Synthesis and characterisation of a new pyridinium salt/crown ether complex and its self-assembly

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The monoprotonated bipyridinium cation can complex with dibenzo-24-crown-8 by means of ion-dipole and charge-transfer interactions. They both thread to form a [2]pseudorotaxane-like complex for further intercomplex association to produce pseudopolyrotaxane arrays through N+–H⋯N hydrogen bonding in the solid state.

Keywords: polyrotaxane, charge-transfer interaction, hydrogen-bonding, 4,4'-bipyridinium cation, DB24C8

Supramolecular complexation of cationic substrates with macrocyclic ethers has attracted ever-increasing attention.[1] In the earlier years Pursiainen[1b,d-f] and his coworkers reported the nature of various biologically important N-heteroaromatic cations complexation of different ring-size crown ethers and pointed out that larger crown ethers {e.g. dibenzo-24-crown-8 (DB24C8)} and functionalised guests would lead to new tailor-made polymers or polyrotaxanes.[1d] We were encouraged to explore whether DB24C8 would complex with the doubly protonated 4,4'-bipyridinium dication just as Loeb reported the complexation of DB24C8 with diprotonated 1,2-bis(4,4'-bipyridinium)ethane.[2] Unexpectedly, the yellow crystals obtained in our study were a 1:1 complex of DB24C8 and monoprotonated bipyridinium[3] by X-ray diffraction. Interestingly, the complex self-assembled to form a supramolecular array *via* head-to-tail N+–H ⋯ N hydrogen bonding of its self-complementary 4,4'-bipyridinium cation moiety as Pursiainen predicted.[4] Herein we report the complexation between **2**·CF₃SO₃ and DB24C8 (Fig. 1), and the noncovalent polymerisation[5] to form a polyrotaxane array[4,6] in the solid state.

The yellow solid was obtained from a CH₃CN solution of diprotonated 4,4'-bipyridinium triflate and DB24C8 by slow evaporation. Much to our surprise, X-ray structural studies[7] show the presence of a [2]pseudorotaxane-like geometry in the solid state in which the cation **2**⁺, protonated 4,4'-bipyridinium monocation, is sandwiched between the two catechol rings of DB24C8 with a C-shaped conformation. The studies also indicate that [**2**/DB24C8]·CF₃SO₃ crystallises with two crystallographically independent 1:1 complexes, **A** and **B** (Fig. 2), in the asymmetric unit. In both conformations, all N⁺ ⋯ O distances lie in the range from 3.120 to 3.667 Å with two exceptions (N3–O7: 4.053, N1–O3: 4.025 Å), indicating that the pseudorotaxane is stabilised by the strong ion-dipole interactions between the positively charged N-atom of the cation and the Lewis basic atoms of the DB24C8 ether. However, the two independent cations differ. The angles between the planes of the two aromatic rings in each cation of A and B are 48.3° and 50.3°, respectively, and furthermore a dihedral angle of 89.2° forms between adjacent bipyridinium units so as to maximise the N⁺ ⋯ O interactions and also magnify the major π-stacking interactions. The distances between both sets of π-electron rich aromatic units vary in **A** and **B** (7.50 and 8.07 Å, respectively), with the shorter ring centroid (catechol ⋯ protonated pyridyl) separations of 3.79 and 4.07 Å, respectively, indicative of strong charge-transfer interactions in the 1:1 complex. C–H ⋯ π interactions were found between DB24C8 and the unprotonated pyridine ring
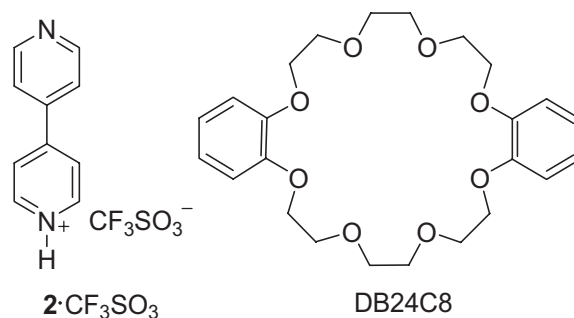
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Fig. 1 Structural formulas of dibenzo-24-crown-8 (DB24C8), and 4,4'-bipyridinium triflate (**2**·CF3SO3).

of the adjacent conformation. The macrocyclic components of **A** and **B** pack (Fig. 3) to furnish channels that extend in the crystallographic *b* direction with the cations threaded in such a manner as to suggest the potential for the formation of polyrotaxanes *via* selfcomplementary N⁺ ⋯ N hydrogen bonds. Furthermore, linear pseudopolyrotaxanes assemble to form 3D supramolecular architecture arrays through C–H ⋯ O hydrogen bonding between the DB24C8 ethers of the adjacent columns.

