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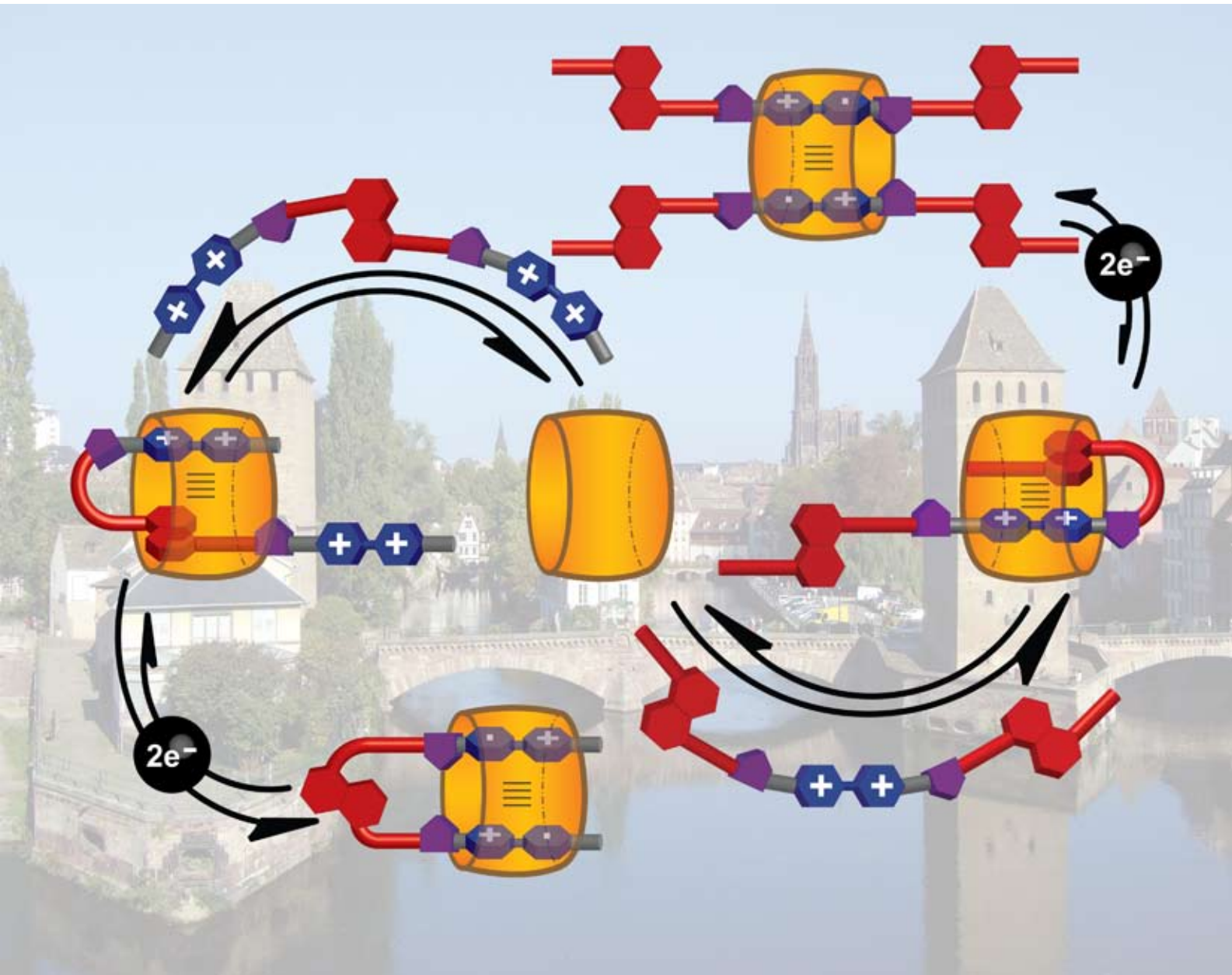

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PAPER
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Redox-driven switching in pseudorotaxanes

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Redox-driven switching in pseudorotaxanes†‡

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Two donor–acceptor thread-like compounds incorporating viologen (V^{2+}) units and 1,5-dihydroxynaphthalene (DNP) stations have been prepared. Their ability to form self-assembled charge-transfer (CT) complexes with cucurbit[8]uril (**CB[8]**) is evidenced by UV-Vis and NMR spectroscopies, as well as by mass spectrometry. Binding studies show the formation of 1 : 1 and 2 : 1 complexes between **CB[8]** and a thread-like compound containing two viologen units, while only a 1 : 1 inclusion complex was observed between **CB[8]** and a thread-like compound containing only a single viologen unit. The switching behavior of the threads within their pseudorotaxane frameworks was investigated by using cyclic voltammetry (CV) and UV-Vis spectroscopy.

Introduction

Artificial molecular switches have received much attention[1,2] in recent years because of their response to external stimuli, such as pH, redox change or light. A wide variety of molecular switches based on rotaxanes,[2] catenanes,[2] molecular muscles,[3] scissors,[4] and elevators[5] have been reported, illustrating these phenomena. Moreover, the switching behavior of these molecules has been harnessed in a range of nanoelectromechanical devices, such as molecular muscle-activated cantilevers,[6,3a] macroscopic liquid transport,[7] molecular electronic devices,[8] and mesoporous silica-mounted nanovalves.[9] Cucurbit[*n*]uril[10] (**CB[*n*]**, n = 5–10), a family of macrocycles comprising n glycoluril units, has been employed, not only in the context of molecular recognition, but also in the construction of a wide range of self-assembled entities including mechanically interlocked molecules[11] and molecular switches.[12,13] In particular, **CB[8]**, with a cavity size comparable to that of γ-cyclodextrin, can include two identical guest molecules to form[10b] a binary 1 : 2 complex, or two different guest molecules to form a ternary 1 : 1 : 1 complex.[14] Kim *et al.*[15] have exploited this redox-coupled, guest-exchange process[16] in designing a molecular machine reminiscent of a loop lock. Although preliminary studies into the use of DNP and viologen as complementary pairs for binding within the cavity of **CB[8]** have been reported[14,15a,b,d,f] previously, quantitative data for these interactions has yet to be obtained and assessed. Virtually all previous studies[14,15] of similar compounds have resulted in qualitative analyses of the resulting supramolecular complexes. The determination of thermodynamic parameters associated with these switchable complexes is a critical next step in the development of useful molecular switches. Herein, detailed studies on both switches and model systems have been performed.

We report the synthesis, characterization and switching behavior of two different [2]pseudorotaxane-based complexes which undergo reversible conversion between inter- and intramolecular motion triggered by electrochemical stimuli.

Results and discussion

Synthesis

Compounds **1**·4Cl and **2**·2Cl were conveniently prepared (Scheme 1) from the appropriate diazide **6** and monoazide **7**, respectively. Tosylation of **5**,[17] followed by reaction with NaN_3, afforded **6** and **7** in 80% and 48% yields, respectively. The highly efficient and functional group tolerant "Cu(I) catalyzed azide/alkyne cycloaddition"[18] was utilized to obtain the final thread-like compounds. Compound **V**·2PF_6 was prepared following a previously reported procedure.[19] Two equivalents of **V**·2PF_6 were allowed to react with diazide **6** (1 equiv.) in Me_2CO in the presence of Cu(I) to afford **1**·4PF_6 in 73% yield; similarly, **V**·2PF_6 (1 equiv.) was reacted with the monoazide **7** (2 equiv.) to give **2**·4PF_6 in 74% yield. Anion exchange to afford the chloride salts was achieved by dissolving the PF_6^- salts in cold MeOH (10 °C) followed by the dropwise addition of concentrated HCl. After 1 h, THF and Et_2O were added to precipitate the product. The precipitates were washed several times with ether before being dried in vacuum to afford **1**·4Cl and **2**·2Cl in 91 and 88% yields, respectively.

