Hydrogen bond assisted helical self-assembly into [*n*]catenane†

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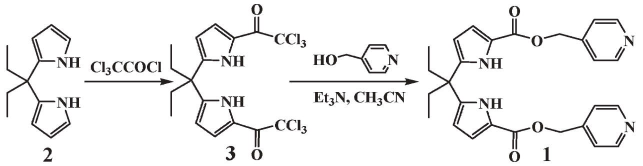
A [*n*]catenane supramolecular structure has been constructed by combination of metal-directed self-assembly with interligand hydrogen bonds which were confirmed by H NMR and DFT calculation.

Crystal engineering based on self-assembly provides a powerful tool for the design and construction of unique supramolecular structures with potentially applicable physical properties.[1–3] Catenanes are an interesting class of compounds and have attracted considerable research attention due to their novel topological structures, intricate self-assembled process, and potential applications in molecular devices.[4–7] The main strategies for the synthesis of catenanes include those based on (1) π-donor/π-acceptor stacking interactions,[8,9] (2) metal ion templating,[10,11] (3) self-assembly of organic bis-monodenate ligands and metal ions,[12,13] and (4) hydrogen bonding template effect of amides.[14] Most recently, a series of [3]catenanes were efficiently prepared by combination of metal-directed self-assembly with π-donor/π-acceptor interactions.[15]

Despite the fact that various catenanes have been prepared by the above methods, the synthesis of catenanes is still a big challenge to chemists. Here, we wish to report a facile catenane formation by combination of metal-directed self-assembly with hydrogen bonds. In this work, a new type of bis-monodentate ligand, *meso*-diethyl-5,5′-di(pyridin-4-yl)methoxycarbonyl-2,2′-dipyrrylmethane (**1**), was designed and synthesized. A [*n*]catenane supramolecular structure has been constructed through self-assembly of the ligand and $HgCl_2$. ^1H NMR studies and DFT calculation revealed that the interligand hydrogen bonding plays an important role in constructing the [*n*]catenane.

The synthesis of the ligand compound **1** is shown in Scheme 1. Diethyl dipyrrolemethane (**2**), which was prepared according to a literature procedure,[16] was allowed to react with an excess of trichloroacetyl chloride to give 2,2′-ditrichlordipyrrolemethane **3**. The reaction of **3** with 4-hydroxymethylpyridine in refluxing CH_3CN then afforded the target molecule **1**. Layering a methanol solution of $HgCl_2$ on a $CHCl_3$ solution of **1** by a routine procedure produced a large amount of white powder, which was recrystallized from methanol to give colorless crystals of $\mathbf{1}_2{\cdot}2HgCl_2{\cdot}H_2O$ in about 60% yield.



Scheme 1 Synthesis of ligand **1**.

An X-ray crystallography study‡ was carried out and demonstrated that there are two types of molecule **1** with different conformation in the crystal of $\mathbf{1}_2{\cdot}2HgCl_2{\cdot}H_2O$. In both types of molecule **1**, the carbonyl groups were all arranged in a way that is *syn* to the pyrrole NH. The dihedral angles of the two pyrrole rings in the same ligand of the two types of molecule **1** are 56.2 and 58.8°, respectively. The two types of molecule **1** form a helical dimer through four N–H···O hydrogen bonds between the pyrrole carbonyl oxygen atoms and the NH protons (Fig. 1). The four hydrogen bonds are different in their N···O distances at a range of 2.882–2.987 Å (Table 1). In a previous study, the hydrogen bonds formed between pyrrole carbonyl groups were shown to be always identical.[17] It is conceived that the varying N···O distances observed here may be caused by a steric effect of the dipyrrolemethane structure.

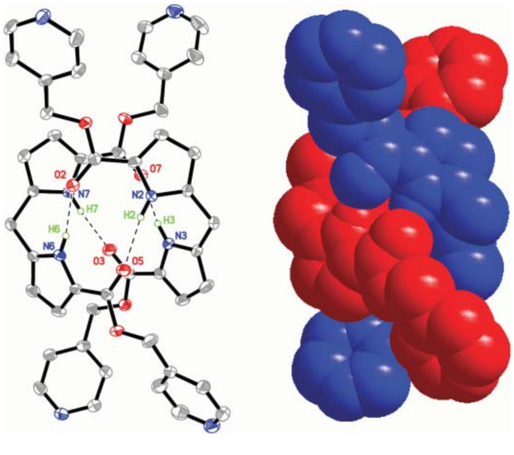


Fig. 1 ORTEP (left, showing 30% probability for ellipsoids) and space filling (right) diagrams of the helical structure of the **1·1** dimer connected by four hydrogen bonds (hydrogen atoms except for the pyrrole NH and ethyl groups are omitted for clarity).

