Supramolecular Chemistry

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Suitanes**

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The making of mechanically interlocked molecular compounds[1] has evolved from a statistical beginning[2] to the use of molecular-recognition-driven, self-assembly protocols[3] that rely upon the operation of covalent,[4] metal,[5] or noncovalent[6] templates,[7] prior to the formation of the mechanical bond(s) by either kinetically or thermodynamically controlled processes, involving either dative[8] or covalent[9] bond formation. Previously, we have speculated[10] about the existence of another class of interlocked molecule beyond the archetypal catenanes[11] and rotaxanes,[12] which are not all that dissimilar from carceplexes[13] and yet are distinguishable from them.[14] In searching for some simple term for this class of mechanically interlocked molecule (Figure 1), which consists of two separate components—a body with two or more limbs that are rigid and protrude outwards, the torso of which carries a close-fitting, all-in-one suit, such that it encompasses the torso of the body—we have come up with the term suitane, in which a number is inserted between "suit" and "ane" to indicate the number of protruding limbs. Thus, the simplest member of the series would be suit[2]ane, a linear structure in which the suit surrounds the body with limbs protruding outwards in opposite directions (180°; Figure 1 a), such that there is no easy way by which the suit can be removed from the body. Likewise, suit[3]ane (Figure 1 b) and suit[4]ane (Figure 1 c) will consist of bodies with three and four limbs, respectively, that are trigonal (120°) and square (90°) planar and ready to be fitted out with the appropriate suit containing three and four holes, respectively.

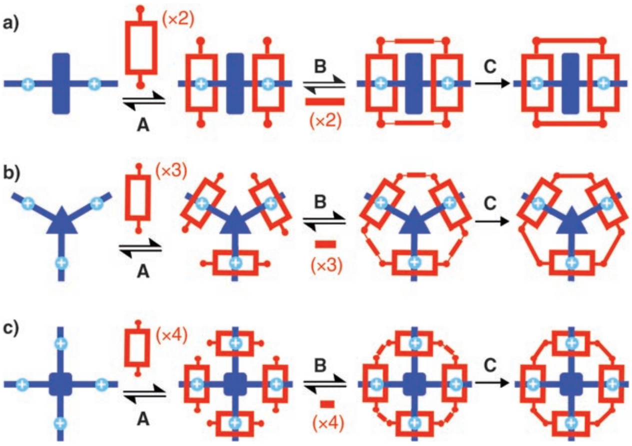

Figure 1. Schematic representations of the approach that is being pursued in the construction of a new class of mechanically interlocked molecular compounds known as suitanes. The construction of a) suit[2]ane, b) suit[3]ane, and c) suit[4]ane. The "+" signs on the protruding limbs of the templates (blue) represent the -NH_2^+- centers on the linear, triangular, and square templates. The (red) rectangles introduced in each case in step A are crown ethers with [24]crown-8 constitutions. In step A, noncovalent bonding leads to complex formation, in which the rectangles are positioned to be covalently linked under thermodynamic control in step B before being kinetically fixed in step C.

A doll dressed up in an all-in-one suit, or a "onesie", provides an analogy with a suit[5]ane (Figure 2).

Let us consider the specific example (Scheme 1) of a linear body template[15] **LBT**-H_2^{2+} carrying two -CH_2-$NH_2^+CH_2$- recognition sites separated from each other by a bulky midriff[16] such that the double linking up of two matching [24]crown-8 rings in the shape of $(CHO)_2$-**DP24C8** units[17] can be achieved reversibly by forming four imine bonds with a diaminobenzene spacer, such as *p*-phenylenediamine (**PPD**). The virtue of employing reversible imine bond formation[18] to clothe the **LBT**-H_2^{2+} dication with two $(CHO)_2$-**DP24C8** units and two **PPD** spacers is that errors can be corrected[19] before the final structure is fixed by

Figure 2. A doll dressed in an all-in-one suit constitutes an example of a suit[5]ane.

