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研究課題名 (和文) Porous metal-organic frameworks with electrically controlled gates: hosts having directional control over the transmission of the guest molecules

研究課題名 (英文) Porous Metal-organic Frameworks with Electrically Controlled Gates: Hosts having Directional Control over the Transmission of the Guest Molecules

研究代表者

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研究成果の概要 (和文) : One of the target FMOFs, having flip-flop rotatable component only on pillars, was obtained and measurements showed good ferroelectric response. Recently, crystal structure of a new FMOF having all edges functionalized with rotatable component was obtained. Ferroelectric measurements are underway.

研究成果の概要 (英文) : The main goal of this research is to fabricate ferroelectric metal-organic frameworks (FMOFs) having electric field-induced flip-flop rotatable components on all edges. This promotes controllable unidirectional transmission of guest molecules and further provides sites for sequencing chemical reactions. One of the target FMOFs, having flip-flop rotatable component only on pillars, was obtained near the end of FY2014 and measurements on its single crystals showed good ferroelectric response. The syntheses of new building blocks and the fabrication of MOF having all edges functionalized with rotatable component were started in mid-FY2015. Recently, crystal structure of the new MOF was obtained. Ferroelectric measurements on its single crystals are underway and will be reported in due course.

研究分野： Materials Chemistry

キーワード： metal-organic framework supramolecular assembly ferroelectricity host-guest chemistry coordination chemistry unidirectional transmission

1. 研究開始当初の背景

The field of nanochemistry is rapidly expanding, and will lead to facile routes to construct sophisticated nano-scale materials. Metal-organic frameworks (MOFs) are an exciting class of materials with excellent potential for real applications. They are coordination polymers of metal ions or clusters and organic bridging ligands that organize into functional porous networks. This research field has been a hot topic to researchers due to the vast applications in gas storage, catalysis and sensor, etc.. MOFs are especially best-known for their application in hydrogen storage owing to their extremely high surface area. Ferroelectrics, on the hand, are another class of materials that have been of interest due to their wide range of applications including random access memories (FeRAMs), electromechanics and microsensors. They are polar substances of either crystalline or polymeric solids, or liquid crystals. These materials response to the direction of the external electric field spontaneously and can be polarized in a reversible manner. A significant phenomenon of ferroelectrics is that they have a remnant polarization even when the applied field becomes zero. There are three types of behaviors that define the origin of ferroelectricity: order-disorder, displacive and proton-transfer. This research aims to combine the intriguing properties of MOFs and ferroelectrics and make a new series of materials that is in the order-disorder category. Based on our previous study on similar ferroelectric system, by applying electrical potential to the sample at elevated temperatures, the polar component can be polarized reversibly with respect to the direction of the electric field (Figure 1).

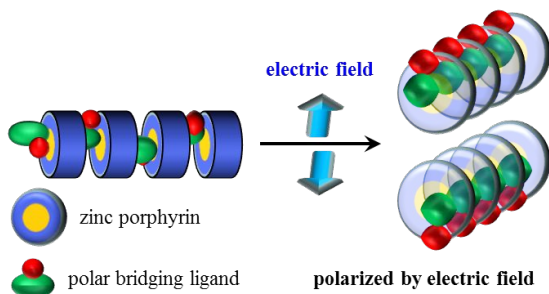


Figure 1. Schematic representation of the one-dimensional coordination polymer and the polarization of the bridging ligands when subject to the external electric field.

MOFs can act as hosts for storing molecules and the guests would enter or exit the frameworks omnidirectionally under normal circumstance (Figure 2). The target ferroelectric MOFs are mesoporous and contain polar moieties that would function as “gates”. By switching the direction of the external electric field, the polarizable “gates” would “open” or “block” the route for the guest molecules to enter or exit the **FMOFs**, resulting in a unidirectional transmission (see Figure 3 for graphical details).

