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A study of the interaction between inverted cucurbit[6]uril and symmetric viologens

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Abstract: The interaction between inverted cucuribit[6]uril (*i*Q[6]) and a series of symmetric viologens bearing aliphatic substituents, namely dicationic dialkyl-4,4′-bipyridinium guests where the alkyl substituent is $CH_3(CH_2)_n$ (n = 1, 3 and 5) or benzyl, has been studied in aqueous solution by ^{1}H NMR spectroscopy, electronic absorption spectroscopy, Isothermal Titration Calorimetry and mass spectrometry. The viologen bearing $C_6H_5CH_2$ substituents has also been investigated. In the case of the dialkyl-derived guests, single crystal X-ray diffraction, on crystals grown in the presence of $CdCl_2$, revealed the compositions to be $2(C_{36}H_{36}N_{24}O_{12})$, $4(C_{14}H_{18}N_2)$,$Cd_5Br_{9.56}Cl_{10.44}2(H_2O).2(H_3O)$; $2(C_{36}H_{36}N_{24}O_{12})$,$C_{18}H_{26}N_2$,$2(CdCl_4)$,$36H_2O$ and $2(C_{36}H_{36}N_{24}O_{12})$,$2(C_{11}H_{17}N)$,$2(CdCl_4)$,$20H_2O$ for the use of n = 1, 3 or 5 respectively. Thus, in the solid state, in the case of both BV^{2+} (n = 3) and HV^{2+} (n = 5), an interaction of viologen with *i*Q[6] was observed and the structure adopted is an external 'dumbbell-type' structure.

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Introduction

Despite the attention that cucurbit[n]urils (Q[*n*]s) are receiving, [1] reports relating to the inverted cucurbit[n]urils (*i*Q[*n*]s) are far more scant. [2, 3] We have embarked upon a programme to investigate the host-guest/inclusion properties of *i*Q[*n*]s, and recently reported the ability of *i*Q[7] to include viologens, namely α,ω-alkyldiammonium guests. [3] In that study, *i*Q[7] was found, in aqueous solution, to partially encapsulate the viologen when R = H, CH_3 or CH_2CH_3 forming 1:1 binary inclusion complexes. By contrast, the use of longer R groups led to 2:1 tertiary complexes with alkyl groups embedded in the *i*Q[7] cavity. In the same study, the presence of $CdCl_2$ led to the formation of pseudorotaxanes for R = 4 and 7 in the solid state. We now extend our hostguest studies of inverted cucurbit[*n*]urils to the *i*Q[6] system, and report our observations on their interaction with dicationic dialkyl-4,4′-bipyridinium guests where the alkyl is $CH_3(CH_2)_n$ (n = 1, 3 and 5), as well as the viologen where the substituents are $C_6H_5CH_2$ (see chart 1). We note that other groups have reported the interaction of Q[*n*]s (n = 6, 7, 8 or 14) with viologens in recent work; [4] viologens are of potential use in electrochromic displays. [5]

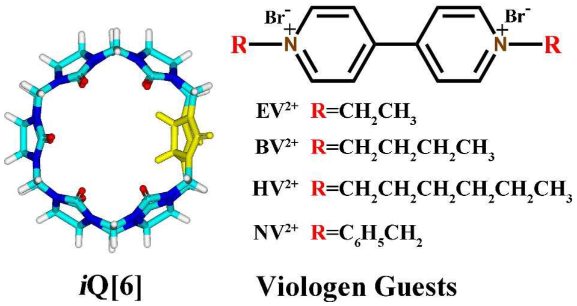

Chart 1. *i*Q[6] and the viologens used in this study.

Results and Discussion

The binding interactions between each of the viologen guests and *i*Q[6] can be conveniently monitored using ^1H NMR spectroscopic data recorded in 1M DCl solution, which is necessary due to the poor solubility in neutral D_2O solution. Figure 1 shows the changes observed in the spectrum of EV^{2+} as progressively larger amounts of *i*Q[6] are added to the solution. There is little evidence of any of the peaks shifting which is consistent with a lack of interaction between *i*Q[6] and the viologen EV^{2+}.

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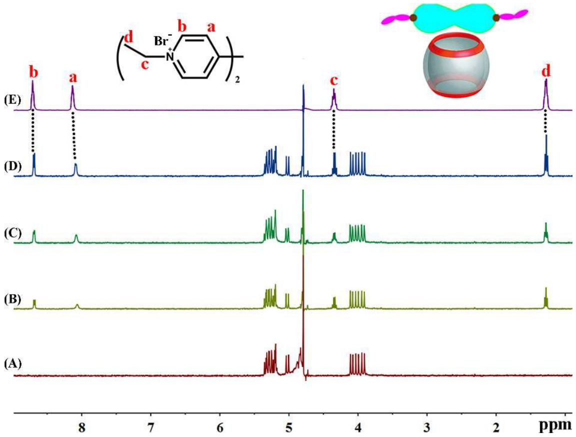

Figure 1. ^{1}H NMR spectra (400 MHz, D_2O) of *i*Q[6] (A) in the absence and in the presence of (B) 0.2, (C) 0.4, (D) 0.8 , (E) 1.1equiv of EV^{2+} and (F) neat EV^{2+} in 1M DCl at 20 °C.

