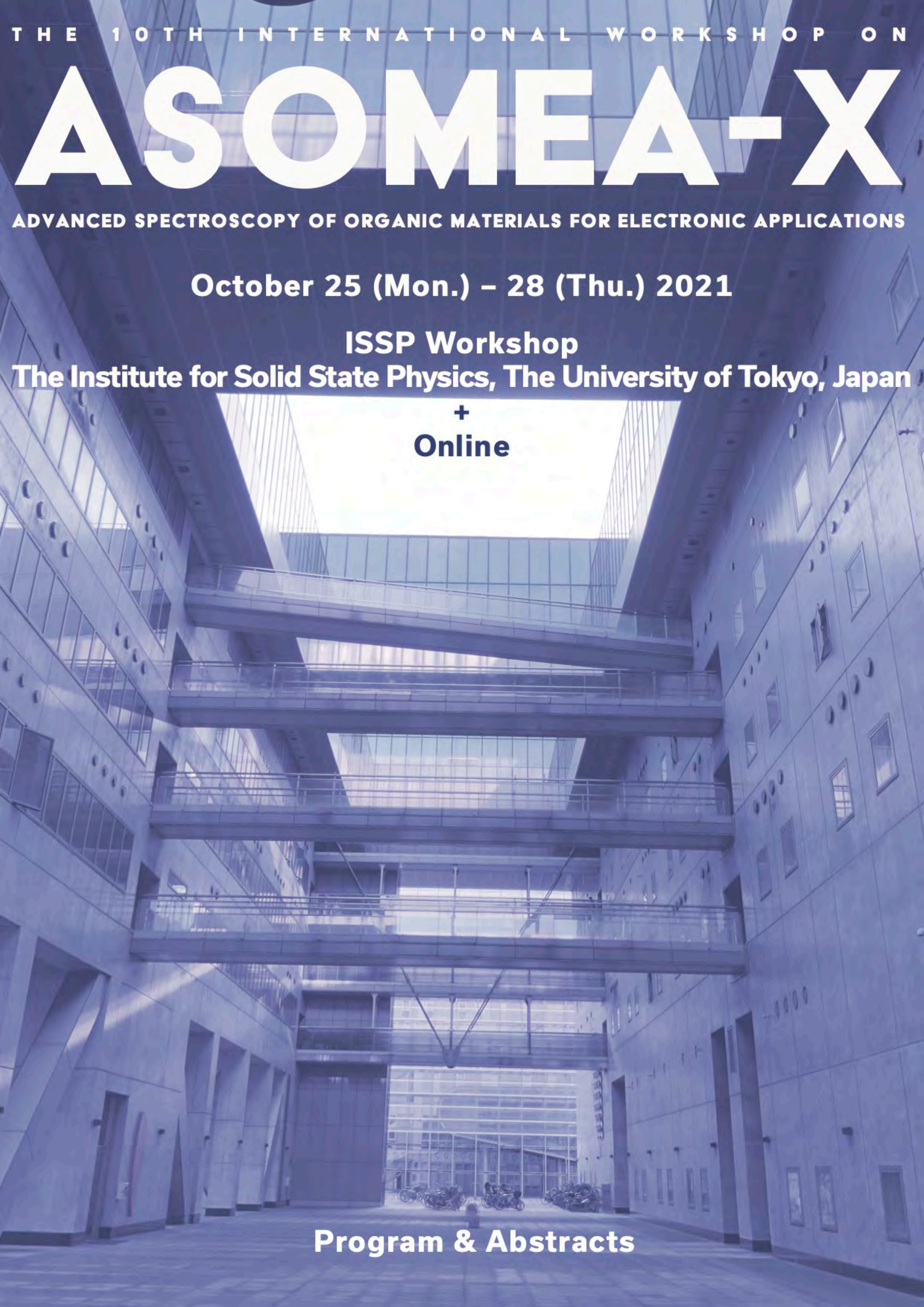


THE 10TH INTERNATIONAL WORKSHOP ON

ASOMEA-X

ADVANCED SPECTROSCOPY OF ORGANIC MATERIALS FOR ELECTRONIC APPLICATIONS

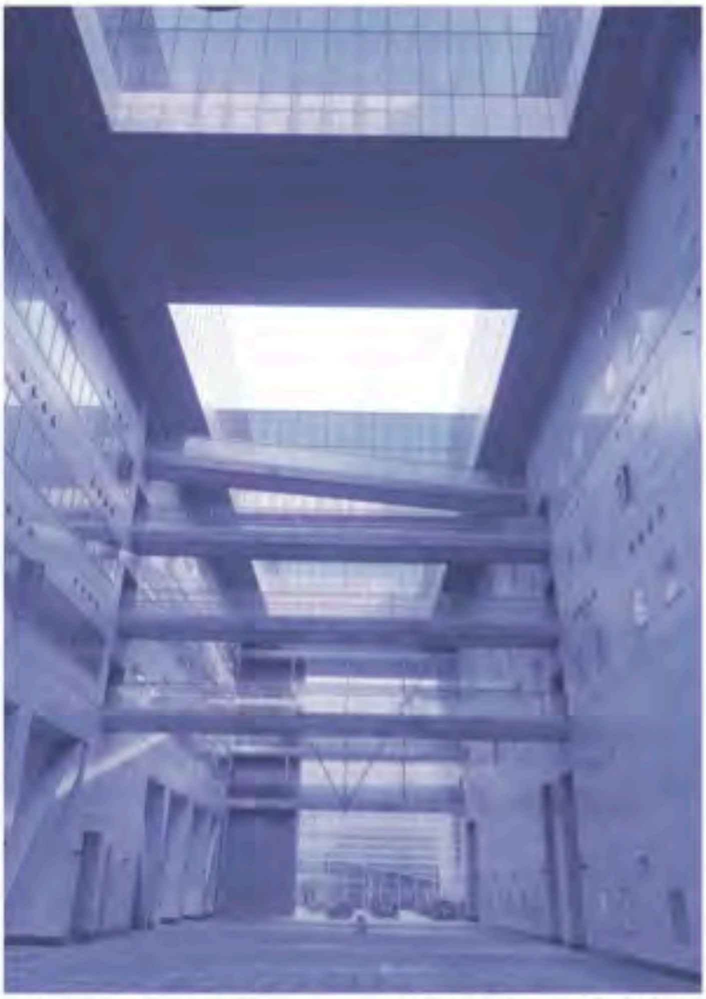
October 25 (Mon.) – 28 (Thu.) 2021

ISSP Workshop
The Institute for Solid State Physics, The University of Tokyo, Japan
+
Online

Program & Abstracts

ASOMEA

X



Oct. 25 Mon. – 28 Thu. 2021

ISSP Workshop
The Institute for Solid State Physics
The University of Tokyo
Japan

ASOMEA-X

The 10th Workshop on Advanced Spectroscopy of Organic Materials for Electronic Applications

October 25 (Monday) – 28 (Thursday), 2021

ISSP Workshop
The Institute for Solid State Physics, The University of Tokyo
Kashiwa-no-ha, Chiba, Japan
+
Online

The series of biannual ASOMEA-workshops began in 2001 as a meeting of Swedish and Japanese scientists working with spectroscopic techniques and theoretical modeling for a better understanding of organic electronic materials and related interfaces. In 2016 the scope of the workshop was widened to include the German community.

In ASOMEA-X (2021), we plan to include Asian communities and the intention to focus on not only organic but also various materials at advanced stages, in-situ/operando techniques, time-resolved spectroscopy and local probe microscopy/spectroscopy.

