



UNIVERSITÀ DI PARMA

ARCHIVIO DELLA RICERCA

University of Parma Research Repository

New Geometries for Calix[6]arene-Based Rotaxanes

This is the peer reviewed version of the following article:

Original

New Geometries for Calix[6]arene-Based Rotaxanes / Bazzoni, Margherita; Zanichelli, Valeria; Casimiro, Lorenzo; Massera, Chiara; Credi, Alberto; Secchi, Andrea; Silvi, Serena; Arduini, Arturo. - In: EUROPEAN JOURNAL OF ORGANIC CHEMISTRY. - ISSN 1434-193X. - 2019:21(2019), pp. 3513-3524. [10.1002/ejoc.201900211]

Availability:

This version is available at: 11381/2857889 since: 2021-10-01T08:16:28Z

Publisher:

Wiley-VCH Verlag

Published

DOI:10.1002/ejoc.201900211

Terms of use:

Anyone can freely access the full text of works made available as "Open Access". Works made available

Publisher copyright

note finali coverpage

(Article begins on next page)

02 May 2026

1 **Calix[6]arene-Based Rotaxanes**

New Geometries for Calix[6]arene-Based Rotaxanes

Margherita Bazzoni,^[a] Valeria Zanichelli,^[a] Lorenzo Casimiro,^[b] Chiara Massera,^[a] Alberto Credi,^[c,d] Andrea Secchi*^[a] Serena Silvi,*^[b] and Arturo Arduini*^[a]

Abstract: Understanding the role played by the nature, number, and arrangement of binding sites anchored to a macrocycle remains a topic of current interest for the synthesis of new interwoven species. We report the synthesis and detailed structural characterization of a new calix[6]arene derivative deco-

rated with two phenylureido groups anchored at the diametrical position of the calix upper rim that adopts a 1,2,3-alternate conformation in solution and in the solid state. Preliminary data on the ability of this host to form redox-active pseudorotaxanes and rotaxanes are reported.

Introduction

16 The nature, number and reciprocal orientation of the binding sites that characterize either natural and synthetic receptors are responsible for their ability to efficiently bind a target guest and perform a programmed function. During these last decades, the supramolecular approach has led to the construction of several
21 stimuli-responsive devices and prototypes of molecular machines that paved the way for the bottom-up approach to the development of nanotechnology.^[1–3] Within this context, calix[6]arenes have demonstrated to be a versatile platform^[4,5] for the construction of interwoven aggregates belonging to the class of pseudorotaxanes and rotaxanes.^[6,7] During the last two decades, we showed that, in apolar media, the tris-(*N*-phenylureido)calix[6]arene **TPU** can take up 4,4'-bipyridinium (viologen) salts and form pseudorotaxanes in a process in which the phenylurea groups at the upper rim of the calixarene play a crucial role in pivoting the unidirectional threading of the cationic viologen through the macrocycle upper rim.^[8–11] This process paved the way for the synthesis of oriented (pseudo)-rotaxanes, characterized by the univocal orientation of the thread termini with respect to the two calix[6]arene
36 rims.^[12–18]

A retrospective perusal of the solid-state structure of pseudorotaxane **TPU**⊃**DOV**, formed by **TPU** and dioctylviologen diiodide (**DOV**) (see the schematic representation of Figure 1),^[8] clearly shows the calix[6]arene macrocycle adopting a flattened

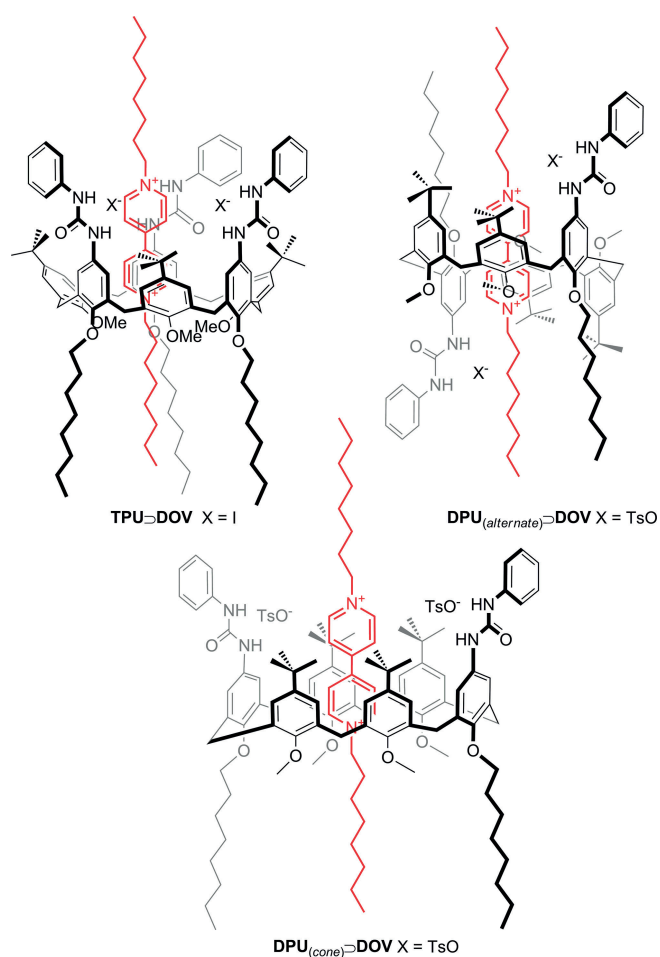


Figure 1. Schematic representation of the interwoven structures formed between tris- and bis-(*N*-phenylureido)calix[6]arene derivatives, **TPU** and **DPU**, respectively, and viologen salts.

[a] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma, Parco Area delle Scienze 17/A, 43124 Parma, Italy
E-mail: arturo.arduini@unipr.it
andrea.secchi@unipr.it

[b] Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, 40126, Italy
E-mail: serena.silvi@unibo.it

[c] Center for Light Activated Nanostructures (CLAN) and Dipartimento di Scienze e Tecnologie Agro-alimentari, Università di Bologna, 40127 Bologna, Italy

[d] Istituto per la Sintesi Organica e la Fotoreattività (ISOF) - CNR Area della Ricerca di Bologna, Via P. Gobetti 101, 40129 Bologna, Italy

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under <https://doi.org/10.1002/ejoc.201900211>.

41 cone conformation in which a defined π -rich aromatic cavity
surrounds the viologen bipyridinium dication, while both the
iodide counteranions are H-bonded to the ureido moieties at
the upper rim of **TPU**. However, while the anion involved in H-
bonds with two urea moieties is completely separated from its
46 pyridinium counteranion deeply engulfed inside the aromatic
cavity, the other, bound by only one urea, remains in intimate
contact with the pyridinium ring protruding from it. Neverthe-
less, the role played by the number and reciprocal position of
the phenylurea binding sites anchored at the calix[6]arene plat-
form is still not fully disclosed.

Van Duynhoven et al. have shown that in low polarity
solvents 1,3,5-trimethoxy-2,4,6-trialkoxy-*para-tert*-butylcalix[6]-
arenes can slowly interconvert from their *flattened cone* con-
formation to their 1,2,3-*alternate* conformation.^[19] The two con-
formations are co-existent at room temperature, one slowly inter-
converting to the other. Such behavior was explained consider-
ing an intra-annulus interconversion of the *tert*-butyl groups.
Jabin et al. recently evidenced the potential of the calix[6]arene
platform to orient its skeleton and to wrap around a specific
61 guest.^[20] Inspired by these studies, we imagined that the latter
geometrical arrangement decorated with H-bond-donor groups
like phenylureas might promote the formation of pseudorotax-
anes and rotaxanes endowed with new properties.

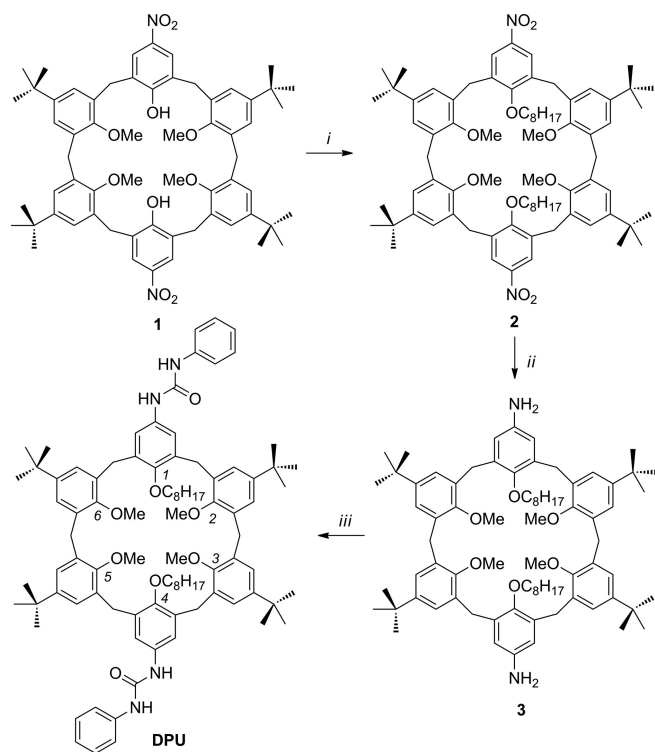
In this paper we present our efforts aimed at the synthesis
66 of a novel hexa-*O*-alkylated heteroditopic calix[6]arene receptor
(**DPU**) characterized by two octyloxy and four methoxy
groups in 1,4 and 2,3,5,6 positions, respectively. Two diametric
N-phenylureido moieties in *para* with respect to the octyloxy

groups complete the structure of the receptor (see Scheme 1).
The objective of the work is also to investigate the conforma-
tional preference adopted by this receptor in solution and in
the solid state and to establish whether the addition of violo-
gen salts as guests would lead to interwoven structures.

