Title	ヒドラゾン骨格を有する機能的共有結合性有機骨格の設計と合成
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Designed Synthesis of Functional Hydrazone-Linked Covalent Organic Frameworks

Doctoral Dissertation

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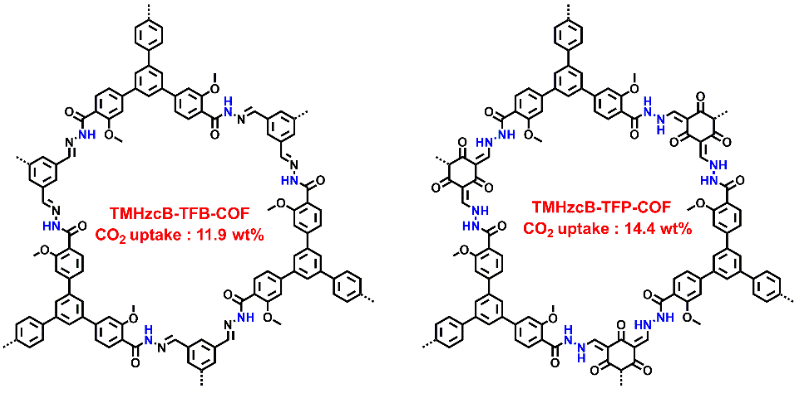
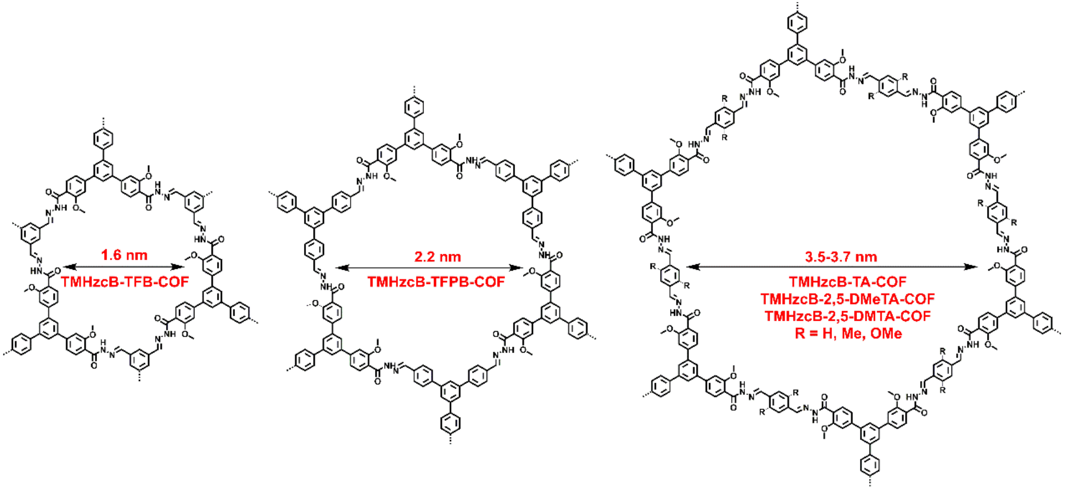
Research Content：

COFs are novel porous crystalline materials that are constructed by organic building units into regular structures with atomic precision through organic chemical reactions. Various reactions have been used to develop different type of COFs, such as B-O, C-N, and C-C linkages. The B-O based COFs were the first example of crystalline frameworks in 2005. Various structures and functions of these COFs were developed in the last few years. However, B-O based COFs are vulnerable in humid conditions, which limited their application in a wide field. To improve the stability of these frameworks, C-C and C-N linkage COFs including imine, azine, hydrazone, and phenazine, were gradually developed. The C-N based COFs usually show excellent chemical stability. Compared to imine, azine, and phenazine linkage, the hydrazone-linked COFs have active N-H units on the walls, which can easily achieve functional applications. For example, active N-H units on the walls of frameworks can enhance carbon dioxide absorption ability. Moreover, the hydrazone linkage can give non-planar linkages for frameworks, which can weaken strong π-π interaction that is derived from adjacent layers to afford light-emitting materials. Therefore, the hydrazone-linked COFs are very useful to design light-emitting and molecule sensing material. This research focused on the design and synthesis of functional hydrazone-linked COFs. Various novel hydrazone-linked COFs including hexagonal and tetragonal structure are designed and synthesized. All hydrazone-linked COFs were characterized using elemental analysis, Fourier transform infrared spectroscopy (FT IR), electronic absorption spectroscopy, field emission scanning electron microscopy (FE SEM), and powder X-ray diffraction measurements (PXRD).



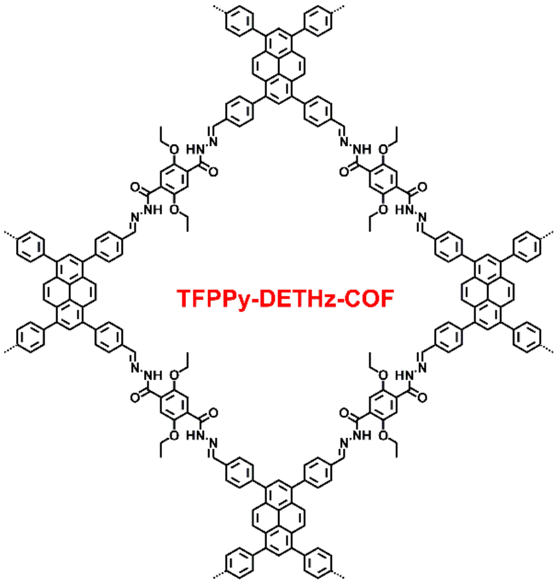
Scheme 1. TMHzcB-TFB-COF and TMHzcB-TFP-COF structures for carbon dioxide adsorption.

