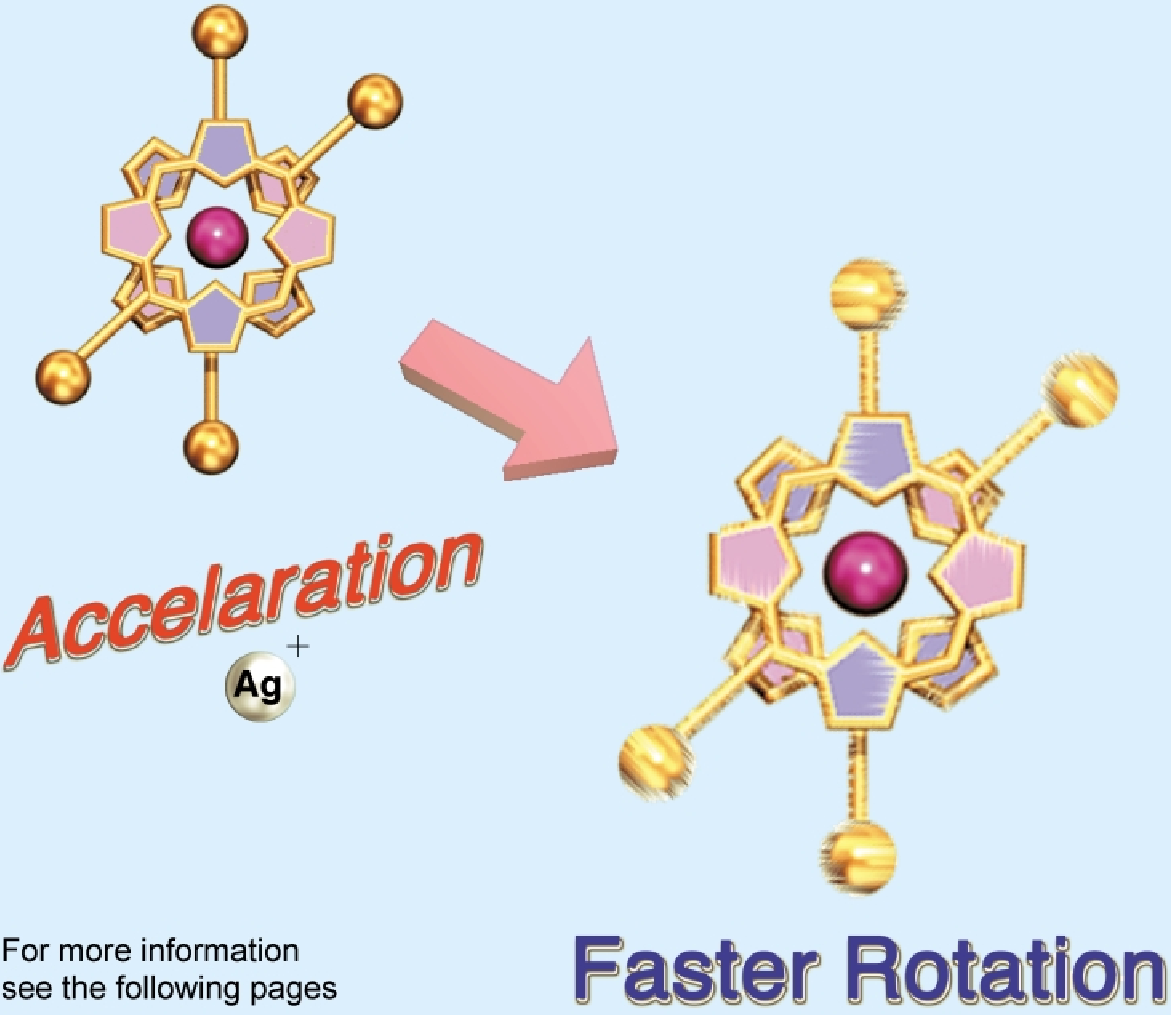
Supramolecular Rotating Module



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Allosteric Binding of an Ag^+ Ion to Cerium(IV) Bis-porphyrinates Enhances the Rotational Activity of Porphyrin Ligands

Masato Ikeda,[a] Masayuki Takeuchi,*[a] Seiji Shinkai,*[a] Fumito Tani,[b] Yoshinori Naruta,[b] Shigeru Sakamoto,[c] and Kentaro Yamaguchi[c]

Abstract: A series of cerium(IV) bis-porphyrinate double-deckers [Ce(bbpp)$_2$] (BBPP = 5,15-bis(4-butoxyphenyl)porphyrin dianion), [Ce(tmpp)$_2$] (TMPP = 5,10,15,20-tetrakis(4-methoxyphenyl)-porphyrin dianion), [Ce(tfpp)$_2$] (TFPP = 5,10,15,20-tetrakis(4-fluorophenyl)porphyrin dianion), [Ce(tmcpp)$_2$] (TMCPP = 5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrin dianion), and [Ce(tmpp)(tmcpp)] was prepared. They bind three Ag^+ ions to their concave porphyrin π subunits (π-clefts) according to a positive homotropic allosteric mechanism with Hill coefficients (n_H) of 1.7–2.7. The rotation rates of the porphyrin ligands in [Ce(bbpp)$_2$] were evaluated to be 200 s^{-1} at 20 °C ($\Delta G^{\ddagger}_{293} = 14.1$ kcal mol^{-1}) and 220 s^{-1} at −40 °C ($\Delta G^{\ddagger}_{233} = 11.0$ kcal mol^{-1}) without and with Ag^+ ions, respectively. These results consistently support our unexpected finding that Ag^+ binding can accelerate rotation of the porphyrin ligand. On the basis of UV-visible, ^{1}H NMR, and resonance Raman spectral measurements, the rate enhancement of the rotational speed of the porphyrin ligands is attributed to conformational changes of the porphyrin in cerium(IV) bis-porphyrinate induced by binding of Ag^+ guest ions in the clefts. This novel concept of positive homotropic allosterism is applicable to the molecular design of various supramolecular and switch-functionalized systems.

Keywords: allosterism · cooperative phenomena · host–guest systems · pi interactions · porphyrinoids

Introduction

The design and construction of artificial molecular machines have been the focus of many research groups.[1] Widely investigated rotating and interlocked modules for such devices include molecular rotors,[2, 3] catenanes,[4] and rotaxanes.[5] The dynamic motion of such molecular machines has been regulated by photo-, electro- (or redox), and host–guest-type chemical interactions.[1–5] Particular features of interest include control of "on/off" switching by external stimuli.

