Highlight Review

Metallo-supramolecular Systems for Synergistic Functions Based on Unique Arrangement of Ligation Sites

Tatsuya Nabeshima,* Shigehisa Akine, Chusaku Ikeda, and Masaki Yamamura

Abstract

Pseudomacrocyclic compounds with 2,2′-bipyridine subunits and multimetal-assisting functional molecules with salamo and dipyrrin moieties as the N_2O_2 ligation moieties are described. The unique and suitable arrangement of these ligation units results in highly synergistic functions in the metallo-supramolecular systems.

♦ Introduction

A variety of molecules bearing functions such as catalytic activity for chemical reactions, molecular recognition, and optical properties have been designed and synthesized in a wide range of chemistry fields.[1] In biological systems, synergistic phenomena such as allostery and feedback play an important role to effectively control the energy and materials balance in the body.[2] Cooperative interactions between functional molecules result in sophisticated functions which cannot be achieved by molecules with a single function. Allosteric events utilize structural change upon effector binding to trigger the next event at the molecular level. Such cooperative structural changes usually amplify molecular functions in a cascade, as seen in the actions of medicines. The cooperative control of molecular functions should be very useful for artificial functional systems to significantly enhance the functions in terms of both quality and quantity. Thus, functional molecules responding to external stimuli have attracted considerable attention from many researchers in various scientific fields. The responding molecules have to possess a moiety receiving an external signal and an intrinsic functional moiety. Upon receiving the signal, conformational change of the responding molecule takes place. Consequently, the original function is modulated. When functional performance increases and decreases, we call this effect positive and negative cooperativity, respectively. We should incorporate a flexible subunit into the responding molecules to induce the conformational change, which usually makes the molecular structure rigid. The structural rigidity is necessary to regulate the functions. In the case of positive cooperativity for molecular recognition, conformational fixation of the binding site inevitably produces a preorganization effect which makes the guest recognition favorable.

Metal complexes are considered to be excellent candidates for constructing the responding functional molecules because various functions are available by selecting the ligand and metal.

In addition, the metal complexes provide diverse structures. Synergistic functions are also expected from the direct interactions between atoms in the metal complexes. The accumulation of typical elements as well as metal elements in a restricted space should cause effective interactions that produce unexpected novel properties of the molecules. For this purpose, the metal complexes possessing organic ligation moieties would be useful for designing and synthesizing element-interacting functional molecular systems.

The appropriate combination of a metal ion and a ligand is crucial for synthesizing metal complexes which exhibit desired molecular functions. However, several functions have to be incorporated into the molecular framework if the synergistic function is required. The functional units should be suitably arranged in the molecules for effective cooperative events.

Hence, we have proposed new concepts and methods to produce cooperative functions on the basis of unique ligand arrangement. We now introduce pseudomacrocyclic systems and multimetal-assisting functional systems by arranging the N_2O_2 ligation moieties. In this review, we focus on metallo-supramolecular systems containing 2,2′-bipyridine, a multi-imine ligand and a dipyrrin subunit because these have been intensively studied due to their strong binding ability to many metal ions and versatile functions of the metal complexes.

♦ Pseudomacrocyclic Compounds for Synergistic Functions

2,2′-Bipyridines show characteristic binding behavior toward metal ions. Their binding strength and selectivity often depend on the position and type of substituents. For example, a substituent at the 6 and/or 6′ position of the bipyridine skeleton prohibits octahedral complexation, but allows a favorable tetrahedral structure. Thus, the tetrahedral Cu^I–6,6′-dimethyl-2,2′-bipyridine complex is very stable under aerobic conditions. The polyether L^1 bearing a 6,6′-dimethyl-2,2′-bipyridine moiety at each end of the chain very smoothly reacts with Cu^I to quantitatively give the stable red complex $L^1 \cdot Cu^I$ (Scheme 1).[3] This macrocycle $L^1 \cdot Cu^I$ is called a pseudocrown ether because the crown ether like structure is maintained by the coordination bond instead of a covalent bond. $L^1 \cdot Cu^I$ exhibits a much higher K^+ selectivity upon ion transport across a liquid membrane than L^1. Thus, a Cu^I ion works as an effector for the ion recognition system. The dynamic conformational change from the linear to the cyclic structure results in a considerable change in ion
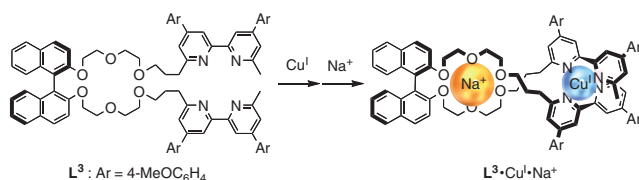
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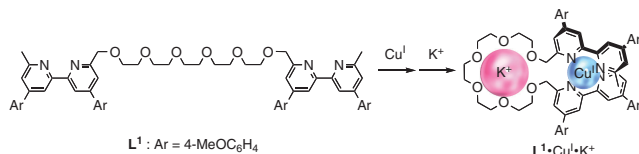
Scheme 1. Formation and K^+ recognition of pseudocrown ether $\mathbf{L^1 \cdot Cu^I}$.
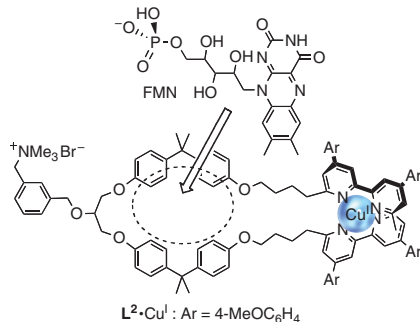
**Scheme 2.** FMN recognition of pseudocyclophane $\mathbf{L^2 \cdot Cu^I}$.

Scheme 3. Chiral transfer in pseudomacrocycle $\mathbf{L^3 \cdot Cu^I}$.

recognition. This conformation conversion effect on the molecular recognition is much more efficient than the conformational modulation of a macrocyclic host via metal-coordination.

