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Formation of sandwich, macrocyclic and box supramolecular assemblies that were controlled by the distance of two oxygen atoms in hydrogen bonding donors†

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Sandwich $\mathbf{1_2{\cdot}2}$, macrocyclic $\mathbf{1{\cdot}3}$ and box $\mathbf{1_2{\cdot}4_2}$ supramolecular assemblies were synthesized by the reaction of 1,8-bis(4-pyridylethynyl)anthracene 1 with hydroquinone 2, resorcinol 3 and 1,5-dihydroxynaphthalene 4 *via* hydrogen-bonding interactions, respectively. The formed sandwiches, macrocycles and boxes can further self assemble to form a double-layer supramolecular polymer, nanotubes and a one-dimensional "iron chain type" supramolecular polymer. Investigation of their crystal structures revealed that the distance between two oxygen atoms in a hydrogen bonding donor play an important role in the formation of supramolecular assemblies.

Hydrogen bonding self-assembly is a quite common phenomenon that existed in biological systems.[1] For example, the secondary structure of a protein α-helix is mainly maintained by hydrogen bonding. The formation of the DNA double helix structure is also through hydrogen bonding. Inspired by Nature, hydrogen bonding has received much attention and been established as the most effective tool in molecular recognition and assemblies because of its stability, dynamics, directionality and reversibility.[2,3] A variety of complex supramolecular assembled structures such as molecule capsules,[4] macrocycles,[5] G-quartets,[6] interpenetrating networks,[7] extended sheet structures,[8] molecular tapes,[9] porous organic hydrogen-bonding frameworks,[10] and columnar and helical assemblies,[11] have been constructed through hydrogen bonding interactions. Hydrogen bonding motifs, such as pyridinone, diaminotriazinyl (DAT), phenol or polyhydroxy compounds and boronic acid, have been widely used in crystal engineering to construct materials with useful properties. Among them, phenol and polyhydroxy compounds[12] have attracted much attention due to the strong O–H⋯N hydrogen bonds in phenol–pyridine/amine complexes. Chen and coworkers[13] reported the synthesis of ladder-like and/or 3D network supramolecular structures using hydroxyl substituted triptycene and 4,4′-bipyridine through hydrogen bonding interactions. Kobayashi's group[14] demonstrated that tetra(4-pyridyl)-cavitand and tetrakis(4-hydroxyphenyl)-cavitand can self-assemble into a heterodimeric capsule *via* four PhOH⋯Py hydrogen bonds. Recently, Natarajan and coworkers[15] described the crystal structure landscape of triazine triphenol (TTP) with its solvates, cocrystals, and polymorphs. Numerous studies have been devoted to construct the phenol–pyridine/amine complexes. However, as far as we know, utilization of the distance between the two oxygen atoms in hydrogen bonding donors to adjust supramolecular assemblies (sandwiches, macrocycles and boxes) based on phenol–pyridine hydrogen bonding interactions has not been reported.

1,8-Bis(4-pyridylethynyl)anthracene, which contains two pyridine groups and an anthracene group, has been used as a donor building block to prepare trigonal prisms through metal coordination interactions.[16] However, the self assembly study of 1,8-bis(4-pyridylethynyl)anthracene with phenol or polyhydroxy compounds is still unexplored. Previously, we[17] utilized 1,8-bis(4-pyridylethynyl)anthracene as a molecular "clip" for the synthesis of a novel water-soluble macrocycle and studied its recognition behavior with guest molecules in water. We believed that 1,8-bis(4-pyridylethynyl)anthracene could be used as a building block to investigate the influence of the distance between the two oxygen atoms in hydrogen bonding donors on supramolecular assemblies.

