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Self-Assembled Nanostructures of Tailored Multi-Metal Complexes and Morphology Control by Counter-Anion Exchange

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Self-assembly is one of the most important and useful techniques for the convenient construction of nanostructures such as particles, fibers, layers,[1] which show a variety of attractive functional molecules and materials for use as a catalyst, sensor, material transporter, and optical material.[2] In most cases, the size and morphology of the nanostructure depend on the components, but the prediction of the overall structure of the nanostructure remains a difficult challenge. The supramolecular nanostructure based on dynamic and directed interactions between the components, such as hydrogen bonding, π-stacking, and coordination bonding with metal ions[3] has been widely used for the formation of shape-defined aggregations, such as wire[3] and tube[4] structures. Such a strategy showed great success for materials composed of a d-block metal complex known as metal–organic frameworks (MOFs).[5] Conversely, the number of reports on an aggregation composed of the f-block metal complex has been recently increasing because the assembly of lanthanide ions shows unique functions such as magnetic[6,7] and luminescent applications.[7] We reported the synthesis of the "trisaloph" ligand, a macrocyclic multidentate ligand composed of three saloph moieties, and its lanthanide–zinc heterotetranuclear complex.[8] Saloph ligands form planar complexes with a variety of metals,[9] which have been developed for supramolecular systems, such as anion-templated assemblies,[10] self-assembled fibers,[11] and liquid crystals.[12] The trisaloph ligand was also utilized as a module for a one-dimensional multi-metal supramolecule.[13] Alkali metal ions caused a stacked tubular aggregation of the trisaloph ligands due to π–π stacking and coordination to the metal ion.[13] The trisaloph lanthanide complex is expected to form a self-assembled aggregation due to the strong interaction between the metal ion and the counter anion of the cationic lanthanide complex that can act as a spacer ligand bridging the lanthanide because the rigid O6 site of the trisaloph fixes the vacant coordination sites of the lanthanide ion in a one-dimensional direction, that is, tailored to a fibril morphology. Herein, the unique aggregation of the trisaloph $Zn^{II}_3La^{III}$ complex bearing PEGylated adamantane units is successfully formed in an aqueous solution by complexation with β-cyclodextrin (β-CD). Additionally, the morphology of the nanostructure is controlled by coordinated anions based on the structural change in the trisaloph complex.

All trisaloph ligands and their complexes reported thus far are insoluble in aqueous media. However, we designed and synthesized a trisaloph ligand bearing adamantane units as an appropriate candidate for water-soluble trisaloph metal complexes by taking advantage of the association of the adamantane units with β-CD.[14] The trisaloph complexes **1** (Figure 1) would be quite versatile because they should be soluble in organic solvents in the absence of β-CD due to high hydrophobicity of the adamantane units. Both aqueous-soluble and solubility-tunable trisaloph complexes have not been reported to the best of our knowledge.

Although the synthesis of the trisaloph ligand bearing adamantane units by the reaction of the phenylenediamine derivative **4** bearing adamantane tags with dialdehyde **5**[15] gave only an inseparable mixture, the same reaction in the presence of three equivalents of $Zn(OAc)_2$ and one equivalent of $La(OAc)_3$ in $CHCl_3$/MeOH/H_2O 10:4:1 gave trisaloph$La^{III}Zn^{II}_3$ complex **1**$(OAc)_3$ in a good yield (94%) due to

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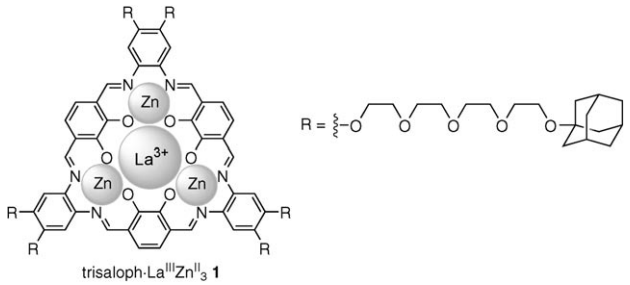
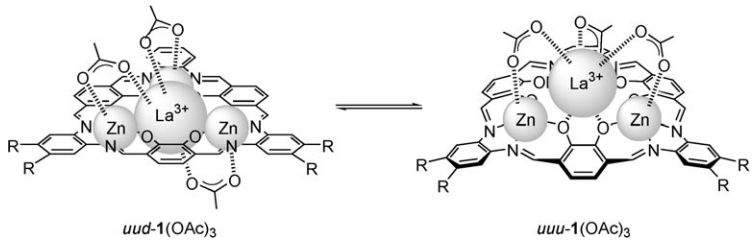