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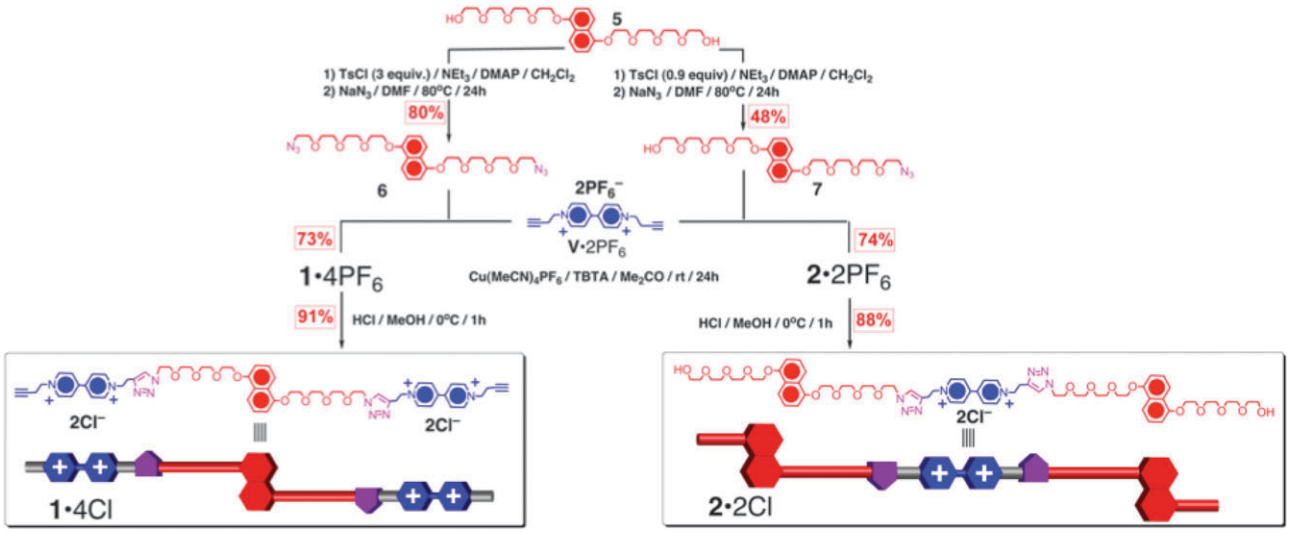
‡ Electronic supplementary information (ESI) available: Further UV-Vis and fluorescence spectroscopic studies, switching properties and NMR spectroscopy studies. See DOI: 10.1039/b819466a



Scheme 1 Synthesis of **1**·4Cl and **2**·2Cl

Spectroscopic properties

The electronic properties of the two donor–acceptor systems, **1**·4Cl and **2**·2Cl, as well as the reference compounds (Fig. 1) **V**·2Cl, **N-1** and **N-2**, were considered and are listed in Table 1. It is also noteworthy that cucurbit[8]uril (**CB[8]**) is not an absorbing species that **V**·2Cl is a not an emitting species and that **1**·4Cl and **2**·2Cl are far less emitting than their **N-1** (**N-2**) counterparts, within the spectral window considered. Assuming that the tetraethyleneglycol (TEG) chains connecting the chromophores are poor electronic relays, **1**·4Cl and **2**·2Cl can be characterized (Fig. 2) by significant hypochromic and moderate bathochromic shifts with respect to their recalculated electronic spectra, which were obtained by summing the electronic spectra of their individual components, **V**·2Cl and **N-1**. In addition, the electronic spectra of **1**·4Cl and **2**·2Cl are characterized by broad and weak absorption bands (λ_{max} = 460 nm; ε^{460} = 390 M^{-1} cm^{-1} for **1**·4Cl and λ_{max} = 475 nm; ε^{475} = 390 M^{-1} cm^{-1} for **2**·2Cl) in the visible region.

These bands can be assigned to charge transfer (CT) interactions between the electron-donating 1,5-dioxynaphthalene ring system and the electron-accepting 4,4′-bipyridinium units present in the two compounds. These CT interactions are also responsible for the large decrease of the emission intensity centered on the electron-rich subunit of the two compounds. These spectroscopic data (Table 1) demonstrate that **1**·4Cl and

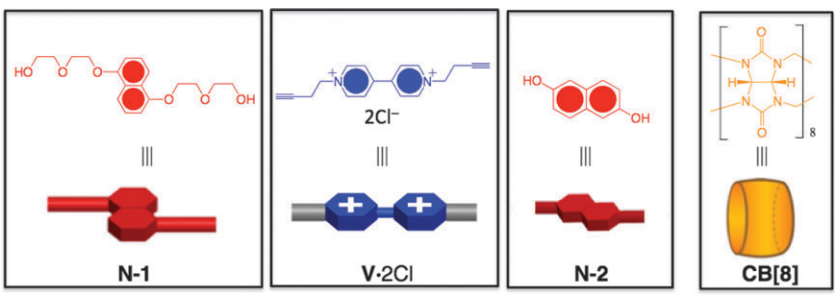


Fig. 1 Structural formulas and graphical representations of the model compounds relevant to the research in this paper.

Table 1 Spectroscopic properties (absorption and emission) of the chromophoric systems in **1**·4Cl, **2**·2Cl, **V**·2Cl, **N-1** and **N-2**[a]

System	Absorption λ_{max}/nm ($10^{-4}\varepsilon^{\lambda max}$/$M^{-1}$ cm^{-1})	Emission λ_{max}/nm	Emission Φ^{abs} (%)
V·2Cl	263 (2.10)	[b]	[b]
N-1	223 (5.53)/283 (0.74)/294 (0.93)/310 (0.68)/324 (0.47)	344/357	11.8
N-2	250 (0.36)/259 (0.42)/269 (0.44)/279 (0.25)/343 (0.27)	374/428	37.0
1·4Cl	225 (3.71)/266 (2.88)/313 (0.57)/326 (0.37)/460 (0.039)	359/424	0.4
2·2Cl	224 (8.40)/274 (2.30)/282 (2.28)/294 (1.91)/311 (1.20)/325 (0.80)/475 (0.039)	354	0.2

[a] Solvent: H_2O, pH 7.0 (phosphate buffer 0.1 M), T = 25.0(2) °C. The errors in λ_{max}, on $\varepsilon^{\lambda max}$ and in Φ^{abs} are ± 1 nm, 5% and 10%, respectively. [b] Non-emitting species.

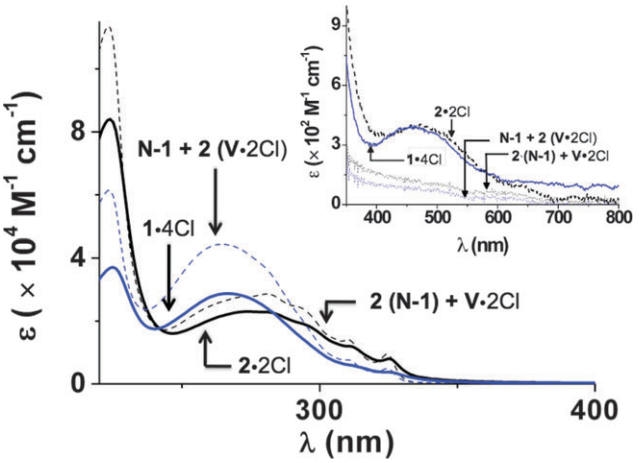


Fig. 2 Electronic spectra of **1**·4Cl (solid blue line) and **2**·2Cl (solid black line) compared to their calculated spectra (dashed lines) obtained by summing the electronic spectra of the individual components **N-1** and **V**·2Cl. Solvent: H_2O, pH 7.0 (phosphate buffer 0.1 M), T = 25.0(2) °C.

2·2Cl can undergo spontaneous self-folding in solution under the experimental conditions (Fig. S1 and S2 in ESI‡).

Binding properties

The thorough study of the inclusion complexes **1**·4Cl and **2**·2Cl within **CB[8]** first requires an examination of the recognition properties of the macrocyclic host towards the monotopic dicationic **V**·2Cl guest in the absence and in the presence of the π-electron donating counterpart, **N-1** or **N-2**. Fig. 3 shows the spectral variation of the viologen-centered electronic transitions upon gradual addition of **CB[8]**. Significant and concomitant hypochromic and bathochromic shifts of π–π* transitions as well as the presence of isosbestic points supports that a 1 : 1 complex is exclusively formed from **V**·2Cl and **CB[8]**. This 1 : 1 complex was further confirmed by a Job's plot[20] (Fig. S3 in ESI‡). The spectrophotometric data were processed by statistical methods[20] allowing us to calculate the association constant of the $\mathbf{V^{2+}}\subset\mathbf{CB[8]}$ species ($\log K_{\mathbf{V^{2+}}\subset\mathbf{CB[8]}}$ = 4.8(2)) as well as its electronic spectrum

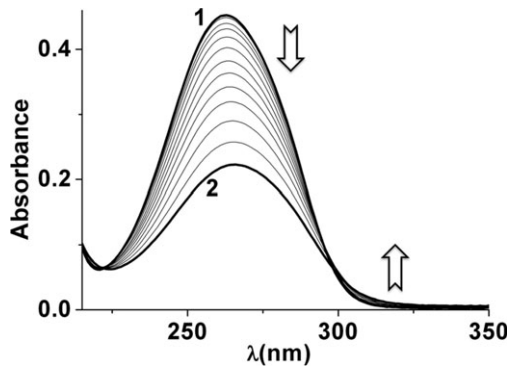


Fig. 3 UV-Visible absorption spectrophotometric titration of the bisalkyneviologen **V**·2Cl by **CB[8]**. Solvent: H_2O, pH 7.0 (phosphate buffer 0.1 M), T = 25.0(2) °C, l = 1 cm, (1) $[\mathbf{V}\cdot2Cl]_{tot} = 2.15\times10^{-5}$ M, (2) $[\mathbf{CB[8]}]_{tot}/[\mathbf{V}\cdot2Cl]_{tot}$ = 3.6.