Results and Discussion

Synthesis of the Host

To synthesize **DPU**, we started from the known tetramethoxy-
dinitro calix[6]arene derivative **1** (see Scheme 1).^[21] Reaction of
1 with 1-iodooctane in refluxing acetonitrile using K_2CO_3 as
base gave **2** that was isolated by precipitation from ethyl acet-
ate in 70 % yield. Its 1H NMR spectrum, taken in $CDCl_3$ (see Fig. 81
S1, Supporting Information, SI), shows, as diagnostic features,
three broad signals in 1:1:1 integration ratio at 7.6, 7.2 and
7.0 ppm, for the aromatic protons, while in its mid-field region
are recognizable: two broad doublets at 3.6 and 4.3 ppm, each
integrating for 4 protons, two overlapped broad signals, overall
86 integrating for 8 protons, at ca. 3.9 ppm, and a singlet at ca.
3.0 ppm integrating for 12 protons. Through routinely 2D COSY
and HSQC NMR experiments (see Fig. S3, SI), the two broad
doublets were assigned to an AX system of coupled geminal
protons belonging to four of the six macrocycle bridging meth-
91 ylene groups. The two overlapped signals were resolved and
assigned to the two remaining bridging methylene groups,
which are in this case magnetically equivalent, and to the two
methylene groups nearby the phenolic oxygen in the two octyl
96 chains, respectively. The singlet at 3 ppm was finally assigned
to the four methoxy groups. Its resonance is quite upfield-
shifted (ca. 1 ppm) with respect to its common values and, as
seen with **TPU**^[18] and other trimethoxy calix[6]arene deriva-
tives,^[19] this shift is usually explained as an anisotropic shield-
ing effect exerted by the aromatic cavity of the macrocycle on 101
vicinal methoxy groups. Despite the general broadness of the
spectrum signals, which confirms a residual fluxionality of the
calix[6]arene macrocycle on the NMR timescale, overall, the re-
sulting signals pattern is consistent with a calix[6]arene macro-
cycle adopting, at room temperature, a 1,2,3-*alternate* confor-
106 mation. Reduction of the nitro groups with hydrazine using
Pd/C as catalyst leads to the formation of the diamino deriva-
tive **3**, which was not isolated but directly reacted with phenyl
isocyanate to afford the target calix[6]arene **DPU** in 80 % of
overall yield. The identity of **DPU** was established through high-
111 resolution (TOF) mass spectroscopy (see Fig. S4, SI) and 1D and
2D NMR measurements (see Fig. S5–12, SI). The 1H NMR spec-
trum, recorded in $CDCl_3$ (see Fig. S5, SI), exhibits several very
broad resonances supporting the hypothesis that, like its pre-
cursor **2**, also **DPU** experiences, on the NMR timescale, a certain
116 fluxionality in solution. Through a perusal of the HSQC spec-
trum (see Fig. S9, SI) we were able to identify two sets of signals,
each set of which likely belonging to two possible conformers
simultaneously present in solution. In particular, we identified
two resonances for the methoxy groups (*a*) (see Figure 2 for 121
labelling), which give rise to a very broad peak at ca. 3.4 ppm
and a sharper singlet at 2.99 ppm, and two for the methylene



Scheme 1. Reagents and conditions: *i*) 1-iodooctane, K_2CO_3 , CH_3CN , reflux, 4 d, 70 %; *ii*) $NH_2NH_2 \cdot H_2O$, Pd/C, EtOH, reflux, 24 h and *iii*) phenyl isocyanate, CH_2Cl_2 , r.t., 2 h, 80 % (two steps).

groups (b) of the octyl chains, that is, an intense triplet at 4.04 ppm and a smaller one at 3.8 ppm. In the corresponding ^{13}C -APT spectrum (see Fig. S5, SI), the carbon nuclei of these groups yield, in the uncrowded spectral window between 50 and 80 ppm, two easily recognizable peaks for (a) at 60.2 and ca. 61 ppm (one still very broad), and two for (b) at 73.7 and 73.3 ppm. The presence of two conformers in solution was subsequently confirmed by verifying the splitting of several other resonances of the proton spectrum. Among the several evidences, for example, in the upfield region of the 2D TOCSY spectrum (see Fig. S11, SI), are easily identifiable two series of multiple correlations, each deriving from one of the conformers, starting from the resonances of the methylene group (b) and propagating to the protons of the respective octyl chains (see Fig. S11, SI). It is important to note that the signals of the two conformers are in a 4:1 integration ratio (see *infra*). The analysis of the signals generated by the macrocycle bridging methylene groups was crucial to determine the geometry adopted by these conformers. As discussed in the introduction, it is known that 1,3,5-trimethoxy-2,4,6-trialkoxy-*para-tert*-butylcalix[6]arenes like **TPU** may adopt, in solution of low polarity solvents, other than the flattened cone conformation also the 1,2,3-alternate one. On the other hand, we have just verified that a 1,2,4,5-tetramethoxy derivative **2** is present in solution in the 1,2,3-alternate conformation. Therefore, we hypothesized that also **DPU** might adopt at least these two conformations (see Figure 2). In particular, we reasoned that, in the cone conformation (C), the protons of the six bridging methylene groups of **DPU** would experience a different magnetic environment and be-

cause of the macrocycle symmetry would give rise to four doublets, with geminal coupling, two for the axial and two for the equatorial protons in the 2:1:1:2 ratio (see Figure 2). However, considering the different functionalization of the aromatic nuclei, we postulated the existence of two different 1,2,3-alternate conformations – **A-1** and **A-2** (see Figure 2) – which differ for the position of the ring bearing the phenylurea groups with respect to the inversion points of the macroring. The bridging methylene groups of these two conformers, because of different symmetry of the macrocycle, would yield very different patterns of signals: conformer **A-1** would give a simpler spectrum of two doublets (equatorial and axial) and a singlet – the bridging methylene (2) – in a 1:1:1 integration ratio. Contrariwise, **A-2** would yield a very complicated pattern of 2 doublets, a 166 singlet and two doublets in 1:1:2:1:1 integration ratio (see Figure 2 for further details).

Analysis of the 2D COSY and HSQC NMR spectra (see Fig. S7–10, SI) showed that, as indicated by black circles in Figure 3, the minor conformer affords two pairs of doublets at 4.31 and 171 4.1 ppm (axial) and 3.56 and 3.71 (equatorial). It thus seems quite clear that the minor conformer is in the cone conformation (C). The major conformer yields instead a pair of doublets for the axial and equatorial methylene protons ($^2J = 15$ Hz) resonating at 4.1 and 3.8 ppm, respectively (see white circles in 176 Figure 3), that is a pattern that did not match for anyone of the conformations proposed in Figure 2. Therefore, we carried out a variable temperature experiment (see Figure 3). The temperature rise did not affect the relative abundance of the two conformers (cf. the intensity of the methoxy resonances in Fig- 181

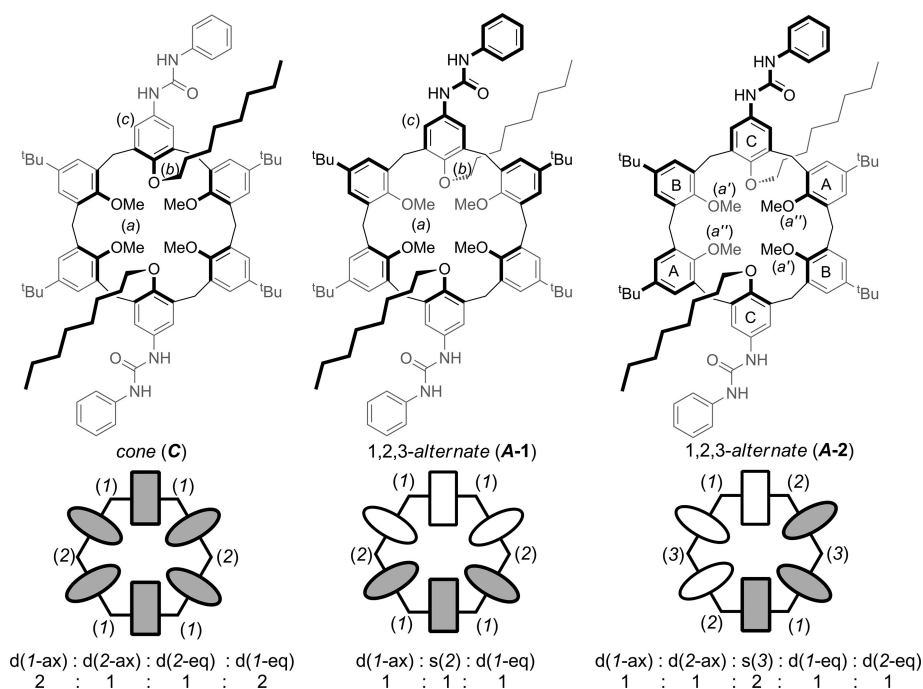


Figure 2. Schematic representation of the three possible conformations adopted by **DPU** in CDCl_3 . The color of the ovals/rectangles indicate the relative position of the phenolic substituent with respect to the plane defined by the bridging methylene groups (hexagon), i.e. grey upward, white downward. The rectangle identifies the phenolic ring substituted with the octyloxy chains, while the ovals those with the methoxy groups. The pattern of the NMR signals yielded by the protons of the bridging methylene groups in each conformation has been placed under the corresponding conformer schematic representation with the multiplicity (doublet or singlet) and relative integration ratio. When the protons are diastereotopic, their axial (ax) or equatorial (eq) geometrical arrangement has been indicated along with the multiplicity and type of methylene group [e.g. $d(1\text{-ax})$].

ure 3), but significantly increased the conformation mobility of the major conformer (see, e.g. the sharpening of the methoxy resonance at 3.4 ppm). Two other very broad resonances at ca. 6 and 4 ppm, barely recognizable at room temperature (see 186 arrows in Figure 3), gradually become sharper as the temperature increases. An HSQC experiment carried out at $T = 325$ K (see Fig. S14, SI) finally allowed to assign these resonances, respectively, to the aromatic protons (*c*), and the bridging methylene group (2) of the macrocycle inversion points (see Figure 2). 191 The correct pattern of signals for the bridging methylene units for the major conformer was thus identified as doublet/singlet/doublet in a 1:1:1 integration ratio. This pattern is consistent with the 1,2,3-*alternate* conformation **A-1**.

