

# MERIT: Report of the Short-term Visit to UK

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## 1. Abstract

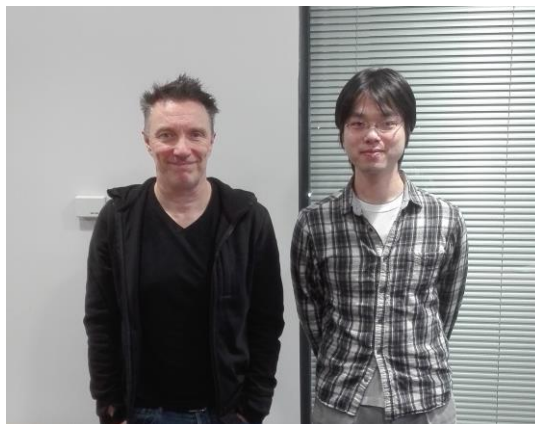
I visited the research group of Prof. Andrew I. Cooper in the University of Liverpool (UK) from 01/09/2017 to 18/01/2018 for the synthesis and structural analysis of novel nanoporous materials.

## 2. Background of the research

Nanoporous materials are defined as solid compounds featuring nanometer-sized continuous voids inside. These nanopores endow the solid with high surface area and high affinity toward the adsorption of guest molecules, and therefore, nanoporous materials can effectively uptake, into their nano pores, small molecules and particles floating in the surrounding media. Representative compounds are zeolite, featuring high affinity toward water, and activated carbon, featuring high affinity toward various types of particles and organic molecules. Amongst them, organic porous crystals are beneficial for the chemical functionalization of their pore surface. Organic porous crystals are made up of small organic molecules and, in some cases, metal ions, which are bound together via non-covalent forces including coordination bond, hydrogen bond and van der Waals interactions. The pore structure of the organic porous crystals is intrinsically uniform. This is in clear contrast to the activated carbon, featuring a branched indefinite shape pores with a diameter ranging from several micrometers to the sub nanometers. Furthermore, chemical properties of the pore surface can be artificially modified by derivatizing the constituent organic molecules. The resultant nanoporous crystals, therefore, can be utilized for the precise molecular sieving, which is often far more effective than the conventional porous materials in terms of the condensation and separation of specific species from a mixture of gaseous or liquid compounds.

In the Ph. D. course study, I serendipitously found a novel porous organic crystal when I recrystallized a newly synthesized mesitylene derivative **1** that was originally designed for the synthesis of geometrically novel coordination polymer. X-ray single

crystal structural analysis revealed that the crystal is solely composed of **1**, which are bound together via C–H···N bonds. C–H···N bond is a noncovalent interaction exerted between a nitrogen atom and a non-acidic hydrogen atom directly connected carbon atom. Due to the small polarity of the C–H bond, the attractive force of C–H···N bond is mainly derived from the dispersion force, and therefore, C–H···N bond is one of the weakest types of non-covalent bonds. To my surprise, despite the weakness of the C–H···N bonds, the obtained porous crystals maintain its porous structure even up to 200 °C. In order to further elucidate the chemical property of the crystal, and to derivatize **1** to afford novel types of porous compounds, I stayed the research group of Prof. Andrew I. Cooper in the University of Liverpool for 6 months.



### 3. Research results

In my stay in UK, I mainly conducted the synthesis and structural analysis of novel porous liquid compounds (theme 3.1) and novel ionic porous crystals (theme 3.2).

**Theme 3.1** When the porous crystals described above is exposed to a hydrogen chloride vapor, the porous structure is completely demolished to afford a white amorphous powdery solid. When the porous crystals are mixed with a 3 eq. amount of formic acid, a viscous liquid is obtained. Since **1** is sterically large, the resultant viscous liquid potentially features extrinsic nanopore in its structure. Motivated with this preliminary result, I methylated all the pyridyl rings of **1**, affording a yellowish viscous liquid **2**. To analyze its extrinsic porosity, I conducted CO<sub>2</sub> adsorption isotherm of **2**. Unfortunately, the volume adsorbed in **2** is almost equivalent to the amount of commercially available ionic liquid, indicating that **2** is not porous.

**Theme 3.2** When **1** was mixed with a commercially available organic molecule having sulfonic acids, white precipitate is immediately formed, indicating that **1** reacts with the sulfonic acid and forms an insoluble salt. Inspired with this result, I mixed **1** with a variety of rigid organic linker featuring multi sulfonic acid groups. Among them, the mixtures of **1** with either pyrene or biphenyl derivative yielded crystals suitable for the

X-ray single crystals structural analysis. Both crystals feature continuous nanometer-sized pores, which are, however, fully occupied by the crystallization solvent molecules. The number of pyridyl rings and that of the sulfonic acid are equal in the cell, indicating that the pyridyl rings and the sulfonic acid groups form a 1:1 complex. The analysis of their permanent porosity is now on going as a collaborative work.

#### **4. Acknowledgement**

I would like to express my grate gratitude to the Prof. Andrew I. Cooper for kindly accepting. I am also grateful to the Dr. Marc Little and other members in the laboratory for their advices and help. I wishes to show my gratitude to the Prof. Takuzo Aida, the professors in the University of Tokyo and Program for Leading Graduate Schools (MERIT) for supporting me to stay abroad for a 6 months.