(Fig. S4 in ESI†). The two components of $\mathbf{V^{2+}}\subset\mathbf{CB[8]}$ are held together by ion–dipole interactions between the positive charges borne by the bipyridinium unit and the polar oxygens of the macrocyclic **CB[8]**. The subsequent high binding affinity of this supramolecule was found to be in excellent agreement with that reported in the literature.[21] Although **CB[8]** has a cavity large enough[10a] to encapsulate two **V**·2Cl molecules, only a single dicationic viologen unit is hosted by the macrocyclic ligand. The formation of the 2 : 1 complex is most likely precluded by the strong electrostatic repulsions between the two **V**·2Cl dications. However, these recognition properties can be tuned by simple redox chemistry and **CB[8]** was shown to be able to accommodate reduced viologen radical cations.[21]

Having established the binding stoichiometry and strength of the complex between **CB[8]** and **V**·2Cl, it was thus of interest to investigate the recognition properties in the presence of a π-electron donating unit such as **N-1** or **N-2**. Cucurbit[8]uril was gradually added to an equimolar solution of **V**·2Cl and **N-1** (or **N-2**) and the UV-Visible spectrophotometric variations were monitored (Fig. S5 and S7 in ESI‡). For the statistical treatment of the data, the electronic spectra and stability constant of $\mathbf{V^{2+}}\subset\mathbf{CB[8]}$ were fixed. It is important to note that **V**·2Cl could interact with **N-1** or **N-2** in the absence of **CB[8]**, as was shown for the two compounds, **1**·4Cl and **2**·2Cl, as well as for closely related systems.[14,22] However, their intermolecular associations lead to rather low stability constants that could not be determined with great accuracy. Their logarithmic values ($\log K_{\mathbf{V^{2+}}\cdot\mathbf{N\text{-}1}}$ and $\log K_{\mathbf{V^{2+}}\cdot\mathbf{N\text{-}2}}$) were, however, estimated to be lower than 2. Therefore, under the experimental conditions employed, $\mathbf{V^{2+}}\cdot\mathbf{N\text{-}1}$ or $\mathbf{V^{2+}}\cdot\mathbf{N\text{-}2}$ associations represent only minor species, which were consequently neglected. Regardless, the nature of the π-electron donating unit (**N-1** or **N-2**), ternary 1 : 1 : 1 complexes, involving one **CB[8]** host and two hetero-guests, namely **V**·2Cl and **N-1** (or **N-2**) were characterized and quantified. Their global stability constants, as well as some relevant spectrophotometric parameters, are given in Tables 1 and 2 (Fig. S6 and S8 in ESI‡). The binding constants given in Table 2 are defined by the following equilibria (**N** = **N-1** or **N-2**):

$$\mathbf{V^{2+}} + \mathbf{CB[8]} \overset{K_{\mathbf{V^{2+}}\subset\mathbf{CB[8]}}}{\rightleftharpoons} \mathbf{V^{2+}}\subset\mathbf{CB[8]};$$

$$K_{\mathbf{V^{2+}}\subset\mathbf{CB[8]}} = \frac{[\mathbf{V^{2+}}\subset\mathbf{CB[8]}]}{[\mathbf{V^{2+}}][\mathbf{CB[8]}]}$$

$$\mathbf{N} + \mathbf{V^{2+}} + \mathbf{CB[8]} \overset{\beta_{\mathbf{V^{2+}}\cdot\mathbf{N}\subset\mathbf{CB[8]}}}{\rightleftharpoons} \mathbf{V^{2+}}\cdot\mathbf{N}\subset\mathbf{CB[8]};$$

$$\beta_{\mathbf{V^{2+}}\cdot\mathbf{N}\subset\mathbf{CB[8]}} = \frac{[\mathbf{V^{2+}}\cdot\mathbf{N}\subset\mathbf{CB[8]}]}{[\mathbf{N}][\mathbf{V^{2+}}][\mathbf{CB[8]}]}$$

$$\mathbf{N} + \mathbf{V^{2+}} \subset \mathbf{CB[8]} \overset{K_{\mathbf{V^{2+}}\cdot\mathbf{N}\subset\mathbf{CB[8]}}}{\rightleftharpoons} \mathbf{V^{2+}}\cdot\mathbf{N}\subset\mathbf{CB[8]};$$

$$K_{\mathbf{V^{2+}}\cdot\mathbf{N}\subset\mathbf{CB[8]}} = \frac{[\mathbf{V^{2+}}\cdot\mathbf{N}\subset\mathbf{CB[8]}]}{[\mathbf{N}][\mathbf{V^{2+}}\subset\mathbf{CB[8]}]}$$

$$\beta_{\mathbf{V^{2+}}\cdot\mathbf{N}\subset\mathbf{CB[8]}} = K_{\mathbf{V^{2+}}\cdot\mathbf{N}\subset\mathbf{CB[8]}} \times K_{\mathbf{V^{2+}}\subset\mathbf{CB[8]}}$$

Table 2 Spectroscopic properties and stability constants of the inclusion complexes with cucurbit[8]uril[a]

Species	$\log\beta$ ($\pm 3\sigma$)	λ^{max}/nm ($10^{-4}\varepsilon^{\lambda max}$/$M^{-1}$ cm^{-1})
$\mathbf{V^{2+}}\subset\mathbf{CB[8]}$	4.8(2)[b]	271 (1.41)
$\mathbf{V^{2+}}\cdot\mathbf{N\text{-}1}\subset\mathbf{CB[8]}$	9.8(9)[b]	272 (2.26)/310 (0.81)/325 (0.53)/445 (0.043)
	8.7(2)[c]	
$\mathbf{V^{2+}}\cdot\mathbf{N\text{-}2}\subset\mathbf{CB[8]}$	9.5(6)[b]	254 (0.72)/263 (0.75)/275 (0.71)/285 (0.67)/298 (0.73)/417 (0.078)/566 (0.077)
	9.4(3)[c]	
$\mathbf{1^{4+}}\subset\mathbf{CB[8]}$	5.8(4)[b]	230 (2.98)/271 (2.55)/580 (0.044)
$\mathbf{1^{4+}}\subset\mathbf{(CB[8])_2}$	9.2(5)[b]	231 (3.13)/276 (2.26)/565 (0.07)
$\mathbf{2^{2+}}\subset\mathbf{CB[8]}$	6.1(2)[b]	283 (2.09)/293 (1.98)/310 (1.31)/325 (0.79)/577 (0.05)

[a] Solvent: water, pH 7.0 (phosphate buffer 0.1 M), T = 25.0(2) °C. The reported errors are given as 3σ with σ = standard deviation. The errors on λ_{max} and on $\varepsilon^{\lambda max}$ are equal to ± 1 nm and 5%, respectively. [b] Determined from absorption titration. [c] Determined from emission titration.

The electron-rich systems, **N-1** or **N-2**, themselves do not bind **CB[8]** in the absence of the dicationic bisalkyneviologen **V**·2Cl. As for **1**·4Cl and **2**·2Cl, the ternary complexes $\mathbf{V^{2+}}\cdot\mathbf{N\text{-}1}\subset\mathbf{CB[8]}$ and $\mathbf{V^{2+}}\cdot\mathbf{N\text{-}2}\subset\mathbf{CB[8]}$ are also characterized by CT absorption bands in the visible region (Table 2), which are clear signatures of the inclusion of the electroactive hetero-pairs in the **CB[8]** host cavity (Fig. 4). It is noteworthy that the position of the CT absorption band of $\mathbf{V^{2+}}\cdot\mathbf{N\text{-}2}\subset\mathbf{CB[8]}$ (λ_{max} = 566 nm; ε^{566} = 770 M^{-1} cm^{-1}) is in agreement with that previously measured[14] for a closely related ternary complex with methylviologen dication (λ_{max} = 580 nm).