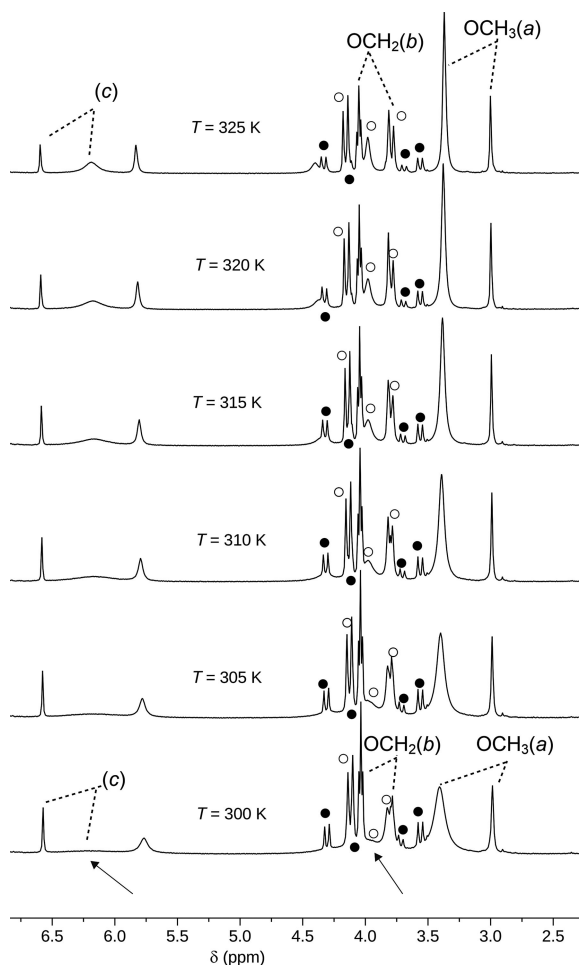


Figure 3. Stack plot of the variable temperature NMR experiment ($T = 300 \rightarrow 325$ K, expanded region, see Fig. S13, SI for the full spectral range) carried out on **DPU** (400 MHz, CDCl_3). The resonances of the bridging methylene protons belonging to conformers **C** and **A-1** (see Figure 2) have been labelled with black and white circles, respectively. Resonances marked as (*a*), (*b*) and (*c*) have been indicated on the molecular sketches of Figure 2.

Encouraged by the previous findings, we wanted to check 196 the effect of the temperature lowering on the mobility of the two conformations. The collection of spectra taken down to $T = 223$ K is gathered in the stack plot of Figure 4. Signals' coalescence was observed at $T = 260$ K,^[19,22] while at $T = 223$ K they were sufficiently resolved to allow the accomplishment of an 201 HSQC experiment (see Fig. S16, SI). The bridging methylene

protons give rise to a pattern of two doublets (axial protons), one broad singlet and two doublets (equatorial protons). Although the central singlet is overlapped with that of the methylene protons (2), the integration ratio between the above resonances seems in agreement with the conformer indicated as **A-206 2** in Figure 2. With respect to the **A-1** geometry, in **A-2** the rings bearing the phenylurea moiety are now shifted adjacent to the methylene bridging units joining the two half-parts of the macrocycle (see Figure 2). Two methoxy signals (*a'*) and (*a''*), in 1:1 ratio, are visible in the spectrum at this temperature. One occurs 211 at its usual fields ($\delta = 3.83$ ppm), while the other is up-field shifted of ca. 0.4 ppm ($\delta = 3.45$ ppm). This suggests that one of the two methoxy groups experiences a higher shielding effect (*vide infra*, crystal structure discussion). Even more straight-forward was the observation that one of the aromatic signals 216 resonates at 4.8 ppm, which is unexpectedly largely up-field shifted (ca. 2.5 ppm). To confirm these hypothesis, we carried out 2D some NOESY and ROESY experiments at $T = 223$ K. Among the multitude of NOE cross-peaks found in both spectra (see Fig. S17–S18 of SI), those correlating the signal of the 221

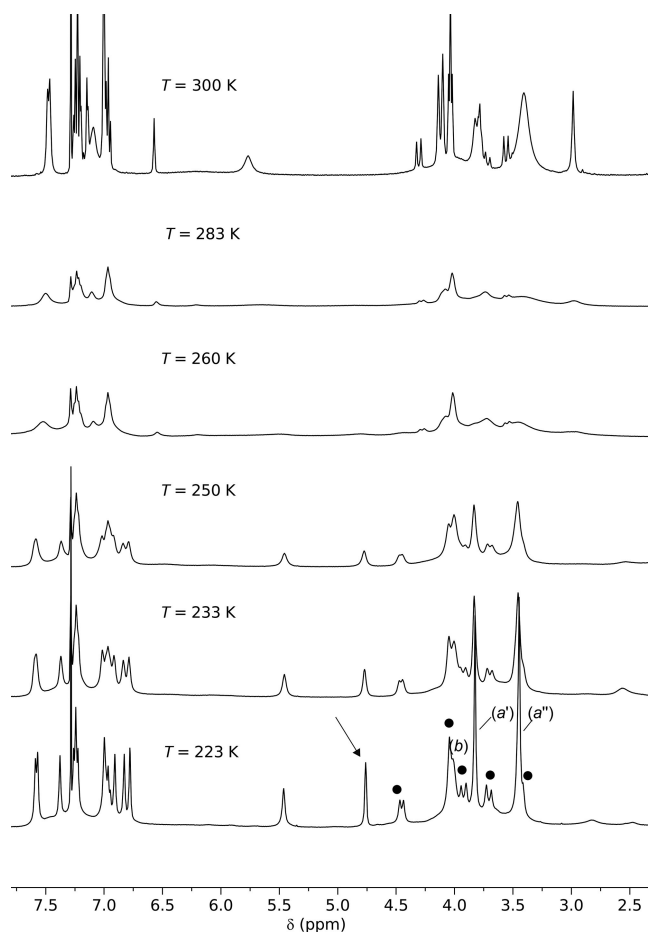


Figure 4. Stack plot of the variable temperature NMR experiment ($T = 300 \rightarrow 223$ K, expanded region, see Fig. S15, SI for the full range) carried out on **DPU** (400 MHz, CDCl_3). The resonances of the bridging methylene protons belonging to conformers **A-2** (see Figure 2) have been labelled with black circles, respectively. Resonances marked as (*a*) and (*b*) have been indicated on the molecular sketches of Figure 2. The arrow highlights one of the macrocycle aromatic protons resonating at unexpectedly high fields.

methoxy protons (*a'*) with *i*) the *tert*-butyl signals at 0.9 and 1.35 ppm, *ii*) the aromatic signals at 4.8 and 7.0 ppm, and *iii*) the NH signal at 5.4 ppm (see Fig. S18 for a schematic representation of the NOE correlations) are all in agreement with a calix[6]arene macrocycle adopting the 1,2,3-alternate conformation **A-2**. In fact, only in the geometrical arrangement described by this conformation, the methoxy protons of ring (A) can be simultaneously close to the *tert*-butyl group of the opposite ring (B) and to the NH protons of the vicinal ring (C), which are both flipped with respect to (A) (see Figure 2 for the rings' labels).

Finally, we planned to verify whether the H-bond donor and acceptor nature of the phenylureas present in **DPU** could promote aggregation phenomena. We thus devised a simple NMR experiment: increasing amounts of deuterated methanol were added to a sample of **DPU** in CDCl₃ kept at room temperature. The competition of the methanol for the H-bonding lead to a progressive simplification of the NMR spectrum (see Figure 5) with an upfield shift of the resonances of the methoxy (*a*) and methylene (*b*) groups of the major conformer (**A-1**). Although less marked, a similar upfield shift was also found for the corresponding resonances of the minor conformer. It thus seems

that upon methanol addition, the protons of groups (*a*) and (*b*) experience a more shielding effect exerted by the aromatic units of **DPU**. On the other hand, the very broad and barely 246 recognizable aromatic resonance at ca. 6.4 ppm (*c*), becomes sharper with an augment of the methanol additions and almost merge with the sharp resonance at 6.7 ppm which was previously ascribed to the minor conformer. The methanol addition also seems to affect the abundance of the two conformers with 251 a shift in favor of the major conformer **A-1** (from 4:1 to 5:1). This result could be tentatively explained supposing the flattened cone conformation is stabilized by an intramolecular H-bonding between the two phenylurea moieties present on the macrocycle. Several 2D NMR experiments were successively accomplished on the sample with the highest amount of deuterated methanol added (50 μ L, CDCl₃/CD₃OD ca. 10:1). In particular, 2D COSY and HSQC experiments (see Fig. S20, S1) allowed us to unequivocally identify the three different signals relative to the bridging methylene protons – two doublets at 4.2 and 261 3.5 ppm and a broad singlet at 3.8 ppm – which are in full agreement with the structure of the 1,2,3-alternate conformer (**A-1**) illustrated in Figure 2.