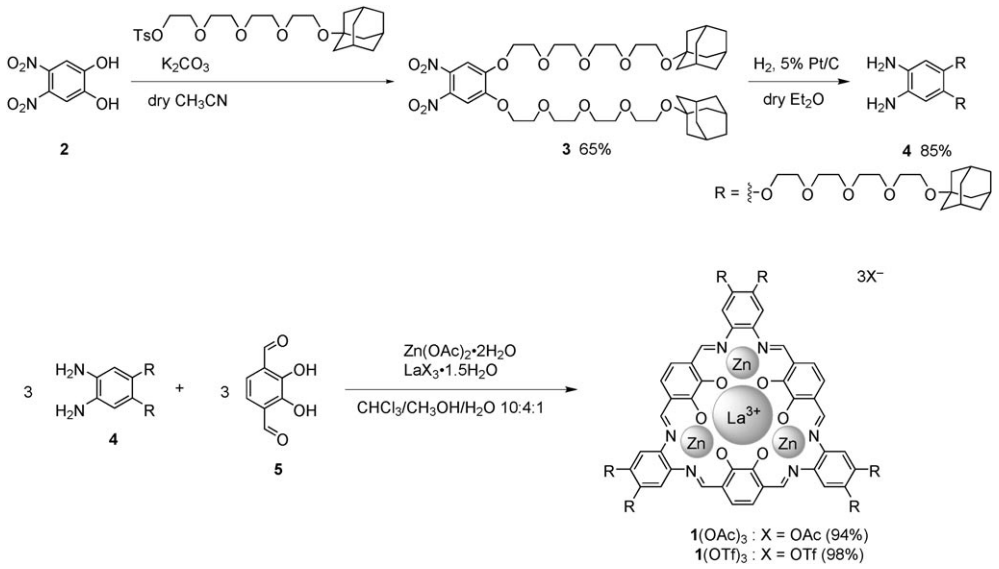
Figure 1. Trisaloph·La^{III}Zn$^{II}_3$ complex bearing PEGylated adamantane units **1**.

the template effect of the metal ions (Scheme 1).[16] The use of another La^{III} source, La(OTf)$_3$ instead of La(OAc)$_3$, successfully formed complexes **1**(OTf)$_3$ (98%). First, the effect of the counter-anion on the structure in DMSO was investigated by ^{1}H NMR spectroscopy. The triflate complex **1**(OTf)$_3$ showed only three broad singlets in [D$_6$]DMSO in the aromatic region reflecting the pseudo D_3 structure (Figure 2a). In contrast, the corresponding signals of **1**(OAc)$_3$ were split into two signals (Figure 2b). The spectral change indicates two isomers based on the different coordination modes of the acetato ligands, that is, the *uuu*-isomer with the three acetato ligands on the upper side and the *uud*-isomer with two on the upper side and one on the under side (Scheme 2). The coalescence of the two signals at higher temperatures proved inter-conversion between two isomers. The ratio of the two isomers did not changed at all at **1**-(OAc)$_3$ concentrations from 0.5 to 5.0 mM, which established no dimerization.[17] The addition of the acetate anion resulted in no change in the ratio, but only broadening of the signals. Therefore, the isomerization is not due to the dissociation to free acetate. Such an effect of the anion motivated us to exchange other counter-anions. The addition of the acetate anion to **1**(OTf)$_3$ showed the same spectrum as the isolated **1**(OAc)$_3$, which suggested the in situ counter-anion exchange (Figure 2c). In the ^{1}H NMR spectrum after the addition of dihydrogenphosphate ($H_2PO_4^-$), three sharp singlets in the aromatic region and signals assigned to diastereotopic methylene protons were observed (Figure 2d). The phosphate complex **1**(H$_2$PO$_4$)$_3$ is considered as only one discrete