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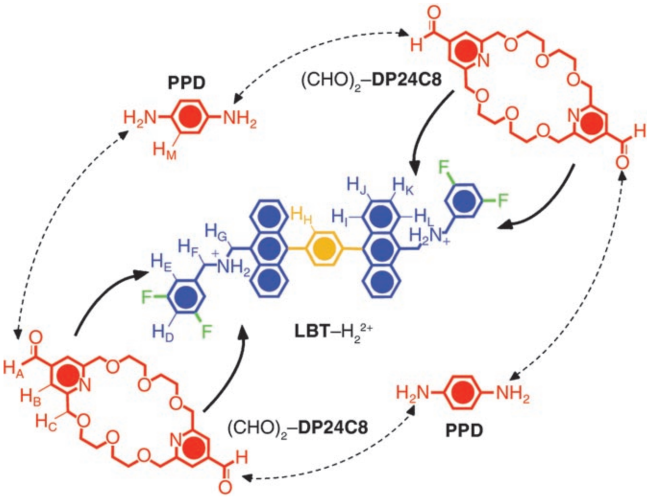

Scheme 1. Synthetic protocol for the construction of suit[2]ane from 1.0 equivalent of **LBT**-H_2^{2+} and 2.0 equivalents each of $(CHO)_2$-**DP24C8** and **PPD**.

reducing the imine functions to amino groups. Herein, we report the efficient self-assembly of a suit[2]ane from five components by using a dynamic covalent synthetic protocol[20] on the back of experimental and computational investigations of the 1:2 complex formed between the **LBT**-H_2^{2+} dication and two equivalents of $(CHO)_2$-**DP24C8** in solution and in the solid state. The tetraimine, which is formed when two equivalents of **PPD** are added to a 2:1 mixture of $(CHO)_2$-**DP24C8** and **LBT**-$H_2 \cdot 2\,PF_6$, is a remarkably stable compound in its own right in solution, from whence it crystallizes. We describe the X-ray crystal (super)structure analysis of both the 1:2 complex and the suit[2]ane.

As a model for the dynamic assembly of a suit[2]ane, the self-assembly of **LBT**-H_2^{2+} and **DP24C8** has been investigated in solution, in the solid state, and by computational methods. When stoichiometric quantities of **DP24C8** were added to **LBT**-$H_2 \cdot 2\,PF_6$ in CD_3NO_2 both the 1:1 and 2:1 (macrocycle/thread) complexes were observed by ^1H NMR spectroscopic analysis. Single crystals, suitable for X-ray analysis, of the [3]pseudorotaxane formed between **LBT**-H_2^{2+} and 2.0 equivalents of **DP24C8** were grown by vapor diffusion of iPr$_2$O into MeCN. Its solid-state superstructure[21] reveals (Figure 3) the anticipated threading of the dicationic spindle through the centers of the two **DP24C8** rings. Complex stabilization is achieved by pairs of $N^+{-}H\cdots N$ and $N^+{-}H\cdots O$ hydrogen bonds, as illustrated in Figure 3a. The 2:1 complex has crystallographic inversion symmetry, and the planes of the terminal 3,5-difluorobenzyl and central phenylene rings are oriented essentially orthogonally to the pair of anthracene ring systems aligned in parallel. The separations of the ring centroids of the two 3,5-difluorobenzyl groups are 22.8 Å, and the distance between the two NH_2^+ centers is 16.0 Å. With a view to constructing the desired macropolycycle in which two **DP24C8** rings are doubly linked through the 4-positions of their pyridyl rings, thus entrapping the central dication, the separations of these 4-positions are important in the context of identifying suitable linking spacer groups. In this 2:1 complex, these distances are approximately 14.5 Å[22].