We are interested in the construction of artificial systems that exhibit positive homotropic allosterism.[6–8] Allosteric complexation with a nonlinear, sigmoidal response can be used to transcribe "digital" behavior at the molecular level, because the behaviors can be switched "on" or "off" only under specific threshold conditions, regulated by, for example, the effector concentration. Thus, positive allosterism can achieve a characteristic nonlinear binding mode in which initial binding of a guest has a positive effect on subsequent host–guest interactions and avoids randomization of information.[1f, 9]

In studies on artificial cooperative recognition utilizing cerium(IV) bis-porphyrinate and *meso–meso*-linked porphyrin dimer, guests such as dicarboxylic acids,[10a–c] K^+ ions,[10d] mono-[10f] and oligosaccharides,[10g–h, 11] and anions[10i] were recognized with high selectivity and affinity according to a positive homotropic allosteric mechanism. In these cases, the first guest binding, although very weak, facilitates binding of the second and third guests by suppressing the rotational freedom of the two porphyrin ligands and providing preorganized binding sites favorable for subsequent guest binding.[6a,b]

Recently, we reported preliminary results on allosteric binding of Ag^+ to [Ce(tmpp)$_2$], in which Ag^+ ions are cooperatively bound to concave π subunits (π clefts) of [Ce(tmpp)$_2$].[10e] On the basis of knowledge obtained from previous studies on cooperative guest recognition with the cerium(IV) bis-porphyrinate scaffold, we assumed a cooperative binding mechanism; that is, Ag^+ binding occurs due to

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successive suppression of the rotational freedom of porphyrins and/or peripheral *meso*-aryl groups in [Ce(tmpp)$_2$] by guest Ag$^+$ ions, and the peripheral π clefts would be effective binding sites for Ag$^+$. However, variable-temperature (VT) ^{1}H NMR measurements on [Ce(tmpp)$_2$] did not give any useful information about the rate of porphyrin rotation, because there is no markable proton which reflects this rate. This preliminary finding stimulated us to further investigate the influence of Ag$^+$ binding on the rotational freedom of porphyrin ligands and the location of the binding sites.[3] Here we report on systematic reinvestigations of Ag$^+$ binding to a series of cerium(IV) bis-porphyrinates by cold spray ionization mass spectrometry (CSI-MS),[12] and UV-visible, ^{1}H NMR, and resonance Raman (RR) spectroscopy. We found that the cerium(IV) bis-porphyrinates can bind three Ag$^+$ ions, mainly within the π clefts defined by the two porphyrin ligands. Moreover, it was found that the rate of rotation of the porphyrin planes is not decelerated but accelerated by the guest Ag$^+$ ions. The interesting, but totally unexpected, mechanistic origin of this cooperative complexation differs from our preliminary assumption and from previously described allosteric host–guest systems. This mechanism offers novel ideas for designing new artificial allosteric systems for the recognition of molecules and ions.

Results and Discussion

Synthesis of double-decker porphyrin complexes: [Ce(bbpp)$_2$], [Ce(tmpp)$_2$], [Ce(tfpp)$_2$], [Ce(tmcpp)$_2$], and [Ce(tmpp)(tmcpp)] were synthesized from the corresponding free-base porphyrins by reaction with [Ce(acac)$_3$] (acac = acetylacetonato) according to the method reported by Buchler et al.[13] The products were identified by tow-dimensional COSY ^{1}H NMR spectroscopy at −40 °C (the peaks were significantly broadened at room temperature), FAB-MS, and elemental analyses.

UV/visible and CSI-MS spectroscopic studies: On addition of CF_3SO_3Ag to a solution of [Ce(bbpp)$_2$] (5.00 μM) in chloroform/methanol (4:1) at 25 °C, the Soret band of [Ce(bbpp)$_2$] shifted from 387.0 to 392.0 nm with distinct isosbectic points (Figure 1). This result implies that the reaction involves only two species in a single equilibrium. A similar bathochromic shift of the Soret band was observed for all the cerium(IV) bis-porphyrinates ([Ce(porph)$_2$]) studied here with Ag$^+$ ions (400.0 to 414.0 nm for [Ce(tmpp)$_2$], 394.0 to 409.0 nm for [Ce(tfpp)$_2$], 398.5 to 409.0 nm for [Ce(tmcpp)$_2$], and 399.5 to 414.0 nm for [Ce(tmpp)(tmcpp)]). These spectral data are summarized in Table 1. No spectral change in both the Soret and the Q-bands of [Ce(bbpp)$_2$] was induced by the addition of sodium, potassium, and cesium ions. Moreover, the Tl$^+$ ion, which tends to bind to π-basic aryl groups by η^6-type cation–π interaction,[14] also did not induce any spectral change.

When an excess of tetrabutylammonium chloride was added to the solution containing [Ce(bbpp)$_2$] and Ag$^+$, AgCl precipitated and the Soret band of the solution shifted back to the original absorption maximum observed in the absence of Ag$^+$. The ^{1}H NMR experiments (see below) showed that all [Ce(porph)$_2$]–Ag$^+$ complexes studied here were diamagnetic and maintained their double-decker structures without dissociation into monomers upon addition of Ag$^+$. These findings show that the Ag$^+$ ion does not undergo a redox reaction with cerium(IV) to yield paramagnetic Ce^{III} or porphyrin π radical cation species, nor is it bound by electrostatic interaction with [Ce^{III}(P)$_2$]$^-$. The redox potentials of [Ce(bbpp)$_2$] (0.51 V vs Ag/AgCl) and [Ce(tmpp)$_2$] (0.55 V) in dichloromethane/methanol (4:1) with 0.1 M tetrabutylammonium perchlorate (TBAP) also support the view that no oxidation by Ag$^+$ (oxidation potential ca. 0.35 V) occurs under these conditions. In other words, the Ag$^+$ ion undergoes cation–π interactions with [Ce(porph)$_2$].[14a, 15]

Importantly, plotting the Soret band absorbance versus CF_3SO_3Ag concentration (Figure 2) resulted in sigmoidal

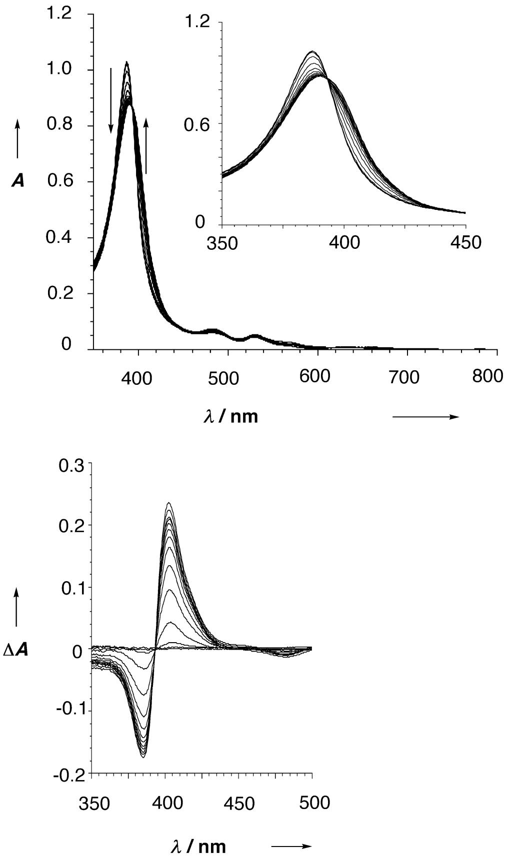


Figure 1. Concentration dependence of the UV-visible spectra (top) and differential spectrum (bottom): [Ce(bbpp)$_2$] = 5.0 μM, CF_3SO_3Ag = 0–100 μM, chloroform/methanol (4:1) at 25 °C.

