Selective Encapsulation of Chloride Ions within Novel Cage Host Complexes in the Presence of Equimolar Amounts of Chloride and Bromide Ions

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Abstract: Four macrotricyclic cage hosts which feature four positive binding sites oriented toward the center of the intramolecular cavity are presented as promising candidates for anion receptors and they have been expected to play a important role in the selective encapsulation of the halide ion Cl^- or Br^-. The complementarity between a macrotricyclic quaternary ammonium ion and Cl^- was achieved by fine-tuning of the four ammonium nitrogen atoms and the endocyclic methylene groups. The cage hosts $[R_4N_4(C_5H_{10})_4(C_6H_{12})_2]^{4+}$ (abbreviated as [556]) showed perfect encapsulation of all chloride ions in acetonitrile at $0 < r = ([Cl^-]_o/[[556]]_o) \leq 1$ within the sensitivity of the ^1H NMR spectra in combination with a rather slow chemical exchange of the Cl^- ion in an encapsulation/decapsulation equilibrium with [556]. Further, the selective encapsulation of all the chloride ions into [556] cage occurs unambiguously at $r = 1$ in the presence of equimolar amounts of Br^-. The structural complementarity of the newly designed [556] host prevails over the Hofmeister-series restraints determined by differences in Gibbs free energy of halide anion solvation.

Keywords: cage compounds · Hofmeister sequence · macrotricycles · receptors · selectivity

Introduction

One of the most important developments in the design of halide anion receptors[1–4] aims at the perfect discrimination of a specific halide among a mixture of different halides. Anion encapsulation into cage hosts occurs after complete desolvation of the anion.[5–7] When the recognition event between the cage host and an encapsulated anion is the more attractive interaction, this recognition will prevail over any other restraints (e.g. the Hofmeister series which were determined by differences in Gibbs free energy of halide anion hydration/solvation). The chloride anion is both ubiquitous in the biosphere and critical for a large number of biological processes. The availability of a Cl^--selective carrier could be of prime utility in clinical problems and monitoring tasks. The preparations of a number of halide-binding receptor have been described,[5–10] but such efforts to date have not been very focused on the characterization of their function in solution as well as on the development of clinically usable Cl^--transport agents and environmentally usable Cl^--selective carriers.

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The exclusive cage host should be able to encapsulate desolvated chloride anion only in the presence of solvated I^-, Br^-, Cl^-, and F^- ions in (non)aqueous solution. The thermodynamic and kinetic stability of X^--encapsulating cage host can be controlled by a deep minimum in intermolecular energy between the host and a central anion as well as a reasonably high energy barrier of the decapsulation process. Thus, the selective encapsulation recognition of the cage host toward a particular anion needs to prevail over any constraints imposed by the Hofmeister series, since the stability of halide anion-encapsulating host complexes depends also on various other factors such as solvent, temperature, and ionic strength. Here, the solvated halide ion stability in water media is well known to follow the order $F^- > Cl^- > Br^- > I^-$ and in organic media $I^- > Br^- > Cl^- > F^-$. The affinity of alkylammonium ion NR_4^+ toward each X^- or the stability of the ion pairs $NR_4^+ \cdot X^-$ in water increases in the sequence I^-, Br^-, Cl^-, and F^-. The differences in the standard molar Gibbs free energy $\Delta G_{0,hyd}(X^-)$ of X^- hydration are -468.1 (F^-), -340.7 (Cl^-), -304.9 (Br^-), and $-274.9\ kJ\,mol^{-1}$ (I^-).[11] Thus, the more negative magnitude for $\Delta G_{0,hyd}(Cl^-)$ is responsible for the lower stability of the Cl^--including supermolecule compared with the Br^--encapsulating cage host in water. For instance, Br^--encapsulating macrotricyclic quaternary ammonium ion $Br^- \subset [(CH_3)_4N_4(C_5H_{10})_2(C_6H_{12})_4]^{4+}$ has a much larger population in the presence of Cl^- in water[12]; it is difficult to design a cage host which encapsulates only Cl^- in the presence of Br^- because of the small difference of only 0.3 Å in their ionic diameters.