The pseudocyclophane $\mathbf{L^2 \cdot Cu^I}$ showed transport ability toward FMN (flavin mononucleotide) sodium salt (Scheme 2).[4] Podand $\mathbf{L^3}$ bearing chiral binaphthyl moieties bound to Cu^I quantitatively produces a pseudocyclophane $\mathbf{L^3 \cdot Cu^I}$ as a 1:1 diastereomeric mixture (Scheme 3).[5] Upon complexation of $\mathbf{L^3 \cdot Cu^I}$ with Na^+, the equilibrium of the diastereomers significantly shifts to the helical species (9:1). This change is ascribed to conformational fixation of the pseudomacrocyclic polyether moiety due to the Na^+ binding. Coordination of the polyether oxygen atoms to the Na^+ ion reduces the flexibility of the chains. Consequently, the chiral information based on the chiral binaphthyl unit was transferred to the Cu·bipyridine moiety to enhance the ratio. Noteworthy is that this chiral transfer is achieved by the achiral ion, Na^+, although chiral structures are generally controlled by a chiral species. Control of the helical sense is a key issue in supramolecular chemistry because chirality inversion and pitch control of helical structures should be very important for regulating functions of biologically important molecules such as DNA and proteins with an α-helix unit. The chirality transfer in $\mathbf{L^3 \cdot Cu^I}$ may lead to chirality amplification because one chiral unit would be sufficient to derive larger polymeric and oligomeric structures with a homo chirality.

Bipyridine derivatives without a substituent at the 6 or 6′ position bind to Fe^{II} to quantitatively give the octahedral 3:1
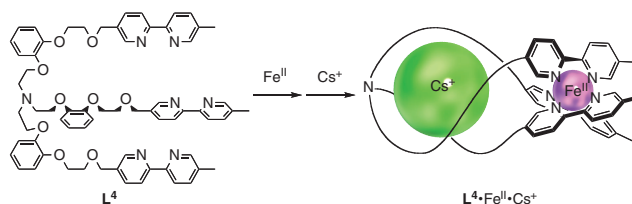
Scheme 4. Formation and Cs^+ recognition of pseudocryptand $\mathbf{L^4 \cdot Fe^{II}}$.
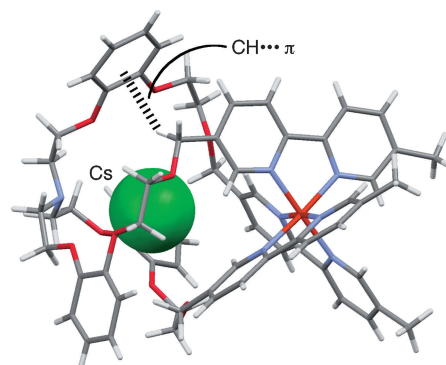

Figure 1. X-ray crystal structure of $\mathbf{L^4 \cdot Fe^{II} \cdot Cs^+}$ with space-filling representation of Cs and capped-stick representation of other atoms.

(bipyridine/Fe^{II}) complex. The complex resists autoxidation. Treatment of tripodand $\mathbf{L^4}$ with Fe^{II} quantitatively affords the 1:1 Fe^{II} complex (Scheme 4).[6] The structure was perfectly characterized by X-ray crystallography. The three polyether chains of $\mathbf{L^4 \cdot Fe^{II}}$ are assembled in a helical fashion to make a cavity favorable for selective guest recognition. $\mathbf{L^4 \cdot Fe^{II}}$ shows much higher and lower affinities to Cs^+ and Na^+, respectively, than $\mathbf{L^4}$. The crystal structure of $\mathbf{L^4 \cdot Fe^{II} \cdot Cs^+}$ reveals that the Cs^+ ion sits in the cavity and is wrapped by the polyether chains (Figure 1). Furthermore, CH$\cdots\pi$ interactions between the benzene ring and one of the methylene protons adjacent to the bipyridine moieties contribute to the Cs^+ binding. The CH$\cdots\pi$ contacts also rationalize the negative cooperativity on the Na^+ binding because the contacts prohibit shrinking of the cavity to fit the smaller Na^+ ion. Similar positive and negative allosteric effects were observed in ion transport experiments.

The concept of the pseudomacrocycles can be used for controlling anion recognition. The host $\mathbf{L^5}$ consists of three urea chains bearing a 2,2′-bipyridine terminal and an isocyanurate core (Scheme 5).[7] The corresponding octahedral Fe^{II} complex $\mathbf{L^5 \cdot Fe^{II}}$ was obtained in high yield. ^1H NMR spectroscopy indicated that $\mathbf{L^5 \cdot Fe^{II}}$ strongly and selectively binds to Cl^- in DMF-d_7. The Cl^- ion in $\mathbf{L^5 \cdot Fe^{II}}$ is captured through hydrogen bonds provided by three protons from the urea moieties. The distance of 3.2 Å between Cl^- and the isocyanurate core strongly suggests an effective anion$\cdots\pi$ interaction. $\mathbf{L^5 \cdot Fe^{II}}$ was found to be redox active and these processes are reversible as seen in the parent tris(2,2′-bipyridine)iron complex.[8] Interestingly, cathodic shifts of the redox potentials were observed in the presence of Cl^-. The binding constants were determined by using the shifts via a nonlinear least-squares-regression. As the positive charge
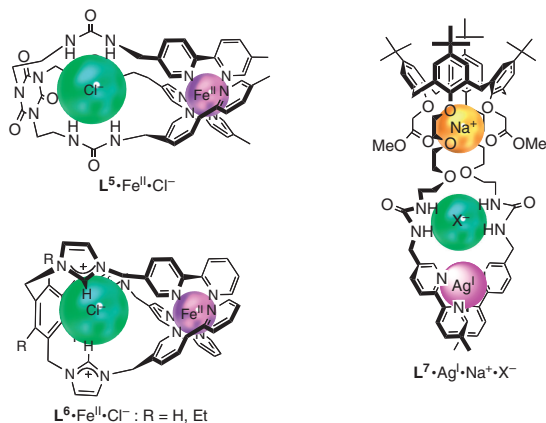
Scheme 5. Pseudomacrocyclic anion receptors.

