RESEARCH ACTIVITIES

Materials Molecular Science

Extensive developments of new functional molecules and their assemblies are being conducted in three Divisions of Electronic Structures, Electronic Properties, and Molecular Functions, and one division for visiting professors and associate professors, in an attempt to discover new phenomena and useful functions. The physical (electric, optical, thermal and magnetic) properties on new functional materials, the chemical properties like enzymes, catalysis and photochemistry, the exploitation of new spectroscopic methods for materials molecular science, and technological applications like fuel cells, solar cells and field effect transistors are investigated in this department.

Exploitation of Novel Spectroscopic Methods for Material and Surface Science

Department of Materials Molecular Science
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Keywords X-Ray Absorption Spectroscopy, Surface & Thin Film Magnetism, Ambient Pressure Hard X-Ray Photoelectron Spectroscopy

For the developments of novel functional materials, it is quite important to exploit simultaneously new analytical methods based on advanced technology. Novel materials and devices often require spatial and/or time resolved analysis to optimize their qualities. In our group, we have been exploiting spectroscopic methods for material and surface science using mainly synchrotron radiation (SR) and partly lasers.

The first subject in our group is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism (UV MCD) photoelectron emission microscopy (PEEM), which allows us to perform real-time and ultrafast magnetic imaging to investigate magnetic dynamics. We have also constructed in situ x-ray magnetic circular dichroism (XMCD) system using a ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The XMCD measurement system contains ultrahigh vacuum sample preparations chamber, with which one can clean substrates (substrate single crystals *etc.*), deposit materials (metallic and molecular magnets *etc.*) and characterize the samples using low energy electron diffraction, reflection high energy electron diffraction and Auger electron spectroscopy. The apparatus is extensively open for public usage and many domestic and foreign researchers visit us every year.

The second subject is the exploitation of near-ambient pressure hard x-ray photoelectron spectroscopy (HAXPES) for polymer electrolyte fuel cells (PEFC) under working conditions. Although usually photoelectron spectroscopic measurement is done under ultrahigh vacuum, recent material science requires ambient pressure measurements under working conditions. We have installed nearly ambient pressure (up to ~5000 Pa) HAXPES apparatus in Beamline 36XU of SPring-8. We have successfully investigated Pt 3d HAXPES of Pt/C, PtCo/C and PtNi/C cathode catalysts in PEFC under working conditions to reveal degradation mechanism of PEFC. This work is supported by the NEDO Fuel Cell project.

The third subject is the pico- and femtosecond pump-and-probe time resolved x-ray absorption fine structure (XAFS) spectroscopy. XAFS is a quite powerful technique for investigating quantitative local structures of very low concentrated non-crystalline element by using the energy-resolved x-ray fluorescence detection technique. Fast time resolved XAFS measurement is difficult since the repetition frequencies of probe SR and pumping lasers are usually far different, requiring pulse picking of the SR probe and resultantly time resolved detection of only energy-integrated x-ray fluorescence. To detect energy- resolved x-ray fluorescence, a picosecond laser with high repetition rate (up to 1 MHz) was installed in Photon Factory Advanced Ring with single bunch operation (794 kHz). This allows us to investigate XAFS of low concentration elements using a slow but energy-resolved x-ray fluorescence detector.

Selected Publications

- T. Nakagawa *et al.*, *Phys. Rev. Lett.* **96**, 237402 (2006).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **110**, 075901 (2013).
- M. Dabrowski *et al.*, *Phys. Rev. Lett.* **113**, 067203 (2014).
- Y. Takagi *et al.*, *Appl. Phys. Lett.* **105**, 131602 (2014).
- Y. Uemura *et al.*, *Angew. Chem., Int. Ed.* **55**, 1364 (2015).
- Y. Wakisaka *et al.*, *Phys. Rev. B* **92**, 184408 (2015).
- K. Eguchi *et al.*, *J. Phys. Chem. C* **119**, 9805 (2015).

1. Ultrafast Structure Determination of Photocarrier in WO_3 Photocatalyst[1)]

The utilization of solar energies is one of the most fascinating and important research subjects to achieve a future society less dependent on fossil fuels. Many photocatalysts have extensively been developed over last several decades in order to produce hydrogen from water without the generation of harmful pollutants. Recently, tungsten trioxide WO_3 has received much attention since its band gap is 2.6–2.8 eV, implying that it functions as an active photocatalyst under visible light irradiation. In the present work, we have investigated femto- and picosecond structure transformation of photoexcited WO_3 by pump-and-probe time-resolved x-ray absorption fine structure (XAFS) spectroscopy using x-ray free electron laser SACLA in Harima and synchrotron radiation PF-AR (single bunch operation) in Tsukuba.

Figure 1 shows the W L_{III}-edge x-ray absorption near edge structure (XANES) of photoexcited WO_3 recorded in SACLA and the time evolution at x-ray energy point C in Figure 1 is depicted in Figure 2. The shift of the edge energy to a lower x-ray energy side is clearly observed, accompanied by the reduction of the white-line intensity. This implies that the W ions are reduced from hexavalent to pentavalent. From Figure 2 and other results of W L_{III}-edge extended x-ray absorption fine structure (EXAFS) and W L_I-edge XANES, we can deduce the photoexcitation process as

1) fast formation of the photocarrier (<0.7 ps)
2) local structural distortion of WO_6 octahedra (140 ps)
3) decay of the photoexcited state (1800 ps).

The local structure distortion of the photocarrier in WO_3 is exemplified, suggesting the usefulness of the time resolved XAFS experiments.

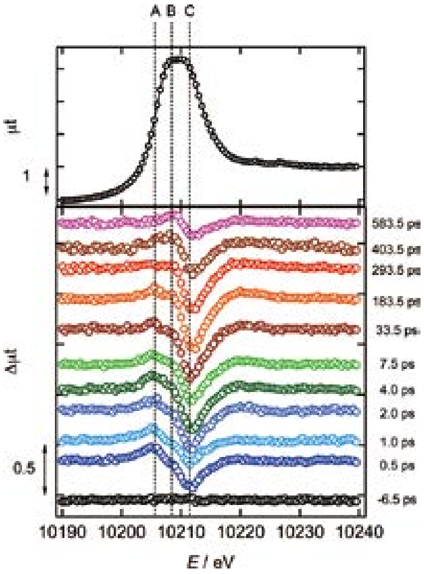

Figure 1. W L_{III}-edge XAFS of the ground state WO_3 and the time evolution of the spectral difference after the photoexcitation (400 nm, 0.070 fs) recorded in SACLA. The time resolving power is ~0.7 ps.

