

# Interaction between cucurbit[8]uril and viologen derivatives

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Received: 10 May 2007 / Accepted: 14 December 2007 / Published online: 8 February 2008  
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**Abstract** The interaction between cucurbit[8]uril (Q[8]) and a series of symmetric viologen derivatives having aliphatic substituents of variable length [*N,N'*-dialkyl-4,4'-bipyridinium dianions; alkyl = CH<sub>3</sub>(CH<sub>2</sub>)<sub>*n*</sub>, *n* = 0 (MV<sup>2+</sup>), 1 (EV<sup>2+</sup>), 2 (PV<sup>2+</sup>), 3 (BV<sup>2+</sup>), 4 (FV<sup>2+</sup>), 5 (HV<sup>2+</sup>) or 6 (SV<sup>2+</sup>); BPY<sup>2+</sup> = diprotonated 4,4-bipyridine], determined by <sup>1</sup>H NMR and electronic absorption spectroscopy methods, is described. Some different binding models were observed in this work when compared to the interactions between cucurbit[7]uril (Q[7]) and these guests. The experimental results revealed that the binding site of the guests by Q[8] depended strongly on the length of the aliphatic substituents on the 4,4'-bipyridinium nucleus. While a 1:2 complex was observed for Q[8]-BPY<sup>2+</sup> under acidic conditions, a 1:1 complex was formed for Q[8]-viologen derivatives with chains shorter than four carbon atoms. However, multiple Q[8] molecules could

be threaded on the longer-chain FV<sup>2+</sup>, HV<sup>2+</sup> or SV<sup>2+</sup> molecules to form 2:1 and even possibly 3:1 complexes.

**Keywords** Cucurbit[8]uril · Viologen derivatives · Binding models · <sup>1</sup>H NMR spectroscopy · Electronic absorption spectroscopy

## Introduction

The cucurbit[*n* = 5,7,8,10]urils (Q[5], Q[7], Q[8] and Q[10]) were reported at the beginning of 2000 by Kim et al. [1] and Day et al. [2, 3]. Prior to this, only one member of the family was known; the structure of this member, now known as cucurbit[6]uril (Q[6]) was determined in 1981 [4]. This family of rigid macrocycles has a unique cavity, rimmed by carbonyl oxygens. A common characteristic of the members of the Q family is their ability to act as molecular hosts. Ingress and egress of molecular guests is primarily controlled by the size of the cavity and the carbonyl portals. Molecular guests as small as gas molecules to small cage compounds can be encapsulated in Q[5]–Q[7] whereas Q[8], with its increased cavity size, can encapsulate larger molecules or pairs of smaller molecules [5–17].

In a series of publications, Kaifer's group recently reported the formation of a variety of inclusion complexes of viologen derivatives with the host Q[7] [18–21]. In addition, they reported a viologen-containing dendrimer, while Jeon et al. [22] reported that Q[8] can form stable 1:1:1 complexes with a viologen derivative and 2,6-dihydroxynaphthalene, which are considered as examples of Fisher's key-and-lock molecular recognition principle.

In this work, we have investigated a series of viologen derivatives having aliphatic substituents on the pyridinium

**Electronic supplementary material** The online version of this article (doi:10.1007/s10847-007-9405-1) contains supplementary material, which is available to authorized users.

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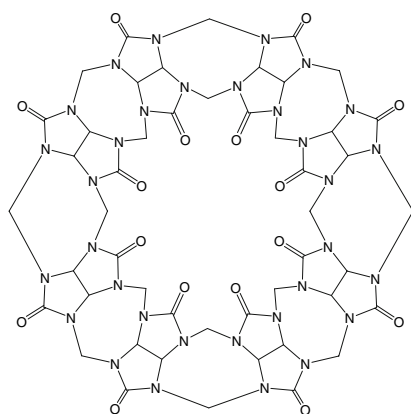
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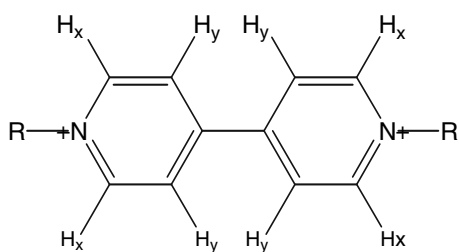
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nitrogens of variable length in order to determine the subtleties in binding resulting from the presence of these substituents. As reported herein, the experimental results reveal that the binding site on the guests (i.e. the location of Q[8] on any part of the guest) depends strongly on the length of the aliphatic substituents on the bipyridinium nucleus; whereas a 1:2 complex for Q[8]-BPY<sup>2+</sup> was observed under acidic conditions, a 1:1 complex was formed for Q[8]-viologen derivatives with chains shorter than four carbon atoms. However, two or three Q[8] molecules could be threaded on the longer-chain FV<sup>2+</sup> and HV<sup>2+</sup> or SV<sup>2+</sup> molecules to form 2:1 and even 3:1 complexes. The influence of pH on interaction of the title host-guest complexes has also been considered.