In the case of BV^{2+} , as shown in Figure 2, only in neat viologen is a shift observed for the resonances (c – f) associated with the alkyl chains. This suggests that only under these conditions are the butyl chains included in the cavity of the host, with the bipyridinium nucleus remaining outside.

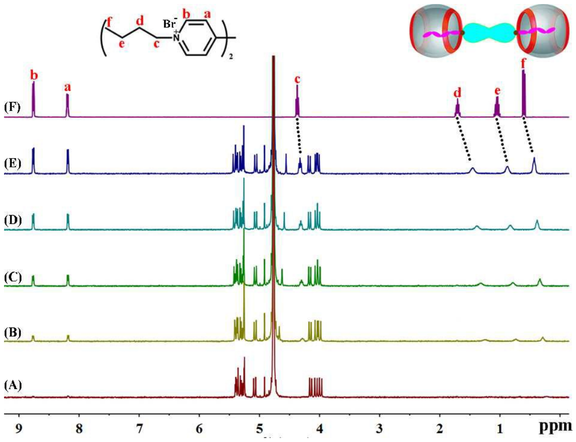

Figure 2. ^{1}H NMR spectra (400 MHz, D_2O) of *i*Q[6] (A) in the absence and in the presence of (B) 0.2, (C) 0.4, (D) 0.8 , (E) 1.1equiv of BV^{2+} and (F) neat BV^{2+} in 1M DCl at 20 °C.

The situation observed for HV2+ (Figure S1) is reminiscent of that for BV^{2+}, the only difference is that the aromatic protons exhibit a slight downfield shift. We propose these observations are again consistent with the formation of a 2:1 host-guest inclusion complex with the two *i*Q[6] molecules encapsulating the aliphatic chains. Interestingly, for *i*Q[7] with the same viologen, the shifts associated with the alkyl chains are more pronounced. [3]

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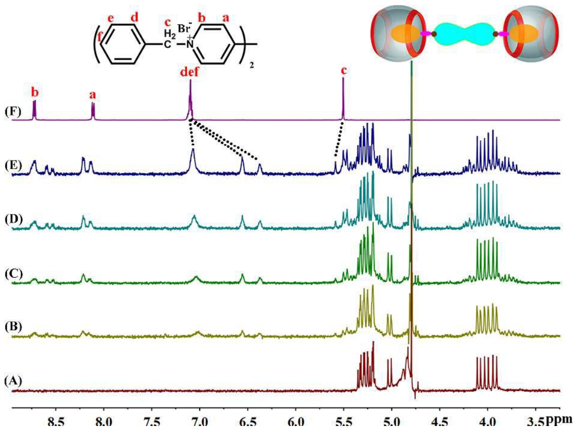

Figure 3. ^{1}H NMR spectra (400 MHz, D_2O) of *i*Q[6] (A) in the absence and in the presence of (B) 0.2, (C) 0.4, (D) 0.8 , (E) 1.1equiv of NV^{2+} and (F) neat NV^{2+} in 1M DCl at 20 °C.

^{1}H NMR spectroscopy was also used to monitor the binding behavior of *i*Q[6] with a viologen bearing $C_6H_5CH_2$ substituents guest NV^{2+} (Figure 3). The shifts associated with the $C_6H_5CH_2$ substituents suggest this portion of the viologen is included in the *i*Q[6] again forming a 2:1 host-guest complex. This is further confirmed by the COSY spectrum of the mixture between *i*Q[6] and NV^{2+} in 1M DCl (Figure S2, in the Supporting Information).

Mass spectrometry

Further evidence for the formation of the inclusion complexes of *i*Q[6] and guests EV^{2+}, BV^{2+}, HV^{2+} and NV^{2+} was provided by the MALDI-TOF mass spectrometry experiments. In their MALDI-TOF MS spectra (Figure 4), the major signals at m/z = 872.098, m/z = 1211.597, m/z=1239.778, and m/z=1245.707 were observed, corresponding to [*i*Q[6]+2EV $^{2+}$]$^{2+}$/2 (calculated 872.509), [2*i*Q[6]+BV^{2+}]$^{2+}$/2 (calculated 1211.928), [2*i*Q[6]+HV^{2+}]$^{2+}$/2 (calculated 1239.983) and [2*i*Q[6]+NV^{2+}]$^{2+}$/2 (calculated 1245.943). The intense signals provide direct support for the formation of the 2:1 stoichiometry of host–guest inclusion complexes 2*i*Q[6]@BV^{2+}, 2*i*Q[6]@HV^{2+} and 2*i*Q[6]@NV^{2+}.

