CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201203483

Co-Conformational Isomerism in a Neutral Ion-Paired Supramolecular System

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Abstract: Two different counter-ion-free host–guest complexes have been prepared and isolated. These compounds were formed from two equally and opposite doubly-charged species, the viologen guests **1a**$^{2+}$ and **1b**$^{2+}$ and the *anti*-disulfodibenzo[24]crown-8 [**DSDB24C8**]$^{2-}$ host, which gave rise to the 1:1 neutral complexes [**1a⋅DSDB24C8**] and [**1b⋅DSDB24C8**]. These species are held together by hydrogen bonding and π stacking, as well as strong electrostatic interactions. The investigation of these neutral ion-paired supramolecular systems in solution and in the solid state allowed us to establish their co-conformational preferences. Compound [**1a⋅DSDB24C8**], with small methyl groups as substituents on the viologen unit, may adopt three different geometries, 1) an *exo* nonthreaded, 2) a partially threaded, and 3) a threaded arrangement, depending on the relative spatial orientation between the host and guest: The partially-threaded structure is preferred in solution and in the solid state. The presence of bulky *tert*-butylbenzyl groups in the viologen moiety in compound [**1b⋅DSDB24C8**] restricts the possible geometrical arrangements to one: The *exo* nonthreaded arrangement. This structure was confirmed in the solid state by X-ray crystallography. The stability of the neutral complexes in solution was determined by UV/Vis spectrophotometry. The stoichiometry of the complexes was established by continuous variation experiments, and overall equilibrium constants and Δ$G°$ values were determined on the basis of dilution experiments. The results observed are a consequence of only the intrinsic stability of the complexes as there are no additional contributions from counter ions.

Keywords: conformation analysis · counter-ion effects · host–guest systems · molecular recognition · supramolecular chemistry

Introduction

The preparation of precise structural molecular ensembles requires the fine design of the molecular components, taking into consideration all possible modes of interaction between them.[1] Some of the most widely investigated supramolecular ensembles are based on viologen derivatives as cationic guests and various kinds of hosts, such as cucurbiturils,[2] cyclodextrins,[3] calixarenes,[4] pillar-arenes,[5] and, in particular, crown ethers.[6]

Because of the ionic nature of many hosts and guests, it is necessary to consider the role played by counter ions in the molecular recognition process and also their possible effect on the association constants.[7] In particular, the association between dibenzo[24]crown-8 (**DB24C8**) and methyl viologen bis(hexafluorophosphate) in acetone has proven to be quite complex.[8,9]

In addition to counter-ion effects, co-conformational isomerism[10] can also contribute to the behavior observed in solution, affecting chemical shifts in NMR spectra and absorption bands in electronic spectroscopy. An example of this behavior was reported by Gibson et al. for the interaction between **DB24C8** and benzylammonium derivatives analyzed by NMR spectroscopy; changes in the ^{1}H chemical shifts of uncomplexed benzylammonium were observed upon mixing the two reagents and attributed to a non-pseudorotaxane *exo*-type complexation with the crown ether.[11] However, a few years later, the same group provided a different explanation based exclusively on ion pairing.[12] Clearly, a new approach must be taken to discriminate between these two effects in solution, along with a careful selection of the host and guest components in the supramolecular complex.

On the other hand, we recently reported neutral [2]pseudorotaxanes based on 1,2-bis(pyridinium)ethane linear dications and a macrocyclic anionic crown ether, *anti*-disulfodibenzo[24]crown-8 [**DSDB24C8**]$^{2-}$, which contains two pendant sulfonate (SO_3^-) functionalities.[13] An increment of two orders of magnitude in the association constant was observed with respect to the neutral analogue of the macrocycle, allowing the formation of stable complexes even in highly competitive solvents such as methanol and water. This observation was explained by significant electrostatic interactions between host and guest. Similar behavior

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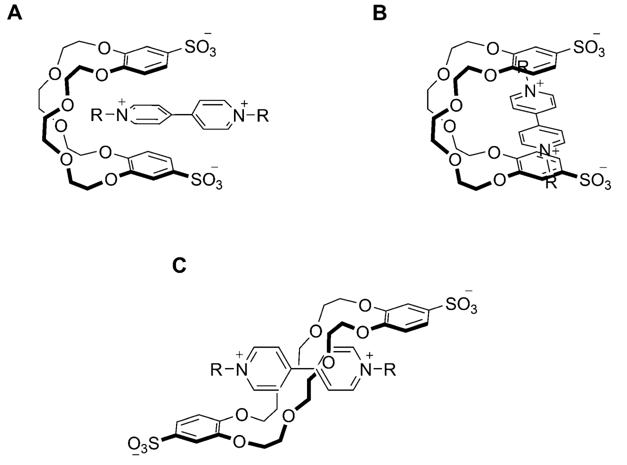
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201203483.