prepared by the treatment of 4,4'-bipyridine with an excess of the corresponding alkyl bromide (see the Supporting Information). The general procedure for the synthesis of (dialkyl)viologens is as follows: A mixture of 4,4'-dipyridyl (1.0 equiv), the corresponding alkyl bromide (6 equiv) and polyethylene glycol (0.05 equiv; present as a phase transfer catalyst) was refluxed for 3 h. The resulting precipitate was filtered, and then loaded onto a silica gel (G200) column, eluted with 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 1:2 ethanol:ether. The crystals were collected, washed with ether, and air-dried. The <sup>1</sup>H NMR data for compounds used in this work follows. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): EV<sup>2+</sup> δ 8.99 (d,



Q[8]



BPY <sup>2+</sup>	R = H
MV <sup>2+</sup>	R = CH <sub>3</sub>
EV <sup>2+</sup>	R = CH <sub>2</sub> CH <sub>3</sub>
PV <sup>2+</sup>	R = CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
BV <sup>2+</sup>	R = CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
FV <sup>2+</sup>	R = CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
HV <sup>2+</sup>	R = CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
SV <sup>2+</sup>	R = CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>

## Experimental

### Materials

Cucurbit[8]uril was prepared and purified according to the method developed in our laboratories [23]. With the exception of methyl viologen (Aldrich), all other viologen guests were

$J = 6$  Hz, 4H,  $\alpha$  of viologen), 8.39 (d,  $J = 6$  Hz, 4H,  $\beta$  of viologen), 4.61 (q,  $J = 7$  Hz, 4H,  $-\text{CH}_2-$ ), 1.55 (t,  $J = 7$  Hz, 6H,  $-\text{CH}_3$ ) ppm; PV<sup>2+</sup> δ 8.84 (d,  $J = 7$  Hz, 4H,  $\alpha$  of viologen), 8.29 (d, 4H,  $\beta$  of viologen), 4.51 (t,  $J = 7$  Hz, 4H,  $-\text{CH}_2-$ ), 1.96 (m,  $J = 7$  Hz, 4H,  $-\text{CH}_2-$ ), 0.85 (t,  $J = 7$  Hz, 6H,  $-\text{CH}_3$ ) ppm; BV<sup>2+</sup> δ 9.01 (d,  $J = 6$  Hz, 4H,  $\alpha$  of viologen), 8.44 (d,  $J = 6$  Hz, 4H,  $\beta$  of viologen), 4.59 (t,  $J = 7$  Hz, 4H,  $-\text{CH}_2-$ ),

1.92 (m,  $J = 7$  Hz, 4H,  $-\text{CH}_2-$ ), 1.26 (m,  $J = 7$  Hz, 4H,  $-\text{CH}_2-$ ), 0.83 (t,  $J = 7$  Hz, 6H,  $-\text{CH}_3$ ) ppm;  $\text{FV}^{2+}$   $\delta$  8.93 (d,  $J = 6$  Hz, 4H,  $\alpha$  of viologen), 8.40 (d,  $J = 6$  Hz, 4H,  $\beta$  of viologen), 4.54 (t,  $J = 7$  Hz, 4H,  $-\text{CH}_2-$ ), 1.95 (m, 4H,  $-\text{CH}_2-$ ), 1.23 (m, 8H,  $-\text{CH}_2-$ ), 0.75 (t,  $J = 7$  Hz, 6H,  $-\text{CH}_3$ ) ppm;  $\text{HV}^{2+}$   $\delta$  8.98 (d,  $J = 6$  Hz, 4H,  $\alpha$  of viologen), 8.40 (d,  $J = 6$  Hz, 4H,  $\beta$  of viologen), 4.59 (t,  $J = 7$  Hz, 4H,  $-\text{CH}_2-$ ), 1.93 (m, 4H,  $-\text{CH}_2-$ ), 1.18 (m, 12H,  $-\text{CH}_2-$ ), 0.72 (t, 6H,  $-\text{CH}_3$ ) ppm;  $\text{SV}^{2+}$   $\delta$  8.97 (d,  $J = 6.4$  Hz, 4H,  $\alpha$  of viologen), 8.53 (d,  $J = 6.4$  Hz, 4H,  $\beta$  of viologen), 4.58 (t,  $J = 7$  Hz, 4H,  $-\text{CH}_2-$ ), 1.94 (m, 4H,  $-\text{CH}_2-$ ), 1.15 (m, 8H,  $-\text{CH}_2-$ ), 1.13 (m, 8H,  $-\text{CH}_2-$ ), 0.72 (t, 6H,  $-\text{CH}_3$ ) ppm.