Table 1. UV-visible spectroscopic data and binding parameters obtained from the Hill plot.[17]

Compound	λ_{max} shift (Soret band)/ $\Delta\lambda_{max}$ [nm]	n_H[a]	log*K*	*R*[b]
[Ce(bbpp)$_2$]	387.0 → 392.0/5.0	2.7	12.8	0.99
[Ce(tmpp)$_2$]	400.0 → 414.0/14.0	2.2	11.2	0.99
[Ce(tmcpp)$_2$]	398.5 → 409.0/10.5	2.1	9.0	0.99
[Ce(tfpp)$_2$]	394.0 → 409.0/15.0	1.7	6.6	0.91
[Ce(tmpp)(tmcpp)]	399.5 → 414.0/13.5	2.6	10.6	0.99

[a] Hill coefficient obtained from Hill equation (see text). [b] Correlation coefficient of Hill plot.

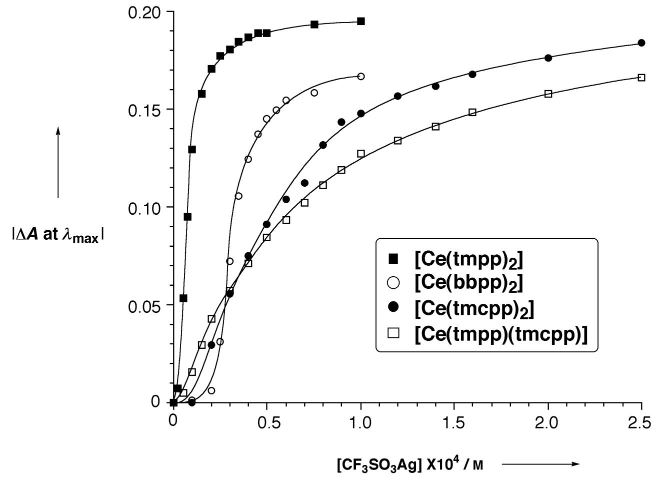


Figure 2. Plots of absorbance change versus CF_3SO_3Ag concentration ($[Ce(porph)_2] = 5\,\mu M$): $\lambda_{max} = 387.0$ for $[Ce(bbpp)_2]$, 400.0 for $[Ce(tmpp)_2]$, 399.5 for [Ce(tmpp)(tmcpp)], and 398.5 nm for $[Ce(tmcpp)_2]$.

curves, that is, the binding of the Ag^+ ions to $[Ce(porph)_2]$ occurs cooperatively (i.e., shows a positive homotropic allosterism).

To analyze these sigmoidal curves and to evaluate the binding constants with Ag^+, we first confirmed the stoichiometry by continuous-variation plots (Job plots) and molar-ratio plots.[16, 17a] Plots of the absorption changes in the Soret band versus $[Ce(porph)_2]/([Ce(porph)_2] + [Ag^+])$ showed a maximum at 0.25, which suggests that the complexes consist of one $[Ce(porph)_2]$ host and three Ag^+ guests. The 1:3 stoichiometry was also confirmed by plotting the absorbance at 468 nm against Ag^+ concentration (molar-ratio plot).[11e] ^1H NMR titration experiments (see below) also revealed that $[Ce(bbpp)_2]$, $[Ce(tmcpp)_2]$, and [Ce(tmpp)(tmcpp)] bind Ag^+ in the stoichiometry 1:3. The stoichiometry of Ag^+ binding was further supported by CIS-MS measurement.[12] The CSI-MS spectrum for $[CF_3SO_3Ag]/[Ce(bbpp)_2] = 25$ in chloroform/methanol (4:1) showed strong peaks at $m/z = 1457.6$, 1713.4, and 1971.5, which can be assigned to $[Ce(bbpp)_2{+}Ag^+]$, $[Ce(bbpp)_2{+}2\,Ag{+}CF_3SO_3{}^+]$, and $[Ce(bbpp)_2{+}3\,Ag{+}2\,CF_3SO_3{}^+]$, respectively (Figure 3).

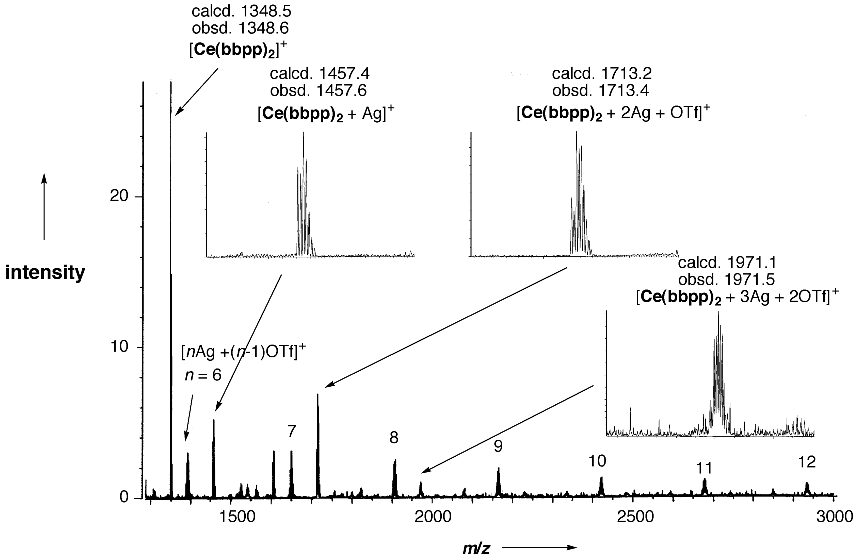


Figure 3. CSI-MS spectrum of $[CF_3SO_3Ag]/[Ce(bbpp)_2]$ (1:25) in chloroform/methanol (4:1).

The cooperative guest bindings were analyzed with the Hill equation[17]: $\log[y/(1-y)] = n_H \log[\text{guest}] + \log K$, in which K, y, and n_H are the association constant, degree of saturation, and the Hill coefficient, respectively, and $y = K/([\text{guest}]^{-n} + K)$. From the slope and the intercept of the linear plots (Hill plots), we obtained $\log K$ and n_H (Table 1). The magnitude of the binding constants decreases in the following order: $[Ce(bbpp)_2] > [Ce(tmpp)_2] > [Ce(tmpp)(tmcpp)] > [Ce(tmcpp)_2] > [Ce(tfpp)_2]$. This clearly shows that the complexation of Ag^+ ions is influenced by the type of substituents in the *meso* positions. The Hill coefficients n_H in the range of 1.7–2.7 indicate that Ag^+ binding occurs cooperatively, since a higher value of n_H is related to a higher degree of cooperativity.[17] The maximum is equal to the number of available binding subunits. Thus, the n_H values (1.7–2.7) are compatible with the 1:3 stoichiometry.