The size and focus of the meeting will support a lively and intimate atmosphere with discussions on the overall progress and recent development of spectroscopic methods.

Scope of this conference

- Spectroscopy of molecular liquids, solids and interfaces
- UV and X-ray photoelectron spectroscopies/microscopies
- X-ray absorption and emission spectroscopies
- Time-resolved/multi-colored spectroscopies
- Ambient pressure/operando spectroscopies
- Nano & atomic scale observation and spectroscopy of surfaces

etc.

Chair

Prof. Jun Yoshinobu, ISSP, Univ. Tokyo, Japan

International Steering Committee

Prof. Joachim Schnadt, Lund Univ., Sweden
Prof. Stacey Sörensen, Lund Univ., Sweden
Prof. Petra Tegeder, Ruprecht-Karls-Univ. Heidelberg, Germany
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Office

Dr. Shunsuke Tanaka, ISSP, Univ. Tokyo
Kozo Mukai, ISSP, Univ. Tokyo
Yukiko Yagihashi, ISSP, Univ. Tokyo

Meeting History

2001 Orenas Castle Glumslov	2003 Shonan Village Kanagawa	
2005 Vadstena	2007 Chiba	
2009 Krusenberg Herrgard Uppsala	2011 Kaga Onsen Ishikawa	
2014 Lund	2016 Okazaki	2018 Schluchsee
Sweden	**Japan**	**Germany**

Financial Supports

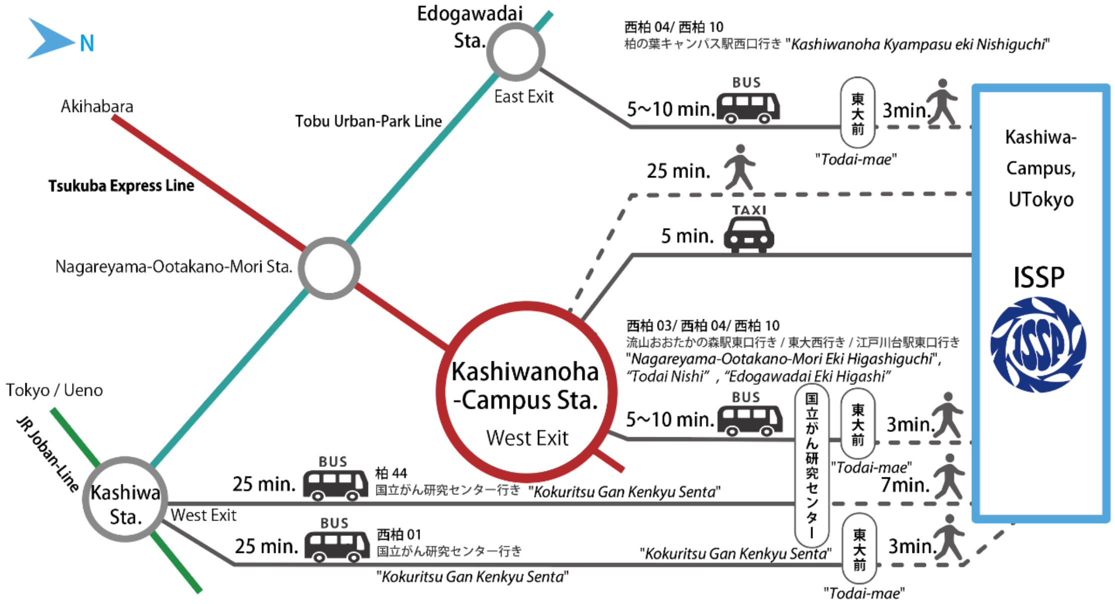
The Murata Science Foundation
The Kajima Foundation
The Institute for Solid State Physics, The University of Tokyo

