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Highly Effective Binding of Methyl Viologen Dication and Its Radical Cation by *p*-Sulfonatocalix[4,5]arenes

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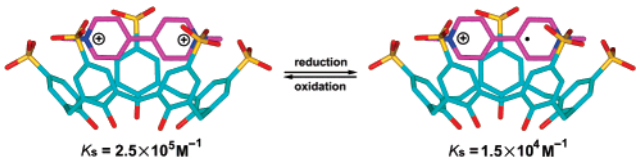

The binding behaviors and thermodynamic origins of *p*-sulfonatocalix[4]arene (C4AS) and *p*-sulfonatocalix[5]-arene (C5AS) with methyl viologen (MV^{2+}) have been investigated by the methods of isothermal titration calorimetry, NMR, and cyclic voltammetry, showing that the binding abilities of C4AS and C5AS and their host selectivity are dramatically pH-controlled, which is closely discussed from the viewpoint of thermodynamics. Moreover, the radical form of $MV^{+\bullet}$ can also be effectively included by C4AS and C5AS.

Viologens are one class of important redox couples,[1] widely utilized as herbicides,[2] as subunits in constructing functional molecular assemblies/machines,[3] as probes to study DNA and zeolites,[4] and as components of electrochromic display devices.[5] Thereinto, viologen radical cations, as odd-electron species, are promised to be suitable electrical conductors and electrochromic displays as solid, crystalline materials.[6] However, a reversible π-dimerization constrains their applications to a certain extent.[5,7] Therefore, endeavors have been made to stabilize viologen radical cations, such as chemical modification and dispersion in appropriate in aprotic matrixes. With development of supramolecular chemistry, the host−guest inclusion complexation emerges to be another effective way for the mission. As an excellent example, Kaifer and co-workers reported that cucurbit-[7]uril can form highly stable complexes with both viologen dications and radical cations and thus largely prevent the dimerization/oligomerization of viologen radical cations.[8]

On the other hand, calix[*n*]arenes are pronounced with regard to the third generation of supramolecular hosts due to their extensive properties.[9] Their water-soluble derivatives, *p*-sulfonatocalix[*n*]arenes (C*n*AS), not only greatly improve the solubility of calixarenes but also can include various guests to form stable complexes, particularly with cation guests.[10] Furthermore, they have been used as artificial signaling acetylcholine receptors,[11] inhibitor of quinine-imine dye deamination,[12] and metalloenzyme models,[13] etc. However, to the best of our knowledge, early studies have only been focused on the complexation of viologens by C6AS, and the inclusion behaviors of C*n*AS with viologen radical cations have not yet been documented.[14] Especially, investigations concerning the inclusion behaviors of C*n*AS with viologen radical cations have never been reported up to now.

In the present work, we report our investigation on the inclusion complexation behaviors of C4AS and C5AS with methyl viologen dication (MV^{2+}) using isothermal titration calorimetry (ITC) and NMR spectroscopy. In addition, the binding abilities of C4AS and C5AS with methyl viologen radical cation ($MV^{+\bullet}$) have also been investigated using cyclic voltammetry. The smaller analogues, C4AS and C5AS, are employed for their stable preorganized cone shapes and anticipated size/shape fits with methyl viologen.

The formation of the inclusion complexes between *p*-sulfonatocalixarenes and MV^{2+} is evident in ^1H NMR spectroscopic experiments in D_2O (Figure 1). In the presence of about 1 equiv of *p*-sulfonatocalixarenes, all the protons of MV^{2+} exhibit a visible upfield shift ($\Delta\delta$) owing to the ring current effect of the aromatic nuclei, which suggests that the MV^{2+} guests are encapsulated into the cavities of *p*-sulfonatocalixarenes. However, the $\Delta\delta$ value for each proton is different, which can be used as a powerful evidence to deduce the host−guest binding manner. Upon addition of C4AS in both acidic (pD 2.0) and basic (pD 12.0) D_2O solution, the $\Delta\delta$ values of MV^{2+} protons are in the order of CH_3 > *a*-H > *b*-H. It indicates that MV^{2+} is immersed into the cavity of C4AS in its axial orientation with the methyl group being included first. The deduced binding manner of C4AS with MV^{2+} is shown in Figure 2a.

