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Self-assembled ring-in-ring complexes from metal–ligand coordination macrocycles and β-cyclodextrin

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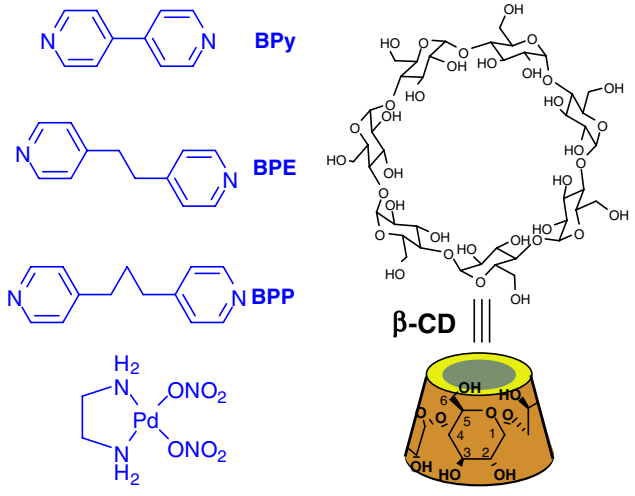
Abstract—Ring-in-ring nanostructures can be assembled from readily available starting materials, including dipyridyl ligands, (en)Pd(NO_3)$_2$, and β-cyclodextrin (β-CD). When a series of dipyridyl ligands are mixed with β-CD and Pd(II) in aqueous solution, various self-assembled geometries can be obtained as a result of a combination of hydrobic interactions and metal–ligand coordinations. In the cases of dipyridyl ligands with flexible linker, dinuclear coordination macrocycles M_2L_2 are formed and included in the cavity of β-CD to form ring-in-ring complexes. When more rigid dipyridyl ligands are used, a tetranuclear coordination macrocycle M_4L_4 prevails and shows no interaction with β-CD, as apposed to the flexible ones.

Cyclodextrins (CDs)[1] are nanometer-sized objects that have been widely used as building blocks in creating supramolecular assemblies[2] thanks to their ability of including guest molecules in the inner hydrophobic cavities. The thus-formed inclusion complexes, most commonly existing in the form of pseudorotaxanes,[3] are precursors of more complex structures such as rotaxanes and catenanes.[4,5] Extensive studies have been directed toward the arrangement of pseudorotaxanes into ordered nanostructures. Among many other interactions, metal–ligand coordination[6–9] has been a powerful tool in assisting the assembly of inclusion complexes containing divalent ligands. For example, necklace-like polypseudorotaxanes were obtained by bridging 1:1 inclusion complexes between β-CD and 4,4′-bipyridine (BPy) with transition metal ions.[10–12] Also, rotaxanes were formed when bulky transition metal complexes were employed as end groups to prevent the dissociation of ligands from the CDs.[13–19]

Self-assembly between dipyridyl ligands, such as BPy, 1,2-bis(4-pyridyl)ethane (BPE) or 1,3-bis(4-pyridyl) propane (BPP), and transition metals (Pd(II) or Pt(II)), (Scheme 1) have been utilized to generate macrocyclic compounds in nearly quantitative yields.[20–26] Depending on the flexibility of the divalent ligands, tetranuclear square-like macrocycle M_4L_4 (L = BPy) or dinuclear macrocycles M_2L_2 (L = BPE or BPP) can be obtained. The versatile Pd-ligand coordination properties prompt us to adapt such chemistry in assembling β-CD-based inclusion complexes. The cyclic structures of β-CD and Pd-ligand complexes, combined with the tendency of the divalent ligands being included in CD cavities, lead to our expectation of hypothetic catenated structures. No detailed studies have been conducted[27] in assembling



Scheme 1. Structural formula of divalent ligands, (en)Pd(NO_3)$_2$, and β-CD.

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the CD rings with these easily accessible macrocycles. Here we describe our studies on the self-assembly behavior of several dipyridyl ligands, transition metals and β-CD in aqueous solution.