was observed by Nikitin and co-workers in a related system based on viologens and dianionic crown ether derivatives of bis-*p*-phenylene[34]crown-10.[14]

In this work, we proposed separating counter-ion effects from co-conformational issues by studying counter-ion-free neutral complexes formed with ionic components, that is, neutral ion-paired supramolecular systems, taking advantage of the strong electrostatic interactions associated with this kind of system in addition to other noncovalent interactions such as hydrogen bonding and π stacking. Based on our previous experience, we chose a dicationic viologen derivative and dianionic crown ether $[\textbf{DSDB24C8}]^{2-}$ as components of the complex. A comprehensive analysis of this supramolecular system provides three possible geometrical arrangements (Scheme 1).

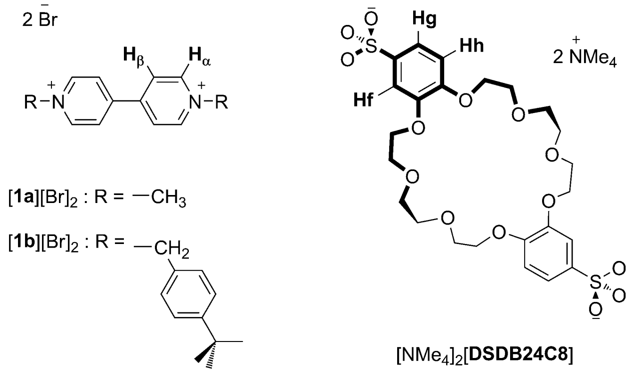


Scheme 1. Possible co-conformational isomers of the neutral 1:1 counter-ion-free complexes formed between viologen derivatives and **DSDB24C8** in solution. Co-conformer **A** = partially threaded, **B** = *exo* nonthreaded, and **C** = fully threaded structures.

Co-conformer **A** represents a partially threaded arrangement in which one of the viologen substituents is located in the center of the host cavity, which adopts a C-type conformation. This particular arrangement results in the shielding of one of the pyridinium rings by the two sulfonated catechol rings. A similar conformation has been observed in the crystal structure of the 2:1 complex formed between methyl viologen and the neutral **DB24C8**.[9] Co-conformer **B** corresponds to an *exo* nonthreaded structure in which the viologen guest is rotated by 90° with respect to its analogue in co-conformer **A**; this is similar to the taco complex reported by Gibson and co-workers, although with a different crown ether.[15] Finally, co-conformer **C** represents the fully threaded arrangement, similar to the topologically interpenetrated structure recently reported by Liu and co-workers in which a methyl viologen penetrates into the cavity of a tetrasulfo-bis-*m*-phenylene[26]crown-8 along the vertical direction to form a [2]pseudorotaxane.[16]

Results and Discussion

Electroneutral complexes: To eliminate any counter-ion effect, we isolated complex [**1a·DSDB24C8**] as an electroneutral salt. This complex was synthesized by a metathesis reaction between the bromide salt [**1a**]$[Br]_2$ and $[NMe_4]_2$[**DSDB24C8**] in water (Scheme 2). Yellow crystals of [**1a·DSDB24C8**] were obtained in good yield by slow evaporation of the solvent and characterized by ^{1}H NMR spectroscopy, UV/Vis spectrophotometry, HRMS (ESI-TOF), and single-crystal X-ray diffraction analysis. Although the components [**1a**]$[Br]_2$ and $[NMe_4]_2$[**DSDB24C8**] are both colorless, the isolated complex [**1a·DSDB24C8**] gives a bright-yellow color in methanol solution ($\lambda_{max} = 380$ nm), which indicates the formation of a charge-transfer complex between the viologen and crown ether.



Scheme 2. Structures of the viologen bromides [**1a**]$[Br]_2$ and [**1b**]$[Br]_2$, and the disulfonated crown ether, *anti*-$[NMe_4]_2$[**DSDB24C8**].

The appearance of color is accompanied by changes in the chemical shifts in the ^{1}H NMR spectrum compared with those of the parent components (Figure 1). Only a single set of resonances is observed, which reveals fast exchange dynamics for the association/dissociation process on the NMR timescale. The observed averaged aromatic signals of the complex, compared with the nonassociated species, are shifted towards lower frequencies (H_α: $\Delta\delta = -0.3$ ppm; H_β: $\Delta\delta = -0.9$ ppm), characteristic of aromatic stacking and consistent with the formation of a charge-transfer complex. In contrast, the methyl signal is shifted to a higher frequency (CH_3: $\Delta\delta = +0.1$ ppm), which suggests that these protons are involved in hydrogen bonding. Moreover, a NOESY experiment (see the Supporting Information) revealed through-space coupling between methyl protons on the viologen guest and methylene protons on the crown ether host, indicative of the spatial proximity of the guest methyl group and the crown ether cavity, in agreement with C−H···O hydrogen bonding. These results support co-conformation **A** as the preferred geometry of [**1a·DSDB24C8**] in solution.