Scheme 6. Design of acyclic bis(N_2O_2) metallohost.

of the Fe complex increases, the binding constants with anions significantly increase. This result clearly indicates that the electrostatic interaction between the iron complex moiety and the Cl^- anion is a key factor for the Cl^- recognition. To the best of our knowledge, this is the first example of the multistep regulation of anion recognition by redox reactions. Although such a multistep control was not shown, two other anion receptors that have a pseudocryptand framework have been reported. The tripodal ligands $\mathbf{L^6}$ possess imidazolium moieties and 2,2′-bipyridine terminals (Scheme 5).[9] The 1:1 complexation of $\mathbf{L^6}$ with Fe^{II} gave the desired Fe complexes, which showed the affinity sequence $Cl^- > Br^- > I^-$.

The other example of multistep anion binding control utilizes metal ions as effectors. The calix[4]arene derivative $\mathbf{L^7}$ has two kinds of cation binding sites and one anion binding site (Scheme 5).[10] The hard cation binding site contains ester groups and diethylene glycol chains. The soft binding sites are bipyridine subunits at the chain terminals. A hydrogen-bond donating urea functionality was employed for the anion binding site. The host $\mathbf{L^7}$ binds Na^+ and Ag^I in the hard and soft binding sites, respectively. The $\mathbf{L^7} \cdot Ag^I$ complex is regarded as a pseudomacrocycle. The complexation of $\mathbf{L^7}$ with either Na^+ or Ag^I made the anion binding more favorable. In the presence of Na^+ and Ag^I, the anion binding site showed a much higher binding strength, thus very weak bases such as the triflate anion can be efficiently captured by the host.

◆ *Cooperative Complexation System Based on Acyclic Oligo(N_2O_2) Ligands*

Salen is one of the most useful constituents of functional molecular systems based on metal centers. Some salen–metal complexes are used as catalysts for organic reactions,[11] models of reaction centers of metalloenzymes,[12] nonlinear optical materials,[13] and building blocks for interlocked molecules.[14] One important feature of the salen–metal complexes is that the complexes show a coordinating ability toward metal cations (Scheme 6a). There are a number of examples in which a salen–metal complex coordinates to another cation such as an alkali metal,[15] an alkaline earth metal,[16] or a lanthanide metal ion.[17] This coordinating ability is mainly ascribed to the negative charge of the phenoxide groups.
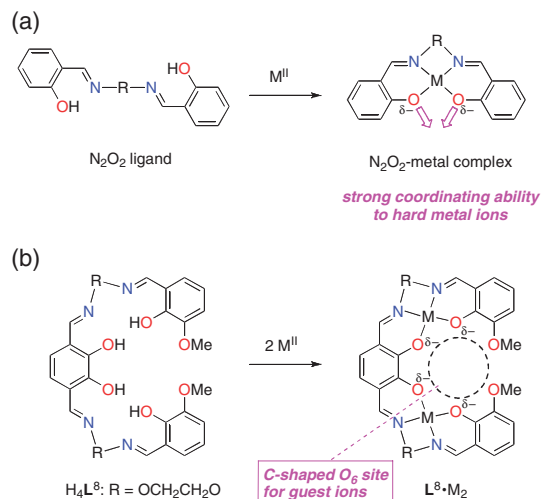
Because of the coordinating ability of the phenoxide groups, host molecules having a salen-type N_2O_2 coordination site are useful for cooperative complexation systems in which the metalation of the N_2O_2 moiety enhances binding to a second (or third) metal ion. In particular, if the molecule contains two or more N_2O_2 moieties, the enhancement effect should be much greater.

A bis(N_2O_2)-type molecule was designed for the development of such a cooperative complexation system (Scheme 6b).[18] The oxime-based chelate moiety, salamo [H_2salamo = 1,2-bis(salicylideneaminooxy)ethane], is used in order to avoid the C=N bond recombination which might give a mixture of oligomers with different chain lengths.[19,20] In fact, the bis(salamo) ligand $H_4\mathbf{L^8}$ was synthesized as stable crystals whereas the synthesis of the bis(salen) and bis(saloph) ligands was difficult due to the C=N bond recombination.[21]