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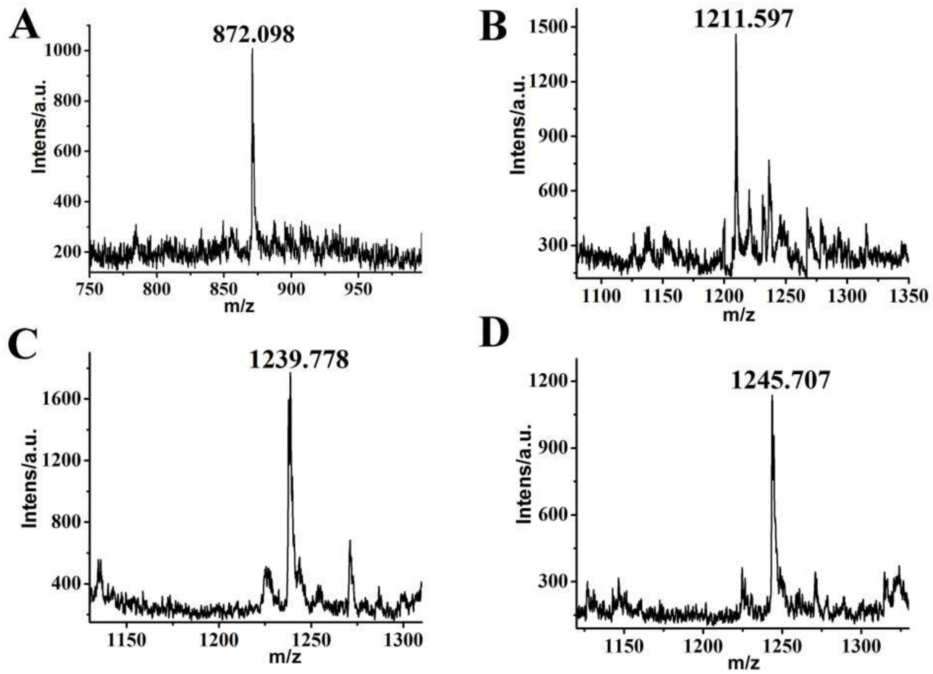

Figure 4. MALDI-TOF mass spectrometry of *i*Q[6]@2EV^{2+} (A), 2*i*Q[6]@BV^{2+} (B), 2*i*Q[6]@HV^{2+} (C) and 2*i*Q[6]@NV^{2+} (D).

UV spectroscopy

To further understand the binding of symmetric viologens to *i*Q[6], we also investigated, by UV-vis spectrometry, the interactions between *i*Q[6] and symmetric viologens. In Figure 5, the UV spectra shown were obtained in 0.1M HCl solutions containing a fixed concentration of viologens and variable concentrations of *i*Q[6]. On gradually increasing the *i*Q[6] concentration in the viologens solution, the absorption band of the guest BV^{2+} exhibits a progressively higher absorbance due to the formation of the host-guest complex 2*i*Q[6]@BV2+ . The absorbance vs. ratios of n(*i*Q[6])/n(BV^{2+}) data can be fitted to a 2:1 binding model. The alkyl moiety of the guests were encapsulated into the cavity of the *i*Q[6] host, generating a 2:1 host–guest inclusion complex. Similar changes in the absorption spectra of the guests HV^{2+} and NV^{2+} were observed as the *i*Q[6] concentration was increased. Thus, these the guests showed similar binding interactions with *i*Q[6] for which the alkyl moiety of the guests is embedded in the *i*Q[6] host. Nevertheless, the absorption band of the EV^{2+} exhibits near invariable absorbance as the ratio of n(*i*Q[6])/n(EV^{2+}) is increased, which is different to the absorption spectra observed for the guests BV^{2+} , HV^{2+} or NV^{2+} on increasing the *i*Q[6] concentration; these observations are

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consistent with the results of the NMR analysis.