The double-decker complexes studied here have two different kinds of π clefts: the porphyrin cores and the *meso*-aryl groups (Figure 4). The Ag^+ ion is known to form complexes with aromatic rings by cation–π interactions.[14a, 15] Here, Ag^+ binding occurs even with $[Ce(tfpp)_2]$, [Ce(tmpp)(tmcpp)], and $[Ce(tmcpp)_2]$, which bear electron-withdrawing COOMe or F substituents on the *meso*-aryl groups. Moreover, $[Ce(bbpp)_2]$ with two *meso*-aryl π clefts can bind three Ag^+ ions. As far as we know, no precedent for a cation–π interaction in solution between Ag^+ and electron-poor π systems bearing methoxycarbonylphenyl or fluorophenyl groups has been reported. We therefore propose that Ag^+ ions interact mainly with the porphyrin ligands themselves; that is, the most likely location of the Ag^+ ion is within the concave porphyrin π cleft (Figure 4B). Kadish et al.[18]

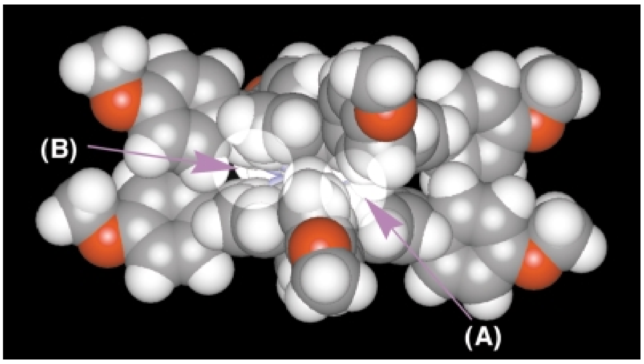


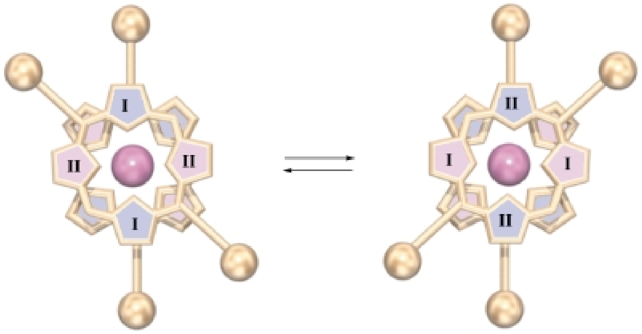
Figure 4. Plausible binding sites for Ag^+: *meso*-aryl π cleft (A) and porphyrin π cleft (B).

reported that *meso*-aryl groups in tetraarylporphyrin metal complexes do not affect the π basicity of the porphyrin core very much, because substituents in the *meso* positions are arranged almost perpendicular to the porphyrin plane. This reasonably explains why the Ag^+-binding porphyrin π clefts in $[Ce(tfpp)_2]$, $[Ce(tmcpp)_2]$, and [Ce(tmpp)(tmcpp)] can accept Ag^+ ions even in the presence of electron-withdrawing groups on the *meso*-aryl rings, although the affinity for Ag^+ ions decreases to some extent.

The λ_{max} of the Soret band of the $[Ce(porph)_2]-3\,Ag^+$ complexes were very close to those of the corresponding cerium(III) complexes, $[Ce^{III}(porph)_2]$, produced by electrochemical reduction. The λ_{max} values of $[Ce^{III}(tmpp)_2]$ and $[Ce^{III}(bbpp)_2]$ obtained from electrochemical reduction[13f] are 415 and 404 nm, respectively. This bathochromic shift due to electrochemical reduction from Ce^{IV} to Ce^{III} is probably attributable not only to the difference in the ionic radius between Ce^{III} (1.14 Å) and Ce^{IV} (0.97 Å), but also to the weaker π–π interactions.[3, 13] In the present study, we have confirmed that neither the redox reaction nor the degradation of $[Ce(porph)_2]$ occurs during the Ag^+ complexation process (vide supra). The mean distance between the pyrrole β-protons in cerium(IV) bis-porphyrinate was estimated to be about 4 Å from the X-ray crystallographic studies.[11b, 13c, 13f] X-ray crystallographic studies show that silver ions bound to benzene molecules lie at the edge of the aromatic ring, where they interact with one of the double bonds with an Ag^+–benzene distance of 2.5 Å.[19] The porphyrin π cleft (Figure 4B) is clearly too narrow to accept a Ag^+ ion by cation–π interaction. Binding of the the first Ag^+ ion to the porphyrin clefts would weaken the π–π interactions between the porphyrins and/or cause a conformational change of $[Ce(porph)_2]$ such as a slight elongation of the porphyrin–porphyrin distance. This facilitates the binding of the second and third Ag^+ ions and induces the bathochromic UV-visible spectral shift, as summarized in Table 1. This binding mechanism should influence the rotation rate of the porphyrin planes in $[Ce(porph)_2]$. This was further investigated by VT ^1H NMR spectroscopy.

^{1}H NMR spectropic studies: We have already reported preliminary ^1H NMR spectroscopic studies on various mixtures of $[Ce(tmpp)_2]$ and CF_3SO_3Ag in CD_2Cl_2/CD_3OD (4:1),[10e] for which we found the following results: $[Ce(tmpp)_2]$ can bind three Ag^+ ions, and in the presence of an excess of Ag^+ (20 equiv), the signals for the 4-methoxyphenyl and pyrrole β-protons of $[Ce(tmpp)_2]$ shift to lower field at all temperatures (−80 to +30 °C). The largest downfield shift was observed for the pyrrole β-protons ($\Delta\delta = 0.43$ at −40 °C). We assumed a conventional binding mechanism in which cooperative Ag^+ binding arises from successive suppression of the rotational freedom of the porphyrin rings and/or the peripheral *meso*-aryl groups in $[Ce(tmpp)_2]$.[10e] However, VT ^1H NMR measurements on $[Ce(tmpp)_2]$, $[Ce(tmcpp)_2]$, $[Ce(tfpp)_2]$, and [Ce(tmpp)(tmcpp)] did not give any useful information about the rate of porphyrin rotation, because they have no markable proton that reflects the rotation rate of the porphyrin rings.[3] Moreover, the rate of the porphyrin-ring rotation in cerium(IV) bis-tetraarylporphyrinate double-deckers is much slower than the NMR timescale.[3, 20, 21] This means that the rotational freedom of the porphyrin rings in $[Ce(tmpp)_2]$, $[Ce(tmcpp)_2]$, $[Ce(tfpp)_2]$, and [Ce(tmpp)(tmcpp)] cannot be evaluated by the VT NMR technique.

To obtain further insight into the Ag^+ complexation and dynamic behavior by VT ^1H NMR spectroscopy, we chose $[Ce(bbpp)_2]$ as a mechanistic probe. In this derivative of cerium(IV) bis-diphenylporphyrinate, the rate of rotation of the porphyrin ligands is comparable to the NMR timescale.[3] $[Ce(bbpp)_2]$ bears four 4-butoxyphenyl groups and has D_2 symmetry. This makes the observation of porphyrin rotation by VT ^1H NMR spectroscopy easier, since two pairs of pyrrole β-protons should exchange during ligand rotation and coalesce with each other at some temperature (Scheme 1).



Scheme 1.