Metalation of the bis(salamo) ligand $H_4\mathbf{L^8}$ with 2 equiv of d-block metal ions (M = Zn, Co, Mn, etc.) was expected to give the corresponding dinuclear metallohost $\mathbf{L^8} \cdot M_2$. Contrary to our expectations, the complexation with $Zn(OAc)_2$ afforded a complex having a stoichiometry of 1:3 (ligand/metal) instead of 1:2, which is evident from the spectroscopic titration (^{1}H NMR and UV–vis).[18,21] The trinuclear structure is confirmed by mass spectra and X-ray crystallographic analysis (Figure 2). It is noteworthy that the complexation process is highly cooperative. No intermediary complexes are observed in the complexation. When two equiv of Zn^{II} ion were added to a solution of the ligand $H_4\mathbf{L^8}$, 2/3 of the $H_4\mathbf{L^8}$ was converted to the trinuclear complex $\mathbf{L^8} \cdot Zn^{II}_3$ and the other 1/3 remained unchanged. In the molecular structure of the trinuclear complex [$\mathbf{L^8}Zn_3$-$(OAc)_2(EtOH)$], Zn^{II} ions are incorporated into the central O_6 site in addition to the N_2O_2 salamo sites (Figure 2). Two acetate ions bridge the trinuclear Zn^{II} core in a μ_2-fashion. These acetate ions probably contribute to the cooperative formation of the trinuclear complex $\mathbf{L^8} \cdot Zn^{II}_3$. The ligand $H_4\mathbf{L^8}$ also forms a similar trinuclear complex with other d-block metal ions such as Mn^{II}, Co^{II}, and Ni^{II} in a cooperative fashion.[21] This cooperativity probably results from the two salamo groups arranged in a convergent fashion.
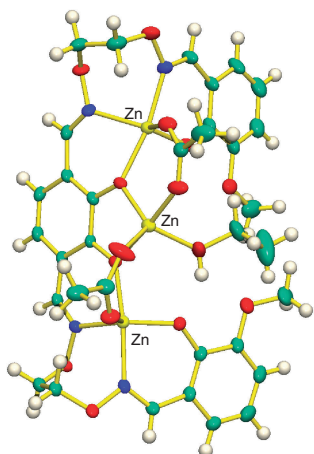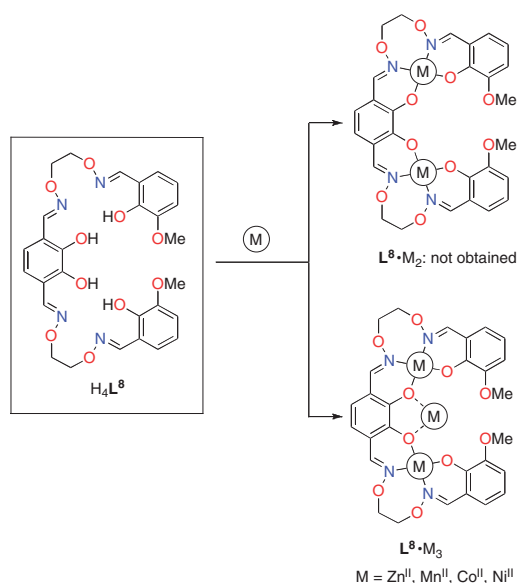
Figure 2. X-ray crystal structure of [**L^8**Zn$_3$(OAc)$_2$(EtOH)].


Scheme 7. Formation of trinuclear complex **L^8**·M$_3$ from bis(N$_2$O$_2$) ligand H$_4$**L^8**.

It is difficult to obtain a dinuclear metallohost in which the O$_6$ recognition site remains vacant, because its C-shaped recognition site is occupied by an additional Zn^{II} ion (Scheme 7). However, the size of the central Zn^{II} ion seems to be too small to fit in the C-shaped O$_6$ site because only two oxygen donor atoms coordinate to the central Zn^{II} ion in the crystalline state. Thus, the central Zn^{II} ion was expected to be replaced by a guest ion with a suitable size for the C-shaped O$_6$ site.

We investigated the guest ion recognition based on the transmetalation of the zinc(II) trinuclear complex **L^8**·Zn^{II}$_3$.[18,22,23] The process is considered to be a metal exchange equilibrium, as shown in Scheme 8, and the binding strength can be discussed by the equilibrium constant K defined as ([**L^8**·Zn^{II}$_2$·G][Zn^{2+}])/ ([**L^8**·Zn^{II}$_3$][G]).

Since the **L^8**·Zn^{II}$_2$ moiety has the C-shaped O$_6$ site similar to the 18-crown-6, the trinuclear complex would recognize alkali metal cations. However, **L^8**·Zn^{II}$_3$ was not converted to any of the complexes with alkali metal cations (G = Na$^+$, K$^+$, Rb$^+$,
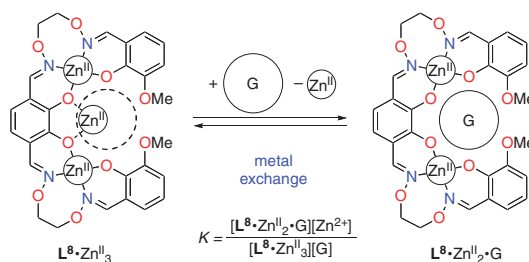
Scheme 8. Ion recognition based on metal exchange.

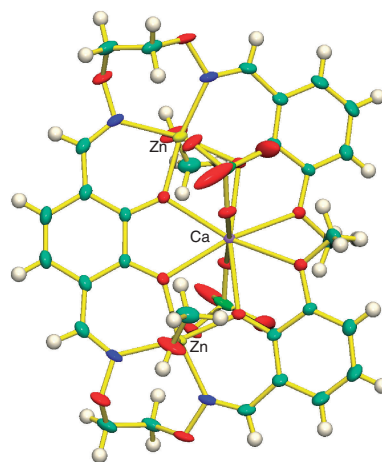**Figure 3.** X-ray crystal structure of [**L^8**Zn$_2$Ca(ClO$_4$)$_2$-(MeOH)$_2$].

and Cs$^+$). On the other hand, the transmetalation efficiently took place to afford the heterotrinuclear complex **L^8**·Zn^{II}$_2$·G when 1 equiv of rare-earth metal ions (G = Sc^{3+}, Y^{3+}, and La^{3+}–Lu^{3+}) was added. The equilibrium constants K for the metal exchange were greater than 1000. The heterotrinuclear complexes **L^8**·Zn^{II}$_2$·G containing lanthanide ions were isolated as yellow crystals and the crystal structure was determined by X-ray crystallography. The C-shaped O$_6$ site is occupied by a lanthanide ion, to which all six oxygen atoms including the phenoxide and methoxy groups coordinate. The ligand moiety forms a single helix around the lanthanide ion.

