

## ビス尿素大環状化合物の結晶構造変化とガス収着

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### Crystal Structural Transformation of Bis-Urea Macrocycles Coupled with Gas Sorption

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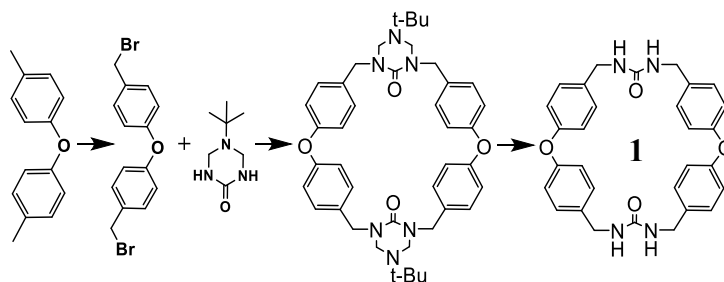
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**【Abstract】** In this study, two kinds of hydrogen-bonding molecular assemblies of bis-urea macrocycle derivative were selectively obtained from various guest molecules. The first one was 1D columnar tube, whereas the second one was 2D interdigitated layer. These two structures could be transformed to each other through the suitable guest absorption-desorption process. Especially, the columnar assembly showed the selective adsorption for CO<sub>2</sub>. Controlling in the structural transformation was achieved by the gas sorption behavior from the vacant state to the selective CO<sub>2</sub> sorption state.

#### 【Introduction】

Hydrogen-bonding urea derivative is a versatile molecular building block to design interesting self-assembly structures. Flexibility of hydrogen-bonding organic frameworks is an important point to form functional materials. Shimizu et al. reported a novel urea-based macrocycle **1** and the hydrogen-bonding one-dimensional (1D) tubular self-assemblies.<sup>[1]</sup> In this study, macrocycle **1** showed structural diversity with different gas absorption performances.



**Fig. 1.** Synthesis of bisurea macrocycle (**1**).

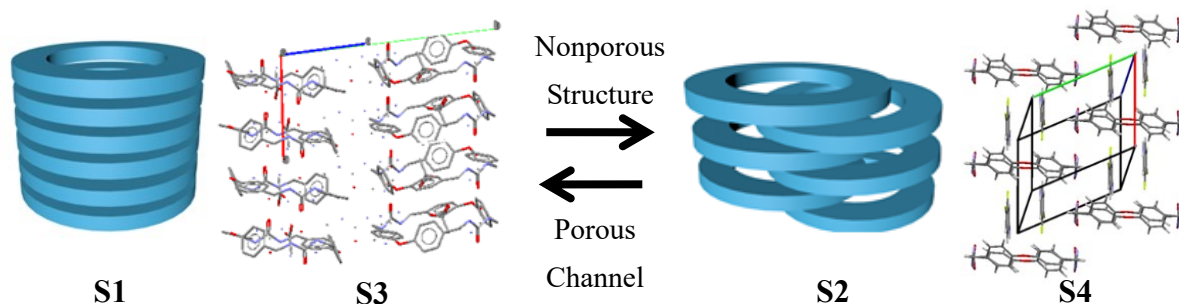
#### 【Experimental】

Synthesis of phenyl ether bis-urea derivative **1** was carried out according to the previous methods.<sup>[1]</sup> N-bromosuccinimide, benzoyl peroxide, and p-tolyl ether in CCl<sub>4</sub> were refluxed during four hours under N<sub>2</sub>, resulting in the white precipitate of 4,4'-oxybis(benzylbromide). 4,4'-oxybis(benzylbromide), triazinanone, and NaH in fresh THF were refluxed during sixty hours under the N<sub>2</sub> condition, then the triazinanone-protected compound was obtained by the recrystallization from CHCl<sub>3</sub>, which was refluxed in 1:1 ratio of 20 % NH(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub> /H<sub>2</sub>O : CH<sub>3</sub>OH overnight due to the deprotection. The needle crystals **1** were obtained by the crystallization from acetic acid.

