



Self-recognition behavior of novel frameworks containing both urea and carboxylate anion motifs



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ABSTRACT

Molecular recognition based on hydrogen bond interaction plays a significant role in supramolecular self-assembly. In this work, we successfully developed a class of novel frameworks containing a urea in the recognition site and a carboxylate anion in the guest unit. The self-recognition model based on the interaction between urea and carboxylate anion could induce the molecules to assemble into a highly organized form. The crystal structures showed that they assembled in highly ordered two-dimensional architectures. The optical properties showed that the position of carboxylate anion on the diphenylacetylene backbone had an obvious influence on optical properties. The self-recognition strategy is useful for the construction of highly ordered self-assembled architectures.

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1. Introduction

Over recent decades, supramolecular self-assembly has developed into one of the most fascinating topics in supramolecular chemistry and a great deal of effort has been made in the design and construction of novel supramolecular architectures. These architectures assemble through many non-covalent intermolecular interactions, such as hydrogen bonding, π - π interaction, van der Waals forces, hydrophobic effect, ionic interactions and coordinative interactions.^{1–12} Supramolecular self-assembly based on hydrogen bond interaction is considered to be one of the most versatile strategies for the construction of highly ordered self-assembling architectures due to many options for hydrogen bond donors and acceptors.^{13–22}

Urea is a popular building block that has been widely applied in self-assembling materials.²³ The NH on the urea unit can be used as a hydrogen bond donor while the carbonyl group can play the role of hydrogen bond acceptor.

Therefore, molecules containing the urea unit can form highly

ordered self-assembled structures through the intermolecular N–H \cdots O hydrogen bond between two urea motifs, as illustrated in Fig. 1A. The hydrogen bond interaction is usually employed as the main driving force in the design of synthetic receptors for anion recognition.²⁴ Over past few decades, urea has been widely applied as a hydrogen bond donor in the recognition of anions.^{25–29} For example, numerous studies have shown that urea can bind to acetate by forming two N–H \cdots O hydrogen bonds in an 8-member ring, similar to the 6-member ring formed in the self-assembling process shown in Fig. 1B.^{30–35}

It is possible that the interaction between urea and the carboxylate anion could also be used as an alternative model in self-assembly when the urea unit and the carboxylate anion are both installed on a molecule. Based on this self-recognition concept, we reported two novel building blocks that both contain a urea in the recognition site and a carboxylate anion in the guest unit. The crystal structures indicated that these building blocks could form two different highly ordered two-dimensional architectures. When the urea unit and carboxylate unit were located in the plane of the diphenylacetylene backbone, the molecule presented a parallel wave-shaped two-dimensional architecture with an intersection angle of 110°. When the urea unit was installed on the para-position of phenylacetylene unit and the carboxylate unit was installed on the meta-position of another phenylacetylene unit, the molecule showed a twisted wave-shaped two-dimensional

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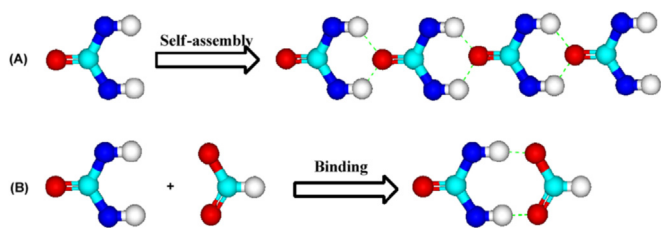


Fig. 1. The schematic representation of the self-assembly of two urea groups (A) and the binding mode between urea and acetate groups (B).

architecture with an intersection angle of ca. 124° . It was worth mentioning that the different angle between the urea-based phenylacetylene backbone and carboxylate group affected the self-assembling behavior.

2. Results and discussion

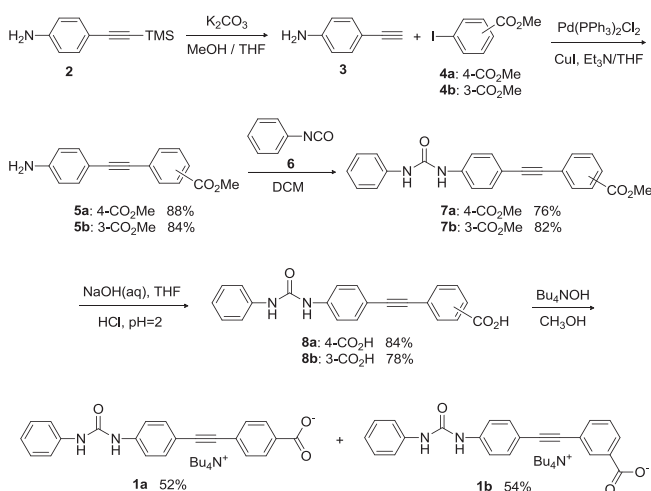
2.1. Synthesis

The synthetic route for the preparation of compounds **1a** and **1b** is outlined in Scheme 1. The deprotection of 4-((trimethylsilyl)ethynyl)aniline **2** formed intermediate **3**, according to previous literature.³⁶ Subsequently, the terminal alkyne **3** was subjected to the palladium-catalyzed Sonogashira coupling reaction with **4a** and **4b**,^{37–39} affording respective compounds **5a** and **5b** in yields of 84–88%. Next, **5a** and **5b** were reacted with isocyanatobenzene **6** for 12 h at room temperature to form respective urea **7a** and **7b** in good yields.⁴⁰ The urea-based carboxylic acids **8a** and **8b** were obtained by the hydrolysis of **7a** and **7b** under alkaline conditions. Subsequent transformation from carboxylic acid to carboxylate anion was performed to give target molecules **1a** and **1b** in the yields of 52–54%, respectively.