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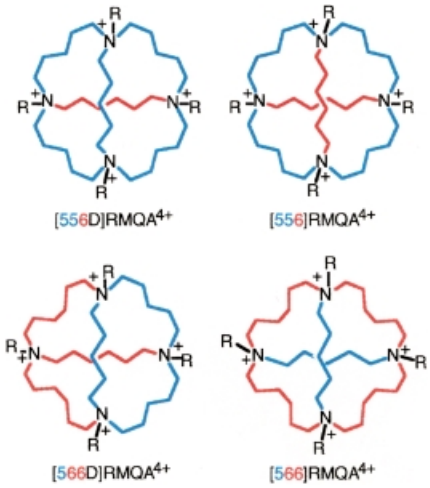
The selective encapsulation of a specific anion into a cage host may be controlled by the binding energy and structural complementarity between cage host and the encapsulated anion, in combination with the anion desolvation. The molecular design based on the above concept may be able to discriminate the slight difference between Cl^- and Br^- and to prevail over the constraints which resulted from the anion desolvation.

We studied the four macrotricyclic cage hosts, with the characteristic feature of having four positive binding sites oriented toward the center of the intramolecular cavity, may play a key role in achieving a good selectivity for Cl^- or Br^-.[5b, 12] The optimal complementarity of the cage host with Cl^- must be achieved by systematic fine-tuning of the combination of three cyclic chains of methylene groups. The macrotricyclic quaternary ammonium ions $RMQA^{4+}$ may be classified as $[R_4N_4(C_5H_{10})_5(C_6H_{12})]^{4+}$ (i.e., [556D]$RMQA^{4+}$), $[R_4N_4(C_5H_{10})_4(C_6H_{12})_2]^{4+}$ (i.e., [556]$RMQA^{4+}$), and $(R_4N_4(C_5H_{10})_3(C_6H_{12})_3]^{4+}$ (i.e., [566D]$RMQA^{4+}$), and $[R_4N_4(C_5H_{IO})_2(C_6H_{12})_4]^{4+}$ (i.e., [566]$RMQA^{4+}$), where R stands for the *exo*-group and the numbers in parentheses, 556 and 566, correspond to the hydrocarbon cycle consisting of three chains of 5, 5, and 6 (or 5, 6, and 6) methylene groups connected by three nitrogen atoms. Here, D in parentheses means that $RMQA^+$ has different triangular planes; [556D]$RMQA^{4+}$ consists of two (555) faces and two (556) faces; [566D]$RMQA^{4+}$ one (555) face and three (566) faces.[5b]



This work reports on the clear discrimination of chloride ions by cage host [556]$MeMQA^{4+}$ (abbreviated as [556]) which can encapsulate one chloride ion and while discriminating almost completely against bromide ions in the presence of Br^- ions.

Results and Discussion

The critical adjustment of intramolecular cavity size was carried out by choosing the different triangular planes through the syntheses of a couple of $RMQA^{4+}$ ions. In the solid state, the crystal structure of $Cl^- \subset$ [566D]$BnMQA^{4+}$ (Bn: benzyl group as *exo*-group)[5b] or $Br^- \subset$ [566]$BnMQA^{4+}$[12] shows unambiguous encapsulation of one chloride or one bromide into the cavity. However, at the solid/liquid interface of NaCl(001) plane in contact with water, the process of encapsulating chloride ions (from the monoatomic layer at the NaCl/water interface) established an ordered array of cage hosts [566D]$MeMQA^{4+}$ (abbreviated as [566D]).[13]