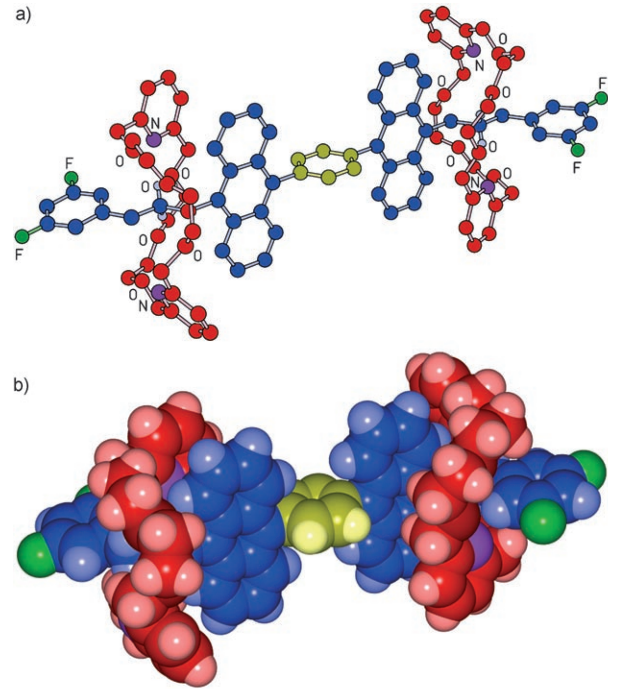

Figure 3. a) Ball-and-stick representation of the solid-state superstructure of the 2:1 complex. The $N^+{-}H\cdots N$ hydrogen bonds have $N^+\cdots N$ and $H\cdots N$ distances of 2.97 and 2.07 Å, respectively, and $N^+{-}H\cdots N$ angles of 179°. The $N^+{-}H\cdots O$ hydrogen bonds have $N^+\cdots O$ and $H\cdots O$ distances of 3.05 and 2.16 Å, respectively, and $N^+{-}H\cdots O$ angles of 168°. b) Space-filling representation of the same superstructure.

Computational force-field modeling[23] predicts the most stable co-conformation of the [3]pseudorotaxane (Figure 4a) in solution to be that in which the macrocycle pyridine rings are involved in π–π stacking interactions with both of the **LBT**-H_2^{2+} anthracene moieties in a manner similar to molecular clips[24] or molecular tweezers.[25] In the structure obtained from modeling, the separation between the 4-positions of the **DP24C8** rings is 8.8 Å, a full 5.7 Å closer than in the solid-state superstructure. Such proximity is ideally suited to form a suit[2]ane upon functionalizing the 4-positions of each pyridine ring with formyl groups and adding two equivalents of **PPD**. The lowest energy co-conformer obtained from modeling of the fully assembled suit[2]ane (Figure 4b) bears an almost uncanny structural resemblance to the modeled [3]pseudorotaxane. In the case of the fully assembled suit[2]ane, the 4-positions of the **DP24C8** rings are separated by 10.1 Å, only 1.3 Å further apart than in the modeled 2:1 precursor complex. This observation is a strong indication that the noncovalent interactions responsible for the self-assembly of the **LBT**-$H_2 \cdot 2\,PF_6$ and the **DP24C8** macrocycles will be preserved in the dynamically assembled suit[2]ane. It may also be anticipated that the p-phenylene ring of **PPD** can impart greater stability to the interlocked suit[2]ane through π–π stacking interactions with the central p-phenylene unit of **LBT**-H_2^{2+}. By comparing the lowest energy structures obtained for **DP24C8**, **LBT**-H_2^{2+}, the [3]pseudorotaxane, the suit[2]ane, and the tetraimine host of suit[2]ane, a semiquantitative evaluation of the binding energies between the host/guest pairs in both the [3]pseudo-