### Instrumentation and measurements

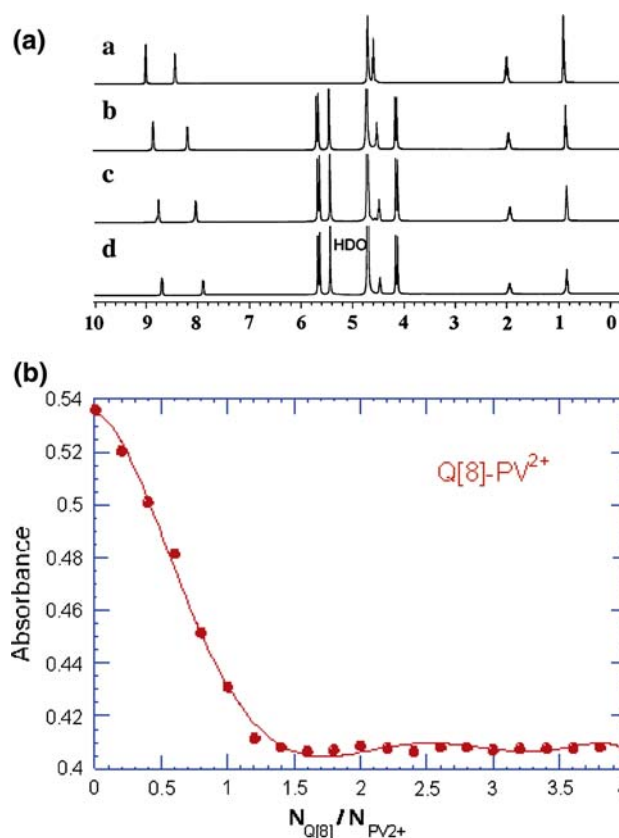
For the study of host–guest complexation of Q[8] and the title guests,  $2.0\text{--}2.5 \times 10^{-3}$  mmol samples of guest in  $0.5\text{--}0.7$  g  $\text{D}_2\text{O}$  were prepared containing increasing concentrations of Q[8], and the  $^1\text{H}$  NMR spectra were recorded at  $20^\circ\text{C}$  on a Varian INOVA-400 spectrometer. Absorption spectra of the host–guest complexes were recorded on an Agilent 8453 spectrophotometer at room temperature. Aqueous solutions of the bromide salts of the dialkyl-4,4'-bipyridinium derivatives were prepared with a concentrations of  $4.0 \times 10^{-4}$  mol/L (for absorption spectra), with no other added salts present. Samples of these solutions were combined with Q[8] to give solutions with a guest:Q[8] ratio of 0, 8:1, 4:1, 2:1, 1:1, 1:2 and so on. The pH of the solution of the host–guest complexes was adjusted if required with NaOH solution, with pH recorded using a S-3C pH meter. Determination of  $K$  values was performed and error analyses carried out as described by us elsewhere recently [24].

### Results and discussion

The doughnut-like Q[8] host has a cavity through which the relatively linear dialkyl-4,4'-bipyridinium ions can pass so that each pyridinium nitrogen extend on opposite side of the host ring for simple 1:1 arrangements—the Q[8] molecule can be considered threaded on the linear dication. For very long linear molecules, it is possible to thread several Q[8] molecules; for example, a 2:1 arrangement would arise where two Q[8] molecules thread onto a single dication, each Q[8] located on an individual alkyl chain and interacting with a different pyridinium centre. An alternate assembly practicable with large-ring cucurbiturils is for the ring to accommodate more than one guest, for example in a 1:2 arrangement. Here, we observe evidence for each of these types of assembly.