The ^1H NMR spectra of $[Ce(bbpp)_2]$ for $[Ce(bbpp)_2]/[CF_3SO_3Ag] = 1{:}0-1{:}5$ and 1:20 were measured at six temperatures. The complexation-induced chemical shifts of the 4-butoxyphenyl and pyrrole β-protons gradually move to lower field up to $[Ce(bbpp)_2]/[CF_3SO_3Ag] = 1{:}3$ and then are saturated at higher CF_3SO_3Ag concentrations. Figure 5 shows

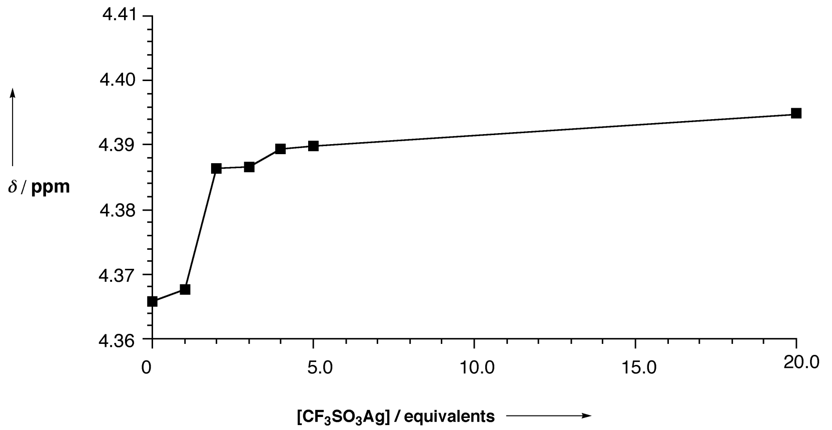


Figure 5. Complex-induced chemical shift of 4-butoxyphenyl groups at 25 °C in CD_2Cl_2/CD_3OD (4:1).

the complex-induced chemical shift of the 4-butoxyphenyl groups. For $[CF_3SO_3Ag]/[Ce(bbpp)_2] < 3$, the peaks assignable to the $[Ce(bbpp)_2]-Ag^+$ complex broaden between 0 and −40 °C and are separate from those of free $[Ce(bbpp)_2]$ at −80 °C (Figure 6). Under the measurement conditions, there are two equilibria—intermolecular Ag^+ exchange and porphyrin rotation—the rates of which are comparable on the NMR timescale. On the other hand, from the spectra at $[CF_3SO_3Ag]/[Ce(bbpp)_2] = 3$, 5, and 20, only one species, which can be assigned to the complex $[Ce(bbpp)_2]-3\,Ag^+$, is identified at all temperatures from the coalescence behavior of the pyrrole β-protons. Hence, the porphyrin rotation rate can be evaluated at $[CF_3SO_3Ag]/[Ce(bbpp)_2] = 3$ by using the coalescence temperature T_c of the pyrrole β-protons. In $[Ce(bbpp)_2]-3\,Ag^+$, the structure should become unsymmetrical. The ^1H NMR spectral pattern of the 1:3 complex is simple under conditions for which the intermolecular Ag^+ exchange is much slower than the NMR timescale. This implies that we observe the averaged ^1H NMR spectrum, because intramolecular Ag^+ exchange is faster than the NMR timescale, even at −80 °C. This could be the reason why the intensities of the pyrrole β-protons are equal in a complex with 1:3 stoichiometry.

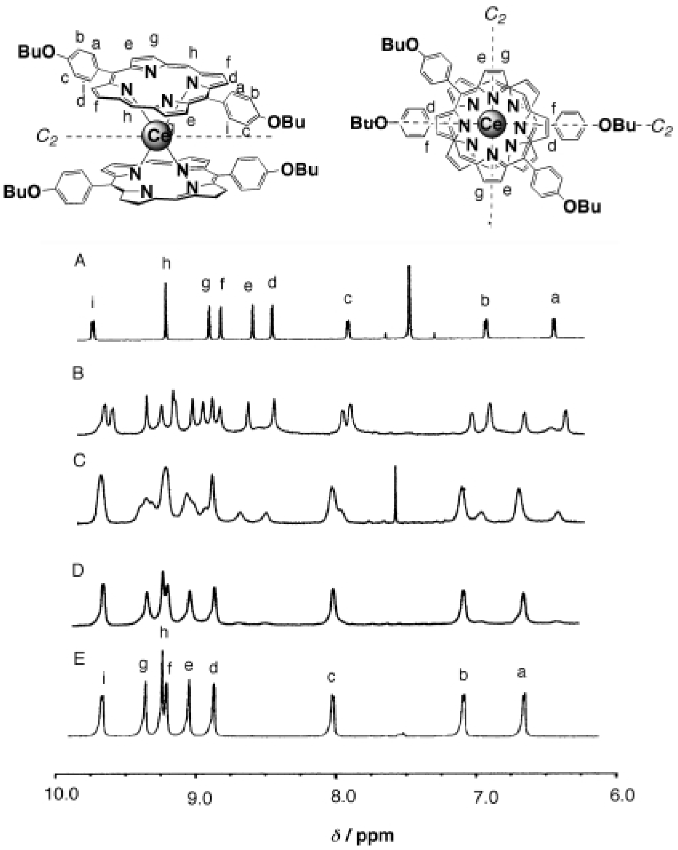


Figure 6. Aromatic region of the ^1H NMR spectra of $[Ce(bbpp)_2]$ (A) at −40 °C (in $CDCl_3/CD_3OD$ 4:1) and mixtures of $[Ce(bbpp)_2]$ with 1 (B), 2 (C), 3 (D) and 20 equiv (E) of CF_3SO_3Ag at −80 °C (in CD_2Cl_2/CD_3OD 4:1).

The rate of porphyrin-ligand rotation in $[Ce(bbpp)_2]$ was estimated in the presence ($[Ce(bbpp)_2]/[CF_3SO_3Ag] = 1{:}20$) and absence of Ag^+. Without Ag^+ at −40 °C in $CDCl_3/CD_3OD$ (4:1), four doublets assignable to the pyrrole β-protons appeared (Figure 7A) at $\delta = 8.43$ (d), 8.58 (e), 8.80 (f), and 8.88 ppm (g), consistent with the symmetry. With increasing temperature, the exchangeable peaks d/e and f/g broaden somewhat at 10 °C and then coalesce with each other at 20 °C due to porphyrin rotation. The exchange rate constant for a pair of pyrrole protons was evaluated to be 200 s^{-1} at 20 °C ($\Delta G^{\ddagger}_{293} = 14.1\ kcal\,mol^{-1}$) by using the Gutowsky and Holm equation.[22] This value is almost comparable to those of the previously reported similar double-decker compounds[3] (Table 2). In the presence of 20 equiv of Ag^+, these peaks coalesce at −40 °C, which corresponds to 220 s^{-1} ($\Delta G^{\ddagger}_{233} = 11.0\ kcal\,mol^{-1}$; Figure 7B and Table 2). It is very surprising that Ag^+ binding lowers T_c by 60 °C rather than increasing it.

