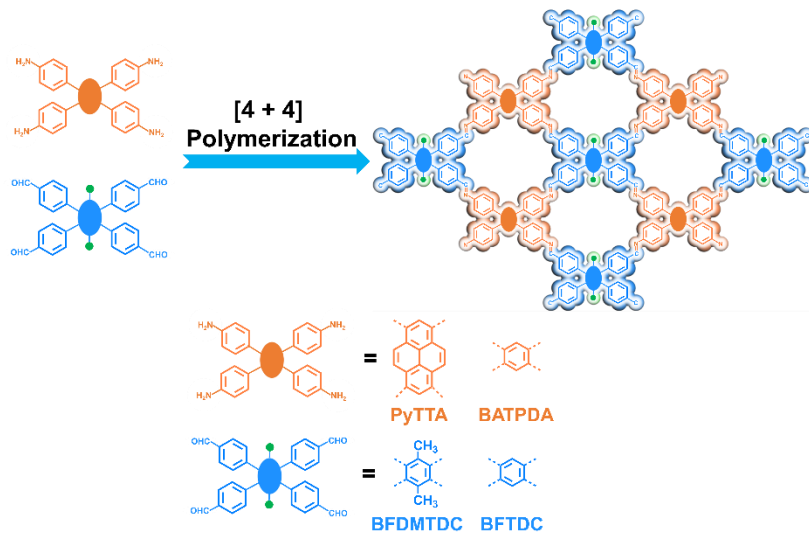


Title	共有結合性有機構造体（COFs）の合成と応用及びCOF誘導炭素材料に関する研究
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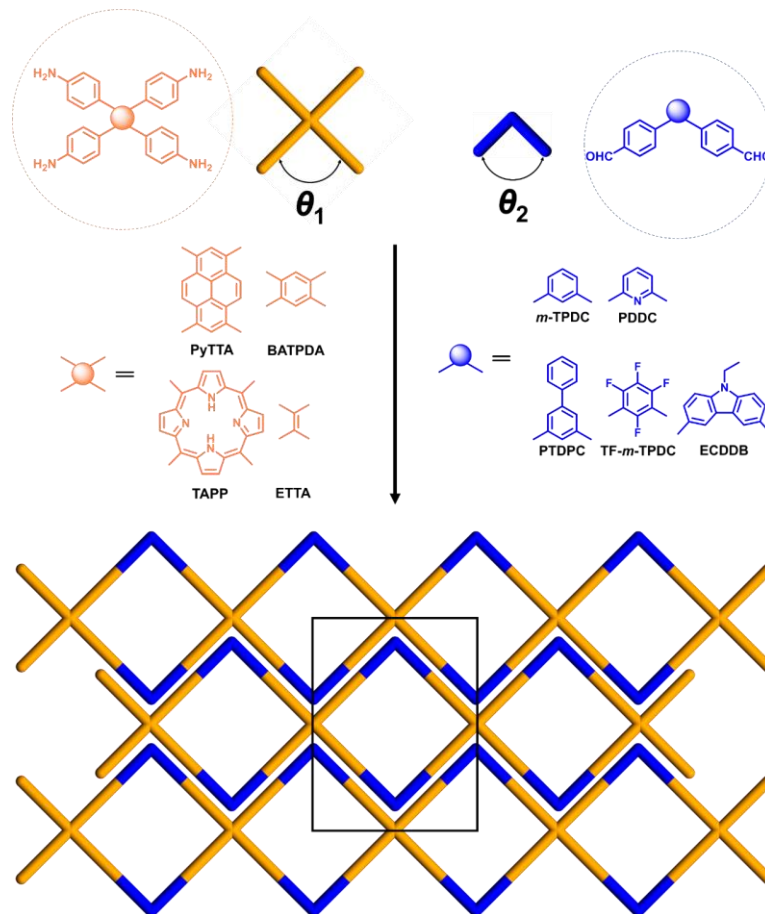
## Abstract

