Construction of hydrogen-bonded organic frameworks with naphthoic acid groups and its structural transition behavior

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Hydrogen-bonded organic frameworks (HOFs) are attractive materials as high-crystalline and regeneratable porous organic materials, but have some problems regarding stability and designability of the porous structure. The construction of stable HOFs with permanent porosity has been reported in recent years, and we also have reported that dibenzo[*g*,*p*]chrysene (DBC) tetracarboxylic acid derivative, namely **CPDBC**, formed a stable HOF.[1)] This stability is resulting from the assembling that non-planer π-conjugated skeletons stacked uniformly (shape-fitted docking). However, the designability of other skeletons is not clear.

In this work, we constructed isostructural DBC HOFs applying analogs with 4'-carboxybiphenyl-4-yl, 4-carboxynaththalen-1-yl or 6-caroboxynaphthalen-2-yl derivatives (**CBPDBC**, **C1NDBC** or **C2NDBC**, respectively, Figure 1a) and investigated the effect of peripheral functional groups. These carboxylic acids were crystallized by the solvent evaporation method with various aromatic solvents as guest molecules. **CBPDBC** and **C1NDBC** were only yield microcrystals. According to the PXRD measurement, both were formed the isostructural HOFs as **CPDBC**. On the other hand, plate crystals of **C2NDCB** were yielded under various poor solvent conditions. From the crystals using 5-*tert*-butyl-*m*-xylene or methyl benzoate, the obtained structures were isostructural HOFs as DBC derivatives (Figure 1b). **C1NDBC** and **C2NDBC** showed different behaviors in the introduction and removal of molecules. Only **C1NDBC** shows reversible structural change.

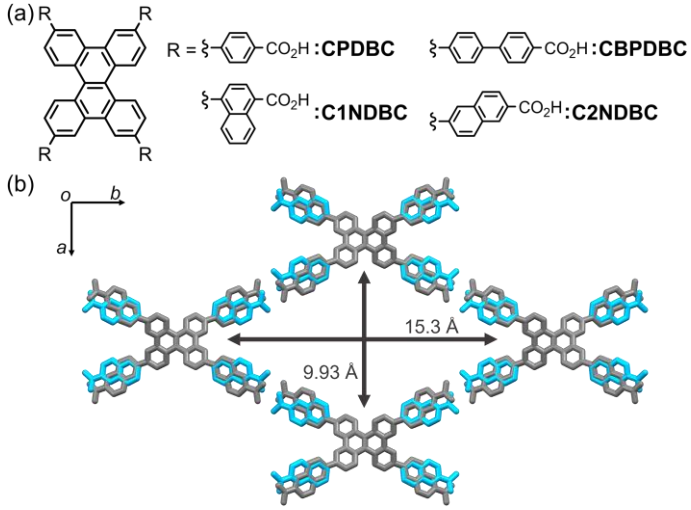

Figure 1. (a) Chemical structures of **C1NDBC** and **C2NDBC**. (b) Obtained crystal structure of **C2NDBC**. Naphthyl groups are disordered in 2 positions, major (gray) and minor (cyan).

In this presentation, we will show the obtained crystal structure, the behavior of the structural change, the stability of the structure and the porosity.

1) Y. Suzuki, N. Tohnai, A. Saeki, I. Hisaki, *Chem. Commun.* **2020**, *56*, 13369-13372.