A 1.0 mM aqueous solution of [**1a·DSDB24C8**] was studied by electrospray mass spectrometry. The mass spectrum shows *m*/*z* peaks corresponding to a sodium adduct of the

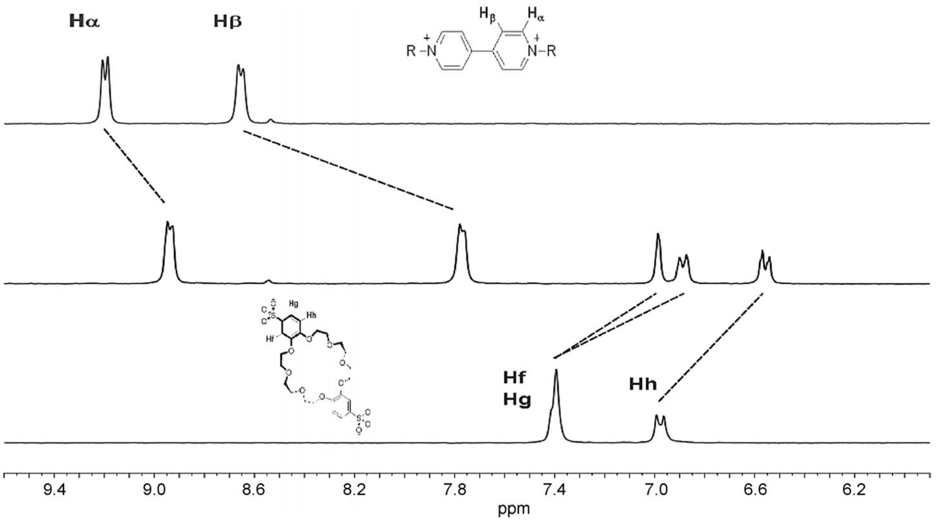


Figure 1. ^{1}H NMR spectra (300 MHz, [D$_4$]methanol, 298 K) of [**1a**][Br]$_2$ (top), [NMe$_4$]$_2$[**DSDB24C8**] (bottom), and [**1a·DSDB24C8**] (middle) at 2 mM.

crown ether [H$_2$**DSDB24C8**+Na]$^+$ (exptl: *m*/*z* 631.1113; calcd: *m*/*z* 631.1126) and the 1:1 complex [**1a·DSDB24C8**+H]$^+$ (exptl: *m*/*z* 793.2295; calcd: *m*/*z* 793.2306), which proves that binding interactions exist between the host and guest in the gas phase (see the Supporting Information). Both the NMR and MS analyses support the formation of a 1:1 neutral supramolecular complex. This was also confirmed by single-crystal X-ray diffraction analysis.

Suitable crystals for X-ray diffraction analysis were obtained by slow evaporation of a saturated aqueous solution of [**1a·DSDB24C8**]. The solid-state structure confirms the 1:1 stoichiometry of the supramolecular complex in which the only ions present are those of the host and guest, thereby proving the electroneutral nature of the association complex (Figure 2). The host–guest complex adopts a partially threaded arrangement (co-conformer **A**) in which the methyl group of the viologen guest occupies the center of the crown ether cavity and weakly interacts with the most basic oxygen atoms (C···O distances varies from 3.37 to 3.44 Å; C−H···O angles varies from 132 to165°). The crown ether adopts a C-type conformation, which favors the interaction between the two electron-rich sulfonated catechol rings and only one of the electron-deficient pyridinium rings of the methyl viologen through face-to-face π-stacking interactions (av 3.7 Å). The expected torsion of the second pyridinium ring is observed (37.7°).

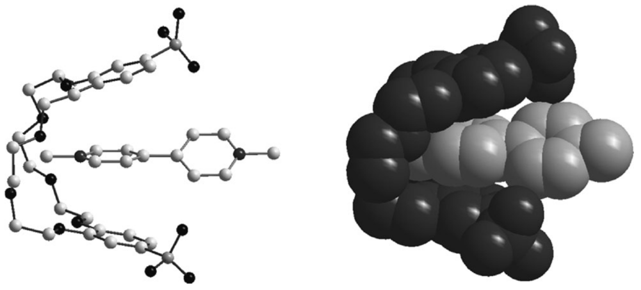


Figure 2. Ball-and-stick and space-filling representations of the X-ray structure of complex [**1a·DSDB24C8**] in the solid state. The complex adopts a partially threaded geometry (co-conformer **A**). C = light gray; S = mid gray; N = gray; O = black.