Among the divalent alkaline earth metal ions (G = Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}), the trinuclear complex **L^8**·Zn^{II}$_3$ selectively recognizes the calcium ion with an equilibrium constant of $K = 32$. The calcium complex **L^8**·Zn^{II}$_2$·Ca^{2+} adopted a structure similar to that of the rare-earth metal complexes, in which the guest metal ion fits nicely into the C-shaped O$_6$ site (Figure 3). Since the trinuclear complex **L^8**·Zn^{II}$_3$ did not recognize the magnesium ion ($K < 0.001$), a significantly high Ca^{2+}/Mg^{2+} selectivity ($>10^5$) was achieved. This selectivity coefficient is comparable with the values of an excellent Ca^{2+}-selective receptor or sensors such as BAPTA or Quin2.[24]

As described above, the trinuclear complex **L^8**·Zn^{II}$_3$ showed a selectivity toward trivalent lanthanide ions. The charge of the guest ion is a significant factor that affects the cation binding ability, because a trivalent cation can interact more strongly with the phenoxide groups of the O$_6$ site. Among the divalent alkaline earth metal ions, **L^8**·Zn^{II}$_3$ showed a selectivity for the calcium ion. The size-fit principle is also

important for this ion recognition. It is evident that the negative charges and the preorganization effect of the C-shaped arrangement of the O_6 donor atoms are the key factors that increase the stability of $L^8 \cdot Zn^{II}_2 \cdot G$ and promote the transmetalation.

When the bis(salamo) derivatives or their longer analogs form a complex with Zn^{II} and guest metal ions, the structures change into a single-helical structure. The helical handedness and the helix inversion rate can be changed depending on the central guest ions.[25] A unique supramolecular superhelical structure was formed by metal complexation of a chiral tris(N_2O_2) ligand.[26] Since some of the metal complexes of the oligo(salamo) ligand exhibit characteristic magnetic[27] or photophysical properties[28] as well as reactivities,[29] the oligo(salamo) framework is useful for the switching of the functions which originate from the helical structures upon guest recognition.

♦ Formation of Multimetal Systems and Molecular Assemblies via N₂O₂ Dipyrrin Derivative Complexation

Dipyrrins (dipyrromethenes) exhibit interesting optical properties based on their conjugated framework. The facile coordination abilities to various metal ions due to the chelate effect are highly attractive for constructing supramolecular architectures. A pioneering study to use a dipyrrin ligand in supramolecular chemistry was performed by Dolphin et al., who reported metallohelicates or cyclic assemblies based on the transition-metal complexes of the oligodipyrrins.[30,31] Later, the formation of bis- or tris-dipyrrin complexes were used in a metal–organic-framework[32] or nanoscale aggregate.[33]

Our approach is to combine the dipyrrin ligand and oxygenated ligand moiety(s) (such as phenol, catechol, and dimethoxybenzene) for preparation of the modified dipyrrins bearing multiple coordination sites. The appropriate arrangement of the coordination sites affords various dipyrrin complexes, which have interesting structural and optical properties. First, we chose the N_2O_2 dipyrrins H_3L^{9a} and H_3L^{9b} bearing 2-hydroxyphenyl groups at the pyrrole α-position of the dipyrrin framework because the metal complexes formed by the N_2O_2-type binding site would serve as a metalloligand, which shows a unique absorption or fluorescence different from the parent dipyrrin (Scheme 9).

In spite of the expected versatile properties, only the boronand N_2O_2 dipyrrin[34] and a few transition-metal complexes[35] have been reported. Furthermore, use of the dipyrrin complexes as a chelating metalloligand has never been reported. We first prepared the aluminum complexes $L^{9a} \cdot Al$ and $L^{9b} \cdot Al$ because the N_2O_2 binding site may serve as a planar equatorial unit for a complex with the octahedral coordination geometry around the aluminum atom. In addition, oxygen atoms in the aluminum complexes should be suitable for subsequent chela-
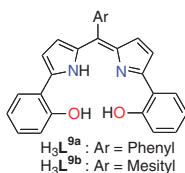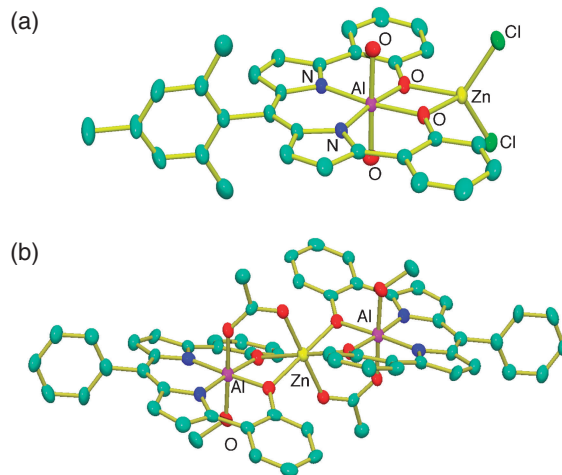

Figure 4. X-ray crystal structures of (a) $L^{9b} \cdot Al \cdot ZnCl_2$ and (b) $(L^{9a} \cdot Al)_2 \cdot Zn(OAc)_2$.

tion to a metal ion due to the negative charge of the Al–O oxygen atoms, which are more negative than those of the B–O bonds. Indeed, we found that these aluminum complexes $L^{9a} \cdot Al$ and $L^{9b} \cdot Al$ work as a metalloligand to form stable complexes with zinc(II) salts such as $ZnCl_2$, $ZnBr_2$, and $Zn(OAc)_2$. In the case of the complex of $L^{9b} \cdot Al$ with a zinc(II) halide, a 1:1 complex such as $L^{9b} \cdot Al \cdot ZnCl_2$ was obtained (Figure 4a). On the other hand, a 2:1 complex $(L^{9a} \cdot Al)_2 \cdot Zn(OAc)_2$ was obtained from a mixture of $L^{9a} \cdot Al$ and zinc(II) acetate (Figure 4b).[36] In both complexes, the aluminum atom has an octahedral coordination environment, and the zinc(II) ion is coordinated by the two μ-phenoxo oxygen atoms. In case of the 2:1 complex, the trinuclear dimeric complex is stabilized by two μ-acetato ligands bridging the aluminum and zinc atoms.