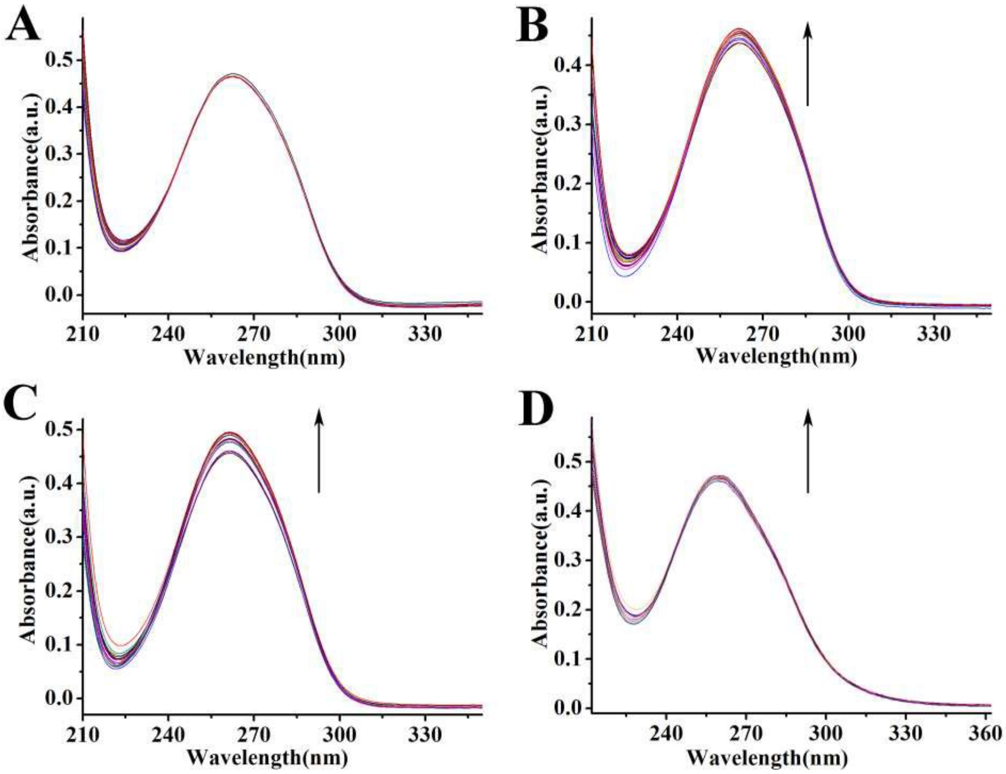

Figure 5. UV spectrum of EV^{2+} (A); BV^{2+} (B); HV^{2+} (C); NV^{2+} (D) at 2 × 10-5 mol L^{-1} upon addition of increasing amounts (0 0.2 0.4 0.6…3.8 4.0 equiv.) of *i*Q[6] with an excitation of 262 nm.

Molecular structures

In the structures, it was not possible to locate hydrogen atoms attached to water. However, the central oxygen atoms can be reliably located. In some of the structures, it is necessary to include H_3O^+ for charge balancing. Although the structures are obtained from a chloride-rich solution there is clear evidence that bromide is present in the n = 1 case (presumably from the $viol^{2+}$ (Br^-) starting material).

The structure of *i*Q[6] with EV^{2+} (n = 1):

Single crystals of the *i*Q[6]- EV^{2+} system suitable for X-ray diffraction were obtained by solvent evaporation of the filtrate in air over a period of about three weeks to afford rhombic colorless crystals. Following treatment with SQUEEZE, the composition of the compound was found to be $2(C_{36}H_{36}N_{24}O_{12}),4(C_{14}H_{18}N_2)$, $Cd_5Br_{9.56}Cl_{10.44}2(H_2O).2(H_3O)$, *ie* 2*i*Q[6]/4EV/$Cd_5Br_{9.56}Cl_{10.44}2(H_2O).2(H_3O)$. Hydrogen atoms were not resolved, whilst the

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anions are 5× CdX_4^{2-} where X is roughly two chloride and two bromide. This is not an inclusion complex, see Figure 6.

This structure is much less well resolved than the other two (see below), perhaps as a result of the absence of an interaction between the viologen and the *i*Q[6]. There is substantial disorder present in the position of the CdX_4^{2-} anions. These anions lie in 1-D channels that extend parallel to the crystallographic c-axis between the organic components. The absence of significant hydrogen bonding to these anions is presumably a cause of the disorder. The *i*Q[6] and viologens are packed alternately in layers in the xy plane; the viologens are aligned with the *b*-axis. This is not an inclusion complex. The ethyl viologen molecules are located between the rims of two *i*Q[6] molecules and are held in place by C−H···O interactions and also some C−H···halide interactions. The H···O distances lie in the range 2.32 to 2.76 Å.

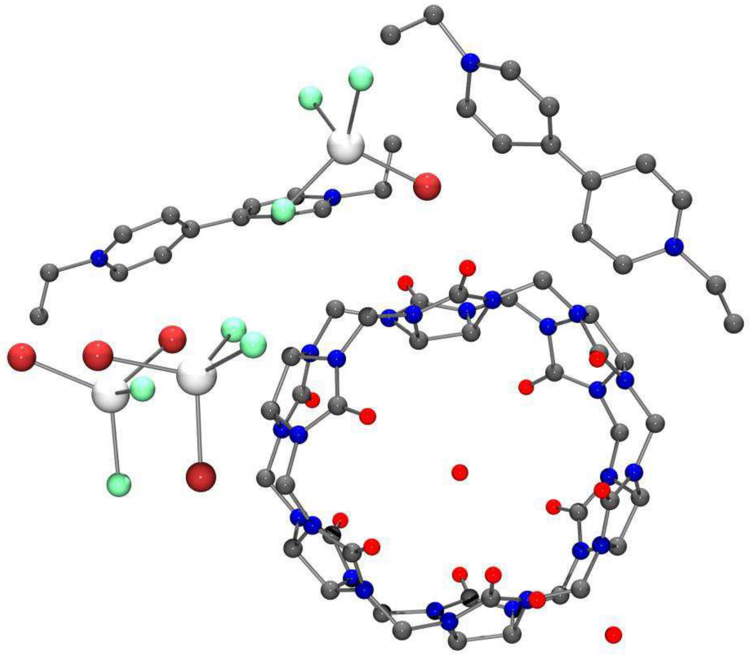

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Figure 6. Molecular structure of 2*i*Q[6]/4EV/$Cd_5Br_{9.56}Cl_{10.44}2(H_2O).2(H_3O)$

The structure of *i*Q[6] with BV^{2+} (n = 3):