In this work, as part of our research interests in supramolecular chemistry,[18] we reported the self assembly study of 1,8-bis(4-pyridylethynyl)anthracene with phenol or polyhydroxy compounds. A variety of supramolecular assemblies could be obtained by simply adjusting the

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distance between the two oxygen atoms in hydrogen bonding donors. The reaction of 1,8-bis(4-pyridylethynyl)anthracene **1** with hydroquinone **2**, resorcinol **3** and 1,5-dihydroxynaphthalene **4** led to the formation of sandwich, macrocyclic and box supramolecular assemblies *via* hydrogen-bonding and π–π stacking interactions, respectively (Fig. 1). Interestingly, the formed sandwiches, macrocycles and boxes can further self assemble to form a double-layer supramolecular polymer, nanotubes and a one-dimensional "iron chain type" polymer, respectively.

Recently, Schmidt and coworkers[19] reported the synthesis and crystal structures of three [2 + 2] supramolecular boxes assembled by halogen bonding. Inspired by their work, we deduced that **1** can also self assemble to form [2 + 2] supramolecular boxes with **2** through hydrogen bonding. By the slow evaporation of a solution of equimolar amounts of **1** and **2** in CH_2Cl_2 at room temperature, we obtained yellow single crystals of adduct $\mathbf{1_2{\cdot}2}$ that are suitable for X-ray analysis. However, to our surprise, a 2 : 1 sandwich complex between **1** and **2** was formed instead of a [2 + 2] supramolecular box. Then we tried to increase the amount of **2** from 1 to 4 equiv. of **1** to get the [2 + 2] supramolecular box, but we still failed and could only get the 2 : 1 sandwich complex. As shown in Fig. 2a, the hydrogen bonding donor **2** was located in the middle of **1** through the strong O–H⋯N hydrogen bonding interactions with the distance of 2.869 Å. The two pyridyl residues of **1** orientate in a nearly face-to-face manner and the distance between two N atoms of pyridyl residues are measured to be 5.674 Å. Moreover, the π⋯π interaction between pyridyl and anthracene groups of **1** with a distance of 3.317 Å was also observed (Fig. 2b). Interestingly, because of these multiple noncovalent interactions, the formed 2 : 1 sandwich complex could further self-assemble to form a double-layer supramolecular polymer (Fig. 2c).

Based on the previous results and considering that pyridine groups are at the 1 and 8 position of **1**, we deduced that it can self assemble with resorcinol **3** which has a short distance between the two oxygen atoms to form a 1 : 1 macrocyclic complex. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of equimolar amounts of **1** and **3** in CH_2Cl_2 at 4 °C. An analysis of the resulting structure (Fig. 3a) revealed that the hydrogen bonding donor **3** was self assembled with **1** to form a 1 : 1 macrocyclic complex through the strong O–H⋯N hydrogen bonding interactions with distances of 2.806 and 2.783 Å, respectively. The two pyridyl residues of **1** orientate in a face-to-face manner and the distance between two N atoms of pyridyl residues are measured to be 4.559 Å which was shorter than the distance of two N atoms of pyridyl residues in the $\mathbf{1_2{\cdot}2}$ sandwich complex, indicating that the distance between two N atoms of pyridyl can be adjusted by hydrogen bonding donors. Moreover, the distance between

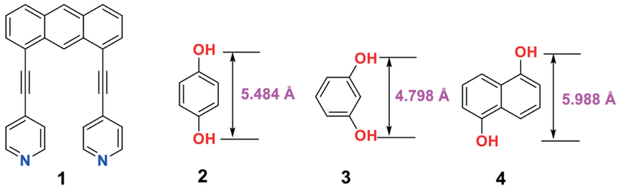

Fig. 1 Structures of **1**–**4** and the distance of two oxygen atoms in **2**, **3** and **4**.

