Chemically controlled self-assembly of [2]pseudorotaxanes based on 1,2-bis(benzimidazolium)ethane cations and 24-crown-8 macrocycles†

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Cations derived from 1,2-bis(benzimidazolium)ethane can penetrate the cavity of dibenzo-24-crown-8 macrocycles to produce a new family of [2]pseudorotaxanes. These supramolecular structures are held together by a series of charge-assisted hydrogen bonds (+)N–H···O, ion-dipole and π-stacking interactions. These new adducts were fully characterised by NMR spectroscopy, ESI mass spectrometry and single-crystal X-ray diffraction. The effect of electron-donating and electron-withdrawing groups on the association constants was also analyzed. Chemical control of the threading/unthreading process was acheived by the alternate addition of acid and base.
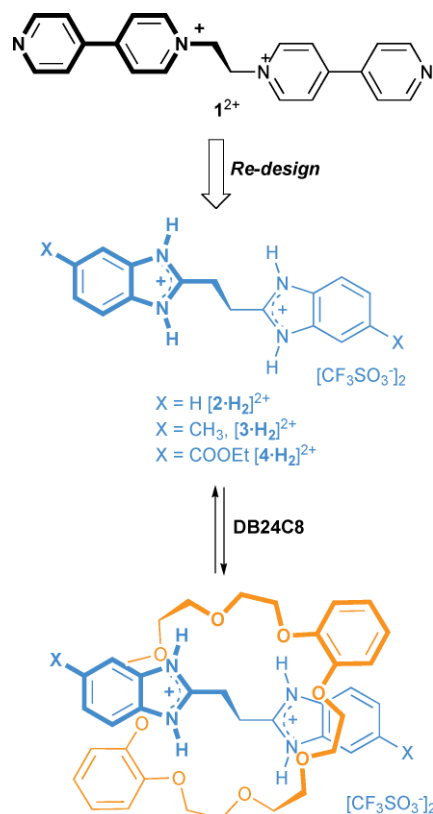
Introduction

The successful development of machines at the molecular scale, based on the bottom-up approach, relies on the precise design and preparation of functional components that can be organized into more sophisticated structures. Some of the most promising systems are based on interlocked molecules.[1] The application of this strategy has generated some of the most interesting and stimulating examples known today, such as molecular elevators,[2] switches,[3] valves,[4] motors[5] and 'muscles'.[6]

An important approach for the synthesis of interlocked molecules is based on the penetration of a linear molecule—the axle–through the cavity of a cyclic molecule—the wheel—to generate an interpenetrated complex or [2]pseudorotaxane, which can be transformed into more elaborate structures, such as rotaxanes and catenanes.[7]

A wide variety of templating motifs for the self-assembly of interpenetrated and interlocked molecules have been investigated, ranging from cationic[8] and neutral[9] to anionic.[10] Among the most versatile cationic systems is the motif pioneered by Loeb[11] based on the linear cation 1,2-bis(4,4′-bipyridinium)ethane 1^{2+} (Scheme 1). This motif has lead to the formation of rotaxanes,[12] polyrotaxanes[13] and catenanes[14] when utilized in combination with dibenzo-24-crown-8 (**DB24C8**) macrocycles.

An essential contribution to the formation of these supramolecular structures is the C–H···O hydrogen bonding between the hydrogens α to the N^+ atoms on the axle with the oxygen atoms on the crown ether.[15] We reasoned that by the substitution of these C–H bonds in the axle for a more acidic version, *i.e.* N–H bonds, but keeping the charge state and geometry intact, we could create a new templating motif that would interact with **DB24C8** through charge-assisted hydrogen bonding, (+)N–H···O, and simultaneously we could gain threading/unthreading control by protonation/deprotonation of the nitrogen atoms on the axle.

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Scheme 1 Re-design of axles and [2]pseudorotaxane formation between 1,2-bis(benzimidazolium)ethane cations and **DB24C8** macrocycles.

A literature survey helped us to identify an excellent candidate, the neutral molecule 1,2-bis(benzimidazolyl)ethane, which affords a dication upon protonation, possesses four N–H bonds and displays an *anti* steplike structure in the solid state,[16] similar to that observed for 1^{2+}.

Herein, we provide computational and experimental evidence of the ability of several 1,2-bis(benzimidazolium)ethane cations that function as templating motifs for the self-assembly of [2]pseudorotaxanes with **DB24C8**, and the use of acid/base chemistry to switch between complexed/uncomplexed states.

