

科学研究費助成事業 研究成果報告書

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研究課題名(和文) Investigation of gated adsorption with time-resolved imaging using XFEL (X-ray Free Electron Laser)

研究課題名(英文) Investigation of gated adsorption with time-resolved imaging using XFEL (X-ray Free Electron Laser)

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交付決定額(研究期間全体)：(直接経費) 3,300,000円

研究成果の概要(和文)：研究の目的は、Spring-8の時にさくらX線自由電子レーザー(XFEL)を使用して解決回折を観察することです。XFELは、時間分解回折が可能な超短パルスX線レーザーです。私たちは、多孔性配位高分子(のPCP)にゲート開口挙動の時間発展を研究するXFELを利用したかったです。のPCPは、ガス吸着することができる結晶性固体、構造変形に伴う分離のユニークなクラスです。ガス投与装置と1レーザーパルスX線回折を利用することにより沿って、私たちは、COガスに銅カゴメPCPの呼吸動作を可視化するために管理しています。我々の研究結果は、ガス分離および保存の領域に影響を与えます。

研究成果の概要(英文)：The objective of the research is to observe time resolved diffraction using the Sakura X-ray Free Electron Laser (XFEL) at Spring-8. XFEL is an intense pulsed X-ray laser which is capable of time-resolved diffraction. We wanted to utilize the XFEL to study the time evolution of gate opening behaviour in porous coordination polymers(PCPs). PCPs are a unique class of crystalline solids which are capable of gas adsorption, separations along with structural deformation. By utilizing one laser pulse X-ray diffraction and along with a gas dosing apparatus, we have managed to visualize breathing behaviour of Copper Kagome PCP in CO gas. Our research results will impact the area of gas separation and storage.

研究分野：化学

キーワード：X線自由電子レーザー 配位高分子 結晶

1. 研究開始当初の背景

Porous Coordination Polymers (PCPs) are a new class of crystalline materials with porosity and designability. Some PCPs can possess different crystal structures dependent on the identity of the guest molecules. The epitome of this is gate-opening behavior, in which the PCP is non-porous until a certain gate opening pressure (P_{go}) is reached and then becomes porous. Gate opening behavior leads to the possibility of selective adsorption and separations. Certain gas pairs such as carbon monoxide/nitrogen or acetylene/carbon dioxide are extremely hard to separate using adsorption due to their similar physicochemical properties. Gate-opening behavior with unprecedented selectivity offers an alternative solution and thus we need to understand more regarding gate-opening behavior.

2. 研究の目的

The aim of this research is to understand about the dynamics of gate-opening behavior by performing real-time in-situ gas adsorption and X-ray diffraction using radiation from a X-ray Free Electron Laser (XFEL). An XFEL with its laser-like intensity and pulsed profile offers a unique opportunity in in-situ diffraction due to the possibility of single shot diffraction.

3. 研究の方法

PCPs with gate-opening properties were synthesized and measured with XFEL radiation from Spring-8 SACLA facility. After successful ambient temperature experiments, the sample was enclosed in a Stirling refrigerator and coupled to a gas-doser.

4. 研究成果

In this project, our progress were restricted by our beam times (2-3 per fiscal year) and the

availability/resolution of our detectors. From the first beam time in H25, the sample cell was an open holder and we could only use a 2-theta 10 degree range for our detector. We measured static samples of **1**, [Zn(ip)(bpy)]; **2**, [Cu(ip)(H₂O)]; **3**, [Zn(5-NO₂-ip)(dpe)] (bpy= bipyridine, H₂ip= isophthalic acid, dpe= 1,2-di(4-pyridyl)ethylene). Note the results are obtained for accumulation of 1000 shots (Figure 1).

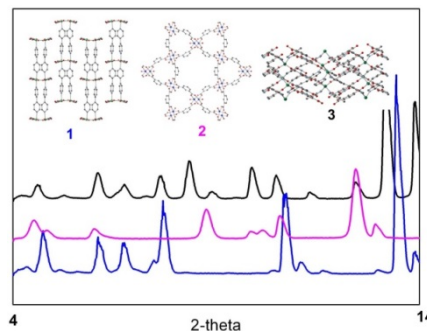


Figure 1: 1000 shot XFEL powder diffraction.