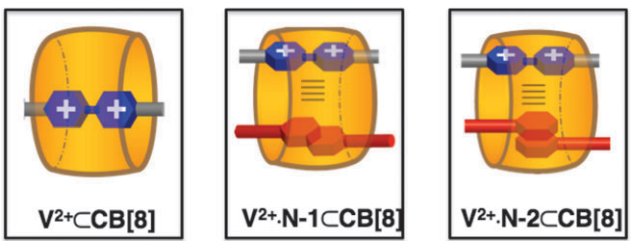


Fig. 4 Schematic representation of the inclusion complexes $\mathbf{V^{2+}}\subset\mathbf{CB[8]}$, $\mathbf{V^{2+}}\cdot\mathbf{N\text{-}1}\subset\mathbf{CB[8]}$ and $\mathbf{V^{2+}}\cdot\mathbf{N\text{-}2}\subset\mathbf{CB[8]}$.

We also took advantage of the emission properties of **N-1**, **N-2** and **V**·2Cl to assess the binding affinities of the ternary complexes by spectrofluorimetric titrations. The two π-electron donating compounds display emission signals in the visible region, while the dicationic π-electron accepting compound is not an emitting species and can act as a fluorescence emission inhibitor. Spectrofluorimetric titrations were carried out and are shown in Fig. 5 (Fig. S9 in ESI‡). These titrations indicate that, upon addition of **CB[8]** to an equimolar mixture of **V**·2Cl and **N-1** (or **N-2**), a significant quenching of the **N-1** (or **N-2**) centered fluorescence emission is observed. As the $\mathbf{V^{2+}}\cdot\mathbf{N\text{-}1}$ or $\mathbf{V^{2+}}\cdot\mathbf{N\text{-}2}$ complexes are minor species in solution, these quenching processes result from CT interactions between the two building blocks $\mathbf{V^{2+}}$ and **N-1** (or **N-2**) within the **CB[8]** cavity, thus leading to stable ternary species. A Stern–Volmer approach[23] was used to calculate the binding constants ($\log K_{\mathbf{V^{2+}}\cdot\mathbf{N\text{-}1}\subset\mathbf{CB[8]}}$ = 3.88(3) and $\log K_{\mathbf{V^{2+}}\cdot\mathbf{N\text{-}2}\subset\mathbf{CB[8]}}$ = 4.57(2)). These values are in close agreement with those obtained (Table 2) from absorption titrations, and clearly emphasize a strong stabilization of the CT complexes by more than two orders of magnitude when **CB[8]** is used. The inclusion of the electron-rich guest is most likely driven by the van der Waals interactions in the hydrophobic cavity of **CB[8]** which

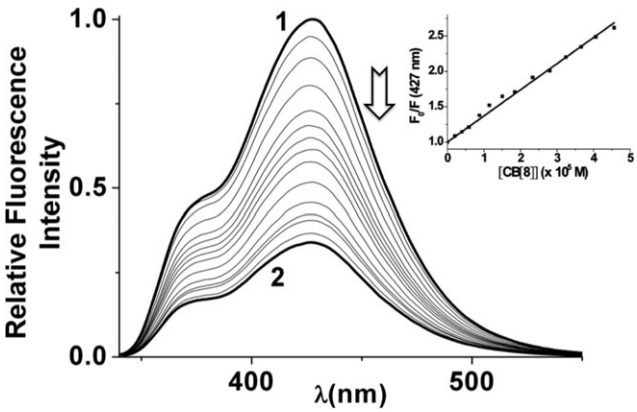


Fig. 5 Fluorescence spectrophotometric titration of **V**·2Cl and **N-2** with **CB[8]**. Solvent: H_2O, pH 7.0 (phosphate buffer 0.1 M), T = 25.0(2) °C, λ_{ex} = 327 nm, emission and excitation slit widths both 6 nm, respectively, $[\mathbf{V}\cdot 2Cl]_{tot} = [\mathbf{N\text{-}2}]_{tot} = 1.73 \times 10^{-5}$ M; (1) $[\mathbf{CB[8]}]_{tot}$ = 0 M, (2) $[\mathbf{CB[8]}]_{tot} = 5.03 \times 10^{-5}$ M. Inset: Stern–Volmer plot at λ = 427 nm ($F_0/F = 1 + K_{\mathbf{V^{2+}}\cdot\mathbf{N\text{-}2}\subset\mathbf{CB[8]}} \times [\mathbf{CB[8]}]_{tot}$) .

are amplified in aqueous solution. Although the formation of a 1 : 1 : 1 complex is entropically unfavorable, the enthalpic stabilization gained by the hydrophobic interactions between **CB[8]** and its guests yield a net stabilizing effect for the complex.

The recognition properties of cucurbit[8]uril towards π-electron rich (**N-1** and **N-2**) and deficient (**V**·2Cl) models being clearly established, we then examined the host–guest complexes with **1**·4Cl and **2**·2Cl and **CB[8]**. Electrospray ionization mass spectrometry (ESI-MS) was used to probe the nature of the host–guest complexes with **CB[8]** (Fig. 6).

We characterized a single complex $\mathbf{2^{2+}}\subset\mathbf{CB[8]}$ with **2**·2Cl, while two species containing one ($\mathbf{1^{4+}}\subset\mathbf{CB[8]}$) and two **CB[8]** ($\mathbf{1^{4+}}\subset\mathbf{(CB[8])_2}$) units were observed (Fig. 7) with **1**·4Cl. All the ESI-MS signals (m/z = 604.0 for $[\mathbf{1^{4+}}\subset\mathbf{CB[8]} - 4Cl]^{4+}$, 936.5 for $[\mathbf{1^{4+}}\subset\mathbf{(CB[8])_2} - 4Cl]^{4+}$ and 1333.5 for $[\mathbf{2^{2+}}\subset\mathbf{CB[8]} - 2Cl]^{2+}$) correspond to multicharged species after losing their chloride counterions.

We have therefore examined, by spectrophotometric means, the formation of the host–guest complexes with **CB[8]** and **1**·4Cl and **2**·2Cl. Absorption spectrophotometric titrations (Fig. S10 and S11, ESI‡) of **1**·4Cl and **2**·2Cl by **CB[8]** were carried out and the corresponding data were processed statistically.[20] The electronic spectra are presented in Fig. 8 and the stability constants are listed in Table 2. Although the electronic spectrum of $\mathbf{2^{2+}}\subset\mathbf{CB[8]}$ is characterized by the

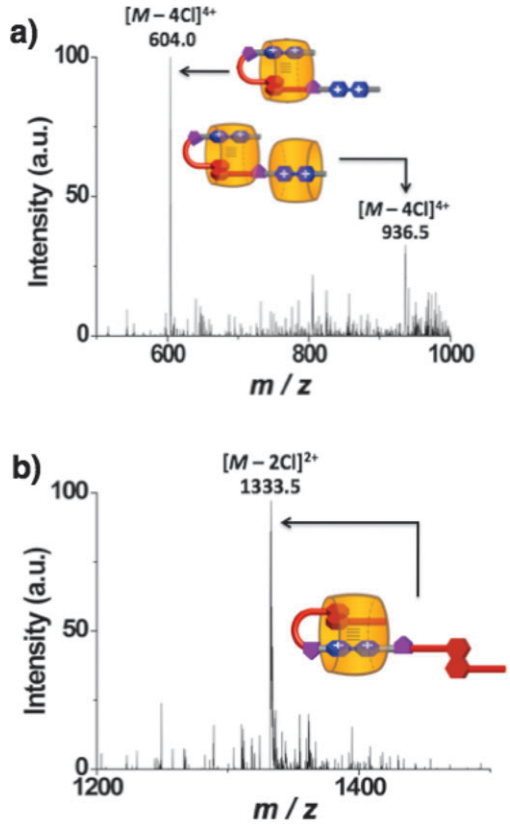


Fig. 6 ESI mass spectra of the host–guest complexes (a) **1**·4Cl and (b) **2**·2Cl, with **CB[8]**. Solvent H_2O–MeOH (80/20 by weight), ESMS+, Skim1 = 40 V, Top: $[\mathbf{1}\cdot 4Cl]_{tot} = 7.5 \times 10^{-6}$ M, $[\mathbf{CB[8]}]_{tot} = 8.5 \times 10^{-6}$ M, Capillary exit = 190 V, Bottom: $[\mathbf{2}\cdot 2Cl]_{tot} = 1.4 \times 10^{-5}$ M, $[\mathbf{CB[8]}]_{tot} = 2.8 \times 10^{-5}$ M, Capillary exit = 270 V.

