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Communication

An interlocked coordination cage based on aromatic amide ligands

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ABSTRACT

An interlocked M_4L_8 coordination cage was synthesized by coordination-driven self-assembly of palladium(II) ions with aromatic amide bidentate ligands. The reaction of the ligand and the metal at 2:1 ratio led to the monomeric M_2L_4 cage as the kinetic product, while the thermodynamic product M_4L_8 cage was obtained by prolongating the reaction. This conversion and the interlocked structure was clearly revealed by using ^{1}H NMR, mass spectrometry and X-ray crystallography. The driving force of interlocking was mainly attributed to the interactions (hydrogen bonding, aromatic stacking and electrostatic interaction) arising from the aptitude of flexibility of the amide ligand.

Coordination cages have attracted considerable attention due to their potential applications in metallasupramolecular materials and biomedical therapy [1–7]. Cages with distinct conformations such as globular, tetrahedral, and columnar shapes have been widely developed and lead to the diversity of features [8–13]. Among these architectures, the mechanically interlocked cages, in which two monomeric cages are interpenetrated with each other, offer a powerful tool to increase complexity of structures and functions [14–25]. The process of interlocking is entropically disfavored, while the gain of enthalpy *via* supramolecular interactions, such as hydrogen bonding, π-π interaction, and electrostatic interaction within the cages is prerequisite. In order to facilitate these interactions, the flexibility of ligand is normally required, whereby the adaptable feature can facilitate the aggregate between the two monomeric cages [26].

The cages made of aromatic amide ligands, reported by us and other groups, possess the flexible character due to the twisting of the amide moieties [27–31]. Following this, we hypothesised that an aromatic amide ligand long enough may also be prone to assemble into an interlocked cage *via* coordination. The target ligand **L** was therefore designed and synthesized by coupling of reported 4,4′-diaminodiphenylmethylamine with commercially available nicotinic acid (Scheme S1 in Supporting information).

The monomeric cage **1** was initially formed by the reaction of **L** with $[Pd(CH_3CN)_4](BF_4)_2$ at 2:1 ratio in CD_3CN for 2 h at 303 K (Scheme 1). ESI mass spectrum verified its structure of a M_2L_4 assembly (Fig. 1a). The observed peaks at *m/z* 1039.2 were assigned to the $[\mathbf{1}(BF_4)_2]^{2+}$ species. The ^{1}H NMR spectrum of the solution also supported the formation of the metal complex **1**: the pyridyl protons, in particular H_a and H_b, showed large downfield shifts, a characteristic of metal-ligand coordination (Figs. 2a and b), while the other aromatic protons displayed much smaller shifts. In addition, only one set of signals for each of the ligand's proton environments was presented for the cage **1**, in agreement with its high symmetry of structure.

Prolongation of the reaction at 333 K led to the quantitative formation of a new species accompanied by a splitting of all the NMR signals into two sets of equal intensity (Scheme 1 and Fig. 2c).

The ESI mass analysis displayed a family of prominent signals at *m/z* 815.0, 1039.2 and 1414.7, which were assigned to the dimeric species $[\mathbf{2}(BF_4)_3]^{5+}$, $[\mathbf{2}(BF_4)_4]^{4+}$ and $[\mathbf{2}(BF_4)_5]^{3+}$, respectively (Fig. 1b). These results suggested that complex **1** converted into a more thermodynamically stable complex **2**, as showed in Scheme 1.