All of the intermediate and target molecules were well characterized by standard spectroscopic techniques such as NMR spectroscopy and mass spectrometry.

2.2. Crystal structures of **1a** and **1b**

The solid-state structure is very significant for the investigation of the self-assembling behavior in supramolecular systems.^{41,42} Great efforts were expended to obtain single crystals of



Scheme 1. Synthetic route of compounds **1a** and **1b**.

compounds **1a** and **1b**. Single crystals of compounds **1a** and **1b** suitable for crystallographic analysis were grown by slow evaporation of methanol (Fig. 2). Crystal structure analysis indicates that **1a** and **1b** were crystallized in the non-centrosymmetric orthorhombic $Fdd2$ and monoclinic $P2_1/c$ space group, respectively. In both their asymmetric units, there are each one host urea derivatives anion and one counter cation $N(t-Bu)_4$. According to their crystal structures, the recognition of urea units and carboxylate moieties play an important role in the crystal packing.^{43–45} The bond lengths and angles of **1a** and **1b** are listed, and the crystal data and structural refinements of **1a** and **1b** are summarized in Tables S1–5.

As shown in Fig. 2, due to a steric effect from the carboxylate group, the molecular conformations in **1a** and **1b** differ from each other largely. For instance, i) the central benzene ring in **1a** make two dihedral angles of $11.20(2)^\circ$ and $8.97(2)^\circ$ with the two neighboring phenyl groups. However, the two angles in **1b** are $23.67(2)^\circ$ and $9.77(2)^\circ$, indicating an apparent molecular non-planarity in **1b**. ii) As for the often generated intermolecular $R^2_2(8)$ hydrogen-bond motif between a urea and a carboxylate group, the urea was twisted away from the carboxylate group by $9.50(2)^\circ$ in **1a**. In comparison, a large angle of $42.26(2)^\circ$ was resulted in **1b** due to a steric effect from the carboxylate.

In their crystal packing, the arrangement of the urea and carboxylate groups of **1a** and **1b** show that they could form well-organized, multi-dimensional architectures by using the hydrogen bonding as the driving force (Figs. 3–4). According to the crystal structure of compound **1a**, the molecules possessed two intermolecular $N-H\cdots O$ hydrogen bonds ($d_{N\cdots O} = 2.713(3)$ Å / $2.896(3)$ Å), forming an $R^2_2(8)$ hydrogen-bonded ring and resulting in the one-dimensional chain along the $[0-13]$ direction by glide-plane symmetry operation (Fig. 3A). Each $[0-13]$ hydrogen-bonding chain may be connected to another by $C-H\cdots O$ interaction or Coulomb electrostatic interactions between the anionic and cationic ions. As for two neighboring groups of 1D chain, regular quadrilateral grids were formed between them. For compound **1b**, similar $R^2_2(8)$ hydrogen-bonded motif consisted of two intermolecular $N-H\cdots O$ hydrogen bonds ($d_{N_2\cdots O_2} = 2.779(2)$ Å and $d_{N_3\cdots O_3} = 2.847(2)$ Å, symmetry code: $x, 3/2 - y, z - 1/2$) could be found to mainly stabilize the $[001]$ chain (Fig. 3B). It is worthy mentioned that the donor plane ($H2/N2/C7/N3/H3$) twisted away from the carboxylate plane ($O2/C21/O3, 1 - x, 2 - y, -z$) with a dihedral angle of $39.0(2)^\circ$, which should be resulted by a steric hindrance of the benzene ring.⁴⁶ Adjacent $[001]$ chains were linked together by one

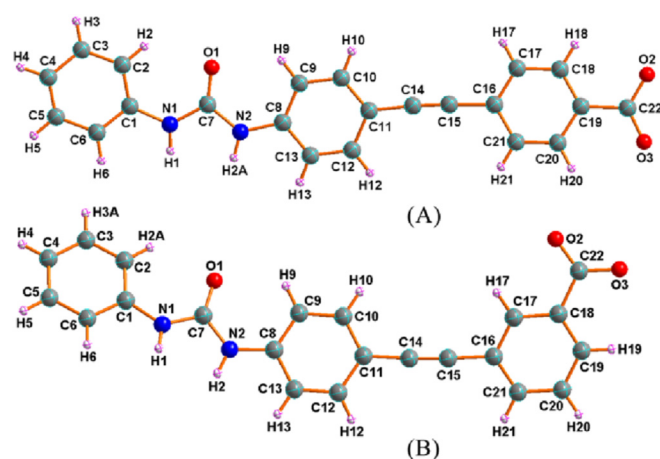


Fig. 2. Top view of the single crystal structures of **1a** (A) and **1b** (B). For clarity, the tetrabutylammonium cations were both omitted in them.

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