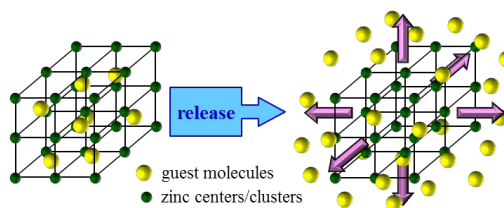


Figure 2. Schematic representation of the omnidirectional transmission of the guest molecules

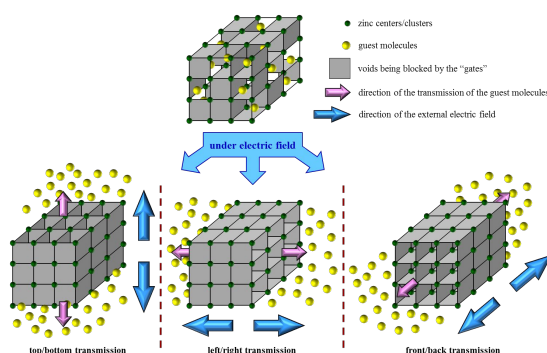


Figure 3. Schematic representation of the unidirectional transmission of the guest molecules when subject to the external electric field.

2. 研究の目的

The ultimate goal is to prepare three-dimensional ferroelectric MOFs (**FMOFs**) with the ability to directionally control the guest molecules from entering and exiting the frameworks upon the application of external electric field. The target **FMOFs** are expected to have high surface areas and pore volumes and their storage capacity for gaseous molecules will be investigated at various temperatures after confirming the framework structures. The most significant scientific characteristic of this research is that the **FMOFs** have rotatable frame that can serve as “gates”, leading to the potential of

controlling the direction of the transmission of the guest molecules. Having directional control of the guest molecules would open up the opportunity of using the voids as sites for performing reactions in sequence. For example, **A** (enter from top/bottom) is stored inside the **FMOFs** first and introducing **B** (enter from left/right) after would yield **A-B**, followed by the addition of **C** (enter from front/back) to obtain **A-B-C** in the correct sequence (Figure 4). Moreover, it is facile to tune the properties of the **FMOFs**, simply by modifying the polar component of the bridging ligands. To the best of our knowledge, no examples of such kind of MOFs have been published to date. The target **FMOFs** are expected to have the ability not only to induce unidirectional transmission of the guest molecules, but also to provide sites for sequencing reactions.

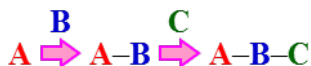


Figure 4. Schematic representation of a sequencing reaction

3. 研究の方法

In order to get the research started, it is necessary to first synthesize the building blocks, which are bridging ligands having polar linker with end groups of dicarboxylic acid or dipyridine (2,1,3-benzothiadiazole-4,7-dicarboxylic acid, **L1**, and 4,7-di-4-pyridyl-2,1,3-benzothiadiazole, **L2**). Incorporation of Zn(II) salt with the ligands would self-assemble into the target **FMOFs**. The MOFs themselves might be good ferroelectric materials given their extended polar structure and thus the polarization of the benzothiadiazole moieties within the frameworks will be scrutinized by extensive ferroelectric measurements. This is also to confirm the open-and-close character of benzothiadiazole moieties functioning as a “gate”. Moreover, the pore sizes and surface areas will be determined by gas adsorption measurements. Studies on the capability of the **FMOFs** having directional control over the transmission of the guest molecules upon the application of electric field will be the ultimate focus of this project.

Two different approaches were carried out to construct the self-assembled three-dimensional mesoporous frameworks

(**FMOF-1** and **FMOF-2**) that will be used as hosts for this project. A graphic representation of the synthetic routes to reach the intermediate goal is as illustrated in Figure 5.

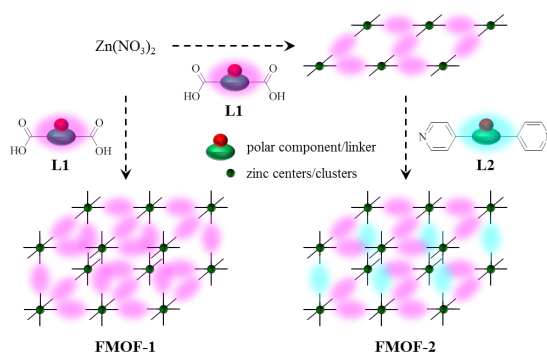


Figure 5. Schematic representation of the formation of **FMOF-1** and **FMOF-2**.