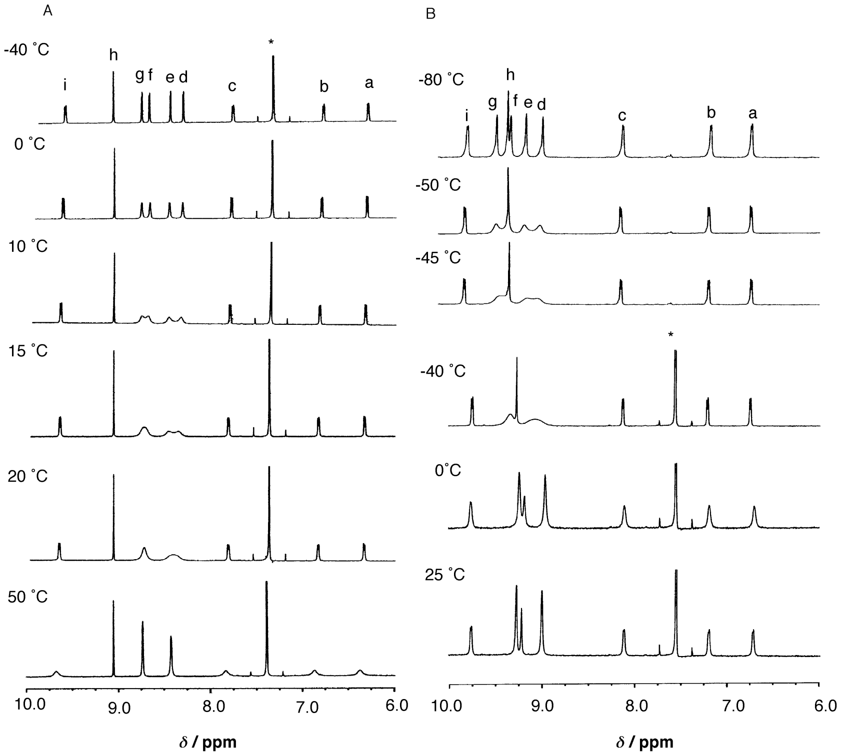


Figure 7. Aromatic region of the ^1H NMR spectra of $[Ce(bbpp)_2]$ (A) and a mixture of $[Ce(bbpp)_2]$ with 20 equiv of CF_3SO_3Ag (B) at various temperatures (+50 °C to −40 °C in $CDCl_3/CD_3OD$ (4:1); −40 °C to −80 °C in CD_2Cl_2/CD_3OD (4:1)). Solvent peaks are marked by an asterisk.

Aida et al.[3] and we[11c, 20, 21] independently reported that the rotational freedom of the porphyrin ligands depends on several factors such as the ionic radius of the central metal atom, the redox state of the porphyrin ligands, protonation of porphyrin ligands,[23] and the bulkiness of the *meso*-aryl groups. The

Table 2. T_c and k_c values for porphyrin-ring rotation (oscillation).

	[Ce(bbpp)$_2$]	[Ce(bbpp)$_2$] + 20 equiv CF$_3$SO$_3$Ag
T_c	20 °C	− 40 °C
k_c[a] at T_c	200 s^{-1}	220 s^{-1}
$\Delta G^{\ne}$[b]	$\Delta G^{\ne}_{293} = 14.1$ kcal mol^{-1}	$\Delta G^{\ne}_{233} = 11.0$ kcal mol^{-1}

[a] $k_c = [(\Delta\delta \times 600) \times \pi/2]^{1/2}$ [s^{-1}]. [b] $\Delta G^{\ne} = 4.576\,T_c[10.319 + \log(T_c/k_c)]$ [cal mol^{-1}].

present study has confirmed by UV-visible and ^{1}H NMR spectroscopy that neither redox reactions to produce paramagnetic species nor degradation of [Ce(porph)$_2$] occurs during the Ag$^+$-complexation process. One can safely eliminate the possibility of the redox reaction between [Ce(porph)$_2$] and Ag$^+$ and/or protonation to give Ce(porph). The above spectral observations therefore suggest that the most likely mechanism is that complexation of Ag$^+$ by the π cleft induces conformational changes in the porphyrin ligands that weaken the π–π interaction and/or slightly lengthen the distance between the two porphyrin ligands and thus reduce the steric crowding. These changes could facilitate rotation. Additional information about a change in the interporphyrin distance due to cooperative Ag$^+$-ion binding might be obtained by the NOE technique with [Ce(tmpp)(tmcpp)]. This hetero bis-porphyrinate has two sets of distinct pyrrole and *meso*-aryl proton signals suitable for NOESY and NOE measurements. However, saturation transfer occurs both in the presence and absence of Ag$^+$ ions, even at − 20 and − 40 °C. This makes it difficult to obtain useful information about the change in the distance between the pyrrole β-protons.

Neverthelss, the trend in the binding constants in Table 1 and the downfield shift of the *meso*-aryl protons induced by Ag$^+$ binding (Figures 5, 6, and 7) show that some assistance of the *meso*-aryl groups in the binding of Ag$^+$ to the porphyrin π clefts cannot yet be ruled out. To reveal the effect of the *meso*-aryl groups on the Ag$^+$ binding to [Ce(porph)$_2$], *meso*-aryl-free cerium(IV) bis(tetranonylporphyrinate) was chosen as a control compound. However, this compound was oxidized by Ag$^+$ ion, and a hypsochromic shift of the Soret band from 398.0 to 394.0 nm was observed instead of a bathochromic shift. This is because its oxidation potential (0.30 V vs Ag/AgCl in dichloromethane/methanol (4:1), 0.1 M TBAP) is lower than that of cerium(IV) bis-tetraarylporphyrinates.[13f, 24] It seems difficult, therefore, to collect further useful information by ^{1}H NMR spectroscopy.

Resonance Raman (RR) spectroscopic studies: We tried many times to obtain a single crystal of a [Ce(porph)$_2$]–Ag$^+$ complex suitable for X-ray crystallographic analysis, but were unsuccessful. Therefore, we performed RR studies in solution. The RR spectra (excitation at 413.1 nm) of [Ce(tmpp)$_2$], [Ce(bbpp)$_2$], and [Ce(tmpp)(tmcpp)] in the range of 400–1800 cm^{-1} in the absence and presence of Ag$^+$ ion are shown in Figure 8. Frequencies of selected vibrational modes ν_1, ν_2, and ν_4 were assigned on the basis of work by Bocian et al.[25] (Table 3). Shelnutt et al. reported systematic solution and solid-state Raman spectroscopic investigations on synthetic nonplanar metalloporphyrins.[26] These studies revealed