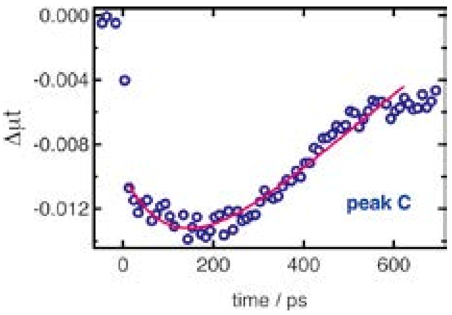

Figure 2. Time evolution of the difference spectra at energy point C in Figure 1.

2. Local Thermal Properties of Functional Materials as Magnetic Alloys[2–4)] and Gold Nanoclusters Studied by Temperature Dependent EXAFS[5)]

We have extensively been studying local thermal properties such as local thermal expansion and local vibrational amplitude between atom pairs by means of the temperature dependent EXAFS technique, together with the computational simulations based on the path-integral effective classical potential theory. In the FeNi invar alloy[2)] that shows almost no thermal expansion up to 400 K, we concluded that the absence of thermal expansion at very low temperature originates from the vibrational quantum effect, and found the different local thermal expansion between Fe and Ni, which cannot be detected with the x-ray diffraction. In the martensitic MnNi alloy,[3)] Mn exhibits large thermal expansion along the tetragonal *a* axis due to the anti-Invar effect and negligibly small thermal expansion along the *c* axis due to the cooperative Invar effect. In metamagnetic FeRh intermetallic compound,[4)] only the Debye-Waller factor of the Fe–Fe pair in the antiferromagnetic phase was found to be enhanced significantly, indicating that the local spin and Fe–Fe distance fluctuations play an important role in driving the metamagnetic transition. In thiolated gold nanoclusters,[5)] we elucidated the hierarchy in the bond stiffness in $Au_{25}(SC_2H_4Ph)_{18}$, $Au_{38}(SC_2H_4Ph)_{24}$ and $Au_{144}(SC_2H_4Ph)_{60}$. Longer and more flexible Au–Au bonds locate at the icosahedral-based gold surface, while shorter stiffer Au–Au bonds are distributed along the radial direction and form a cyclic structural backbone of the rigid Au–SR oligomers.

References

1) Y. Uemura, D. Kido, Y. Wakisaka, H. Uehara, T. Ohba, Y. Niwa, S. Nozawa, T. Sato, K. Ichiyanagi, R. Fukaya, S. Adachi, T. Katayama, T. Togashi, S. Owada, K. Ogawa, M. Yabashi, K. Hatada, S. Takakusagi, T. Yokoyama, B. Ohtani and K. Asakura, *Angew. Chem., Int. Ed.* **55**, 1364 (2015).
2) T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
3) T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **110**, 075901 (2013).
4) Y. Wakisaka, Y. Uemura, T. Yokoyama, H. Asakura, H. Morimoto, M. Tabuchi, D. Ohshima, T. Kato and S. Iwata, *Phys. Rev. B* **92**, 184408 (2015).
5) S. Yamazoe, S. Takano, W. Kurashige, T. Yokoyama, K. Nitta, Y. Negishi and T. Tsukuda, *Nat. Commun.* **7**, 10414 (2016).

Magnetic Resonance Studies for Functional Molecular-Based Solids

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Keywords Organic Conductor, Electron Spin Resonance (ESR), Nuclear Magnetic Resonance (NMR)

Magnetic resonance measurements are advantageous for studying fundamental electronic properties and for understanding the detailed electronic structures of molecular based compounds. Developing an understanding of the electronic phases and functionality of these materials enables us to perform systematic investigations of low-dimensional, highly-correlated electron systems and functional materials. Competition between the electronic phases in molecular-based conductors has attracted much attention. The investigations of such electronic phases by magnetic resonance measurements are important to understanding unsolved fundamental problems in the field of solid state physics, and to explore novel functionalities in the field of material science.

In this study, we performed broad-line NMR and ESR measurements on molecular-based conductors to understand electron spin dynamics and functionality in low-temperature electronic phases.

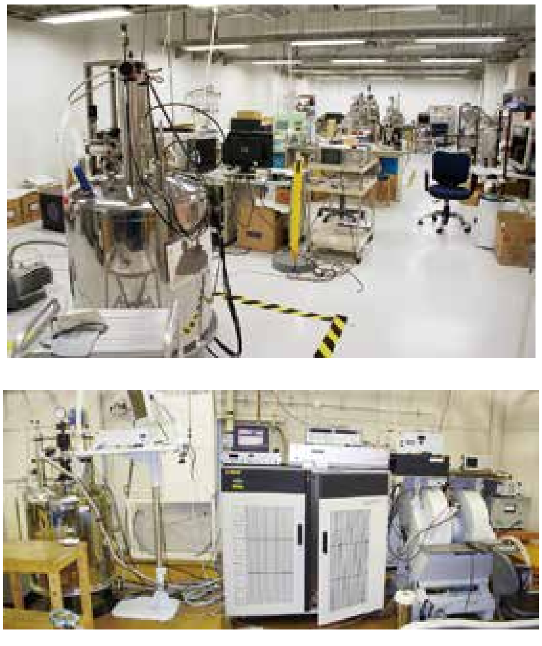

Figure 1. Solid-state broad-line NMR system (above). Multi-frequency pulsed ESR system (below).

Selected Publications

- T. Nakamura, K. Furukawa, T. Terauchi and Y. Kobayashi, " Microscopic Evidence of a Metallic State in the One-Pot Organic Conductor, Ammonium Tetrathiapentalene Carboxylate," *Phys. Status Solidi RRL* **9**, 480–484 (2015).
- M. Yoshida, M. Kondo, T. Nakamura, K. Sakai and S. Masaoka, "Three Distinct Redox States of an Oxo-Bridged Dinuclear Ruthenium Complex," *Angew. Chem., Int. Ed.* **53**, 11519–11523 (2014).

