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Layered Assembly Formed by Benzyl Viologen and *p*-Sulfonatothiacalix[4]arene and Their Complexation Thermodynamics

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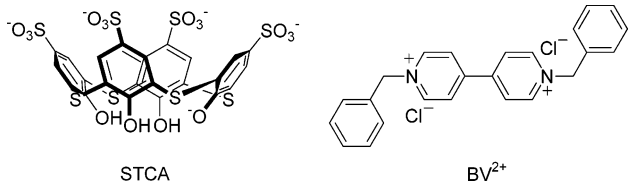
ABSTRACT: A novel layered assembly, possessing 5,11,17,23-tetrasulfonatothiacalix[4]arene (STCA) and benzyl viologen dication (BV^{2+}), has been prepared in the solid state. The crystal structure of the layered assembly reveals that the intermolecular interaction between STCA and BV^{2+} is a 1:2 stoichiometry, and meanwhile, the STCA forms a layered array in an up-and-down fashion. To investigate the thermodynamic origin of the inclusion complexation between STCA and dicationic BV^{2+} molecules, microcalorimetric titrations have been performed in phosphate buffer solution (pH 7.2) at 25 °C to calculate the complex stability constants (K_S) and thermodynamic parameters ($\Delta G°$, $\Delta H°$, and $T\Delta S°$) for stepwise binding to form the stoichiometric 1:2 inclusion complex between STCA and BV^{2+}. Thermodynamically, the resulting complex of BV^{2+} with STCA is absolutely enthalpy-driven in buffer solution, typically showing larger negative enthalpy changes due to the hydrophobic, electrostatic, and $\pi-\pi$ interactions. ^{1}H NMR spectroscopic investigations indicate that not only the resulting complex between STCA and BV^{2+} but also two BV^{2+} guest molecules bond to the upper and lower rim of STCA in sequence. Therefore, the comprehensive evaluation of the binding behavior in solution and the solid state by thermodynamics and crystallography will serve us in designing and preparing the claylike materials, in which organic or inorganic counterparts are intercalated to the organic−organic layer.

Introduction

The water soluble *p*-sulfonatocalix[*n*]arenes, possessing a rich π-electron cavity, were employed as model systems for the investigation of the inclusion behavior of species such as metal cations,[1−4] paraffin,[5] amino acids,[6−8] acetylcholine,[9] dye molecules, and aromatic cations, etc.,[10−18] which are encountered in many recognition processes in both biology and chemistry. Much research work has already been devoted to the binding behavior investigations on inclusion complexes where a guest is located within such a cavity.[19−21] The pH dependence experiments indicate that the driving forces of formation in the inclusion complexes are electrostatic, hydrophobic, or $\pi-\pi$ interactions.[17] However, almost all reports focus on the formation of a 1:1 host−guest inclusion complex, in which guest organic cations are bound into the cavity of calix[4]arene. To the best of our knowledge, the present work is the first example that two guest molecules stepwise bond to the upper and lower rim of thiacalix[4]arenesulfonate. In this article, we prepared a novel layered assembly composed of 5,11,17,23-tetrasulfonatothiacalix[4]arene (STCA) and benzyl viologen dication (BV^{2+}); the crystal structure of the assembly revealed that STCA formed a layered structure by interlocking calixarenes in an up−down fashion, and BV^{2+} molecules intercalated into the organic−organic layer. Pentaaquo sodium ions as connectors link the different organic layers through hydrogen bond interactions to form an inorganic and organic layered assembly. On the other hand, microcalorimetric titrations investigated the complexation thermodynamics of guest BV^{2+} molecules with STCA in the phosphate buffer solution (pH 7.2) (Chart 1). Combined with the ^{1}H NMR and microcalorimetric results, it can be deduced that the BV^{2+} molecule prefers to bind at the wider rim of STCA accompanied with a larger favorable enthalpic contribution and a somewhat unfavorable entropic loss resulting from the fixation of conformation. Thermodynamic parameters for the complexation of calixarene and organic cations will serve to further our understanding of the inclusion complexation mechanism in order to design novel claylike organic−inorganic materials from the view of thermodynamic points.

Chart 1



Experimental Section

STCA was synthesized according to the method reported by Miyano et al.[22] Benzyl viologen dichloride was purchased from Tokyo Kasei (Japan). Disodium hydrogen phosphate and sodium dihydrogen phosphate were dissolved in distilled, deionized water to make a 0.10 M phosphate buffer solution of pH 7.20 for calorimetric titration.