Table 1 Parameters of hydrogen bonds in the **1·1** dimer

D–H	*d*(D–H)/Å	*d*(H···A)/Å	*d*(D···A/Å	∠DHA/°	A
N2–H2	0.86	2.046	2.882	163.80	O5
N3–H3	0.86	2.125	2.947	159.76	O7
N6–H6	0.86	2.134	2.987	171.70	O2
N7–H7	0.86	2.148	2.972	160.27	O3

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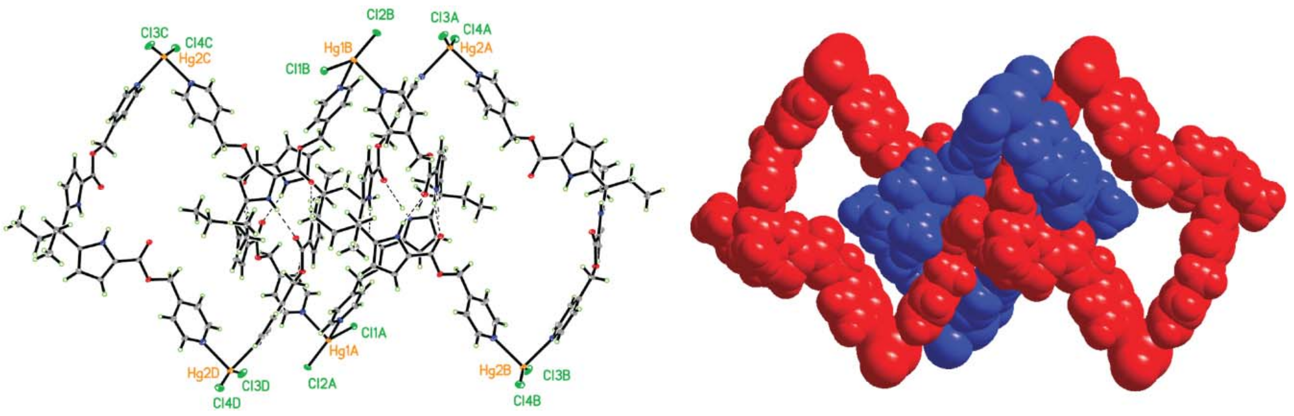

Fig. 2 A part of the infinite [*n*]catenane structure in $\mathbf{1}_2\cdot 2HgCl_2\cdot H_2O$ (left: ORTEP diagram showing 50% probability for ellipsoids and right: space filling diagram).

In the **1·1** dimer, the remaining four N atoms in the pyridine moieties coordinate with Hg^{II} atoms and consequently form a [*n*]catenane supramolecular structure (Fig. 2), where the Hg^{II} atoms are in a distorted-tetrahedral HgN_2Cl_2 geometry and are coordinated with the two Cl anions and two N atoms of separated ligands. The bond angles of $N–Hg^{II}1–N^{i}$ (i: $-x + 1, -y, -z + 1$) and $N–Hg^{II}2–N^{ii}$ (ii: $-x, -y + 1, -z + 1$) are 82.8 and 91.2°, respectively. The $Hg^{II}1\cdots Hg^{II}1$ and $Hg^{II}2\cdots Hg^{II}2$ distances in the macrocycles are 20.109 and 19.581 Å, respectively.

In the literature, various types of bis-monodentate ligands were prepared and the self-assembly with metal ions were also studied. Different types of supramolecular structures such as macrocycles, helical chains, and others were demonstrated.[18–22] However, only a few examples of catenane structure have been reported.[12,13] Schalley and co-workers have previously synthesized some organic [2]catenanes and rotaxanes.[14] In their system, the formation of catenanes and rotaxanes was attributed to the hydrogen bonding template effect of amide. On the other hand, in our earlier work, we have reported that the pyrrole-2-carboxylate moieties prefer to form dimers through strong hydrogen bonds.[17] Upon comparing the structure of **1** with other bis-monodentate ligands, we thought that the intermolecular hydrogen bond-forming ability of **1** should also play an important role in constructing the catenane structure. To test this, ^1H NMR experiments and DFT calculations were conducted.