The analyzed crystal belongs to the triclinic space group $P\bar{1}$ with one crown ether, one methyl viologen, and seven water molecules per asymmetric unit.[17] The presence of seven water molecules was confirmed by the 13.6% weight loss observed by thermogravimetric analysis (see the Supporting Information).

In fact, although the methyl viologen guest forms a 1:2 dicationic complex with the neutral crown ether dibenzo[24]crown-8 in the solid state,[9] in the electroneutral complex [**1a·DSDB24C8**], only one dicationic guest and one dianionic host are needed to form a stable association complex with a 1:1 stoichiometry.

So far we have established the existence of a neutral ion-paired association complex for [**1a·DSDB24C8**] in the solid state and in solution that adopts the partially threaded co-conformation **A**. To determine its relative stability in solution, we undertook ^{1}H NMR titration experiments (see the Supporting Information). Unexpectedly, the results were not conclusive, mainly because different association constants were obtained depending on which proton was used for evaluation purposes; something similar occurred when continuous variation experiments, also based on ^{1}H NMR data, were performed. It is widely known that the existence of simultaneous equilibria can affect these kinds of measurements.[18] Thus, we hypothesized that the NMR signal-dependency of the association constants could be due to the presence of minor amounts of other co-conformational isomers of [**1a·DSDB24C8**] co-existing in solution with co-conformer **A**, thereby affecting the observed chemical shifts and hindering the direct determination of the association constant by ^{1}H NMR spectroscopy.

To confirm the hypothesis that other co-conformational isomers exist in solution, especially co-conformer **B**, we decided to investigate another viologen derivative bearing bulkier groups at both ends of the molecule, namely guest **1b**$^{2+}$ with *tert*-butylbenzyl substituents (Scheme 2). With the same host, the steric hindrance at the ends of the viologen unit would prevent the formation of the threaded (co-conformer **C**) and partially threaded (co-conformer **A**) geometries, and therefore only co-conformer **B** would exist.

The electroneutral complex [**1b·DSDB24C8**] was synthesized in a similar way to [**1a·DSDB24C8**] and again characterized by ^{1}H NMR spectroscopy, UV/Vis spectrophotometry, and HRMS (ESI-TOF) (see the Supporting Information). The yellow color of the complex in methanol solution ($\lambda_{max} = 415$ nm) and the changes in the chemical shifts in the ^{1}H NMR spectrum in [D$_4$]methanol indicate the formation of a charge-transfer complex with fast exchange dynamics on the NMR timescale. The aromatic signals (H_α: $\Delta\delta = -0.2$ ppm; H_β: $\Delta\delta = -0.4$ ppm) as well as the benzyl signal (-CH$_2$-: $\Delta\delta = -0.1$ ppm) are shifted towards lower frequencies, which suggests that aromatic stacking is the predominant interaction between the host and guest and is consistent with the proposed spatial arrangement of co-conformer **B**. Further proof of the different geometrical arrangements of complexes [**1a·DSDB24C8**] and [**1b·DSDB24C8**] in solution was obtained from ^{1}H NMR titration experiments: The shielding effect caused by aromatic stacking of the sulfonated catechol rings in the host and the pyridinium rings in both guests is quite different. This is especially clear for proton H_β (Figure 3). Although the initial chemical shifts of this proton in both guests are practically the same, there is a pronounced shift of $\Delta\delta = 1.7$ ppm in the case of [**1a·DSDB24C8**] and only $\Delta\delta = 0.5$ ppm for [**1b·DSDB24C8**] after the addition of 6 equivalents of the host.

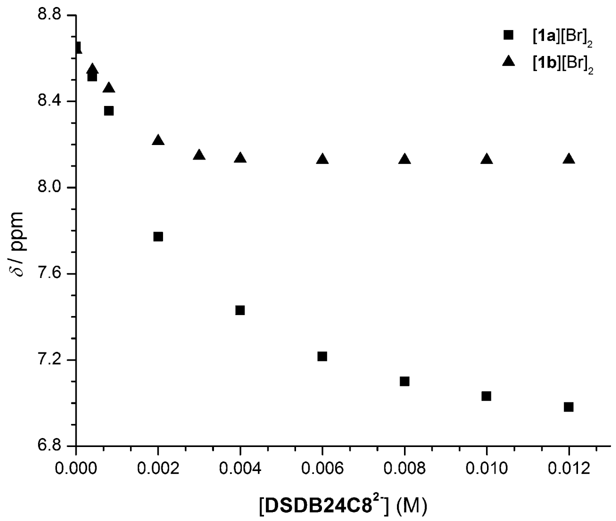


Figure 3. ^{1}H NMR (300 MHz, [D$_4$]methanol, 298 K) chemical shifts for H_β in titration experiments of guest solutions of [**1a**][Br]$_2$ and [**1b**][Br]$_2$ (both 2 mM) with host [NMe$_4$]$_2$**DSDB24C8**.