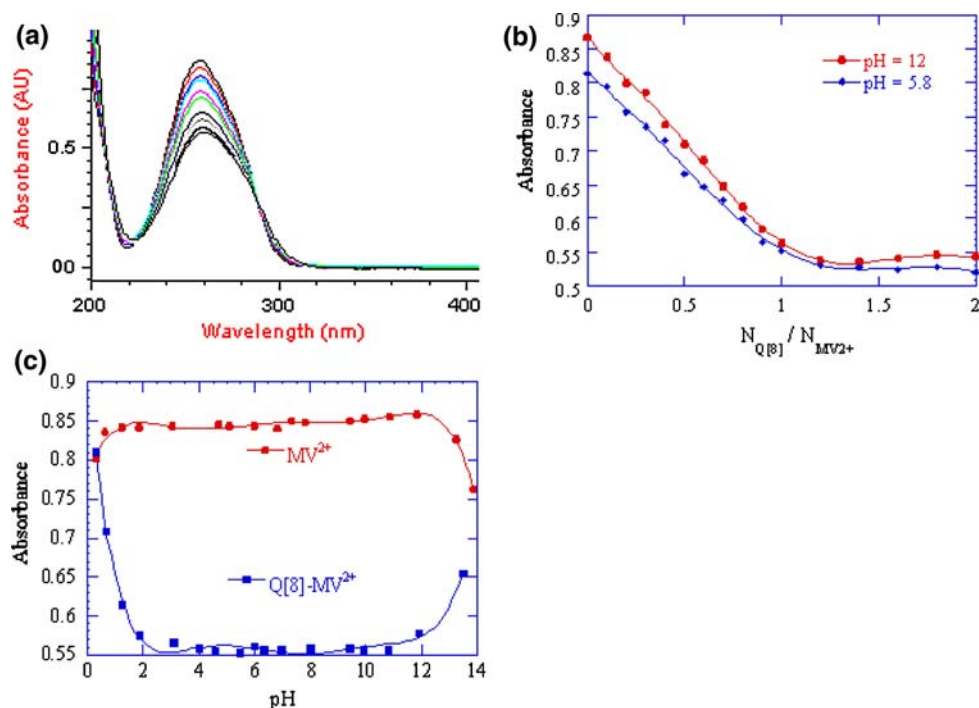
### 1:1 Q[8]:Guest interactions

The simplest interactions of association for complexes of 1:1 were found between Q[8] and guests with alkyl chains no more than four carbon atoms long ( $\text{MV}^{2+}$ ,  $\text{EV}^{2+}$ ,  $\text{PV}^{2+}$  and  $\text{BV}^{2+}$ ). To exemplify this behaviour, Fig. 1 shows the  $^1\text{H}$  NMR titration spectra of  $\text{PV}^{2+}$  in  $\text{D}_2\text{O}$  recorded in the absence of Q[8] (a) and in increasing proportions of Q[8] at 0.25 (b), 0.33 (c) and 0.72 (d) molar equivalents (pH 5.7–5.8). A gradual upfield shift of the aromatic proton resonances is observed as the proportion of Q[8] is increased. At 0.72 equiv of Q[8], the resonances of the aromatic protons  $\text{H}_x$  and  $\text{H}_y$ , respectively, show upfield shifts of 0.32 and 0.55 ppm compared to positions in the free  $\text{PV}^{2+}$ . A downfield shift by 0.15 ppm is observed for the methylene proton resonances of the propyl substituent closest to the N of the viologen nucleus, whereas the terminal  $-\text{CH}_2\text{CH}_3$  protons on the aliphatic propyl chains are not significantly shifted. Similar  $^1\text{H}$  NMR titration spectra between Q[8] and the guests  $\text{MV}^{2+}$ ,  $\text{EV}^{2+}$ ,  $\text{BV}^{2+}$  were also recorded (see the Supporting Information). We mostly observed only one set of  $^1\text{H}$  NMR resonances for the guest we have examined,



**Fig. 1** Interaction of  $\text{PV}^{2+}$  and Q[8]: (a)  $^1\text{H}$  NMR spectra (400 MHz,  $\text{D}_2\text{O}$ ) of  $\text{PV}^{2+}$  ( $\sim 4$  nM) in the absence (a) and in the presence of 0.25 equiv (b), 0.33 equiv (c), and 0.7 equiv (d) of Q[8]; (b) absorbance at 260 nm vs. an extended  $N_{\text{Q[8]}}/N_{\text{PV}^{2+}}$  ratio, indicating only 1:1 binding applies

**Fig. 2** Absorption spectra of aqueous solutions containing a fixed concentration (24  $\mu\text{M}$ ) of  $\text{MV}^{2+}$  and variable concentrations of Q[8] (a), and (b) the experimental absorbances at 260 nm at two pH values. The lower panel (c) shows the expected absence of variation in absorbance at 260 nm with pH for  $\text{MV}^{2+}$  and the fully formed Q[8]- $\text{MV}^{2+}$  adduct, except at pH extrema



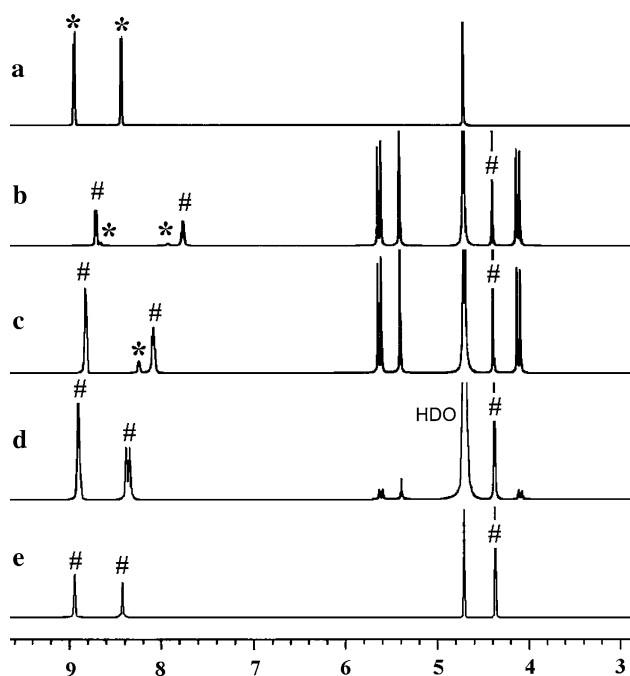
and these are generally sharp. This implies that the exchange rates between the included guests and the free guests are moderate to fast on the NMR time scale. We attempted to measure the interaction ratio between Q[8] and the guests by a  $^1\text{H}$  NMR titration method, but the limitation of the solubility of the host Q[8] frustrated our attempts at ratios of Q[8]:guest of more than 1:1. The systems do not display fluorescence, so this technique is not available either. However, we were able to obtain good data on the interaction between Q[8] with viologen guests through UV absorption spectroscopy. The Q[8]: $\text{PV}^{2+}$  interaction investigated by NMR was also examined by UV absorbance spectroscopy, where the absence of change at high ratios (up to 1:4) supports a simple and persistent 1:1 model (Fig. 1). A further example appears in more detail in Fig. 2, which shows the UV spectra obtained with aqueous solutions containing a fixed concentration of  $\text{MV}^{2+}$  (24  $\mu\text{M}$ ) and variable concentrations of Q[8]. The absorption band of the  $\text{MV}^{2+}$  exhibits progressively lower absorbance as the ratio of  $N_{\text{Q}[8]}/N_{\text{MV}^{2+}}$  is increased. The absorbance vs. ratios of  $N_{\text{Q}[8]}/N_{\text{MV}^{2+}}$  data can be fitted to a 1:1 binding model at both pH 5.8 and 12.0. Similar changes in the absorption spectra of the guests  $\text{EV}^{2+}$ ,  $\text{PV}^{2+}$  and  $\text{BV}^{2+}$  were observed as the Q[8] concentration was increased (see the Supporting Information). Thus, these four guests showed similar binding interactions with Q[8]. The symmetrical  $^1\text{H}$  NMR spectra imply that these guests are completely threaded through the host and that the main binding site for the host is the aromatic nucleus of the viologen residue.