In solution, [566]$MeMQA^{4+}$ (Me: methyl group, abbreviated as [566]) shows a higher selectivity for Br^- in water containaing both Cl^- and Br^-; the stability constants are $110\,M^{-1}$ for Cl^- and $990\,M^{-1}$ for Br^-.[12] ^1H NMR spectroscopic data (Figure 3 in ref. [12]) revealed that the [566] cavity is too large to retain a preference for $Cl^- \subset$ [566] in the presence of the larger Br^- in water. On the other hand, the selectivity of [566D] toward halide ions in aqueous solution has been studied by ^1H NMR measurements, since it is not yet clear, whether the cage host [566D] prefers to encapsulate the smaller Cl^- or the larger Br^- in water. The addition of Cl^- or Br^- led to a downfield shift of the ^1H NMR peaks of endocyclic α- and β-protons (Figure 1). The new peaks were assigned to the α- and β-protons of the Cl^-/Br^- encapulated complexes $Cl^-/Br^- \subset$ [566D]. However, the peak intensities hardly increase with increasing $r\,(=[X^-]_0/[566D]_0)$: Cl^- or Br^- was able to be encapsulated into less than 7% $[566D]_0$ in water at $1 < r < 2$. No selectivity of [566D] toward Cl^- or Br^- in the presence of equimolar Cl^- and Br^- was shown in Figure 1, inset c) and e): the ^1H NMR shifts are located

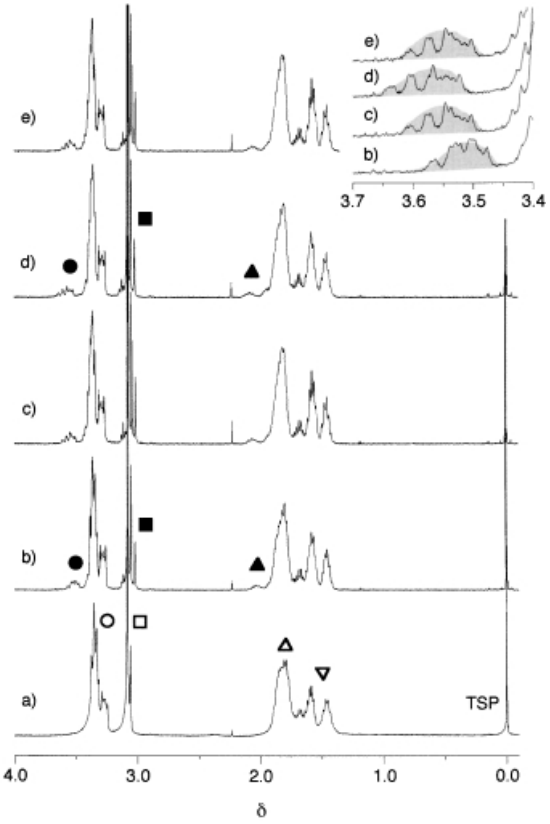


Figure 1. Selectivity of [566D] toward chloride ion in the presence of equimolar Cl^- and Br^- in water at 30 °C, $r\,(=[X]_0/[566D]_0) = 2$ and 5 mM [566D] from the ^1H NMR spectra of a) [566D], b) a)+Cl^-, c) b)+Br^-, d) a)+Br^-, and e) d)+Cl^-. Ionic strength is equal to 0.1 M KNO_3. ○, ●: α-CH_2; □, ■: *exo*-CH_3; △, ▲: β-CH_2; ▽, ▼: γ-CH_2, where the open symbols are for the free hosts and the filled symbols for the Cl^--encapsulated [556D].

between the shifts for the respective Cl^- and Br^- solutions. Both [556D] and [556] have been newly designed and synthesized, since the [566D] and [566] receptors were unsuitable without any higher affinity for Cl^-.

The addition of Cl^- to an aqueous [556D] solution showed no ^1H NMR peak that would correspond to $Cl^- \subset$ [556D] because its distorted cavity may be too small for Cl^- encapsulation. However, upon fluoride addition to aqueous [556D] solution at $r = 1$ the observed ^{19}F NMR data showed two signals at $\delta = 0$ and about -20 which were attributed to the hydrated (i.e., free) and encapsulated fluoride. Now, the cage host [556] is the center of attention, since its spherical cavity must be slightly larger than that of [556D]. The chloride anion titration showed the deformed profile associated with downfield shift in ^1H NMR spectra in acetonitrile at $0 < r(=[Cl^-]_0/[556]_0) < 1$, as shown in Figure 2b)–d). The deformed and broad peaks are due to the slow chemical exchange between the Cl^- encapsulation/decapsulation into/from [556]. The assignment of ^1H NMR spectra of free [556] (Figure 2a)) was determined as follows: α-H1 and 2 at $\delta \approx 3.25$ show a typical triplet coupling and they face to the outside of intramolecular cavity; while α-H3/5 and α-H4/6 at $\delta = 3.17$ face perfectly or partially toward the inside, respectively. Here, the geometry among the protons of the three α-CH_2 protons next to each nitrogen atom (Figure 3) was estimated by the crystal structures of $I^- \subset$ [666], $Br^- \subset$ [566], and $Cl^- \subset$ [566D].[5b, 12, 14] The downfield shift of $Cl^- \subset$ [556] was observed in ^1H NMR spectra at $r = 1$, but not for the free [556] cage host (Figure 2).