As an emerging class of ordered conjugated organic polymer materials, covalent organic frameworks (COFs) possess many unique properties such as predictability, inherent porosity, structural periodicity, large surface area, and high stability. The design and synthesis of COFs are based on the reticular chemistry and geometry of building blocks, which play a very significant role on the formation, topology and porosity of COF. Due to simultaneous polymerization and crystallization, it is key to keep the balance between dynamic error correction and non-covalent interlayer interaction. In this regard, the linkers in 2D COFs via [3 + 2], [3 + 3], [4 + 2] or [6 + 2] pathways should be small molecules in order to tune the free movement of monomers as well as thermodynamic and kinetic of system. However, forming 2D COFs via [4 + 4] pathway in the solution phase remains a big challenge when both of building units are tetrafunctional so that they can not twist or bend in a large range like bi- or tri-functional building blocks. On the other hand, stable and porous 1D COFs have not been reported due to the lack of relevant knowledges of controlling the covalent interaction and non-covalent interaction. However, tuning the dimension is an important and fundamental issue because 1D nanostructures always exhibit a distinct property with their 2D or 3D counterparts. In addition, owing to the thermal stability and designable heteroatoms, COFs also might be ideal precursors for metal-free carbon nanomaterials as electrocatalysts.

In this thesis, various 2D [4 + 4] COFs and 1D COFs were synthesized and characterized by Fourier transform infrared (FT-IR), solid-state NMR, powder X-ray diffraction (PXRD), high resolution transmission electron microscope (HR-TEM), X-ray photoelectron spectra (XPS), nitrogen sorption, computing simulation and so on.



**Scheme 1.** Schematics for the synthesis of 2D [4 + 4] COFs.



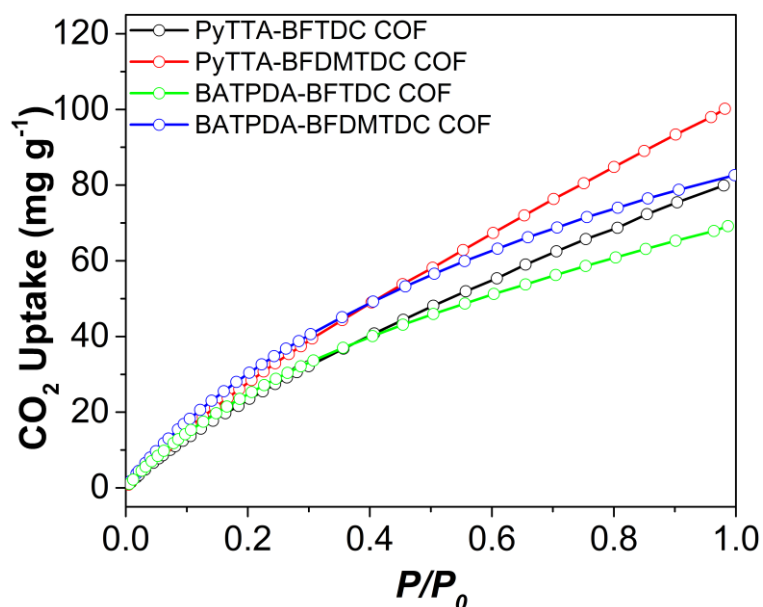
**Scheme 2.** A general designing strategy of 1D COFs.

2D [4 + 4] COFs were successfully synthesized in solvothermal method. Due to the good matching between building blocks, trade off between interlayer interaction and crystallization, and special connection pathway, high porosity (BET surface areas:

650~1100 m<sup>2</sup> g<sup>-1</sup>) and micropores (~1 nm) can be achieved. In addition, methyl groups can be decorated to modify the pore surface of 2D [4 + 4] COFs.

Moreover, 1D COFs were first reported. By designing a series of bifunctional V-type linkers to combine with tetragonal knots, the covalent extension is limited in only one direction. These microporous 1D COFs are very designable since they can be modified by various heteroatoms and functional groups and tuned by the angle of building blocks. Due to the high microporosity, 1D COF exhibits a good performance for CO<sub>2</sub> separation.