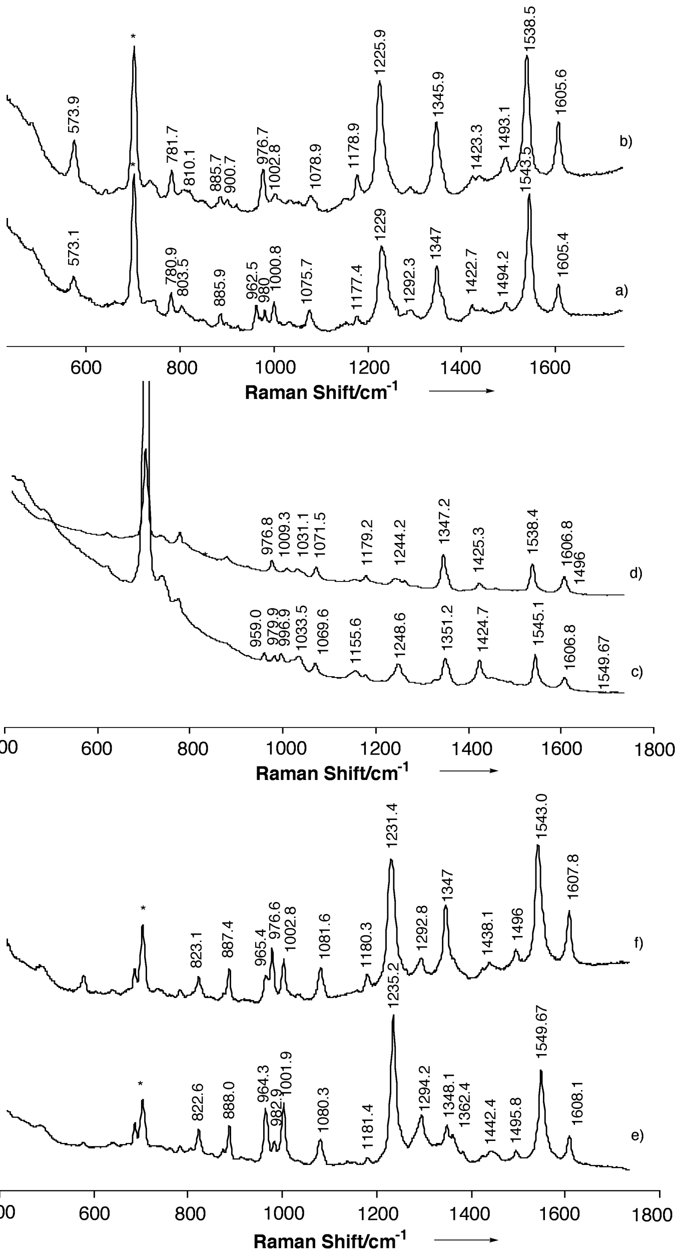


Figure 8. High-frequency region of the 413.1 nm excitation resonance Raman spectra. a) [Ce(tmpp)$_2$], b) [Ce(tmpp)$_2$] with 20 equiv of AgOTf, c) [Ce(bbpp)$_2$], d) [Ce(bbpp)$_2$] with 50 equiv of AgOTf, e) [Ce(tmpp)(tmcpp)], and f) [Ce(tmpp)(tmcpp)] with 50 equiv of AgOTf in dichloromethane/methanol (4:1). Solvent peaks are marked by an asterisk.

Table 3. Selected resonance Raman frequencies [cm^{-1}] of the [Ce(porph)$_2$].[a]

Complex	ν_2	ν_4	ν_1
[Ce(tmpp)$_2$][b]	1543.5	1347.0	1229.0
[Ce(tmpp)$_2$]–Ag complex	1538.5 (− 5.0)[c]	1345.9 (− 1.1)	1225.9 (− 3.1)
[Ce(bbpp)$_2$][b]	1545.1	1351.2	1248.6
[Ce(bbpp)$_2$]–Ag complex	1538.4 (− 6.7)	1347.2 (− 4.0)	1244.2 (− 3.4)
[Ce(tmpp)(tmcpp)][b]	1549.7	1348.1	1235.2
[Ce(tmpp)(tmcpp)]–Ag complex	1543.0 (− 6.7)	1347.0 (− 1.1)	1231.4 (− 3.8)

[a] Spectra of all [Ce(porph)$_2$] complexes obtained with $\lambda_{ex} = 413.1$ nm. [b] Mode numbering and assignments follow ref. [25]. [c] Frequencies in parentheses are differences between [Ce(porph)$_2$] and [Ce(porph)$_2$]–Ag$^+$.

that the bands ν_2 and ν_4 are structure-sensitive and the oxidation-state marker line, respectively. Moreover, they have demonstrated that increasing the nonplanar distortion of the porphyrins causes a shift to lower frequency in the band ν_2, a longer metal–nitrogen distance of the pyrrole moieties, and a bathochromic shift of the Soret band.[25] In this work, the ν_1, ν_2, and ν_4 bands of the [Ce(porph)$_2$]–3 Ag$^+$ complexes were all shifted to lower frequency relative to [Ce(porph)$_2$]. Especially the structure-sensitive line ν_2 shifted to lower frequency by 5.0–6.7 cm^{-1}, whereas the oxidation-state marker line ν_4 was less strongly shifted (1.1–4.0 cm^{-1}). These spectral changes indicate that the distortion of the porphyrin ligand planes in [Ce(porph)$_2$] is induced by the guest Ag$^+$ ions. Since [Ce(porph)$_2$] has a square-antiprismatic coordination geometry,[13f] we propose that the deformation arises from a conformational change in the porphyrin planes to a more domed structure. This is consistent with our proposal, based on other spectral evidence, that the slight conformational changes in the porphyrin ligands take place by cooperative Ag$^+$-ion complexation so as to weaken the π–π interactions and enhance the rotational activity of the ligands.

Conclusion

In conclusion, we have demonstrated that cerium(IV) bis-porphyrinate double-deckers show positively homotropic allosterism in Ag$^+$ binding, and the peripheral π clefts of the porphyrin ligands act as effective Ag$^+$ binding sites. Moreover, the rate of the porphyrin ligand rotation is nonlinearly accelerated with increasing Ag$^+$ ion concentration. Such an allosteric behavior can be regarded as a sort of "on/off" switching function. In other words, cerium(IV) bis-porphyrinate double-deckers can behave as rotating modules which can switch their rotational speed at the right time and in the right place by means of the Ag$^+$ concentration. More important is the finding that the origin of the positive homotropic allosterism in the present system is different from those reported earlier. The typical mechanism so far reported is that binding of the first guest suppresses the molecular motion of the host, and this entropically facilitates the binding of the second and third guests. In the present system, the binding of the first Ag$^+$ ion guest would adjust the size of the π cleft and thus makes it suitable for binding further Ag$^+$ and instead enhances the molecular motion of the host. This offers a new concept for designing positive homotropic allosterism as well as rotating molecular modules with a switching function. Therefore, we believe that further elaboration of the present system should lead to a more generalized concept for designing allosteric modules, not only in artificial systems but also in biological systems.

Experimental Section

General: All starting materials and solvents were purchased from Tokyo Kasei Organic Chemicals or Wako Organic Chemicals and used as received. The ^{1}H NMR spectra were recorded on a Brucker AC250 (250 MHz) or Brucker DRX600 (600 MHz) spectrometer. Chemical shifts are reported in downfield from tetramethylsilane as internal standard. Mass spectral data were obtained on a Perseptive Voyager RP MALDI-TOF mass spectrometer and/or a JEOL JMS HX110A high-resolution magnetic-sector FAB mass spectrometer. UV-visible spectra were recorded with a Shimadzu UV-2500 PC spectrophotometer. Resonance Raman spectra were obtained on a SpectraPro-300i (Action Research Co.) spectrograph (operating with a 2400-groove grating) with a SpectraPhysics Beamlok 2060 Kr Ion Laser (413.1 nm) and a liquid-N$_2$-cooled CCD detector. The spectra for solution samples were collected in spinning cells (2 cm diameter, 1500 rpm) with a laser power of 20 mW, 90° scattering geometry, and 5 min data accumulation. Peak frequencies were calibrated relative to indene and CCl$_4$ standards and were accurate to ±1 cm^{-1}. During each Raman experiment, UV-visible spectra were simultaneously collected on a Hamamatsu PMA-11 CCD spectrophotometer with a Photal MC-2530 as light source (D$_2$/W$_2$).