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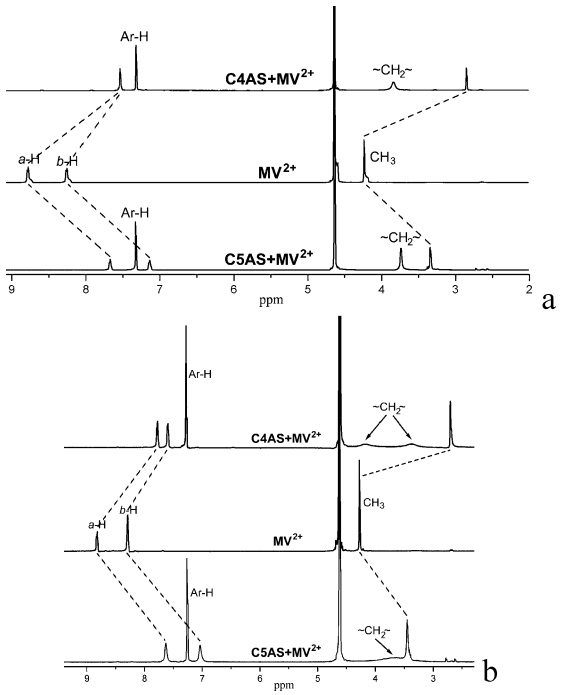

FIGURE 1. The ^{1}H NMR spectra of MV^{2+} in the absence (and presence) of C4AS or C5AS: (a) pD = 2.0; (b) pD = 12.0.

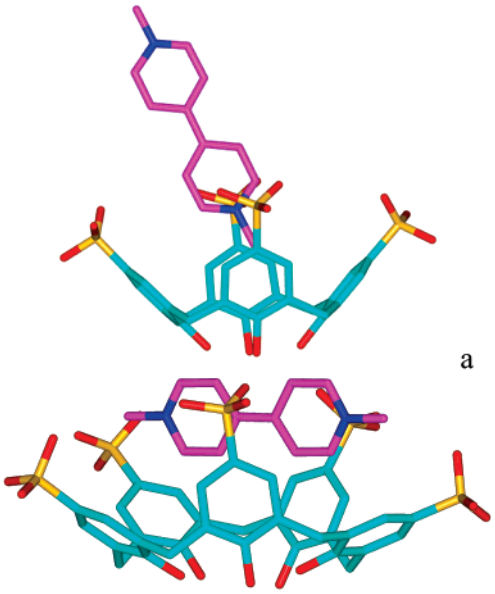

FIGURE 2. The deduced binding manners of C4AS (a) and C5AS (b) with MV^{2+} according to NMR spectra.

C5AS possesses similar cone shape to C4AS, but with a wider size. However, C5AS provides distinct binding geometry for MV^{2+} from C4AS. According to complex-induced shifts of MV^{2+} protons by C5AS, the $\Delta\delta$ sequence by C5AS (*b*-H > *a*-H > CH_3) is reversed from that by C4AS in both acidic and basic conditions. Judged from the present ^{1}H NMR results, MV^{2+} may undergo two possible modes when included into the cavity of C5AS. One is that MV^{2+} penetrates through the cavity of C5AS in the longitudinal orientation; the other is that MV^{2+} lies at the upper-rim midsection of C5AS in the latitudinal orientation. To clarify, 2D ROESY NMR experiments were carried out to obtain complementary information on the inclusion