Single-crystal X-ray analysis unambiguously reveals the formation of the dimeric, interlocked cage **2** (Fig. 3). The interlocking produces three internal cavities of the structure with nearly equal volumes, whereby one tetrafluoroborate ion is encapsulated per cavity to balance the positive charges. Interestingly, in the solid state, the structure of **2** displays severe distortion compared to other reported interlocked cages [20–26]. Firstly, the tertiary aniline segments in the central of each ligand adopt a distorted conformation (the dihedral angles range from 28.4° to 88.3°) within the non-coplanarity of the two phenyl rings. Besides, the amide moieties twist as well with respect to the pyridyl rings, and

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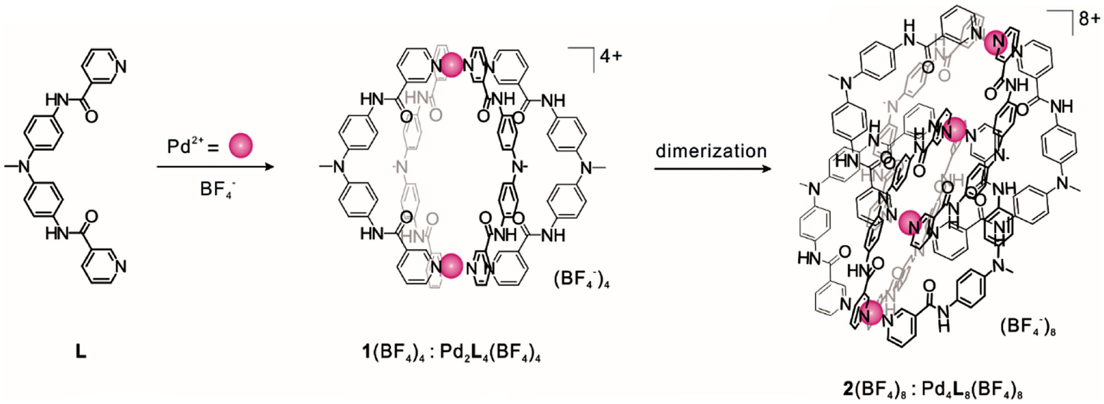

Scheme 1. Synthesis of the monomeric and the dimeric cages. The reaction of **L** (2 equiv.) with [Pd(CH_3CN)$_4$](BF_4)$_2$ (1 equiv.) in acetonitrile at 303 K led to the formation of **1**. Prolongation of the reaction at 333 K gave rise to the interlocked complex **2**.

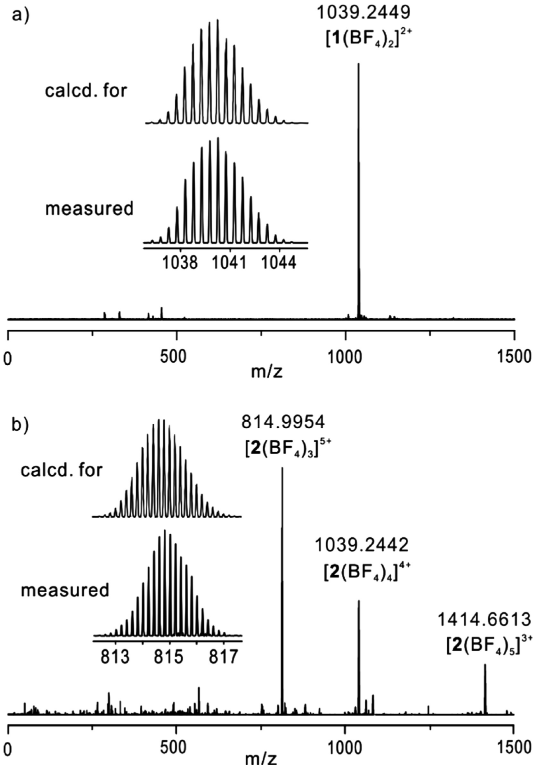

Fig. 1. The high-resolution ESI-MS of (a) the monomeric cage **1** and (b) the dimeric cage **2**.