Results and discussion

DFT calculations using the deMon2k[17] suite of programs were performed to estimate the interaction energy between [2], [2·H]+ and [2·H2]2+ with **DB24C8** (see ESI†). These values (17.8, 31.6 and 70.5 kcal mol−1, respectively) clearly indicate an increase in pseudorotaxane stability as the charge and number of protons is increased on the axle, with an important electrostatic contribution in addition to the expected role of hydrogen bonding. These calculations support the feasibility of pseudorotaxane formation between [2·H2]2+ and **DB24C8** and discard any significant interaction with [2], opening the possibility to switch between the pseudorotaxane and the free components by acid/base control.

The synthesis of neutral 1,2-bis(benzimidazolyl)ethane from 1,2-phenylenediamine and succinic acid was performed following a previously reported procedure.[18] The addition of two equivalents of trifluoromethanesulfonic acid to an acetonitrile solution of this compound rendered the product [2·H2][CF3SO3]2 as a soluble salt (Scheme 1). The cation thus formed possesses two positive charges delocalized in each imidazolium ring and four N–H bonds that can be used for hydrogen bonding with the crown ether.

When equimolar solutions of axle [2·H2][CF3SO3]2 and **DB24C8** were mixed together at room temperature in CD3CN or CD3NO2, a new species was observed in the 1H NMR spectrum, in addition to the corresponding signals for the uncomplexed cation and the crown (Fig. 1), indicating slow exchange on the NMR timescale.
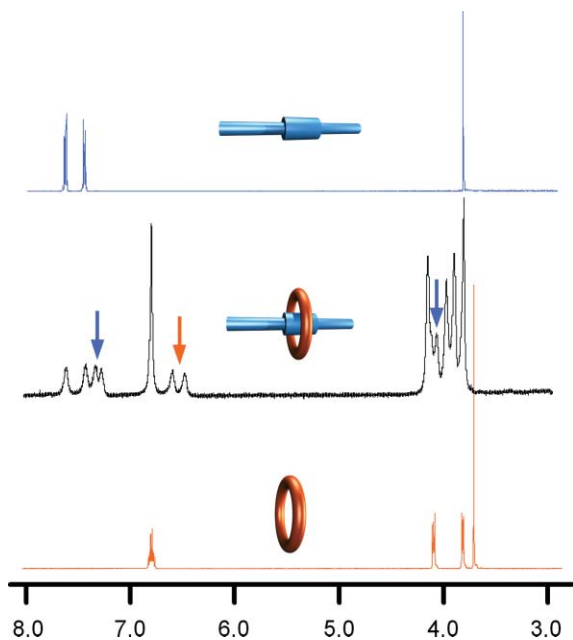

Fig. 1 1H NMR spectra of [2·H2][OTf]2 (top), **DB24C8** (bottom) and a 1 : 1 mixture of [2·H2][OTf]2 and **DB24C8** at 2×10^{-3} M (middle).

The resonances of the new species are consistent with the formation of an interpenetrated complex, the peak for the -C*H*2- protons being shifted to higher frequency compared to the free axle ($\Delta\delta = +0.30$ ppm) as a consequence of their participation in C–H⋯O hydrogen bonding with the crown ether. The aromatic protons, both in the axle and the crown, are shifted to lower frequencies ($\Delta\delta = -0.25$ ppm, $\Delta\delta = -0.28$ ppm), probably due to a parallel arrangement of the aromatic rings, maximizing

π-stacking interactions. The 1 : 1 stoichiometry of the new complex was directly determined from integration of the spectrum.

Further evidence of chemical exchange was obtained by variable-temperature NMR (see ESI†) and EXSY experiments. In the EXSY spectrum (Fig. 2), cross-peaks relating the complexed and uncomplexed species were observed.
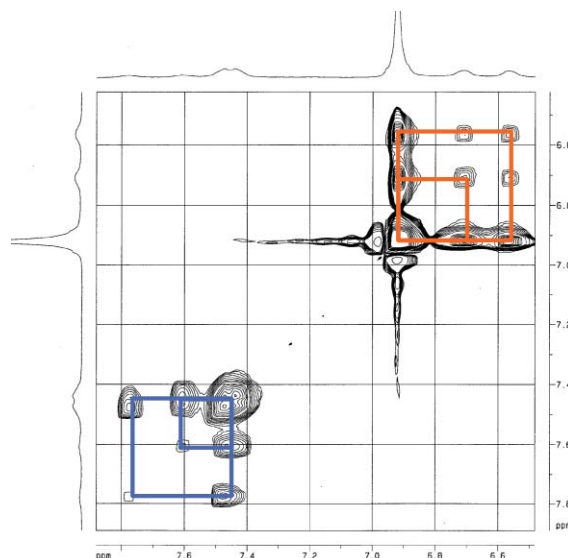