Scheme 2. Equilibrium between *uud*- and *uuu*-isomers of **1**(OAc)$_3$.

isomer, a C_3 symmetrical *uuu*-**1**(H$_2$PO$_4$)$_3$ because only one singlet of **1**(H$_2$PO$_4$)$_3$ in the ^{31}P NMR (δ_P 4.5 ppm) separately appeared as compared with the NMR spectrum of free H$_2$PO$_4$ anion (δ_P 0.3 ppm). The formation of *uuu*-**1**(H$_2$PO$_4$)$_3$ is noteworthy because reaction of mononuclear saloph·Zn^{II} complex with H$_2$PO$_4$ dissociated the complex to give the free ligand.[10] Assembled Zn$^{II}_3$La^{III} multi-metal ions play an important role in forming *uuu*-**1**(H$_2$PO$_4$)$_3$ owing to the bridging ligation. This structure was also supported by the DFT calculations. The large energy (ΔE) for the isomerization from *uud*-**1**(H$_2$PO$_4$)$_3$ to *uuu*-**1**(H$_2$PO$_4$)$_3$, −68 kJ mol^{-1},



Scheme 1. Synthesis of trisaloph complexes **1**(OAc)$_3$ and **1**(OTf)$_3$.

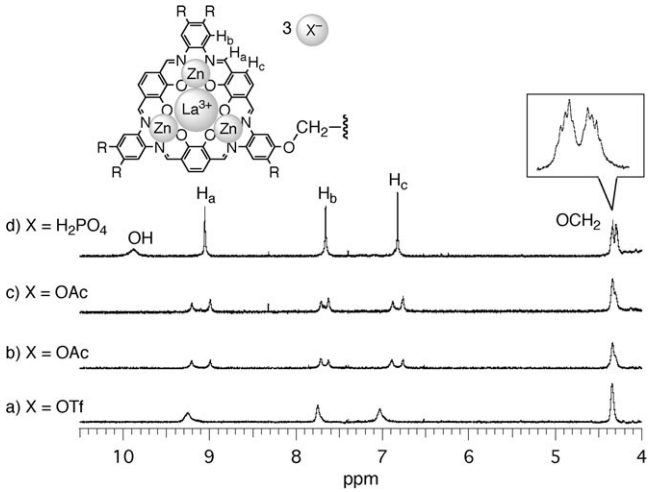


Figure 2. ^{1}H NMR spectra of a) **1**$(OTf)_3$, b) **1**$(OAc)_3$, c) **1**$(OAc)_3$ prepared in situ from **1**$(OTf)_3$ and nBu$_4$N(OAc), and d) **1**$(H_2PO_4)_3$ prepared in situ from **1**$(OTf)_3$ and nBu$_4$N(H_2PO_4), 600 MHz, [D$_6$]DMSO, 298 K.

