

Title	ヒドロ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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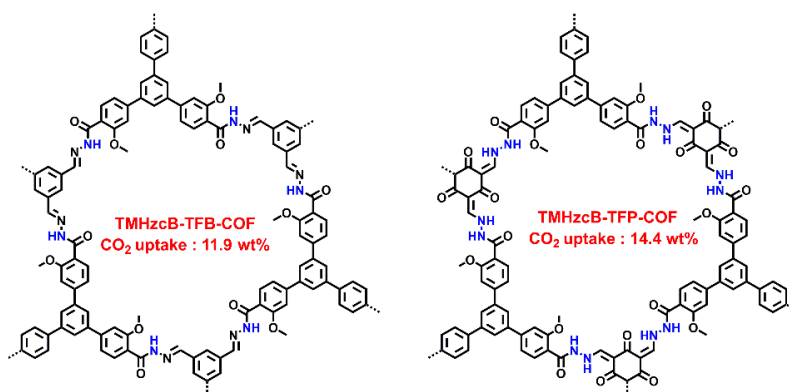
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論文の内容の要旨

Research Content :

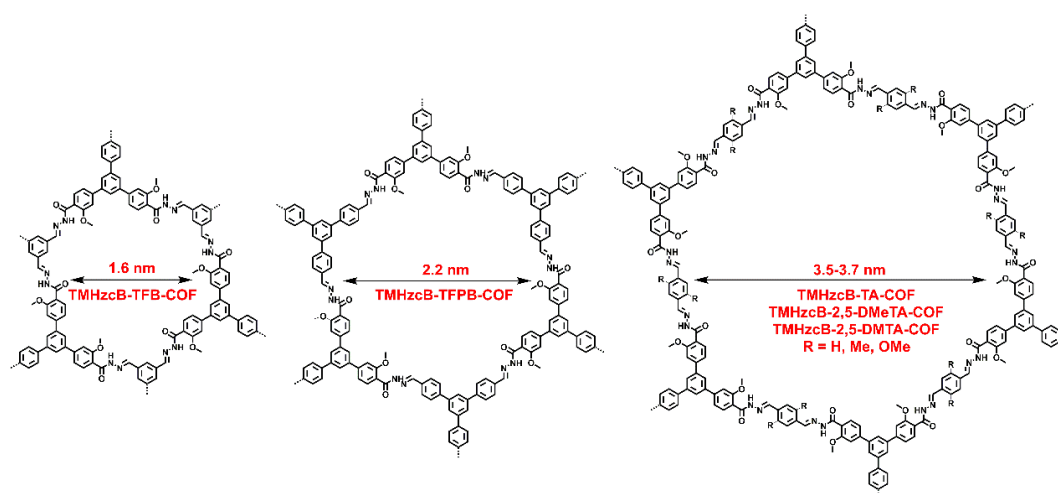
COFs are novel porous crystalline materials that are constructed by organic building units into regular structures with atomic precision through organic chemical reactions. Various reactions have been used to develop different type of COFs, such as B-O, C-N, and C-C linkages. The B-O based COFs were 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).



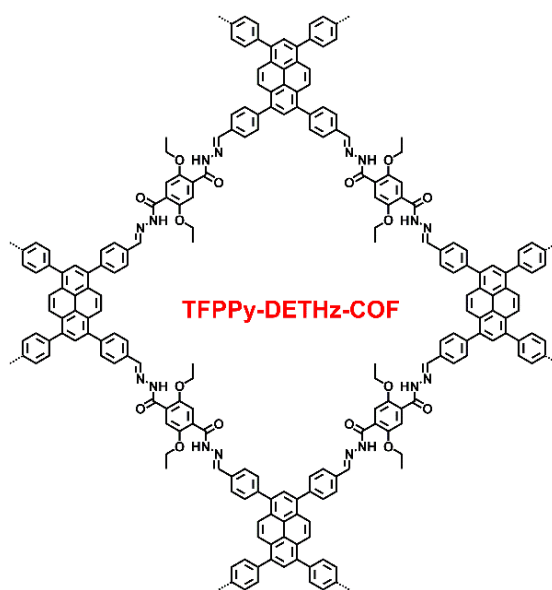
Scheme 1. TMHzcB-TFB-COF and TMHzcB-TFP-COF structures for carbon dioxide adsorption.

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.

論文審査の結果の要旨

本論文では、ヒドラゾン骨格を有する共有結合性有機骨格構造(COF)を多数合成し、CO₂吸蔵、発光およびアニオンセンシング（フッ化物イオン）に関する機能性 COF を新規に創成した。

COF は多孔性材料の 1 つとして知られ、分子レベルで構成ブロックを精密に組み立てることが可能である。これまでに機能性 COF では、ガス吸蔵、触媒、プロトン伝導、TNT センサー、pH センサー、アンモニアセンサー、電気伝導体等が報告されている。これまでに報告された機能性 COF の中には水に対して不安定であるものが多く、水や酸・アルカリ下で安定な機能性 COF の開発が課題となっている。彼は水や酸・アルカリ下において骨格が安定で、発光にとって有利な骨格の柔軟性を有するヒドラゾン骨格に着目し、機能性 COF の開発を行った。

第 2 章では、細孔サイズが異なるヒドラゾン骨格を有する結晶性 COF を 2 種合成し、273K において CO₂ を 14.4 wt% 取り込む COF が見出された。これらの COF は酸やアルカリ下においても骨格が安定であることが明らかにされた。この値はチャンピオンレコードではないが、細孔サイズと CO₂ の吸蔵量の傾向から、細孔サイズが大きいほど CO₂ を必ずしも多量に含有するわけではなく、COF の細孔壁の塩基点が CO₂ の吸蔵に重要な役割を果たすことが明らかにされた。

第3章では、ヒドラゾン骨格を有する結晶性の発光性 COF を5種合成することに成功した。これらの COF は酸やアルカリ下においても骨格が安定であることが明らかにされた。発光の量子収率を向上させるために、バルキーな置換基を骨格に導入し、 $\pi-\pi$ スタッキングを弱めることで、ヒドラゾン骨格の COF でチャンピオンレコードである 19.5%の発光量子収率を達成した。また、細孔の大きさや骨格の柔軟性の違いで発光波長を緑（大きな細孔）から青（小さな細孔）の範囲で制御できることが明らかにされた。

第4章では、ペリレンを導入したヒドラゾン骨格を有する結晶性の COF を合成し、フッ化物イオンのセンシングが示された。得られた COF は酸・アルカリにおいて安定であり、ハロゲン族の中でフッ化物イオンにのみ発光強度が選択的に応答し、発光強度を増大させることが明らかにされた。2種のハロゲンイオンを混合させても、フッ化物イオンのみに応答した。また、酸を添加することで発光強度を元に戻すことが可能であり、ppb レベルのフッ化物イオンでも十分にセンシングできることが見出された。

以上から、本論文は、機能性 COF の分野について新しい知見を与えたものであり、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。