Generally, the pH of a solution can influence the interaction in a host–guest system, but in the present case the charge on the viologens is independent of pH. Consequently, the plots of the absorbance vs. pH for  $\text{MV}^{2+}$  and the Q[8]- $\text{MV}^{2+}$  complex with a host:guest ratio of 1:1 (Fig. 2) exhibit a significant and constant absorbance difference between the guest and the inclusion complex across most of the pH range ( $2 < \text{pH} < 12$ ). The curves become equivalent only at  $\text{pH} < 0.5$  or  $\text{pH} > 13$ , which infers breakdown of the host–guest assembly under these limiting conditions, possibly associated with protonation of the host at low pH or competition by sodium ion, and decomposition of the viologens at high pH. The other systems in this work show a similar behaviour (see Supporting Information).

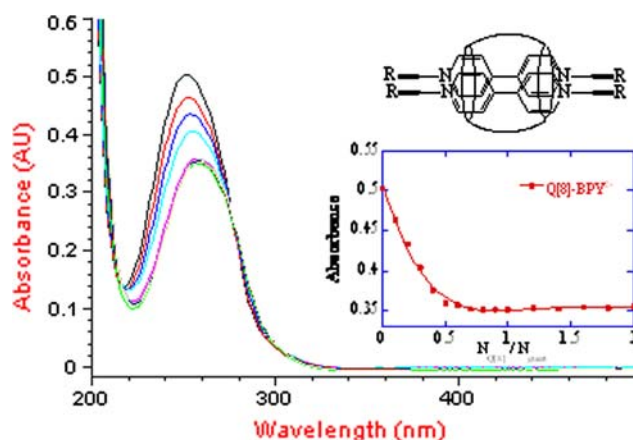
#### 1:2 Q[8]:Guest interactions

We also attempted to investigate the binding interactions between Q[8] and the guest  $\text{BPY}^{2+}$  by  $^1\text{H}$  NMR, but only the resonances of free  $\text{BPY}^{2+}$  were observed, as a consequence of the poor solubility of Q[8] in the presence of this potential guest. This problem was resolved by pre-dissolving Q[8] as an association complex with  $\text{MV}^{2+}$ , and measuring displacement by another guest; the Q[8]- $\text{MV}^{2+}$  complex proved to be useful in elucidating the Q[8] interactions with  $\text{BPY}^{2+}$ . This type of approach is valid when the guest being displaced has a weaker interaction than the incoming guest;  $\text{BPY}^{2+}$  was found to have stronger

interactions. However, at concentrations required for  $^1\text{H}$  NMR, large amount of precipitation were observed following the addition of  $\text{BPY}^{2+}$  and the Q[8] resonances are reduced in intensity relative to those of the  $\text{MV}^{2+}$  complex. Figure 3, for example, shows the  $^1\text{H}$  NMR titration spectra of Q[8]- $\text{MV}^{2+}$  in  $\text{D}_2\text{O}$  recorded with addition of increasing amounts of  $\text{BPY}^{2+}$ . A significant feature of the spectra in Fig. 3 is the reduction in intensity of Q[8] resonances and the persistence of the resonances for  $\text{MV}^{2+}$  (marked #) as  $\text{BPY}^{2+}$  is added (from Fig. 3b–d). An upfield shift of the aromatic proton resonances (marked \*) of  $\text{BPY}^{2+}$  indicates that  $\text{BPY}^{2+}$  can be bound within the cavity. At lower concentrations precipitation was not a problem, and UV adsorption spectra were recorded with increasing concentrations of Q[8]- $\text{MV}^{2+}$  which established that the complex formed was Q[8]- $(\text{BPY}^{2+})_2$  with a binding ratio of 1:2 (see Fig. 4). The absorption band of the  $\text{BPY}^{2+}$  also exhibits progressively lower absorbance as the ratio of  $N_{\text{Q[8]}}/N_{\text{BPY}^{2+}}$  is increased. The absorbance vs. ratio of  $N_{\text{Q[8]}}/N_{\text{BPY}^{2+}}$  (inset, Fig. 4) or  $N_{\text{Q[8]}}/N_{\text{EV}^{2+}}$  data plots fit a 1:2 binding model. In contrast to the previous three systems discussed, Q[8]- $\text{BPY}^{2+}$  binding modes are best interpreted as Q[8] threaded by two guests, and the main binding site for the host as indicated by  $^1\text{H}$  NMR is the aromatic viologen residue (model in Fig. 4). The ternary complex may involve two singly protonated 4,4'-bipyridine cations