same set of absorption bands as free **2**·2Cl, it is, however, significantly shifted. Indeed, the absorption band of the viologen unit undergoes a significant hypochromic shift, which clearly points to its inclusion within the **CB[8]** cavity. In addition, the CT absorption band is preserved but significantly red-shifted (Table 2), thus indicating that stronger CT interactions take place between the π-electron accepting bipyridinium unit and one of the two π-electron donating dioxynaphthalene groups, located within the **CB[8]** cavity. Therefore, $\mathbf{2}^{2+}\subset\mathbf{CB[8]}$ most likely adopts (Fig. 7) an "*end-to-interior loop*"[24] superstructure in which an intramolecular CT complex is included in the **CB[8]** cavity, leaving one 1,5-dioxynaphthalene unit free. The stability constant of $\mathbf{2}^{2+}\subset\mathbf{CB[8]}$ (Table 2) is more than one order of magnitude higher than that measured for $\mathbf{V}^{2+}\subset\mathbf{CB[8]}$, thus supporting the formation of a stable intramolecular CT complex. The

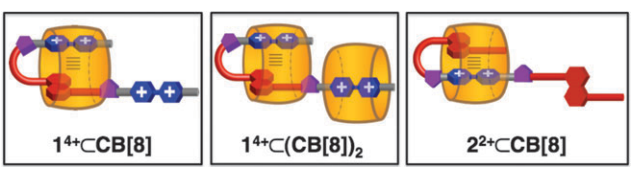


Fig. 7 Schematic representation of the inclusion complexes of guests $\mathbf{1}^{4+}$ and $\mathbf{2}^{2+}$ with the host **CB[8]**.

same behavior is also valid for the $\mathbf{1}^{4+}\subset\mathbf{CB[8]}$ complex. Its electronic spectrum is characterized by a hypochromic shift of the viologen-centered transitions, as well as a significant bathochromic shift of the CT absorption band (Table 2 and Fig. 8). The complex $\mathbf{1}^{4+}\subset\mathbf{CB[8]}$ most likely adopts (Fig. 7) the same "*end-to-interior loop*" arrangement as $\mathbf{2}^{2+}\subset\mathbf{CB[8]}$, as shown (Table 2) by their comparable association constants. In contrast to $\mathbf{2}^{2+}\subset\mathbf{CB[8]}$, complex $\mathbf{1}^{4+}\subset\mathbf{CB[8]}$ contains a non-hosted viologen residue, which can behave similarly to the **V**·2Cl reference compound. In the presence of excess **CB[8]**, a second complex $\mathbf{1}^{4+}\subset\mathbf{(CB[8])_2}$ (Fig. 7) has indeed been identified from both spectrophotometric and mass spectrometric studies. The electronic spectrum of $\mathbf{1}^{4+}\subset\mathbf{(CB[8])_2}$ is characterized by a further hypochromic effect with respect to $\mathbf{1}^{4+}\subset\mathbf{CB[8]}$, and the maximum of the CT absorption band remains unchanged. These spectrophotometric data indicate that a second **CB[8]** macrocycle interacts with the free viologen unit of $\mathbf{1}^{4+}\subset\mathbf{CB[8]}$ to afford the ternary complex, $\mathbf{1}^{4+}\subset\mathbf{(CB[8])_2}$. The respective stability constants have been determined ($\log K_{\mathbf{1}^{4+}\subset\mathbf{CB[8]}} = 5.8(4)$ and $\log K_{\mathbf{1}^{4+}\subset\mathbf{(CB[8])_2}} = 3.4(4)$, Table 2). The value of $\log K_{\mathbf{1}^{4+}\subset\mathbf{(CB[8])_2}}$ can be directly compared to that of $\mathbf{V}^{2+}\subset\mathbf{CB[8]}$ ($\log K_{\mathbf{V}^{2+}\subset\mathbf{CB[8]}} = 4.8(2)$) and emphasizes that the formation of $\mathbf{1}^{4+}\subset\mathbf{(CB[8])_2}$ is destabilized by more than one order of magnitude with respect

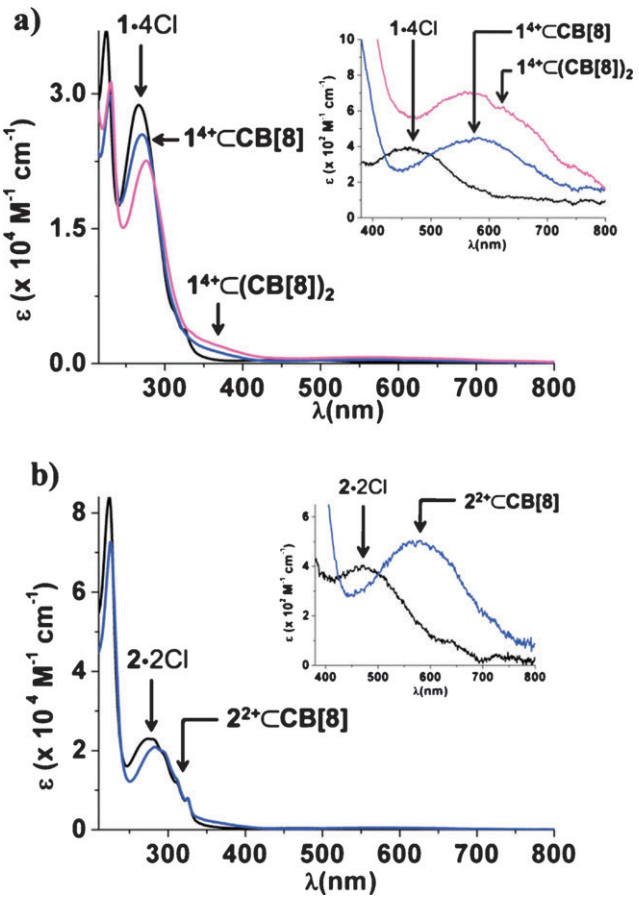


Fig. 8 Electronic spectra of the host–guest complexes. (a) **1**·4Cl, $\mathbf{1}^{4+}\subset\mathbf{CB[8]}$, and $\mathbf{1}^{4+}\subset\mathbf{(CB[8])_2}$, (b) **2**·2Cl and $\mathbf{2}^{2+}\subset\mathbf{CB[8]}$. Solvent: H_2O, pH 7.0 (phosphate buffer 0.1 M), $T = 25.0(2)$ °C.

to $\mathbf{V}^{2+}\subset$**CB[8]**, most likely as a consequence of strong steric interactions that inhibit the binding of a second **CB[8]** from one side of $\mathbf{1}^{4+}\subset$**CB[8]**.[25] In addition, the UV-Vis data are supported by ^{1}H NMR spectroscopy (Fig. S13 and S14 in ESI‡).

Switching properties

The mechanical switching of the two [2]pseudorotaxane molecular machines (Fig. 9) were studied by cyclic voltammetry (CV) and UV-Vis spectroscopy. Typical cyclic voltammograms of each thread **1**·4Cl and **2**·2Cl and its relative [2]pseudorotaxane $\mathbf{1}^{4+}\subset$**CB[8]** (1 : 1, 1 mM) and $\mathbf{2}^{2+}\subset$**CB[8]** (1 : 1, 1 mM) are shown in Fig. 10. The two threads **1**·4Cl (**2**·2Cl) undergo two consecutive two-electron (one-electron) processes with a sharp second peak that indicates strong adsorption of the fully reduced species $\mathbf{1}^{0}$ and $\mathbf{2}^{0}$ on the electrode. The 1 : 1 complex is present in >95% in solution.[26] Compared to **1**·4Cl, however, $\mathbf{1}^{4+}\subset$**CB[8]** exhibits a splitting of the first reduction peak (−0.42 V) into two different peaks (−0.44 and −0.82 V), corresponding to two electrochemically different viologen units. One is involved in the CT complex formation with the DNP unit (at −0.82 V), of **1**·4Cl, inside **CB[8]**, while the other is free (at −0.44 V). The second reduction peak of compound **1**·4Cl (−0.78 V) shows a very large shift in the presence of **CB[8]** (−1.21 V).