To further investigate the nature of their complexation, we synthesised the monoprotonated 4,4'-bipyridinium triflate by the reaction of an excess of 4,4'-bipyridyl with triflic aãd. Treatment of **2**·CF₃SO₃ with one equiv. of DB24C8 in CH₃CN at room temperature resulted in a yellow solution on account of the charge-transfer interactions between the π-electron rich and defiãent entities in the two components. The stoichiometry of the complex between **2**·CF₃SO₃ and DB24C8 was determined to be 1:1 using the Job's plot method. The nature of the suprastructure present in CD₃CN was investigated by ¹H NMR spectroscopy. At equimolar (50 mM) proportions of **2**·CF₃SO₃ and DB24C8 (Fig. 4), the relatively large Δδ values for the catechol aromatic protons (Δδ = –0.15 ppm) in DB24C8 and β-CH protons (Δδ = –0.34 ppm) in **2**·CF₃SO₃ reveal that the DB24C8 and the cation **2**⁺ must lie in close proximity to each other – a geometry consistent with the presence of π–π stacking between these two components in the complex. Moreover, only one set of signals for the bipyridinium aromatic protons in the absence or presence of DB24C8 was observed, and it suggests fast proton exchange and complexation equilibrium on the NMR time scale. A K_a value for the 1:1 complex of 116 ± 20 dm³ mol⁻¹ was determined by dilution methods in CH₃CN using ¹H NMR probe protons in DB24C8 and recording their chemical shift changes (Δδ) for an equimolar mixture of DB24C8 and **2**·CF₃SO₃.

In summary, an interesting complexation between the monoprotonated 4,4'-bipyridinium triflate and dibenzo-
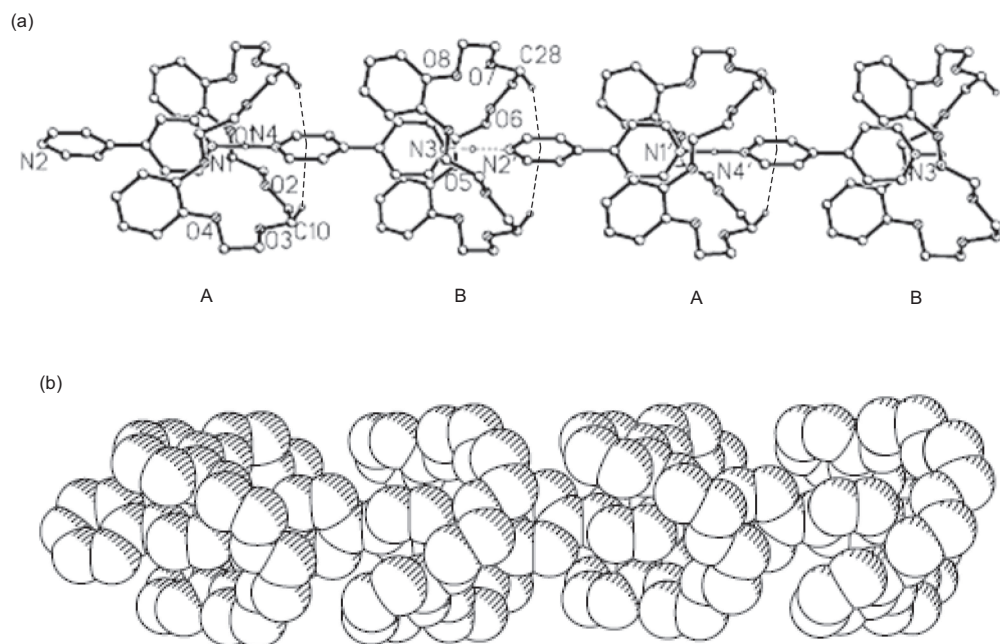
Fig. 2 (a) Partial ball-and-stick representation of the pseudorotaxane in the X-ray crystal structure composed of alternating A and B. (b) Partial space-filling representation of the pseudopolyrotaxane.
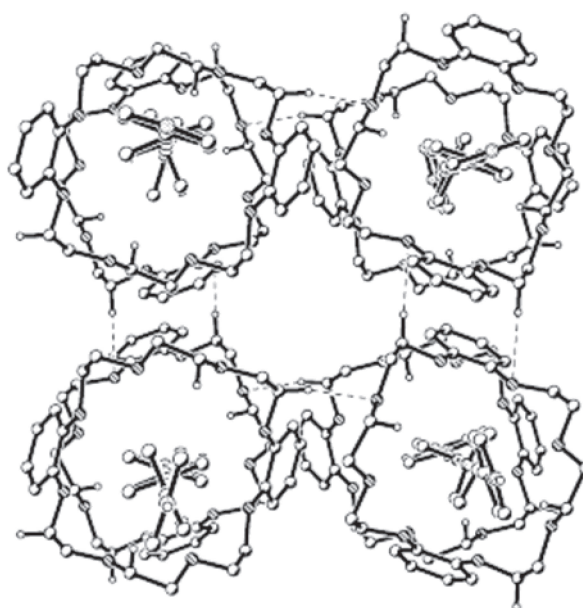

Fig. 3 A view down the b direction in the crystals of the [2]pseudorotaxane showing the DB24C8 channels and H-bonding (dashed lines) between the adjacent columns.