1. Curious Electronic Phases and ESR Behaviors in One-Dimensional Organic Conductors (TMT*C*F)$_2X$

One-dimensional conductors based on (TMTCF)$_2X$ (C = S, Se) are some of the most extensively studied materials among organic conductors. They possess various ground states including the spin-singlet (SS), commensurate antiferromagnetic state (C-AF), incommensurate spin density wave (IC-SDW) and superconductivity (SC), with applied pressures or counter anions, X. Moreover, findings of charge-ordering (CO) and related phenomena in (TMTTF)$_2X$ have attracted significant recent attention.

(TMTTF)$_2$Br undergoes antiferromagnetic transition at 16 K (T_N). But it is located on the proximity between C-AF and IC-SDW phase in the generalized phase diagram. Previously, we examined the magnetic structure of the antiferromagnetic state of (TMTTF)$_2$Br by ^{1}H-NMR spectroscopy at 4.2 K. We clarified that the wave-number of the antiferromagnetic state is commensurate Q = (1/2, 1/4, 0) with amplitude 0.14μ_B/molecule at 4.2 K.$^{1)}$ The commensurate antiferromagnetic state of (TMTTF)$_2$Br was also confirmed by ^{13}C-NMR measurements. Recently anomalous ^{13}C-NMR spectra change was observed in (TMTTF)$_2$Br below 4.2 K.$^{2)}$ This observation suggests possible successive phase transition around 4.2 K. Hence we also investigated antiferromagnetic resonance (AFMR) of a single crystal of (TMTTF)$_2$Br. The X-band ESR experiments were carried out using Bruker Elexsys 500 with Oxford Cryostat E910. The temperature range was between 1.5 K and 10 K. Figure 2 shows the angular dependence of the antiferromagnetic resonance (AFMR) modes (normal mode and spin-flop mode) at 4.8 K and 1.5 K. The AFMR modes seem to enhance at 1.5 K, indicating development of the magnetic moment of the AF sub-lattices even at low-temperatures ($T \ll T_N/2$). Temperature dependence of the two AFMR modes also shows anomalous increase below 5 K. According to the detailed analysis of the AFMR experiment results, the shift of the AFMR field suggests change of the magnetization of the AF sub-lattice (namely, the amplitude of the AF).$^{3)}$ Possible sub-phases in the antiferromagnetic state are discussed.

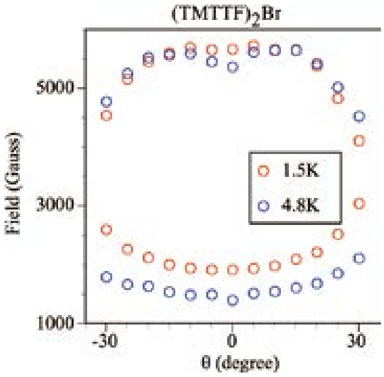

Figure 2. Angular dependence of the anti-ferromagnetic resonance in (TMTTF)$_2$Br (easy-intermediate plane: 9.5 GHz).

2. Effect of Spin–Orbit Interaction and Topological Gap for ESR Spectra in Low-Dimensional Organic Conductors

Recently theoretical investigation by Oshikawa proposed that strong spin–orbit interaction causes additional ESR satellite signal and g-shift in 1D metallic system.$^{4)}$ So, we reexamined detailed X-band ESR spectra (satellite, line-shape, line-width) for low-dimensional metallic systems. Firstly, we focused on a 1D organic conductor (TMTSF)$_2$ClO$_4$, which shows stable metallic state down to 1 K. Since the TMTSF molecule contains heavy selenium elements, there are considerable spin–orbit interactions. When we apply the static magnetic field along 1D conducting direction ($H_0//a$), a tiny satellite peak was appeared below 12 K. In the case of $H_0//c^*$, we cannot observed any satellite peak. We also performed 2D metallic system, BEDT-TTF salts. A series of BEDT-TTF salts with low-symmetry shows anomalous g-shift at low-temperatures. We discuss relationship between the tiny band gap and anomalous ESR behavior observed in low-dimensional metallic systems.

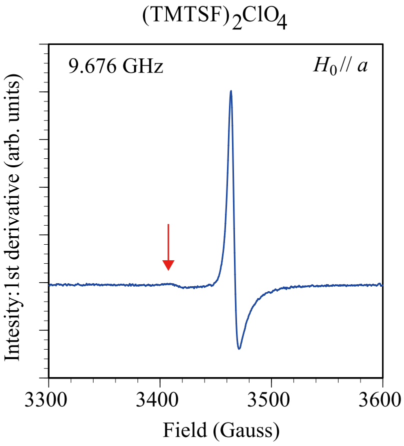

Figure 3. ESR spectra of (TMTSF)$_2$ClO$_4$ at 8 K with the static magnetic field along 1D conducting direction ($H_0//a$). A tiny satellite peak was appeared below 12 K.

These works were supported by a Grant-in-Aid for Scientific Research B (No. 20340095) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1) T. Nakamura, T. Nobutoki, Y. Kobayashi, T. Takahashi and G. Saito, *Synth. Met.* **70**, 1293 (1995).
2) T. Ihachi *et al.*, *JPS Spring meeting 2015*, 21aAs-2 (2015).
3) H. Ohta, N. Yamauchi, T. Nanba, M. Motokawa, S. Kawamata and K. Okuda, *J. Phys. Soc. Jpn.* **62**, 785 (1993).
4) M. Oshikawa, *54th SEST (Japan ESR society) annual meeting* SB-05 (2015.11).