**Fig. 3**  $^1\text{H}$  NMR titration spectra (400 MHz,  $\text{D}_2\text{O}$ ) obtained by adding  $\text{BPY}^{2+}$  to a solution of a pre-formed Q[8]- $\text{MV}^{2+}$  ( $\sim 4$  mM) complex: (a)  $\text{BPY}^{2+}$  only; (b) Q[8]: $\text{MV}^{2+}$ : $\text{BPY}^{2+}$  = 1:1.1:0.1; (c) Q[8]: $\text{MV}^{2+}$ : $\text{BPY}^{2+}$  = 1:3.5:0.7; (d) Q[8]: $\text{MV}^{2+}$ : $\text{BPY}^{2+}$  = 1:19:1.4; (e)  $\text{MV}^{2+}$  only. Peaks of  $\text{BPY}^{2+}$  and  $\text{MV}^{2+}$  are marked with \* and #, respectively; the peak at  $\sim 4.7$  ppm is due to HDO



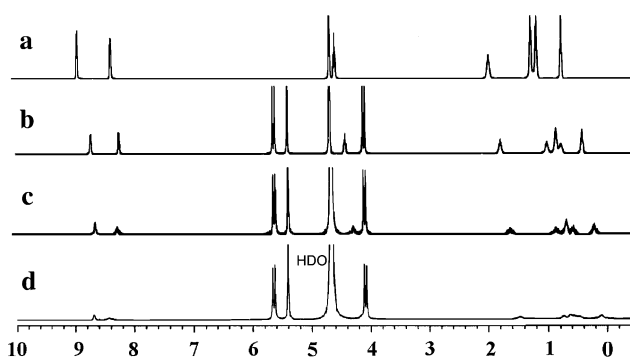
**Fig. 4** Absorption spectra of aqueous solutions containing a fixed concentration ( $24 \mu\text{M}$ ) of  $\text{BPY}^{2+}$  and variable concentrations of Q[8] at pH 5.3. The inset shows the experimental absorbances at 260 nm (filled circles) and the best fit line at pH 5.3; experimental results at pH 12.0 are also shown, illustrating the clear pH dependence of the interaction seen in this case only. The possible interaction model ( $\text{R}=\text{H}$ ) is also presented

rather than two diprotonated cations; a higher  $K$  value compared with the viologens may support the latter (4+) compared with the former (2+) assembly, however. Nevertheless, there is a clear pH dependence observed in this case only, as expected, associated with protonation–deprotonation phenomena associated with the 4,4'-bipyridine nitrogen centres.

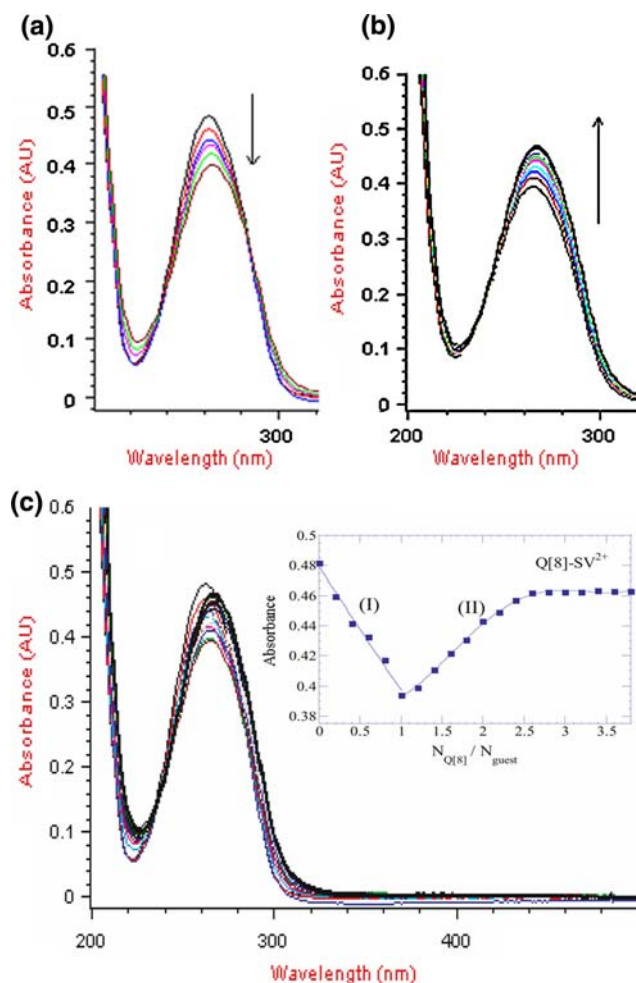
#### 2:1 and Higher Q[8]:guest interactions