Supporters

The Japan Society of Applied Physics
The Chemical Society of Japan
The Japan Society of Vacuum and Surface Science
The Physical Society of Japan

Venue (On-site)

The Institute for Solid State Physics (ISSP) Main Bldg., Lecture Room A632 Kashiwa Campus, The University of Tokyo



From Kashiwanoha-campus Station (TX13), Tsukuba Express Line

From #1 bus station at the west exit, take the public buses headed for

- "Nagareyama-Otakanomori-eki higashi guchi" (Nagareyama-Otakanomori Station east exit) / " Todai nichi" (Tokyo University west)
- "Edogawadai-eki higashiguchi" (Edogawadai Sta. east exit)

Get off after 10 minutes ride at "Todai mae", Fare: 170 yen.

From Edogawadai Station (TD20), Tobu Urban Park Line (Noda Line)

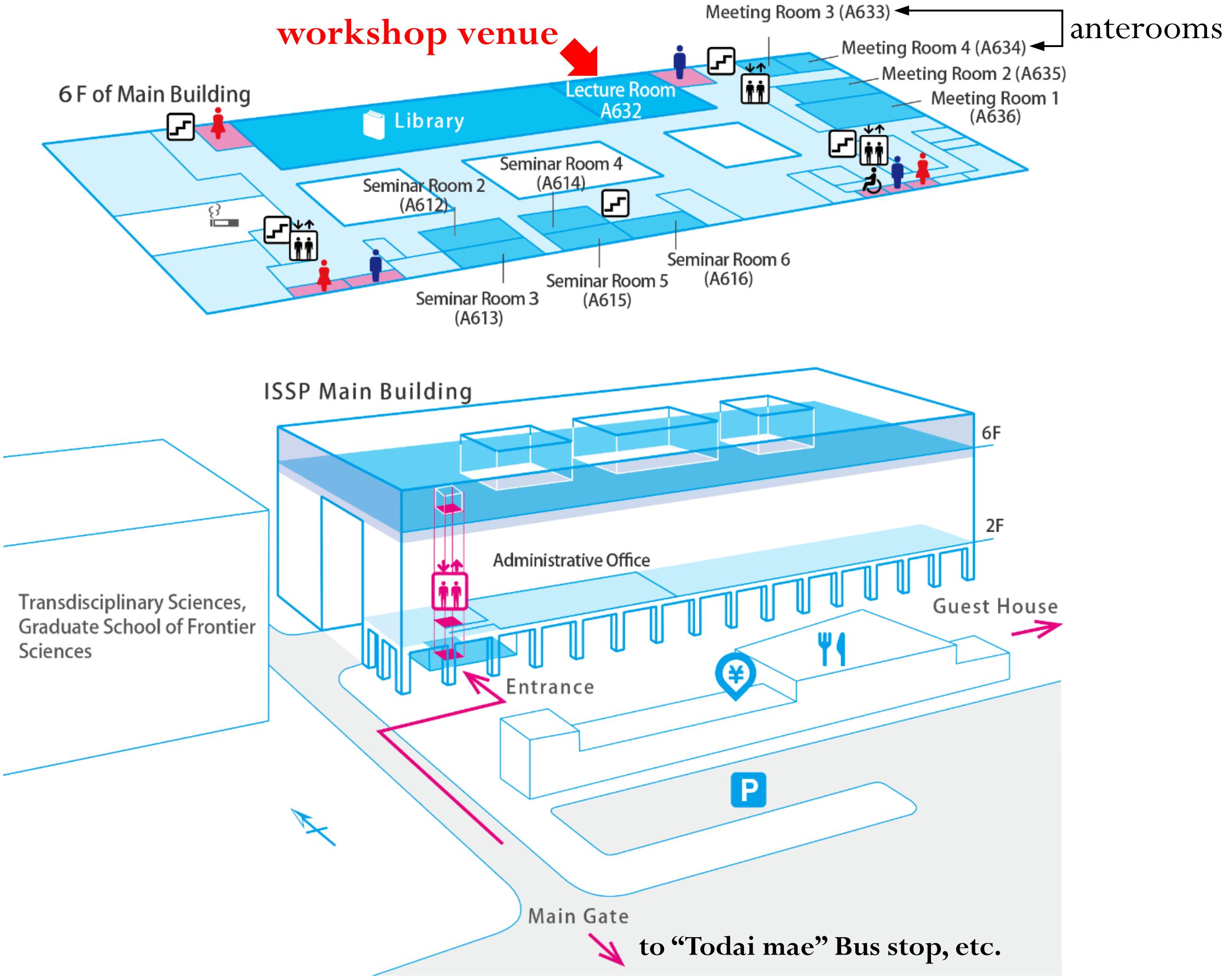
From bus station at east exit, take the public bus headed for"Kashiwanoha Campus eki Niishi guchi (Kashiwanoha Campus Station west exie)"