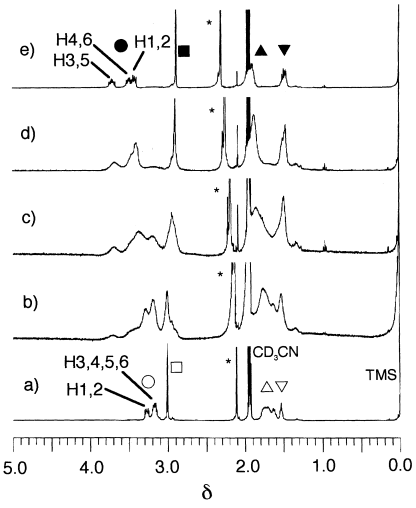


Figure 2. $r(=[Cl^-]_0/[[556]]_0)$ dependence of the ^1H NMR spectra in CD_3CN at 30 °C and 5 mM [556]: a) $r = 0$, b) 0.3, c) 0.6, d) 0.8, and e) 1; * means the protons of DHO. For symbols, see Figure 1.

A simulation of the observed ^1H NMR profile based on encapsulation after desolvation of Cl^- resulted in a good fit between the observed and calculated spectra (Figure 2 and 4). After the almost perfect encapsulation of all chloride ions at $r = 1$, the four α-protons α-H3–6 at $\delta = 3.17$ and $r = 0$ separated into two α-protons (H3/5) at $\delta \approx 3.7$ and another two α-protons (H4/6) at $\delta \approx 3.5$ for $r = 1$. Protons H1/2 at $\delta = 3.25$ and $r = 0$ showed the smallest downfield shift to $\delta = 3.45$

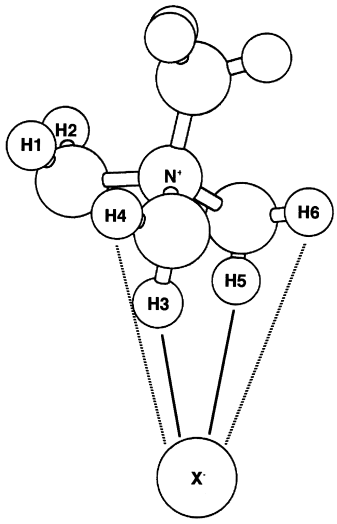


Figure 3. Typical geometry of six protons of α-methylene groups around each nitrogen atom: the geometry was given by X-X-ray crystalline molecular structure of the cage compounds as mentioned in text.

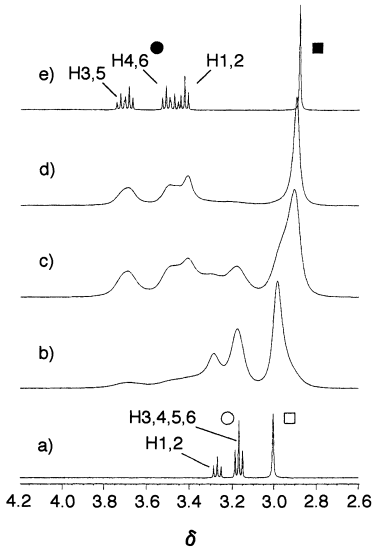


Figure 4. Kinetic simulation of r dependence of ^1H NMR spectra observed for the α-methylene groups and *exo*-methyl group: a) $r = 0$, b) 0.3, c) 0.6, d) 0.8 and e) 1. For symbols, see Figure 1.