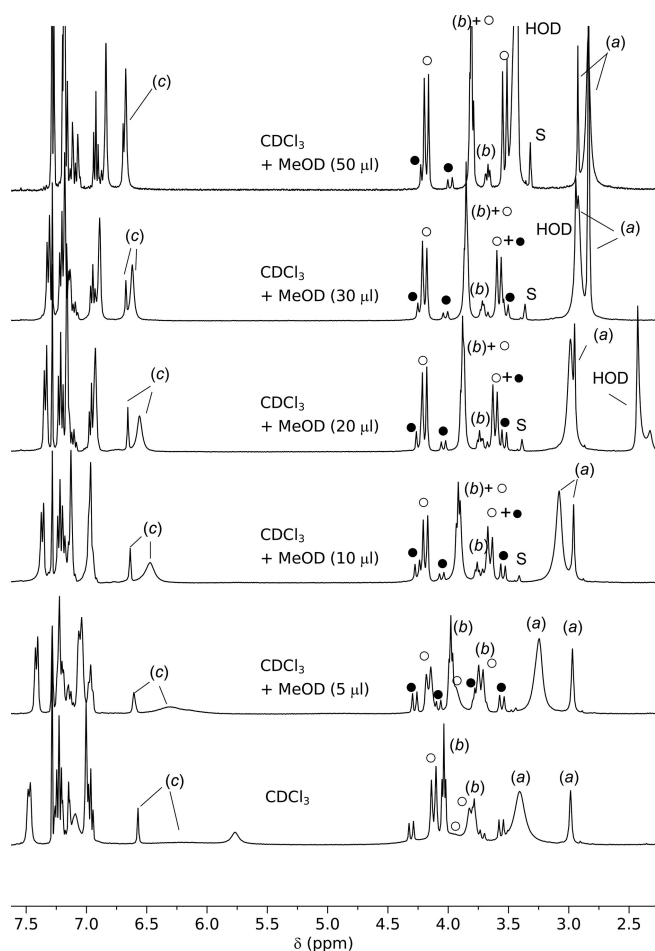


Figure 5. NMR stack plot (400 MHz, expanded region, see Fig. S19, S1, for full range) recorded upon addition of increasing amount of CD₃OD to a solution of **DPU** in CDCl₃ at *T* = 300 K. The most significant resonances affected by methanol addition have been labelled according to Figure 3.

Description of the Crystal Structures

The crystal structure of compound **DPU** was determined via 266 synchrotron X-ray diffraction data on single crystals obtained by slow evaporation of a CHCl₃/CH₃OH solution. In the unit cell, three different molecules co-exist, indicated in the discussion as **I**, **II** and **III** (see Figure 6). For each calix[6]arene of general formula C₉₂H₁₂₀N₄O₈·2/3 molecules of CHCl₃, 4/3 molecules of 271 CH₃OH and 10/3 molecules of H₂O are present in the unit cell. For all the three macrocycles only half of the molecule is independent, while the other half is generated by symmetry [symmetry codes: (i) 1 - *x*, 1 - *y*, 2 - *z*; (ii) = 1 - *x*, 1 - *y*, 1 - *z* and (iii) = -*x*, *y*, 1 - *z* for **I**, **II** and **III**, respectively]. The three independent aromatic rings forming the walls are labelled A, B, C (**I**), D, E, F (**II**) and G, H, I (**III**); the conformation of the cavity is always 1,2,3-alternate. The molecular structures **I-III** assume a geometry compatible with the 1,2,3-alternate conformation indicated in the previous discussion as **A-2** (cf. Figure 2 and Figure 281 ure 6). With respect to the mean plane passing through the six methylene bridges, the mean planes passing through the aromatic rings are inclined of 67.4(2), 36.8(3), 63.4(2), 74.3(4), 62.7(3), 40.7(3), 79.1(2), 44.2(2) and 68.8(3)° for A, B, C (**I**), D, E, F (**II**), G, H and I (**III**) (the values reported are always those 286 smaller than 90°). In **III**, the phenylureido moiety is not parallel to the aromatic walls of the macrocycle like in **I** and **II**, but it is inclined towards the cavity as evidenced by the torsion angles C4-N1-C16-N2 [C4A-N1A-C16A-N2A = 176.6(3)° (**I**); C4D-N1D-C16D-N2D = -161.5(3)° (**II**); C4G-N1G-C16G-N2G = 291 -9.2(4)° (**III**)]. These findings confirmed the results previously obtained in the variable temperature NMR experiment (see Figure 4).

In each calixarene, two methoxy groups point inside the cavity, namely O1B-C8B (**I**), O1F-C8F (**II**), O1H-C8H (**III**) and their 296 symmetry-related equivalents, forming C-H... π interactions with the aromatic walls which stabilize the **A-2** conformer

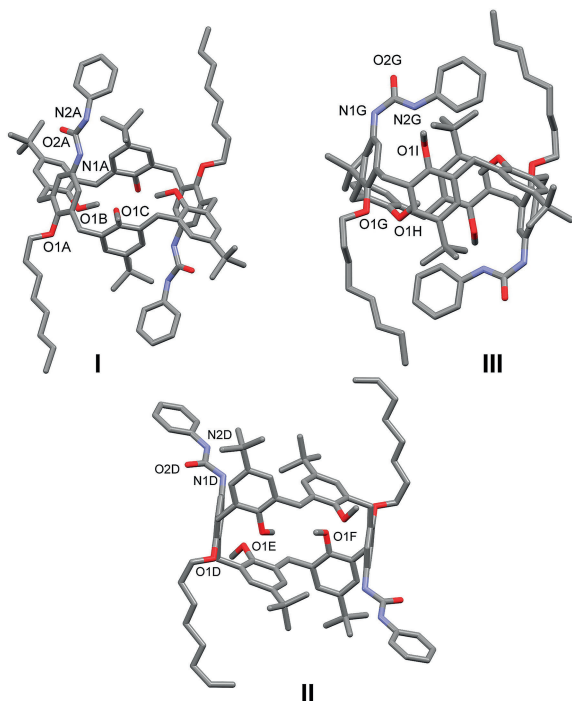


Figure 6. Molecular structure of **I–III** with partial labelling scheme for the atoms in the asymmetric unit. Hydrogen atoms and solvent molecules have been omitted for clarity.

[C8B–H8B3...C5A, 3.576(2) Å and 132.2(3)°; C8B–H8B1...C6C–(1 – x, 1 – y, 2 – z), 3.407(4) Å and 126.9(5)°; C8F–H8F1...C2E, 3.451(3) Å and 128.0(5)°; C8F–H8F3...C5D(1 – x, 1 – y, 1 – z), 3.759(3) Å and 133.8(4)°; C8H–H8H3...Cg1, 3.779(1) Å and 157.9(3)°; C8H–H8H2...C2I(–x, –y, 1 – z), 3.526(5) Å and 143.8(3)°; C8H–H8H2...C3I(–x, –y, 1 – z), 3.725(4) Å and 145.3(3)°. C6C, C2E, C5D C2I and C3I belongs to the rings C1A–C6A, C1C–C6C, C1E–C6E, C1D–C6D and C1I–C6I, respectively. Cg1 is the centroid of the benzene ring C1G–C6G]. In the lattice, the three molecules are connected through H bonds involving the ureido groups, with the N–H atoms behaving as donors and the oxygen atoms as acceptors [see Figure 7; N1A–H1A...O2D, 2.891(3) Å and 161.4(2)°; N2A–H2A...O2D, 2.916(3) Å and 14.46(2)°; N1D–H1D...O2G, 2.820(3) Å and 129.3(2)°; N2D–H2D...O2G, 2.933(3) Å and 140.2(2)°]. The overall crystal packing results in a supramolecular sheet formed by the three independent molecules **I** (green), **II** (blue) and **III** (red). The sheet is parallel to the (1–10) plane and consists of alternating adjacent chains following the pattern ABAB, where the chain A is formed by H-bonded calixarenes **II** and **III**, while chains B comprise calixarenes **I**, H-bonded to water, methanol and chloroform molecules (not shown in the figure). In order to investigate the influence of the solvent on the crystal structure, calix[6]arene **DPUs** was crystallized from ethyl acetate, yielding the monosolvate form **IV**, whose molecular structure can be seen in Fig. S21 of the SI. The asymmetric unit, crystallizing in the monoclinic space group C2/c, comprises half of a molecule of the macrocycle and of ethyl acetate. With respect to the mean plane passing through the six methylene bridges, the mean planes passing through the aromatic rings are inclined of 69.5(2), 45.3(3) and 68.8(3)° for rings A, B and C, respectively (in good agreement

with the values found for **I**, **II** and **III**; the same labelling scheme has been used). The torsion angle C4A–N1A–C16A–N2A (which characterizes the position of the phenylureido moiety with respect to the aromatic walls) is –177.8(3)°, similar to forms **I** and **II**. Also in this case, the methoxy group O1B–C8B and its symmetry-related equivalent point inside the cavity, forming C–H... π interactions with the aromatic rings C1A–C6A and C1C–C6C [C8B–H8B1...C6A, 3.510(2) Å and 145.0(4)°; C8B–H8B3...C6C(1 – x, 1 – y, 1 – z), 3.326(3) Å and 128.0(3)°], stabilizing the **A-2** conformer. The main supramolecular feature in **IV** is the presence of two strong H-bonds between the N–H groups of the phenylureido moiety and the oxygen atom O1 of the 341 acetate solvent [N1A–H1A...O1, 2.960(6) Å and 155.3(2)°; N2A–H2A...O1, 2.904(5) Å and 153.5(5)°]. These strong interactions are also present in the crystal structure of the three independent calixarenes **I**, **II** and **III**, but in that case, the H-bond acceptors are the oxygen atoms of the phenylureido unit of adjacent 346 calixarenes, thus also influencing the packing of the compound. In **IV**, the overall crystal structure is mainly driven by van der Waals interactions, yielding layers parallel to the *ab* plane (see Fig. S22, SI).