Microcalorimetric Titration. An isothermal calorimeter was used for all microcalorimetric experiments. The microcalorimetric titrations were performed at atmospheric pressure and 25 °C in aqueous phosphate buffer solution (pH 7.20). All solutions were degassed and thermostated using a ThermoVac accessory before the titration experiment. In each run, a buffer solution of BV^{2+} in a 0.250 mL syringe was sequentially injected with stirring at 300 rpm into a phosphate buffer solution of thiacalix[4]arenesulfonate in the sample cell (1.4227

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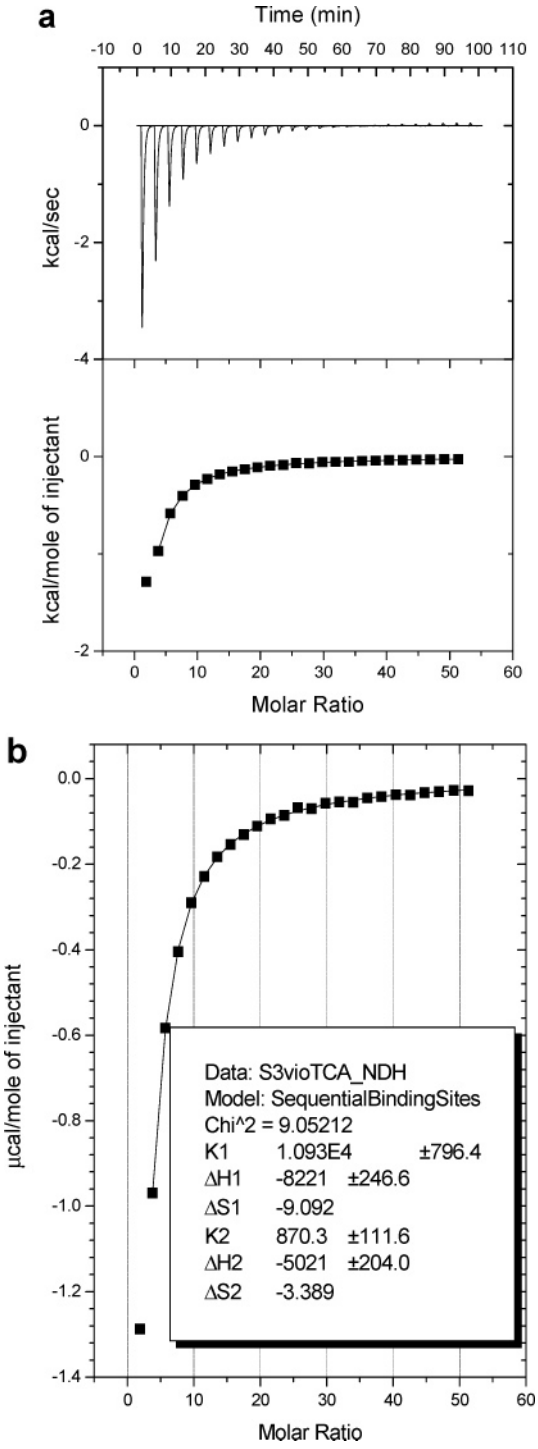

Figure 1. (a) Heat effects of complexation of benzyl viologen (BV^{2+}) with thiacalix[4]arenesulfonate for each injection during the titration microcalorimetric experiment. (b) "Net" heat effect obtained by subtracting the heat of dilution from the heat of reaction, which was analyzed by computer simulation using the two sequential two binding sites model.

mL volume). Each titration experiment was composed of 25 successive injections (9 μL per injection). The ORIGIN software (Microcal) allowed us to simultaneously determine the binding constant (K_S) and reaction enthalpy ($\Delta H°$) with the standard derivation on the basis of the scatter of data points from a single titration experiment.

