Supramolecular Chemistry of Macrocyclic Oligomers of Metal Chelating Units

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Macrocyclic oligomers of metal chelating units serve as unique ligands to synthesize multinuclear complexes that assemble coordination sites in the cavity (**Fig. 1a**).[1–4] Such metallomacrocycles can realize precise molecular binding by utilizing multi-point coordination and rigidity of the metal complex units. Desymmetrization of macrocycles is another approach to create functional molecules, because they can employ their unsymmetrically arranged interaction moieties (**Fig. 1b**).[1–3,5]

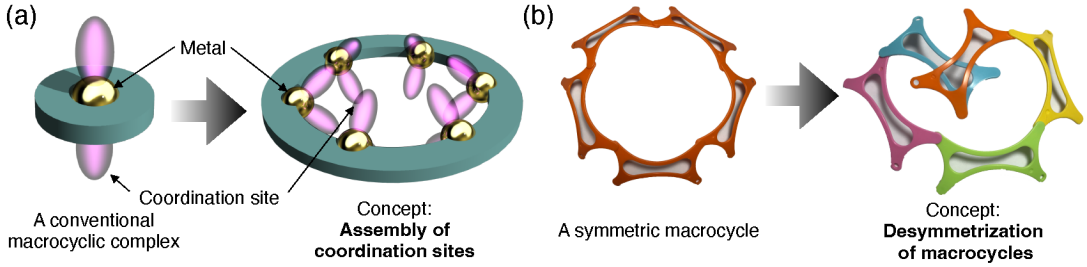

Figure 1. (a) Assembly of coordination sites. (b) Desymmetrization of macrocycles.

Pyridylmethylene-aminophenol (pap) hexamer and its Pd complexes as a metallohost[2d]

We have developed multinuclear complexes of hexapap, macrocyclic ligands with six pyridylmethylene-aminophenol (pap) units.[2] A hexanuclear Pd^{II} complex of hexapap $[\mathbf{1}Pd_6L_6](OTf)_6$ (L: exchangeable ligand) has six inward coordination sites. Because of the planarity of one monomeric [Pd(pap)L] unit, $[\mathbf{1}Pd_6L_6](OTf)_6$ can take two conformations. One is an *Alternate* conformation, in which six coordination sites of pap alternatively point to *Up-Down-Up-Down-Up-Down*. The other is a *Twisted* conformation, in which the coordination sites direct *Up-Middle-Down-Up-Middle-Down* (**Fig. 2**).

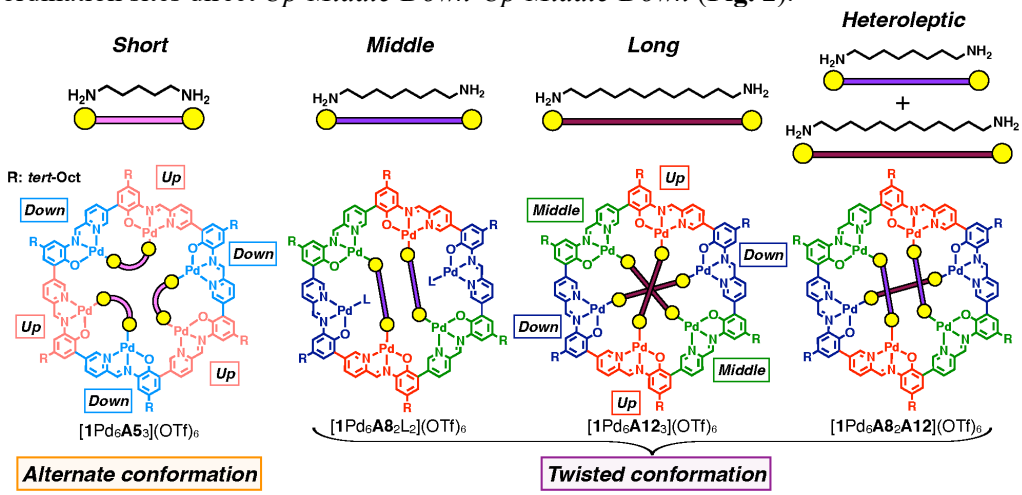

Figure 2. Site-selective ligand bridging of $[\mathbf{1}Pd_6L_6](OTf)_6$ and its conformational regulation.

