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High affinity of *p*-sulfonatothiacalix[4]arene with phenanthroline-diium in aqueous solution†

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The molecular binding behavior of three sulfonated calixarene hosts, *p*-sulfonatocalix[4]arene (SC4A), *p*-sulfonatocalix[5]arene (SC5A), and *p*-sulfonatothiacalix[4]arene (STC4A), with two phenanthroline-diium guests, 5,6-dihydropyrazion[1,2,3,4-*lmn*][1,10]phenanthroline-4,7-diium (DP^{2+}) and 6,7-dihydro-5*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-4,8-diium (PPQ^{2+}), were systemically investigated in neutral phosphate buffer solutions by microcalorimetry, cyclic voltammetry, NMR spectroscopy, and molecular mechanics calculation. We found that the phenanthroline-diium guests were captured by SC4A, SC5A, and STC4A from their aromatic moieties. Furthermore, STC4A displays a high affinity with phenanthroline-diium guests in the order of magnitude of 10^5 M^{-1}. It is the reported highest binding order of magnitude for STC4A up to now, although the binding constants of SC4A and SC5A with phenanthroline-diium guests are still a little larger.

Introduction

p-Sulfonatothiacalix[4]arene (STC4A), the analogue of *p*-sulfonatocalix[*n*]arenes (SC*n*As, $n = 4$–8), was first prepared by Miyano *et al.*[1] Rather than a simple substitution for conventional calixarenes, thiacalix[4]arene should be regarded as a unique molecular framework because replacement of the methylene linkages of calix[4]arenes by sulfur atoms provides various intrinsic characteristics of thiacalix[4]arene,[2] such as a wider cavity, lower electron density, more flexibility, additional coordination sites of sulfur, and so on. As anticipated, STC4A shows much different inclusion behavior toward some organic molecules and metal ions in water as compared with SC*n*As.[3] Therefore, STC4A should have been widely used as an important supramolecular building block. However, unlike SC*n*As, which have been popularly applied in many fields,[4–6] such as amphiphile,[7] polymer,[8] enzyme mimic/enzyme assay,[9] and biomedicine,[10] in the past three decades due to their robust inclusion properties with numerous guest molecules,[11–18] STC4A is by far less explored owing to its much weaker affinity with model guest.

We previously studied the structures and thermodynamics for the intermolecular complexation of *p*-sulfonatocalix[4]arene (SC4A), *p*-sulfonatocalix[5]arene (SC5A), and STC4A with methyl viologen (MV^{2+}) and diquat (DQ^{2+}) in neutral phosphate buffer solutions on account of the biological environment of serum (pH *ca.* 7.3). We found that MV^{2+} displayed the high affinities with SC4A and SC5A around 10^5 M^{-1},[15e] which have been applied in the MV^{2+} detoxification.[10b,d] However, the binding constant of STC4A + MV^{2+} complex is only in the order of magnitude of 10^3 M^{-1} under the same condition.[10b] We also found that the position of the nitrogen atoms in guests also exerted dramatic influence on the complex stabilities, and upon complexation with the same host, the binding constants of DQ^{2+} were always larger than those of MV^{2+}.[10b] However, we noted that the DQ^{2+}/MV^{2+} selectivity for STC4A was much lower than that for SC4A and SC5A. Therefore, the affinity of STC4A + DQ^{2+} complex is still moderate.

In this study, to further enhance the affinities of sulfonated calixarene hosts with model guests, we synthesized two phenanthroline-diium guests, 5,6-dihydropyrazion[1,2,3,4-*lmn*][1,10]phenanthroline-4,7-diium (DP^{2+}) and 6,7-dihydro-5*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-4,8-diium

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† Electronic supplementary information (ESI) available: Experimental section; ^1H and ^{13}C NMR spectra of SC4A, SC5A, STC4A, DP^{2+}, and PPQ^{2+} in D_2O; elemental analysis data of SC4A, SC5A, STC4A, DP^{2+}, and PPQ^{2+}; pictures showing the color of DP^{2+} solutions upon complexation with 1 equiv. of sulfonated calixarenes; ^1H NMR spectra of DP^{2+} guest in the presence of sulfonated calixarene hosts at different temperatures; "Net" heat effects of complexation of DP^{2+} and PPQ^{2+} with SC4A, SC5A, and STC4A for each injection, obtained by subtracting the dilution heat from the reaction heat, which was fitted by computer simulation using the "one set of binding sites" model. See DOI: 10.1039/c4ra15047c.

