（別紙様式２）

フォトンサイエンス国際卓越大学院プログラム（XPS）

光科学特別実習　報告書

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In this winter (16^{th} – 21^{st} December 2021), I joined in the 2021 International Chemical Congress of Pacific Basin Societies, Pacifichem 2021, to make poster presentation in English.

Originally, we were planning to visit Hawaii to participate in this conference and also to communicate with researchers from various countries. But unfortunately, in last October, it was determined to conduct the conference only in virtual due to the spread of COVID-19. I was really sorry to hear that because it can be my first and possibly the last chance to go abroad to take part in the international conference and to send my research progress to various people. I had expected that it would have become the great motivation and stimulation for my future works. On the other hand, this determination also made it possible for me to easily go to hear the many presentation offered. Actually, I successfully utilized this chance to gather information from researches of various countries and various fields. Especially, it was impressing for me to directly hear the oral presentation from famous Chinese or New Zealander professors, ones of the leading persons in the supramolecular chemistry or MOF chemistry.

As for my own poster, I gave the presentation in the title of "Dynamic structural transformation of a porous metal–macrocycle framework driven by effector binding to a local allosteric site" in the session of "Responsive Nanospace of Porous Compounds (#329) " of " (08) Materials" topic area. (**Figure 1**) I would like to explain the content of my presentation in below.

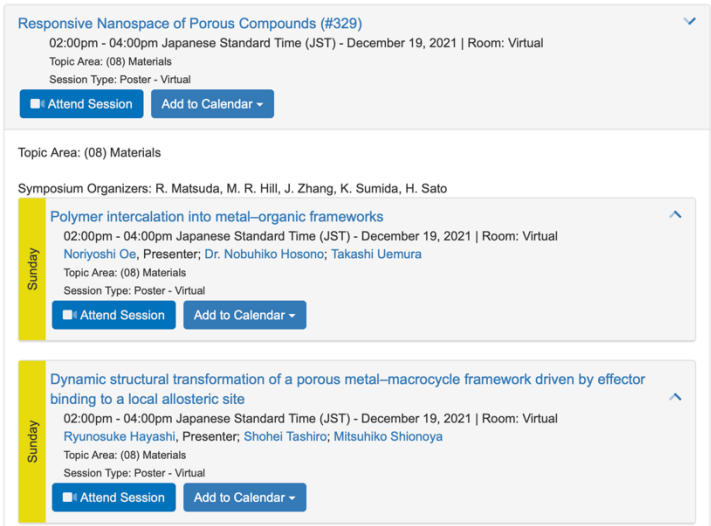

Figure 1. The time schedule of Pacifichem 2021 to exhibit my presentation

<u>The introduction of my presentation</u>

Recently as functional nano-materials, flexible porous crystals whose structure can be variously controlled by incorporated guest molecules are widely studied for sophisticated molecular separation *etc*.. However, in general cases, the guest molecules occupy the most part of the active inner-space to induce the structural change, so further pore functionalization becomes difficult due to their limited space.

On the other hand, in biological systems, the 3D structure of proteins can be controlled just by recognition of effector molecules in the local allosteric site to change the whole non-covalent interactions, and then their activity can be regulated. If we can manipulate the structure of artificial porous materials by recognition of an allosteric effector, it should be beneficial in terms of further functional applications. Thus, we focused to variously control the structure and functions of a porous crystal by addition of allosteric effectors in a local binding site.

In our group, we have developed a porous supramolecular crystal named metal-macrocycle framework, which is constructed by self-assembly of four stereoisomeric twisted Pd_3 macrocyclic complexes based on H-bondings or Pd-Pd interactions. MMF has a low-symmetric 1D channel with various molecular recognition sites on the inner wall to specifically adsorb incorporated molecules. Previously, we have reported the site-selective arrangement of multiple guest molecules in the channel via non-covalent interactions. Also, we have already discovered the space-specific reactions in this nano-channel. This time, we worked on dynamic structural transformation of this MMF crystal based on the molecular.

Based on this background, I reported my recent progress consisting of three parts, 1. [Effector-induced anisotropic structural transformation of MMF crystals.], 2. [Stepwise anisotropic structural transformation driven by change of effector due to external stimuli.], 3. [Allosteric effects of structural transformation on the guest binding ability.]

In the first part, I introduced the structural transformation of the framework induced by effector adsorption on the local binding site located in the bottom corner of the channel. Experimental results based on X-ray diffraction analyses indicated that the molecule bound to the local binding site can work as an effector to induce the reversible structural change via rearrangement of intermolecular interactions among whole Pd_3-macrocyclic complexes. This mechanism enabled anisotropic transformation in effector-dependent manner.

In the second part, I showed that precise molecular design of effectors enables the stepwise structural transformation via heat-induced conformational change of the effector in the allosteric site. When as-crystalized MMF was just soaked in some effector (*Effector A*) at 20 °C for 1 day, the metastable structure can be obtained through low crystal phase transition energy. Upon heating, the non-covalent interactions were significantly rearranged while changing the binding mode of the *Effector A*. As a result, more effective interaction network was formed to generate remarkably expanded structure as the thermionically most stable state.

So far, it was claimed that the crystal structure of MMF is variously controlled according to the type and binding mode of effector molecules at local allosteric sites. At last part, I focus on the application and reported allosteric effects of structural transformation on guest recognition ability. When a guest molecule (*Guest B*) was introduced into the as-crystalized MMF channel, no adsorption was observed due to lack of effective interactions. On the other hand, upon introducing into the extended MMF channel accommodating an effector, the guest adsorption via multiple CH-pi interactions between the lateral and the bottom wall of MMF channel was clearly observed. It indicates that the structural change leads to the formation of binding site which is suitable for *Guest B* to achieve its adsorption and immobilization. In conclusion, the arrangement of the guest molecules in the channel was allosterically controlled by structural transformation.

As for perspectives, I will attack the rational regulation of catalytic reactions in the channel.