TABLE 1. Complex Stability Constants (K_S/M^{-1}), Enthalpy [$\Delta H°$/(kJ·mol^{-1})], and Entropy Changes [$T\Delta S°$/(kJ·mol^{-1})] for 1:1 Intermolecular Complexation of MV^{2+} with *p*-Sulfonatocalixarenes in Phosphate Buffer Solution (pH 2.0, 7.2, 12.0) at 298.15 K

conditions	complexes	log K_S	$\Delta H°$	$T\Delta S°$
pH = 2.0	**C4AS** + $\mathbf{MV^{2+}}$	4.49 ± 0.01	−28.18 ± 0.01	−2.53 ± 0.03
	C5AS + $\mathbf{MV^{2+}}$	3.74 ± 0.01	−20.58 ± 0.06	0.79 ± 0.08
pH = 7.2	**C4AS** + $\mathbf{MV^{2+}}$	4.97 ± 0.00	−31.98 ± 0.03	−3.62 ± 0.01
	C5AS + $\mathbf{MV^{2+}}$	5.40 ± 0.01	−31.52 ± 0.06	−0.67 ± 0.11
pH = 12.0	**C4AS** + $\mathbf{MV^{2+}}$	4.97 ± 0.01	−32.83 ± 0.29	−4.46 ± 0.25
	C5AS + $\mathbf{MV^{2+}}$	5.53 ± 0.02	−33.11 ± 0.05	−1.53 ± 0.15

geometry of C5AS with MV^{2+}. The ROESY spectrum (Figure S1) of the complex of C5AS with MV^{2+} exhibits three clear cross-peaks representing the correlations of *a*-H, *b*-H, and CH_3 with aromatic protons of C5AS, respectively. The correlations between methylene protons of C5AS and protons of MV^{2+} are not observed, which excludes the possibility of the former manner (if MV^{2+} penetrates through the cavity of C5AS, the distances from methylene protons to *a*-H or *b*-H should be in the region of Overhauser effect). Therefore, we determine the binding manner of C5AS with MV^{2+}, as shown in Figure 2b. This result is consistent with our previous study that 4,4′-dipyridinium was accumbently included into the cavity of C5AS from the upper rim.[15]

To further quantitatively determine the inclusion complexation abilities of *p*-sulfonatocalixarenes with MV^{2+}, the isothermal titration calorimetry (ITC) experiments were performed at acidic, neutral, and basic conditions. ITC is a powerful tool for measuring the host−guest complex interactions because it not only gives the complex stability constants (K_S) but can also yield their thermodynamic parameters (enthalpy and entropy changes $\Delta H°$ and $\Delta S°$). The data obtained are listed in Table 1. In all cases, the titration data can be well fitted by computer simulation using the "one set of binding sites" model and repeated as 1:1 complex formation, thereby the higher-order complexes did not need to be postulated.

As can be seen from Table 1, C4AS and C5AS can all form stable complexes with the MV^{2+} guest ($K_S = 10^3$−10^5 M^{-1}), which is different from the larger C6AS that just shows weak inclusion complexation (K_S = 220 M^{-1}) for MV^{2+} with the alternative conformation.[14b] Moreover, the pH conditions also play a crucial role in manipulating the complex stability constants (K_S) upon inclusion of the MV^{2+} guest. The K_S values are in the order of C5AS < C4AS at pH 2.0 and in the order of C4AS < C5AS at pH 7.2 and 12.0. That is to say, the host selectivity for C4AS/C5AS pairs is reversed when the pH increases from acidic to neutral (basic) conditions. According to the pK_a values of lower-rim phenolic hydroxyls (pK_a values of C4AS = 3.08, 12.02; C5AS = 4.31, 7.63, 10.96),[16] all the phenolic hydroxyls of C4AS and C5AS are in the protonated form at pH 2.0. In this case, C4AS possesses the most compact framework and highest π-electron density of the cavity, leading to more effective π-stacking interactions with MV^{2+}, and then forms a stable complex with MV^{2+} almost 1 order of magnitude higher than C5AS. This fact can be reflected from the much more favorable enthalpy change ($\Delta H°_{C4AS+MV2+,pH2.0}$ − $\Delta H°_{C5AS+MV2+,pH2.0}$ = −7.60 kJ·mol^{-1}).

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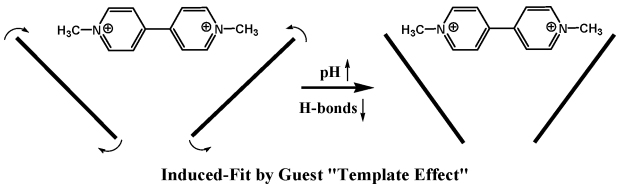

FIGURE 3. The conformational pinch of C5AS induced by complexation with MV^{2+} accompanied with pH increase.