In chapter 2, the microporous hydrazone-linked COFs, TMHzcB-TFB-COF and TMHzcB-TFP-COF (Scheme 1), were synthesized through the condensation of 1,3,5-tris(3'-methoxy-4'-hydrazinecarbonylphenyl)benzene (TMHzcB) and 1,3,5-triformylbenzene (TFB)/triformylphloroglucinol (TFP) under solvothermal conditions. These COFs showed high crystallinity, permanent micropores, excellent thermal and chemical stability, and abundant heteroatom activated sites on the walls. Interestingly, TMHzcB-TFP-COF showed good carbon dioxide uptake of 14.4 wt% at 273 K and 1 bar.



Scheme 2. Structure of light-emitting hydrazone-linked COFs.

In chapter 3, a series of light-emitting hydrazone-linked COFs was successfully synthesized (Scheme 2). The pore size of hydrazone-linked COFs can be tunable from micropore (1.3 nm) to mesopore (3.7 nm) through changing different symmetrical linkers or knots. These COFs not only showed excellent porosity but also displayed good stability in organic solvents, water, acid and base conditions for 24 h at the room temperature. The light-emitting activity of COFs can be improved through introducing flexible building units or functional active groups including methoxy and methyl groups. As a result, the luminescence of COFs can be tuned over a broad range of colors from blue to green. Notably, COF-TMHzcB-2,5-DMeTA showed the highest fluorescence quantum yield over 19.5 % at solid state, which is higher than most reported azine, imine, and hydrazone based COFs.



Scheme 3. Structure of TFPPy-DETHz-COF.

In chapter 4, the hydrazone-linked TFPPy-DETHz-COF (Scheme 3) was successfully constructed through the Schiff-base condensation reaction under solvothermal conditions. The N-H bond in linkage on the walls can be deprotonated by fluoride anion via acid-base reaction to form an anionic species, which can eliminate the nitrogen-related fluorescence quenching pathway. The addition of fluoride anion eliminates the photoinduced electron transfer pathway and directly improves the light-emitting activity. Surprisingly, the emission is switched on in the presence of fluoride anion and its intensity is enhanced in a linear proportion to the amount of fluoride anion. The absolute fluorescence quantum yield increases to 17%, which is 3.8-fold as high as that of as-synthesized TFPPy-DETHz-COF. In contrast, other halogen anions, including chloride, bromide, and iodide, retain inactive. The detection limit of fluoride anions can be down to a ppb level.

Research Purpose：

Various novel hydrazone-linked COFs including hexagonal and tetragonal structure with high porosity, crystallinity, and stability, can be designed and synthesized. The pore size of COFs can be adjustable from micropores (1.6 nm) and mesopores (3.7 nm), which also

enriches the diversity of the COFs' structure. Moreover, fluorescence COFs showed the highest quantum yield than most reported COFs through changing flexible units and auxiliary chromophore. I also used the pinpoint surgery on the N−H unit of the hydrazone-linked COFs and the first example of COFs for anion sensing. The investigated results displayed in this thesis demonstrate functional hydrazone-linked COFs that open a new phase for not only high adsorptive media but also light-emitting materials for chemical sensing. The active N-H sites can be possibly applied in the removal and separation of molecules through hydrogen bond interaction in the future.

Keyword: Covalent organic frameworks, carbon dioxide, light-emitting, pinpoint surgery, and anions.

Research Accomplishments：

1. **Zhongping Li**, Ning Huang, Ka Hung Lee, Yu Feng, Shanshan Tao, Qiuhong Jiang, Yuki Nagao, Stephan Irle and Donglin Jiang. Light-emitting covalent organic frameworks: fluorescence improving via pinpoint surgery and selective switch-on sensing of anions. *J. Am. Chem. Soc.* **2018**, *140*, 12374−12377.
2. Ping Wang, Qing Xu, **Zhongping Li**, Weiming Jiang, Qiuhong Jiang and Donglin Jiang. Exceptional iodine capture in two-dimensional covalent organic framework. *Adv. Mater*. **2018**, *30*, 1801991.
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4. Design and light-emitting functions of hydrazone-linked covalent organic frameworks. 日本化学会北陸地区講演会と研究発表会. **Dec. 2017**, Ishikawa, Japan. Style of Presentation: Poster.
5. Design and light-emitting functions of hydrazone-linked covalent organic frameworks. The 98th Annual Meeting. **Mar. 2018**, Funabashi, Japan. Style of Presentation: Oral.
6. Design and light-emitting functions of hydrazone-linked covalent organic frameworks. 10th Singapore International Chemistry Conference 2018 (SICC-10). **Dec**. **2018**, Singapore. Style of Presentation: Poster.
7. Designing covalent organic frameworks for light emitting and anion Sensing. The 99th Annual Meeting. **Mar**. **2019**, Kobe, Japan Style of Presentation: Oral.