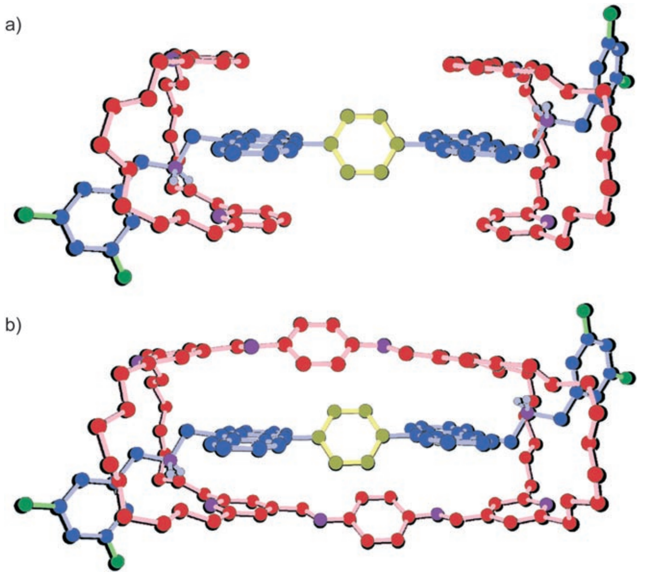

Figure 4. a) Profile representation of the lowest energy co-conformation of the model 2:1 complex obtained from computational modeling. The solution-phase modeling predicts that π–π stacking interactions between the **DP24C8** and anthracene moieties may, upon functionalization of the **DP24C8** rings with formyl groups, facilitate the formation of the fully assembled suit[2]ane on the addition of **PPD**. b) The lowest energy co-conformation of the fully assembled suit[2]ane obtained from modeling bears a striking resemblance to the modeled 2:1 complex.

rotaxane and the suit[2]ane can be made.[26] Such a comparison leads to the conclusion that the binding of **LBT**-H_2^{2+} by the tetraimine host is 1.1 kcal mol^{-1} more favorable than binding of **LBT**-H_2^{2+} by two equivalents of **DP24C8**. Such a small energy difference is, however, well within the error of these force-field calculations, and the two binding energies of the two compounds should, therefore, be taken to be roughly identical. These modeling results indicate, at the very least, that formation of the suit[2]ane and concomitant co-conformational change in the [3]pseudorotaxane host/guest complex do not disrupt, and perhaps even enhance, the binding of **LBT**-H_2^{2+}.

With these encouraging predictions to hand, the dipyrido[24]crown-8 derivative $(CHO)_2$-**DP24C8** was prepared and added to a solution of **LBT**-H_2^{2+} in CD_3NO_2 in a 2:1 ratio. Nearly quantitative formation of the corresponding [3]pseudorotaxane is observed (Figure 5) by ^{1}H NMR spectroscopy within 5 minutes of mixing. The effects and efficiency of complexation is reflected in shifts of the signals corresponding to protons on both the $(CHO)_2$-**DP24C8** macrocycles as well as on the **LBT**-$H_2 \cdot 2PF_6$ once the latter finds itself threaded through two equivalents of the former. For example, methylene protons H_F and H_G, which are adjacent to the $-CH_2NH_2^+CH_2-$ centers of **LBT**-H_2^{2+}, appear as singlets at $\delta = 4.8$ and 5.8 ppm, respectively, in the free template (Figure 5b). Upon complexation, H_F and H_G appear (Figure 5c) as multiplets and shift to $\delta = 5.1$ and 5.5 ppm, respectively, as they are involved in hydrogen-bonding interactions with the $(CHO)_2$-**DP24C8** macrocycles. The signal for the benzylic methylene protons of $(CHO)_2$-**DP24C8** shifts from being a singlet centered at $\delta = 4.7$ ppm when uncomplexed to two doublets ($\delta = 4.6$ and 4.2 ppm) as a result of their diastereotopic relationship when complexed. Furthermore, the anthracene protons H_I, which point "inward" toward the central *p*-phenylene unit of **LBT**-H_2^{2+}, undergo a downfield shift of $\Delta\delta = 0.4$ ppm upon complexation ($\delta = 8.4$–8.0 ppm). This observation suggests that π–π stacking occurs between the $(CHO)_2$-**DP24C8** pyridine rings and the anthracene units of **LBT**-H_2^{2+}, similar to that predicted by computational modeling (Figure 4a).