Crystallographic Data for the Layered Assembly. The X-ray intensity data of assembly were collected on a standard Siemens SMART CCD Area Detector System equipped with a normal focus molybdenum target X-ray tube (λ = 0.71073 Å)

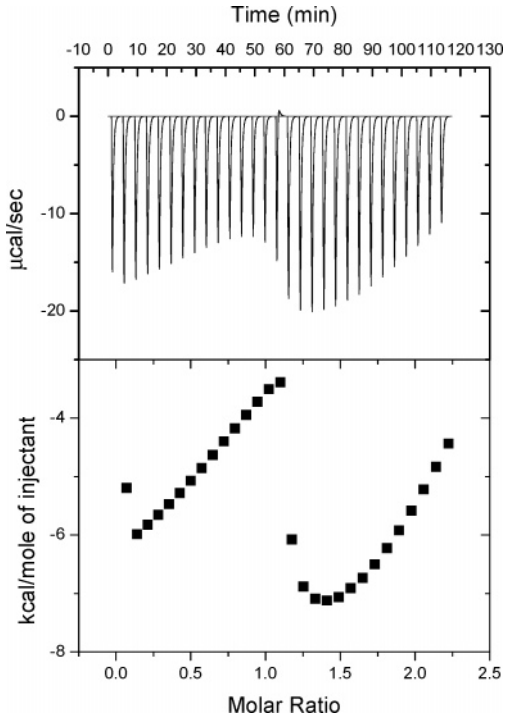

Figure 2. Two step binding of heat effects of complexation of benzyl viologen (BV^{2+}) (10.5 mmol) with thiacalix[4]arenesulfonate (1.06 mmol) for each injection during the titration microcalorimetric experiment.

operated at 2.0 kW (50 kV, 40 mA) and a graphite monchromator; T = 293 K. Crystal data for $C_{72}H_{55}N_4NaO_{16}S_8 9.5H_2O$: M_r = 1682.8, monoclinic $P2(1)/c$, a = 15.099(4) Å, b = 35.962(10) Å, c = 14.662(4) Å, α = 90°, β = 102.290(5)°, γ = 90°, V = 7779(4) Å^3, Z = 4, 1.437 g cm^{-3}, μ(Mo Kα) = 0.316 mm^{-1}, T = 293 K, 39242 reflections measured, 13632 unique (R_{int} = 0.0830), R_1 =0.0809, wR_2 = 0.1710, [data $I > 2\sigma(I)$], and GOF = 1.029. The structures were solved by using a direct method and refined employing full-matrix least-squares on F2 (Siemens, SHELXTL, version 5.04). CCDC 212763 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre).

Results and Discussion

Isothermal titration calorimetry was utilized to investigate the thermodynamics of association between thiacalix[4]arenesulfonate and BV^{2+}. The calorimetric titrations were performed by adding BV^{2+} to a solution of thiacalix[4]arenesulfonate at 25 °C in pH 7.2 phosphate buffer (I = 0.1 M) according to the method reported before.[23,24] Obviously, the experimental curve does not fit the simple 1:1 model. Similarly, the simultaneous 2:1 binding model failed to fit to the experimental data. Thus, the simplest choice to give a satisfactory fit is a stepwise 2:1 complexation model (Figure 1). Actually, we have repeated the calorimetric experiment many times through a change to the ratio of guest and host up to 300 for the determination stoichiometry and precise thermodynamic parameters.

Carefully observing the titration curve under the relative lower ratio of host (thiacalix[4]arenesulfonate sodium) and guest (BV^{2+}), it is easy to find that there are two exothermic reaction processes, with the joint point around the equimolar ratio of host and guest