Notable is that an enhanced fluorescence was observed when the aluminum complexes $L^{9a} \cdot Al$ and $L^{9b} \cdot Al$ were converted into the corresponding Al^{III}–Zn^{II} complexes. The fluorescence quantum yield of $L^{9a} \cdot Al$ increased from 0.23 to 0.55 upon binding to zinc(II) chloride. $L^{9b} \cdot Al$, bearing mesityl groups at the meso-position, showed a higher quantum yield ($\Phi_F = 0.72$ and 0.83 for $L^{9b} \cdot Al$ and $L^{9b} \cdot Al \cdot ZnCl_2$, respectively) due to the restricted rotation of the mesityl group.[37] The enhanced emission of the complex of $L^{9a} \cdot Al$ and $L^{9b} \cdot Al$ with a zinc(II) halide is partly ascribed to the increased rigidity of the dipyrrin skeleton caused by the chelation, which reduces the loss of energy via a nonradiative decay.

The N_2O_2 binding site is effective for synthesizing boron–dipyrrins bearing an arylboronate center with a unique coordination geometry.[38] The boron–dipyrrins bearing one or two aryl group(s) at the boron center (*Ar*-BODIPY) are very interesting because the optical properties would be modified by changing the aromatic groups on the boron center. In addition, introduction of an aromatic group that has a guest binding site would lead to effective fluorescent sensors for an appropriate guest. However, the reported synthesis of the *Ar*-BODIPY involved the substitution of the fluorine atoms of the BF_2 complex of dipyrrin and the yields were not high.[39,40] In sharp contrast, *Ar*-BODIPYs containing an arylboronate center were readily obtained from the reaction with the N_2O_2 dipyrrin and arylboronic acids. For example, the boron complex $HL^{9b} \cdot B$–Ph, which shows an
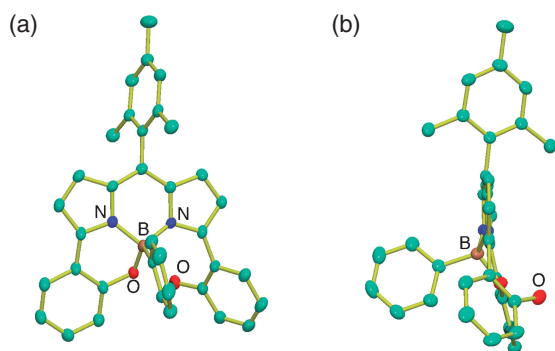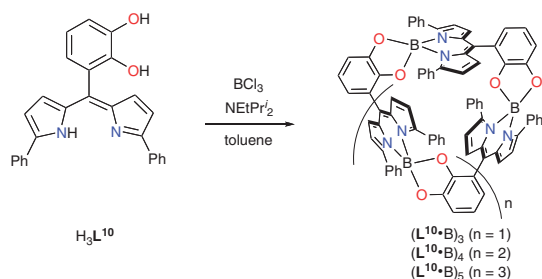
Ar

H_3L^{9a} : Ar = Phenyl
H_3L^{9b} : Ar = Mesityl

Scheme 9.

Figure 5. X-ray crystal structure of HL^{9b}·B–Ph. (a) Top view; (b) side view. Only one of the enantiomers is shown.

Scheme 10. Synthetic scheme of self-assembled cyclic boron–dipyrrin oligomers.

intense fluorescence at 614 nm with a quantum yield of 0.65, was quantitatively obtained from the reaction of the N$_2$O$_2$ dipyrrin and phenylboronic acid (Figure 5).

The strategy for the *Ar*-BODIPY preparation is highly useful because a variety of boronic acids can be used as a starting material for the derivatization of the *Ar*-BODIPY. These dipyrrins may show unique fluorescence properties, which depend on the aromatic substituent. In addition, the chiral boron center is expected to be applicable for chiral recognition. A ^{1}H NMR spectral study using a chiral shift reagent showed that racemization at the boron center does not occur at least on the NMR timescale.

Self-assembled oligodipyrrins were well synthesized via a heteroleptic coordination. The dipyrrin derivatives were cyclicly arranged in a head-to-tail fashion. The cavity of the cyclic self-assembled complex was found to behave as a guest-recognition site. The dipyrrin bearing catecholyl groups gave cyclic oligodipyrrin assemblies (L^{10}·B)$_3$, (L^{10}·B)$_4$, and (L^{10}·B)$_5$ upon the reaction of H$_3$L^{10} with BCl$_3$ (Scheme 10).[41]

X-ray crystallographic analysis showed that (L^{10}·B)$_3$ and (L^{10}·B)$_4$ have triangular- and square-prism structures, which are connected by the boron atom coordinated to the two pyrrolic nitrogens and the two catecholate oxygen atoms (Figure 6).

The cavity of (L^{10}·B)$_3$, which is formed by the catecholate oxygens as well as the electron-rich pyrrolic planes, was suitable for alkali-metal ion recognition. A ^{1}H NMR spectroscopic study indicated high binding constants with K$^+$, Rb$^+$, and Cs$^+$. Interestingly, among the alkali metal ions, the highest binding constant was observed with Cs$^+$ ($K_a \geq 5.5 \times 10^6\,M^{-1}$), which has a larger ionic radius (1.67 Å) than the cavity (1.4 Å). This result suggests that (L^{10}·B)$_3$ captures the Cs$^+$ ion in a binding
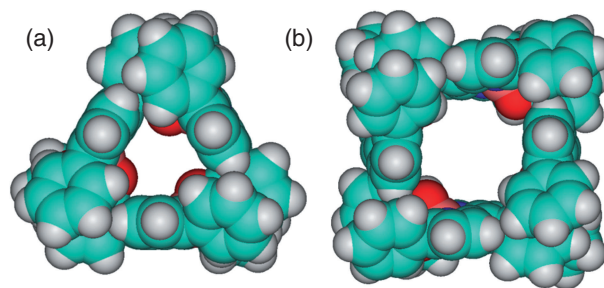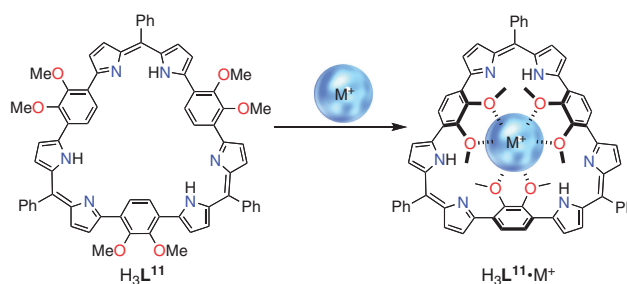

Figure 6. X-ray crystal structures of (a) (L^{10}·B)$_3$ and (b) (L^{10}·B)$_4$ with the space-filling representation.