The NMR, UV/Vis, and MS data point towards the existence of [**1b·DSDB24C8**] as a 1:1 complex in solution with co-conformer **B** as the only possible geometry. After several attempts, we finally managed to grow single crystals from an aqueous solution of [**1b**][Br]$_2$ and *syn*/*anti*-[NMe$_4$]$_2$-[**DSDB24C8**].[19] Although the isolated crystals were of low quality, they allowed us to establish that the complex has an *exo* nonthreaded structure in the solid state, that is, it exists as co-conformer **B** (Figure 4).

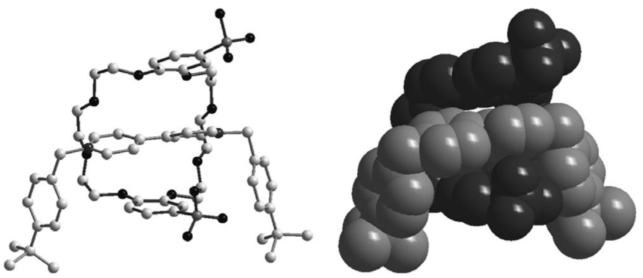


Figure 4. Ball-and-stick and space-filling representations of the X-ray structure of complex [**1b**·*syn*-**DSDB24C8**]. The complex adopts a nonthreaded geometry (co-conformer **B**). C = light gray; S = mid gray; N = gray; O = black.

Stability of the neutral complexes in solution: Due to the lack of reliability of the relative stability of complexes [**1a·DSDB24C8**] and [**1b·DSDB24C8**] determined in solution by using NMR data, we turned to electronic absorption spectroscopy. By using this technique we would be able to obtain reliable data regardless of the co-conformers present in solution.

As expected, the UV/Vis spectra of electroneutral complexes [**1a·DSDB24C8**] and [**1b·DSDB24C8**] in methanol show intermolecular charge-transfer bands at 380 and 415 nm, respectively, associated with the electronic interaction between electron-rich catechol units in the crown ether and electron-poor pyridinium rings in the viologen guests $\mathbf{1a}^{2+}$ and $\mathbf{1b}^{2+}$. To corroborate the stoichiometries of the complexes in solution, continuous variation experiments were performed. In both cases, a maximum molar ratio was observed at 0.5 (Figure 5), which confirms the 1:1 stoichiometries determined by single-crystal X-ray diffraction and mass spectrometry.

So far we have demonstrated that the neutral supramolecular complexes [**1a·DSDB24C8**] and [**1b·DSDB24C8**] both exist in a 1:1 stoichiometry with the association/dissociation equilibrium shown in Equation (1). Their dissociation guarantees an equimolar solution of host and guest.

$$[\mathbf{1}\cdot\mathbf{DSDB24C8}] \rightleftharpoons \mathbf{1}^{2+} + \mathbf{DSDB24C8}^{2-}$$
$$K_d = \frac{[\mathbf{1}^{2+}][\mathbf{DSDB24C8}^{2-}]}{[\mathbf{1}\cdot\mathbf{DSDB24C8}]} \tag{1}$$

Dissociation constants using equimolar solutions of host and guest were determined by using Equation (2), which is based on the Beer–Lambert and mass action laws, and was adapted from a method previously reported by Ray.[20] For a complete demonstration, see the Supporting Information.

$$\frac{c_o}{A_{obs}} = \left(\frac{K_d}{\varepsilon l}\right)^{1/2}\frac{1}{A_{obs}^{1/2}} + \frac{1}{\varepsilon l} \tag{2}$$

In Equation (2), C_o represents the nominal concentration of the electroneutral salt [**1a·DSDB24C8**] or [**1b·DSDB24C8**], A_{obs} is the absorbance at λ_{max}, K_d is the global dissociation constant for the 1:1 complex in solution, ε is the extinction coefficient of the charge-transfer band, and l is the optical path length, which is 1 cm. The slope of a