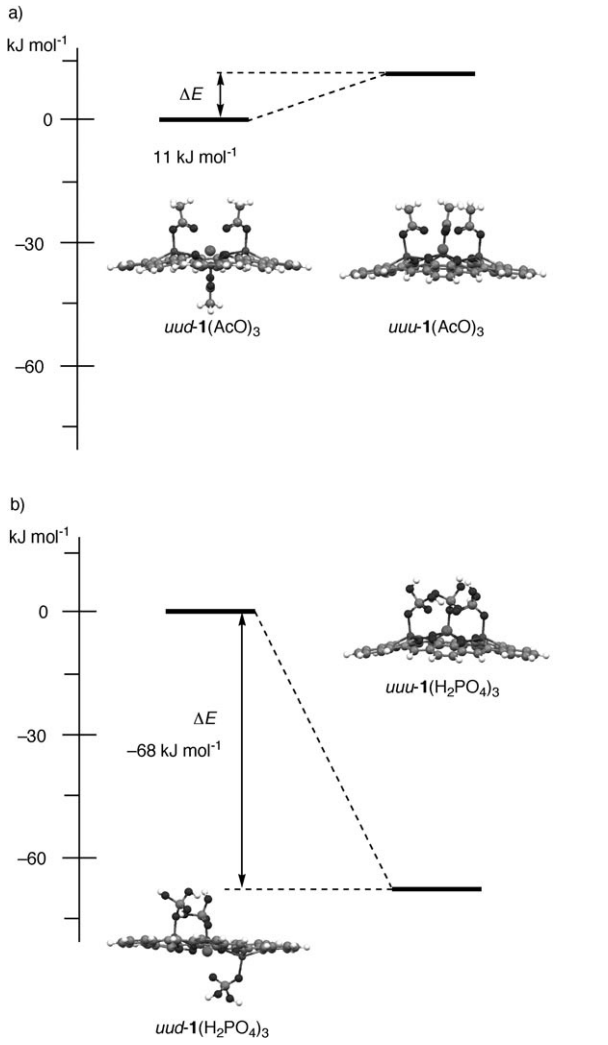


Figure 3. Relative energy diagram of isomerization between *uud*- and *uuu*-isomers of a model analogue of a) **1**$(AcO)_3$ and b) **1**$(H_2PO_4)_3$. The PEGylated adamantane unit was substituted with hydrogen atom for the present calculations.

compared to *uud*-**1**$(H_2PO_4)_3$ proved the quantitative formation of *uuu*-**1**$(H_2PO_4)_3$ (Figure 3).[18] Three intramolecular hydrogen bonds were shown in the optimized structure of a **1**$(H_2PO_4)_3$ analogue without any side chains. The stability of *uuu*-**1**$(H_2PO_4)_3$ would be due to these hydrogen bonds. On the contrary, the ΔE for two isomers of the **1**$(OAc)_3$ analogue is 11 kJ mol^{-1}. This small energy difference is consistent with the fact that two isomers, *uuu*- and *uud*-**1**$(OAc)_3$, were observed at an approximately equal ratio.

At first, the behavior of the complexes in aqueous media was investigated by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of a 9:1 mixture of a D_2O solution of β-CD and a [D$_6$]DMSO solution showed a drastic increase in the signal intensity of complex **1** dependent on the β-CD concentration, indicating that both **1**$(OTf)_3$ and **1**$(OAc)_3$ were well solubilized in the aqueous solution by host-guest complexation of β-CD with the adamantane moieties.[19] The upfield shift of the inner H3 and H5 protons of β-CD and downfield shift of the outer H2 and H4 protons from the free β-CD were observed as seen in the reported complexes between β-CD and the adamantane derivatives.[20,21] The formation of an inclusion complex was directly proved by the ROE correlation peaks between the inner protons of the β-CD and those of adamantane. As shown in many complexes between the β-CD and adamantane derivatives,[21] H3 showed stronger ROE cross-peaks with the proton of adamantane than H5 (Figure 4). Isothermal titration calorimetry (ITC) was used to confirm the affinity of the adamantane···β-CD interaction.[22] First, the ITC of tetraethyleneglycol adamantyl ether (**6**), a tag unit of **1**, was performed as a comparable experiment. The result showed that **6** gave a 1:1 host–guest pair with a typical binding constant and enthalpy change ($K_a = (7.1 \pm 0.6) \times 10^3$ M^{-1}, $\Delta H° = -25.1 \pm 0.4$ kJ mol^{-1}).[19] On the contrary, the heat change during the titration of **1**$(OTf)_3$ was too small to estimate the accurate thermodynamic parameters. However, the small heat change indicates the interaction of **1**$(OTf)_3$ with β-CD.[23] The UV/Vis spectral titration of **1**$(OTf)_3$ with β-CD also showed little change, but this result excludes the inhibition of the complexation by precipitation. Therefore, the most reasonable explanation is the formation of **1**$(OTf)_3$ driven by a hydrophobic effect that disturbs the hydrophobic interaction of the adamantane·β-CD in an aqueous solution.