Thus, the cyclic voltammetric behavior of $\mathbf{1}^{4+}\subset$**CB[8]** suggests that the two-electron reduction of the [2]pseudorotaxane $\mathbf{1}^{4+}\subset$**CB[8]** with an *end-to interior loop* structure results in the generation of a species containing two terminal viologen radical cation units, which then undergo a rapid intramolecular pairing process inside **CB[8]** to form the stable [2]pseudorotaxane, $\mathbf{1}^{2(+\bullet)}\subset$**CB[8]**, with an *end-to-end loop* structure. On the other hand, the [2]pseudorotaxane $\mathbf{2}^{2+}\subset$**CB[8]** exhibits a large shift for the first reduction peak (−0.67 V) compared to the monoviologen thread **2**·2Cl (−0.45 V). This large shift indicates the formation of a CT inclusion complex in the cavity of the **CB[8]**. The second reduction peak of the monoviologen compound, **2**·2Cl (−0.78 V), is split into two peaks in the presence of **CB[8]** (−0.78 and −1.20 V) corresponding to two electrochemically different viologen units. The peak at −0.78 V corresponds to the viologen radical cation ($\mathbf{V}^{+\bullet}$) threaded with **CB[8]**, but not dimerized. The second peak at −1.20 V corresponds to the formation of the [3]pseudorotaxane $(\mathbf{2}^{+\bullet})_2\subset$**CB[8]** and four terminal **DNP** units. The peak at −1.20 V is more visible at 50 mV s^{-1} than at 200 mV s^{-1} (Fig. S12, ESI‡), reflecting a slower dimerization of the viologen radical cation in the case of **2**·2Cl than in **1**·4Cl. The formation of these complexes was confirmed by UV-Vis spectroscopy (Fig. 11). The treatment of a solution containing $\mathbf{1}^{4+}\subset$**CB[8]** or $\mathbf{2}^{2+}\subset$**CB[8]** with $Na_2S_2O_4$ results in the appearance of new absorption bands at $\lambda \approx 380$, 550 and > 900 nm which reflect the dimerization of the viologen radical cation units in the cavity of the **CB[8]**. Upon exposure to air, the viologen radical cations were oxidized back to their original dicationic state. The "*end-to-interior loop*" structures, as evidenced by the CT band, were thus regenerated (Fig. 11).

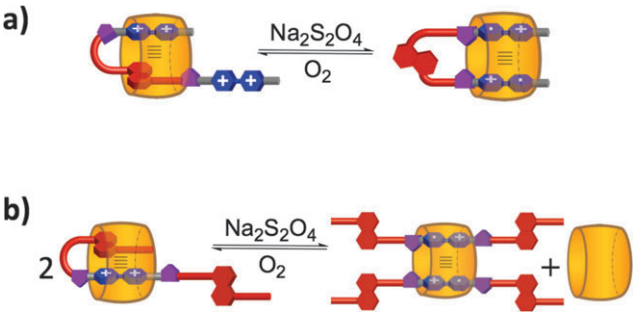


Fig. 9 Chemically-triggered interconversions in host–guest complexes: (a) reduction of $\mathbf{1}^{4+}\subset$**CB[8]** with "*end-to-interior loop*" superstructure to form an "*end-to-end loop*" superstructure and (b) reduction of $\mathbf{2}^{2+}\subset$**CB[8]** with "*end-to-interior loop*" superstructure leads to the formation of a [3]pseudorotaxane superstructure.

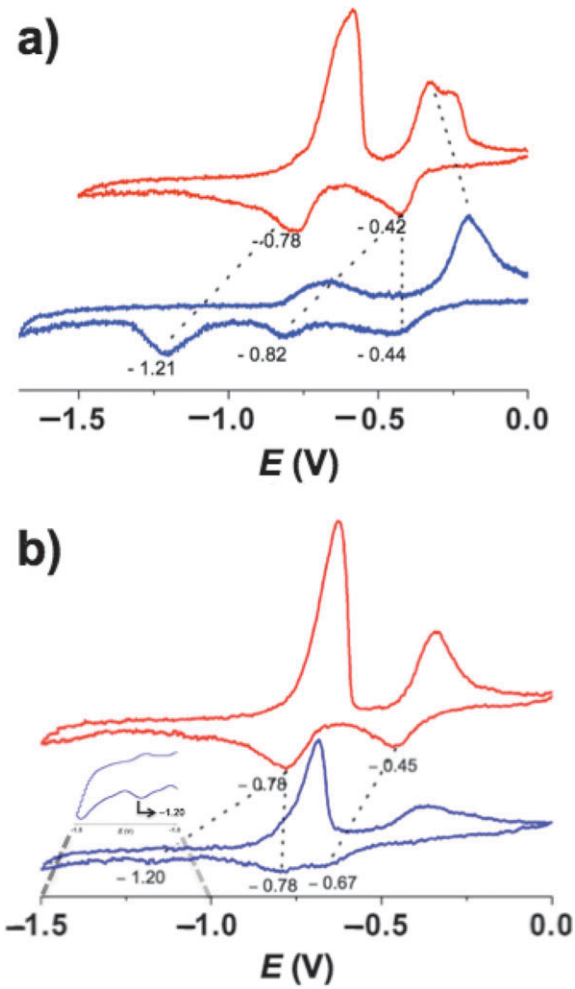


Fig. 10 Cyclic voltammograms of 1 : 1 mixture of (a) 1 mM of **1**·4Cl (red) and $\mathbf{1}^{4+}\subset$**CB[8]** (blue), (b) 1 mM of each **2**·2Cl (red) and $\mathbf{2}^{2+}\subset$**CB[8]** (blue). Supporting electrolyte: 0.1 M phosphate buffer (pH 7.0). Scan rate: 200 mV s^{-1}.

Conclusions

Two donor–acceptor thread-like compounds, incorporating viologen units and 1,5-dihydroxynaphthalene ring systems have been prepared. Their ability to form an *end-to-interior*

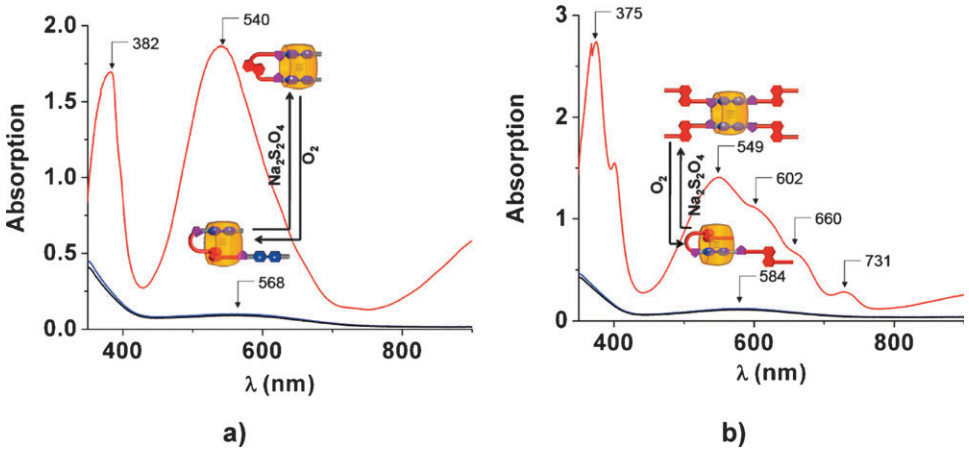


Fig. 11 Absorption spectra of (a) $\mathbf{1}^{4+}\subset$**CB[8]** (1 mM) and (b) $\mathbf{2}^{2+}\subset$**CB[8]** (1 mM), before (blue), after (red) reduction with $Na_2S_2O_4$, and following (black) reoxidation with air (10 min), in phosphate buffer 0.1 M (pH = 7.0), l = 1 cm.

superstructure with cucurbit[8]uril has been demonstrated by UV-Vis spectroscopic studies. The appearance of a charge transfer band is a phenomenon which is characteristic of an intramolecular interaction between a viologen and a dihydroxynaphthalene ring system in the cavity of the cucurbituril. In the case of the bisviologen thread, the reduction of the viologen units results in an intramolecular motion (Fig. 9(a)), which can be contrasted with the intermolecular motion observed (Fig. 9(b)) in the case of the monoviologen thread.