Fig. 2 Aromatic portion of the EXSY spectrum of an equimolar mixture (2×10^{-3} M) of [2·H2][OTf]2 and **DB24C8**. Exchanging peaks are indicated by squares (blue: axle, orange: macrocycle).

The association constant (K_a) of [2·H2]2+ with **DB24C8** was determined in CD3CN using two different counterions, [BF4−] and [CF3SO3−] (Table 1). The K_a values are comparable to those reported for other cationic templating motifs[8,11] in similar solvents. When trifluoroacetate [CF3COO−] was utilized as the counterion, no significant association occurred, probably as a consequence of strong ion-pairing in solution.[19]

The new complex was crystallized from acetonitrile and the structure determined by X-ray diffraction,[20] displaying the expected interpenetrated geometry [2·H2]2+⊂**DB24C8** (Fig. 3). The axle and macrocycle lie about a common inversion centre which is at the midpoint of the ethane C–C bond. The [2]pseudorotaxane structure is held together by a series of non-covalent interactions: i) two charge-assisted hydrogen bonds (+)N–H⋯O (N⋯O 2.933(4) Å, N–H⋯O 150°), ii) four weak C–H⋯O contacts (C⋯O$_{Ar}$ 3.543(5) Å, C–H⋯O$_{Ar}$ 156° and C⋯O$_{Ali}$ 3.686(4) Å, C–H⋯O$_{Ali}$ 153°), iii) ion–dipole interactions (3.289(3) Å from

Table 1 Association constants with **DB24C8** determined by 1H NMR

Compound	$K_a \times 10^2 / M^{-1}$ [a]	$\Delta G° / kJ\ mol^{-1}$
[2·H2][CF3SO3]2	4.0 (0.3)	−14.8 (0.2)
[2·H2][BF4]2	4.8 (0.4)	−15.3 (0.2)
[2·H2][CF3COO]2	~0.0	0.0
[3·H2][CF3SO3]2	2.5 (0.4)	−13.6 (0.5)
[4·H2][CF3SO3]2	5.4 (0.6)	−15.6 (0.3)

[a] Determined at 25 °C, in CD3CN, average values are shown with standard deviations from three independent measurements by the single-point method using a 2×10^{-3} M concentration.
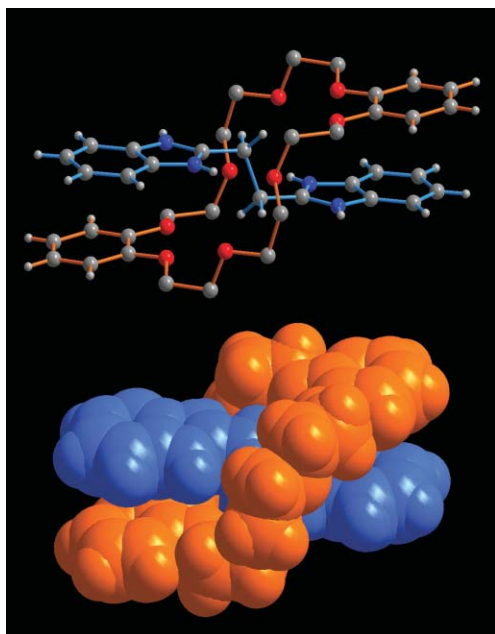
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Org. Biomol. Chem., 2007, **5**, 2252–2256 | 2253

Fig. 3 Ball-and-stick (top) and space-filling (bottom) representations of the crystal structure of $[2 \cdot H_2]^{2+} \subset$ **DB24C8** showing the interpenetrated nature of the complex. Solvent and anions are omitted for clarity.

the centroid of the five membered-ring to one aromatic oxygen atom in the crown ether), and iv) offset π-stacking between the electron-poor benzimidazolium rings on the axle and the electron-rich catechol rings on the crown, confirming the presence of all the interactions observed in solution by NMR. Surprisingly, only two N–H groups on the axle are involved in hydrogen bonding with the crown ether; a closer look revealed that the other two N–H groups are hydrogen bonded to acetonitrile molecules ($N \cdots N$ 2.918(6) Å, $N–H \cdots N$ 152°). To evaluate a possible solvent effect, the same complex was crystallized from nitromethane, a less coordinating solvent. In this case, the same basic interpenetrated structure is observed, with the main difference being that the N–H bonds previously hydrogen bonded to the solvent are now bound to the anions (see ESI†).