A further variation to binding modes was found for the guests  $\text{SV}^{2+}$  and  $\text{HV}^{2+}$ . In these examples the substituents are relatively long aliphatic chains, which were expected to also compete as binding sites as a result of their lipophilic nature. The  $^1\text{H}$  NMR spectra showed that this was the case (see Fig. 5). The proton resonances of both the aromatic nucleus and the aliphatic chains of the  $\text{SV}^{2+}$  are shifted upfield upon addition of Q[8]. At a molar ratio of 1.4:1 of Q[8]: $\text{SV}^{2+}$ , this is particularly distinctive, and in addition leads to a broadening of the signals (Fig. 5d). At a small molar ratio of 0.3:1 there is still a significant shift upfield of the aromatic and aliphatic proton resonances, but the peaks are sharper (Fig. 5b, c). This indicates that the interaction model for Q[8]- $(\text{SV}^{2+})_n$  is much more complex, with the number of guests ( $n$ ) less clear. The UV absorption spectra were examined to try to answer this Q[8]-guest ratio question (Fig. 6). The absorption band of the  $\text{SV}^{2+}$  exhibits progressively lower absorbance when the ratio of  $N_{\text{Q[8]}}/N_{\text{MV}^{2+}}$  is between 0 and 1, with the curve of absorbance vs.  $N_{\text{Q[8]}}/N_{\text{MV}^{2+}}$  giving an almost straight line (Fig. 6a; curve(I), inset); subsequently, the absorption band





**Fig. 5** <sup>1</sup>H NMR spectra (400 MHz, D<sub>2</sub>O) of SV<sup>2+</sup> (~4 mM) in the absence (a) and in the presence of 0.3 equiv (b), 0.7 equiv (c), and 1.4 equiv (d) of Q[8]



**Fig. 6** Absorption spectra of aqueous solutions containing a fixed concentration (24 μM) of SV<sup>2+</sup> and variable concentrations of Q[8]. The inset shows the experimental absorbances at 260 nm (filled squares)

of the SV<sup>2+</sup> exhibits progressive increases in absorbance as the ratio of  $N_{Q[8]}/N_{MV^{2+}}$  was increased with a maximum at 2.5 (Fig. 6b; curve(II), inset). Part (I) of the absorbance vs.

$N_{Q[8]}/N_{MV^{2+}}$  shows a curve typical for a 1:1 ratio of Q[8]:SV<sup>2+</sup> ( $K = 2.7 \times 10^4$ ) whereas part (II) can be best fitted to an ~2:1 ratio of Q[8]:SV<sup>2+</sup> ( $K \leq 10^4$ ). Based on the information obtained from the <sup>1</sup>H NMR titration spectra and the absorption spectrophotometric measurements, it is conceivable that there are multiple bonding models for the Q[8] and SV<sup>2+</sup> host–guest interaction. When the ratio of Q[8]:SV<sup>2+</sup> is less than 1, SV<sup>2+</sup> provides the viologen nucleus and the long hydrophobic aliphatic chains as binding sites for a single Q[8] molecule, with a 1:1 species forming dominantly. From the <sup>1</sup>H NMR spectra, there would appear to be little differentiation between binding at the aromatic viologen residue or the aliphatic chains. Thus, averaged upfield resonances of the SV<sup>2+</sup> were observed in the <sup>1</sup>H NMR spectra (Fig. 5). The UV spectra may indicate a preference for aromatic nucleus binding, as demonstrated by the reduced absorbance. At higher proportions of Q[8], the nucleus would appear to be more exposed, as indicated by the increase in the UV spectra. A possible equilibrium binding model, depicted in Fig. 7, illustrates the likely shift in the balance as the concentration of Q[8] is increased; 1:1 association adducts (with possible modes of interaction represented schematically by a, b and c) occur at ratios of  $N_{Q[8]}/N_{SV^{2+}} < 1$ , with the 2:1 adduct (d) predominating at ratios  $> 1$ .

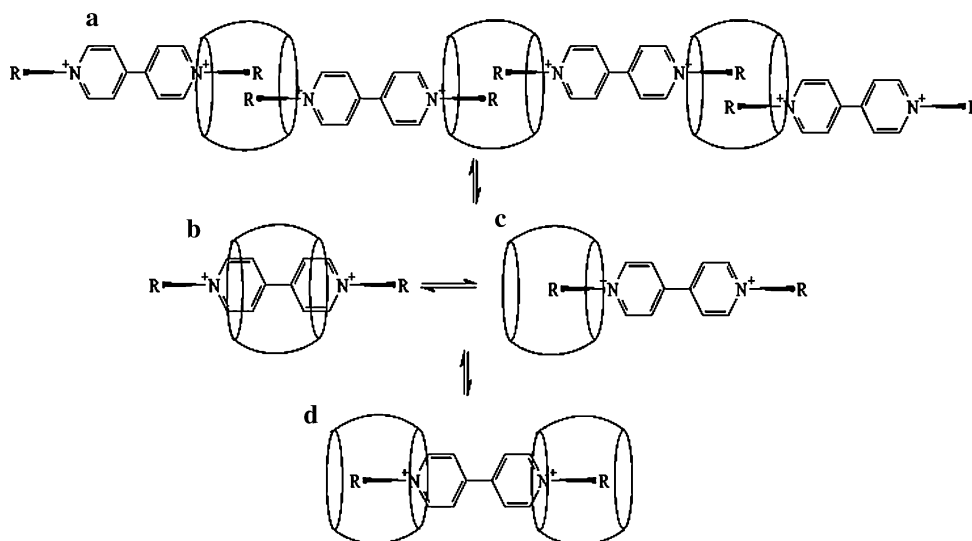
Similar <sup>1</sup>H NMR titration spectra were observed between Q[8] and the guests FV<sup>2+</sup> and HV<sup>2+</sup>, and the variation in the absorption bands of the FV<sup>2+</sup> or HV<sup>2+</sup> and the curves of the absorbance vs. ratios of  $N_{Q[8]}/N_{FV^{2+}}$  or  $N_{Q[8]}/N_{HV^{2+}}$  are similar to those observed in the Q[8]-SV<sup>2+</sup> system (see Supporting Information). Thus it is assumed that these exhibit the same binding model as discussed above for SV<sup>2+</sup>.