The DOSY experiment afforded the diffusion coefficients of **1**$(OTf)_3$ in the presence of β-CD, that is, 9.7×10^{-11} m^{2}s^{-1} (Figure 5a). The corresponding hydrodynamic diameter[24] is 4.1 nm which is similar to the molecular size calculated by the molecular modeling of the monomeric **1** (Figure 5b). Dynamic light scattering (DLS) clearly showed the aggregation of **1** under the same condition. The DLS experiment of **1**$(OAc)_3$ gave a significant single peak with a hydrodynamic diameter of 141 nm obtained by CONTIN analysis for the continuous size distribution.[25] This result is almost the same as the average diameter obtained by the cumulated analysis,

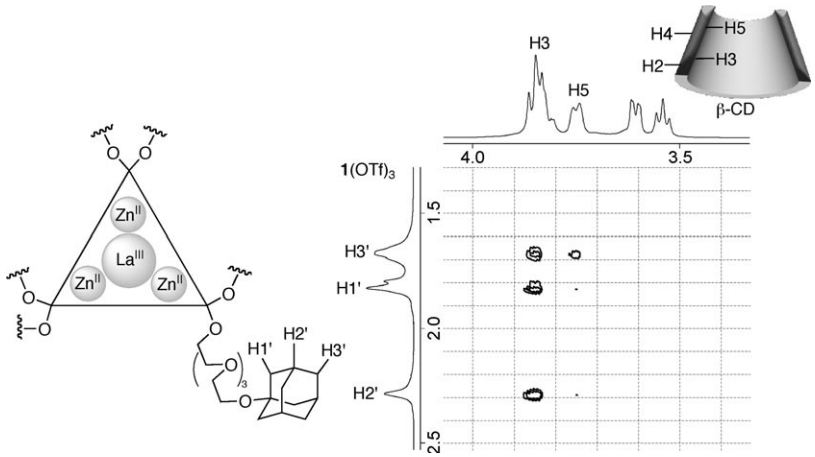


Figure 4. ROESY spectrum of **1**$(OTf)_3$ (1.0 mM) and β-CD (12 equiv) with presaturation at 4.75 ppm assigned to residual water, 600 MHz, D_2O/[D_6]DMSO 9:1, 300 K.

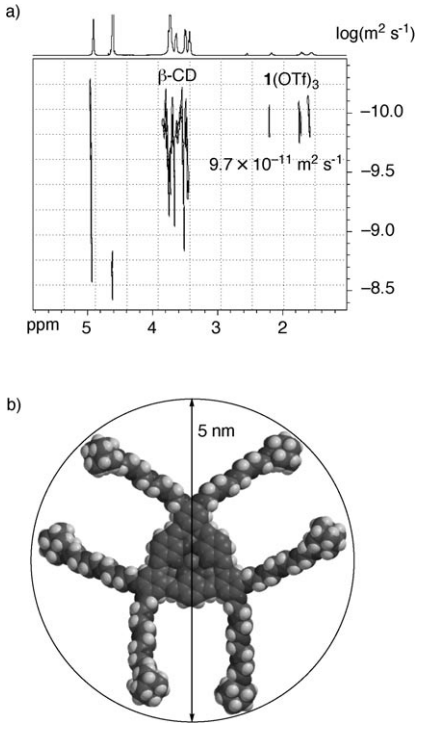


Figure 5. a) DOSY spectrum of **1**$(OTf)_3$ (0.5 mM) and β-CD (30 equiv) 600 MHz, D_2O/[D_6]DMSO 9:1, 300 K and b) structure based on molecular modeling studies of **1** by molecular mechanics calculations using the MMFF force field.

136 nm, indicating the formation of particles with a narrow size distribution in solution. The hydrodynamic diameter, which is much larger than the monomer estimated by the DOSY experiment, shows the formation of nanoaggregates. A comparison with the DOSY experiment indicates the equilibrium between the monomer and nanoaggregate of **1**-$(OAc)_3$. Centrifugation of the aqueous solution of **1**$(OAc)_3$ and β-CD, and successive washing with water afforded the aggregate isolated as a red paste. The aggregate was confirmed by scanning electron microscopy (SEM) to have an average diameter of about 120 nm, consistent with the size observed by DLS (Figure 6a). The morphology of the particles is spherical. Considering no observation of the aggregate of **1**-$(OAc)_3$ by ^{1}H NMR spectroscopy in the [D_6]DMSO solution, the main driving force for the aggregation in an aqueous medium is probably a hydrophobic effect as shown in the self-assembled system using the adamantane···β-CD interaction.[26] Conversely, no particle formed in either the similarly prepared sample of **1**$(OTf)_3$ nor the sample prepared by filtration using a 100 nm Millipore filter. An SEM image of the aggregated **1**$(OAc)_3$ prepared in the absence of β-CD showed a condensed layered plate.[23] This morphology is similar to that of the thin layer of **1**$(OAc)_3$ prepared by casting of the chloroform solution followed by drying in air, therefore, β-CD plays a crucial role in constructing the spherical aggregation.

