

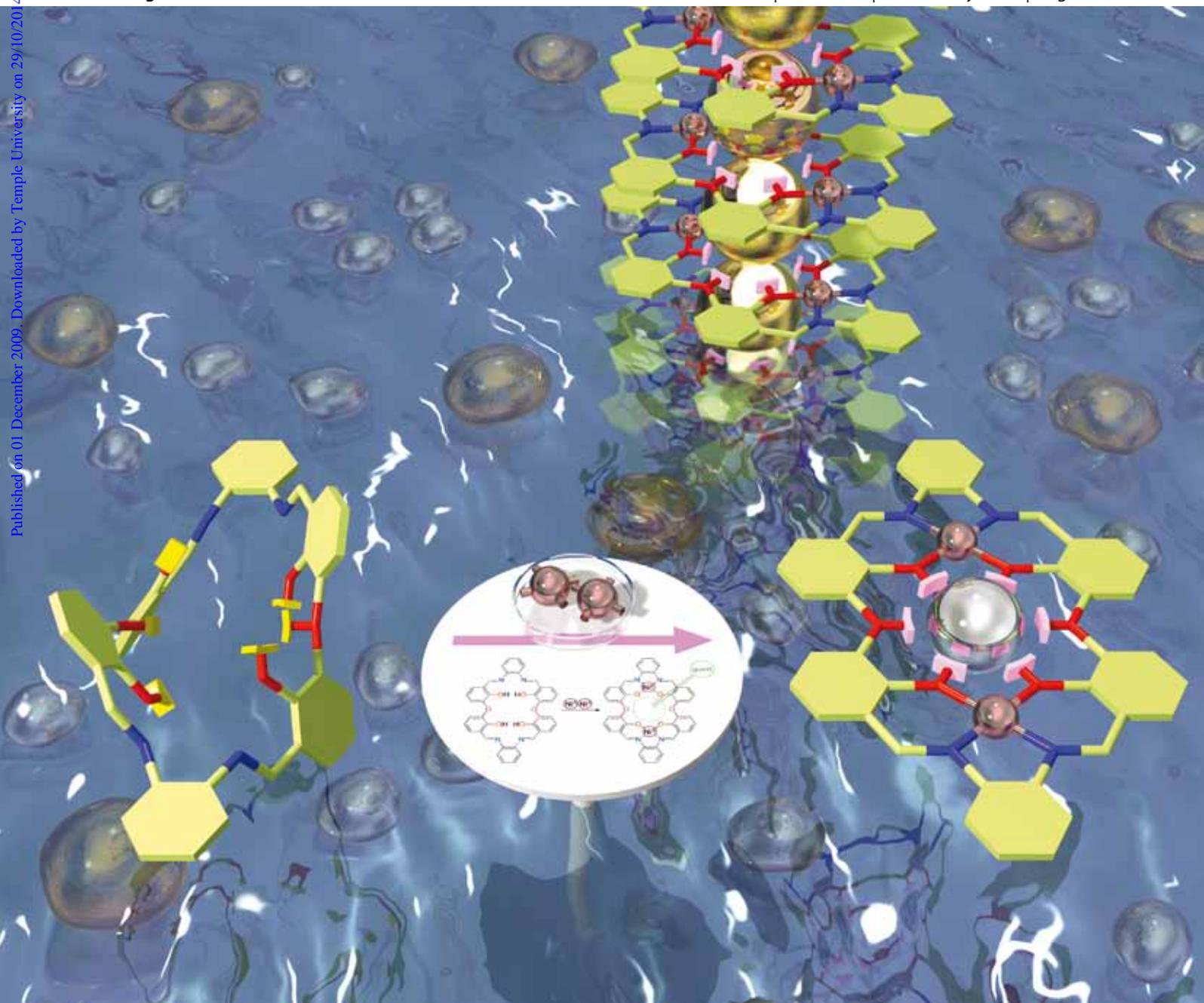
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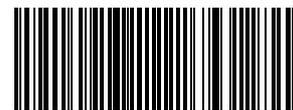
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FEATURE ARTICLE

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Highly efficient regulation of cation recognition and promotion of self-assembly by metalation of a macrocyclic bis(N₂O₂) ligand with nickel(II)[†]

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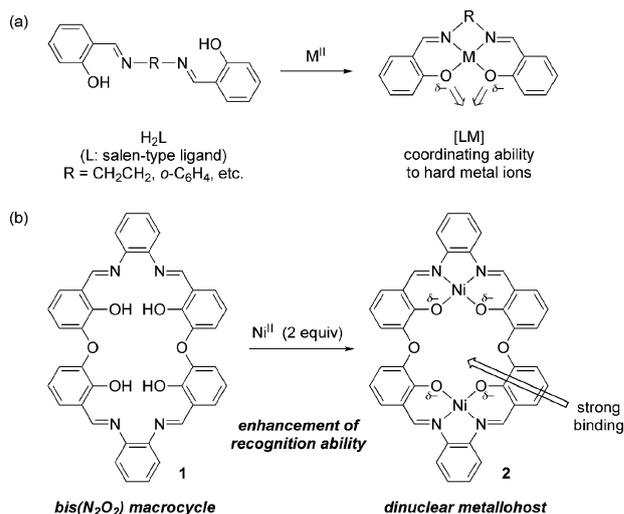
Metalation of a bis(N₂O₂) macrocyclic ligand **1 with nickel(II) acetate afforded a dinuclear metallohost **2**, resulting in a significant enhancement of recognition ability of alkali metal ions and the promotion of self-aggregation.**