(PPQ^{2+}), because they have much more conjugated structures as compared with DQ^{2+}. Then we studied the molecular binding behaviors between sulfonated calixarene hosts and phenanthroline-diium guests in neutral phosphate buffer solutions by microcalorimetry, cyclic voltammetry, NMR spectroscopy, and molecular mechanics calculation. We found that the phenanthroline-diium guests were captured by SC4A, SC5A and STC4A from their aromatic moieties. Furthermore, in contrast to the higher DQ^{2+}/MV^{2+} selectivity for SC4A and SC5A, we excitingly note that the DP^{2+} (or PPQ^{2+})/DQ^{2+} selectivity for STC4A is much higher. As a result, STC4A displays the high affinities with phenanthroline-diium guests in the order of magnitude of 10^5 M^{-1}. To the best of our knowledge, it is the reported highest binding order of magnitude for STC4A complex up to now. The high affinity of STC4A with phenanthroline-diium would be beneficial to explore the supramolecular application of STC4A by designing suitable guest. For example: the high affinity between STC4A and phenanthroline-diium is highly desirable as the reporter pair of supramolecular tandem assay, particularly for potential application in high-throughput screening for drug discovery;[9i,19] modifying hydrophilic phenanthroline-diium with a hydrophobic group may lead to the formation of a supramolecular amphiphile upon complexation with STC4A;[7] synthesizing bis-phenanthroline-diium may lead to the formation of a supramolecular polymer upon complexation with lower-rim-linked bis-STC4A;[8b] and so on.

Results and discussion

Binding ability and thermodynamics

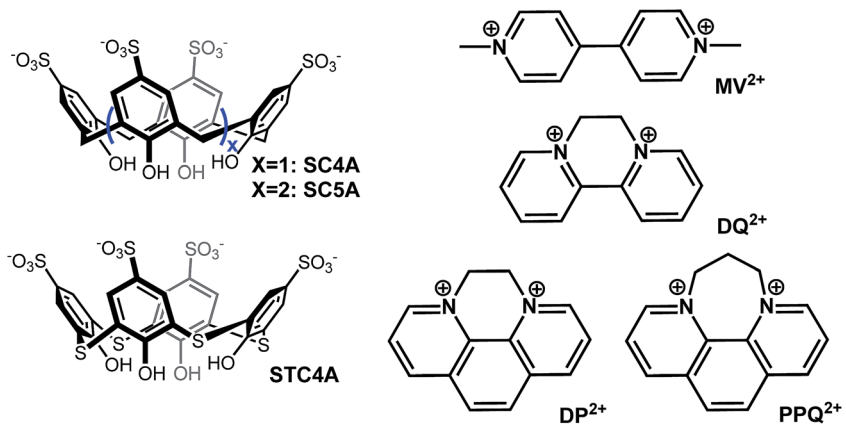
To compare quantitatively the selective binding behaviors of sulfonated calixarenes with diquaternary salts (Scheme 1), the microcalorimetric experiments for the intermolecular complexation of SC4A, SC5A, and STC4A with DP^{2+} and PPQ^{2+} were performed in pH 7.2 phosphate buffer solutions, which could not only give the binding affinities (K_s) between hosts and guests, but also show the accompanied enthalpy (ΔH°) and entropy ($T\Delta S^\circ$) changes. The obtained results are listed in Table 1 together with our previous thermodynamic results for the intermolecular complexation of MV^{2+} and DQ^{2+} with the three sulfonated calixarenes under the same conditions.[10b,15e] All the stoichiometric ratios (N values) that we observed from curve-fitting results of the binding isotherm fell within the range of 0.90–1.10 : 1. This clearly indicates that all the inclusion complexes have a 1 : 1 stoichiometry.