In order to assess the electronic effect of the substituent groups on the association constants, two new axles, $[3 \cdot H_2]^{2+}$ and $[4 \cdot H_2]^{2+}$, were synthesized (Scheme 1). The mixing of the new axles with **DB24C8** in solution results in pseudorotaxane formation (according to NMR) in a similar fashion to $[2 \cdot H_2]^{2+}$. Axle $[3 \cdot H_2]^{2+}$ possesses electron-donating methyl groups (EDGs), while axle $[4 \cdot H_2]^{2+}$ presents electron-withdrawing ethyl ester groups (EWGs) in their structures. The association constants follow the expected trend based on the electronic nature of the substituents; there is a significant increase for $[4 \cdot H_2]^{2+}$, which possesses an EWG (-COOEt), and a decrease for $[3 \cdot H_2]^{2+}$ with an EDG (-CH$_3$), both compared to $[2 \cdot H_2]^{2+}$ (Table 1).

With the aim of investigating the ability of the new motif to perform association/dissociation with the crown ether by pH control, we synthesized a more soluble axle bearing four methyl groups on the aromatic rings $[5 \cdot H_2][CF_3SO_3]_2$ (Scheme 2). The neutral compound [5] is unable to associate with **DB24C8**, while $[5 \cdot H_2]^{2+}$ forms a [2]pseudorotaxane with $K_a = 1.2 \times 10^2$ M^{-1} in acetonitrile. This allows ~95% control of the threading/unthreading process by the alternate addition of triflic acid and triethylamine
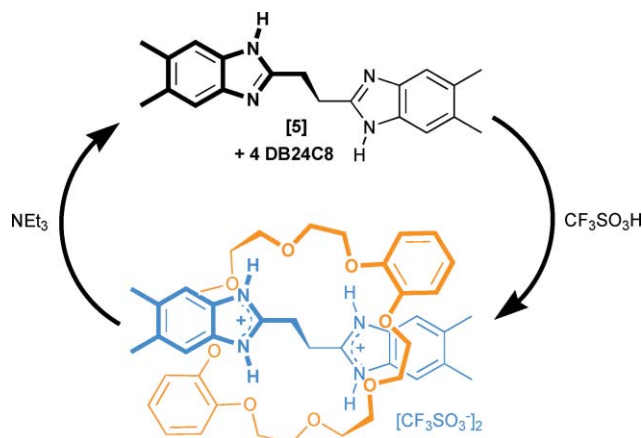
Scheme 2 Acid/base control of [2]pseudorotaxane formation.

(Scheme 2) in the presence of four equivalents of crown ether. After 4 cycles there is no significant evidence of decomposition by ^{1}H NMR; this behaviour is similar to that displayed by dibenzylammonium[21] and benzylanilinium[22] axles. The size and position of the substituents in the axle did not modify significantly the ability of the axle to penetrate the cavity of **DB24C8**, although equilibrium is reached after a longer period of time compared to $[2 \cdot H_2]^{2+}$.

Furthermore, the new adducts were characterized by mass spectrometry using electrospray ionization (see ESI†). In all cases, singly-charged species were simultaneously observed in the spectra: $[axle \cdot H_2 \subset$ **DB24C8** $+ BF_4]^+$, $[axle \cdot H \subset$ **DB24C8**$]^+$, $[axle \cdot H_2 + BF_4]^+$, $[axle \cdot H]^+$ and $[Na \subset$ **DB24C8**$]^+$.