The host-guest molecular crystals were obtained by the recrystallization of **1** from the corresponding solvents. The structure transformation was studied by exposing a host **1** to solvent vapor in a seal chamber, and the guest absorption followed for 3-7 days. The structures were confirmed by PXRD.

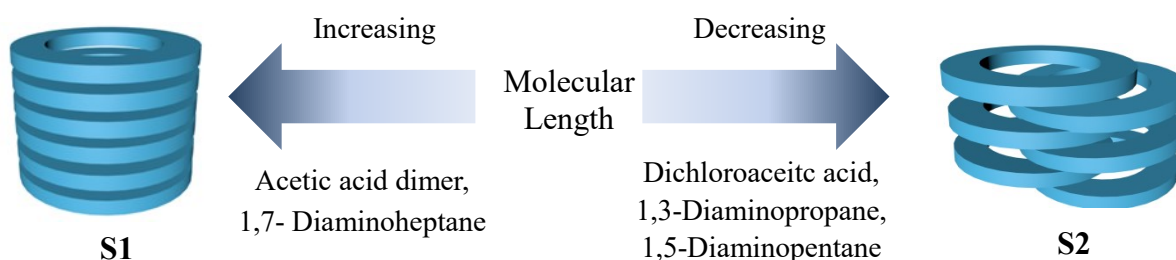
## 【Results and Discussion】

The 1D columnar structure (**S3**) was filled by AcOH by the crystallization of **1** from AcOH. After the desorption of AcOH from tube, the apohost **1** (**S1** state) was exposed to various solvent vapors. The flexibility of vacant **S1** was found during the absorption study. Depending on the guest molecules, the host-guest complexes were classified as two different structures, including 1D columnar **S3** and interdigitated **S4** (guest is 3,4-difluoroaniline). After the desorption of guests, whether **S1** or **S2** were obtained. Surprisingly, **S2** can be converted to **S3** by AcOH re-adsorption, suggesting reversible **S1** - **S2** transform by suitable guests sorption.



**Fig. 2.** Schematic structural transformation and crystal structures of **1** with guests.

A variety of guests were loaded into **S1** to study the factor which can affect the transformation. From the result, it is clear to see that the molecular length play an important role to control the structures after desorption. Though single acetic acid molecule is short, it can form dimer in the porous channel, hindering the structure transformation. In contrast, dichloroacetic acid was not able to form dimer in the tortuosity channel due to the big size of chlorine.

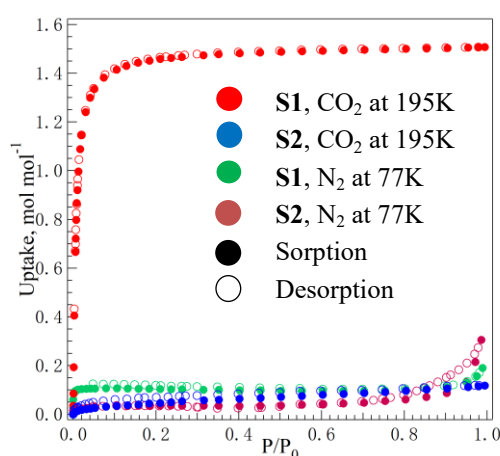


**Fig. 3.** Schematic of architecture transformation induced by guests.

The porosity of **S1** and **S2** states was confirmed by  $N_2$  and  $CO_2$  gas sorption measurements. There was no  $N_2$  sorption behavior in both **S1** and **S2** states, whereas **S1** state showed significantly higher  $CO_2$  absorption behavior. The size matching effect between the  $CO_2$  and pore diameter played an essential role. On the contrary, **S2** state did not show the sorption behavior due to shrinking after the removal of guests. Through controlling in the structure conversion, the gas sorption abilities from non-sorption of **S2** state can change to selective sorption **S1** state for  $CO_2$ .

## 【References】

[1] L. S. Shimizu, A. D. Hughes, M. D. Smith, M. J. Davis, B. P. Zhang, H. C. Zur Loye, K. D. Shimizu, *J. Am. Chem. Soc.*, **125**, 14972–14973. (2003)



**Fig. 4.** Adsorption-desorption isotherms of **S1** and **S2** for  $N_2$  and  $CO_2$ .