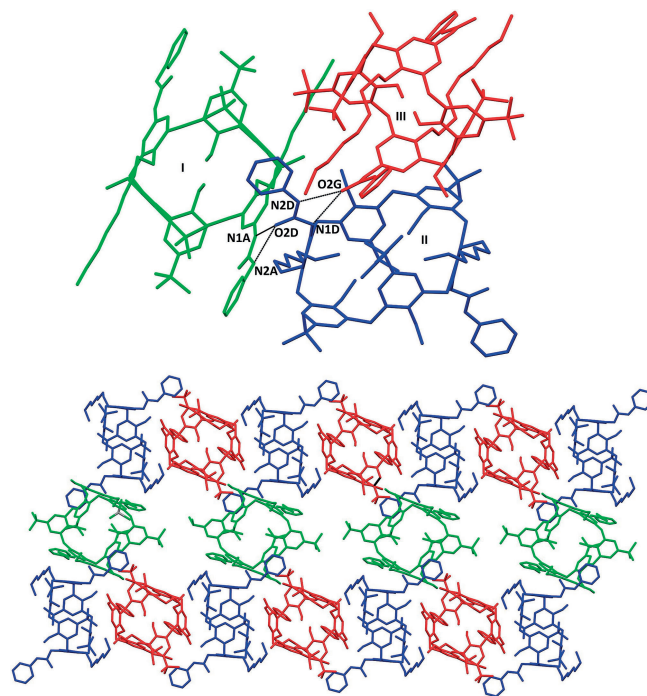


Figure 7. (top) The set of H bonds involving the three independent molecules **I**, **II** and **III**, with partial labelling scheme. Hydrogen atoms and solvent molecules have been omitted for clarity. H bonds are shown as black lines; (down) view of the supramolecular sheet formed by **I** (green), **II** (blue) and **III** (red) macrocycles. Hydrogen atoms and solvent molecules have been omitted for clarity.

Synthesis and Characterization of the Interwoven Structures

351

The ability of **DPUs** to form pseudorotaxane complexes with viologen salts was initially tested in CDCl₃ solution using 1,1'-diethyl-4,4'-bipyridinium ditylosylate (**DOV**) as the axle (see

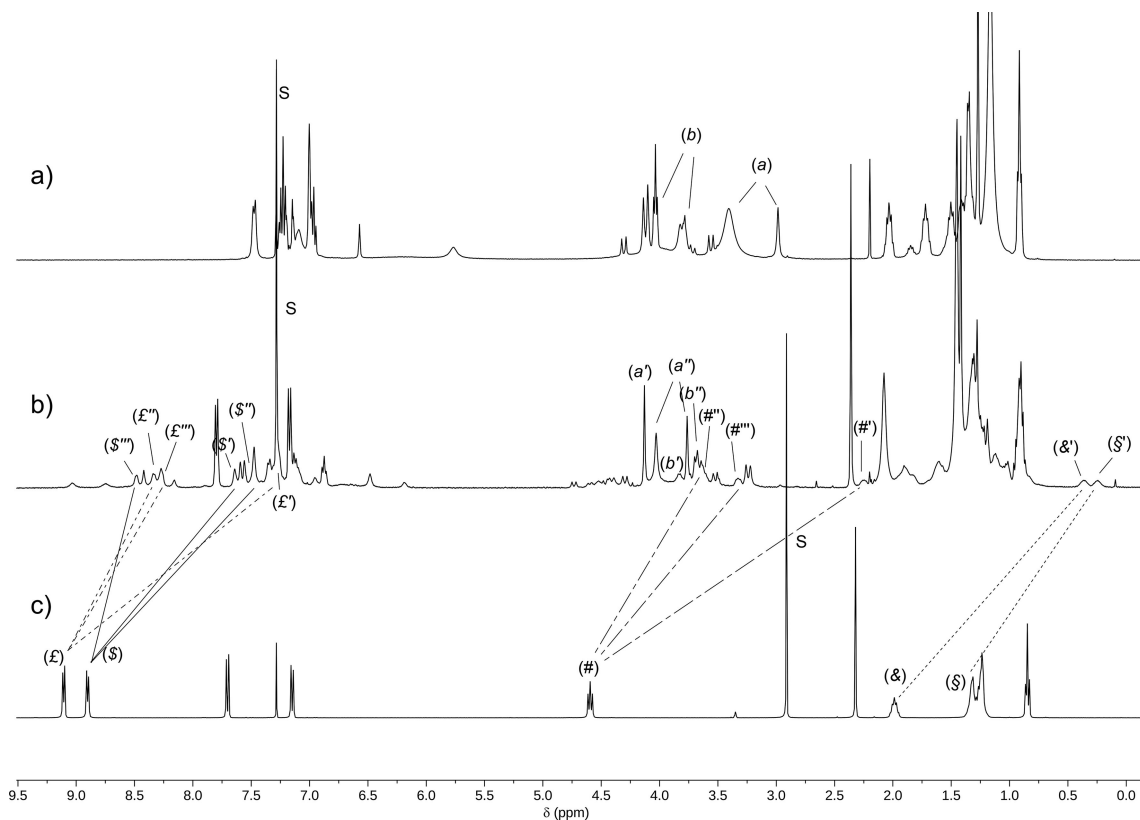


Figure 8. ^1H NMR stack plot (400 MHz) of a) **DPU**, b) pseudorotaxanes **DPU** \rightarrow **DOV** in CDCl_3 and c) **DOV** in $\text{CDCl}_3/\text{CD}_3\text{OD} = 10:1$. For the labels see text and Scheme 2.

considering that in low polarity solvents **DOV** is present as a tight ion pair that, to allow the threading of the dication inside the aromatic cavity, must be separated. This process will likely be more favored for the *cone* conformer since it has the urea moieties on the same side of the macrocycle (*vide infra*).

For the synthesis of the rotaxane **4**, we used the 1,1'-bis(12-426 hydroxydodecyl)-4,4'-bipyridinium ditosylate (**DDOV**) as the axle. Indeed, upon complexation, this thread might promote the rotaxation reaction by the insertion of bulky diphenylacetyl chloride groups on its hydroxyl termini. Following a procedure verified in previous studies,^[10,12,14] the solid **DDOV** was 431 mixed with a solution of **DPU** in CH_2Cl_2 to promote the formation of pseudorotaxanes (**DPU** \rightarrow **DDOV**). After 12 hours of mixing at room temperature, the undissolved salt was eliminated by filtration and the resulting homogeneous solution treated with diphenylacetyl chloride to complete the stoppering reaction (see Scheme 2). In this way, rotaxanes **4** was isolated in 48 % yield after chromatographic separation. HR-MS measurements confirmed the identity of the isolated rotaxane (see Fig. S31, SI). The ^1H NMR spectrum in CDCl_3 of **4** (see Fig. S32, SI) shares several common features with the spectrum of the pseudorotaxane **DPU** \rightarrow **DOV** (cf. Figure 8). In particular, the presence of two broad peaks (S' and $\&'$) in the upfield (0.1–0.5 ppm) region of the spectrum is indicative of the formation of an interwoven structure, while the occurrence of a pattern of three signals for both the methoxy (*a*) and the octyloxy OCH_2 methylene (*b*) groups is consistent with the presence in solution of approx. equimolar mixture of two rotaxanes. As seen before for

the pseudorotaxanes with **DOV**, what distinguishes also rotaxanes **4** is the *cone* and 1,2,3-alternate conformation assumed by the calix[6]arene wheel surrounding the viologen thread. This hypothesis was verified by the analysis of a series of 1D and 451 2D NMR spectra (see Fig. S33–37, SI). The effectiveness of the rotaxation reaction was verified by the presence in the spectrum of several signals belonging to the diphenylacetic stopper. The methine proton of the stopper (α) apparently yields a single signal at ca. 5 ppm, but after peak deconvolution, the presence of three resonances consistent with the above mixture of two rotaxanes was revealed (see inset of Fig. S32, SI).

UV/Vis Characterization

The interwoven structures were characterized by UV/Vis spectroscopy. The absorption spectrum of **DPU** is characterized 461 by an intense band in the UV, with $\lambda_{\text{max}} = 260$ nm and $\epsilon = 38000 \text{ M}^{-1} \text{ cm}^{-1}$. This band is red shifted and less intense with respect to the parent calixarene bearing three phenyleureido moieties (**TPU**).^[9] These differences can be ascribed to the lack of one chromophoric unit, but also the different conformations 466 assumed by the molecule in solution.

Upon titration of a solution of **DOV** with **DPU**, the solution turns red, and a characteristic charge-transfer band appears, with a maximum around 500 nm. This band was also observed in related pseudorotaxanes based on **TPU** calixarenes, and it is 471 ascribed to the charge transfer interaction between the bi-

pyridinium unit and the aromatic rings of **DPU** (Figure 9). The association constant determined by fitting the data with a 1:1 binding model is $3.2 \times 10^6 \text{ M}^{-1}$. Indeed, the results of the thermodynamic investigation would suggest that the number of phenylurea moieties does not affect the stability of the pseudorotaxane. The corresponding rotaxane **4** was characterized by UV/Vis spectroscopy, and, as expected, it displays the same features of the pseudorotaxane: an intense band in the UV and a weak and broad band in the visible region of the spectrum. In line with the observations reported on the **DPU** ring component, the absorption coefficient at λ_{max} is lower with respect to the parent rotaxanes bearing a **TPU** macrocycle.^[10,14]

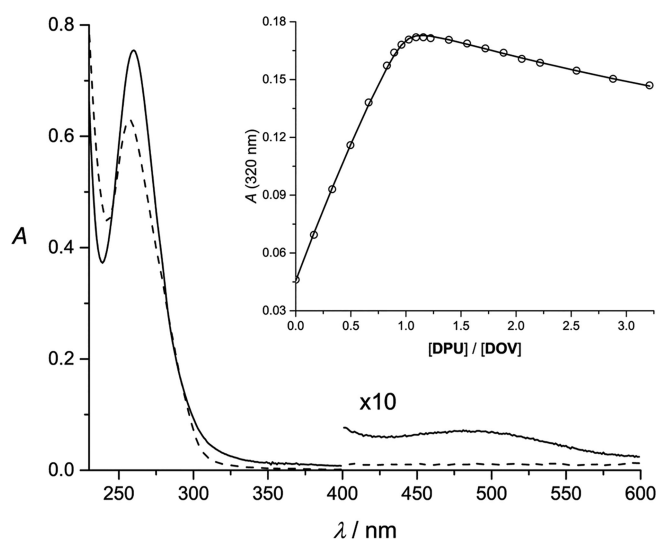


Figure 9. Sum of the absorption spectra (dashed line) and the absorption spectrum of the mixture (solid line) of CH_2Cl_2 solutions of **DOV** ($1.4 \times 10^{-5} \text{ M}$) and **DPU** ($1.2 \times 10^{-5} \text{ M}$). The inset shows the absorption changes at 320 nm together with the fitted curve upon titration of a $7.4 \times 10^{-5} \text{ M}$ solution of **DOV** with concentrated **DPU**.