Table 1 Complex stability constants (K_s/M^{-1}), enthalpy (ΔH°/(kJ mol^{-1})), and entropy ($T\Delta S^\circ$/(kJ mol^{-1})) changes for 1 : 1 intermolecular complexations of sulfonated calixarenes with diquaternary salts in pH 7.2 phosphate buffer solutions at 298.15 K

Hosts	Guests	K_s	ΔH°	$T\Delta S^\circ$
SC4A[a]	MV^{2+}	9.33×10^4	−31.98	−3.62
SC5A[a]		2.51×10^5	−31.52	−0.67
STC4A[b]		8.68×10^3	−31.01	−8.53
SC4A[b]	DQ^{2+}	7.95×10^5	−33.90	−0.21
SC5A[b]		3.23×10^6	−32.78	4.39
STC4A[b]		4.57×10^4	−32.26	−5.65
SC4A	DP^{2+}	$(1.55 \pm 0.07) \times 10^6$	−36.94 ± 0.21	−1.59 ± 0.10
SC5A		$(2.43 \pm 0.18) \times 10^6$	−31.85 ± 0.10	4.61 ± 0.09
STC4A		$(1.86 \pm 0.01) \times 10^5$	−36.15 ± 0.01	−6.05 ± 0.01
SC4A	PPQ^{2+}	$(1.59 \pm 0.02) \times 10^6$	−38.05 ± 0.07	−2.64 ± 0.10
SC5A		$(3.60 \pm 0.33) \times 10^6$	−32.57 ± 0.05	4.86 ± 0.28
STC4A		$(2.81 \pm 0.01) \times 10^5$	−38.02 ± 0.03	−6.91 ± 0.04

[a] Ref. 15e. [b] Ref. 10b.

Among several weak noncovalent interactions working between calixarene hosts and model guests, hydrogen bond, π-stacking, and van der Waals interactions mainly contribute to the enthalpy changes, while electrostatic interaction,[12a] conformation change, and desolvation effect contribute to the entropy changes. As shown in Table 1, all the intermolecular complexations between sulfonated calixarenes and diquaternary salts are driven by the favorable enthalpy changes (ΔH° = −31.01 to −38.05 kJ mol^{-1}), accompanied by small positive (favorable) or negative (unfavorable) entropy changes ($T\Delta S^\circ$ = −8.53 to 4.86 kJ mol^{-1}), which indicates that the governing factor for these complexations is the inclusion of guests into the host cavity,[13f,g] and hydrogen bond, π-stacking, and van der Waals interactions are the main driven forces.



Scheme 1 Structural illustration of sulfonated calixarenes (SC4A, SC5A, and STC4A) and diquaternary salts (MV^{2+}, DQ^{2+}, DP^{2+}, and PPQ^{2+}).