at $r = 1$. The r dependence of the population P_A or P_B of $Cl^- \subset$ [556] (= A) or free [556] (= B), which was obtained from the above-mentioned simulation of the observed ^1H NMR profile, gave a high stability constant of the complex with Cl^- encapsulated by [556] being at least more than $10^4\,M^{-1}$. The stability constant of $Cl^- \subset$ [556] is much larger than that of $Br^- \subset$ [556], $\approx 340\,M^{-1}$ estimated from the simulation of the observed ^1H NMR profile for the α-protons (Figure 5d)). The equilibrium between A and B at $0 < r < 1$ gave the relationship $\tau_A^{-1} P_A = \tau_B^{-1} P_B$, where τ_A or τ_B stands for the life time of A or B. The parameter τ_0 $(=\tau_A P_B = \tau_B P_A)$ at 30 °C between $r = 0.3$ and 0.8 (Figure 2) was calculated as follows: $\tau_0 \approx 20$ ms and $\tau_0(\nu_A - \nu_B) \approx 4$, where ν_A and ν_B stand for the chemical shift values of α-H3/5 of A and B. The chemical exchange process between $Cl^- \subset$ [556] and free [556] is not slow, but not fast either. In conclusion, the complex with Cl^- encapsulated by [556] is characterized by the thermodynamically high and

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kinetically low stability in acetonitrile. A new series of anion receptors combining ferrocene and pyrrole moieties showed a high affinity for Cl^- compared with Br^- in acetonitrile (i.e., for macrocyclic receptor $K_{st}(Cl^-)/K_{st}(Br^-) = 11$ and $K_{st}(Cl^-) = 9030\,M^{-1}$; for acyclic analogue $K_{st}(Cl^-)/K_{st}(Br^-) = 19$ and $K_{st}(Cl^-) = 1260$). But these receptors are previously selective for F^- over the other halides Cl^- and Br^- (i.e., $K_{st}(F^-) > 10^5$).[6a]

The almost perfect selectivity of [556] toward Cl^- in the presence of Cl^- and Br^- in acetonitrile has been revealed by ^1H NMR measurements (Figure 5). Figure 5c) and e) demonstrate that the cage host [556] has a higher affinity for Cl^- in the presence of both Cl^- and Br^-; $Br^- \subset$ [556] was not detected by ^1H NMR measurements using equimolar Cl^- and Br^- solution at each $r = 1$. The observed ^1H NMR data showing UV-spectra-type changes may be explained by the bimolecular interchange reaction between Cl^- and Br^-, $Br^- \subset$ [556]+Cl^-(solv) $\rightarrow Cl^- \subset$ [556]+Br^-(solv). A drastic change was observed in ^1H NMR spectra (Figure 5), since the thermodynamic stability is very different between the respective chloride or bromide inclusion complexes of [556]. No change in the ^1H NMR spectra was observed after the addition of equimolar F^- into a [556] solution, although the smaller F^- can be encapsulated into [556].

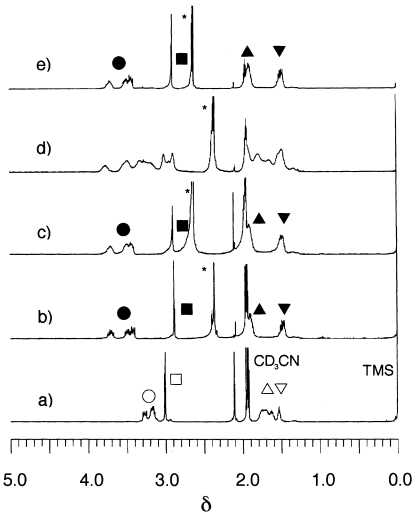

Figure 5. Selectivity of [556] toward chloride ion in the presence of equimolar Cl^- and Br^- in CD_3CN at 30 °C, $r = 1$ and 5 mM [556] from the ^1H NMR spectra of a) [556], b) a)+Cl^-, c) b)+Br^-, d) a)+Br^- and e) d)+Cl^-. For symbols, see Figure 1.