Organic Solar Cells

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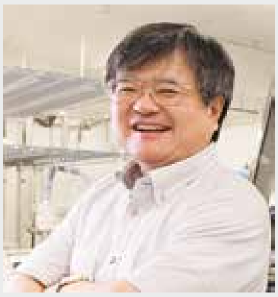

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Keywords Organic Semiconductors, Organic Solar Cells, ppm-Doping

Organic solar cells have been intensively studied due to many advantages like flexible, printable, light, low-cost, fashionable, *etc*. We have been focused on the establishment of “bandgap science for organic solar cells.” We believe that the following features are indispensable. (a) Organic semiconductors purified to sub-ppm level, at least seven nines (7N; 0.1 ppm), should be used. (b) A ppm-level doping technique should be developed. (c) Every individual organic semiconductor should be capable of displaying both *n*- and *p*-type characteristics by impurity doping alone, *i.e.*, complete *pn*-control should be developed. (d) Unintentional and uncontrollable doping by oxygen and water from air should be completely eliminated. (e) The doping technique should be applicable not only to single organic semiconductor films, but also to codeposited films consisting of two kinds of organic semiconductors since a key element for exciton dissociation in organic solar cells is having a co-deposited films.

Recently, we have showed that in principle, almost all single organic semiconductors can be controlled to both *n*-type and *p*-type by doping alone, similar to the case of inorganic semiconductors (Figure 1). This can be regarded as a foundation for the construction of high efficient organic solar cells.

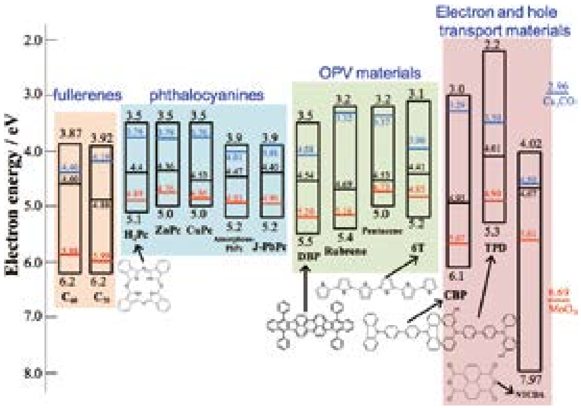

Figure 1. Energy diagrams of various organic semiconductor films. The black, red, and blue lines show the energetic position of E_F for non-doped, acceptor dopant (MoO_3)-doped, and donor dopant (Cs_2CO_3)-doped films. The doping concentration is 3,000 ppm. E_F values for MoO_3 and Cs_2CO_3 films (100 nm) are also shown.

Selected Publications

- C. Ohashi, Y. Shinmura, M. Kubo and M. Hiramoto, “ppm-Doping Effects in the Simplest n^+p-Homojunction Organic Photovoltaic Cells,” *Org. Electron.* **27**, 151–154 (2015).
- M. Hiramoto, M. Kubo, Y. Shinmura, N. Ishiyama, T. Kaji, K. Sakai, T. Ohno, M. Izaki and M. Hiramoto, “Bandgap Science for Organic Solar Cells,” *Electronics* **3**, 351–380 (2014).
- M. Kubo, K. Iketaki, T. Kaji and M. Hiramoto, “Conduction Type Control of Fullerene Films from *n*- to *p*-Type by Molybdenum Oxide Doping,” *Appl. Phys. Lett.* **98**, 023302 (3 pages) (2011).

1. Effects of Doping at the ppm Level in Simple n^+p-Homojunction Organic Photovoltaic Cells

We believe that a doping technique for very low concentrations of the order of parts per million should be developed. In this study, we adopted the simplest n^+p-homojunction cell that has a one-sided abrupt junction (Figure 2). The acceptor ($FeCl_3$) doping concentration in the p-layer was varied from the extremely low concentration of 1 ppm up to 1,000 ppm.

Figure 3(a) shows the dependences of short-circuit photocurrent (J_{sc}) and the fill factor (FF) on doping concentration. The doping effect of extremely low concentrations of the order of 1 ppm was confirmed. The doping effects can be divided into three regions. From 0 to 10 ppm, both FF and J_{sc} increase rapidly. From 10 to 100 ppm, J_{sc} still increases while FF maintains a constant value. From 100 to 1,000 ppm, both J_{sc} and FF decrease.

Figure 3(b) shows the dependences of the fill factor (FF) and the cell resistance (R_s) on doping concentration from 0 to 100 ppm. Clearly, R_s decreases and FF increases from 0 to 10 ppm. Once acceptor doping is performed, holes and electrons inevitably act as majority and minority carriers, respectively. Thus, we conclude that the increase in FF at 10 ppm doping is due to the appearance of majority carriers in the p-layer.

Figure 3(c) shows the dependences of J_{sc} and the built-in potential (V_{bi}) on doping concentration from 0 to 1,000 ppm. Clearly, there is a close relationship between J_{sc} and V_{bi}. In particular, there are simultaneous increases in J_{sc} and V_{bi} at the relatively low doping concentrations of 10 and 100 ppm. Based on these considerations, we conclude that the increase in J_{sc} is due to the increase in V_{bi}, that is, the formation of an n^+p-homojunction.

The decreases in FF and J_{sc} from 100 to 1,000 ppm doping (Figure 3(a)) are caused by the decrease in mobility of the majority carriers as a result of the disturbance of hopping transport by dopant molecules and by the decrease in the width of depletion layer, respectively.

The most important technical significance of the doping is the intentional design of built-in potentials in the cells. We believe that a new design concept that includes the doping technology needs to be developed in order to realize a high-performance cell.

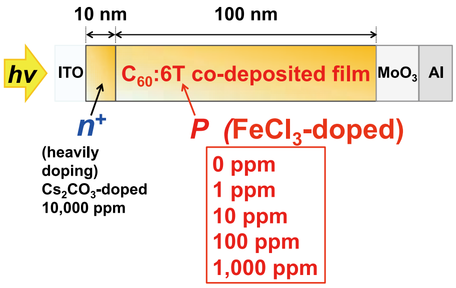

Figure 2. Structure of n^+p-homojunction cell with a one-sided abrupt junction.