Fig. 4 Partial ^{1}H NMR spectra (500 MHz, CD$_3$CN, 298 K) of (a) **2**·CF$_3$SO$_3$, (b) DB24C8, and (c) an equimolar mixture of **2**·CF$_3$SO$_3$ and DB24C8.

24-crown-8 has been presented. The complex is stabilised mainly by ion-dipole and charge-transfer interactions, and can noncovalently polymerise to a supramolecular polyrotaxane array via head-to-tail N$^+$–H···N hydrogen bonding in the solid state. The possible complexation between the doubly protonated 4,4'-bipyridinium axle and DB24C8 remains under study.

Experimental

Commerãally available reagents and solvents were used as received. The ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz (Bruk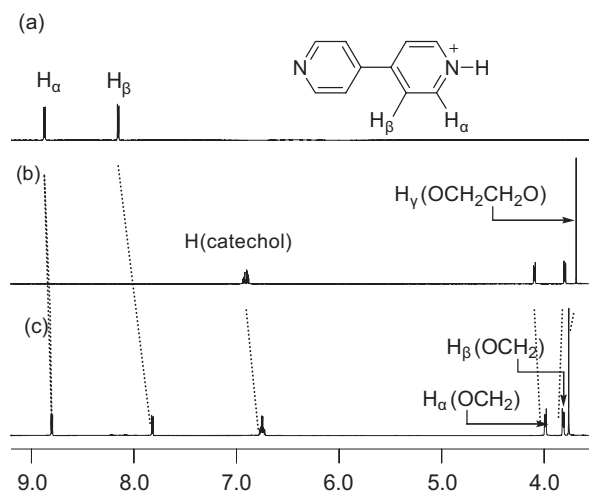er AM), respectively. The residual proton shift was used as standard reference. The UV-vis spectra were measured at 298 K by a SHIMADZU UV-2450 spectrophotometer.

Determination of the stoichiometry by Job's method [8]
The stoichiometry of the complex between DB24C8 and **2**·CF$_3$SO$_3$ was determined using the continuous variation method (Job's method). The same concentrations of guest solution were added to the sample cell and reference cell. The molar fraction of **2**·CF$_3$SO$_3$ varied in the range 0.2–0.8 in the sample cell when [DB24C8]$_0$ + [**2**·CF$_3$SO$_3$]$_0$ = 10.0 mM. UV spectra for each sample were taken at 298 K, and the absorbance at λ_{max} 337 nm recorded for the Job plot as the free DB24C8 ether has no absorption significant enough to affect the measurement of the stoichiometry at the investigated wavelength range.

Determination of assoãation constant [1a]

An equimolar CD_3CN solution of DB24C8 and **2**·CF_3SO_3 was diluted in seven steps from 50 to 0.5 mM. At each step the solution was left standing for 30 min at 25ºC and an ^{1}H NMR spectrum was recorded. The chemical shift change ($\Delta\delta$) observed for H^γ on DB24C8 was plotted against the concentration (c). The assoãation constant (K_a) and the maximum chemical shift change ($\Delta\delta_m$) were determined by fitting the NMR data into the following equation with Origin's nonlinear regression method (Version: Origin 6.1) based on Levenberg–Marquardt (LM) algorithm on a PC computer.

$$\Delta\delta_o = \frac{\Delta\delta_m + 2cK_a\Delta\delta_m - \sqrt{\Delta\delta_m{}^2 + 4cK_a\Delta\delta_m{}^2}}{2cK_a}$$

Supplementary information

The details on the Job plot and assoãation constant determination for **2**·CF_3SO_3/DB24C8 are available from the authors on request.

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7 *Crystal data* for (**2**/DB24C8)·CF_3SO_3: yellow block, $C_{35}H_{41}F_3N_2O_{11}S$, fw = 754.76, orthorhombic, T = 294(2) K, *Pbcn, a* = 19.539(3), b = 19.289(3), c = 19.541(3) Å, V = 7365(2) Å^3, Z = 8, μ = 0.164 mm^{-1}, independent reflections: 7894 (R_{int} = 0.1021). final R indices [$I > 2\sigma I$]: $R1$ = 0.0497, $wR2$ = 0.0955, R indices (all data): $R1$ = 0.1467, $wR2$ = 0.1260, Goodness-of-fit ($F2$) = 0.984. CCDC 608599 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.ãf.
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