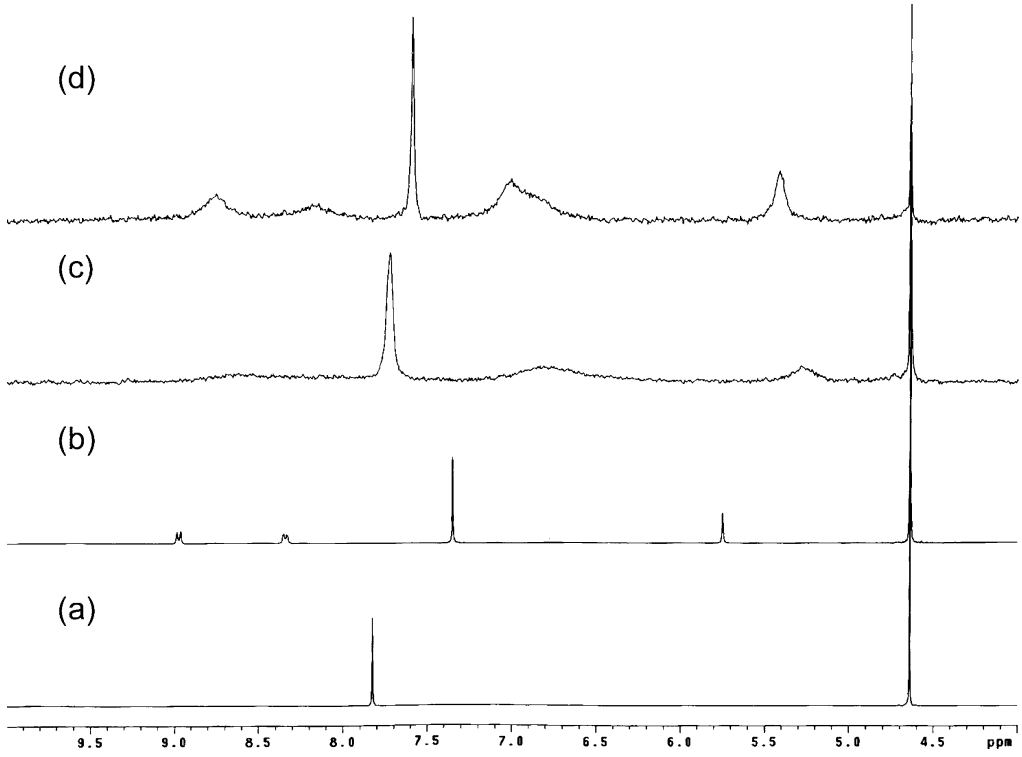

Figure 3. ^{1}H NMR spectra of (a) STCA, (b) BV^{2+}, (c) STCA:BV^{2+} = 1:1 (molar ratio), and (d) STCA:BV^{2+} = 1:2 (molar ratio).

(Figure 2). One reasonable explanation for this phenomenon is that two BV^{2+} stepped bind into STCA and the first binding affinity is much stronger than the second one. To obtain evidence for the first BV^{2+} molecule binding preferentially the upper rim or lower rim of **1**, we carried out ^{1}H NMR experiments in D_2O (Figure 3). The chemical shifts of protons in BV^{2+} molecule shift unexceptionally to upfield in the presence of STCA, accompanying peaks to become broad, and the shift values in an equimolar mixture of STCA with BV^{2+} are more remarkable than those in a 1:2 mixture. This is reasonable that the negatively charged sulfonate groups of calix[4]arenes could shield effectively the hydrogen protons in BV^{2+} resulting in a remarkable upfield shift, but the effect of electron cloud in the lower rim of STCA to the hydrogen protons in BV^{2+} is almost negligible. The above results suggest that the BV^{2+} molecule must coordinate preferentially with the upper rim of thiacalix[4]arenesulfonate. Upon the addition of BV^{2+}, the initial free guests rapidly and closely "deposit" onto the negatively charged hydrophilic moiety of **1** ($\log K_1 = 4.1 \pm 0.2$) with a favorable enthalpic contribution ($\Delta H_1 = -34.6 \pm 0.3$ kJ mol^{-1}) primarily arising from the electrostatic attraction between the double cationic BV^{2+} and the sulfonate groups of the host as well as the C−H···π, π−π stack, and hydrophobic interactions. In the meanwhile, the fixation of configuration of STCA and BV^{2+} leads to entropic loss ($T\Delta S_1 = -11.2 \pm 0.4$ kJ mol^{-1}), which exceeds the entropic contribution of desolvation. Subsequently, the second binding constant ($\log K_2 = 2.9 \pm 0.2$ kJ mol^{-1}) is less than that of the first one ($\log K_1$). It seems to be logical because BV^{2+} molecules located in the lower rim of STCA are only stabilized by weak C−H···O, C−H···π, and van der Waals interactions. This weak binding ability directly results in a relatively less enthalpic

