

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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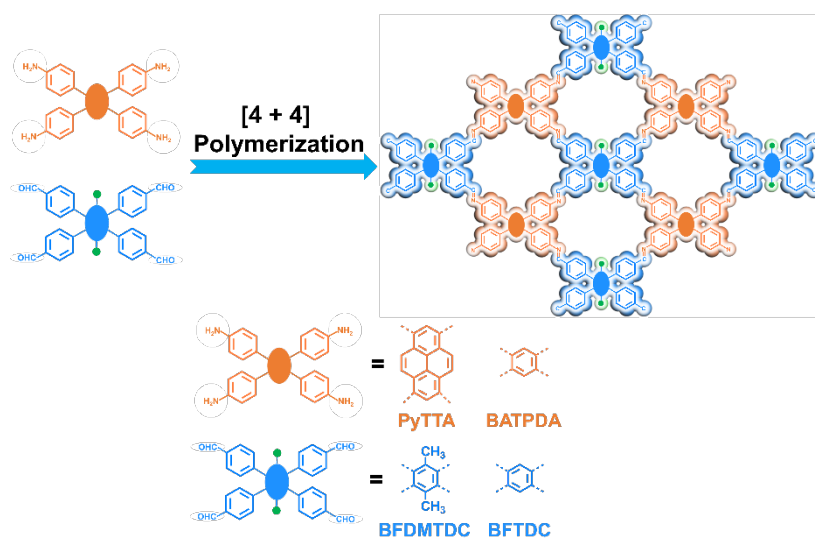
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論文題目	Synthesis and Application of Covalent Organic Frameworks (COFs) and COF Derived Carbons		
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論文の内容の要旨

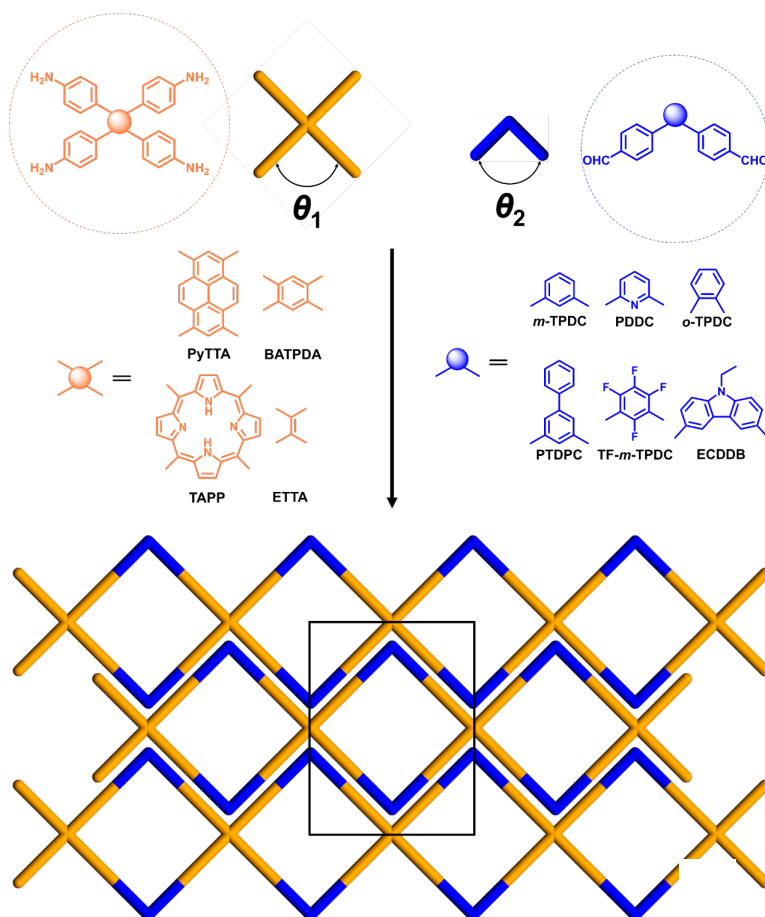
As an emerging class of ordered conjugated organic polymer materials, covalent organic frameworks (COFs) possess many unique properties such as predictability, inherent porosity, structural periodicity, large surface area, and high stability. The design and synthesis of COFs are based on the reticular 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.



