JAIST Repository
https://dspace.jaist.ac.jp/

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
Author(s)	Yang, Chao
Citation	
Issue Date	2019-09
Type	Thesis or Dissertation
Text version	ETD
URL	http://hdl.handle.net/10119/16189
Rights	
Description	Supervisor:前之園　信也，先端科学技術研究科，博士

JAIST
JAPAN
ADVANCED INSTITUTE OF
SCIENCE AND TECHNOLOGY

Japan Advanced Institute of Science and Technology

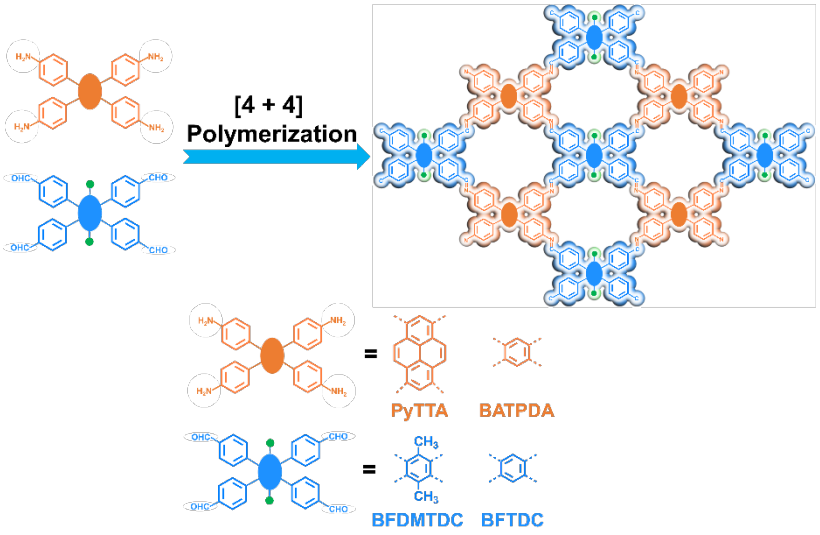
氏名	YANG, Chao		
学位の種類	博士(マテリアルサイエンス)		
学位記番号	博材第 478 号		
学位授与年月日	令和元年 9 月 24 日		
論文題目	Synthesis and Application of Covalent Organic Frameworks (COFs) and COF Derived Carbons		
論文審査委員	主査	前之園 信也	北陸先端科学技術大学院大学 教授
		藤本 健造	同 教授
		高村 由起子	同 准教授
		谷池 俊明	同 准教授
		牧浦 理恵	大阪府立大学工学研究科 准教授

論文の内容の要旨

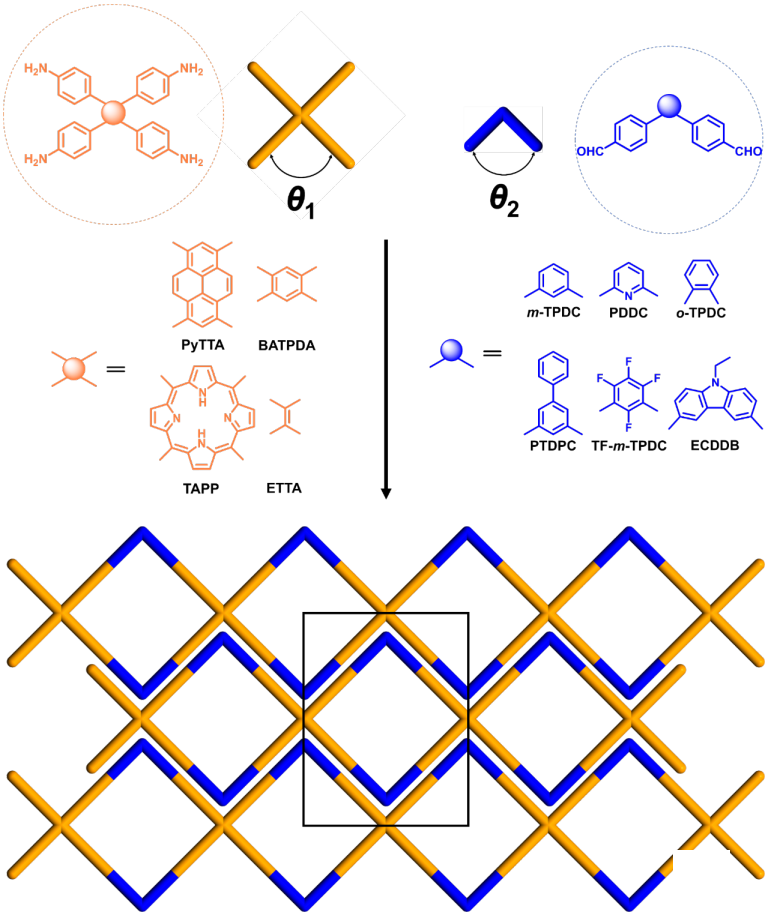
As an emerging class of ordered conjugated organic polymer materials, covalent organic frameworks (COFs) possess many unique properties such as predictability, inherent porosity, structural periodicity, large surface area, and high stability. The design and synthesis of COFs are based on the reticular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