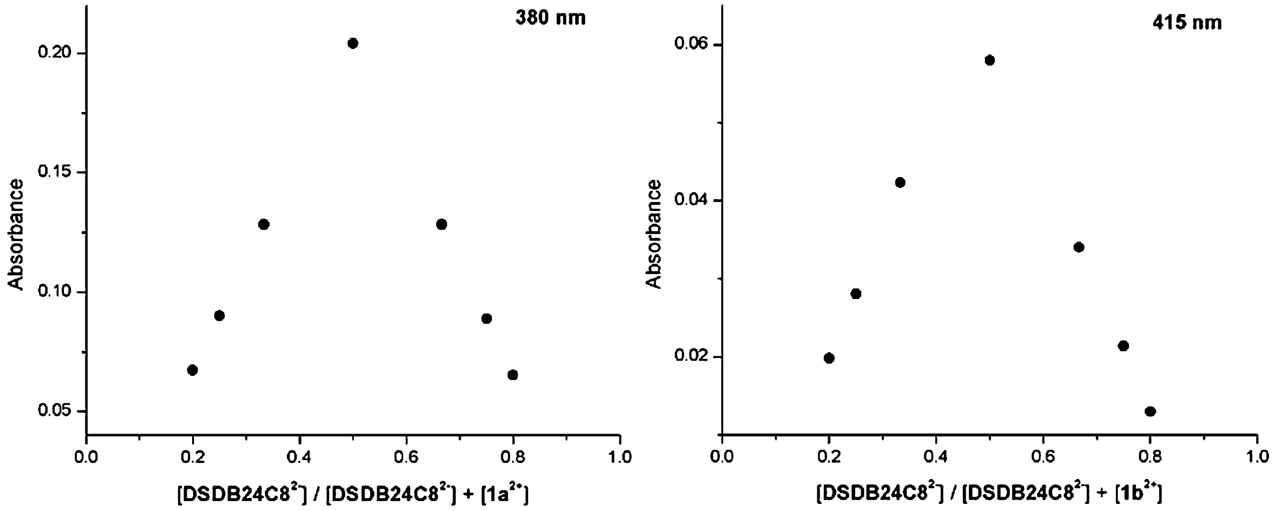


Figure 5. Job plots for complexes [**1a·DSDB24C8**] ($\lambda_{max}=380$ nm) and [**1b·DSDB24C8**] ($\lambda_{max}=415$ nm) in methanol.

plot of C_o/A_{obs} against $1/(A_{obs})^{1/2}$ yields $(K_d/\varepsilon l)^{1/2}$ and the intercept is equivalent to $1/\varepsilon l$.

We designed and performed dilution experiments for [**1a·DSDB24C8**] and [**1b·DSDB24C8**] in methanol in the concentration ranges 2–0.2 and 3–0.3 mM, respectively. Linear plots of C_o/A_{obs} against $1/(A_{obs})^{1/2}$ are shown in Figure 6 with correlation coefficients of 0.9960 and 0.9975, respectively. The dissociation constants and ε values were obtained from these plots; the association constant, K_a, is simply the inverse of the dissociation constant, K_d. The association constants and extinction coefficients determined for complexes [**1a·DSDB24C8**] and [**1b·DSDB24C8**], and their corresponding ΔG° values, are summarized in Table 1.

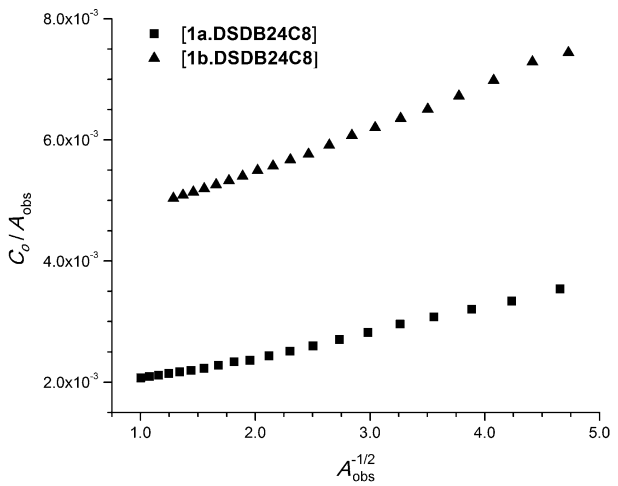


Figure 6. Linear plots of C_o/A_{obs} against $1/(A_{obs})^{1/2}$ for different concentrations of complexes [**1a·DSDB24C8**] and [**1b·DSDB24C8**].

Table 1. Comparison of the extinction coefficients, association constants, and free energies of association for the complexes formed between host **DSDB24C8**$^{2-}$ and guests **1a**$^{2+}$ and **1b**$^{2+}$.[a]

	ε [10^2 M^{-1} cm^{-1}][b]	K_a [10^3 M^{-1}]	ΔG° [kJ mol^{-1}][c]
[**1a·DSDB24C8**]	6.2 ± 0.1	9.8 ± 1.6	−22.8 ± 0.2
[**1b·DSDB24C8**]	2.5 ± 0.1	8.1 ± 1.9	−22.3 ± 0.2

[a] All values were determined by UV/Vis absorption spectrophotometry at 298 K in methanol. The errors were obtained as reported by Nygaard et al. (see ref. [21]). [b] $\lambda_{max}=380$ and 415 nm for [**1a·DSDB24C8**] and [**1b·DSDB24C8**], respectively. [c] $\Delta G° = -nRT\ln K$ ($T=298$ K).