Get off after 5-10 minutes ride at "Todai mae", Fare: 190-200 yen.

From Kashiwa Station (JJ07, JL28), JR Joban Line

From #2 bus station at the west exit, take the public bus headed for"Kenmin Plaza Keiyu Kokuritsu Gan Kenkyuu Senta (National Cancer Center via Kenmin Plaza)"

Get off after 25 minutes ride at "Todai mae", Fare: 300 yen.



for response to COVID-19, visitors must see

http://www.issp.u-tokyo.ac.jp/maincontents/visitors-covid19_en.html

Access Information (Online)

The workshop is held in an **on-site/online hybrid** manner. Tutorial lectures and oral sessions (including Poster Short Presentations) are simultaneously distributed as Zoom® meetings.

The virtual space for the poster presentations are open throughout the duration of the workshop for casual discussion, where all participants are able to log-in at any time.

Details for accessing the oral and poster sessions has been announced to the participants upon registration via Google Forms.

Instruction for the Oral Presentations

✓ Tutorial Lectures: 50 min. Lecture + 10 min. Q&A
✓ Invited Presentations: 25 min. Talk + 5 min. Q&A
✓ Contributed Oral Presentations: 10 min. Talk + 5 min. Q&A

Each invited and contributed oral presenter is requested to have a 15 min individual Breakout Room Session after her/his talk for extended discussion.

Instruction for the Poster Presentations

The poster session consists of short presentations (5 min for each, in Zoom®) and following core-time discussions (1 h, in SpatialChat®).
The poster should be in A-series documents of landscape (horizontal) orientation.
The preferred file format is jpeg or png, and the file size should be less than 10 MB.
Each presenter is requested to upload her/his poster by October 20, 2021 (JST) via the website given below:

https://yoshinobu.issp.u-tokyo.ac.jp/ASOMEAX_web/PosterSubmission/index.html

Timetable

JST	Mon. 25/Oct.	Tue. 26/Oct.	CST	IST	CEST	MDT
10:30		**I-7** **S. Masuda**	9	7	3	18 (−1)
11:00		**I-8** **S. Duhm**	10		4	19 (−1)
11:30		Breakout		8		
		Lunch				
12:00			11		5	20 (−1)
12:30				9		
13:00	Welcome: H. Mori Opening: J. Yoshinobu	**T-1** **[Tutorial]** **T. Ozaki**	12		6	21 (−1)
13:30	**I-1** **W. Chen**			10		
14:00	**I-2** **Q. Bao**	*Break*	13		7	22 (−1)
		O-4: Y. Hamamoto				
14:30	O-1: M. S. Al Mamun	O-5: M. Shibuta		11		
	Breakout	**I-9** **I. Hamada**				
15:00	*Break*		14		8	23 (−1)
	I-3 **J. Tang**	O-6: S. Kera				
15:30		Breakout		12		
	I-4 **J. Zhu**	*Break*				
16:00		O-7: A. Opitz	15		9	0
	O-2: A. Fleurence	O-8: Q. Wang				
16:30	Breakout	**I-10** **F. C. Bocquet**		13		
	Break					
17:00	**I-5** **T. Komeda**	O-9: Y. Nakayama	16		10	1
		Breakout				
17:30	**I-6** **J. Weissenrieder**	*Break*		14		
		I-11 **P. Tegeder**				
18:00	O-3: K. Takeyasu		17		11	2
	Breakout	Breakout				
18:30	Poster Short Presentation P-1 − P-6	Poster Short Presentation P-7 − P-12		15		
19:00	Poster Session Core-time: P-1 − P-6	Poster Session Core-time: P-7 − P-12	18		12	3
19:30				16		

<u>note</u> T: tutorial lecture, I: invited, O: contributed oral, P: poster

Timetable

(continued)