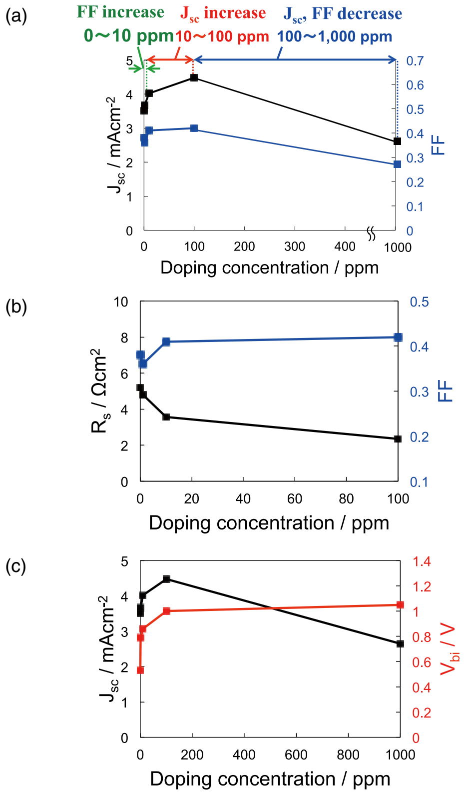

Figure 3. (a) Dependences of short-circuit photocurrent (J_{sc}) and the fill factor (FF) on doping concentration. (b) Dependences of FF and the cell resistance (R_s) on doping concentration. (c) Dependences of J_{sc} and the built-in potential (V_{bi}) on doping concentration.

Two-Dimensional Polymers and Covalent Organic Frameworks

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Professional Employment

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Awards

2006	The Young Scientists' Prize, The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology, Japan
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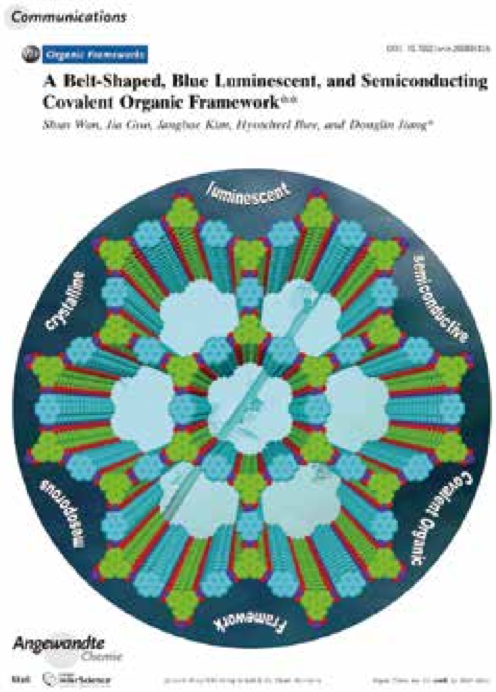
Keywords Two-Dimensional Covalent Polymer, Covalent Organic Frameworks, Porous Organic Polymers

Two-dimensional (2D) polymers and their layered frameworks (covalent organic frameworks: COFs) are a class of crystalline porous materials that enable precise integration of organic components into periodicities. Different from conventional polymers and typical porous zeolite materials in the aspects structure, synthesis, and functions, COF materials have emerged as a new platform for designing advanced multiple functional materials, including gas adsorption, catalysts, semicoductors, light-emitters, and active materials for batteries and solar cells. We have pioneered the field of COFs by exploring molecular design principle, synthetic reactions, functions and applications.



Communications

Organic Frameworks

A Belt-Shaped, Blue Luminescent, and Semiconducting Covalent Organic Framework**

Figure 1. The first semiconducting 2D COF.

Selected Publications

- X. Feng, X. Ding and D. Jiang*, "Covalent Organic Frameworks," *Chem. Soc. Rev.* **41**, 6010–6022 (2012).
- S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang*, "A Belt-Shaped, Blue Luminescent and Semiconducting Covalent Organic Framework," *Angew. Chem., Int. Ed.* **47**, 8826–8830 (2008) (VIP).
- S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang*, "A Photoconductive Covalent Organic Framework: Self-Condensed Arene Cubes with Eclipsed 2D Polypyrene Sheets for Photocurrent Generation," *Angew. Chem., Int. Ed.* **48**, 5439–5442 (2009).
- J. Guo, Y. Honsho, M. A. Addicoat, J. Kim, A. Saeki, H. Ihee, S. Seki, S. Irle, M. Hiramoto, J. Gao and D. Jiang*, "Conjugated Organic Framework with Three-Dimensionally Ordered Stable Polymer with Delocalized π Clouds," *Nat. Commun.* **4**: 2736 doi: 10.1038/ncomms3736 (2013).

1. Radical Covalent Organic Frameworks for Capacitive Energy Storage

Organic radicals have received considerable attentions because their unpaired electrons endow the materials with unusual electronic, magnetic, optical, and redox properties. In this study, we developed a facile and general strategy that converts a conventional COF to an outstanding redox-active platform for energy storage *via* post-synthetic channel-wall functionalization with organic radicals. With this achievement, we show a new platform based on radical COFs for energy storage. We demonstrated this strategy using a conventional imine-linked NiP-COF (Figure 2) as a scaffold with nickel porphyrin at the vertices and TEMPO radicals on the walls.

The radical frameworks with open-accessible polyradicals immobilized on the pore walls undergo rapid and reversible redox reactions, leading to capacitive energy storage with high capacitance, high-rate kinetics, and robust cycle stability. The results suggest that channel-wall functional engineering with redox-active species will be a facile and versatile strategy to explore COFs for energy storage. Our results reveal the enormous potential of COFs as an appealing platform for construction of electrode materials for energy storage. We anticipate that the present post-synthetic channel-wall engineering strategy will be critical to exploring COF materials for high-performance energy storage and power supply.

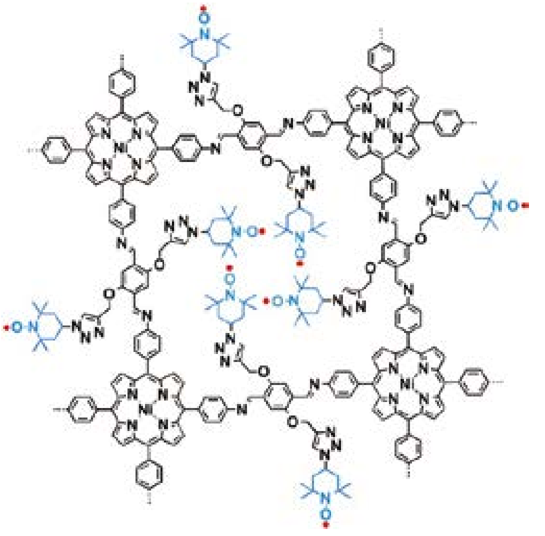


Figure 2. A NiP-COF with TEMPO radicals immobilized on the walls.