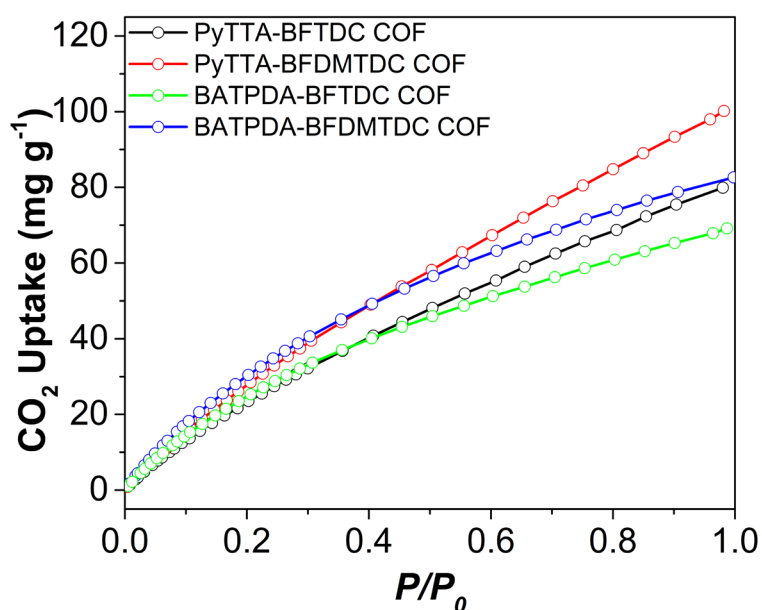
Scheme 2. A general designing strategy of 1D COFs.

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 m² g⁻¹) 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 CO₂ separation.

2D [4 + 4] COFs also exhibit good performances for CO₂ capture. Methyl group decorated COFs achieve an enhanced capture (100 mg g⁻¹) and separation (w/w, 26/1, CO₂ over N₂) of CO₂ at 1 atm and 273 K due to the increased microporosity and the strong affiliation between COFs and

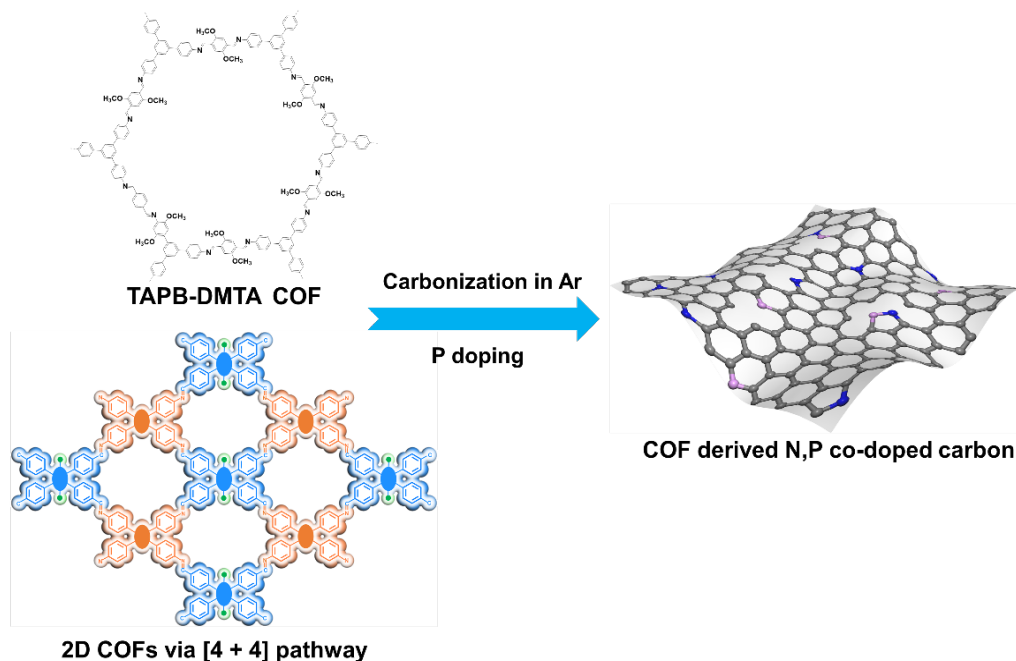


Scheme 3. CO₂ uptake curves at 273 K for 2D [4 + 4] COF.