JST	Wed. 27/Oct.	Thu. 28/Oct.	CST	IST	CEST	MDT
10:30	**I-12** **S. Park**	**I-17** **J. Guo**	9	7	3	18 (−1)
11:00	**I-13** **O. L. A. Monti**	O-16: K. Ozawa	10		4	19 (−1)
		O-17: R. Ugalino				
11:30	Breakout	Breakout		8		
	Lunch	*Lunch*				
12:00			11		5	20 (−1)
12:30				9		
13:00	**T-2** **[Tutorial]** **S. Shin**	**T-3** **[Tutorial]** **J. Takeya**	12		6	21 (−1)
13:30				10		
14:00	*Break*	*Break*	13		7	22 (−1)
	O-10: L. T. Ta	O-18: H. Yoshida				
14:30	O-11: S. Tanaka	O-19: H. Ishii		11		
	I-14 **K. Dani**	**I-18** **T. Suzuki**				
15:00			14		8	23 (−1)
	O-12: I. Matsuda	O-20: M. Horio				
15:30	Breakout	Breakout		12		
	Break	*Break*				
16:00	O-13: R. Wallauer	O-21: A. Sahu	15		9	0
	O-14: T. K. Yamada	O-22: A. Patra				
16:30	**I-15** **J. Uhlig**	**I-19** **A. Ishizaki**		13		
17:00	O-15: J. Schnadt	**I-20** **M. Rossi**	16		10	1
	Breakout					
17:30	*Break*	Breakout		14		
	I-16 **T. Fritz**	Closing S. Kera + α				
18:00			17		11	2
	Breakout					
18:30	Poster Short Presentation P-13 – P-18			15		
19:00	Poster Session Core-time: P-13 – P-18		18		12	3
19:30				16		

Monday, 25/Oct./2021

13:00		Welcome (Hatsumi Mori, Director of ISSP, Univ. Tokyo)
13:05		Opening Remarks (Jun Yoshinobu, Chair of ASOMEA-X)
		Chair: Jianxin Tang (Soochow Univ.)
13:30	I-1	**Wei Chen**, *National University of Singapore, Singapore* “Interface Engineering Enabled Ohmic Contacts for 2D Materials”
14:00	I-2	**Qinye Bao**, *East China Normal University, China* “Interface Energetics in Perovskite Solar Cells”
14:30	O-1	**Muhammad Shamim Al Mamun**, *Tohoku University, Japan* “UV/Thermally Induced Isomerization of Nitro-spiropyran on MoS_2 Lattice Observed by MoS_2 Field Effect Transistor”
14:45		Breakout Room Session (I-1, I-2, O-1)
15:00		Break
		Chair: Qinye Bao (East China Normal Univ.)
15:15	I-3	**Jianxin Tang**, *Soochow University, China* “Interfacial “Anchoring Effect” Enables Efficient Blue Perovskite LEDs”
15:45	I-4	**Junfa Zhu**, *University of Science and Technology of China, China* “In-situ Investigations of Metal Electrodes/Perovskite Interfacial Structures”
16:15	O-2	**Antoine Fleurence**, *Japan Advanced Institute of Science and Technology, Japan* “Band Engineering in an Epitaxial Two-dimensional Honeycomb $Si_{6-x}Ge_x$ Alloy”
16:30		Breakout Room Session (I-3, I-4, O-2)
16:45		Break

Monday, 25/Oct./2021

(continued)

Chair: Ryuichi Arafune (NIMS)

17:00 I-5 **Tadahiro Komeda**, *Tohoku University, Japan*
"Spin State of Single Molecule Magnet Adsorbed on Superconducting NbSe$_2$ Surface Using Scanning Tunneling Microscopy"

17:30 I-6 **Jonas Weissenrieder**, *Royal Institute of Technology, Stockholm, Sweden*
"Synthesis and Reactivity of a Model Catalyst: Isolated Fe$_1$O$_3$ Sites on Pt(111) and Cu$_2$O(100)"

18:00 O-3 **Kotaro Takeyasu**, *University of Tsukuba, Japan*
"Role of Pyridinic Nitrogen in the Mechanism of the Oxygen Reduction Reaction on Carbon Electrocatalysts"

18:15 Breakout Room Session (I-5, I-6, O-3)

Chair: Hiroyuki Yoshida (Chiba Univ.)

18:30 Poster Session: Short Presentation

P-1 **Yoshihisa Harada**
P-2 **Tsuyoshi Takaoka**
P-3 **Younghyun Choi**
P-4 **Kaishu Kawaguchi**
P-5 **Xiaoni Zhang**
P-6 **Fumihiko Ozaki**

19:00 Poster Session: Core-time discussions for P-1 – P-6 (~20:00)

Tuesday, 26/Oct./2021

Chair: Ikutaro Hamada (Osaka Univ.)

10:30	I-7	**Shigeru Masuda**, *The University of Tokyo, Japan* "Electronic States at Organic-metal Interface Studied by MAES, UPS, and DFT Calculation"
11:00	I-8	**Steffen Duhm**, *Soochow University, China* "Photoelectron Spectroscopy Reveals Inversion Layers in Hybrid Organic-Silicon Heterojunctions"
11:30		Breakout Room Session (I-7, I-8)
11:45		Lunch

Chair: Jun Yoshinobu (ISSP, Univ. Tokyo)

13:00	T-1	**Taisuke Ozaki**, *ISSP, The University of Tokyo, Japan* **[Tutorial Lecture]** "Theory of Core-level Photoelectron Spectroscopy"
14:00		Break

Chair: Steffen Duhm (Soochow Univ.)