A mixture of equimolar β-CD and BPE in D_2O is sonicated until all solid dissolves to give a clear solution. The resulting ^1H NMR spectrum suggests the inclusion of BPE inside the CD cavity as indicated by the characteristic shifts of the H-3 and H-5 resonances of the glucoside units in β-CD (Fig. 1a and b). In a separate experiment, an equimolar mixture of (en)$Pd(NO_3)_2$ and BPE (8.2 mM each) is shown by ^1H NMR spectroscopy to form a highly symmetrical dinuclear macrocycle M_2L_2,[20] accompanied by small amount of oligomeric byproducts (Fig. 1d). After the addition of 1 equiv β-CD into this solution, no significant chemical shift changes are observed for the coordination macrocycle M_2L_2, suggesting that the metal–ligand coordination is not disrupted by β-CD. Meanwhile, an upfield shift of the H-3 resonance of β-CD is observed, (Fig. 1c) suggesting that the cavity of β-CD is occupied by guests, which appears to be the coordination macrocycle M_2L_2. To determine the stoichiometry between M_2L_2 and β-CD in the complex, a continuous variation method (Job's plot)[28] is employed and the ratio is determined to be 1:1 (Fig. 2). The highly symmetric spectrum of the three-component mixture suggests that the interactions between the two macrocyclic objects are undergoing fast equilibrium at the ^1H NMR timescale.

The facts that (1) the cavity of β-CD is occupied, and (2) β-CD forms a 1:1 complex with the coordination M_2L_2 macrocycle suggest that either a [2]catenane or a ring-in-ring complex is formed. A catenated structure can be excluded, however, based on the observed highly symmetric spectrum, since a non-degenerated spectrum would be expected on account of the different chemical environments of the inside and outside BPE units in the hypothetic [2]catenane. Thus the formation of a ring-in-ring complex can be concluded. It is interesting to note that although the Pd(II) complexes prepared at 8.2 mM contains small amount of oligomers, addition of β-CD to the 1:1 mixture of BPE and (en)$Pd(NO_3)_2$ drives the equilibrium to the complete formation of M_2L_2 to give a ring-in-ring complex. Such host-stimulated, self-correcting reorganization exemplifies an 'induced-fit' molecular recognition process that is enabled by the labile nature of Pd-ligand coordination bond.

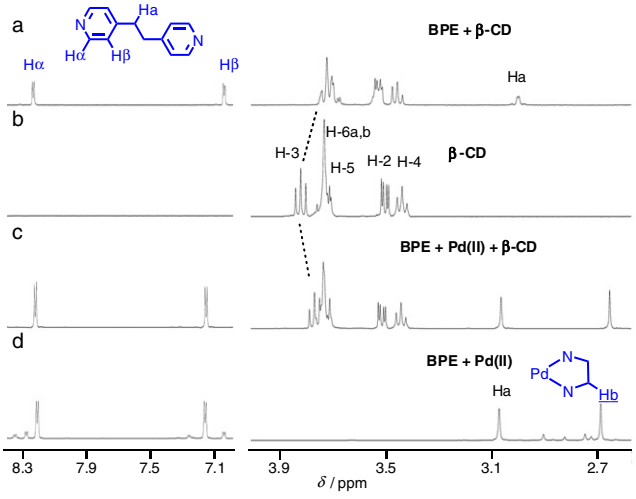


Figure 1. ^1H NMR spectra of (a) 1:1 mixture of BPE and β-CD, (b) free β-CD, (c) 2:2:1 mixture of BPE, (en)$Pd(NO_3)_2$ and β-CD, and (d) 1:1 mixture of BPE and (en)$Pd(NO_3)_2$.