The association constants determined for these complexes are several orders of magnitude higher than those reported for related systems with neutral crown ethers in acetone or acetonitrile.[8,9,22] This is probably due to a number of noncovalent interactions being enhanced by electrostatic cooperative effects.[13] Note that the results are a consequence of only the intrinsic stability of the complexes as there are no additional contributions from counter ions.

Although complex [**1b·DSDB24C8**] can only form a nonthreaded structure, that is, co-conformer **B**, its ΔG° value indicates that it is fairly stable in solution. Unfortunately, the association constants for [**1a·DSDB24C8**] and [**1b·DSDB24C8**] cannot be directly compared due to the different nature of the guests. However, it seems reasonable to consider that complex [**1a·DSDB24C8**] exists in solution predominantly as co-conformer **A** with a smaller quantity of co-conformer **B**. So far, no direct experimental evidence for the presence of co-conformer **C** has been obtained.

Conclusions

We have demonstrated that it is possible to eliminate counter-ion effects in solution and in the solid state by isolating two neutral ion-paired supramolecular systems formed from two equally and opposite doubly-charged species, the viologen guests **1a**$^{2+}$ and **1b**$^{2+}$ and the *anti*-disulfodibenzo[24]-crown-8 [**DSDB24C8**]$^{2-}$ host. The components of the two complexes are held together by hydrogen bonding and π stacking as well as strong electrostatic interactions.

These counter-ion-free complexes stay almost completely associated in methanol solutions ($K_a \approx 1\times10^4\,\text{M}^{-1}$), which allowed us to investigate their co-conformational equilibria. With small groups as substituents in the viologen, such as methyl, we proved the co-existence of two co-conformations, namely partially threaded and *exo* nonthreaded arrangements. With bulky substituents in the viologen, such as *tert*-butylbenzyl groups, the number of co-conformations is restricted to just one, the *exo* nonthreaded arrangement. These results should allow a more specific design of supramolecular ensembles leading to better structural control.

The results presented herein suggest that neutral ion-paired supramolecular complexes allow the intrinsic stability and structural features to be determined in the absence of interfering counter ions. Further work in this direction is in progress.

Experimental Section

General methods: Dicationic guests [**1a**][Br]$_2$ and [**1b**][Br]$_2$ were synthesized by direct alkylation of 4,4′-bipyridine with the corresponding alkyl or benzyl derivative. Dianionic host [NMe$_4$]$_2$[**DSDB24C8**] was prepared and isolated as its *anti* isomer according to a published method.[13] All reactions were carried out in air and solvents were used without any prior purification. ^{1}H NMR spectra were recorded on a Bruker DP300 spectrometer at 300.1 MHz, locked to the deuterated solvent. High-resolution mass spectra were obtained on an Agilent G1969A electrospray-ionization time-of-flight mass spectrometer. UV/Vis spectra were recorded on an Agilent 8453A spectrophotometer. Thermogravimetric analysis was performed with a TA Instruments Q500 Thermogravimetric Analyzer.

Synthesis of [1a·DSDB24C8]: Guest compound [**1a**][Br]$_2$ (0.053 g, 0.15 mmol) was dissolved in water (15 mL) to afford a colorless solution. Host compound [NMe$_4$]$_2$[**DSDB24C8**] (0.117 g, 0.15 mmol) was added to the solution, which immediately turned yellow. This solution was heated at 80 °C for 1 h with stirring. Yellow crystals were removed by filtration after 4 days of slow evaporation of the solvent and washed with cold water (3×2 mL) to yield [**1a·DSDB24C8**] as yellow crystals (0.102 g, 0.13 mmol, 87 %). ^{1}H NMR (300 MHz, [D$_4$]methanol, 25 °C, TMS): δ = 8.93 (d, ^2J(H,H) = 6 Hz, 4H; H$_\alpha$), 7.73 (d, ^2J(H,H) = 6 Hz, 4H; H$_\beta$), 6.98 (s, 2H; H$_f$), 6.88 (d, ^2J(H,H) = 6 Hz, 2H; H$_g$), 6.55 (d, ^2J(H,H) = 6 Hz, 2H; H$_h$), 4.58 (s, 6H; CH$_3$), 4.01–3.89 ppm (m, 24H; CH$_2$); HRMS (ESI-TOF+): *m*/*z* calcd for $C_{36}H_{45}N_2O_{14}S_2^+$: 793.2306 [*M*+H]$^+$; found: 793.2295.