14:15	O-4	**Yuji Hamamoto**, *Osaka University, Japan* "Hybrid Image Potential States in Lead Phthalocyanine on Graphene"
14:30	O-5	**Masahiro Shibuta**, *Osaka City University, Japan* "Confined Hot Electron Relaxation at the Molecular Heterointerface of the Size-Selected Plasmonic Noble Metal Nanocluster and Layered C_{60}"
14:45	I-9	**Ikutaro Hamada**, *Osaka University, Japan* "Toward Accurate Description of Organic Semiconductors and Organic/Metal Interfaces from First Principles"
15:15	O-6	**Satoshi Kera**, *Institute for Molecular Science, NINS, Japan* "Energy Band Dispersion Modified by Phonon and Vibronic Couplings"
15:30		Breakout Room Session (I-9, O-4, O-5, O-6)
15:45		Break

Tuesday, 26/Oct./2021

(continued)

Chair: Kouki Akaike (AIST)

16:00 O-7 **Andreas Opitz**, *Humboldt-Universität zu Berlin, Germany*
“Fermi Level Pinned Molecular Donor/Acceptor Junctions: Reduction of Induced Carrier Density by Interfacial Charge Transfer Complexes”

16:15 O-8 **Qi Wang**, *Soochow University, China*
“Studies of Organic Heterostructures on Coinage Metal Substrates”

16:30 I-10 **François C. Bocquet**, *Forschungszentrum Jülich GmbH, Germany*
“Insights into the Collective Electronic Losses at Surfaces with Momentum Resolution”

17:00 O-9 **Yasuo Nakayama**, *Tokyo University of Science, Japan*
“Exciton Energy-momentum Dispersion in the Single Crystal Pentacene Probed by Low-energy Angle-resolved Electron Energy-loss Spectroscopy”

17:15 Breakout Room Session (I-10, O-7, O-8, O-9)

17:30 Break

Chair: Yasuo Nakayama (Tokyo Univ. Sci.)

17:45 I-11 **Petra Tegeder**, *Ruprecht-Karls-Universität Heidelberg, Germany*
“Electronic Properties of Interfaces with N-Heteropolycyclic Molecules”

18:15 Breakout Room Session (I-11)

Chair: Yoichi Yamada (Univ. Tsukuba)

18:30 Poster Session: Short Presentation

P-7	**Takashi Yamada**	P-10	**Syed A. Ab Rahman**
P-8	**Yuri Hasegawa**	P-11	**Masato Iwasawa**
P-9	**Haruki Sato**	P-12	**Yuki Gunjo**

19:00 Poster Session: Core-time discussions for P-7 – P-12 (~20:00)

Wednesday, 27/Oct./2021

Chair: Keshav Dani (OIST)

10:30	I-12	**Soohyung Park**, *Korea Institute of Science and Technology, Republic of Korea* "Study on the Electronic Structure of van der Waals Heterointerfaces: 2D Semiconductor with Functional Organic Molecules"
11:00	I-13	**Oliver L. A. Monti**, *University of Arizona, USA* "Tailoring the Optical and Electronic Response in 2D Materials"
11:30		Breakout Room Session (I-12, I-13)
11:45		Lunch

Chair: Kozo Okazaki (ISSP, Univ. Tokyo)

13:00	T-2	**Shik Shin**, *The University of Tokyo, Japan* **[Tutorial Lecture]** "Ultrahigh Resolution Laser Photoelectron Spectroscopy"
14:00		Break

Chair: Takeshi Kondo (ISSP, Univ. Tokyo)

14:15	O-10	**Luong Thi Ta**, *Osaka University, Japan* "Adsorption of Toxic Gases on Borophene: Surface Deformation Links to Chemisorptions"
14:30	O-11	**Shunshuke Tanaka**, *ISSP, The University of Tokyo, Japan* "Multipole Plasmon Excitation at a Multilayer Structure of Cs/graphene/Cs on Ir(111)"
14:45	I-14	**Keshav Dani**, *Okinawa Institute of Science & Technology Graduate University, Japan* "Imaging Excitonic States with Time-resolved Photoemission Spectroscopy in 2D Semiconductor Heterostructures"
15:15	O-12	**Iwao Matsuda**, *ISSP, The University of Tokyo, Japan* "Environmental Effects in Layer-dependent Dynamics of Dirac Fermions in Quasi-crystalline Bilayer Graphene"
15:30		Breakout Room Session (I-14, O-10, O-11, O-12)
15:45		Break

Wednesday, 27/Oct./2021

(continued)

Chair: Kenichi Ozawa (TIT)

16:00 O-13 **Robert Wallauer**, *Philipps-Universität Marburg, Germany*
"Tracing Orbital Images at Surfaces and Interfaces on Ultrafast Time Scales by Photoemission Tomography"

16:15 O-14 **Toyo Kazu Yamada**, *Chiba University, Japan*
"On-surface Construction of Host-guest Molecular System: Absorption of Guest Atom / Molecule on Host Crown Ether Array"

16:30 I-15 **Jens Uhlig**, *Lund University, Sweden*
"Resolving Dynamics in Real World Complexes with Rime-resolved X-ray Spectroscopy"

17:00 O-15 **Joachim Schnadt**, *Lund University, Sweden*
"Beyond the Ligand Exchange Model: Time-Resolved APXPS Studies of the Atomic Layer Deposition of HfO_2 on InAs"

17:15 Breakout Room Session (I-15, O-13, O-14, O-15)

17:30 Break

Chair: Soohyung Park (KIST)

17:45 I-16 **Torsten Fritz**, *Friedrich-Schiller-Universität Jena, Germany*
"Aromatic Molecules Decoupled from Metals via Modern 2D Materials beyond Graphene"

18:15 Breakout Room Session (I-16)

Chair: Yasuo Nakayama (Tokyo Univ. Sci.)