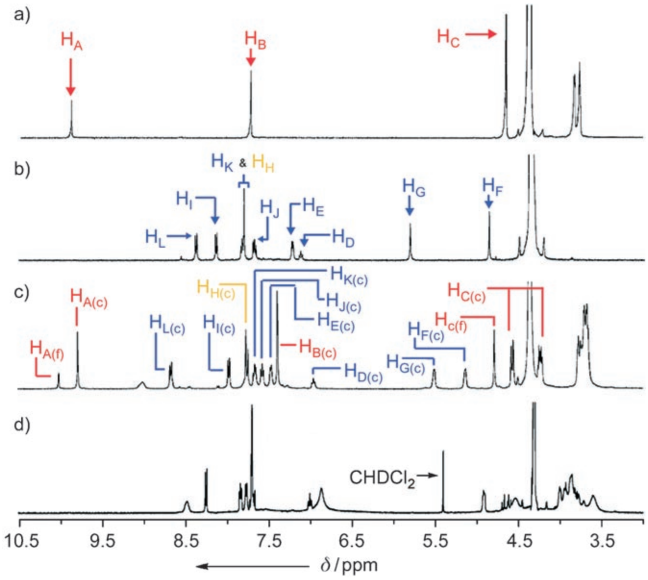

Figure 5. Partial ^{1}H NMR spectra recorded at 500 MHz in CD_3NO_2 showing a) free $(CHO)_2$-**DP24C8**, b) free **LBT**-$H_2 \cdot 2PF_6$, c) [3]pseudorotaxane, and d) suit[2]ane after equilibration. For the proton (H) assignments, see Scheme 1.

The addition of 2 equivalents of **PPD** to the [3]pseudorotaxane formed from a solution of **LBT**-$H_2 \cdot 2PF_6$ and $(CHO)_2$-**DP24C8** (1:2) in CD_3NO_2 results, initially, in a mixture of kinetic products. The ^{1}H NMR spectrum recorded after 29 days (Figure 5d) of equilibration corresponds to the formation of one dominant, highly symmetric, thermodynamic product in solution. No significant spectroscopic changes were observed after 29 days. The disappearance of the aldehyde peak at $\delta = 9.8$ ppm and appearance of a sharp imine peak at $\delta = 8.2$ ppm, which integrates to give four protons, strongly indicate the formation of the suit[2]ane. X-ray-quality single crystals were grown by vapor diffusion of iPr$_2$O into Me$_2$CO, and the solid-state structure,[21,27] corresponding to suit[2]ane, was obtained (Figure 6a,b). The similarity between the suit[2]ane structure as predicted by computational modeling (Figure 4b) and that obtained from X-ray crystallographic analysis is quite remarkable. The solid-state structure of the suit[2]ane reveals the desired encapsulation of the central aromatic core, containing the two anthracene rings and their linking phenylene unit, within the macropolycycle. In addition to the mechanical interlocking of the two components, secondary stabilization is achieved by a combination of $N^+–H \cdots N$, $N^+–H \cdots O$, $C–H \cdots O$, and $C–H \cdots \pi$ interactions, as illustrated in Figure 6a. The overall