As can be seen from Table 1, MV^{2+} displays the high affinities with SC4A and SC5A around 10^5 M^{-1}, while the binding constant of STC4A + MV^{2+} complex is only in the order of magnitude of 10^3 M^{-1} under the same condition. The weaker binding ability of STC4A originates mainly from the more unfavorable entropy change. It indicates that the cavity size and preorganized structure of STC4A do not fit well with MV^{2+} guest, leading to a greater loss of conformational degrees of freedom and structure freezing upon complexation.[10b] The position of the nitrogen atoms in guests also exerts dramatic influence on the complex stabilities, and upon complexation with the same host, the binding constants of DQ^{2+} are always larger than those of MV^{2+}. Both the enthalpy changes and the entropy changes for the intermolecular complexations of DQ^{2+} with SC4A, SC5A, and STC4A are relatively more favorable than those of MV^{2+} with the three sulfonated calixarene hosts. It indicates that, on one hand, in comparison with MV^{2+}, DQ^{2+} is more prone to form π-stacking and van der Waals interactions with sulfonated calixarenes and then shows the more favorable enthalpy changes; on the other hand, the complexation of DQ^{2+} with sulfonated calixarenes gives rise to smaller conformational loss and more favorable desolvation effect, and then shows the more relatively favorable entropy changes.[10b] After careful analysis of the data, we can also see that the DQ^{2+}/MV^{2+} selectivity for STC4A ($K_{s(STC4A+DQ^{2+})}/K_{s(STC4A+MV^{2+})}$ = 5.3) is much lower than that for SC4A ($K_{s(SC4A+DQ^{2+})}/K_{s(SC4A+MV^{2+})}$ = 8.5) and SC5A ($K_{s(SC5A+DQ^{2+})}/K_{s(SC5A+MV^{2+})}$ = 12.9). It means that the binding constant of STC4A increases only a little upon complexation from MV^{2+} to DQ^{2+}. Therefore, the affinity of STC4A + DQ^{2+} complex is still moderate. However, the K_s value of DQ^{2+} with SC5A has displayed a high affinity over 10^6 M^{-1} accompanied by a large increasement of the binding constant of SC5A upon complexation from MV^{2+} to DQ^{2+}. The SC5A/STC4A selectivity for DQ^{2+} is as high as 70.7.

To further enhance the affinities of sulfonated calixarenes with model guests, we synthesized two phenanthroline-diium salts for the reason that they have much more conjugated structures with one more benzene ring in their molecules as compared with DQ^{2+}. As can be seen from Table 1, upon complexation with SC4A and STC4A, the K_s values of DP^{2+} and PPQ^{2+} are indeed larger than those of DQ^{2+}. However, differing from the DQ^{2+}/MV^{2+} selectivity, the DP^{2+} (or PPQ^{2+})/DQ^{2+} selectivity for SC4A and STC4A is only governed by the favorable enthalpy changes, accompanied by the unfavorable entropy changes. In comparison with DQ^{2+}, much more conjugated DP^{2+} and PPQ^{2+} are more prone to form π-stacking and van der Waals interactions with sulfonated calixarenes and then shows the more favorable enthalpy changes. However, the cavity size and preorganized structure of SC4A and STC4A do not fit with larger phenanthroline-diium guests, leading to a greater loss of conformational degrees of freedom and structure freezing upon complexation. Moreover, in contrast to the DQ^{2+}/MV^{2+} selectivity, we excitingly find that the DP^{2+} (or PPQ^{2+})/DQ^{2+} selectivity for STC4A ($K_{s(STC4A+DP^{2+})}/K_{s(STC4A+DQ^{2+})}$ = 4.1; $K_{s(STC4A+PPQ^{2+})}/K_{s(STC4A+DQ^{2+})}$ = 6.1) is much higher than that for SC4A ($K_{s(SC4A+DP^{2+})}/K_{s(SC4A+DQ^{2+})}$ = 1.9; $K_{s(SC4A+PPQ^{2+})}/K_{s(SC4A+DQ^{2+})}$ = 2.0). Furthermore, SC5A even displays the comparable binding affinities with phenanthroline-diium guests and DQ^{2+} accompanied by the similar enthalpy and entropy changes. As a result, STC4A displays the high affinities with phenanthroline-diium guests in the order of magnitude of 10^5 M^{-1}. To the best of our knowledge, it is the reported highest binding order of magnitude for STC4A complex up to now, although the binding constants of SC4A and SC5A with phenanthroline-diium guests are still a little larger. One possible explanation for this phenomenon is that STC4A has a much more flexible structure by replacement of the methylene linkages of calix[4]arenes by sulfur atoms, and then can bind larger conjugated guest well by adjusting its structure. The above results also reveal that stronger binding does not always mean higher selectivity.