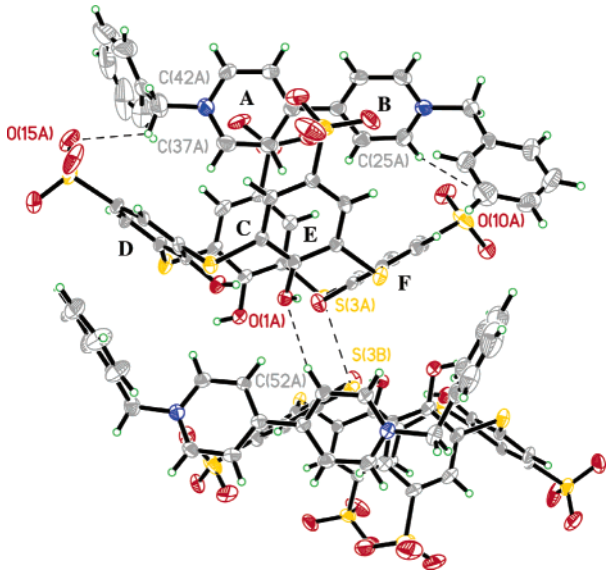

Figure 4. View of a section of the structure illustrating the arrangement of two BV^{2+} molecules. One is complexed by the hydrophobic cavity of the thiacalix[4]arenesulfonate. Rings A and B are sandwiched and π−π stacked by rings C and E of the host (the centroid distances and dihedral between the rings A−C and the rings B−E are 4.947 Å, 18.8°, 5.126 Å, and 18.4°) and are almost perpendicular to rings D and F of the host. C_{37} belonging to guest forms C−H···π interactions with ring D (the distance and angle of C−H···π are 2.827 Å and 165.8°). The cavity of calixarene from the ideal C_{4v} symmetry cone configuration to one of distorted C_{2v} symmetry. The S···S (trans) approaches are 8.0 and 13.4 Å. The other BV^{2+} molecule is seen to be intercalated into another layer of calixarene.

contribution ($\Delta H_2 = -21.1 \pm 0.2$ kJ mol^{-1}) as compared with ΔH_1, which is ascribed to the fact that the enthalpic change of the π···π stack is more favored than those of C−H···π interactions.[25] On the other hand, an en-