Scheme 11. Macrocyclic trisdipyrrin H$_3$L^{11} and the guest binding.

mode different from those for K$^+$ and Rb$^+$. The Hartree–Fock calculation indicates that the Cs$^+$ ion locates above the central O$_3$ cavity and the structure is stabilized by coordination with the oxygen atoms as well as the cation⋯π interaction with the pyrrolic rings. In contrast, K$^+$ fits well within the cavity only by the coordination of the three oxygen atoms.

We also prepared another macrocyclic trisdipyrrin H$_3$L^{11}, because H$_3$L^{11} would exhibit good binding affinity to guests. In H$_3$L^{11}, 2,3-dimethoxy-1,4-phenylene moieties connect the dipyrrin units.[42] The 2,3-dimethoxy-1,4-phenylene rings may contribute to the macrocyclic conjugation depending on the tilting angle with the neighboring aromatic rings, as known for other macrocyclic oligodipyrrins.[43] If the methoxy groups on the 2,3-dimethoxy-1,4-phenylene moieties interact with a cationic guest such as alkali metal ions, changes in the absorption spectra would take place due to the tilting angle change (Scheme 11).

An X-ray crystallographic study revealed that the H$_3$L^{11} has a planar triangle structure, in which the six pyrrole rings locate in a nearly coplanar fashion. The ^{1}H NMR study indicated the fast flipping of the 2,3-dimethoxy-1,4-phenylene moieties in solution because atropisomers were not detected.

Notable is the absorption spectral changes observed in H$_3$L^{11} upon the addition of alkali metal ions. Large bathochromic shifts of 50–60 nm are observed upon the addition of K$^+$, Rb$^+$, and Cs$^+$. These spectral changes are probably attributed to the elongation of the effective π-conjugation along the macrocycle due to conformational change upon complexation with the cationic guests. The Hartree–Fock calculation suggests the cation binding structures of H$_3$L^{11}, in which all the methoxy groups face to the inside and the guest cation locates in the center of the triangle core. The cations are captured by cation–dipole interactions between the guest cation and the six oxygen atoms.

♦ *Conclusion*

A conformational change of a functional molecule induced upon the metal complexation is quite useful to cooperatively change the functions because the molecular functions generally depend on the molecular structure. The accumulation of metal ions by utilizing unique ligand arrangement is also very effective for cooperative functions. In particular, a suitable spatial arrangement of chelating ligands such as 2,2′-bipyridines and N_2O_2 type ligands is essential to create these metallosupramolecular systems with synergistic functions. We believe that the strategy shown here will open a new way to synthesize cooperatively controllable molecular catalysts, and multiresponding functional molecules and materials.

References and Notes

1 J.-M. Lehn, *Supramolecular Chemistry*, VHC, Weinheim, **1995**.

2 C. R. Cantor, P. R. Schimmel, *Biophysical Chemistry*, W. H. Freeman and Company, New York, **1980**, Part 3, pp. 849–1371.

3 T. Nabeshima, T. Inaba, N. Furukawa, *Tetrahedron Lett.* **1987**, *28*, 6211; T. Nabeshima, T. Inaba, N. Furukawa, T. Hosoya, Y. Yano, *Inorg. Chem.* **1993**, *32*, 1407.

4 T. Nabeshima, A. Hashiguchi, S. Yazawa, T. Haruyama, Y. Yano, *J. Org. Chem.* **1998**, *63*, 2788.

5 T. Nabeshima, A. Hashiguchi, *Tetrahedron Lett.* **2002**, *43*, 1457; T. Nabeshima, A. Hashiguchi, T. Saiki, S. Akine, *Angew. Chem., Int. Ed.* **2002**, *41*, 481.

6 T. Nabeshima, Y. Yoshihira, T. Saiki, S. Akine, E. Horn, *J. Am. Chem. Soc.* **2003**, *125*, 28.

7 T. Nabeshima, S. Masubuchi, N. Taguchi, S. Akine, T. Saiki, S. Sato, *Tetrahedron Lett.* **2007**, *48*, 1595.

8 Y. Kaizu, T. Yazaki, Y. Torii, H. Kobayashi, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2068; P. S. Braterman, J.-I. Song, R. D. Peacock, *Inorg. Chem.* **1992**, *31*, 555; B. R. Serr, K. A. Andersen, C. M. Elliott, O. P. Anderson, *Inorg. Chem.* **1988**, *27*, 4499; S. Ferrere, C. M. Elliott, *Inorg. Chem.* **1995**, *34*, 5818.

9 V. Amendola, M. Boiocchi, B. Colasson, L. Fabbrizzi, M.-J. R. Douton, F. Ugozzoli, *Angew. Chem., Int. Ed.* **2006**, *45*, 6920; K. Sato, Y. Sadamitsu, S. Arai, T. Yamagishi, *Tetrahedron Lett.* **2007**, *48*, 1493.