Attempts to obtain **FMOF-1** were done through a one-pot synthesis as depicted by the left route in Figure 5. Zinc(II) nitrate reacted with the polar dicarboxylic-acid-containing ligand **L1**. The zinc centers first combined with the carboxylate end groups of ligand **L1**, leading to the formation of tetranuclear supertetrahedral zinc clusters that further organized into three-dimensional mesoporous framework **FMOF-1** through the polar linker of the bridging ligand. Hydrothermal technique, a good method for getting single crystals of MOFs for X-ray diffraction structural analyses, was utilized to perform the reaction. The same hydrothermal technique was used to prepare **FMOF-2** by reacting zinc(II) nitrate with **L1** and dipyridyl ligand **L2** *in situ*. Ligand **L2** functioned as a pillar and that led to the assembly of the two-dimensional network into the target three-dimensional framework **FMOF-2**. Prior to undertaking the ferroelectric measurements, the framework structures of **FMOF-1** and **FMOF-2** were investigated by X-ray crystallography in order to confirm the syntheses being successful.

Based on our previous work on similar ferroelectric system, it is believed that the target **FMOFs** are good candidates to exhibit ferroelectric behavior. In fact, it is important for **FMOF-1** and **FMOF-2** to show ferroelectric-like response upon the application of external electric field. Such phenomenon would indicate the polar moieties within the frameworks can be polarized reversibly and the “gates” can be “opened” or “closed” in accordance

to the direction of the electric field. Crystals of the **FMOFs** will undergo extensive ferroelectric measurements. The tentative setup involves having both ends of the sample crystals being connected to the electrodes (prepared from dried gold paste on a piece of ceramic substrate) through gold wires (Figure 6).

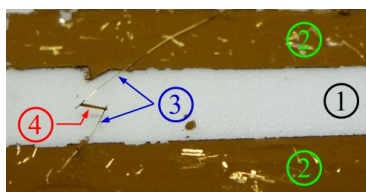


Figure 6. 1 = ceramic substrate, 2 = gold electrodes (prepared from dried gold paste), 3 = gold wire, 4 = sample crystal

Once the **FMOFs** are proven to be ferroelectrics, the next important task is to find evidence for supporting the frameworks being capable of accepting and releasing guest molecules unidirectionally with the use of electric field. It is important to first understand the pore volumes and sizes of the frameworks, which can be determined by taking the gas adsorption measurements. **FMOF-1** and **FMOF-2** will then undergo a variety of investigations against different gaseous molecules and organic/inorganic compounds in solution, which will be monitored by the second harmonic generation (SHG) measurements while applying electric field. It is believed that the SHG signals will be able to denote any directional or angular difference in the transmission of the guest molecules.

FMOF-1 and **FMOF-2** are classified as the first generation **FMOFs** of this research. According to the pore sizes of the frameworks, benzothiadiazole might not be big enough to function as a “gate” and cover the void. Therefore, the size of the “gates” needs to be tuned correspondingly. If satisfactory results could be observed with the proposed system, i.e., if the polar moieties within the frameworks can be polarized reversibly in regard to the direction of the external electric field and the ferroelectric data support the “gates” having the open-and-close character, this project will be carried on further by modifying the linkers with bigger polarizable component.