It was found that α,ω-diaminoalkanes $H_2N(CH_2)_nNH_2$ (**A*n***) bridged the inner coordination sites of [**1**Pd_6L_6](OTf)$_6$ in different binding modes according to the number of methylene groups (*n*). **A4**–**A7** linked adjacent pap units to form [**1**Pd_6**A*n***$_3$](OTf)$_6$ (*n* = 4–7) with *Alternate* conformation. **A8** connected 2 next pap units to yield [**1**Pd_6**A8**$_2L_2$](OTf)$_6$ with *Twisted* conformation. **A12** connected diagonal Pd centers to result in [**1**Pd_6**A12**$_3$](OTf)$_6$, again with *Twisted* conformation. Furthermore, in the case of **A8**:**A12** = 2:1, heteroleptic bridging was achieved to give [**1**Pd_6**A8**$_2$**A12**](OTf)$_6$ (**Fig. 2**).

Pyridylbenzoxazole (pbo) trimer and its unsymmetric conversion[3)]

Synthesis of macrocycles with unsymmetric frameworks often suffers from multi-step reactions and low yields to sequentially connect different units. The use of dynamic covalent bonds is usually not effective for the synthesis of an unsymmetric macrocycle as a single product. We have achieved a high-yield 3-step synthesis of an unsymmetric macrocycle composed only of irreversible bonds (**Fig. 3**).

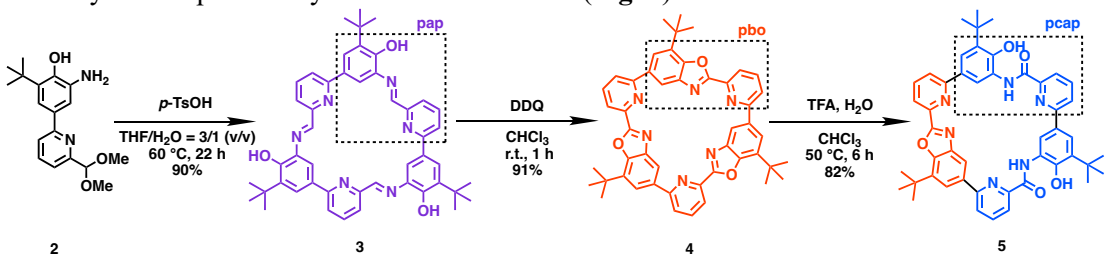

Figure 3. Synthesis of pcap-pbo mixed macrocycle **5** utilizing dynamic covalent bond

The three steps are comprised of macrocyclization, oxidation, and unsymmetric conversion. The first step is the macrocyclic oligomerization of the bifunctional monomer **2**, which has *o*-aminophenol and 2-formylpyridine subunits, utilizing imine bonds formation to yield the pap macrocycle **3**. The second step is the oxidation of the pap units of **3** to benzoxazole (pbo) units to yield the macrocycle **4** composed only of irreversible bonds. The last step is the unsymmetric conversion, that is, the selective addition reaction of water to only two of three pbo units of **3** to convert them into pyridylcarboxamidephenol (pcap) units, to obtain the unsymmetric macrocyclic ligand **5**. Moreover, the unsymmetric macrocycle **5** forms an interesting 2:1 complex with Zn^{II}, which holds the metal ion like a pearl in bivalve shells (**Fig. 4**).

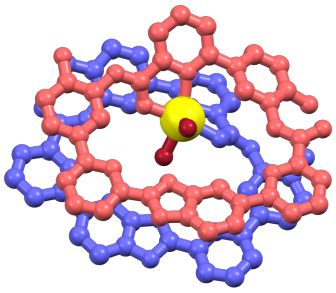

Figure 4. Structure of [**5**$_2$Zn(H$_2$O)$_2$]$^{2+}$ determined by X-ray crystallography

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