18:30 Poster Session: Short Presentation

P-13 **Noriyuki Tsukahara**
P-14 **Yoichi Yamada**
P-15 **Hiroshi Okuyama**
P-16 **Ryohei Tsuruta**
P-17 **Gota Endo**
P-18 **Taiyo Nakanishi**

19:00 Poster Session: Core-time discussions for P-13 – P-18 (~20:00)

Thursday, 28/Oct./2021

Chair: Yoshihisa Harada (ISSP, Univ. Tokyo)

10:30	I-17	**Jinghua Guo**, *Advanced Light Source, Lawrence Berkeley National Laboratory, USA* "In-situ/Operando Soft X-ray Spectroscopy Study Charge Transfer and Structural Formation of Electrochemical Interfaces"
11:00	O-16	**Kenichi Ozawa**, *Tokyo Institute of Technology, Japan* "Time-resolved XPS Study of the Effect of Stacking Order on Exciton Dissociation in a Bilayer Photovoltaic System"
11:15	O-17	**Ralph Ugalino**, *ISSP, The University of Tokyo, Japan* "Electronic Signature of a "Breathing" Transition in a Metal-organic Framework by Resonant Inelastic X-ray Scattering (RIXS)"
11:30		Breakout Room Session (I-17, O-16, O-17)
11:45		Lunch

Chair: Satoshi Kera (IMS)

13:00	T-3	**Jun Takeya**, *The University of Tokyo, Japan* **[Tutorial Lecture]** "Present Status and Future of Organic Device"
14:00		Break

Chair: Akihito Ishizaki (IMS)

14:15	O-18	**Hiroyuki Yoshida**, *Chiba University, Japan* "Energy Band Structure of the Lowest Unoccupied Molecular Orbital and Polaron Formation in High-Mobility Organic Semiconductors"
14:30	O-19	**Hiroyuki Ishii**, *University of Tsukuba, Japan* "Impact of Small Polaron with Low-Frequency Molecular Vibration on Electron Mobility of Organic Semiconductors"
14:45	I-18	**Takeshi Suzuki**, *ISSP, The University of Tokyo, Japan* "Time- and Angle-resolved Photoemission Study on Quantum Materials"
15:15	O-20	**Masafumi Horio**, *ISSP, The University of Tokyo, Japan* "Surface-doping Induced Mott Breakdown in Ca_2RuO_4"
15:30		Breakout Room Session (I-18, O-18, O-19, O-20)
15:45		Break

Thursday, 28/Oct./2021

(continued)

Chair: Takeshi Suzuki (ISSP, Univ. Tokyo)

16:00	O-21	**Arundhati Sahu**, *National Institute of Science and Technology, Berhampur, India* “Exploring Effective Surface Passivation of CdS QD’s with Gallic Acid: from Green Synthesis to Highly Fluorescent Molecular Probe”
16:15	O-22	**Asutosh Patra**, *Berhampur University, India* “Charge Transfer Interaction of Citric Acid Passivated CdS QD’s with Natural Dyes Under Visible Light Irradiation”
16:30	I-19	**Akihito Ishizaki**, *Institute for Molecular Science, NINS, Japan* “Investigating Excited-state Dynamics in Molecules with Quantum Light”
17:00	I-20	**Mariana Rossi**, *MPSD, Max-Planck-Gesellschaft, Germany* “Unraveling Structural and Dynamical Properties of (Quantum) Nuclei in Diverse Materials”
17:30		Breakout Room Session (I-19, I-20, O-21, O-22)
17:45		Closing Remarks (Satoshi Kera, International Advisory Board)

List of Poster Presentations

Monday, 25/Oct./2021

Short Presentation 18:30 – 19:00, Core-time discussion 19:00 – 20:00 (JST)

P-1 **Yoshihisa Harada**, *ISSP, The University of Tokyo, Japan*
"Electronic Structure of Ultrafine Water Cluster Deposited on a Hydrophobic Surface Explored by Soft X-ray Emission Spectroscopy"

P-2 **Tsuyoshi Takaoka**, *Tohoku University, Japan*
"Spectra of the Photocurrent of CuPc-adsorbed MoS_2-FET"

P-3 **Younghyun Choi**, *ISSP, The University of Tokyo, Japan*
"AP-XPS Study of Methane and Carbon Dioxide for Methane Dry Reformation on a Pt(997) Surface"

P-4 **Kaishu Kawaguchi**, *ISSP, The University of Tokyo, Japan*
"Time-, Spin- and Angle-resolved Photoemission Spectroscopy of Spin-polarized Surface States with the 10.7-eV Extreme-ultraviolet at 1-MHz Repetition Rate"

P-5 **Xiaoni Zhang**, *ISSP, The University of Tokyo, Japan*
"Electronic Structure of Borophane, Studied by X-ray Spectroscopy"