In $CDCl_3$ solution, the ^1H NMR spectrum of compound **1** was observed to be concentration dependent. An increase in the concentration of compound **1** in the range of 0.8–20 mM caused a significant downfield shift of the pyrrole NH signal (Fig. 3). In DMSO-d$_6$, however, the spectrum was found to be concentration independent. This clearly shows that intermolecular association through hydrogen bonds has taken place in $CDCl_3$ solution. Using the non-linear curve fitting procedure,[23] the K_{ass} of dimerization was calculated to be 452 M^{-1}. The 2D NMR spectra of **1** were recorded both in $CDCl_3$ and DMSO-d$_6$. The most noteworthy feature in the two spectra is that in $CDCl_3$ solution the C–H groups of methylene show NOE with the C–H groups of ethyl, whereas NOE was not detected in DMSO-d$_6$ solution (see ESI†). This phenomenon may be explained by the formation of an interlocking-type **1·1** dimer in $CDCl_3$ solution through hydrogen bonds, whereas no such dimer was formed in DMSO-d$_6$ solution due to the high polarity of the solvent that prevented formation of hydrogen bonds between the two molecules of **1**. At the B3LYP/6-31G* level, the intermolecular hydrogen bond energy of the **1·1** dimer was calculated using the Gaussian 98 program[24] on the basis of its crystal structure. Stabilization energies resulting from hydrogen bond interactions in the **1·1** dimer were computed as the difference in the energy between the **1·1** dimer and its two isolated monomers.[17,25] The calculated energy is 9.78 kcal mol^{-1}, indicating that the intermolecular hydrogen bonds should be strong enough to hold two ligands together in apolar solvents but may be easily destroyed in polar solvents. This agrees well with ^1H NMR observation. Moreover, attempts to prepare crystals of $\mathbf{1}\cdot HgCl_2$ from methanol failed, and led to a large amount of unidentified powder. Thus, it should be reasonable to propose a two-step mechanism for the formation of [*n*]catenane: namely, the interlocked **1·1** dimers were first constructed in $CHCl_3$ by combination of two molecules of **1** through hydrogen bonding, then subsequently, the dimers were connected to each other with Hg^{II} atoms as linkers through coordination bonds to form the infinite [*n*]catenane.

In summary, a [*n*]catenane supramolecular structure constructed through self-assembly of ligand **1** and $HgCl_2$ is reported. The

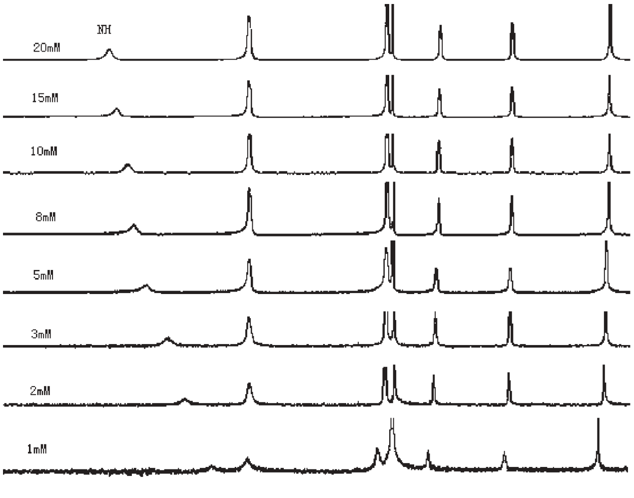

Fig. 3 Parts of the ^1H NMR spectrum of **1** in $CDCl_3$ solution showing the dimerization induced shift changes (concentrations from bottom to top: 1, 2, 3, 5, 8, 10, 15, 20 mM).

5,5′-dicarbonyl dipyrrylmethane ligand assembled into a helical structure with the assistance of four hydrogen bonds. The ^{1}H NMR study and DFT calculation revealed that the interligand hydrogen bonds played a critical role in self-assembling of **1** with $HgCl_2$. Self-assembly with other metal ions is under current investigation.

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Notes and references

‡ *Crystal data* for $\mathbf{1}_2 \cdot 2HgCl_2 \cdot H_2O$: $C_{54}H_{58}Cl_4Hg_2N_8O_9$, $M_r = 1506.06$, $T = 293(2)$ K, triclinic, space group $P\bar{1}$, $a = 12.7414(9)$, $b = 14.6499(11)$, $c = 16.8512(13)$ Å, $\alpha = 71.0860(10)$, $\beta = 80.2820(10)$, $\gamma = 79.0090(10)^\circ$, $V = 2901.6(4)$ Å^3, $Z = 2$, $D_c = 1.7.23$ g cm^{-3}, $\mu = 5.529$ mm^{-1}, $F(000) = 1474$, reflections collected: 15900, independent reflections, 10118 ($R_{int} = 0.0215$), Final R indices [$I > 2\sigma(I)$], $R_1 = 0.0487$, $wR_2 = 0.1069$; R indices (all data), $R_1 = 0.0739$, $wR_2 = 0.1179$, GOF on F^2, 1.029. CCDC 640218. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703591h

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