Electrochemical behavior

We previously found that the shift values for the first reduction potential of MV^{2+} upon complexation with SC4A and SC5A were −52 mV and −66 mV, and those of DQ^{2+} increased dramatically to −87 mV and −100 mV upon complexation with SC4A and SC5A, respectively (SC4A: shift value (DQ^{2+}) − shift value (MV^{2+}) = −35 mV; SC5A: shift value (DQ^{2+}) − shift value (MV^{2+}) = −34 mV).[15e] However, upon complexation with STC4A, that shift value only changes from −11 mV of MV^{2+} to −30 mV of DQ^{2+} (STC4A: shift value (DQ^{2+}) − shift value (MV^{2+}) = −19 mV).[10b] Compared with the complexation of STC4A, the larger change of the shift value from MV^{2+} to DQ^{2+} upon complexation with SC4A and SC5A is well in accordance with the much higher DQ^{2+}/MV^{2+} selectivity for SC4A and SC5A. The large shift values for the first reduction potential of MV^{2+} and DQ^{2+} upon complexation with SC4A and SC5A are also in accordance with the high affinities of SC4A and SC5A with MV^{2+} and DQ^{2+}.

Herein, the electrochemical behaviors of DP^{2+} in the absence and presence of SC4A, SC5A, and STC4A were also investigated in pH 7.2 phosphate buffer solutions by cyclic voltammetry. To focus on the first reduction potentials, the selected partial cyclic voltammetric curves of DP^{2+} before and after complexation by SC4A, SC5A, and STC4A are shown in Fig. 1. We can see that the

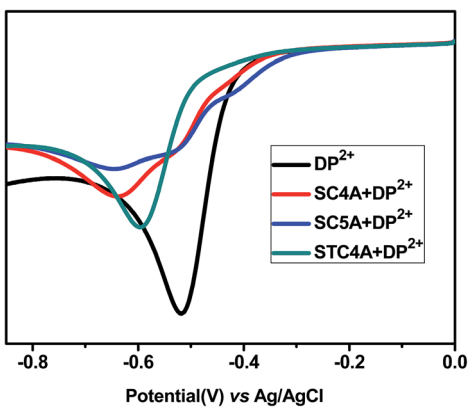


Fig. 1 Selected partial cyclic voltammetric curves for the first reduction potentials of DP^{2+} (1.0 mM in pH 7.2 phosphate buffer solution) in the absence and presence of 1 equiv. of SC4A, SC5A, and STC4A. The scan rate is 100 mV s^{-1}.

first reduction potential of DP^{2+} also shifts to more negative values upon complexation with these hosts, indicating that DP^{2+} is more difficult to be reduced after complexation by sulfonated calixarenes. Differently, the shift value for the first reduction potential of DP^{2+} increases dramatically to −77 mV from −30 mV of DQ^{2+} upon complexation with STC4A (STC4A: shift value (DP^{2+}) − shift value (DQ^{2+}) = −47 mV). However, these shift values of DP^{2+} only increase to −121 mV and −127 mV from −87 mV and −100 mV of DQ^{2+} upon complexation with SC4A and SC5A, respectively (SC4A: shift value (DP^{2+}) − shift value (DQ^{2+}) = −34 mV; SC5A: shift value (DP^{2+}) − shift value (DQ^{2+}) = −27 mV). The larger change of the shift value from DQ^{2+} to DP^{2+} upon complexation with STC4A is also well in accordance with the above thermodynamic results that, in contrast to the higher DQ^{2+}/MV^{2+} selectivity for SC4A and SC5A, STC4A displays a much higher DP^{2+}/DQ^{2+} selectivity. Meanwhile, the large shift value for the first reduction potential of DP^{2+} upon complexation with STC4A is also in accordance with the high affinity of STC4A with phenanthroline-diium guest.