Syntheses: Cerium(IV) bis-porphyrinate double-deckers were synthesized from the corresponding free-base porphyrins according to the method of Buchler et al.[13] [Ce(tmpp)$_2$],[13c] [Ce(tmcpp)$_2$],[13a] and BBPPH$_2$[27] were synthesized according to methods reported previously.

[Ce(tmpp)$_2$]: ^{1}H NMR (CH$_2$Cl$_2$, −40 °C, 600 MHz): $\delta = 4.15$ (s, 24 H), 6.48 (d, $J = 8.0$ Hz, 8 H), 6.91 (d, $J = 8.0$ Hz, 8 H), 7.77 (d, $J = 8.0$ Hz, 8 H), 8.37 (s, 16 H) , 9.54 (d, $J = 8.0$ Hz, 8 H); MALDI-TOF MS: m/z calcd for [M^++H]: 1606.76; found: 1606.88; elemental analysis (%) calcd for $C_{96}H_{72}CeN_8O_8 \cdot 0.75\,C_6H_3Cl_3$: C 69.21, H 4.42, N 6.42; found: C 69.51, H 4.79, N 6.22.

[Ce(tmcpp)$_2$]: ^{1}H NMR (CH$_2$Cl$_2$, 25 °C, 600 MHz): $\delta =$ 4.15 (s, 24 H), 6.49 (brs, 8 H), 7.96 (brs, 8 H), 8.27 (s, 16 H), 8.83 (brs, 4 H) , 9.62 (brs, 4 H); MALDI-TOF MS: m/z calcd for [M^++H]: 1830.85; found: 1830.94; elemental analysis (%) calcd for $C_{104}H_{72}CeN_8O_{16} \cdot 2\,H_2O$: C 66.94, H 4.11, N 6.01; found C 66.74, H 4.24, N 5.64.

5,15-bis(4-butoxyphenyl)porphyrin (BBPPH$_2$): ^{1}H NMR (25 °C, CDCl$_3$, 250 MHz): $\delta = 1.13$ (t, 6 H), 1.68 (s, H), 2.07 (s, 8 H), 4.29 (t, 4 H), 7.34 (d, 4 H), 8.18 (d, 4 H), 9.13 (d, 4 H), 9.39 (d, 4 H), 10.30 (s, 2 H); MALDI-TOF MS: m/z calcd for [M^++H]: 607.31; found: 607.91.

[Ce(bbpp)$_2$]: [Ce(acac)$_3$]·3 H$_2$O (320 mg, 3 equiv) was added to a stirred solution of 5,15-bis(4-butoxyphenyl)porphyrin (BBPPH$_2$; 100 mg, 0.165 mmol) in 1,2,4-trichlorobenzene (15 mL). The mixture was heated to reflux for 5 h under nitrogen atmosphere. After cooling to room temperature, the solvent was removed in vacuo. The residue was purified by column chromatography (silica, chloroform) and size-exclusion chromatography (Bio-beads SX-1, chloroform) to yield [Ce(bbpp)$_2$] as a purple solid (15 mg, 13 %). ^{1}H NMR (−40 °C, CDCl$_3$/CD$_3$OD 4:1, 600 MHz): $\delta =$ 1.19 (t, 12 H), 1.78 (s, 8 H), 2.07 (s, 8 H), 4.38 (t, 8 H), 6.41 (d, 4 H), 6.90 (d, 4 H), 7.89 (d, 4 H), 8.43 (d, 4 H), 8.58 (d, 4 H), 8.80 (d, 4 H), 8.88 (d, 4 H), 9.19 (s, 4 H), 9.71 (d, 4 H); FAB-MS (magic bullet): m/z calcd for [M^++H]: 1349.4809; found: 1349.4518; elemental analysis (%) calcd for $CeC_{80}H_{72}N_8O_4 \cdot 0.5\,CHCl_3$: C 70.40, H 5.59, N 7.61; found: C 70.20, H 5.59, N 8.19.

[Ce(tfpp)$_2$]: [Ce(acac)$_3$]·3 H$_2$O (325 mg, 3 equiv) was added to a stirred solution of 5,10,15,20-tetrakis(4-fluorophenyl)porphyrin (TFPP; 150 mg, 0.22 mmol) in 1,2,4-trichlorobenzene (15 mL). The mixture was heated to reflux for 24 h under nitrogen atmosphere. After cooling to room temperature the solvent was removed in vacuo. The residue was purified by column chromatography (silica, chloroform) and size-exclusion chromatography (Bio-beads SX-1, chloroform) to yield [Ce(tfpp)$_2$] as a purple solid (15 mg, 9 %). ^{1}H NMR (−40 °C, CDCl$_3$, 600 MHz): $\delta = 6.31$ (m, 8 H), 6.97 (m, 8 H), 7.86 (m, 8 H), 8.27 (s, 16 H), 9.51 (d, 8 H); FAB-MS (magic bullet): m/z calcd for [M^++H]: 1509.3007; found: 1509.3016.

[Ce(tmpp)(tmcpp)]: [Ce(acac)$_3$]·3 H$_2$O (353 mg, 3 equiv) was added to a stirred solution of 5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrin (TMPP; 200 mg, 0.24 mmol) and 5,10,15,20-tetrakis(4-methoxyhenyl)porphyrin (TMCPP; 208 mg, 0.29 mmol) in 1,2,4-trichlorobenzene (30 mL). The mixture was heated to reflux for 36 h under nitrogen atmosphere. After cooling to room temperature the solvent was removed in vacuo. The residue was purified by column chromatography (silica, dichloromethane/acetone 100/1) and size exclusion chromatography (Bio-beads SX-1, chloroform) to yield [Ce(tmpp)(tmcpp)] as a purple solid (10 mg, 10 % based on TMCPP). ^{1}H NMR (−40 °C, CDCl$_3$/CD$_3$OD 4:1, 600 MHz): $\delta =$ 4.13 (s, 24 H), 6.48 (d, 4 H), 6.63 (d, 4 H), 6.92 (d, 4 H), 7.73 (d, 4 H), (d, 4 H), 7.99 (d, 4 H), 8.35 (s, 8 H), 8.42 (s, 8 H) 8.88 (d, 4 H), 9.44 (d, 4 H), 9.74 (d, 4 H); FAB-MS (magic bullet): m/z calcd for [^+M+H]: 1717.4402; found: 1717.4459.

Binding-isotherm analysis: Cooperative guest binding was analyzed according to the Hill equation[16]: $\log(y/(1-y)) = n\log[\text{guest}] + \log K$, where K, y, and n_H are the association constant, extent of complexation, and Hill coefficient, respectively. From the slope and the intercept of the linear plots one can estimate K and n_H, which are useful measures of the cooperativity.[16] In the analysis of the binding isotherm by Hill plot, we evaluated the concentration of unbound Ag^+ by assuming that 100% 1:3 complex is formed when the absorption change is saturated.

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