With the solution adjusted from acidic to neutral (basic), some of the phenolic hydroxyls of calixarenes begin to be deprotonated,[16] and therefore, the cavities of calixarenes become more electron-rich and are capable of providing stronger π-stacking interactions. The enhanced binding constants K_S going with pH value are absolutely driven by the enthalpy term. Dramatically, C5AS presents much stronger binding ability to MV^{2+} than C4AS once the solution is adjusted to neutral or basic. For example, the inverted host selectivity for C5AS/C4AS pairs is 2.7 times at pH 7.2 and up to 3.6 times at pH 12.0, which differs from the host selectivity for C4AS/C5AS pairs of 5.6 times at pH 2.0. Although the augmentation of π-electron density of calixarenes arising from the deprotonation of phenolic hydroxyls plays an important role in the enhancement of binding ability for *p*-sulfonatocalixarenes ($K_{S,C4AS+MV2+,pH7.2}/K_{S,C4AS+MV2+,pH2.0} = 3.0$), it is not effective enough to enhance the binding ability of C5AS with MV^{2+} to such a large extent ($K_{S,C5AS+MV2+,pH7.2}/K_{S,C5AS+MV2+,pH2.0} = 45.7$) because the augmentations of π-electron density are considered to be almost identical between C4AS and C5AS when the condition changes from pH 2.0 to 7.2. One reasonable explanation for the profound pH-subtle selectivity of C5AS with MV^{2+} can be inferred from the viewpoint of binding manner. As proved by the aforementioned NMR experiments, the wider cavity of C5AS can accommodate the MV^{2+} guest with the accumbent manner. At acidic condition of pH 2.0, the restriction of the lower-rim hydrogen bonds makes the cavity of C5AS appear more like a shallow dish with a certain rigidity,[17] and the size/shape fit between C5AS and MV^{2+} is not very good. Upon increasing pH value to neutral (and basic) conditions, some hydrogen bonds are destroyed, leading to more conformational flexibility of C5AS, which makes the cavity of C5AS more adaptable to better accommodate MV^{2+}. As illustrated in Figure 3, the conformational micro-adjustment of C5AS upon complexation with MV^{2+} allows the methyl groups of the MV^{2+} guest to be more adjacent to the sulfonate groups of C5AS, which can form strong hydrogen-bonding interactions, and further strengthens the host−guest complexation to much extent. This can not only be reflected from the enthalpy term ($\Delta H^\circ_{C5AS+MV2+,pH7.2} - \Delta H^\circ_{C5AS+MV2+,pH2.0} = -10.94$ kJ·mol^{-1}) but also be validated by the entropy term. Compared with that in acidic condition, the framework of calixarenes is more flexible in neutral and basic conditions owing to the deprotonation of phenolic hydroxyls. However, the entropy change is more unfavorable during the course of complexation of C5AS with MV^{2+} at pH 7.2 than that of pH 2.0 ($T\Delta S^\circ_{C5AS+MV2+,pH7.2} - T\Delta S^\circ_{C5AS+MV2+,pH2.0} = -1.46$ kJ·mol^{-1}). This is mainly originated from the large loss of conformational degree of freedom for C5AS and structure freezing upon strong complexation with MV^{2+} at pH 7.2.

On the other hand, the interpretation can also be validated by the comparison of the binding abilities of C5AS between pH 7.2 and 12.0. The stability of complex C5AS+MV^{2+} at pH 12.0 is enhanced from that at pH 7.2 by 1.3 times. From pH 2.0 to 7.2, there should be one hydroxyl deprotonated in C5AS, and from pH 7.2 to 12.0, there should be another two hydroxyls deprotonated in C5AS. It can be seemingly deduced that the enhancement of K_S value from pH 7.2 to 12.0 should be as prominent as, or even possibly larger than, that from pH 2.0 to 7.2 if only the augmentation of π-electron density originated from the deprotonation of hydroxyls plays the crucial role during the course of complexation of C5AS with MV^{2+} at different pH values. However, the factual results do not support the hypothesis. Therefore, according to the close comparison of K_S-(C5AS+MV^{2+}) values among the three pH conditions, we can deduce that the outstanding enhancement of complex stability from pH 2.0 to 7.2 is mainly attributed to the induced-fit interaction between the conformation-flexible C5AS and MV^{2+} by template effect of guest, while the accepted enhancement of complex stability from pH 7.2 to 12.0 is rationally attributed to the augmentation of π-electron density of C5AS as a result of the deprotonation of phenolic hydroxyls.