10 T. Nabeshima, T. Saiki, J. Iwabuchi, S. Akine, *J. Am. Chem. Soc.* **2005**, *127*, 5507.

11 E. N. Jacobsen, in *Catalytic Asymmetric Synthesis*, ed. by I. Ojima, VCH, New York, **1993**; T. Katsuki, *Coord. Chem. Rev.* **1995**, *140*, 189; E. N. Jacobsen, *Acc. Chem. Res.* **2000**, *33*, 421.

12 T.-T. Tsou, M. Loots, J. Halpern, *J. Am. Chem. Soc.* **1982**, *104*, 623; M. F. Summers, L. G. Marzilli, N. Bresciani-Pahor, L. Randaccio, *J. Am. Chem. Soc.* **1984**, *106*, 4478.

13 S. Di Bella, I. Fragalà, *Synth. Met.* **2000**, *115*, 191; P. G. Lacroix, *Eur. J. Inorg. Chem.* **2001**, 339.

14 I. Yoon, M. Narita, T. Shimizu, M. Asakawa, *J. Am. Chem. Soc.* **2004**, *126*, 16740.

15 D. Cunningham, P. McArdle, M. Mitchell, N. Ní Chonchubhair, M. O'Gara, F. Franceschi, C. Floriani, *Inorg. Chem.* **2000**, *39*, 1639.

16 L. Carbonaro, M. Isola, P. La Pegna, L. Senatore, F. Marchetti, *Inorg. Chem.* **1999**, *38*, 5519.

17 G. Condorelli, I. Fragalà, S. Giuffrida, A. Cassol, *Z. Anorg. Allg. Chem.* **1975**, *412*, 251.

18 S. Akine, T. Taniguchi, T. Nabeshima, *Angew. Chem., Int. Ed.* **2002**, *41*, 4670.

19 H$_2$salamo: 1,2-bis(salicylideneaminooxy)ethane. See: S. Akine, T. Taniguchi, T. Nabeshima, *Chem. Lett.* **2001**, 682; S. Akine, T. Taniguchi, W. Dong, S. Masubuchi, T. Nabeshima, *J. Org. Chem.* **2005**, *70*, 1704.

20 For related salamo complexes, see: S. Akine, T. Taniguchi, T. Nabeshima, *Inorg. Chem.* **2004**, *43*, 6142; S. Akine, T. Nabeshima, *Inorg. Chem.* **2005**, *44*, 1205; S. Akine, T. Taniguchi, T. Nabeshima, *Chem. Lett.* **2006**, *35*, 604; S. Akine, W. Dong, T. Nabeshima, *Inorg. Chem.* **2006**, *45*, 4677; S. Akine, A. Akimoto, T. Shiga, H. Oshio, T. Nabeshima, *Inorg. Chem.* **2008**, *47*, 875.

21 S. Akine, T. Taniguchi, T. Nabeshima, *Inorg. Chem.* **2008**, *47*, 3255.

22 S. Akine, T. Taniguchi, T. Saiki, T. Nabeshima, *J. Am. Chem. Soc.* **2005**, *127*, 540.

23 S. Akine, T. Taniguchi, T. Nabeshima, *J. Am. Chem. Soc.* **2006**, *128*, 15765.

24 R. Y. Tsien, *Biochemistry* **1980**, *19*, 2396.

25 S. Akine, T. Taniguchi, T. Matsumoto, T. Nabeshima, *Chem. Commun.* **2006**, 4961.

26 S. Akine, T. Matsumoto, T. Nabeshima, *Chem. Commun.* **2008**, 4604.

27 S. Akine, T. Matsumoto, T. Taniguchi, T. Nabeshima, *Inorg. Chem.* **2005**, *44*, 3270.

28 S. Akine, F. Utsuno, T. Nabeshima, *IOP Conf. Ser.: Mater. Sci. Eng.* **2009**, *1*, 012009.

29 S. Akine, S. Kagiyama, T. Nabeshima, *Inorg. Chem.* **2007**, *46*, 9525.

30 Y. Zhang, A. Thompson, S. J. Rettig, D. Dolphin, *J. Am. Chem. Soc.* **1998**, *120*, 13537.

31 A. Thompson, S. J. Rettig, D. Dolphin, *Chem. Commun.* **1999**, 631.

32 S. R. Halper, L. Do, J. R. Stork, S. M. Cohen, *J. Am. Chem. Soc.* **2006**, *128*, 15255.

33 H. Maeda, M. Hasegawa, T. Hashimoto, T. Kakimoto, S. Nishio, T. Nakanishi, *J. Am. Chem. Soc.* **2006**, *128*, 10024.

34 J. Chen, J. Reibenspies, A. Derecskei-Kovacs, K. Burgess, *Chem. Commun.* **1999**, 2501.

35 S. M. Bloom, P. P. Garcia, U.S. Patent 3 691 161, **1972**.

36 C. Ikeda, S. Ueda, T. Nabeshima, *Chem. Commun.* **2009**, 2544.

37 I. V. Sazanovich, C. Kirmaier, E. Hindin, L. Yu, D. F. Bocian, J. S. Lindsey, D. Holten, *J. Am. Chem. Soc.* **2004**, *126*, 2664.

38 C. Ikeda, T. Maruyama, T. Nabeshima, *Tetrahedron Lett.* **2009**, *50*, 3349.

39 C. Goze, G. Ulrich, L. J. Mallon, B. D. Allen, A. Harriman, R. Ziessel, *J. Am. Chem. Soc.* **2006**, *128*, 10231.

40 A. Harriman, G. Izzet, R. Ziessel, *J. Am. Chem. Soc.* **2006**, *128*, 10868.

41 C. Ikeda, T. Nabeshima, *Chem. Commun.* **2008**, 721.

42 C. Ikeda, N. Sakamoto, T. Nabeshima, *Org. Lett.* **2008**, *10*, 4601.

43 M. Stępień, L. Latos-Grażyński, N. Sprutta, P. Chwalisz, L. Szterenberg, *Angew. Chem., Int. Ed.* **2007**, *46*, 7869.