In order to investigate the dynamics of the threading process, kinetic experiments were performed using a stopped-flow apparatus. **DPU** and **DOV** were mixed in equimolar amounts and the absorption changes were followed in the UV and visible regions (Figure 9 and Figure 10). The kinetic traces were fitted with an equilibrium model, by fixing the equilibrium constant to the value determined upon titration. The rate constants for threading and dethreading resulted to be, respectively, $3.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ and $1.1 \times 10^{-3} \text{ s}^{-1}$. These values are three orders of magnitude lower with respect to the parent pseudorotaxane with **TPU**.^[9,16] Phenylurea moieties are good anion receptors,^[23,24] and it is well known that in this kind of systems they play a crucial role in driving the formation of the supramolecular adduct. In particular, it has been hypothesized the involvement of a transition state wherein the counterions are no more paired with the bipyridinium unit, but they are already engaged with the calixarene.^[9] The present results would support this hypothesis, confirming the role of the phenylurea units in the stabilization of this transition state. As the electrochemical experiments were performed in the presence of a 100-fold excess of tetrabutylammonium hexafluorophosphate (TBAPF_6) as the supporting electrolyte (vide infra), thermodynamic inves-

tigations were also performed in these experimental conditions. Indeed, the shape of the titration curve (Figure S38, SI) suggests a lower association, and the value of the stability constant determined by fitting the data with a 1:1 binding model is $7 \times 10^4 \text{ M}^{-1}$. An effect of the concentration and the nature of the anions on the stability of the supramolecular complex is not unexpected, considering the double role played by the counterions in the formation and stabilization of the pseudorotaxane:^[9] not only the phenylurea moieties are good anion receptors, as mentioned above, but also the formation of the pseudorotaxane is in competition with the ion-pairing between the bipyridinium ion and its counteranions.^[25,26]

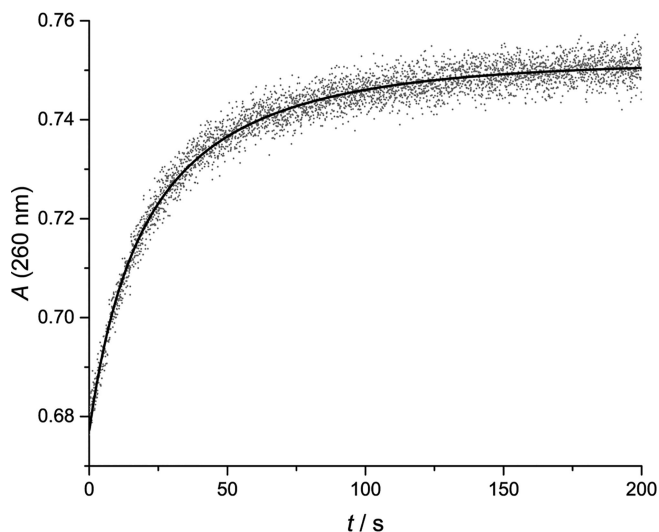


Figure 10. Absorption changes at 260 nm upon rapid mixing of equimolar amounts of **DOV** and **DPU**. The concentration of the reactants after mixing was $1.3 \times 10^{-5} \text{ M}$.

Electrochemical Experiments

Cyclic voltammetry and differential pulse voltammetry experiments were performed on the pseudorotaxane and rotaxane molecules, in CH_2Cl_2 , in the presence of a 100-fold excess of TBAPF_6 as supporting electrolyte. The bipyridinium moiety of **DOV** is characterized by two reversible and mono-electronic reduction processes, at $E_{1/2}' = -0.27 \text{ V}$ and $E_{1/2}'' = -0.83 \text{ V}$. When the viologen is included in the cavity of a calix[6]arene macrocycle, the reduction processes are shifted to more negative potential values, on account of the host-guest electron transfer interactions (Figure 11).^[10,14] Indeed, the cyclic voltammetric curves of rotaxane **4** are characterized by two quasi-reversible waves, with $E_{1/2}' = -0.65 \text{ V}$ and $E_{1/2}'' = -1.18 \text{ V}$. As observed for related **TPU**-based rotaxanes,^[9] these processes are affected by slow heterogeneous electron-transfer kinetics. The pseudorotaxane obtained by mixing **DPU** and **DOV** in equimolar amounts shows the typical cyclic voltammetry curves described by an electrochemical process followed by a chemical reaction (EC square scheme) (Figure 11).^[9,27,28] A fraction of free **DOV** is still present in solution, as evidenced by the small cathodic process around -0.3 V . This is not unexpected from the association constant determined in the presence of an excess of PF_6^- ions and

541 of the effect of the ion pair dissociation on the formation of
the complex.^[25,26] Indeed the intensity of this signal decreases
on increasing the concentration of **DPU**. On the other hand, the
encapsulated **DOV** is reduced at more negative potential val-
ues, but, after the first reduction, the complex dissociates and
546 the second reduction process of free **DOV** is displayed at
−0.82 V. Upon re-oxidation, only the processes of free **DOV** are
observed: as a matter of fact, the first reduction process is char-
acterized by a large separation between the cathodic and
anodic peaks. This pattern can be modelled with an EC square
551 scheme mechanism and is indicative of slow kinetics of the
monoreduced bipyridinium.^[9,27,28] Therefore, in analogy with
parent **TPU**-based systems, pseudorotaxanes based on the **DPU**
wheel can be disassembled by electrochemical reduction of the
bipyridinium axle. Indeed, the results of the electrochemical in-
556 vestigation suggest that the two different conformers behave in
a similar way and the 1,2,3-*alternate* and the *cone* conformation
assumed by the interlocked structure cannot be distinguished
in our experimental conditions.

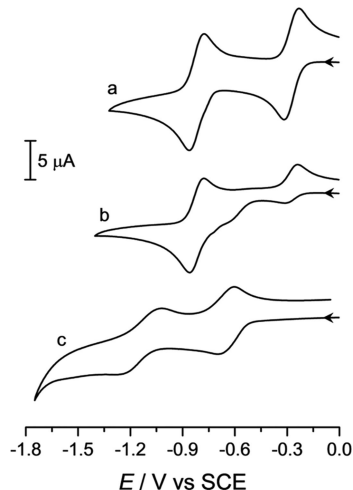


Figure 11. Cyclic voltammetric curves for the first and second reduction of the bipyridinium unit in (a) **DOV** ($c = 3.0 \times 10^{-4}$ M), (b) **DPU**→**DOV** ($c = 3.0 \times 10^{-4}$ M), and (c) **4** ($c = 1.1 \times 10^{-4}$ M) (CH_2Cl_2 , 100-fold TBAPF₆, scan rate 100 mV/s).

Conclusions

561 A new calix[6]arene-based host (**DPU**) functionalized with two
phenylurea moieties in 1,4-diametral position was synthesized
and structurally characterized. Detailed NMR studies evidenced
that in solution of low polarity solvents this host mainly adopts
a 1,2,3-*alternate* conformation. The determination of the crystal
566 structure via X-ray diffraction on single crystals showed that
DPU assumes this conformation also in the solid state. The abil-
ity of **DPU** to act as a wheel for the formation of pseudorotax-
ane and rotaxane species with viologen-based salts was investi-
gated in a solution of low polarity solvents through NMR,
571 UV/Vis and electrochemical measurements. The NMR studies
evidenced that the formation of interwoven structures occurs
with the host adopting both the *cone* and 1,2,3-*alternate* con-
formation. Kinetic experiments showed that the rate constants

for threading and dethreading of the viologen salts are three
orders of magnitude lower with respect to the parent pseudo-576
rotaxane with **TPU** that, in low polarity solvents, is in the *cone*
conformation. These findings thus account for the crucial role
played by the number, orientation and reciprocal arrangement
of the phenylurea binding groups in promoting the threading
of the dicationic portion of the ion-paired viologen salts. The 581
ability of **DPU** to exploit its particular 1,2,3-*alternate* conforma-
tion and self-assemble to yield polyrotaxane structures is cur-
rently undergoing in our laboratories.

Experimental Section

Synthesis and Characterization

586

Solvents were dried following standard procedures; all other rea-
gents were of reagent grade quality, obtained from commercial
sources and used without further purification. Chemical shifts are
expressed in ppm using the residual solvent signal as an internal
reference. Mass spectra were determined in ESI mode. Calix[6]arene 591
1,^[21] axles **DOV**^[9] and **DDOV**^[8,10] ditosylate were synthesized ac-
cording to reported procedures.