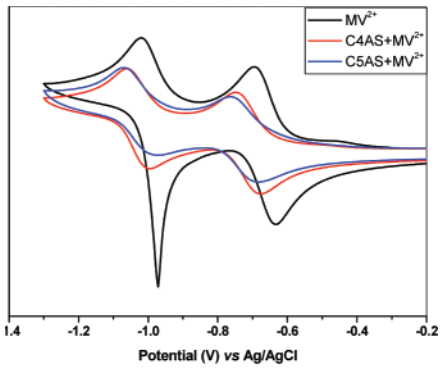

FIGURE 4. Cyclic voltammetric curves of MV^{2+} (1.02 mM in pH 7.2 phosphate buffer solution) in the absence and presence of 1 equiv of C4AS and C5AS. Scan rate is 100 mV/s.

Furthermore, the electrochemical behaviors of MV^{2+} in the absence and presence of *p*-sulfonatocalixarenes were also investigated to determine the binding abilities of C4AS and C5AS with the methyl viologen radical cation ($MV^{+\bullet}$). The selected cyclic voltammetric (CV) curves for MV^{2+} before and after complexation by *p*-sulfonatocalixarenes are shown in Figure 4. In the presence of *p*-sulfonatocalixarenes, the half-wave potential ($E_{1/2}^1$) of the first one-electron reduction of MV^{2+} ($MV^{2+} \rightarrow MV^{+\bullet}$) is obviously shifted to more negative values. It indicates that MV^{2+} becomes more difficult to be reduced, reflecting the stabilization offered by the complexation of *p*-sulfonatocalixarenes. In line with this interpretation, the shifts of $E_{1/2}^1$ in the presence of *p*-sulfonatocalixarenes are more and more pronounced from C4AS to C5AS, which is in the same order of K_S values. Moreover, the shifts of $E_{1/2}^1$ also imply that the stability of complexes of *p*-sulfonatocalixarenes with MV^{2+} decreases upon one-electron reduction. It is reasonable that the first one-electron reduction decreases the π-electron acceptor and hydrogen-bonding donor abilities of MV^{2+} and thereby destabilizes the structure of complexes. Despite the disadvantageous influence arising from the one-electron reduction, *p*-sulfonatocalixarenes can also effectively include $MV^{+\bullet}$, which is reflected from the shifts of $E_{1/2}^2$. Besides the first reduction progress, the second one-electron reduction progress ($MV^{+\bullet} \rightarrow MV$) is also affected to some extent in the presence of *p*-sulfonatocalixarenes. It implies that the $MV^{+\bullet}$ likewise

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becomes more difficult to be reduced upon complexation by *p*-sulfonatocalixarenes.

Along with the continuous addition of C5AS, $E_{1/2}{}^1$ is further shifted to negative values more and more and becomes almost balanceable upon addition of 1.44 equiv of C5AS. Moreover, primary calculation from the K_S value of C5AS with MV^{2+} implies that MV^{2+} exists mostly in C5AS+MV^{2+} complex form. Therefore, the $E_{1/2}{}^1$ in the presence of 1.44 equiv of C5AS should represent the corresponding half-wave potential of the C5AS+MV^{2+} complex. Thus, the complex stability constant (K_S*) of C5AS with $MV^{+\bullet}$ can be determined by eq 1.

$$E_{1/2}{}^1(MV^{2+}) = E_{1/2}{}^1(C5AS + MV^{2+}) + \frac{RT}{nF}\ln\frac{K_S}{K_S*} \quad (1)$$