It is of interest to contrast the interaction between Q[7] and Q[8] and the series of aliphatic substituent viologens. For the former, BV<sup>2+</sup> (4 carbon chains) represents the limiting case where Q[7] steps from 1:1 to 2:1 inclusion [5], whereas FV<sup>2+</sup> (5 carbon chains) behaves as the limiting case for Q[8], presumably due to the larger cavity of Q[8]. We have found a tendency for dual occupancy in the larger Q[8] for BPY<sup>2+</sup>, but only single occupancy (1:1 adducts) for MV<sup>2+</sup> to BV<sup>2+</sup>. Single occupancy of Q[8] was also found for FV<sup>2+</sup>, HV<sup>2+</sup> and SV<sup>2+</sup>, except that these guests can accommodate two Q[8] hosts when the host:guest ratio increases.

#### Binding constants of host–guest inclusion complexes

In previous studies [25–30], several methods have been used to measure binding constants for the inclusion complexes involving with Q[n]s, such as NMR spectroscopy, electronic absorption spectroscopy and fluorescence spectroscopy. As

**Fig. 7** Proposed binding modes for interaction between Q[8] and  $SV^{2+}$  with different host–guest ratios. Different 1:1 arrangements (a) and (b) are in equilibrium and dominate at high Q[8]: $SV^{2+}$  ratios, with the 2:1 form (d) becoming dominant as the ratio of Q[8]: $SV^{2+}$  is decreased



**Table 1** Inclusion constants for the host–guest complexes of Q[8] with dialkyl-4,4'-bipyridinium guests determined at pH  $\sim$ 5.5 using electronic absorption spectroscopy

Guest	$K$	Guest	$K$
BPY $^{2+}$	$(1.5 \pm 0.4) \times 10^5$	BV $^{2+}$	$(3.3 \pm 0.4) \times 10^4$
MV $^{2+}$	$(2.7 \pm 0.4) \times 10^4$ <sup>a</sup>	FV $^{2+}$	$(4.3 \pm 0.5) \times 10^4$ <sup>b</sup>
EV $^{2+}$	$(4.1 \pm 0.3) \times 10^4$	HV $^{2+}$	$(5.3 \pm 0.3) \times 10^4$ <sup>b</sup>
PV $^{2+}$	$(4.8 \pm 0.2) \times 10^4$	SV $^{2+}$	$(3.5 \pm 0.3) \times 10^4$ <sup>b</sup>

<sup>a</sup> A value of  $1.1 \pm 0.3 \times 10^5$  was reported earlier in different conditions [16]

<sup>b</sup> Based on the data of curve I (region where 1:1 complexation dominates)

mentioned above, the absorbance (Figs. 2, 4, 6 and supporting information) vs. the ratio of  $N_{Q[8]}/N_{\text{guest}}$  fit well to a 1:1 binding model for the Q[8]-guest systems where the guests are MV $^{2+}$ , EV $^{2+}$ , PV $^{2+}$  and BV $^{2+}$ , and partially fitted to 1:1 binding model for the Q[8]-guest systems, where the guests are longer-chain FV $^{2+}$ , HV $^{2+}$  and SV $^{2+}$ . There is some evidence that there are multiple interaction models with different ratio of the host and guest. This is clearly evident for the systems where the substituents are relatively long aliphatic chains ( $\geq 5$  carbons), but we have observed that BV $^{2+}$  (4 carbon chain) also shows some variation in absorbance at high host:guest ratios that suggests 2:1 species may be forming under these conditions. Table 1 shows the binding constants measured for the 1:1 host–guest complexes in the present system. Measuring  $K$  for the host–guest system in this work under different pH conditions for the dialkylammonium species shows there are no significant differences, consistent with the permanent nature of the charge on the alkylated N centres in these dications; only 4,4'-bipyridine exhibits a clear pH dependence, as expected. The stability of the host–guest interaction complexes formed is high even in

aqueous solution, consistent with the high charge on the cations and their favourable fit to the host.

**Acknowledgments** Support of the National Natural Science Foundation of China (NSFC; No. 20662003), the International Collaborative Project Fund of the Chinese Ministry of Science and Technology (Grant No. 2003DF000030), the ‘‘Chun-Hui’’ Fund and the America and Pacific Region Research Collaboration Fund of the Chinese Ministry of Education, the Science and Technology Fund of Guizhou Province (Grant No. J-2005-2012) and the Governor Foundation of Guizhou Province, P.R. China, are gratefully acknowledged.

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