Calix[6]arene 2: In a 100 mL Schlenk flask, to a solution of calix-
arene **1** (1 g, 1 mmol) and 1-Iodoctane (0.72 g, 3 mmol) in dry
596 acetonitrile (50 mL), K₂CO₃ (0.41 g, 3 mmol) was added. After two
vacuum/nitrogen cycles, the flask was sealed, and the heterogene-
ous reaction mixture was refluxed for 4 days. After cooling to room
temperature, the solvent was evaporated to dryness under reduced
pressure, and the sticky residue was taken up with dichloromethane
(50 mL) and with a 10 % aqueous solution of HCl (30 mL). The 601
separated organic phase was washed thrice with distilled water,
dried with anhydrous Na₂SO₄, filtered and the solvents evaporated
to dryness under reduced pressure. The solid residue was triturated
with hot ethyl acetate to give, after Buchner filtration, 0.85 g of
pure **2** (70 % yield) as a white solid compound. Mp > 300 °C; ¹H
606 NMR (400 MHz, CDCl₃): δ = 0.90 (t, 6 H, ³J_{H,H} = 8 Hz,
−OCH₂CH₂(CH₂)₅CH₃), 1.22, 1.3–1.5 and 1.6 (s, m, br. s, 56 H, ^tBu and
−OCH₂CH₂(CH₂)₅CH₃), 1.9 (br. s, 4 H, −OCH₂CH₂(CH₂)₅CH₃), 3.0 (br. s,
12 H, ArOCH₃), 3.6 (br. d, 4 H, Ar-CH₂-Ar (equatorial)), 3.92 (br. s, 8
H, −OCH₂CH₂(CH₂)₅CH₃ and Ar-CH₂-Ar), 4.3 (br. d, 4 H, Ar-CH₂-Ar 611
(axial)), 6.96 (s, 4 H, Ar-H), 7.22 (br. s, 4 H, Ar-H), 7.64 (br. s, 4 H, Ar-
H); ¹³C NMR (100 MHz, CDCl₃): δ = 14.0, 22.6, 26.2, 29.2, 29.5, 30.4,
30.7, 30.8, 31.3, 31.8, 34.2, 59.7, 74.0, 123.0, 126.4, 126.9, 132.1,
133.9, 136.5, 143.5, 146.4, 154.1, 160.0 ppm; Elemental Analysis
calcd. for C₇₈H₁₀₆N₂O₁₀: C, 76.06; H, 8.67; N, 2.27; found C, 76.5; H,
616 8.88; N, 1.93; ESI-MS(+): *m/z* (%) = 1253.9 (100) [M + Na]⁺, 1254.9
(70) [M + Na + 1]⁺, 1269.9 (70) [M + K]⁺, 1270.9 (60) [M + K + 1]⁺.

Bis(N-phenylureido)calix[6]arene DPU: In a two-neck flask kept
under inert atmosphere, to a solution of **2** (0.7 g, 0.57 mmol) in
ethanol (150 mL), hydrazine monohydrate (1.42 g, 28 mmol) and a 621
tip of spatula of 10 % Pd/C catalyst were added. The resulting mix-
ture was refluxed for 48 h and then filtered, still warm and under
an inert atmosphere, through a celite pad to remove the palladium
catalyst. The filtered solution was evaporated to dryness under re-
duced pressure. The residue was taken up in dichloromethane 626
(50 mL), and the resulting organic phase was washed thrice with
water to remove the excess of hydrazine. The separated organic
phase was dried with anhydrous CaCl₂, filtered and the solvents
evaporated to dryness under reduced pressure. The residue was
dissolved in anhydrous dichloromethane (50 mL) and placed in a 631
two-neck flask kept under an inert atmosphere. To the resulting
homogeneous solution, phenyl isocyanate (0.17 g, 1.4 mmol) was

added. The reaction mixture was stirred at room temperature for 24 h; then the solvent was removed under reduced pressure. Purification of the residue by column chromatography (eluent *n*-hexane/ethyl acetate, 75:25) afforded **DPU** in 80 % yield as a white solid compound. Mp. 236–238 °C; ¹H NMR (400 MHz, CDCl₃/CD₃OD = 10:1): δ = 0.8 (t, 6 H, ³J_{H,H} = 8 Hz, -OCH₂CH₂(CH₂)₅CH₃), 1.1 (s, 36 H, ^tBu), 1.2–1.3 (m, 20 H, -OCH₂CH₂(CH₂)₅CH₃), 1.4–1.5 (m, 4 H, OCH₂CH₂(CH₂)₅CH₃), 1.7–1.8 (m, 4 H, -OCH₂CH₂(CH₂)₅CH₃), 2.8 (br. s, 12 H, ArOCH₃), 3.5 (br. d, 4 H, Ar-CH₂-Ar (equatorial)), 3.8 (br. s, 8 H, -OCH₂CH₂(CH₂)₅CH₃ and Ar-CH₂-Ar), 4.2 (br. d, 4 H, Ar-CH₂-Ar (axial)), 6.7 (br. s, 4 H, Ar-H), 6.8 (br. s, 4 H, Ar-H), 6.9 (m, 2 H, Ar-H), 7.2 (br. s, 8 H, Ar-H), 7.3 (br. s, 4 H, Ar-H); ¹³C NMR (100 MHz, CDCl₃/CD₃OD = 10:1): δ = 14.0, 22.6, 26.3, 29.3, 29.6, 30.5, 31.2, 31.8, 34.1, 59.7, 60.2, 73.7, 119.0, 121.1, 122.5, 122.9, 126.3, 126.7, 126.9, 128.7, 132.1, 132.8, 134.1, 135.4, 136.5, 138.9, 143.5, 146.4, 146.6, 150.4, 152.6, 154.1 ppm. HR-MS(+): *m/z* (%) = 1409.9155 (9) [M + H]⁺, 1426.9436 (100) [M + NH₄]⁺, 1431.8998 (45) [M + Na]⁺.

Rotaxane 4: Calix[6]arene **DPU** (0.05 g, 0.035 mmol) was dissolved in dry dichloromethane and 1,1'-bis(12-hydroxydodecyl)-4,4'-bipyridinium ditosylate **DDOV** (0.034 g, 0.039 mmol) was added. The solution was stirred at room temperature for 12 hours, filtered to remove the undissolved salt, and then diphenylacetyl chloride (0.021 g, 0.089 mmol) and triethylamine (0.011 g, 0.11 mmol) were added. The reaction mixture was stirred at room temperature overnight. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography (eluent: CH₂Cl₂/MeOH = 92:2). To assure the total exchange of the viologen counteranions as tosylates, the solid residue recovered from the chromatographic separation was dissolved in 25 mL of dichloromethane and the resulting organic phase was washed thrice with a saturated solution of sodium tosylate and twice with distilled water. After evaporation of the organic phase under reduced pressure, rotaxane **4** was isolated in 48 % yield as a red solid compound. HR-MS (+): *m/z* (%) = 1161.7550 (78) [M - 2TsO]²⁺.

X-ray Data Collection and Crystal Structure Determination

The crystal structures of the methanol/chloroform (**I–III**) and ethyl acetate (**IV**) solvates of **DPU** were determined by X-ray diffraction methods. Crystal data and experimental details for data collection and structure refinement are reported in Tables S1–S2 of the SI. Intensity data and cell parameters were recorded at 100(2) K at the ELETTRA Synchrotron Light Source (CNR Trieste, strada statale 14, Area Science Park, 34149, Basovizza, Trieste, Italy) for **I–III**, and at 150(2) K on a Bruker D8 Venture PhotonII diffractometer equipped with a CCD area detector, using a CuK_α radiation (λ = 1.54178) for **IV**. The raw frame data were processed using the program package CrysAlisPro 1.171.38.41^[29] for **I–III**, and the programs SAINT and SADABS^[30] for **IV**. The structures were solved by Direct Methods using the SIR97 program^[31] and refined on F_o² by full-matrix least-squares procedures, using the SHELXL-2014/7^[32] program in the WinGX suite v.2014.1.^[33] All non-hydrogen atoms were refined with anisotropic atomic displacements, except for some disordered alkyl chains or solvent molecules. The carbon-bound and the nitrogen-bound H atoms were placed in calculated positions and refined isotropically using a riding model with C–H ranging from 0.93 to 0.97 Å and U_{iso}(H) set to 1.2–1.5U_{eq}(C), N–H equal to 0.86 and U_{iso}(H) set to 1.2U_{eq}(N), and O–H equal to 0.82 and U_{iso}(H) set to 1.5U_{eq}(O). The weighting schemes used in the last cycle of refinement were w = 1/[σ²F_o² + (0.4534P)²] and w = 1/[σ²F_o² + (0.5768P)²] where P = (F_o² + 2F_c²)/3, for **I–III** and **IV**, respectively.

CCDC 1894692 (for **I–III**), and 1894693 (for **IV**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data

Centre. (≠ Author: please check that the correct compound was assigned to each CCDC number. – two CCDC numbers but obviously 4 structures?).