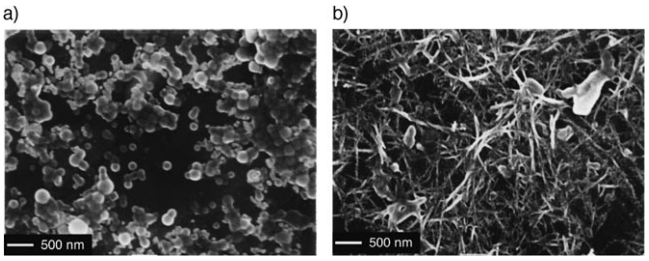


Figure 6. SEM images of the aggregates of a) **1**$(OAc)_3$ and b) **1**$(H_2PO_4)_3$ prepared by centrifugation from a H_2O/DMSO 9:1 solution of β-CD (12 mM).

The aggregate from **1**$(H_2PO_4)_3$ was similarly formed in an aqueous solution, and its SEM image showed a fibril morphology with a diameter of approximately 50 nm (Figure 6b). In the aggregate of **1**$(H_2PO_4)_3$, the apparent anisotropy allowed assembly in a one-dimensional direction. The DFT calculations suggested that the most possible interaction for the linear aggregation is intermolecular hydrogen bonding. In the optimized structure, one hydroxy group of each H_2PO_4 is directed to the upper side and the oxygen atoms of the saloph moiety, which are negatively charged hydrogen-bonding acceptor,[27] are arranged at the underside. As a result, three intermolecular hydrogen bonds can be formed by the three H_2PO_4 of one *uuu*-**1**$(H_2PO_4)_3$ molecule and three of the six oxygen atoms of the trisaloph moiety of another (Figure 7). In the optimized dimeric and trimeric structures, the trisaloph complexes are linearly

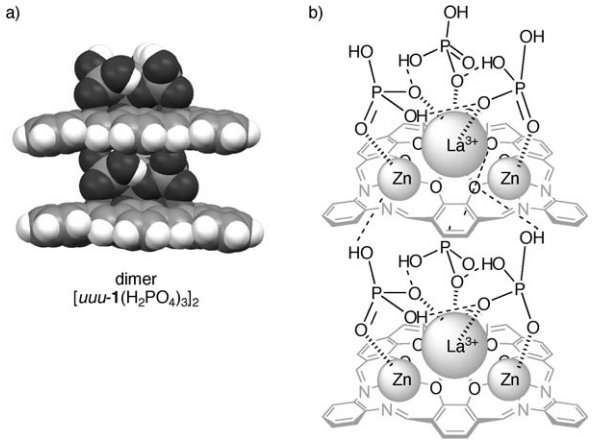


Figure 7. Model compound of dimer [*uuu*-**1**$(H_2PO_4)_3]_2$ with a) the space-filling and b) schematic representation. The PEGylated adamantane unit was substituted with hydrogen atom for the present calculations.

stacked through intermolecular hydrogen bonding (Figure 8). The interaction energy (ΔE) of the trimer, $-53\ kJ\,mol^{-1}$, is similar to that of the dimer, $-43\ kJ\,mol^{-1}$. The infinite one-dimensional aggregation of **1**$(H_2PO_4)_3$ can be formed with an interaction energy at each stacking. Considering the diameter of the fibril, the one-dimensional aggregate must be stacked in a side-by-side direction to form a thick fibril.