2. A Photoresponsive Smart Covalent Organic Framework

Materials with structures that are transformable in response to external stimuli, such as light, heat and pressure, are attracting increasing attention because of their broad applications in various fields. In particular, when the structural transformations are accompanied by changes in physiochemical properties, these materials are considered “smart” and “dynamic” and can function as stimuli-responsive materials. Two-dimensional covalent organic polymers (2D COPs) and their layered covalent organic frameworks (COFs) are a class of crystalline porous polymers that allow atomically precise integration of organic units into periodic columnar π-arrays and ordered one-dimensional (1D) open channels. The integration of stimuli-responsive π-units into COFs is likely to yield structurally-dynamic frameworks in which the structure can be transformed upon external stimulation. However, a “smart” COF is unprecedented and the possibility of structural transformation is to be exemplified.

The anthracene units stacked in the π-columns of Ph-An-COF are responsive to irradiation, which induces interlayer $[4\pi + 4\pi]$ cycloaddition reactions, causes conformational changes of the π-columns, and triggers a structural transformation of the layers. These photoinduced hierarchical transformations are reversible by virtue of the thermally allowed reversibility of the cycloaddition reaction. Notably, the structural transformations are accompanied by profound changes in properties and functions, including gas adsorption, π-electronic adsorption and luminescence. Our results demonstrate the first example of photoresponsive structurally-dynamic COFs and suggest that COFs could be designed as “smart” materials whose gas-adsorption, molecular storage, sensing, and semiconducting properties are controllable by external stimuli.

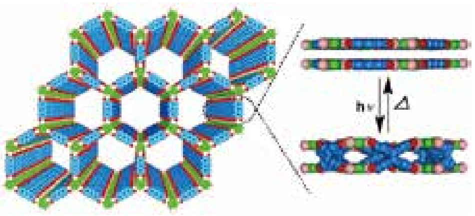


Figure 3. Anthracene-based photoresponsive COF.

References

1) S. Dalapati, M. Addicoat, S. Jin, T. Sakurai, J. Gao, H. Xu, S. Irle, S. Seki and D. Jiang, *Nat. Commun.* **6**:7786 (2015).
2) N. Huang, R. Krishna and D. Jiang, *J. Am. Chem. Soc.* **137**, 7079–7082 (2015).
3) S. Jin, M. Supur, M. Addicoat, K. Furukawa, L. Chen, T. Nakamura, S. Fukuzumi, S. Irle and D. Jiang, *J. Am. Chem. Soc.* **137**, 7817–7827 (2015).
4) N. Huang, X. Ding, J. Kim, H. Ihee and D. Jiang, *Angew. Chem., Int. Ed.* **54**, 8704–8707 (2015). (VIP)
5) F. Xu , H. Xu, X. Chen, D. Wu, Y. Wu, H. Liu, C. Gu, R. Fu and D. Jiang, *Angew. Chem., Int. Ed.* **54**, 6814–6818 (2015).
6) X. Chen, M. Addicoat, E. Jin, L. Zhai, H. Xu, N. Huang, Z. Guo, L. Liu, S. Irle and D. Jiang, *J. Am. Chem. Soc.* **137**, 3241–3247 (2015).
7) C. Gu, N. Huang, F. Xu, J. Gao, and D. Jiang, *Sci. Rep.* **5**, 8867 (2015).
8) F. Xu, S. Jin, H. Zhong, D. Wu, X. Yang, X. Chen, H. Wei, R. Fu and D. Jiang, *Sci. Rep.* **5**, 8225 (2015)..
9) N. Huang, X. Chen, R. Krishna and D. Jiang, *Angew. Chem., Int. Ed.* **54**, 2986–2990 (2015).

Solid-State NMR for Molecular Science

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1994 B.S. Himeji Institute of Technology (University of Hyogo)
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Keywords Solid State NMR, Biomolecules, Developments

In order to elucidate functions of molecules, characterization of the molecule is the first step. There are varieties of important molecules which are insoluble to any solvents and functional at amorphous state. Solid-state NMR enables to obtain variety of information at atomic resolution without damages of molecules and significant restrictions. Thus solid-state NMR is one of the essential tools for the characterization of those molecules.

We have been working on methodology and hardware developments of solid-state NMR and their applications for structural biology and material science. We study characterization of membrane proteins and peptides, organic materials, natural products and synthetic polymers. Characterizations of those molecules based on solid-state NMR are under investigations through collaborations with several research groups.

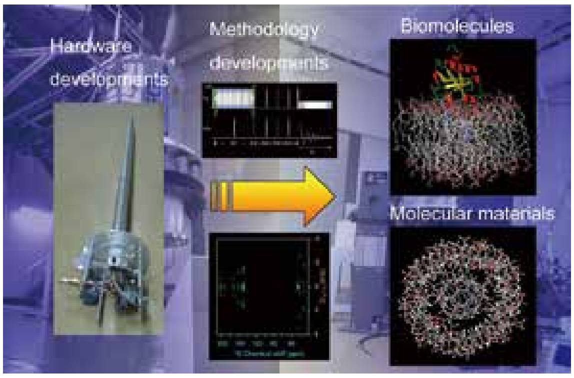

Figure 1. Outline of our studies.