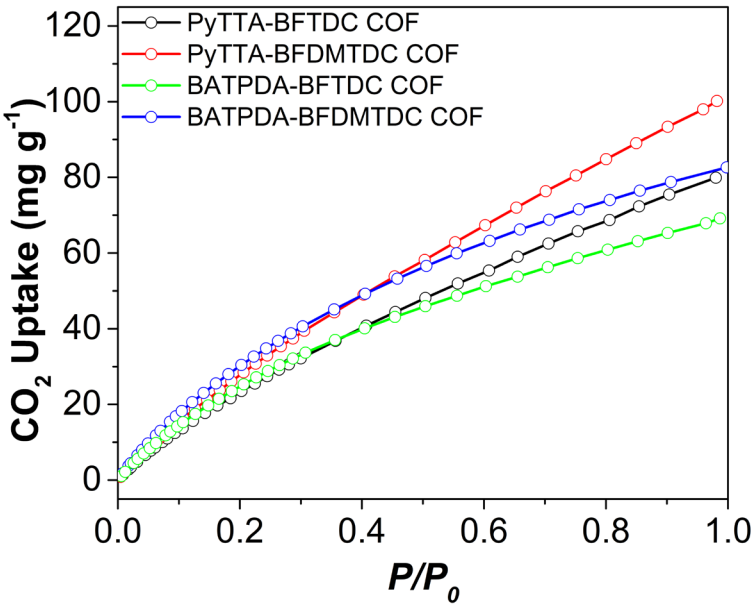
Scheme 2. A general designing strategy of 1D COFs.

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 patyway, high porosity (BET surface areas: 650~1100 m^2 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 CO_2 separation.

2D [4 + 4] COFs also exhibit good performances for CO_2 capture. Methyl group decorated COFs achieve an enhanced capture (100 mg g^{-1}) and separation (w/w, 26/1, CO_2 over N_2) of CO_2 at 1 atm and 273 K due to the increased microporosity and the strong affiliation between COFs and

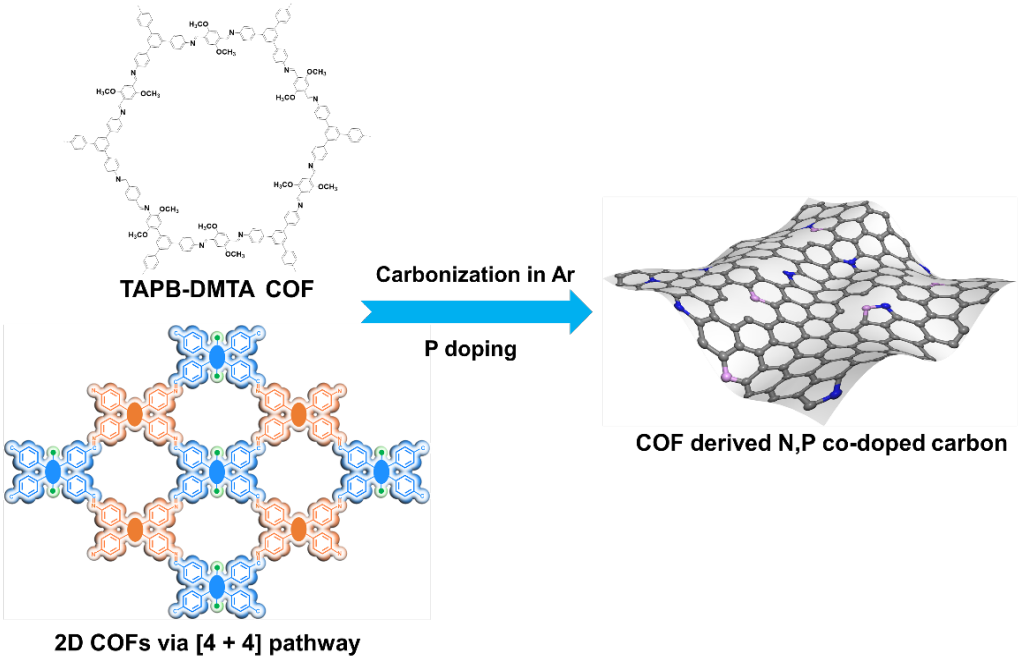


Scheme 3. CO_2 uptake curves at 273 K for 2D [4 + 4] COF.

CO_2 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 CO_2 capture and separation, suggesting the promising prospect of these COFs and the effect of methyl groups for CO_2 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_2 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CO_2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-tetrayl)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CO_2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CO_2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、リンをドープすることによって、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。