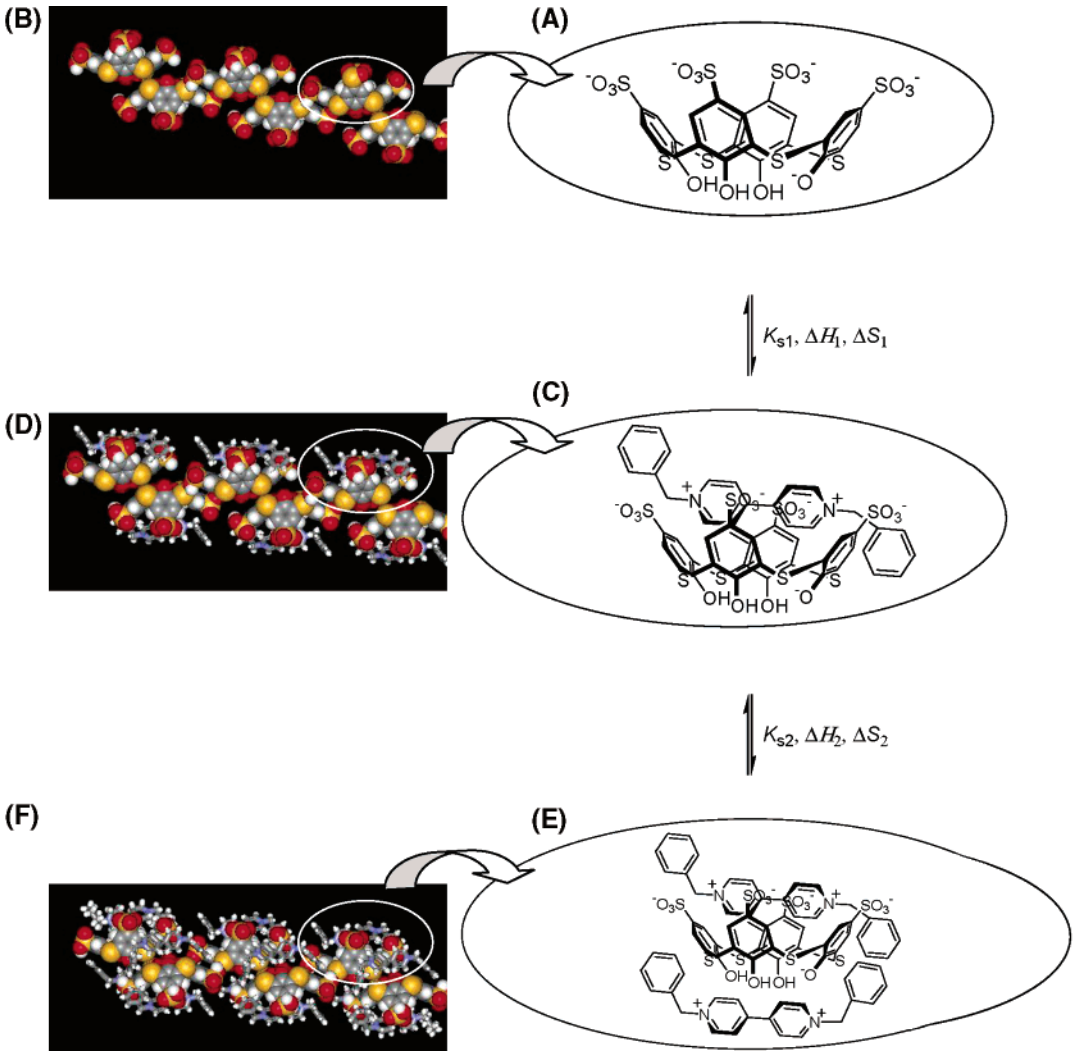

Figure 5. Schematic representation of the self-assembly of (A) *p*-sulfonatothiacalix[4]arene anions STCA into the layer structure (B) morphologies (hydrated sodium ions and water molecules were omitted for clarity). (C) In the presence of a guest, the first BV^{2+} molecule is included into the hydrophobic cavity of thiacalix[4]arenesulfonate. (D) BV^{2+} molecule located on the surfaces of the layer. (E) With the addition of BV^{2+}, the second binding site on the lower rim of the thiacalix[4]arenesulfoante. (F) BV^{2+} molecules intercalated into the organic layer in the second step binding process through van der Waals and electrostatic interactions. In the representation, *p*-sulfonatothiacalix[4]arene anions are shown in space-filled view and BV^{2+} molecules are in stick models. Elements are colored as follows: C, gray; H, white; N, blue; O, red; and S, yellow.

tropic change ($T\Delta S_2 = -4.2 \pm 0.4$ kJ mol^{-1}) of the second, stepwise bind process indicates that the loss of the freedom degrees is smaller than the first binding process. In other words, the resulting complex of the second stepwise binding is loose as compared with the first one.

After the titration, the resulting complex was transferred to a tube and sealed, and the yellow crystals were formed 3 days later. A crystal was selected and cut to a size suitable for single-crystal X-ray diffraction. The crystal cell consists of a [thiacalix[4]arene sulfonate]$^{5-}$ anion, a sodium ion, two BV^{2+} counterions, and 9.5 water molecules (Figure 4). One of the phenolic protons of the thiacalix[4]arene has been eliminated, and the resulting negative charge on the molecule is counterbalanced by the Na^+ cation, which is filled by five water molecules. Four water molecules of the pentaaquo complex interact via hydrogen bonding with the sulfonate groups of three thiacalix[4]arenes in the opposite layers. It should be noted that the neighboring thiacalix[4]arenes in the hydrophobic layer were linked by the bridged sulfur atoms through a S···S (3.355 Å) interaction[26−28] besides the conventional van der Waals contacts existing in calix[4]arenesulfonate layer structures (Figure 5).[29]

Conclusion

A unique layered assembly was prepared through inclusion complexation of STCA and BV^{2+} molecules. In the assembly, STCA displayed an interlocked layered array in an up-and-down fashion through van der Waals and S···S interactions, and organic BV^{2+} dications are located into the organic layer. Furthermore, the pentaaquo sodium ions, as connectors, linked the different organic layer through hydrogen bond interactions to form an inorganic and organic layered structure in the solid state. On the other hand, ^{1}H NMR and microcalorimetric titration experiments validated that two guest molecules were stepwise bound to the STCA in sequence, accompanying typically larger negative enthalpy changes. The inclusion complexation between

BV^{2+} and STCA was absolutely enthalpy driven. The comprehensive investigations on the binding behavior of the inclusion complex both in solution and in the solid state not only elucidate helpfully the complexation mechanisms but also afford significant information on the controlled preparation of claylike organic−inorganic hybrid materials.

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Supporting Information Available: CIF file of the crystal structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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