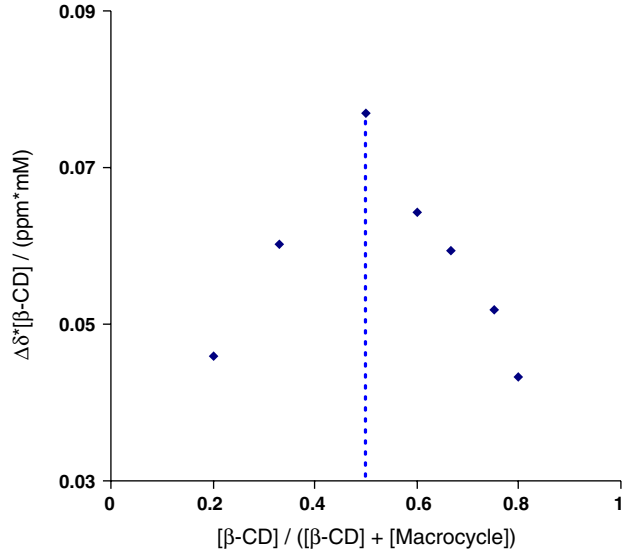
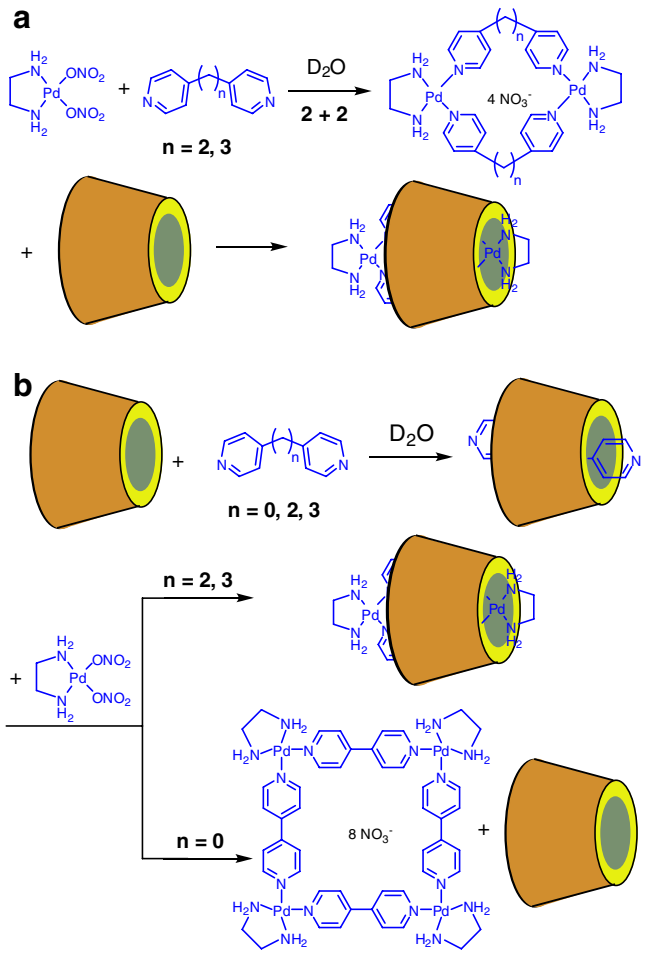


Figure 2. Job plot showing the 1:1 stoichiometry of the coordination macrocycle and β-CD in the ring-in-ring complex. The chemical shift changes of H-4 of β-CD glucoside unit were used in this plot. [β-CD] + [Macrocycle] = 10 mM.

It is also shown that the formation of ring-in-ring complex is irrelevant to the order of the addition of individual components (Scheme 2b). Upon the addition of Pd(II) into a solution of the preformed β-CD ⊃ BPE inclusion complex, the same ring-in-ring complex is obtained. A reasonable pathway is that the introduction of Pd(II) dethreads the divalent ligand from the inclusion complex, followed by the formation of M_2L_2 coordination macrocycles and its inclusion by β-CD to give a ring-in-ring complex.