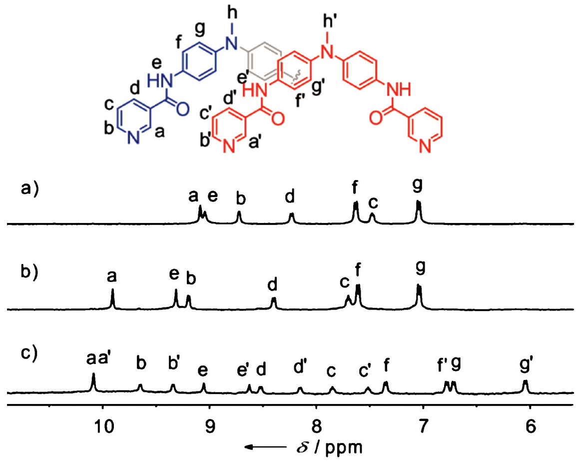

Fig. 2. ^{1}H NMR spectra of (a) the ligand **L**, (b) the monomeric cage **1** and (c) the dimeric cage **2** in CD_3CN.

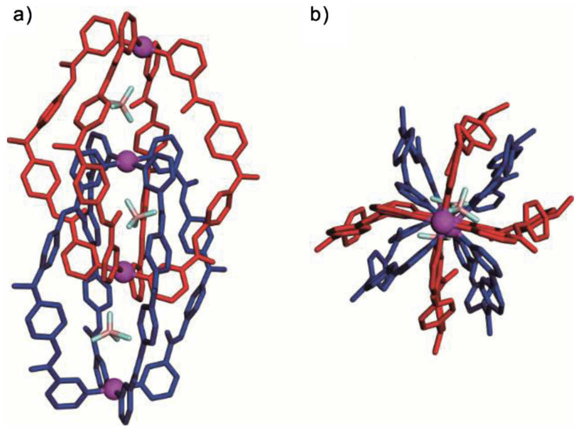

Fig. 3. The single crystal structures of **2**. The solvent molecules, anions outside of cavity and disorders have been removed for clarity.

exhibit two roughly distinct arrangements. More specially, half of amide groups orients their C=O groups inward of the cavity, while the other half directs the C=O groups outward. These twist events thus result in the loss of the possible C_4 symmetric of the structure.

We inferred that this structural torsion was mainly due to the requirement of the enthalpy gain in the compact structure. The CH-π and π-π interactions between the neighboring bridging ligands were evident in the crystal structure. Their proximities could also be verified by the NOESY experiment, in which the NOE cross peaks were obviously observed between the inner pyridine protons and the aniline aromatic protons (Fig. S2 in Supporting information). A total of eight hydrogen bonds (N-H···O, N-H···F) between the amide groups of the neighboring ligands as well as between the amide groups and the tetrafluoroborate anions were presented in the structure. All these interactions (hydrogen bonds, CH-π and π-π) arising from the twisting of the tertiary amine and amide moieties as well as the electrostatic interaction between the metals and the encapsulated anions contributed to stability of the interlocked cage.

The encapsulation of the BF_4^- anions were further supported by ^{19}F NMR spectra, in which new peaks appeared except the free BF_4^- resonances (Fig. S3 in Supporting information). The competitive titration experiments showed that halide ions bound stronger to the cage than that of BF_4^-, while other anions such as PF_6^-, trifluoromethanesulfonate (OTf^-) or bis(trifluoromethane)solfonimide (NTf_2^-) displayed little or none bind ability (Fig. S4 in Supporting information). Unexpectedly, addition of NO_3^- led to a decomposition of the cage. The control experiments showed that the interlocked cage could not be assembled when using NO_3^- or OTf^- rather than BF_4^- as counter-anion. These results hint that the BF_4^- may be a template for assembly of the interlocked cage. The structural stability of **2** was examined by concentration- and temperature-variable NMR experiments subsequently. No evidence was found for decomposition of the complex either by diluting the solution to 0.01 mmol/L, or by raising temperature to 343 K, revealing its high thermodynamically stability.

In summary, we have synthesized a new interlocked cage, which is formed quantitatively through self-assembly of palladium (II) ions and the aromatic amide ligands. Due to the flexibility of the ligand, the multiple supramolecular interactions are prone to be involved in stabilizing the structure. The twisting of amide moiety may also bring about the helical chirality of the system, which is currently being investigated in our laboratory and will be reported in due course.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2020.11.002.

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