CO₂ induced by methyl groups.

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⁻² in acid medium.



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

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 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 CO₂ capture and separation, suggesting the promising prospect of these COFs and the effect of methyl groups for CO₂ 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; CO₂ capture; Dimension; Doped carbon.

論文審査の結果の要旨

本博士学位論文は、新規な低次元の共有結合性有機構造体 (covalent organic frameworks: COFs) の創製とその応用 (水素発生触媒や CO₂ 分離膜など) に関するものである。これまで多孔質材料といえばゼオライトやメソポーラスシリカなどの無機材料が一般的であったが、近年、新たな多孔質材料として金属-有機構造体 (metal organic frameworks: MOFs) や COFs が注目されている。特に COFs は、金属元素を含まない有機物で構成され、優れた熱安定性を示すため、ガス貯蔵や電気化学触媒など様々な応用が期待されている。

一般に、2次元 COFs は、*m* 官能性モノマー (ノット) と *n* 官能性モノマー (リンカー) とを縮合反応によって共有結合させていくことで合成され、 $[m + n]$ の組み合わせとしては、 $[3 + 2]$ 、 $[3 + 3]$ 、 $[4 + 2]$ 、 $[6 + 2]$ などが報告されている。しかし、より細孔径を小さくするなど、2次元骨格構造の更なる精密制御には、新たなモノマーの開発と合成経路の開拓が重要となる。

そこで YANG 氏は、4, 4', 4'', 4'''-(pyrene-1, 3, 6, 8-tetra-yl) tetraaniline (PyTTA)、4', 5'-bis(4-aminophenyl)-1, 1': 2', 1''-terphenyl-4, 4''-diamine (BATPDA)、4', 5'-bis(4-formylphenyl)-1, 1': 2', 1''-terphenyl-4, 4''-dicarbaldehyde (BFTDC)、4', 5'-bis(4-formylphenyl)-3', 6'-dimethyl-[1, 1': 2', 1''-terphenyl]-4, 4''-dicarbaldehyde (BFDMTDC) などの 4 官能性モノマーを合成し、それらを縮合させることで、PyTTA-BFTDC、PyTTA-BFDMTDC、BATPDA-BFTDC、BATPDA-BFDMTDC などの $[4 + 4]$ 2次元 COFs を創製することに成功したほか、1, 1': 3', 1''-terphenyl-4, 4''-dicarbaldehyde (*m*-TPDC) などの非直線的 2 官能性モノマーを合成し、 $[4 + 2]$ 1次元 COFs の合成も試み、PyTTA-*m*-TPDC や BATPDA-*m*-TPDC などの 1次元 COFs の創製にも成功した (第 2 章)。

続いて、合成した PyTTA-BFTDC、PyTTA-BFDMTDC、BATPDA-BFTDC、BATPDA-BFDMTDC の 4 種類の $[4 + 4]$ 2次元 COFs の CO₂ 吸着性能を調べ、従来の COFs と比較しても高い性能を有していることを明らかにした。また、分子構造にメチル基を有する BFDMTDC を用いた 2次元 COFs のほうがメチル基の無い BFTDC を用いた 2次元 COFs よりも CO₂ 吸着性能は高いことを見出した (第 3 章)。

さらに、 $[4 + 4]$ 2次元 COFs を炭化し、リンをドーピングすることによって、含窒素・リンカーボンを作製し、その酸素還元反応 (ORR) や水素発生反応 (HER) に対する触媒活性を調べたところ、高い電気伝導率、多孔性、窒素とリンの最適空間配置、および高い欠陥密度などの特徴から、ORR と HER の両方に活性を有する二機能性触媒として有望であることを示した (第 4 章)。

本博士学位論文は、COF ライブラリーに新たな一頁を加えることに資するものであり、幅広い関連分野において学術的に貢献するところが大きい。よって博士 (マテリアルサイエンス) の学位論文として十分価値あるものと認めた。