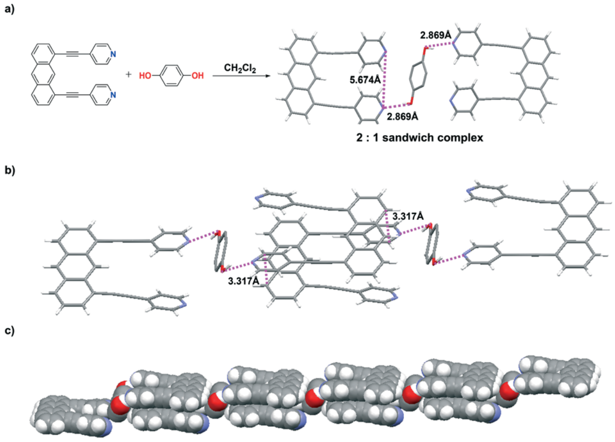

Fig. 2 (a) The synthesis and crystal structure of $\mathbf{1_2{\cdot}2}$; (b) formation of a double-layer supramolecular polymer *via* π⋯π interactions; (c) the space-filling model of the double-layer supramolecular polymer.

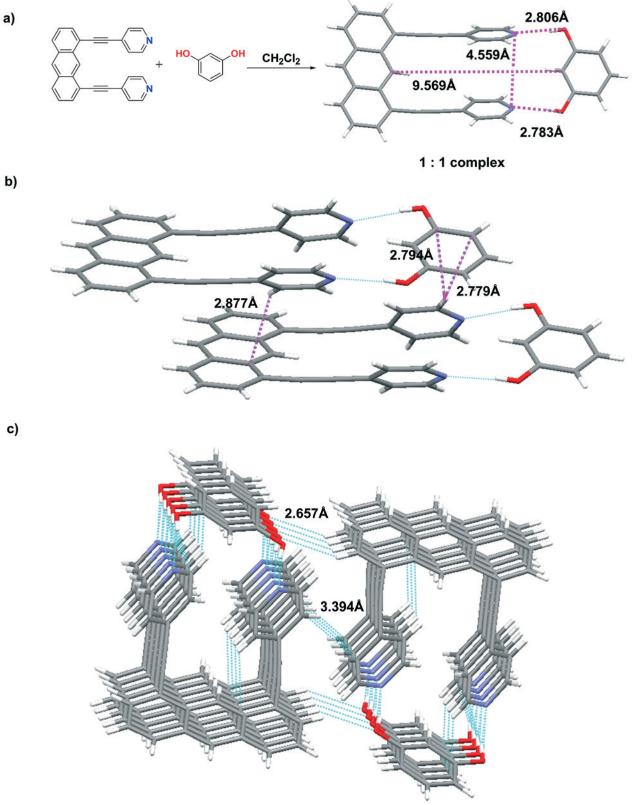

Fig. 3 (a) The synthesis and crystal structure of **1·3**; (b and c) formation of nanotubes *via* hydrogen bonding and π⋯π interactions.

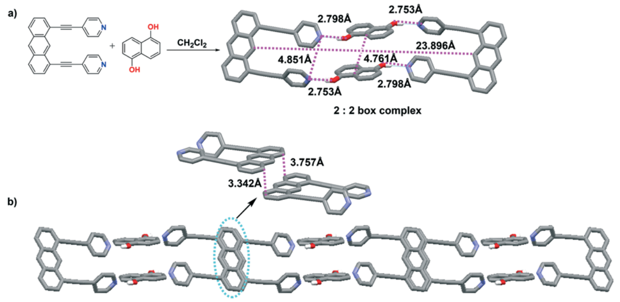

Fig. 4 (a) The synthesis and crystal structure of $\mathbf{1}_2{\cdot}\mathbf{4}_2$; (b) formation of a one-dimensional “iron chain type” supramolecular polymer *via* π⋯π interactions.

two middle C atoms of **1** and **3** was measured to be 9.569 Å, suggesting the larger cavity of the formed **1·3** macrocyclic complex. Interestingly, π⋯π interactions existed in the two formed macrocyclic complexes. As shown in Fig. 3b, the π⋯π interactions between **1·3** macrocycle's pyridyl residues and resorcinol, and another **1·3** macrocycle's anthracene and pyridyl groups with distances of 2.877, 2.794 and 2.783 Å were also observed, respectively. Surprisingly, because of these multiple noncovalent interactions, the formed 1 : 1 macrocyclic complex could further self-assemble to form nanotubes (Fig. 3c). There are many hydrogen bonding and π⋯π interactions existed between two nanotubes with distances of 2.657 and 3.394 Å respectively. These weak interactions further promote the formation of nanotubes.