Synthesis of [1b·DSDB24C8]: Guest compound [**1b**][Br]$_2$ (0.10 g, 0.16 mmol) was dissolved in hot water (50 mL) to afford a colorless solution. Host compound [NMe$_4$]$_2$[**DSDB24C8**] (0.12 g, 0.16 mmol) was added to the solution, which immediately turned orange. This solution was heated at 80 °C for 1 h with stirring. Orange crystals were removed by filtration after 4 days of slow evaporation of the solvent and washed with cold water (3×2 mL) to yield [**1b·DSDB24C8**] as orange crystals (0.155 g, 0.15 mmol, 94 %). ^{1}H NMR (300 MHz, [D$_4$]methanol, 25 °C, TMS): δ = 9.14 (d, ^2J(H,H) = 6 Hz, 4H; H$_\alpha$), 8.13 (d, ^2J(H,H) = 6 Hz, 4H; H$_\beta$), 7.64 (s, 8H; Ar-H), 7.00 (d, ^2J(H,H) = 6 Hz, 2H; H$_g$), 6.58 (s, 2H; H$_f$), 6.13 (d, ^2J(H,H) = 6 Hz, 2H; H$_h$), 5.85 (s, 4H; N$^+$-CH$_2$), 3.91–3.42 (m, 24H; CH$_2$), 1.34 ppm (s, 18H; *t*Bu); HRMS (ESI-TOF-): *m*/*z* calcd for $C_{56}H_{67}N_2O_{14}S_2^-$: 1055.4039 [*M*-H]$^-$; found: 1055.4028.

Single-crystal X-ray diffraction: Single crystals were grown by slow evaporation of saturated aqueous solutions of the complexes. X-ray diffraction data were collected at 298 K on an Enraf–Nonius Kappa diffractometer fitted with a CCD-based detector by using Mo$_{K\alpha}$ radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97-2. Least-squares refinement based on F^2 was carried out by the full-matrix method of SHELXL-97-2.[23] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and refined with an isotropic fixed thermal parameter by using a riding model. Neutral atom scattering factors and anomalous dispersion corrections were taken from International Tables for Crystallography.[24] Molecular structure drawings were generated by using DIAMOND for Windows.[25]

X-ray crystallographic data for [1a·DSDB24C8]: Chemical formula: $C_{36}H_{48}N_2O_{21}S_2$, M_w = 908.88, T = 293(2) K, Mo$_{K\alpha}$ radiation (0.71073 Å), triclinic, $P\bar{1}$, a = 12.006(2), b = 14.099(3), c = 14.310(3) Å, α = 77.73(3), β = 85.60(3), γ = 70.72(3)°, V = 2234.2(8) Å^3, Z = 2, ρ_{calcd} = 1.351 g cm^{-3}, μ = 0.200 mm^{-1}, F(000) = 956, yellow, 0.34×0.25×0.09 mm^3, Enraf–Nonius Kappa diffractometer, 27353 independent reflections, 7584 with $I > 2\sigma$, min. and max. transmission: 0.9352 and 0.9823, 5 restraints, 568 parameters, $R1$ = 0.0959, $wR2$ = 0.2562 [$I > 2\sigma$], $R1$ = 0.1241, $wR2$ = 0.2845 [all data], GOF = 1.042, largest diff. peak and hole: 0.89 and −0.76 e Å^{-3}.

X-ray crystallographic data for [1b·DSDB24C8]: Chemical formula: $C_{56}H_{68}N_2O_{17}S_2$, M_w = 1105.24, T = 293(2) K, Mo$_{K\alpha}$ radiation (0.71073 Å), triclinic, $P\bar{1}$, a = 12.7187(6), b = 13.1703(7), c = 21.8508(14) Å, α = 77.247(2), β = 89.403(2), γ = 66.612(4)°, V = 3264.4(3) Å^3, Z = 2, ρ_{calcd} = 1.124 g cm^{-3}, μ = 0.143 mm^{-1}, F(000) = 1172, yellow, 0.43×0.25×0.20 mm^3 crystal, Bruker Enraf–Nonius Kappa diffractometer, 10736 independent reflections, 8562 with $I > 2\sigma$, min. and max. transmission: 0.9409 and 0.9719, 0 restraints, 695 parameters, $R1$ = 0.2115, $wR2$ = 0.4974 [$I > 2\sigma$], $R1$ = 0.2808, $wR2$ = 0.5280 [all data], GOF = 1.865, largest diff. peak and hole: 1.08 and −0.54 e Å^{-3}.

CCDC-903399 [**1a·DSDB24C8**] and CCDC-903400 [**1b·DSDB24C8**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was financially supported by CONACYT (Project No. 128419). We thank Marco Leyva for his assistance in obtaining X-ray data, Geiser Cuellar for HRMS measurements and Myriam Campos for thermogravimetric analyses.

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Received: September 29, 2012