In subsequent beam times, we tried to obtain structural data via light stimuli by attempting [2+2] photodimerization with XFEL laser at 260 nm on **4**, [Zn(isophthalic)(bpy)], which we have previously published. Since the sample cells were sealed capillaries, we repeated the same irradiation under an atmosphere of CO₂. However we did not observe any significant changes in the diffraction pattern (Figure 2) after numerous attempts.

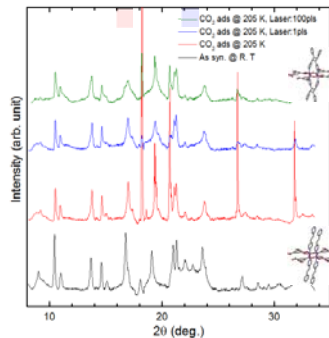


Figure 2: XFEL powder diffraction from sample in capillary with/without light irradiation.



Figure 3: Sterling refrigerator and gas dosing apparatus.

In our last beam time (H27), we were able to successfully incorporate our gas dosing apparatus and Sterling refrigerator into the XFEL hutch (Figure 3). We were able to obtain time resolved (at 30 Hz resolution) X-ray diffraction of **5**, [Cu(C₃F₇-isophthalate)] under pressure swing adsorption (0->100 kPa, 100->0 kPa) of CO (Figure 4). This is promising and subsequent work will focus on obtaining better data and extending the range of our MPCCD detectors.

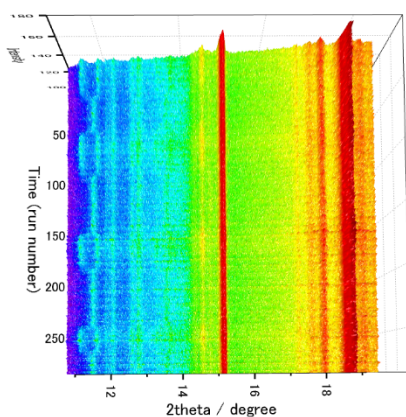


Figure 4: Time-resolved XFEL powder diffraction of **5 under pressure swing adsorption of CO.**

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 2 件)

1. L. Li, R. Matsuda, I. Tanaka, H. Sato, P. Kanoo, H. J. Jeon, M.L. Foo, A. Wakamiya, Y. Murata, S. Kitagawa

A Crystalline Porous Coordination Polymer Decorated with Nitroxyl

Radicals Catalyzes Aerobic Oxidation of Alcohols

Journal of the American Chemical Society **136**(21), 7543-7546 (2014).
(peer reviewed)

2. M.L. Foo, R. Matsuda, S. Kitagawa

Hybrid Functional Porous Coordination Polymers

Chemistry of Materials **26**(1), 310–322(2014).

(peer reviewed)

[学会発表] (計 8 件)

All talks and posters were given by Dr Maw Lin Foo.

1. International: (Invited talk) Jan 28-30 2015, Wuhan University of Geosciences, Wuhan, China

2. International: (poster talk) Sep 28-Oct 1 2014, Metal Organic Framework (MOF) 2014, Kobe Convention Center, Kobe, Japan

3. Domestic: (poster) Sept 18-20 2014, Japanese Coordination Chemistry Conference, Chuo University, Tokyo

4. International: (Invited talk) July 21-25 2014, International Chemistry Conference 41, Suntech Convention Center, Singapore

5. Domestic: (poster) Mar 27-30 2014, 94th Chemistry Society of Japan Annual Conference (Nienkai), Nagoya

University (Higashiyama campus),
Nagoya

6. International: (poster) Nov 4-7, 2013,
Asian Coordination Conference,
International Convention Center,
Cheju island, South Korea

7. Domestic: (poster) Nov 2-4 2013,
Japanese Coordination Chemistry
Conference, University of the Ryukyus
(Senbaru campus), Okinawa

8. International: (poster) June 30- July
5 2013, ICMAT conference, Suntech
Convention Center, Singapore

〔図書〕 (計 件)

〔産業財産権〕

○出願状況 (計 件)

名称：
発明者：
権利者：
種類：
番号：
出願年月日：
国内外の別：

○取得状況 (計 件)

名称：
発明者：
権利者：
種類：
番号：
出願年月日：
取得年月日：
国内外の別：

〔その他〕

ホームページ等

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