Again, crystals suitable for X-ray diffraction were obtained from the filtrate upon slow evaporation. The best estimate of the composition of the crystal is $2(C_{36}H_{36}N_{24}O_{12})$, $C_{18}H_{26}N_2$, $2(CdCl_4)$, $36H_2O$, *ie* 2*i*Q[6]/ BV/$2(CdCl_4)$, $36H_2O$. Charge balancing is not obvious in this case. As shown in Figure 7, the crystal structure contains two unique *i*Q[6] molecules, two $CdCl_4^{2-}$ ions and one dibutyl viologen cation in the asymmetric unit and there is water of crystallisation that is poorly resolved. Presumably for the purposes of charge balancing some of the water is present as H_3O^+. Importantly, the viologen is encapsulated within two symmetry-related *i*Q[6]; every viologen is encapsulated and every *i*Q[6] is involved in this process. The dumbbells formed are packed in a C-centred array according to the space group symmetry. Between these exist large regions of space that are occupied by water. The butyl viologen resides with each of the alkyl chains located within the *i*Q[6] cavity of a different *i*Q[6] molecule. There are no classical hydrogen bonds but a raft of C−H···O interactions between the viologen and the *i*Q[6]. These interactions are between the C=O and CH_2 groups and also aromatic C−H on the viologen. The H···O distances lie in the range 2.38 to 2.77 Å. The formally positively-charge nitrogen atom is displaced slightly from the centre of the ring to form C=O···N distances in the range 3.28 to 4.53 Å. Presumably the displacement from the centre maximises this favourable interaction.

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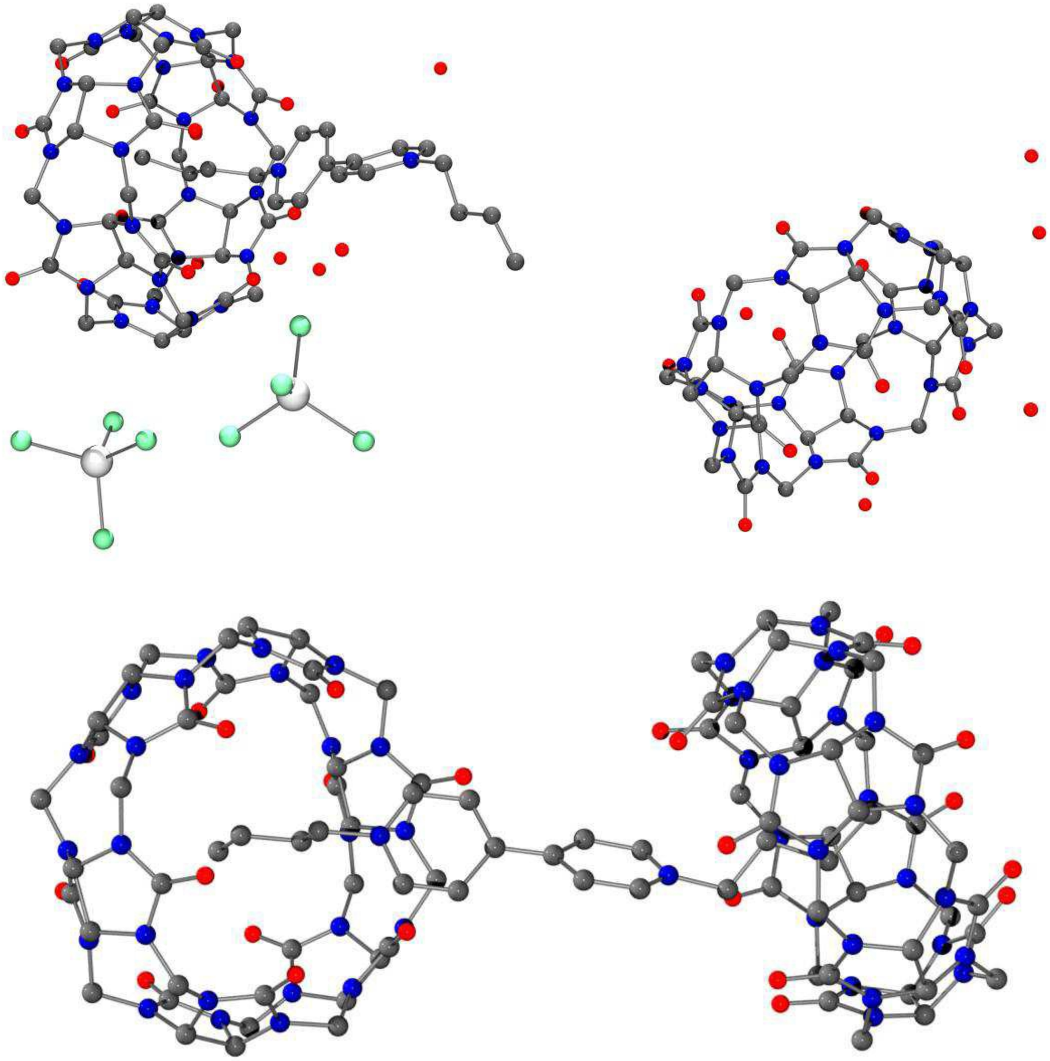

Figure 7. Molecular structure of 2*i*Q[6]/ BV/2($CdCl_4$), $36H_2O$. Top: the asymmetric unit. Bottom: the docking between the viologen and *i*Q[6].