The obtained K_S* value of C5AS with $MV^{+\bullet}$ at pH 7.2 is $1.52 \times 10^4\ M^{-1}$, which decreases obviously by comparing with the K_S value ($2.51 \times 10^5\ M^{-1}$) of C5AS with MV^{2+}. Nevertheless, the stable complexation of C5AS with $MV^{+\bullet}$ still represents a typical example of calixarene-stabilizing radicals. The binding behaviors of *p*-sulfonatocalixarenes with some other radicals have been studied before, showing that *p*-sulfonatocalixarenes cannot act as ideal hosts for radicals.[18] In the same way, the K_S* value of C4AS with $MV^{+\bullet}$ at pH 7.2 is also gained as $1.13 \times 10^4\ M^{-1}$. The effective inclusion of C4AS and C5AS with $MV^{+\bullet}$ is promised to prevent the unsatisfactory π-dimerization of viologen radical cations, which endows the more effective use of viologens as components of electrochromic display devices and other applications.[2−5] In addition, taking into account the binding manners, C5AS may be a more suitable receptor than C4AS.

In summary, both C4AS and C5AS can form stable complexes with MV^{2+} while their binding manners are distinct from each other. MV^{2+} penetrates into the cavity of C4AS in the axial orientation, while the wider cavity of C5AS accommodates MV^{2+} at its upper-rim midsection with the accumbent manner. The particular binding geometry of C5AS with MV^{2+} allows the right induced fit between host and guest accompanied with the augmentation of pH value. As a result, C5AS presents much stronger binding ability to MV^{2+} than C4AS at neutral (basic) conditions and displays the reversed host selectivity from that at acidic conditions, as well. Moreover, C4AS and C5AS can also effectively include $MV^{+\bullet}$ with the strength of over $10^4\ M^{-1}$. The strong complexation of *p*-sulfonatocalixarenes with both MV^{2+} and $MV^{+\bullet}$ is potentially valuable because of the versatile applications of viologens.

Experimental Section

Materials. The two *p*-sulfonatocalixarenes {i.e., *p*-sulfonatocalix[4]arene tetrasodium (C4AS)[19] and *p*-sulfonatocalix[5]arene pentasodium (C5AS)}[16b] were synthesized and purified according to the literature reports. Guest molecule, methyl viologen diiodide (MV^{2+}), was prepared by the direct reaction of 4,4′-dipyridine with iodomethane in DMF. The phosphate buffer solution of pH 2.0 was prepared by dissolving sodium dihydrogen phosphate in distilled, deionized water to make a 0.1 mol·dm^{-3} solution, which was then adjusted to pH 2.0 by phosphoric acid. The phosphate buffer solution of pH 7.2 was prepared by dissolving disodium hydrogen phosphate ($Na_2HPO_4{\cdot}12H_2O$, 25.79 g) and sodium dihydrogen phosphate ($NaH_2PO_4{\cdot}2H_2O$, 4.37 g) in distilled, deionized water (1000 mL) to make a 0.1 mol·dm^{-3} solution. The phosphate buffer solution of pH 12.0 was prepared by dissolving disodium hydrogen phosphate in distilled, deionized water to make a 0.1 mol·dm^{-3} solution, which was then adjusted to pH 12.0 with sodium hydroxide.

Measurements. ^{1}H NMR and 2D ROESY (rotating frame Overhauser effect spectroscopy) spectra were recorded in D_2O solution (pH adjusted by DCl or NaOD) at 25 °C. Chemical shifts (δ, ppm) in water were externally referenced to 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an external reference in order to avoid any possible interaction with hosts as well as with the guest molecule. A thermostated and fully computer-operated isothermal calorimetry (VP-ITC) instrument was used for all microcalorimetric experiments. The cyclic voltammetry (CV) measurements were carried out on an electrochemical analyzer with a C3 cell stand in phosphate buffer (pH 7.2) at 25 °C.

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Supporting Information Available: Two-dimensional NMR, ITC, and CV experiments of C5AS (C4AS) with MV^{2+}. This material is available free of charge via the Internet at http://pubs.acs.org.

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