Selected Publications

- J. Hu, R. Fu, K. Nishimura, L. Zhang, H. X. Zhou, D. D. Busath, V. Vijayvergiya and T. A. Cross, "Histidines, Heart of the Hydrogen Ion Channel from Influenza A Virus: Toward an Understanding of Conductance and Proton Selectivity," *Proc. Natl. Acad. Sci. U.S.A.* **103**, 6865–6870 (2006).
- N. Uekama, T. Aoki, T. Maruoka, S. Kurisu, A. Hatakeyama, S. Yamaguchi, M. Okada, H. Yagisawa, K. Nishimura and S. Tuzi, "Influence of Membrane Curvature on the Structure of the Membrane-Associated Pleckstrin Homology Domain of Phospholipase C-δ1," *Biochim. Biophys. Acta, Biomembr.* **1788**, 2575–2583 (2009).
- T. Iijima and K. Nishimura, "^{2}H Quadrupolar Carr-Purcell-Meiboom-Gill NMR for Paramagnetic Solids," *Chem. Phys. Lett.* **514**, 181–186 (2011).
- K. Yazawa, F. Suzuki, Y. Nishiyama, T. Ohata, A. Aoki, K. Nishimura, H. Kaji and T. Asakura, "Determination of Accurate ^{1}H Positions of Alanine Tripeptide with Anti-Parallel and Parallel β-Sheet Structures by High Resolution ^{1}H Solid State NMR and GIPAW Chemical Shift Calculation," *Chem. Commun.* **48**, 11199–11201 (2012).
- M. Tanio and K. Nishimura, "Intramolecular Allosteric Interaction in the Phospholipase C-δ1 Pleckstrin Homology Domain," *Biochim. Biophys. Acta, Proteins Proteomics* **1834**, 1034–1043 (2013).
- M. Yagi-Utsumi, K. Kato and K. Nishimura, "Membrane-Induced Dichotomous Conformation of Amyloid β with the Disordered N-Terminal Segment Followed by the Stable C-Terminal β Structure," *PLoS One* **11**, 0146405 (10 pages) (2016).

1. Membrane Induced Dichotomous Conformation of Amyloid β (1-40) Bound to Lipid Bilayers(1)

Various neurodegenerative disorders are ascribed to pathogenic molecular processes involving conformational transitions of amyloidogenic proteins into toxic aggregates characterized by their β-structure. Accumulating evidence indicate that neural cell membranes provide platforms for such conformational transitions of pathogenic proteins. Amyloid β (Aβ) is a major player in the onset and developments of Alzheimer's disease. Prof. K. Kato group in IMS has successfully determined monomeric structure of Aβ (1-40) bound to glycolipid GM1 embedded in micelles using solution NMR. However the membrane bound Aβ are not accessible with solution NMR techniques, because of its slow molecular tumbling. So we collaborate with Prof. K. Kato group to characterize Aβ oligomers induced on the surface of lipid bilayers composed of neutral lipids prior to formation of amyloid fibril using solid-state NMR.

Fully hydrated uniformly ^{13}C-, and ^{15}N isotope enriched Aβ (1-40) bound to DMPC vesicles were lyophilized immediately after preparation of sample in order to capture oligomeric state of Aβ and used for solid-state NMR measurements. Sequential signal assignments were carried out using solid-state NMR techniques of ^{13}C homonuclear scholar coupling based homonuclear correlation experiment of *constant time uniform cross peak COSY* (CT-UCCOSY) under magic angle spinning (MAS), in conjunction with ^{13}C observed *double cross polarization* (DCP) based NCO and NCA heteronuclear correlation experiments. All of observed signals were successfully assigned to C-terminal segment of Aβ (1-40) from Val$_{24}$ to Val$_{39}$. Through the inspection of conformational dependent isotropic chemical shifts using TALOS-N, the conformation of C-terminal segment of Aβ (1-40) was identified to as β-structure. In order to clarify intermolecular packing of the C-terminal segment of Aβ (1-40), dipolar coupling based through-space homonuclear correlation experiments of *dipolar assisted rotational resonance* (DARR) were carried out with various mixing times up to 400 ms to obtain correlation among carbons up to 6 Å apart. The DARR spectra exhibited correlation peaks among carbons in same and adjacent residues. Therefore, intermolecular arrangement of the C-terminal segments of Aβ (1-40) was identified to as parallel β-sheet structure. The obtained structure of Aβ (1-40) bound to DMPC bilayers differs from any of reported ones such as monomer on lipids and fibrils conformed in the absence and the presence of lipids. The oligomeric structure of Aβ on DMPC bilayers suggests structural transition of Aβ from α to β is occurred at oligomeric state on lipid bilayers.

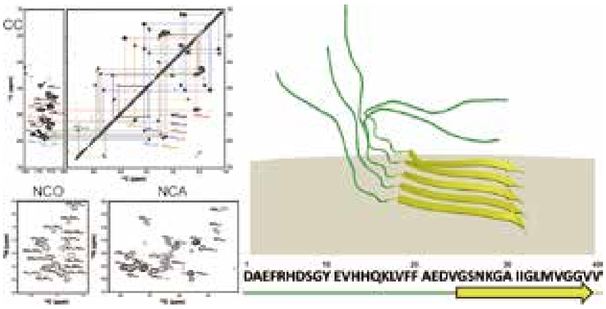

Figure 2. ^{13}C- homonuclear and ^{13}C-^{15}N heteronuclear correlation spectra of [U-^{13}C, ^{15}N] Aβ (1-40) bound to DMPC lipid bilayers acquired by solid-state NMR (right side). The proposed topology model of Aβ (1-40) bound to DMPC lipid bilayers (left side).

2. Characterizations of Organic and Inorganic Materials Based on Solid-State NMR through Observations of Natural Abundant Isotopes(2,3)

There are a number of organic materials, which are insoluble to any solvents. Solid-state NMR is one of the most powerful tools to provide molecular information for such samples at intact conditions. Especially, for small organic molecules and polymers consisting of repeated local structures, ^{1}H and ^{13}C solid-state NMR spectra through the observations of those natural abundant isotopes retain reasonable spectral sensitivities. Combination of ultra high-field and ultra high-speed MAS also enables high-resolution spectra for ^{1}H as demonstrated in the past collaboration works.

We have been collaborated with several research groups to characterize molecular structures of various types of materials using solid-state NMR. During a year, our group contributed to provide molecular information of several molecular materials such as newly designed synthetic polymers(2) for collaboration with Prof. Jiang group in JAIST and also inorganic materials(3) for collaboration with Prof. Iijima group in Yamagata Univ.

Currently, we are also collaborating with several other research groups for characterization studies of natural products, newly designed synthetic polymers, functional materials and *etc.* based on solid-state NMR.

References

1) M. Yagi-Utsumi, K. Kato and K. Nishimura, *PLoS One* **11**, 0146405 (10 pages) (2016).

