# Joint Studies Programs

As one of the important functions of an inter-university research institute, IMS facilitates joint studies programs for which funds are available to cover the costs of research expenses as well as the travel and accommodation expenses of individuals. Proposals from domestic scientists are reviewed and selected by an interuniversity committee.

## (1) Special Projects

### (a) Construction of Synthetic Microdomains to Artificially Assemble Biological Polymers on Lipid Membranes Using Metal Complex Lipids

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KINOSHITA, Masanao (*Kyushu Univ.*)
YANAKA, Saeko (*IMS*)
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Cell membranes are nonuniform entities characterized by heterogeneous molecular assemblies that mediate biological processes exemplified by signal transduction. Accumulating evidence has indicated that these microdomains comprise various lipid molecules including glycosphingolipids and cholesterol and serve as molecular platforms where specific biomolecules accumulate to perform sophisticated functions. To gain a deeper understanding of these complex membrane functions, we employed a multilateral approach in an attempt to artificially control membrane properties and their molecular assembly.

In this project, we created and applied *metal complex lipids* for (1) manipulating lipid membrane properties such as curvature and viscosity to construct synthetic domain architectures and (2) controlling assemblies of biological polymers thereon. The metal complex lipid consists of a metal complex moiety as its hydrophilic head and an alkyl chain as its hydrophobic tail. It exhibits different physical properties from those of natural lipid species, which further impacts lipid membrane properties. Through investigation of the influence of the metal complex lipids on phase-transition and molecular-assembling behaviors of both artificial and cell membranes, we successfully constructed an artificial phase separation system with micro-sized rigid domains consisting of metal complexes in living cell membranes. Furthermore, we succeeded in synthesizing a new metal complex lipid which could provide unique fluid–fluid phase separation in lipid membranes. The metal complex lipid not only exhibits such domain formation property but also offers a possibility to hybridize with biomolecules via the click chemistry approach due the head part incorporating an ethynyl substituent. We expect that this metal complex lipid will be applicable to assembling and accumulating biomolecules in lipid membranes, which is now underway.

We held a collaboration meeting in 2020 to extensively discuss our research progress and future planning. The meeting was held at on-line on July 29th, 2020. This project has achieved two published papers (R. Ohtani *et al. Angew. Chem., Int. Ed.* **61**, 13603–13608 (2021), R. Ohtani *et al. Angew. Chem., Int. Ed.* **59**, 17931–17937 (2020)).

### (b) *Operando* Structural Studies on the Reacting Species of the Cross-Coupling Catalysis

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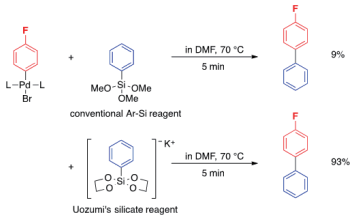
TAKAYA, Hikaru (*Kyoto Univ. and IMS (cross appointment)*)
NAGASAKA, Masanari (*IMS*)
OKUMURA, Shintaro (*IMS*)
UOZUMI, Yasuhiro (*IMS*)

The palladium-catalyzed cross-coupling reactions have been recognized as the most powerful synthetic means of carbon–carbon bond formation. Coupling of aryl halides and organosilicon reagents, the so-called Hiyama coupling, is one of the representatives. Recently, Uozumi at IMS developed aryl silicate reagents which exhibited remarkably high reactivity toward the Hiyama coupling with aryl halides (Scheme 1). These observations prompted us to examine the operando structural studies on the aryl silicates as well as conventional aryl silyl reagents under the actual coupling reaction conditions by *in situ* NEXAFS measurements. For the preliminary measurements, the electronic structures of phenyl groups in




**Scheme 1.** The Hiyama Coupling Reactions with Uozumi's Aryl Silicate.

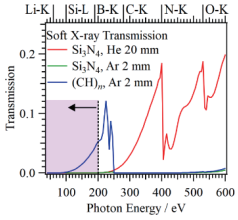



**Figure 1.** Calculated soft X-ray transmission at several conditions of liquid cells.

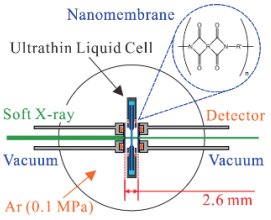



**Figure 2.** The schematic of an ultrathin liquid cell including Si-free nanomembranes.

organosilicon compounds were investigated by C K-edge NEXAFS (280 eV) at BL3U of UVSOR-III (by Nagasaka, Okumura). From the soft X-ray transmission calculations (Figure 1), on the other hand, the Si L-edge NEXAFS (100 eV) needs the ~2 mm optical length of argon gas and Si-free nanomembranes. Thus, this project combines (1) a new coupling reaction (by Uozumi, Okumura) and (2) an ultrathin liquid cell that achieves the 2.6 mm optical length of argon gas (by Nagasaka, Takaya) including novel Si-free nanomembranes developed by Fujikawa at Kyusyu University (Figure 2) at once to realize the *operando* structural studies of the highly reactive Hiyama coupling reaction. Though, in 2021, this project team have never had the on-site collaborations because of the COVID catastrophe, we have prepared the reacting reagents, Si-free nanomembranes, and an ultrathin liquid NEXAFS cell at each site. This *in situ* NEXAFS method will pave the way for studying various organic reaction with organosilicon, organolithiums, organoboranes, and so on.

## (2) Research Symposia

(From Oct. 2020 to Sep. 2021)

| Dates | Theme | Chair |
|---|---|---|
| Oct. 28–29, 2020 | Next Generation Spectro-Mircroscopy and Micro-Spetroscopy Workshop | **OHIGASHI, Takuji** |
| Dec. 4– 5, 2020 | New Development of Molecular Manipulation and Reaction Control Interwoven by Nanospace and Light | **MINAMIMOTO, Hiro**<br>**OKAMOTO, Hiromi** |
| Mar. 11–12, 2021 | The Potential for Academic Development Originating in Coordination Chemistry | **MATSUDA, Ryotaro**<br>**KUSAMOTO, Tetsuro** |
| Jul. 12–13, 2021 | IMS-FHI Symposium “Emerging Techniques of Scanning Probe Microscopy” | **KUMAGAI, Takashi** |
| Aug. 31, 2021 | The Morino Discussion 2021 | **MUNAKATA, Toshiaki**<br>**SUGIMOTO, Toshiki** |
| Aug. 16–19, 2021 | The 60$^{th}$ Summer School of Molecular Science by Young Scientistse | **TOKITA, Tsukasa**<br>**SUGIMOTO, Toshiki** |

## (3) Numbers of Joint Studies Programs

| Categories | | Oct. 2020–Mar. 2021 | | Apr. 2021–Sep. 2021 | | | Total | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Regular | NanoPlat | Regular | NanoPlat | NMRPlat | Regular | NanoPlat | NMRPlat | Sum |
| Special Projects | | 1 | | 1 | | | 2 | | | 2 |
| Research Symposia | | 3 | | 2 | | | 5 | | | 5 |
| Research Symposia for Young Researchers | | 0 | | 2 | | | 2 | | | 2 |
| Cooperative Research | | 30 | 27 | 20 | 30 | 3 | 50 | 57 | 3 | 110 |
| Use of Facility | Instrument Center | | 74 | | 69 | | 0 | 143 | | 143 |
| | Equipment Development Center | 1 | 5 | 0 | 5 | | 1 | 10 | | 11 |
| Use of UVSOR Facility | | 15 | 1 | 101 | 1 | | 116 | 2 | | 118 |
| Use of Facility Program of the Computer Center | | | | | | | 271* | | | 271* |

* from April 2020 to March 2021