Experimental

General

All reagents and starting materials were purchased from Aldrich and used without further purification. Compounds **7** and **V**·2PF_6 were prepared according to literature procedures.[15] Thin-layer chromatography (TLC) was performed on silica gel 60 F245 (E. Merck). Column chromatography was carried out on silica gel 60F (Merck 9385, 0.040-0.063). Deuterated solvents (Cambridge Isotope Laboratories) for NMR spectroscopic analyses were used as received. NMR spectra were recorded on Varian 500 spectrometer, with working frequencies of 500.13 MHz for ^{1}H nuclei, and 100 MHz for ^{13}C nuclei, respectively. Chemical shifts are quoted in ppm relative to tetramethylsilane with the residual solvent peak as a reference standard. High-resolution mass spectra were measured either on an Applied Biosystems Voyager DE-PRO MALDI TOF mass spectrometer (HR-TOF), or on a Finnigan LCQ ion-trap mass spectrometer (HR-ESI). Electrochemical experiments were carried out at room temperature in argon-purged 100 mM phosphate buffered solutions (pH 7.0) with a Princeton Applied Research 263 A Multipurpose instrument interfaced to a PC. Cyclic voltammetry experiments were performed by using a glassy carbon working electrode (0.018 cm^2, Cypress system). The electrode surface was polished routinely with 0.05 μm alumina/water slurry on a felt surface immediately before use. The counter electrode was a Pt coil and the reference electrode was a Ag/AgCl electrode. The concentration of the samples were 1 mM and the scan rate was set to 200 mV s^{-1}. UV-Vis absorption spectra were recorded on a Varian Cary-300 spectrophotometer.

Synthesis

6. The ditosylate derivative of **5** (500 mg, 0.54 mM) and NaN_3 (105 mg, 1.5 mM) were heated in DMF (20 mL) at 90 °C overnight. After the removal of the solvent by evaporation, the residue was dissolved in CH_2Cl_2, and the insoluble material was removed by filtration. Concentration under reduced pressure gave **6** (90%) as an orange oil.

1·**4Cl.** A solution (10 mL) of the DNP-diazide **6** (1.0 g, 1.5 mM) in Me_2CO was added dropwise at room temperature over 2 h to a solution of the bisalkyneviologen (**V**·2PF_6) (4.14 g, 7.5 mM) and a catalytic amount of tetrakis(acetonitrile)-copper(I) hexafluorophosphate and tris(benzyltriazolylmethyl)-amine (TBTA). The reaction mixture was left to stand overnight. After the removal of the solvent by evaporation, the residue was purified by column chromatography (SiO_2, Me_2CO plus 2% ammonium hexafluorophosphate). Concentration under vacuum afforded **1**·4PF_6 (73%) as a red, glassy product. The thread **1**·4Cl was obtained in 91% yield as a red, glassy product as described in the results and discussion section. ^{1}H NMR (500 MHz, D_2O) δ 2.55 (t, 1H, J = 2.5 Hz), 2.98 (td, 2H, J = 6.5, 2.5 Hz), 3.31 (t, 2H, J = 6.5 Hz), 3.56 (m, 4H), 3.64–3.68 (m, 2H), 3.73–3.80 (m, 5H), 3.95 (br m, 2H), 4.14 (br m, 1H), 4.43 (m, 2H), 4.74 (t, 2H, J = 7 Hz), 4.72 (d, 1H, J = 7.5 Hz), 7.08 (t, 1H, J = 8 Hz), 7.25 (d, 1H, J = 8.5 Hz), 7.75 (s, 1H), 8.08 (d, 2H, J = 7 Hz), 8.25 (d, 2H, J = 7 Hz), 8.58 (d, 2H, J = 7 Hz); ^{13}C NMR (100 MHz, D_2O) δ 20.1, 26.7, 49.9, 60.0, 61.3, 67.8, 68.6, 69.3, 69.4, 69.7, 69.8, 70.3, 74.4, 78.5, 106.4, 114.2, 124.9, 125.4, 126.2, 126.4, 141.7, 145.0, 145.6, 148.9, 149.1, 153.4. HRMS (HR-ESI): m/z calc. for $C_{62}H_{74}N_{10}O_8$: 271.6; found: 271.8.

2·**2Cl.** Compounds **7** (400 mg, 0.744 mM) and **V**·2PF_6 (205 mg, 0.372 mM) were mixed in Me_2CO (50 mL). A catalytic amount of tetrakis(acetonitrile)copper(I) hexafluoro-phosphate and TBTA were added at room temperature. The mixture was left to stand overnight. After the removal of the solvent by evaporation, the residue was purified by column chromatography (SiO_2, Me_2CO plus 2% ammonium

hexafluorophosphate). Concentration *in vacuo* afforded **2**·2PF$_6$ (74%). The thread **2**·2Cl was obtained in 88% yield as described in the results and discussion section. ^{1}H NMR (500 MHz, D_2O) δ 3.34 (t, 2H, J = 6 Hz), 4.46 (m, 3H), 3.5–3.6 (m, 16H), 3.65 (br m, 4H), 3.75 (t, 3H, J = 4 Hz), 3.79 (br s, 3H), 3.82 (br s, 2H), 4.00 (br s, 2H), 4.07 (br s, 2H), 4.24 (t, 2H, J = 4 Hz), 4.73 (t, 2H, J = 6 Hz), 6.65 (d, 1H, J = 8 Hz), 6.69 (d, 1H, J = 8 Hz), 7.05 (t, 1H, J = 8 Hz), 7.13 (t, 1H, J = 8 Hz), 7.35 (d, 1H, J = 9 Hz), 7.45 (d, 1H, J = 9 Hz), 7.80 (s, 1H), 7.91 (d, 2H, J = 6.5 Hz), 8.55 (d, 2H, J = 6.5 Hz); ^{13}C NMR (100 MHz, D_2O) δ 26.6, 49.9, 60.3, 61.1, 67.7, 68.7, 69.2, 69.3, 69.5, 69.6, 69.7, 70.0, 70.2, 71.7, 106.4, 106.6, 114.2, 114.3, 124.9, 125.8, 125.8, 125.9, 125.9, 141.8, 144.9, 148.0, 153.6, 153.7. HRMS (HR-ESI): m/z calc. for $C_{70}H_{96}N_8O_{18}$: 668.4; found: 668.5.

Physico-chemical measurements. **2**·2Cl ($C_{70}H_{96}Cl_2N_8O_{18}$, MW = 1408.46 g mol^{-1}), **1**·4Cl ($C_{62}H_{74}Cl_4N_{10}O_8$, M. W. = 1229.13 g mol^{-1}), the bisalkyneviologen **V**·2Cl ($C_{16}H_{14}Cl_2N_2$, MW = 305.22 g mol^{-1}) and 1,5-bis[2-(2-hydroxyethoxy)-ethoxy]naphthalene (**N-1**) ($C_{18}H_{24}O_6$, MW = 336.38 g mol^{-1}) were prepared and purified as described above. Naphthalene-2,6-diol (**N-2**) ($C_{10}H_8O_2$, MW = 160.17 g mol^{-1}) (Alfa Aesar) and cucurbit[8]uril (**CB[8]**) ($C_{48}H_{48}N_{32}O_{16}$, MW = 1329 g mol^{-1}) (Aldrich) are commercial products, which were used without further purification. All solutions were prepared in distilled H_2O which was further purified by passing it through a mixed bed of ion-exchanger (Bioblock Scientific R3-83002, M3-83006) and activated carbon (Bioblock Scientific ORC-83005). It was then boiled and de-oxygenated using CO_2 and O_2 free argon prior to use (Sigma Oxiclear cartridge). All stock solutions were prepared using an AG 245 Mettler Toledo analytical balance (precision 0.01 mg), and complete dissolution in phosphate buffer was achieved using an ultrasonic bath. The experiments were carried out at 25.0(2) °C maintained with the help of Haake FJ thermostats. In all the solutions, the pH was maintained at 7.00 ± 0.05 by the use of a 0.1 M phosphate buffer, which was prepared by mixing 30.5 mL of $Na_2HPO_4{\cdot}2H_2O$ (0.2 M) (Prolabo) with 19.5 ml of NaH_2PO_4 (0.2 M) (Prolabo) and diluting to 100 mL. The final pH of the solution was then adjusted to the required value by using phosphoric acid (85%, Labosi). The pH was measured with an Ag/AgCl combined glass electrode (Metrohm 6.0234.500, long life) filled with 0.1 M NaCl (Fluka, p.a.) in H_2O. Standardization of the millivoltmeter and the verification of the linearity of the electrode response were performed using a set of commercial Merck buffered solutions (pH 1.68, 4.00, 6.86, 7.41 and 9.18).