4. 研究成果

The main goal of this research is to fabricate ferroelectric metal-organic frameworks (**FMOFs**) having electric field-induced flip-flop rotatable components on all edges. This could lead to controllable unidirectional transmission of guest molecules and further provide sites for sequencing chemical reactions. Single crystals of both **FMOF-1** and **FMOF-2** were grown by the hydrothermal method and their respective structural frameworks were confirmed by X-ray crystallography. Ferroelectric measurements on the single crystals of **FMOF-2**, having flip-flop rotatable component only on pillars, revealed good response at room temperature (Figure 7). Our previous work on similar electric field-induced flip-flop rotational system observed ferroelectric hysteresis behavior only at high temperatures, so the result of **FMOF-2** is considered as a breakthrough. Ferroelectric measurements on the single crystals of **FMOF-1** and gas adsorption measurements on both **FMOFs** are underway and the results will be reported in due course.

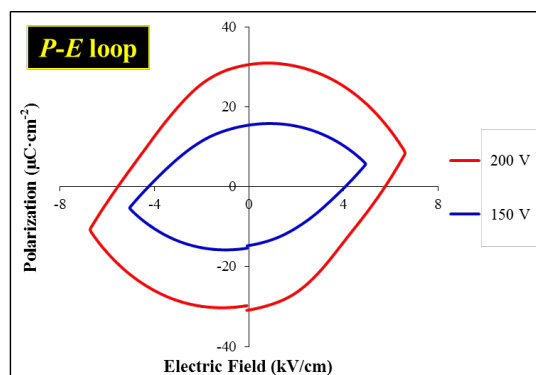


Figure 7. The *P-E* loop of **FMOF-2** recorded at 150 and 200 V, 0.1 Hz, 298 K and 50 cycles

5. 主な発表論文等

(研究代表者、研究分担者及び連携研究者には下線)

〔雑誌論文〕(計 0 件)

〔学会発表〕(計 8 件)

Presenter: Joseph Hui

Title: Ferroelectric Coordination Polymers Self-assembled from Liquid Crystalline Zinc(II) Porphyrin and Dipyridyl Ligands

Conference: The International Chemical Congress of Pacific Basin Societies

Location: Hawaii Convention Center,

Hawaii, USA

Date: December 15th-20th, 2015

Presenter: Shinya Uchino

Title: Development of Ferroelectric Zn Porphyrin Complexes Cross-Linked by Dipolar Axial Ligands

Conference: 日本化学会 第 96 春季年会

Location: 同志社大学 京田辺キャンパス

Date: March 24th-27th, 2016

Presenter: Ryosuke Yamamoto

Title: 大きな永久双極子を有する液体の超分子ゲル化と誘電特性

Conference: 日本化学会 第 95 春季年会

Location: 日本大学 理工学部船橋キャンパスノ薬学部

Date: March 26th-29th, 2015

Presenter: Ryosuke Yamamoto

Title: 機能性液体の超分子ゲル化と誘電特性の制御

Conference: 第 52 回化学関連支部合同九州大会

Location: 北九州国際会議場

Date: June 27th-28th, 2015

Presenter: Ryosuke Yamamoto

Title: 極性芳香族液体の超分子ゲル化と特異な誘電ヒステリシス特性

Conference: 第 64 回高分子討論会

Location: 東北大学 川内キャンパス

Date: September 15th-17th, 2015

Presenter: Ryosuke Yamamoto

Title: Supramolecular Gelation of Polar Aromatic Liquids and Their Dielectric Polarization Properties

Conference: 九州韓国ジョイントシンポジウム

Location: International Center, Dong-A University Bumin Campus, Busan, Korea

Date: November 12th-14th, 2015

Presenter: Ryosuke Yamamoto

Title: 極性芳香族液体の超分子ゲル化と誘電特性の制御

Conference: 高分子学会九州支部

Location: 休暇村「志賀島」, 福岡市

Date: December 3rd-4th, 2015

Presenter: Ryosuke Yamamoto

Title: Supramolecular Gelation of Functional Liquids and Their Dielectric Properties

Conference: The International Chemical Congress of Pacific Basin Societies

Location: Hawaii Convention Center, Hawaii, USA

Date: December 15th-20th, 2015

〔図書〕(計 0 件)

〔産業財産権〕

○出願状況(計 0 件)

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発明者:

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番号:

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〔その他〕

ホームページ等

6. 研究組織

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