Also, in order to investigate possible electrochemical control of the association/dissociation process, an electrochemical study was performed (Fig. 4). The cyclic voltammogram of compound $[2 \cdot H_2][BF_4]_2$ exhibited two overlapping reduction waves, from

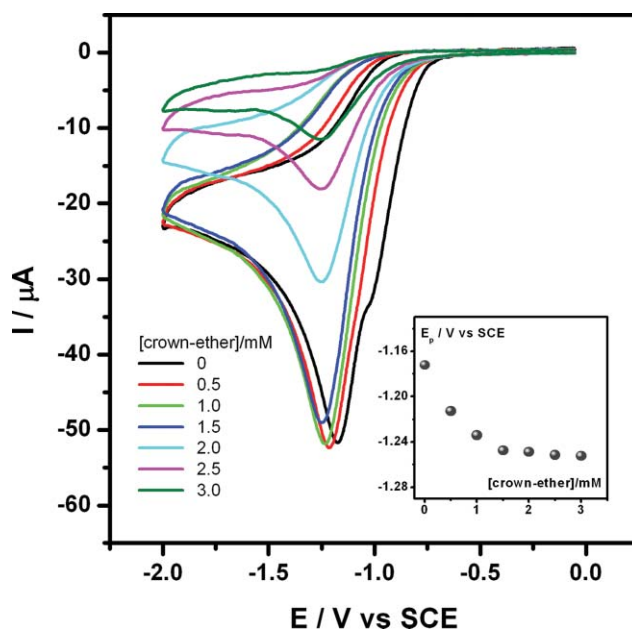**Fig. 4** Cyclic voltammetry of 2 mM $[2 \cdot H_2][BF_4]_2$ in the presence of various concentrations of **DB24C8** in acetonitrile on a glassy carbon electrode at 0.1 V s^{-1}. Inset: E_p values at various **DB24C8** concentrations.

−1.03 to −1.17 V *vs.* SCE, corresponding to the stepwise reduction of the two positive redox centres. Due to the chemically irreversible nature of these waves, it is likely that the reduced species are unstable radicals, preventing any kind of electrochemical control. Nevertheless, a significant shift (∼0.15 V) in the reduction waves towards a more negative potential was observed in the presence of **DB24C8**, in agreement with the stabilisation of the positive charges in $[2\cdot H_2]^{2+}$ by effect of its association with **DB24C8**, supporting the formation of a pseudorotaxane under electrochemical conditions.[23]

Conclusions

The results presented herein provide evidence of the ability of 1,2-bis(benzimidazolium)ethane cations to function as a templating motif for the self-assembly of [2]pseudorotaxanes with **DB24C8**. These adducts are held together by a series of non-covalent interactions: charge-assisted hydrogen bonding (+)N–H···O, ion-dipole and π-stacking interactions. We have shown that the strength of the interactions can be modified by varying the substituent groups on the axle, electron-withdrawing groups providing an increase in the electrostatic interactions and therefore an increase in the association constants. Moreover, control of the threading/unthreading process was accomplished by adding an acid/base. We are currently investigating further properties of this pseudorotaxane motif and its incorporation into the structure of permanently interlocked molecules.

Experimental

General

All chemicals were purchased from Aldrich and used without further purification. The solvents were dried and distilled prior to use. ^{1}H NMR spectra were recorded on Jeol Eclipse 400 MHz or Jeol GSX 270 MHz spectrometers locked to the deuterated solvent. Mass spectra were obtained on an Agilent G1969A electrospray-ionization time-of-flight spectrometer. Electrochemical measurements were performed in a Radiometer Potentiostat IMT102-DEA332 with positive feedback resistance compensation in a three-electrode cell (a glassy carbon disk 3 mm in diameter, a platinum screen and an aqueous saturated calomel electrode) in acetonitrile at 25 °C under an argon atmosphere using 0.2 M n-Bu$_4$NPF$_6$ as the supporting electrolyte.

General procedure for the syntheses of 1,2-bis(benzimidazolium)ethane derivatives 2–5

A mixture of succinic acid (236 mg, 2.0 mmol) and 1,2-phenylenediamine (519 mg, 4.8 mmol) was ground and mixed with silica gel (2 g). The solid mixture was irradiated in a conventional microwave oven (LG MS-0745V, 700 W) for 30 min (3 × 10 min). The reaction mixture was washed with 5% aqueous sodium bicarbonate (3 × 20 mL) and water (3 × 20 mL). The product was extracted from the remaining solid using hot ethanol (3 × 10 mL). The solvent was removed by rotary evaporation and the solid residue was recrystallized from ethanol to yield an off-white solid. Yields: 10% for **2**; 12% for **3**; 15% for **4**; and 20% for **5**. These solids were first converted to the chloride salts by the addition of aqueous hydrochloric acid and then anion exchanged

in situ with different sodium salts to render the corresponding salts in quantitative yields.