Although we have obtained the supramolecular assembly of the $\mathbf{1}_2{\cdot}\mathbf{2}$ sandwich complex and **1·3** macrocyclic complex, we still want to obtain the [2 + 2] box complex. Then, we pay our attention to the hydrogen bonding donor 1,5-dihydroxynaphthalene **4**. The distance between the two oxygen atoms in **4** is longer than the distance between the two oxygen atoms in **2** and **3**, which indicates that the distance between two N atoms of pyridyl may be adjusted to form a new [2 + 2] box complex. Through slow evaporation of equimolar amounts of **1** and **4** in CH_2Cl_2 at 4 °C, yellow single crystals suitable for X-ray diffraction analysis were obtained. Fortunately, we obtained the [2 + 2] box complex $\mathbf{1}_2{\cdot}\mathbf{4}_2$. An analysis of the resulting structure (Fig. 4a) revealed that the hydrogen bonding donor **4** was self assembled with hydrogen bonding acceptor **1** to form a [2 + 2] box complex through the strong O–H⋯N hydrogen bonding interactions with distances of 2.798 and 2.753 Å, respectively. The $\mathbf{1}_2{\cdot}\mathbf{4}_2$ box (Fig. 4a) has a length of 23.896 Å (anthracene–anthrance distance) and a height of 4.761 Å (the distance between two 1,5-dihydroxynaphthalene molecules). Moreover, the angle between the planes formed by the two pyridyl residues of **1** is close to 65° and the distance between two N atoms of pyridyl residues are measured to be 4.851 Å which was longer than the distance of two N atoms of pyridyl residues in $\mathbf{1}_2{\cdot}\mathbf{2}$ and **1·3** complexes, indicating that increasing the distance between the two oxygen atoms in hydrogen bonding donors can lead to the increase of the distance between two N atoms of pyridyl in **1**. As shown in Fig. 4b, the π⋯π interactions between the anthracene groups of two boxes with distances of 3.757 and 3.342 Å were also observed. Because of these π⋯π interactions, the formed [2 + 2] box complex could further self-assemble to form a one-dimensional “iron chain type” supramolecular polymer (Fig. 4b).

In conclusion, we demonstrated the synthesis of sandwich $\mathbf{1}_2{\cdot}\mathbf{2}$, macrocyclic **1·3** and box $\mathbf{1}_2{\cdot}\mathbf{4}_2$ supramolecular assemblies by the reaction of 1,8-bis(4-pyridylethynyl) anthracene **1** with hydroquinone **2**, resorcinol **3** and 1,5-dihydroxynaphthalene **4** *via* hydrogen-bonding and π–π stacking interactions, respectively. Further investigation of their crystal structures revealed that the distance between the two oxygen atoms in the hydrogen bonding donor play an important role in the formation of supramolecular assemblies. Moreover, the formed sandwiches, macrocycles and boxes can further self assemble to form a double-layer supramolecular polymer, nanotubes and a one-dimensional “iron chain type” supramolecular polymer, respectively. To the best of our knowledge, this system is the first time to reveal the importance of the distance between the two oxygen atoms in a hydrogen bonding donor that influence the formation of supramolecular assemblies. The ability of the supramolecular boxes described here to possibly host flat aromatic compounds with complimentary quadrupole moment is under investigation, and we believe that the results presented here will be useful for the design and construction of new supramolecular materials.

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Conflicts of interest

There are no conflicts to declare.

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