Macrocyclic host molecules having several chelating moieties have been used to prepare cooperative recognition systems that can regulate guest recognition by metalation with transition metals.^{1,2} In particular, salen (H₂salen = *N,N'*-bis(salicylidene)-ethylenediamine) and its analogues are useful as a constituent for such a host molecule.² We can introduce various kinds of metal ions in the salen-type tetradentate coordination site. Metalation of the salen moiety makes the phenoxo groups more negative. Due to these negative charges, the phenoxo groups tend to coordinate to another cation (Scheme 1(a)). In addition, the four coordination bonds from the salen ligand fix the phenoxo groups suitably for chelate coordination. Indeed, salen-containing crown ethers are useful for cooperative metal coordination.² We have investigated the complexation behavior of macrocyclic tris(salen)-type ligands,³ which are effective for the formation of a homonuclear cluster with a bowl-shaped structure.⁴ However, it is difficult to selectively introduce transition metal ions into the salen-type coordination sites, because the transition metal ions intended for the salen-type coordination sites also occupy the guest-binding site consisting of six phenoxo groups. If such macrocyclic metallo-salen compounds have a vacant cavity or the transition metal ions do not compete with the guest in the binding, the central binding site will exhibit a strong affinity toward guest cations due to the negative charges.^{2,4,5} In addition, metallohosts having square-planar metals are expected to form stacked aggregated structures because of the increased molecular planarity. We have now designed a new bis(salen)-type macrocycle **1** which has a diaryl ether oxygen between the neighboring salen units. The metalation of the macrocycle **1** with nickel(II) efficiently afforded the dinuclear metallohost **2**, which showed a dramatic enhancement of the recognition ability toward alkali metal ions (Scheme 1(b)) and promoted the formation of the stacked aggregate structure. To the best of our knowledge, this is the

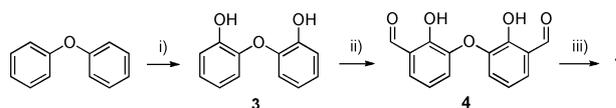
first example of a stacked one-dimensional array of a metallo-salen macrocycle bearing both transition metal and alkali metal ions,⁶ which would show unique physical and chemical properties.

The synthesis of the macrocycle **1** is shown in Scheme 2. The diol **3** was obtained by dilithiation of diphenyl ether⁷ followed by the reaction with trimethyl borate and subsequent treatment with hydrogen peroxide under basic conditions.

After the *ortho*-bromination of the diol **3** with NBS/diisopropylamine,⁸ the dibromide was lithiated and then allowed to react with DMF to afford the dialdehyde **4**. The reaction of the dialdehyde **4** with *o*-phenylenediamine in a 1 : 1 molar ratio in acetonitrile afforded the macrocycle **1** in 64% yield as orange crystals. In the ¹H NMR spectrum, the CH and OH protons of the salicylalimine moiety appeared as singlets at 8.97 and 13.52 ppm, respectively, being consistent with a highly symmetric cyclic structure. The ESI mass



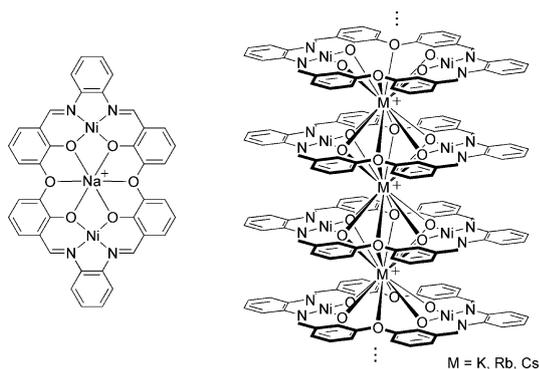
Scheme 1 (a) Metalation of salen-type ligand promotes the binding to hard metal cations. (b) Design of bis(salen)-type macrocycle **1** and the conversion to dinuclear metallohost **2**.



Scheme 2 Synthesis of macrocycle **1**. Reagents and conditions: (i) (1) *n*-BuLi, TMEDA, hexane; (2) B(OMe)₃, (3) H₂O₂, KOH, yield 71%; (ii) (1) NBS, *i*-Pr₂NH, (2) NaH, *n*-BuLi, (3) DMF, yield 28%; (iii) *o*-C₆H₄(NH₂)₂, CH₃CN, yield 64%.