The structure of *i*Q[6] with HV^{2+} (n = 5):

Single crystals of the *i*Q[6]@HV^{2+} system suitable for X-ray diffraction were obtained by solvent evaporation of the filtrate in air over a period of about three weeks to afford colorless crystals of the solid products. HV1 was treated with SQUEEZE to pick up a little tiny bit of poorly ordered water. Best estimate of the composition of the crystal is 2($C_{36}H_{36}N_{24}O_{12}$), ($C_{22}H_{34}N_2$), 2($CdCl_4$), $18H_2O$.2(H_3O), *ie* 2*i*Q[6]/HV/2$CdCl_2$$18H_2O$.2($H_3O$), see Figure 8. The asymmetric unit contains one *i*Q[6], one $CdCl_4$ anion, and one half of the

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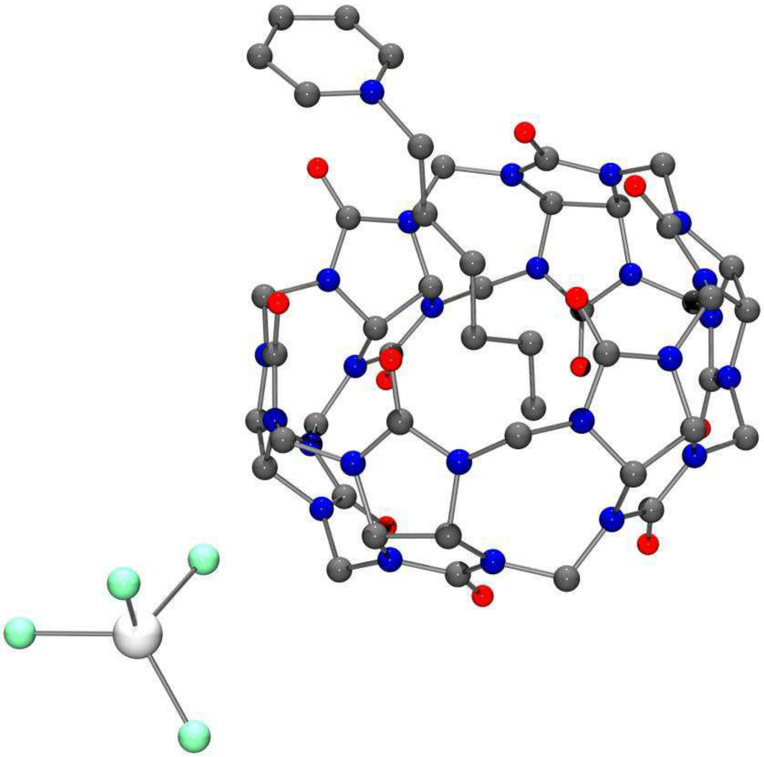
hexyl viologen and some isolated water molecules. The second half of the viologen is generated by symmetry; each viologen is located with the hexyl group located encapsulated within the viologen ring. Dumbbells of viologen between two *i*Q[6] are packed in a highly symmetric arrangement aligned in layers in the *yz* plane alternately along the [011] and [01-1] directions. Between these are the CdX_4^{2-} anions. Again, this structure is best considered as a dumbbell-type inclusion complex. The alkyl chain shows some disorder towards its end, but there are discernible C−H···O interactions between CH_2 groups and the rim of the *i*Q[6]. Four H···O distances lie in the range 2.48 to 2.63 Å. There is a single aromatic C−H···O interaction (H···O 2.51 Å). The positively-charged nitrogen atom is located out of the centre of the ring almost directly about two C=O groups at O···N distances of 3.69 and 3.88 Å.



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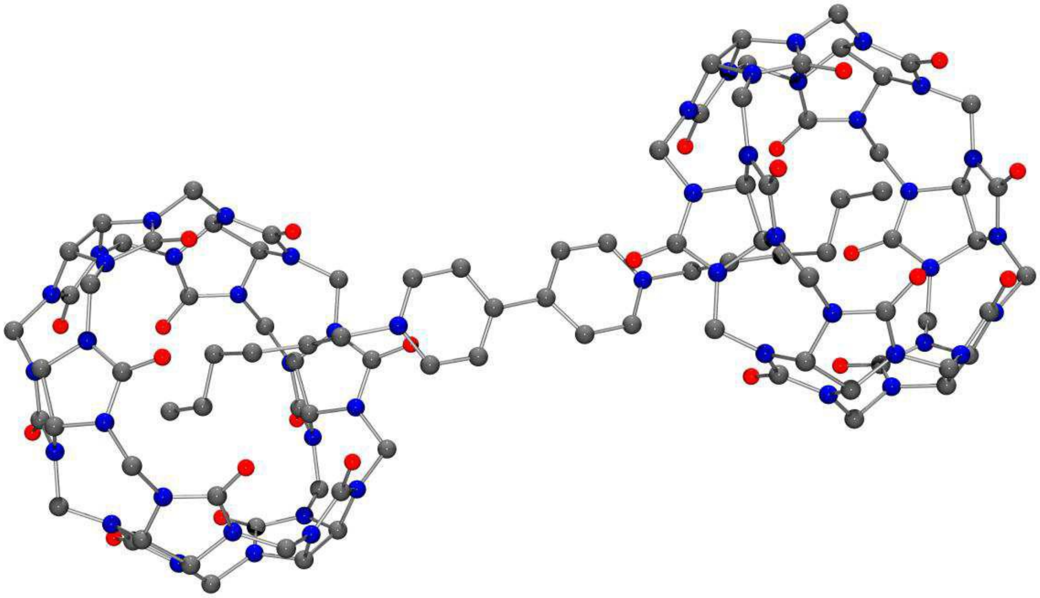