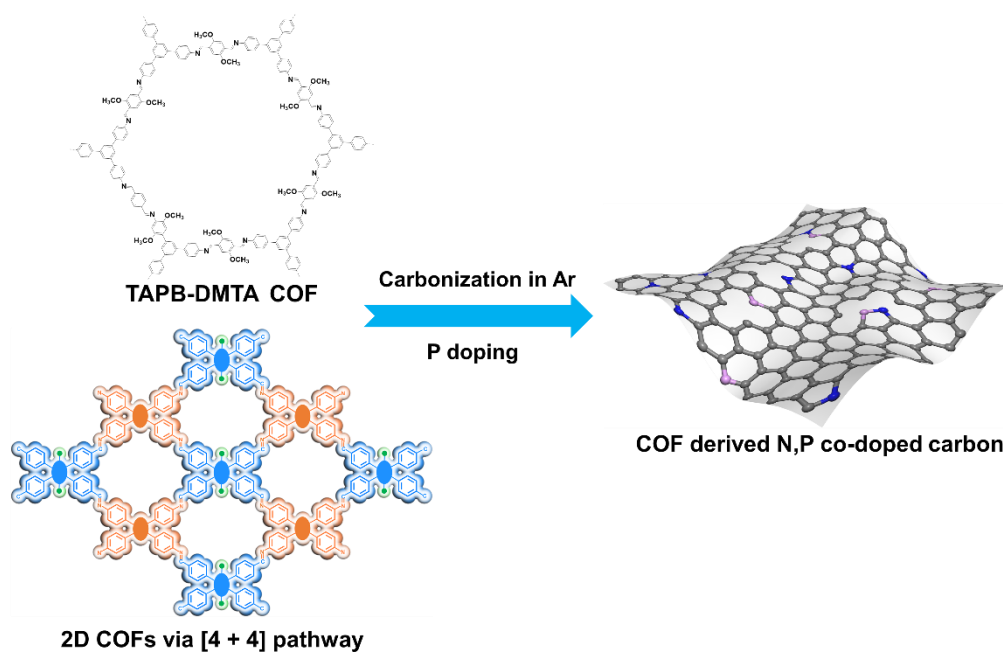
2D [4 + 4] COFs also exhibit good performances for CO<sub>2</sub> capture. Methyl group decorated COFs achieve an enhanced capture (100 mg g<sup>-1</sup>) and separation (w/w, 26/1, CO<sub>2</sub> over N<sub>2</sub>) of CO<sub>2</sub> at 1 atm and 273 K due to the increased microporosity and the strong affiliation between COFs and CO<sub>2</sub> induced by methyl groups.



**Scheme 3.** CO<sub>2</sub> uptake curves at 273 K for 2D [4 + 4] COF.

Porous and metal-free N,P co-doped carbons via carbonizing and phosphorizing 2D [4 + 4] COFs and TAPB-DMTA COF exhibit remarkable performances as ORR/HER electrocatalysts with the half-wave potential of 0.81 V vs. RHE in alkaline medium and overpotential of 260 mV at 10 mA cm<sup>-2</sup> in acid medium.

Various 2D and 1D COFs were designing and successfully synthesized under solvothermal conditions mainly considering the geometry, angle, functional group and symmetry of building blocks. The topology, dimension and pore surface can be tuned



**Scheme 4.** Fabrication process of 2D COF derived N,P co-doped carbon.

controllably. Especially, the finding of 1D COFs will overturn the traditional view that COFs are 2D and 3D rather than 1D. This will much enrich the diversity of COFs and promote the development of chemistry of COFs. Moreover, microporous 2D [4 + 4] COFs with methyl groups and 1D COFs show a good performance for CO<sub>2</sub> capture and separation, suggesting the promising prospect of these COFs and the effect of methyl groups for CO<sub>2</sub> application. On the other hand, the remarkable electrochemical performance of N,P co-doped carbons derived from 2D COFs will open a new way to synthesize high-performance metal-free electrocatalysts and broaden the application of emerging COF-derived carbons.

**Keywords:** Covalent organic frameworks; Topology; CO<sub>2</sub> capture; Dimension; Doped carbon.