosson, S. Otto, Y.-F. Ng, A. D. Bond, J. K. M. Sanders, *Angew. Chem.* **2004**, *116*, 1993; *Angew. Chem. Int. Ed.* **2004**, *43*, 1959; f) R. Jäger, F. Vögtle, *Angew. Chem.* **1997**, *109*, 966; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 930; g) T. Clifford, A. Abushamleh, D. H. Busch, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4830; h) N. Watanabe, T. Yagi, N. Kihara, T. Takata, *Chem. Commun.* **2002**, 2720.

[4] See for example: a) P. L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M. T. Gandolfi, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vicent, D. J. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 193; b) S. A. Vignon, T. Jarrosson, T. Iijima, H.-R. Tseng, J. K. M. Sanders, J. F. Stoddart, *J. Am. Chem. Soc.* **2004**, *126*, 9884; c) G. Kaiser, T. Jarrosson, S. Otto, Y.-F. Ng, A. D. Bond, J. K. M. Sanders, *Angew. Chem.* **2004**, *116*, 1993; *Angew. Chem. Int. Ed.* **2004**, *43*, 1959; d) F. Huang, A. L. Rheingold, C. Slebodnick, A. Ohs, K. A. Switek, H. W. Gibson, *Tetrahedron* **2005**, *61*, 10242.

[5] See for example: a) F. Diederich, L. Echegoyen, M. Gomez-Lopez, R. Kessinger, J. F. Stoddart, *J. Chem. Soc. Perkin Trans. 2* **1999**, 1577; b) F. Huang, L. Zhou, J. W. Jones, H. W. Gibson, M. Ashraf-Khorassani, *Chem. Commun.* **2004**, 2670.

[6] See for example: a) T. Kraus, M. Budesinsky, J. Cvacka, J.-P. Sauvage, *Angew. Chem.* **2006**, *118*, 264; *Angew. Chem. Int. Ed.* **2006**, *45*, 258; b) C. Hamann, J.-M. Kern, J.-P. Sauvage, *Dalton Trans.* **2003**, 3770; c) D. B. Amabilino, C. O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.* **1996**, *118*, 3285.

[7] For examples, see: a) R. A. Bartsch, N. K. Dalley, V. S. Talanov, D. W. Purkiss, H. E. Vogel, *Tetrahedron* **2005**, *61*, 8351; b) M. J. Pugia, D. H. Desai, R. A. Bartsch, *J. Org. Chem.* **1987**, *52*, 4387.

[8] For a recent example, see: a) D. P. Cormode, S. S. Murray, A. R. Cowley, P. D. Beer, *Dalton Trans.* **2006**, 5135; b) For a comprehensive review, see: P. D. Beer, P. A. Gale, *Angew. Chem.* **2001**, *113*, 502; *Angew. Chem. Int. Ed.* **2001**, *40*, 486.

[9] a) G. V. Oshovsky, D. N. Reinhoudt, W. Verboom, *J. Org. Chem.* **2006**, *71*, 7441; b) G. V. Oshovsky, D. N. Reinhoudt, W. Verboom, *Eur. J. Org. Chem.* **2006**, 2810; c) D.-S. Guo, H.-Y. Zhang, C.-J Li, Y. Liu, *Chem. Commun.* **2006**, 2592.

[10] a) F. Huang, J. W. Jones, C. Slebodnick, H. W. Gibson, *J. Am. Chem. Soc.* **2003**, *125*, 14458; b) J. W. Jones, H. W. Gibson, *J. Am. Chem. Soc.* **2003**, *125*, 7001.

[11] M. Asakawa, M. Higuchi, G. Mattersteig, T. Nakamura, A. R. Pease, F. M. Raymo, T. Shimizu, J. F. Stoddart, *Adv. Mater.* **2000**, *12*, 1099.

[12] a) G. J. E. Davidson, S. J. Loeb, N. A. Parekh, J. A. Wisner, *J. Chem. Soc. Dalton Trans.* **2001**, 3135; b) S. J. Loeb, *Chem. Commun.* **2005**, 1511.

[13] a) T. Sasaki, S. Umetani, M. Matsui, S. Tsurubou, T. Kimura, Z. Yoshida, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 371; b) S. Umetani, T. Sasaki, M. Matsui, S. Tsurubou, T. Kimura, Z. Yoshida, *Anal. Sci.* **1997**, *13*, 123.

[14] The original publications (see Ref. [13]) on the preparation of H_2DSDB24C8 and various salts of DSDB24C8^{2-} did not successfully separate the *syn* and *anti* isomers. In earlier applications of DSDB24C8^{2-}, the statistical 50:50 mixture of the two isomers was used with the assumption that this had no significant effect on the properties being studied. This is very likely an incorrect assumption, as Gibson and co-workers showed that *syn* and *anti* isomers of related DB24C8 derivatives had different association constants with the same axles; see Ref. [15].

[15] H. W. Gibson, H. Wang, K. Bonrad, J. W. Jones, C. Slebodnick, L. N. Zackharov, A. L. Rheingold, B. Habenicht, P. Lobue, A. E. Ratliff, *Org. Biomol. Chem.* **2005**, *3*, 2114.

[16] S. J. Loeb, J. Tiburcio, S. J. Vella, J. A. Wisner, *Org. Biomol. Chem.* **2006**, *4*, 667.

[17] S. L. Cockroft, C. A. Hunter, *Chem. Soc. Rev.* **2007**, *36*, 172.

[18] DIAMOND 3.1—CRYSTAL IMPACT, Postfach 1251, 53002 Bonn, Germany, **2007**.

[19] S. J. Loeb, J. A. Wisner, *Angew. Chem.* **1998**, *110*, 3010; *Angew. Chem. Int. Ed.* **1998**, *37*, 2838.

[20] I. R. Hanson, D. L. Hughes, M. R. Truter, *J. Chem. Soc. Perkin Trans. 2* **1976**, 972.

[21] a) S. J. Loeb, J. A. Wisner, *Chem. Commun.* **1998**, 2757; b) G. J. E. Davidson, S. J. Loeb, P. Passaniti, S. Silva, A. Credi, *Chem. Eur. J.* **2006**, *12*, 3233; c) N. Georges, S. J. Loeb, J. Tiburcio, J. A. Wisner, *Org. Biomol. Chem.* **2004**, *2*, 2751.

[22] A. L. Hubbard, G. J. E. Davidson, R. H. Patel, J. A. Wisner, S. J. Loeb, *Chem. Commun.* **2004**, 138.

[23] a) S. J. Loeb, J. Tiburcio, S. J. Vella, *Chem. Commun.* **2006**, 1598; b) S. J. Loeb, J. Tiburcio, S. J. Vella, *Org. Lett.* **2006**, *8*, 3421.

[24] a) S. J. Loeb, *Chem. Soc. Rev.* **2007**, *36*, 226; b) D. J. Hoffart, S. J. Loeb, *Angew. Chem.* **2005**, *117*, 923; *Angew. Chem. Int. Ed.* **2005**, *44*, 901; c) G. J. E. Davidson, S. J. Loeb, S. J. *Angew. Chem.* **2003**, *115, 78; Angew. Chem. Int. Ed.* **2003**, 42, 74; *Angew. Chem. Int. Ed.* **2003**, *42*, 74.