The addition of I^- cannot change any ^1H NMR spectra of the [556] solution containing equimolar F^-, Cl^-, and Br^-, since the cavity of [556] is smaller than [566] by ≈0.5 Å and the addition of I^- to the acetonitrile solution containing [566] and equimolar amounts of Cl^- and Br^- ions shows no significant change in the ^1H NMR profile, as shown in Figure 6c) and d). The [566] prefers to encapsulate Br^- in the presence of Cl^- in acetonitrile as well as in water (Figure 6c) in this work and Figure 4 in ref. [12]). In conclusion, [556] and [566] can discriminate between Cl^- and Br^- in the presence of any other halide ions, respectively. In aqueous [556] solution, no change in ^1H NMR chemical shifts was observed after the addition

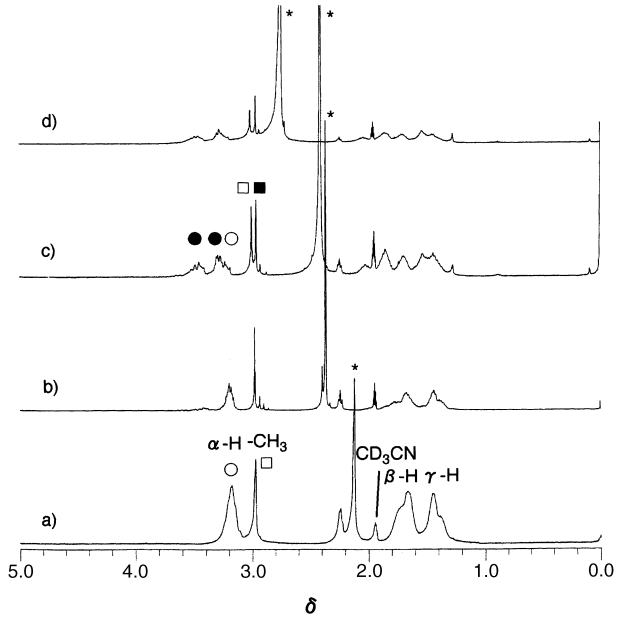

Figure 6. Selectivity of [566] toward bromide ion in the presence of Cl^- and I^- in CD_3CN at 30 °C, $r = 2$ and 5 mM [566] from the ^1H NMR spectra of a) [566], b) a)+Cl^-, c) b)+Br^- and d) c)+I^-. For symbols, see Figure 1.

Cl^-, since the Gibbs free energy barrier ΔG^* for Cl^- inclusion into an intramolecular cavity of [556] may be much higher because of the Cl^- diameter which is closer to the (556) face size than to the (566) face size and the larger stability of hydrated Cl^- compared with the solvated Cl^- in acetonitrile.

The newly designed [556] has prevailed over the constraints which result from the sequence of the standard molar Gibbs energy changes $\Delta G_{0,solv}(X^-)$ of $-298.2\,kJ\,mol^{-1}$ (Cl^-) < -277.0 (Br^-) < -255.9 (I^-) for X^- solvation in acetonitrile. The electrostatic interaction between encapsulated Cl^- and four ammonium ions in the cage host [556] and the CH_2 (of endomethylene groups)$\cdots Cl^-$ hydrogen-bonding interaction[15, 16] may provide the efficient complementarity for molecular recognition. The almost perfect selectivity of [556] toward Cl^- as well as the much larger stability constant of $Cl^- \subset$ [556] have been realized in the presence of other halide anions (Figure 2 and 5). Here, the hydrogen bonding of $CH_2\cdots Cl^-$ has been confirmed by the fact that the distances between α-H3/5 and X^-, and the bond angles < Cα-H3/5 X^- are equal to ≈2.5–3.0 Å and ≈140–180° for $Cl^- \subset$ [556]; ≈2.6–3.1 Å and ≈130–170° for $Cl^- \subset$ [566D];[5b] and ≈2.8–3.3 Å and ≈130–170° for $Br^- \subset$ [566].[12]