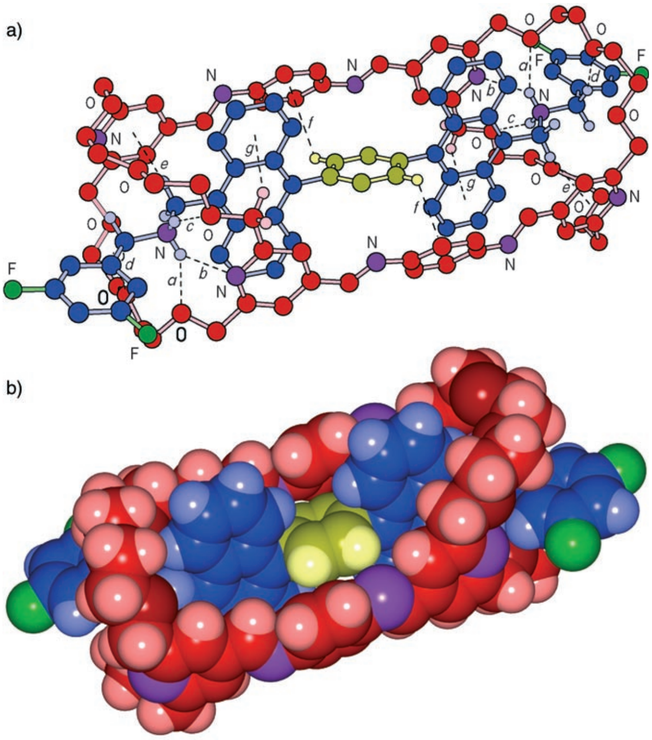

Figure 6. a) Ball-and-stick representation of the solid-state structure of a suit[2]ane. The X^{+}–H···X and H···X hydrogen bonds labeled *a–d* have X^{+}···N, H···X distances [Å] and X^{+}–H···X angles [°], respectively, of 2.94, 2.13, 150 (*a*); 2.95, 2.28, 130 (*b*); 2.86, 2.03, 154 (*c*); and 3.27, 2.35, 160 (*d*). The C–H···π interactions labeled as *e–g* have H···π [Å] distances and C-H···π angles [°], respectively, of 2.70, 132 (*e*); 2.91, 120 (*f*); and 2.97, 145 (*g*). b) Space-filling representation of the solid-state structure of the suit[2]ane.

dimensions of the dication are changed little from those observed in the 2:1 complex with a centroid–centroid separation of the two terminal 3,5-difluorobenzyl ring systems of 23.2 Å and of the nitrogen centers of 16.2 Å. This linking of the 4-positions of the **DP24C8** rings by **PPD** spacers causes decreases of approximately 4.0 Å in the separations of the two pairs of **DP24C8** rings relative to those observed in the 2:1 complex. The parallel-aligned **PPD** ring systems have an interplanar separation of approximately 8.2 Å.

The successful template-directed synthesis of this suit[2]ane echoes the painstaking efforts that went into designing its constituent parts with crucial input from computational chemistry. On reflection, **LBT**-H_2^{2+} is a fairly rigid template which becomes trapped as the "guest" inside a relatively flexible "host" built up of a couple of difunctionalized crown ethers $(CHO)_2$-**DP24C8** that can embrace the $-CH_2-NH_2^{+}CH_2-$ recognition sites at both ends of the **LBT**-H_2^{2+} dication. In the final analysis, it is the choice—herein it is **PPD**—of the linker that matters: it must not be too short nor too long so that it dictates a successful outcome for this first stab (Figure 1 a) at making suit[2]anes, which employs dynamic covalent and noncovalent chemistries.

Before we can claim that the compound we call suit[2]ane is a molecule, we have to gather evidence that it is truly a mechanically interlocked molecular compound. Although minor changes were observed in the relative intensities of some of the signals in the ^{1}H NMR spectrum when a sample of the compound was heated at 70 °C in CD_3CN for 30 days, the chemical shifts δ remained essentially unchanged. Moreover, there was no evidence, after the 30 days of heating, for the presence of free **LBT**-H_2^{2+} dications, or indeed of the free tetraimine host. These observations demonstrate the integrity and stability of this class of mechanically interlocked molecular compounds.[28]

Our success in the template-directed synthesis of suit[2]ane holds out hope for being able to self-assemble suit[3]anes (Figure 1 b) and suit[4]anes (Figure 1 c) around trigonal and square planar templates, respectively. When this "two-dimensional" goal is realized then there is no reason why entering the third dimension with tetrahedral and octahedral scaffolds should not be contemplated. Supramolecular assistance to covalent synthesis, in which the template is consumed stoichiometrically, can be regarded as a forerunner to template-directed reactions[29] in which the template keeps expressing or even copying itself.

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[13] "Carceplexes are comprised of host and guest components that cannot separate from one another without the breaking of covalent bonds. Their existence does not depend upon host–guest interactions nor on other than gross size complementarity. Rather their existence depends upon physical envelopment of guests during shell closures leading to carceplexes." This quote is taken from D. J. Cram, J. M. Cram in *Container Molecules and Their Guests* (Ed.: J. F. Stoddart), The Royal Society of Chemistry, Cambridge, **1994**, p. 147.

[14] The class of mechanically interlocked molecules we propose to call suitanes differ from carceplexes in so far as their existence is established by host–guest interactions during their template formation. These interactions will normally live on in the molecules afterwards, provided the recognition sites are not switched off by some means or another. Herein, the recognition in the form of noncovalent bonds would have their strength considerably diminished and impaired by the addition of base.

[15] The synthesis of **LBT**-$H_2 \cdot 2PF_6$ is reported in the Supporting Information.