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Scheme 3 Plausible structure of complexes between metallohost **2** with alkali metal cations.

added, broad signals separately appeared from the free metallohost **2** (Fig. 2(c)). The addition of 1 equiv. of Rb^+ or Cs^+ resulted in the appearance of several sets of signals (Fig. 2(d) and (e)). These results indicate that the self-assembly and complexation/decomplexation process with these ions is slow and that several kinds of complexes were formed upon the complexation.

To clarify the complexation behavior, the ESI mass spectra of **2** in the presence of K^+ , Rb^+ and Cs^+ were investigated. It is noteworthy that several kinds of aggregated species, such as $[\text{2}_2\cdot\text{M}]^+$, $[\text{2}_3\cdot\text{M}_2]^{2+}$ or $[\text{2}_4\cdot\text{M}_3]^{3+}$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$), were observed in addition to the 1 : 1 complex $[\text{2}\cdot\text{M}]^+$ (Fig. 3(b) for $\text{M} = \text{Rb}$). The diffusion coefficients determined by DOSY experiments were 2.2×10^{-10} and $1.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for the 1 : 1 mixture of **2** with Na^+ and Cs^+ , respectively. The smaller diffusion coefficient of the Cs^+ complex coincides with the observation of aggregated species in the mass spectrum.

It is known that 18-crown-6 ethers can form a 2 : 1 or 3 : 2 complex with Rb^+ and Cs^+ .¹⁰ In addition, salen-nickel(II) complexes are known to form an infinite sandwich assembly or triple-decker sandwich complexes with alkali metal cations through μ -phenoxo bridges.¹¹ Since the cyclic array of oxygen atoms in a metallohost **2** is similar to the 18-crown-6 and contain salen-metal moieties, the observed oligomeric species would adopt a sandwich or club sandwich structure, in which two or more flat metallohosts are held together by the metal ions (Scheme 3). This is evidenced from the upfield shifted signals of the aromatic protons of the Rb^+ and Cs^+ complexes that appeared at around 5.8 ppm, which is attributed to the stacking structure.

Therefore, the conversion from the macrocycle **1** into the metallohost **2** not only enhances the ion recognition ability toward alkali metal cations, but also induces the metal-assisted assembly with stacking structures. This conversion makes the molecular structure more rigid and planar, favorable for the formation of the stacking aggregates. In addition, the resultant metallohost has the phenoxo groups with negative charges, which contribute to the aggregate formation induced by the alkali metal ions due to the $-\text{M}-\text{O}-\text{M}-\text{O}-$ bridging. This may suggest that the stabilization by the stacking structures and phenoxo bridging is greater than the destabilization due to the electrostatic repulsion between the guest cations.

In conclusion, the conversion of the macrocyclic imine **1** into the nickel(II) dinuclear metallohost **2** greatly enhances the

alkali metal ion recognition in the central O_6 site. The macrocycle worked as an on/off regulation system of ion recognition. The metalation also induces the aggregated molecular array structure when the metallohost **2** binds to larger guest cations. The stacking of the planar metal complexes has a significant influence on the physical and chemical properties of the metal complexes due to the inter-plane interactions between the metal centers. We are now investigating the changes in the properties induced by the inclusion of alkali metal cations.

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Notes and references

† Crystallographic data: **1**·2MeCN ($\text{C}_{44}\text{H}_{34}\text{N}_6\text{O}_6 = 742.77$): orthorhombic, *Pbcn*, $a = 21.7674(9)$, $b = 8.3961(4)$, $c = 20.4083(9)$ Å, $V = 3729.8(3)$ Å³, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.090 \text{ mm}^{-1}$, $D_c = 1.323 \text{ g cm}^{-3}$, $F(000) = 1552$, $T = 120 \text{ K}$, $R_1 = 0.0488$ (3681 data with $I > 2\sigma(I)$), $wR_2 = 0.1425$ (all 4248 data; $R_{\text{int}} = 0.0290$), GOF = 1.064.¹²
2·4DMSO ($\text{C}_{48}\text{H}_{48}\text{N}_4\text{Ni}_2\text{O}_{10}\text{S}_4 = 1086.56$): triclinic, *P* $\bar{1}$, $a = 11.2439(8)$, $b = 11.7378(8)$, $c = 11.7488(9)$ Å, $\alpha = 63.3210(18)$, $\beta = 66.059(2)$, $\gamma = 60.3036(16)^\circ$, $V = 1169.48(15)$ Å³, $Z = 1$, $\mu(\text{Mo-K}\alpha) = 1.048 \text{ mm}^{-1}$, $D_c = 1.543 \text{ g cm}^{-3}$, $F(000) = 564$, $T = 120 \text{ K}$, $R_1 = 0.0475$ (4514 data with $I > 2\sigma(I)$), $wR_2 = 0.1345$ (all 5298 data; $R_{\text{int}} = 0.0312$), GOF = 1.080.¹²

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