The encapsulation of halide ions into [556] or [566] have been investigated by molecular mechanics calculations (MM2).[17, 18] The steric energy ΔE of the system consisting of [556]/[566] and X^-, referring to free [556]/[566] and free X^-, was calculated at every 0.2 Å for the distances between X^- and N^+ located at the other side of a center of the (556)/(566) face, through which X^- penetrates into its cavity. The two minima ΔE versus the above-mentioned distance correspond to the two states in which X^- is encapsulated into the intramolecular cavity of [556]/[566] and in which it is only slightly encapsulated. A maximum shows an activated state associated with energy barrier $\Delta\Delta E^*$, which is equal to the difference, ΔE^* (a maximum of ΔE in the activated state)

$-\Delta E_0$ (a minimum of ΔE in the encapsulated state). The lower $\Delta\Delta E^*$ indicates the kinetically unstable X^--inclusion complexes, such as $F^- \subset$ [556]/[566]: the much higher $\Delta\Delta E^*$ obtained for I^- corresponded to no observation of I^--inclusion complex. The negative minimum ΔE_0 in the encapsulated state and the positive maximum ΔE^* magnitude in the activated state are more substantial and indispensable for the complexation and selectivity of [556] toward Cl^- or [566] toward Br^-. Thus, the cage receptor [556] will be utilized as Cl^--selective carrier in the presence of any halide ions in aqueous acetonitrile by generating the potential response using bilayer membrane[19] or ion-selective electrodes of liquid membrane.[20]

Experimental Section

Synthesis: The synthetic route of [556] and [556D] involves the three successive cyclization to prepare the construction of macrotricyclic amine using modified conventional methods.

[556] was identified by ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.59-1.83$ (m, 40H; β-, γ-CH_2), 3.14 (s, 12H; CH_3), 3.32–3.43 (m, 24H; α-CH_2); elemental analysis calcd (%) for [556]4$BF_4^-\cdot H_2O$ ($C_{36}H_{78}N_4B_4F_{16}O$): C 46.48, H 8.45, N 6.02; found: C 46.17, H 8.16, N 5.90.

[556D] was identified by ^{1}H NMR: $\delta = 1.57-1.69$ (m, 14H; γ-CH_2), 1.78–1.86 (m, 24H; β-CH_2), 3.12 (s, 12H; CH_3), 3.32–3.35 (br, 24H; α-CH_2); elemental analysis calcd (%) for [556D]4BF_4^- ($C_{35}H_{74}N_4B_4F_{16}$): C 46.96, H 8.33, N 6.25; found: C 46.89, H 8.38, N 6.29.

The water (ca. 3% *v/v*) in acetonitrile was supplied by the addition of aqueous KF, KCl, KBr, and KI for the ^{1}H NMR measurements. The observed downfield shift of DHO, denoted by * in Figure 2, 5 and 6, may show the MX-concentration dependence.

Simulation: In the simulation (gNMR Analysis Package provided by Cherwell Scientific Limited) of the observed ^{1}H NMR spectra, the geometry of the six protons of α-CH_2 around each nitrogen atom before inclusion was assumed to be equal to the Cl^--encapsulated host. The exchange rate between two sites $Cl^- \subset$ [556] and free [556] occurs in solution, associated with the Cl^- encapsulation and decapsulation. The coupling constant of α-CH_2 with of β-CH_2 was set to to 7 Hz and $\tilde{\nu}_{1/2}$ to 1 Hz and the coupling of α-CH_2 with nitrogen nucleus was neglected. For *exo*-methyl group, $\delta = 3.0$ and $\tilde{\nu}_{1/2} = 2.3$ Hz at $r = 0$; $\delta = 2.9$ and $\tilde{\nu}_{1/2} = 1.9$ Hz at $r = 1$.

Calculations: Molecular mechanics calculation was accomplished with the molecular mechanics packages provided by the Tektronix CAChe System, Version 3.7. The initial structures of $X^- \subset$ [556] and $X^- \subset$ [566] were given by X-ray structure of $Br^- \subset$ [566]BnMQA^{4+} and modified by the replacement of -$CH_2C_6H_5$(Bn) to -CH_3 (Me) as *exo*-groups. The lowest energy structures of the system consisting of [556]/[566] and X^- were optimized for 3.0 Å to 15.0 Å at intervals of 0.12 Å. In this calculation no contribution from water or acetonitrile as solvent was included.

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