UV/Vis Absorption Spectroscopy

All spectroscopic measurements were performed on air-equilibrated CH₂Cl₂ (Uvasol) solutions at room temperature in 1 cm path-length quartz cuvettes. UV/Vis spectra were recorded with a Cary 300 (Agilent) spectrophotometer. Spectrophotometric titrations were performed adding a concentrated solution of the host to a more diluted solution of the guest. The apparent stability constants of the pseudorotaxanes were obtained by fitting the absorbance changes with software SPECFIT/32,^[34] according to a 1:1 binding model. **Stopped-Flow Kinetics:** Threading kinetics were investigated on air-equilibrated CH₂Cl₂ (Uvasol) solutions at room temperature using a stopped-flow spectrophotometer equipped with a 1 cm pathlength cell and a driving ram for the mixing system at the 711 N₂ pressure of 8.5 bar. Under these conditions, the time required to fill the cell is lower than 2 ms. The resulting absorption changes were then analyzed with software SPECFIT/32^[34] to obtain the rate constants for the threading process, according to a mixed order (second order threading–first order dethreading) kinetic model. 716

Electrochemical Measurements

Cyclic voltammetry (CV) experiments were carried out in argon-purged dry CH₂Cl₂ (Sigma-Aldrich) with an Autolab 30 multipurpose instrument interfaced to a PC. The working electrode was a glassy carbon electrode (Amel, 0.07 cm²), carefully polished with an alumina-water slurry on a felt surface, immediately before use. The counter electrode was a Pt wire, separated from the solution by a frit, and an Ag wire was employed as a quasi-reference electrode. Ferrocene was present as an internal standard. Tetrabutylammonium hexafluorophosphate was added in a 100-fold proportion with respect to the sample concentration, as supporting electrolyte. Cyclic voltammograms were obtained at sweep rates varying from 0.05 to 5 V s⁻¹. The IR compensation implemented within the software was employed to minimize the resistance of the solution. In any instance, the full electrochemical reversibility of the voltammetric wave of ferrocene was taken as an indicator of the absence of uncompensated resistance effects. 731

Acknowledgments

The authors thank Centro Interdipartimentale di Misure of the University of Parma for NMR and MS measurements. This work was supported by the University of Parma, the University of Bologna, and by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement no. 692981). C. M. wishes to thank the CNR of Trieste, and in particular Dr Nicola Demitri, for the single crystal XRD data collected at the ELETTRA synchrotron facility. Chiesi Farmaceutici SpA is acknowledged for the support with the D8 Venture X-ray equipment. 741

Keywords: Rotaxanes · Calixarenes · Conformation analysis · Structure elucidation · Electrochemistry 746

- [1] S. Kassem, T. Van Leeuwen, A. S. A. S. Lubbe, M. R. Wilson, B. L. B. L. Feringa, D. A. D. A. Leigh, *Chem. Soc. Rev.* **2017**, *46*, 2592–2621.
- [2] E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem. Int. Ed.* **2007**, *46*, 72–191; *Angew. Chem.* **2007**, *119*, 72.
- [3] V. Balzani, A. Credi, M. Venturi, *Chem. Eur. J.* **2002**, *8*, 5524–5532. 751

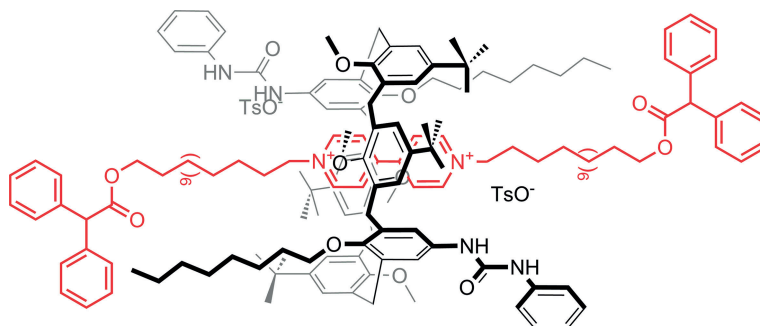
- [4] A. Arduini, G. Orlandini, A. Secchi, A. Credi, S. Silvi, M. Venturi, in *Calixarenes Beyond* (Eds.: P. Neri, J. L. Sessler, M.-X. Wang), Springer International Publishing, Cham, **2016**, pp. 761–781.
- [5] A. Arduini, G. Orlandini, A. Secchi, A. Credi, S. Silvi, M. Venturi, in *Ref. Module Chem. Mol. Sci. Chem. Eng.* Elsevier, **2014**, pp. 1–26.
- 756 [6] M. Xue, Y. Yang, X. Chi, X. Yan, F. Huang, *Chem. Rev.* **2015**, *115*, 7398–7501.
- [7] W. Yang, Y. Li, H. Liu, L. Chi, Y. Li, *Small* **2012**, *8*, 504–516.
- [8] A. Arduini, R. Ferdani, A. Pochini, A. Secchi, F. Uguzzoli, *Angew. Chem. Int. Ed.* **2000**, *39*, 3453–3456; *Angew. Chem.* **2000**, *112*, 3595.
- 761 [9] A. Credi, S. Dumas, S. Silvi, M. Venturi, A. Arduini, A. Pochini, A. Secchi, *J. Org. Chem.* **2004**, *69*, 5881–5887.
- [10] A. Arduini, R. Bussolati, A. Credi, A. Pochini, A. Secchi, S. Silvi, M. Venturi, *Tetrahedron* **2008**, *64*, 8279–8286.
- 766 [11] F. Uguzzoli, C. Massera, A. Arduini, A. Pochini, A. Secchi, *CrystEngComm* **2004**, *6*, 227–232.
- [12] V. Zanichelli, M. Bazzoni, A. Arduini, P. Franchi, M. Lucarini, G. Ragazzon, A. Secchi, S. Silvi, *Chem. Eur. J.* **2018**, *24*, 12370–12382.
- [13] V. Zanichelli, G. Ragazzon, G. Orlandini, M. Venturi, A. Credi, S. Silvi, A. Arduini, A. Secchi, *Org. Biomol. Chem.* **2017**, *15*, 6753–6763.
- 771 [14] V. Zanichelli, G. Ragazzon, A. Arduini, A. Credi, P. Franchi, G. Orlandini, M. Venturi, M. Lucarini, A. Secchi, S. Silvi, *Eur. J. Org. Chem.* **2016**, *2016*, 1033–1042.
- [15] A. Arduini, R. Bussolati, A. Credi, S. Monaco, A. Secchi, S. Silvi, M. Venturi, *Chem. Eur. J.* **2012**, *18*, 16203–16213.
- 776 [16] A. Arduini, R. Bussolati, A. Credi, A. Secchi, S. Silvi, M. Semeraro, M. Venturi, *J. Am. Chem. Soc.* **2013**, *135*, 9924–9930.
- [17] A. Arduini, F. Ciesca, M. Fragassi, A. Pochini, A. Secchi, *Angew. Chem. Int. Ed.* **2005**, *44*, 278–281; *Angew. Chem.* **2005**, *117*, 282.
- 781 [18] A. Arduini, F. Calzavacca, A. Pochini, A. Secchi, *Chem. Eur. J.* **2003**, *9*, 793–799.
- [19] J. P. M. van Duynhoven, R. G. Janssen, W. Verboom, S. M. Franken, A. Casnati, A. Pochini, R. Ungaro, J. de Mendoza, P. M. Nieto, *J. Am. Chem. Soc.* **1994**, *116*, 5814–5822.
- [20] R. Lavendomme, D. Ajami, S. Moerkerke, J. Wouters, K. Rissanen, M. Luhmer, I. Jabin, *Chem. Commun.* **2017**, *53*, 6468–6471.
- [21] J. de Mendoza, M. Carramolino, F. Cuevas, P. M. Nieto, P. Prados, D. N. Reinhoudt, W. Verboom, R. Ungaro, A. Casnati, *Synthesis* **1994**, *1994*, 47–50.
- [22] The resonances of the methoxy group assigned to conformers **A-1** and **791 C** ($\Delta\nu = 148$ Hz at $T = 325$ K) coalesce at $T = 260$ K. From this datum, an energy barrier ΔG^\ddagger ca. 28 kJ mol⁻¹ for the interconversion between the conformers was preliminarily determined, see e.g. F. P. Gasparro, N. H. Kolodny, *J. Chem. Educ.* **1977**, *54*, 258.
- [23] V. Amendola, L. Fabbri, L. Mosca, *Chem. Soc. Rev.* **2010**, *39*, 3889–3915.
- 796 [24] L. Pescatori, A. Arduini, A. Pochini, F. Uguzzoli, A. Secchi, *Eur. J. Org. Chem.* **2008**, *2008*, 109–120.
- [25] J. W. Jones, H. W. Gibson, *J. Am. Chem. Soc.* **2003**, *125*, 7001–7004.
- [26] F. Huang, J. W. Jones, C. Slebodnick, H. W. Gibson, *J. Am. Chem. Soc.* **2003**, *125*, 14458–14464. 801
- [27] A. E. Kaifer, M. Gómez-Kaifer, *Supramolecular Electrochemistry*, Wiley, **2008**.
- [28] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd Edition, John Wiley & Sons, **2000**.
- [29] *CrysAlisPro*, Rigaku Oxford Diffraction, **2015**. 806
- [30] G. M. Sheldrick, *SADABS v2.03: Area-Detector Absorption Correction*, University of Göttingen, Germany, **1999**.
- [31] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119. 811
- [32] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
- [33] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849–854.
- [34] R. A. Binstead, *SPECFIT/32*, Fitting Software, Spectrum Software Associates, Chapel Hill, **1996**.

Received: February 7, 2019

816

Calix[6]arene-Based Rotaxanes

M. Bazzoni, V. Zanichelli, L. Casimiro,
C. Massera, A. Credi, A. Secchi,*
S. Silvi,* A. Arduini* 1–13

New Geometries for Calix[6]arene-
Based Rotaxanes

A bis(*N*-phenylureido)calix[6]arene that adopts a 1,2,3-alternate conformation has been synthesized, and its structure has been established in solution of low polarity solvents and in the

solid state. Its ability to act as a wheel and form interwoven systems with viologen salts was studied through structural characterization and electrochemical measurements.

826

Authors: Please check that the ORCID identifiers listed below are correct. We encourage all authors to provide an ORCID identifier for each coauthor. ORCID is a registry that provides researchers with a unique digital identifier. Some funding agencies recommend or even require the inclusion of ORCID IDs in all published articles, and authors should consult their funding agency guidelines for details. Registration is easy and free; for further information, see <http://orcid.org/>.

831

Margherita Bazzoni <http://orcid.org/0000-0002-4701-6267>

Valeria Zanichelli <http://orcid.org/0000-0003-2642-1578>

Lorenzo Casimiro <http://orcid.org/0000-0002-8818-5913>

Chiara Massera <https://orcid.org/0000-0003-0230-1707>

836 Alberto Credi <https://orcid.org/0000-0003-2546-9801>

Andrea Secchi <http://orcid.org/0000-0003-4045-961X>

Serena Silvi <http://orcid.org/0000-0001-9273-4148>

and Arturo Arduini <http://orcid.org/0000-0003-2774-0095>

DOI: 10.1002/ejoc.201900211