Figure 8. Molecular structure of 2*i*Q[6]/HV/2CdCl$_2$18H$_2$O.2(H$_3$O). Top: the asymmetric unit. Bottom: the docking between the viologen and *i*Q[6].

Experimental Section

All ^{1}H NMR spectra, including those for the titration experiments, were recorded at 20°C on a JEOL JNM-ECZ400S spectrometer. 1M DCl was used as a field-frequency lock, and the observed chemical shifts are reported in parts per million (ppm). MALDI-TOF mass spectrometry was recorded on a Bruker BIFLEX III ultra-high resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with a-cyano-4-hydroxycinnamic acid as matrix. Absorption spectra of the host-guest complexes were performed with an Aglient 8453 spectrophotometer at room temperature. The host and guests were dissolved in deionized water. UV-visible spectra was obtained at a concentration of 2.00-4.00×10^{-5} mol·L^{-1} guest and different *i*Q[6] concentrations for the *i*Q[6]@guest system.

Starting materials and solvents for syntheses were purchased commercially and used as supplied without further purification. *i*Q[6] was prepared and purified according to our previously published procedure. [2a, 6] With the exception of methyl viologen and N,N′-diheptyl-4,4′-bipyridinium dibromide (Aldrich), all other viologen guests were prepared by the treatment of 4,4′-bipyridine with an excess of the corresponding alkyl bromide.

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The general procedure for the synthesis of (dialkyl) viologens is as follows: A mixture of 4,4′-dipyridyl (1.0 equiv.) and the corresponding alkyl bromide (6 equiv.) were refluxed for 3 h. The resulting precipitate was filtered, and then loaded onto a silica gel (G200) column, eluted with a 3:1 acetone:acetic acid mixture and the second major species eluted was collected. The eluate was reduced *in vacuo* to a small volume, separated, and recrystallized from a solvent system comprising 1:2 ethanol:ether. The crystals were collected, washed with ether, and then air-dried.

UV-Vis Absorption Spectra

All UV spectra were recorded with an Agilent 8453 spectrophotomete at room temperature. The solutions of *i*Q[6] (1.0×10^{-4} mol/L) were prepared by directly dissolving host in 0.1M HCl. The solutions of viologen guests (1.0×10^{-3} mol/L) were prepared for absorption spectra determination. Samples of these solutions were combined to give guest:host ratios of 0, 0.2:1, 0.4:1, 0.6:1,… 4:1 respectively. The data were then analyzed using ORIGIN 8.0 and photoshop software.

Nuclear Magnetic Resonance Measurements

To analyze the host-guest complexation of *i*Q[6] and viologen guests, all ^{1}H NMR spectra, including those for the titration experiments, were recorded at 20°C on a JEOL JNM-ECZ400S spectrometer. 1M DCl was used as a field-frequency lock and the observed chemical shifts are reported in parts per million (ppm) relative to that for the internal standard (TMS at 0.0 ppm). The ratio of viologen guests *versus* *i*Q[6] was calculated by the ratio of their integral are as for special peaks. The concentrations of the viologen guests are 1.0×10^{-4} mol/L in the ^{1}H NMR spectroscopic experiments.

Preparation of single crystals *i*Q[6]@EV^{2+}, *i*Q[6]@BV^{2+} and *i*Q[6]@BV^{2+}

Similar processes were used to prepare crystals of this series of samples (see below). Complex *i*Q[6]@EV^{2+}: weigh accurately about 59 mg *i*Q[6](0.05mmol), 55mg $CdCl_2$ (0.3mmol) and 150 mg EV^{2+} (0.4mmol) into a 25 mL beaker and dissolve in 12mL of 3M HCl solution, The mixture was heated at 50°C with stirring until the *i*Q[6] and guest dissolved completely. The solution was then allowed to slowly evaporate under air at room temperature, whilst being kept in a shaded environment. Colorless and needlelike crystals were obtained in the beaker over about three weeks.

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Complex *i*Q[6]@BV^{2+}: weigh accurately about 59 mg *i*Q[6](0.05mmol), 55 mg $CdCl_2$ (0.3mmol) and 173 mg BV^{2+} (0.4mmol) into a 25 mL beaker and dissolve in 12mL of 3M HCl solution, The mixture was heated at 50℃ with stirring until the *i*Q[6] and guest dissolved completely. The solution was allowed to slowly evaporate under air at room temperature, whilst being kept in a shaded environment. Colorless and needlelike crystals were obtained in the beaker over about three weeks.