Binding mode

^{1}H NMR spectroscopy is a powerful tool that can be used to determine the structures of calixarene complexes.[13a] Herein, to obtain the binding modes of DP^{2+} with SC4A, SC5A, and STC4A under neutral conditions, ^{1}H NMR spectra of DP^{2+} in the absence and presence of these hosts were measured in pD 7.2 phosphate buffer solutions. To ensure a fully complexation between sulfonated calixarenes and DP^{2+}, the concentrations of host and guest were employed as 10 mM according to the measured binding constants above between host and guest. As can be seen from Fig. 2, all DP^{2+} protons exhibit visible upfield shifts upon complexation due to the ring current effect of the aromatic nuclei of sulfonated calixarene hosts, which suggests that the DP^{2+} guests are included into the cavities of the three hosts. Moreover, the DP^{2+} protons are still observed as a single resonance after complexation, indicating a fast exchange between a free DP^{2+} guest and a calixarene-complexed one on the NMR time scale. The corresponding chemical shift changes ($\Delta\delta$) of guest protons in the presence of the three sulfonated calixarene hosts are listed in Table 2. We can see that the $\Delta\delta$ values differ from each other, which can be used to deduce the binding modes of host–guest complexes because the proton with the largest $\Delta\delta$ value would be affected mostly by the ring current effect of the aromatic nuclei of sulfonated calixarene hosts. As shown in Table 2, upon complexation with SC4A, SC5A, and STC4A, the $\Delta\delta$ values of DP^{2+} protons are in the similar order of H2, H3, and H4 > H1 > H5. The $\Delta\delta$ values of H5 are even negligible. Moreover, the DP^{2+} solutions changed from colorless to yellow upon addition of sulfonated calixarenes (Fig. S13†), suggesting the formation of charge-transfer complexes. All these results indicate that DP^{2+} is encapsulated into the cavities of the three sulfonated calixarene hosts from its aromatic moiety accompanied by the favorable π-stacking and van der Waals interactions. The deduced binding modes of phenanthroline-diium guest with sulfonated calixarene hosts are also stable by taking the expected electrostatic interactions between positively charged N^+ in guest and negatively charged SO_3^- in host into account. The ^{1}H NMR spectra of DP^{2+} in the presence of these hosts were further measured at a reduced temperature as low as possible (Fig. S14†). Compared with the NMR signals at room temperature, the signals at a reduced temperature only become a little broaden, especially for SC5A + DP^{2+} complex. No other differences were observed. These results imply that DP^{2+} guest may prefer to be included into the host cavities only with one minimum-energy structure. Next, preliminary molecular modeling studies were performed to give the computational minimum-energy structures between sulfonated calixarene hosts and DP^{2+} guest. The results show that the cavities of sulfonated calixarenes prefer binding the aromatic moiety of DP^{2+} guest (Fig. 3), which is in accordance with the deduced binding modes above by ^{1}H NMR spectroscopy. The above thermodynamic results show that there are no significant differences for the binding affinities and accompanied enthalpy and entropy changes for the intermolecular complexation of DP^{2+} and PPQ^{2+} with the same sulfonated calixerene host, although PPQ^{2+} has one more methylene in its structure as compared with DP^{2+}. The binding structures of phenanthroline-diium guest with sulfonated calixerene hosts can also explain this phenomenon well: the methylene moieties

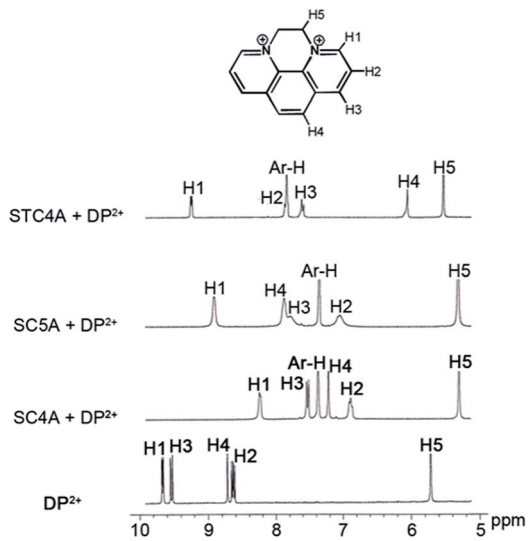


Fig. 2 ^{1}H NMR spectra of DP^{2+} in the absence and presence of SC4A, SC5A, and STC4A at pD 7.2. The host and guest were mixed in a 1 : 1 stoichiometry at 10 mM.