Similar ring-in-ring complex is also observed when 1,3-bis(4-pyridyl)propane (BPP) is employed instead of BPE. No ring-in-ring complex is formed, however, when a shorter and more rigid divalent ligand BPy is used. An inclusion complex of BPy and β-CD is obtained from co-crystallization[10] and dissolved in D_2O. The ^1H NMR spectrum indicates (Fig. 3a) the 1:1 stoichiometry and upfield shifts of H-3 and H-5 resonances of the glucoside units, suggesting the inclusion of BPy inside the cavity of β-CD. Upon the addition of 1 equiv Pd(II), a ^1H NMR spectrum (Fig. 3d) identical to the sum of pure β-CD (Fig. 3b) and M_4L_4 macrocycle (Fig. 3c) was obtained, indicating the co-existence of two discrete species with little or no mutual recognition. The different self-assembly behavior of these rigid divalent ligands can



Scheme 2. Different pathways indicating the addition of (en)Pd(NO_3)$_2$ (a) before and (b) after the formation of β-CD ⊃ Ligand inclusion complex. Both lead to the same ring-in-ring complexes when flexible ligands are used.

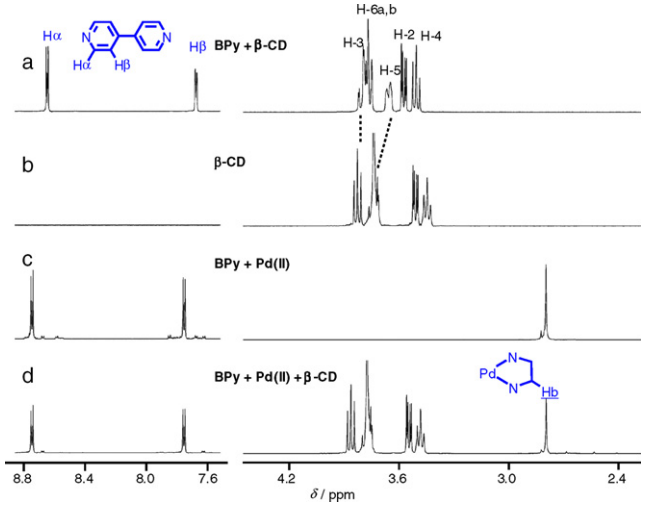


Figure 3. ^{1}H NMR spectra of (a) 1:1 mixture of BPy and β-CD, (b) free β-CD, (c) 1:1 mixture of BPy and (en)Pd(NO_3)$_2$, and (d) 2:2:1 mixture of BPy, (en)Pd(NO_3)$_2$ and β-CD.

be explained by the size mismatch between β-CD and the coordination macrocycle—the more flexible BPE and BPP ligands form dinuclear macrocycles with Pd(II) to give a smaller macrocycle that can be included inside the cavity of β-CD, while in the cases of more rigid BPy–Pd tetranuclear coordination macrocycle, it can neither be included by β-CD nor catenate with β-CD by threading one edge of the squares through the cavity of β-CD.

In summary, we have shown that ring-in-ring complexes can be assembled non-covalently from several components with pre-programed recognition forces. The investigated components include dipyridyl ligands, (en)Pd(NO_3)$_2$, and β-CD. The dipyridyl ligands can form inclusion complexes with β-CD in aqueous solution as a result of hydrophobic interactions. On the other hand, the dipyridyl ligands can coordinate with Pd(II) to form symmetric macrocyclic structures. In the presence of β-CD, dinuclear coordination macrocycles M_2L_2 from dipyridyl ligands with flexible linkers can be included in the cavity of β-CD to form ring-in-ring complexes. It is also shown that the presence of β-CD reinforces the formation of cyclic M_2L_2 as a result of induced-fit effect. When more rigid dipyridyl ligand is used, the tetranuclear coordination macrocycle M_4L_4 prevails, which shows no interaction with β-CD. No catenated product is observed in all cases. The studies disclose a facile approach to ring-in-ring complexes through an error-checking self-assembly process. Complexes with such geometry have been rarely reported[29–31] and are topologically interesting as they are potential forerunners of more complex structures such as borromean rings.[32–34]

Acknowledgments

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