Complex *i*Q[6]@HV^{2+}: weigh accurately about 59 mg *i*Q[6] (0.05mmol), 55mg $CdCl_2$ (0.3mmol) and 195mg HV^{2+} (0.4mmol) into a 25 mL of beaker and dissolve in 12mL of 3M HCl solution, The mixture was heated at 50℃ with stirring until the *i*Q[6] and guest dissolved completely. The solution was allowed to slowly evaporate under air at room temperature, whilst being kept in a shaded environment. Colorless and needlelike crystals were obtained in beaker in air over about three weeks.

Conclusions

In summary, we have investigated the binding interactions of *i*Q[6] with a series of dialkyl-viologen dicationic guests using ^1H NMR spectroscopy and X-ray crystallography. In aqueous solution, the alkyl chains of the viologens (BV^{2+} and HV^{2+}) were engulfed into the cavity of the *i*Q[6] host, forming 2:1 ternary complexes. The viologen bearing $C_6H_5CH_2$ substituents (NV^{2+}) behaves in a similar fashion. This result is consistent with the binding behavior of Q[6] and its derivatives, tetramethylcucurbit[6]uril ($Me_4Q[6]$) and cyclohexanocucurbit[6]uril ($Cy_6Q[6]$), with dialkyl-viologens.[7] By contrast, there was no significant interaction between *i*Q[6] and the viologen EV^{2+}, which is different to the observations for Q[6] and its derivatives. [7, 8] This is thought to be due to the smaller cavity of *i*Q[6] which contains a single inverted glycoluril units. The strong binding of *i*Q[6] to viologens is presumably due to the favorable ion–dipole interactions between the positively charged guest and the portal oxygen atoms of *i*Q[6] in addition to hydrophobic effects. Single crystals grown in the presence of $CdCl_2$, revealed solid-state structures best described as external 'dumbbell' type in the case of both BV^{2+} (n = 3) and HV^{2+} (n = 5) with *i*Q[6].

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Single-crystal X-ray crystallography

Single crystals of complexes were grown from 3 M HCl solution containing $CdCl_2$ salt by slow evaporation. In each case, the structure was treated with the SQUEEZE routine to model disordered water contained within the structure and the formulas reflects the composition obtained from SQUEEZE. Diffraction data were collected at 293 K with a Bruker SMART Apex-II CCD diffractometer using graphite-monochromated Mo-Kα radiation (wavelength = 0.71073 Å). Empirical absorption corrections were performed by using the multiscan program SADABS. Structural solution and full-matrix least-squares refinement based on F 2 were performed with the SHELXS-2014 and SHELXL-2018/1 program packages, respectively. [9, 10] All non-hydrogen atoms were treated anisotropically in all cases. All hydrogen atoms were introduced as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom.

CCDC 1823647-1823649 contain the supplementary crystallographic data for this paper.

Table 1. Crystallographc data

Compound	*i*Q[6] with EV^{2+}	*i*Q[6] with BV^{2+}	2*i*Q[6]@HV^{2+}
Formula	$C_{128}H_{144}Br_{9.56}Cd_5Cl_{10.44}N_{56}O_{30}$	$C_{90}H_{98}Cd_2Cl_8N_{50}O_{36}\bullet 15H_2O$	$C_{94}H_{106}Cd_2Cl_8N_{50}O_{43}$
Formula weight	4642.844	2964.58	3132.68
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	C c	C $^{2}/_{c}$
Unit cell dimensions			
a (Å)	14.9882(11)	25.637(11)	23.0853(19)
b (Å)	15.3355(11)	16.148(7)	24.898(2)
c (Å)	23.6644(17)	35.826(15)	24.780(3)
α (Å)	83.034(2)	90	90
β (Å)	79.110(2)	97.719(6)	111.814(2)
γ (Å)	61.125(2)	90	90
V ($Å^3$)	4674.4(6)	14697(11)	13223(2)
Z	1	4	4
Temperature (K)	296(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Calculated density (Mg m^{-3})	1.649	1.340	1.574

Absorption coefficient (mm^{-1})	2.828	0.518	0.584
Transmission factors (min/max)	0.977 and 0.981	0.845 and 0.884	0.193 and 0.252
Crystal size (mm^3)	0.210 x 0.180 x 0.178	0.260 x 0.220 x 0.190	0.280 x 0.230 x 0.220
ϑ (max) (°)	25.0	26.1	27.6
Reflections measured	59315	40079	86705
Unique reflections	16518	19604	15260
R_{int}	0.0671	0.0427	0.042
Reflections with $F^2 > 2\sigma(F^2)$	9862	13326	10243
Number of parameters	1053	1616	831
R_1 [$F^2 > 2\sigma(F^2)$]	0.1773	0.0528	0.0608
wR_2 (all data)	0.5171	0.1513	0.2117
GOOF, S	1.960	0.951	1.040
Largest difference peak and hole (e Å^{-3})	9.339 and -5.667	0.657 and -0.580	1.469 and -0.710

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