Table 2 Chemical shift changes ($\Delta\delta$, ppm) of DP^{2+} protons in the presence of SC4A, SC5A, and STC4A at pD 7.2[a,b]

Host	H1	H2	H3	H4	H5
SC4A	−1.39	−1.68	−1.96	−1.44	−0.40
SC5A	−0.76	−1.59	−1.76	−0.84	−0.40
STC4A	−0.43	−0.78	−1.94	−2.66	−0.19

[a] $\Delta\delta = \delta$(presence of 1 equiv. of host) − δ(free guest). Negative values indicate upfield shift. [b] The host and guest were mixed in a 1 : 1 stoichiometry at 10 mM.

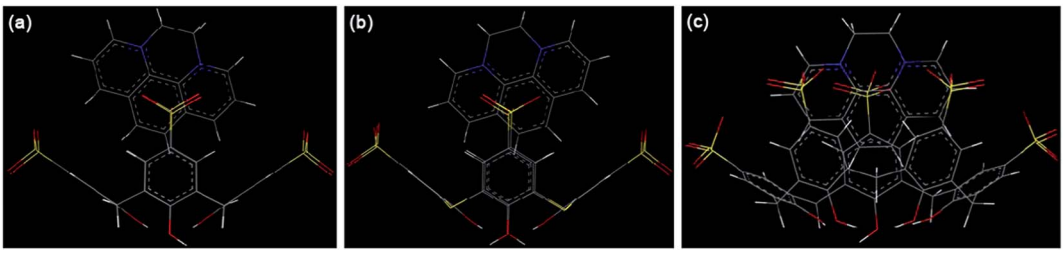


Fig. 3 Energy-minimized structures of SC4A + DP^{2+} complex (a), STC4A + DP^{2+} complex (b), and SC5A + DP^{2+} complex (c), which were optimized by the molecular mechanics method with a Dreiding force field.

of the phenanthroline-diium guest are not included into the cavities of the sulfonated calixerene hosts, and they are directed to the solvent. Therefore, the one more methylene in PPQ^{2+} could not affect its binding properties with sulfonated calixerene hosts essentially.

Conclusions

In conclusion, the molecular binding behaviors of sulfonated calixerene hosts (SC4A, SC5A, and STC4A) with phenanthroline-diium guests (DP^{2+} and PPQ^{2+}) were systemically investigated in neutral phosphate buffer solutions. Phenanthroline-diium guests are encapsulated into the cavities of the sulfonated calixarene hosts from their aromatic moieties. Furthermore, in contrast to the higher DQ^{2+}/MV^{2+} selectivity for SC4A and SC5A, STC4A displays a much higher DP^{2+} (or PPQ^{2+})/DQ^{2+} selectivity. As a result, STC4A shows the high affinities with phenanthroline-diium guests in the order of magnitude of 10^5 M^{-1}. It is the reported highest binding order of magnitude for STC4A complex up to now. The present results will help us to understand the inclusion phenomena, recognition mechanisms, and thermodynamic origins of sulfonated calixarenes in aqueous solution more systematically and comprehensively. Moreover, the high affinity of STC4A with phenanthroline-diium would be beneficial to explore the supramolecular application of STC4A by designing suitable guest, particularly in the fields of supramolecular tandem assays, supramolecular amphiphile, and supramolecular polymer.

Conflict of interest

The authors declare no competing financial interest.

Acknowledgements

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