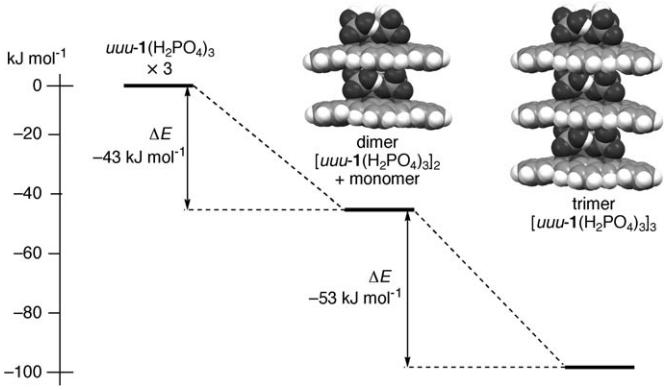


Figure 8. Optimized structures and energy diagram in oligomerization of a model compound of **1**$(H_2PO_4)_3$.

In conclusion, the trisaloph·$La^{III}Zn^{II}_3$ complex **1** having adamantane tags associated with β-CD in aqueous media produces a self-assembled aggregations driven by a hydrophobic effect. Interestingly, the morphology was changed by the counter anion. Such an aggregate containing metal clusters is attractive as materials having lanthanide ions, which potentially develop anion-dependent functions of the aggregate based on a morphology change.

Experimental Section

Synthesis of 1(OAc)$_3$: A solution of **4** (71.5 mg, 85% purity, 80 μmol) in chloroform (10 mL) was added under N_2 atmosphere at room temperature to a solution of $La(OAc)_3{\cdot}1.5H_2O$ (9.1 mg, 27 μmol) in water (1.0 mL) including $Zn(OAc)_3{\cdot}2H_2O$ (15.4 mg, 70 μmol) and **5** (11.6 mg, 70 μmol) dissolved in methanol (4.0 mL). After stirring at 60 °C for 12 h, evaporation and reprecipitation from chloroform/hexane gave dark red solid of **1**$(OAc)_3$ (70.4 mg, 94%). ^1H NMR (600 MHz, $CDCl_3/CD_3OD$ 9:1): $\delta = 1.55$–1.67 (m, 36H), 1.71–1.77 (m, 45H), 2.14 (br s, 18H), 3.55–3.64 (m, 24H), 3.64–3.72 (m, 24H), 3.72–3.76 (m, 12H), 3.76–3.82 (m, 12H), 3.91–3.99 (m, 12H), 4.27–4.34 (m, 12H), 6.80 (s, 6H), 7.38 (s, 6H), 8.80 ppm (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3/CD_3OD$ 9:1): $\delta = 23.6$ (*C*H$_3$), 30.6 (*C*H), 36.5 (*C*H$_2$), 41.5 (*C*H$_2$), 59.3 (*C*H$_2$), 69.1 (*C*H$_2$), 69.7 (*C*H$_2$), 70.6 (*C*H$_2$), 70.7 (*C*H$_2$), 70.9 (*C*H$_2$), 71.2 (*C*H$_2$), 72.7 (*C*), 101.4 (*C*H), 118.2 (*C*), 119.3 (*C*H), 133.9 (*C*), 149.7 (*C*), 158.8 (*C*H), 164.0 (*C*), 178.4 ppm (*C*); ESI-MS: *m*/*z*: 1530.21 [$M^{2+}-2(CH_3COO)$]; elemental analysis calcd (%) for $C_{156}H_{213}LaN_6O_{42}Zn_3{\cdot}2H_2O$: C 58.27, H 6.80, N 2.41; found: C 58.13, H 6.69, N 2.54.

Preparation of nanoparticles of 1(OAc)$_3$: A DMSO solution of **1**$(OAc)_3$ (2.5 mM, 0.4 mL) was added at room temperature to an aqueous solution of β-CD (8.3 mM, 3.6 mL). After sonication for 1 h and standing for 12 h at room temperature, centrifugation at 10000 rpm, decantation, and washing with water twice afforded a red paste. The suspension of the red paste in water was dropped on an aluminium plate followed by drying in vacuo vacuum, and then the aluminium plate was coated with Pt/Pd using an ion coater for SEM observation.

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Keywords: cyclodextrins · lanthanides · multi-metal complexes · self-assembly · trisaloph

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