General procedure for the K_a measurements

A ^{1}H NMR spectrum of an equimolar solution (2.0×10^{-3} M) of 1,2-bis(benzimidazolium)ethane salt and dibenzo-24-crown-8 ether in CD$_3$CN was recorded at 25 °C. The concentration of all the species at equilibrium was determined using the initial concentrations and integration of the aromatic resonances of the uncomplexed and complexed species. See ESI for the NMR assignments.†

[2·H$_2$][CF$_3$SO$_3$]$_2$. 1,2-Bis(benzimidazolium)ethane triflate. ^{1}H NMR (CD$_3$CN): δ (ppm) 7.79 (m, 4H, b), 7.58 (m, 4H, c), 3.70 (s, 4H, a). HR-MS–ESI: m/z [2·H]$^+$ [C$_{16}$H$_{14}$N$_4$ + H]$^+$ calc.: 263.1291, found: 263.1294 (error: 1.1 ppm).

[3·H$_2$][CF$_3$SO$_3$]$_2$. 1,2-Bis(4′-methylbenzimidazolium)ethane triflate. ^{1}H NMR (CD$_3$CN): δ (ppm) 7.65 (d, 2H, J = 8.4 Hz, b), 7.57 (s, 2H, d), 7.36 (d, 2H, J = 8.4 Hz, c), 3.64 (s, 4H, a), 2.51 (s, 6H, e). HR-ESI-MS: m/z [3·H]$^+$ [C$_{18}$H$_{18}$N$_4$ + H]$^+$ calc.: 291.1604, found: 291.1609 (error: 1.6 ppm).

[4·H$_2$][CF$_3$SO$_3$]$_2$. 1,2-Bis(4′-ethoxycarbonylbenzimidazolium)-ethane triflate. ^{1}H NMR (CD$_3$CN): δ (ppm) 8.41 (d, 2H, J = 1.5 Hz, d), 8.20 (dd, 2H, J = 8.6 Hz, J = 1.5 Hz, c), 8.01 (d, 2H, J = 8.6 Hz, b), 4.34 (q, 4H, J = 7.2 Hz, e), 3.80 (s, 4H, a), 1.38 (t, 6H, J = 7.2 Hz, f). HR-ESI-MS: m/z [4·H]$^+$ [C$_{22}$H$_{22}$N$_4$O$_4$ + H]$^+$ calc.: 407.1714, found: 407.1704 (error: 2.4 ppm).

[5·H$_2$][CF$_3$SO$_3$]$_2$. 1,2-Bis(4′,5′-dimethylbenzimidazolium)ethane triflate. ^{1}H NMR (CD$_3$CN): δ (ppm) 7.52 (s, 4H, b), 3.52 (s, 4H, a), 2.39 (s, 12H, c). HR-ESI-MS: m/z [5·H]$^+$ [C$_{20}$H$_{22}$N$_4$ + H]$^+$ calc.: 319.1917, found: 319.1907 (error: 3.4 ppm).

[2·H$_2$]$^{2+}$⊂[DB24C8][CF$_3$SO$_3$]$_2$. ^{1}H NMR (CD$_3$CN) δ (ppm) 7.47 (broad, 4H, b), 7.41 (broad, 4H, c), 6.68 (broad, 4H, d), 6.55 (broad, 4H, e), 4.03 (s, 4H, a), 3.97 (broad, 8H, f), 3.90 (broad, 8H, h), 3.81 (broad, 8H, h). HR-ESI-MS: m/z [2·H⊂DB24C8]$^+$ [C$_{40}$H$_{46}$N$_4$O$_8$ + H]$^+$ calc.: 711.3388, found: 711.3384 (error: 0.69 ppm).

[3·H$_2$]$^{2+}$⊂[DB24C8][CF$_3$SO$_3$]$_2$. ^{1}H NMR (CD$_3$CN): δ (ppm) 7.36 (overlapped, 2H, c), 7.21 (d, 2H, J = 8.1 Hz, b), 7.16 (s, 2H, d), 6.70 (m, 4H, f), 6.54 (m, 4H, g), 3.97 (m, 8H, h), 3.92 (s, 8H, j), 3.89 (m, 8H, j), 3.96 (s, 4H, a), 2.41 (s, 6H, e). HR-ESI-MS: m/z [3·H⊂DB24C8]$^+$ [C$_{42}$H$_{50}$N$_4$O$_8$ + H]$^+$ calc.: 739.3701, found: 739.3699 (error: 0.37 ppm).

