

**【Grant-in-Aid for Scientific Research (S)】**  
**Science and Engineering (Chemistry)**



**Title of Project : Synthesis of Functional Nanostructures by Interfacial Coordination Programming and Creation of Chemical Devices**

Hiroshi Nishihara  
(The University of Tokyo, Graduate School of Science, Professor)

Research Project Number : 26220801 Researcher Number : 70156090

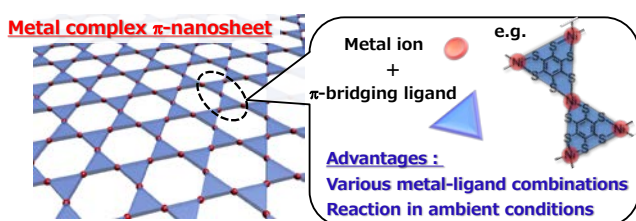
Research Area : Inorganic Chemistry

Keyword : Molecular Wire, Two-dimensional Metal Complex, Bio-conjugated Material

**【Purpose and Background of the Research】**

The current target of research for technological innovation of photo, electro, and electrochemical devices is to establish the methodology to utilize functional molecular materials together with inorganic semiconductors by bottom-up synthetic procedures.

In the present research, we aim to produce molecular networks with unique characteristics by employing *interfacial coordination programming*, and to develop original high-performance chemical devices. One of the target materials is  $\pi$ -conjugated metal complex wires synthesized by stepwise connection of metal ions and bridging ligands on surface (vertical coordination programming). Inclusion of various functionalities such as redox activity, electronic conductivity, external stimuli responsivity, photoelectron conversion ability in the molecular wires will be investigated. Hybrid systems of molecular wires with photo-responsive bio-component, PSI and PSII are also studied. Another target material is metal complex  $\pi$ -nanosheets. This new kind of two-dimensional materials is prepared by horizontal coordination programming at the liquid-liquid or gas-liquid interface. Their unique electrochemical and electronic properties will be used for developing novel chemical devices.



**Fig. 1.** Metal complex  $\pi$ -nanosheet.

**【Research Methods】**

The research is made of three steps: 1) synthesis of metal complex wires and nanosheets using various combination of metals and bridging ligands, 2) analysis of their structures and physical properties, and 3) development of electronic and electrochemical devices based on their unique properties. As for metal complex wires, intelligent systems including external stimuli responsive molecular units such as PSI and PSII are

constructed. As for metal complex nanosheets, multilayer sheets with  $\mu\text{m}$  thickness and atomic layer sheets with nm thickness are prepared by the liquid-liquid and gas-liquid interfacial reactions, respectively. The nanosheets undergoing rapid redox reaction accompanying drastic color change will be used for electrochromic devices, those with electronic conductivity for high-performance FET, and those behaving as topological insulator for spin transition torque (STT) devices.

**【Expected Research Achievements and Scientific Significance】**

The material useful for the single molecular devices is an intelligent molecular network with various functions responsive to external stimuli such as photons, electrons and magnetic field. For the purpose to create such molecular networks, coordination programming is an effective way as the sequence of the molecular units and the length and shape of the molecular network can be controlled at will. In the present research, new  $\pi$ -conjugated redox molecular networks in one and two-dimensions with unique properties will be created. Their application to chemical devices will contribute greatly to the advance of molecular-scale devices.

**【Publications Relevant to the Project】**

- $\pi$ -Conjugated Nickel Bis(dithiolene) Complex Nanosheet, T. Kambe, R. Sakamoto, K. Hoshiko, K. Takada, J. Ryu, S. Sasaki, J. Kim, K. Nakazato, M. Takata, H. Nishihara, *J. Am. Chem. Soc.* **2013**, *135*, 2462-2465.
- Coordination Programming-A Concept for the Creation of Multifunctional Molecular Systems, H. Nishihara, *Chem. Lett.* **2014**, *43*, 388-395. (Highlight Review)

**【Term of Project】** FY2014-2018

**【Budget Allocation】** 150,100 Thousand Yen

**【Homepage Address and Other Contact Information】**

<http://www.chem.s.u-tokyo.ac.jp/users/inorg/nishihara@chem.s.u-tokyo.ac.jp>