2) N. Huang, L. Zhai, D. E. Coupry, M. A. Addicoat, K. Okushita, K. Nishimura, T. Heine and D. Jiang, *Nat. Commun.* **7**, 12325 (12 pages) (2016).

3) T. Iijima, T. Yamase and K. Nishimura, *Solid State Nuc. Magn. Reson.* **76–77**, 15–23 (2016).

Development of Novel Heterocyclic Compounds and Their Molecular Assemblies for Advanced Materials

Safety Office

TOMURA, Masaaki
Assistant Professor

Heterocycles containing sulfur and/or nitrogen atoms are useful as components of functional organic materials since heteroatoms in their rings are helpful to stabilize ions or ion-radical species. In addition, intermolecular interactions caused by heteroatom contacts can be expected to form unique molecular assemblies. In this project, novel functional organic materials based on various heterocycles were synthesized and their physical and structural properties were investigated.

1. X-Ray Crystallographic Analyses of Heterocyclic and Aromatic Compounds

The X-ray crystallographic analyses of five heterocyclic and aromatic compounds have revealed their interesting structural natures and unique molecular aggregations. A large number of short intermolecular S···S and S···N contacts are observed in the crystal structures of [1,3]dithiolo[4,5-*c*][1,2,5]thiadiazole-5-thione, 2-thioxo-[1,3]dithiolo[4,5-*b*]pyrazine-5,6-dicarbonitrile and dimethyl 2-([1,3]dithiolo[4,5-*c*][1,2,5]thiadiazol-5-ylidene)-1,3-dithiole-4,5-dicarboxylate. In the bis(tetra-*n*-butylammonium) bis(5,6-dicyanopyrazine-2,3-dithiolato-κ^2*S*,*S*')nickel(II) complex, the centrosymmetric dianion is planar, with an r.m.s. deviation of 0.031(1) Å. We have also found a novel hydrate isomer of cyananilic acid, dihydrate derivative. The cyananilate dianion molecule is planar with an r.m.s. deviation of 0.011(2) Å and is located on an inversion center. The cyananilate molecules are linked via the oxonium ions with intermolecular O–H···O and O–H···N interactions.

Multifunction Integrated Macromolecules for Molecular-Scale Electronics

Safety Office

TANAKA, Shoji
Assistant Professor

Recently a single electron tunnel device (**SET**) has attracted much attention as an ultra-low-power device. In this project, to establish an innovative fabrication process for **SET** systems, we have been developing step-wise synthetic protocols for mono-molecular single-electron tunnel devices and their integrated circuits (**MOSET IC**).

1. Synthesis of 10 nm-Long Molecular Linkers for Supramolecular Architecture

We have already established the synthetic process for a series of "single-nanometer scale" devices. In the current study, we have synthesized long molecular linkers for supramolecular approaches, which are one of the key parts for the integration of nanosize devices to "deca~hecto-nanometer scale" electronic circuits. Figure 1 shows the examples.

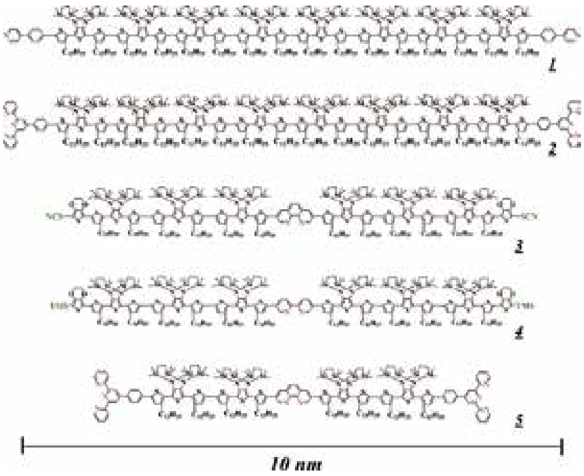

Figure 1. Examples of long molecular linkers with coordination sites.

Visiting Professors

Visiting Professor

NAKAMURA, Masakazu *(from Nara Institute of Science and Technology)*

Giant Seebeck Effect in Pure Fullerene Thin Films

The small thermal conductivity of molecular solids is beneficial for their thermoelectric applications. If Seebeck coefficients were sufficiently large to compensate for the relatively small electrical conductivity, these materials would be promising candidates for thermoelectric devices. In this work, the thermoelectric properties of C_{60} were studied by in situ measurements under ultrahigh vacuum after the deposition of a pure C_{60} thin film. An exceptionally large Seebeck coefficient of more than 150 mV/K was observed as a steady-state thermoelectromotive force. Even considering several extreme but realistic conditions, conventional semi-classical thermoelectric theories cannot explain this giant Seebeck effect.

Visiting Associate Professor

YOSHIKAWA, Hirofumi *(from Kwansei Gakuin University)*

Development of High Performance Rechargeable Batteries Using Various Molecular Materials

Recently, much attention has been focused on development of high-performance rechargeable batteries due to the global energy and environmental crises. Our research interest is to find novel cathode materials toward the next-generation rechargeable battery. In order to realize a high capacity, a stable cycle performance, a rapid charging, and so on, we examine battery performances of various materials such as organic and inorganic compounds, nanomaterials *etc.*, which can take the place of the present general cathode materials, transition metal oxides. We also try to nano-hybridize these materials with nano-carbons such as single-walled carbon nanotubes, graphenes, and mesoporous carbons, to increase electrochemical performances by utilizing electrical double layer capacitance of nanocarbons. Finally, we reveal these electrochemical reaction mechanism by using operando XAFS, XRD, solid-state NMR *etc.* and it is utilized to investigate new materials with high battery performances.

Visiting Associate Professor

TAJIMA, Naoya *(from Toho University)*

Quantum Transport Phenomena in Molecular Massless Dirac Fermion Systems

Two dimensional (2D) massless Dirac fermion systems was realized in an organic conductor α-(BEDT-TTF)$_2$I$_3$ under pressure. This material with layered structure and tilted Dirac cones belongs to a broad category of 2D massless Dirac fermion systems. Moreover, the interaction between Dirac particles are strong. Thus, this system provides us with a testing ground for the quantum transport of multilayered massless Dirac fermion systems. In this work, we develop the field effect transistor channeled by this system and then aim at the detection of (fractional) quantum Hall effect.