[4·H$_2$]$^{2+}$⊂[DB24C8][CF$_3$SO$_3$]$_2$. ^{1}H NMR (CD$_3$CN): δ (ppm) 7.98 (d, 2H, J = 0.8 Hz, d), 7.86 (dd, 2H, J = 8.3 Hz, J = 0.8 Hz, c), 7.56 (d, 2H, J = 8.2 Hz, b), 6.63 (m, 4H, g), 6.48 (m, 4H, h), 4.30 (q, 4H, J = 9.0 Hz, e), 4.13 (m, 8H, i), 4.05 (s, 4H, a), 4.04 (s, 8H, k), 3.80 (m, 8H, j), 1.36 (t, 6H, J = 9.0 Hz, f). HR-ESI-MS: m/z [4·H⊂DB24C8]$^+$ [C$_{46}$H$_{54}$N$_4$O$_{12}$ + H]$^+$ calc.: 855.3811, found: 855.3805 (error: 0.76 ppm).

[5·H$_2$]$^{2+}$⊂[DB24C8][CF$_3$SO$_3$]$_2$. ^{1}H NMR (CD$_3$CN): δ (ppm) 7.15 (s, 4H, b), 6.68 (m, 4H, d), 6.52 (m, 4H, e), 3.97 (m, 8H, f), 3.93 (s, 4H, a), 3.92 (s, 8H, h), 3.88 (m, 8H, g), 2.30 (s, 12H, c). HR-ESI-MS: m/z [5·H⊂DB24C8]$^+$ [C$_{44}$H$_{54}$N$_4$O$_8$ + H]$^+$ calc.: 766.3942, found: not observed.

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Org. Biomol. Chem., 2007, **5**, 2252–2256 | 2255

X-Ray crystal structure determination

Crystals were grown by slow evaporation of saturated solutions containing [2·H$_2$][BF$_4$]$_2$ and three equivalents of **DB24C8** in CH$_3$CN or CH$_3$NO$_2$. Crystals were mounted on a glass fibre. A full hemisphere of data were collected with 30 s frames on an Enraf–Nonius Kappa diffractometer fitted with a CCD-based detector using MoKα radiation (0.71073 Å). Diffraction data and unit-cell parameters were consistent with the assigned space groups. The structures were solved by direct methods, completed by subsequent Fourier syntheses and refined with full-matrix least-squares methods against $|F^2|$ data. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library.[24] Ball-and-stick diagrams were prepared using DIAMOND 3.0.[25]

Crystal structure data for [2·H$_2$][BF$_4$]$_2$⊂DB24C8·(CH$_3$CN)$_2$. C$_{44}$H$_{54}$B$_2$F$_8$N$_6$O$_8$, $M = 968.55$, monoclinic, $a = 11.5985(4)$, $b = 14.1871(5)$, $c = 14.5743(6)$ Å, $\beta = 100.842(2)°$, $V = 2355.4(2)$ Å^3, $T = 293(2)$ K, space group $P2_1/c$, $Z = 2$, $D_c = 1.366$ g cm^{-3}, $\mu(\text{MoK}\alpha) = 0.114$ mm^{-1}, $R1 = 0.0991$ ($2540F_o > 4\sigma F_o$) and 0.1453 (all data), $wR_2 = 0.2662$, GOF = 1.038. CCDC reference number 634481. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707211b

Crystal structure data for [2·H$_2$][BF$_4$]$_2$⊂DB24C8·(CH$_3$NO$_2$)$_2$. C$_{42}$H$_{54}$B$_2$F$_8$N$_6$O$_{12}$, $M = 1008.53$, triclinic, $a = 8.9189(3)$, $b = 11.0803(4)$, $c = 12.0622(4)$ Å, $\alpha = 81.660(2)$, $\beta = 79.928(1)$, $\gamma = 77.557(2)°$, $V = 1138.93(7)$ Å^3, $T = 293(2)$ K, space group $P\bar{1}$, $Z = 1$, $D_c = 1.470$ g cm^{-3}, $\mu(\text{MoK}\alpha) = 0.127$ mm^{-1}, $R1 = 0.0608$ ($2690F_o > 4\sigma F_o$) and 0.0970 (all data), $wR_2 = 0.1327$, GOF = 1.017. CCDC reference number 634482. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707211b

Acknowledgements

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