[16] The formation of the 2:1 complexes—or [3]pseudotoraxane—is assisted principally by $N^+-H\cdots O$ hydrogen bonds and $C-H\cdots O$ interactions between the $-CH_2NH_2^+CH_2-$ recognition sites on the **LBT**-H_2^{2+} dication and the matching dipyrido[24]crown-8 rings in $(CHO)_2$-**DP24C8**. For reviews on the use of this particular recognition motif as a template, see: a) P. T. Glink, C. Schiavo, J. F. Stoddart, *Chem. Commun.* **1996**, 1438–1490; b) T. J. Hubin, A. G. Kolchinski, A. L. Vance, D. H. Busch, *Adv. Supramol. Chem.* **1999**, *6*, 237–357; c) T. J. Hubin, D. H. Busch, *Coord. Chem. Rev.* **2000**, *200–2002*, 5–52; d) S. J. Cantrill, A. R. Pease, J. F. Stoddart, *J. Chem. Soc. Dalton Trans.* **2000**, 3715–3734.

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[21] Crystal data for [(**DP24C8**)$_2$(**LBT**-H_2)]: $[C_{94}H_{98}F_4N_6O_{12}]$-$(PF_6)_2 \cdot 2\,MeCN$, $M_r = 1951.83$, monoclinic, $P2_1/n$ (no. 14), $a = 12.6367(14)$, $b = 26.388(3)$, $c = 15.594(2)$ Å, $\beta = 111.060(8)°$, $V = 4852.6(11)$ Å^3, $Z = 2$ (C_i symmetry), $\rho_{calcd} = 1.336\ g\,cm^{-3}$, $\mu(Cu_{K\alpha}) = 1.222\ mm^{-1}$, $T = 293$ K, colorless prisms; 7207 independent measured reflections, F^2 refinement, $R_1 = 0.133$, $wR_2 = 0.364$, 2730 independent observed reflections ($|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 120°$), 659 parameters.

[22] It should be noted that, in the solid-state superstructure, two co-conformations of relative occupancies 0.65:0.35 were observed for the **DP24C8** rings, and the separations of the carbon atoms in the 4-positions of the pyridine rings in the two different co-conformations were 14.3 and 14.6 Å, respectively; Figure 3 depicts the major conformer.

[23] Computations were performed using the program Maestro v 3.0.038 with the AMBER* force-field and GB/SA solvent model for $CHCl_3$. Full details of computational procedures can be found in the Supporting Information.

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[26] The [3]pseudorotaxane binding energy was taken as the difference in energy between the fully optimized structures of the [3]pseudorotaxane and that of the fully separated **LBT**-H_2^{2+} and two equivalents of $(CHO)_2$-**DP24C8**. The binding energy of suit[2]ane was taken as the difference in energy between the fully optimized structures of the suit[2]ane and those of the fully separated **LBT**-H_2^{2+} plus the tetraimine host.

[27] Crystal data for suit[2]ane: $[C_{110}H_{106}F_4N_{10}O_{12}](PF_6)_2 \cdot 8\,Me_2CO$, $M_r = 2590.61$, monoclinic, $P2_1/n$ (no. 14), $a = 16.3400(3)$, $b = 21.1680(3)$, $c = 20.7430(4)$ Å, $\beta = 110.5770(6)°$, $V = 6717.0(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.281\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 0.123\ mm^{-1}$, $T = 123$ K, pale yellow plates; 12156 independent measured reflections, F^2 refinement, $R_1 = 0.083$, $wR_2 = 0.232$, 7171 independent observed absorption-corrected reflections ($|F_o| > 4\sigma$-$(|F_o|)$, $2\theta_{max} = 51°$), 837 parameters. CCDC-608949 ([(**DP24C8**)$_2$-(**LBT**-H_2)]) and -608950 (suit[2]ane) 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.

[28] The four imine bonds in suit[2]ane constitute a fairly stable entity. In principle, as we have shown with numerous other polyimine macrocycles, it should be possible to reduce them with reagents, such as BH_3–THF or BH_3–lutidine—and, in so doing, fix the structure for all time in a kinetic regime.

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