Electrospray ionization mass spectrometric measurements. ESI Mass spectra of **1**·4Cl, **2**·2Cl and their respective complexes formed with **CB[8]** were obtained with an ion-trap instrument (Bruker Esquire 300plus, Bruker Daltonic, Bremen, Germany), equipped with an Agilent electrospray (ESI) ion source (Agilent Headquarters, Palo Alto, CA). The solutions of **1**·4Cl (1.5×10^{-5} M) and **2**·2Cl (1.5×10^{-5} M) and their complexes with **CB[8]** ([$\mathbf{1}^{4+}$] = 1.4×10^{-5} M; [**CB[8]**] = 2.8×10^{-5} M); ([$\mathbf{2}^{2+}$] = 7.5×10^{-6} M; [**CB[8]**] = 8.5×10^{-6} M), prepared in the mixed solvent H_2O–MeOH (80/20 by weight), were continuously introduced into the mass spectrometer source with a syringe pump (Cole–Parmer Instrument Company, Vernon Hills, IL) at a flow rate of 3.33 μL min^{-1}. For electrospray ionization, the drying gas was heated at 300 °C ($\mathbf{1}^{4+}$) or 350 °C ($\mathbf{2}^{2+}$). Its flow was set at 5 L min^{-1}, with 43.5 psi nebulizer pressure. The capillary and skimmer voltage were set at 4000 and 40 V, respectively. The capillary exit was adjusted at 125 V ($\mathbf{1}^{4+}$), 230 V ($\mathbf{2}^{2+}$), 190 V ($\mathbf{1}^{4+}$/**CB[8]**) or 270 V ($\mathbf{2}^{2+}$/**CB[8]**). Scanning was performed from m/z = 200 to 2000.

Spectrophotometric titrations. The spectrophotometric titrations of $\mathbf{V}^{2+}$ (2.15×10^{-5} M) and of $\mathbf{2}^{2+}$ (1.32×10^{-5} M) with cucurbit[8]uril (**CB[8]**) were carried out in a Hellma quartz optical cell (l = 1 cm). It is noteworthy that **CB[8]** has a low solubility in H_2O at pH 7.0 ($\sim 2 \times 10^{-4}$ M). Microvolumes of a concentrated solution of **CB[8]** (1.9×10^{-4} M) were added to 2 mL of $\mathbf{V}^{2+}$ or $\mathbf{2}^{2+}$ with the help of a microburette (Eppendorf). The $[\mathbf{CB[8]}]_{tot}/[\mathbf{V}^{2+}]_{tot}$ and $[\mathbf{CB[8]}]_{tot}/[\mathbf{2}^{2+}]_{tot}$ ratios were varied from 0 to 3.6 and from 0 to 6.7, respectively. Special care was taken to ensure that complete equilibration was attained. After each addition, a UV-Vis spectrum was recorded from 230 to 800 nm on a Cary 300 (Varian) spectrophotometer maintained at 25.0(2) °C by the flow of a Haake NB 22 thermostat. In order to determine the association constants of the 1 : 1 : 1 ternary complexes formed with the electron-donor/electron-acceptor pair $\mathbf{V}^{2+}{\cdot}\mathbf{N\text{-}1}{\subset}\mathbf{CB[8]}$ or $\mathbf{V}^{2+}{\cdot}\mathbf{N\text{-}2}{\subset}\mathbf{CB[8]}$, aliquots (2 mL) of an equimolar mixture of **N-1** (or **N-2**) and $\mathbf{V}^{2+}$ were titrated by adding microvolumes of a concentrated solution of **CB[8]**. Special care was taken to ensure that complete equilibration was attained and UV-Vis spectra were recorded. For $\mathbf{1}^{4+}$, a batch titration was required to ensure that all the sample did reach the equilibrium and thus favored the formation of the $\mathbf{1}^{4+}{\subset}(\mathbf{CB[8]})_2$ complex. The concentration of $\mathbf{1}^{4+}$ was fixed at 9.36×10^{-6} M and the ratio $[\mathbf{CB[8]}]_{tot}/[\mathbf{1}^{4+}]_{tot}$ was varied from 0 to 18.6. UV-Vis spectra were recorded from 230 to 800 nm on a Cary 300 (Varian) spectrophotometer maintained at 25.0(2) °C by the flow of a Haake NB 22 thermostat. The spectrophotometric data were processed using the Specfit program[27] which adjusts the stability constants and the corresponding extinction coefficients of the species formed at equilibrium. Specfit uses factor analyses to reduce the absorbance matrix and to extract the eigenvalues prior to the multi-wavelength fit of the reduced data set according to the Marquardt algorithm.[28]

Spectrofluorimetric titrations. For the spectrofluorimetric titrations, solutions were prepared in such concentrations to get absorbances smaller than 0.1 at wavelengths $\geq \lambda_{exc}$ in order to avoid any errors due to the inner filter effect. Moreover, the excitation wavelengths correspond to isosbestic points, where both complexed and uncomplexed species exhibit the same molar absorption coefficient. The excitation wavelengths were set at 325(1) nm and 327(1) nm for **N-1** and **N-2**, respectively. An aliquot (2 mL) of an equimolar mixture of **N-1** (or **N-2**) and $\mathbf{V}^{2+}$ ([**N-1**] = [$\mathbf{V}^{2+}$] = 1.51×10^{-5} M and [**N-2**] = [$\mathbf{V}^{2+}$] = 1.73×10^{-5} M) was introduced into a 1 cm Hellma quartz optical cell. Microvolumes of a concentrated solution of **CB[8]** were added, and the $[\mathbf{CB[8]}]_{tot}/[\mathbf{N}/\mathbf{V}^{2+}]_{tot}$ ratios were varied from 0 to 5 for **N-1** (from 0 to 2.9 for **N-2**).

The formation of the ternary complexes was evidenced by the quenching of the fluorescence centered on **N-1** or **N-2**. After each addition, special care was taken to ensure that complete equilibration had been attained. The luminescence spectra were recorded from 300 to 600 nm on a Perkin-Elmer LS-50B instrument maintained at 25.0(2) °C by the flow of a Haake FJ thermostat. The excitation and emission bandwidths were set at 5 nm for the ternary complex with **N-1** and at 6 nm for that with **N-2**. The source was a pulsed xenon flash lamp with a pulse width at half peak height <10 μs and power equivalent to 20 kW. Fluorescence quantum yields were determined relative to fluorescent standard quinine sulfate ($\Phi_{abs} = 0.546$ in 0.5 M H_2SO_4) with the possibility of correcting for differences between the refractive index of the reference n_r, and the sample solutions n_s using the expression:

$$\phi_f(s) = \phi_f(r)\frac{\int I_s(\lambda)D_r n_s^2}{\int I_s(\lambda)D_s n_r^2}$$

The indices s and r denote sample and reference, respectively. The integrals over I represent areas of the corrected emission spectra, D is the optical density at the wavelength of excitation. The spectrofluorimetric data were analysed using the Microcal Origin program.[29]

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25 Although $\mathbf{1}^{4+}$ contains two seemingly identical terminal viologen units, they are actually located in different chemical environments when in the presence of **CB[8]**. One terminal viologen unit forms an *end-to-interior loop* structure with the central π-electron donating dioxynaphthalene moiety, both of which are encircled by **CB[8]**, while the other viologen unit remains free. The free π-electron accepting viologen residue in $\mathbf{1}^{4+}\subset$**CB[8]** is able to bind an additional **CB[8]**. When compared with the **V**·2Cl model, the second binding event for $\mathbf{1}^{4+}\subset$**CB[8]** is considerably less favorable than that of its **V**·2Cl counterpart. The lower stability constant for $\mathbf{1}^{4+}\subset$**(CB[8])$_2$** is most likely a result of the fact that only one side of the free terminal viologen is available for inclusion in **CB[8]**, the other side being substituted by the bulky binary complex. This effect was not observed (or expected) in the **V**·2Cl model.

26 Under the experimental conditions (1 : 1 ratio **1**·4Cl : **CB[8]**, 1 mM in 0.1 M phosphate buffer, pH 7.0), the 2 : 1 complex is present in $<5\%$ on account of the low stability of $\mathbf{1}^{4+}\subset$**(CB[8])$_2$** (see Table 2).

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