P-6 **Fumihiko Ozaki**, *ISSP, The University of Tokyo, Japan*
"Interaction between the Functionalized MoS_2 Basal Surface and Hydrogen"

Tuesday, 26/Oct./2021

Short Presentation 18:30 – 19:00, Core-time discussion 19:00 – 20:00 (JST)

P-7 **Takashi Yamada**, *Osaka University, Japan*
"Correlation between Superstructure, Photoluminescence, and Excited-state Dynamics of Polyaromatic Hydrocarbon Thin Films on Graphite"

P-8 **Yuri Hasegawa**, *Ritsumeikan University, Japan*
"Impact of Weak Electronic Coupling on the Electronic Structure at the Molecule/Graphite Interface"

P-9 **Haruki Sato**, *Chiba University, Japan*
"Measurement of LUMO Band Structure of Organic Semiconductor"

P-10 **Syed A. Ab Rahman**, *Chiba University, Japan*
"Evidence of Polaron Formation in Organic Semiconductor from Temperature-dependent HOMO/LUMO Bandwidth"

P-11 **Masato Iwasawa**, *University of Tsukuba, Japan*
"Momentum Microscopy of Highly Oriented Organic Thin Films on Ag(110)"

P-12 **Yuki Gunjo**, *Tokyo University of Science, Japan*
"Interface Structures and Electronic States of Tetraaza-acenes on Single Crystal Pentacene"

Wednesday, 27/Oct./2021

Short Presentation 18:30 – 19:00, Core-time discussion 19:00 – 20:00 (JST)

P-13 **Noriyuki Tsukahara**, *National Institute of Technology, Gunma College, Japan*
"Competition between Adsorbate-adsorbate Coupling and Adsorbate-substrate Interaction in the Superstructure Formation of Molecular Layers"

P-14 **Yoichi Yamada**, *University of Tsukuba, Japan*
"Direct Visualization of Nearly-free-electron States Formed by Superatom Molecular Orbitals in Li@C_{60} Monolayer"

P-15 **Hiroshi Okuyama**, *Kyoto University, Japan*
"Fano Interference in Electron Transport through Individual CuPc Molecules on Cu(100)"

P-16 **Ryohei Tsuruta**, *University of Tsukuba, Japan*
"Crystal Structure of C_{70} Fullerene on Organic Single Crystals"

P-17 **Gota Endo**, *Tokyo University of Science, Japan*
"Crystal Structures of Pentacene Thin Films Grown on the Epitaxial C_{60} on the Single Crystal Rubrene"

P-18 **Taiyo Nakanishi**, *Tokyo University of Science, Japan*
"H_2O-iduced Crystallization of Organic Luminescent Thin Films by Direct Film Storage in a High Vacuum"

Monday

25/Oct./2021

Interface Engineering Enabled Ohmic Contacts for 2D Materials

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Two-dimensional (2D) layered materials like graphene and transition metal dichalcogenides (TMDs) have been considered as promising building blocks for the next generation nanoelectronic devices, showing great potentials to extend the scaling limits existing in silicon based complementary metal-oxide-semiconductor field-effect-transistors (CMOS-FET) as well as to serve as a high mobility alternative to organic semiconductors for flexible electronic and optoelectronic devices. However, the existence of large contact resistance at the interface between the TMDs semiconductor and any bulk (or 3D) metal drastically restrains the intrinsic transport properties of materials and the performance of realistic devices. Thus, it is a crucial to optimize the contacts and lower the contact resistance between 2D semiconductors and metal electrodes.

In this talk, I will summarize and discuss our recent work for the development of scalable Ohmic contact engineering approaches to 2D materials that can be easily integrated into existing semiconductor device production processes. We will focus on the Ohmic contact to 2D materials enabled by surface charge transfer doping induced semiconductor-to-metal phase transition, and the demonstration of high performance 2D materials based electronic devices with Ohmic contact.

Interface Energetics in Perovskite Solar cells

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Organic-inorganic halide perovskites have drawn worldwide attention because they have many exceptional optoelectronic properties such as high absorption coefficients, long carrier diffusion lengths, and adjustable band gaps, which enable them to be a promising semiconductor for new-generation photovoltaic technology. Perovskite interface plays a critical role in many key electronic processes, *e.g.* charge injection/extraction and recombination, significantly governing the final device efficiency and lifetime. In this talk, we will discuss our recent work on the electronic structures at 2D Ruddlesden–Popper perovskite/electron transport layer interface [1], and direct observation of perovskite surface region energetics transformation from p- to n-type during defect passivation [2-3]. These results could provide guidance for design high-performance perovskite solar cells with reduced energy loss.

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UV/Thermally Induced Isomerization of Nitro-Spiropyran on MoS$_2$ Lattice Observed by MoS$_2$ Field Effect Transistor

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Abstract: Nanotechnology is being considered as a mainstream technology of the 21st century due to its aspects of observing and modifying matter at the nano level.[1] Molecules with very specific functional groups can be modulated by outside stimuli are of great interest for sensing and optoelectronics.[2] In this report, we observe the photo/thermal induced structural switching of spiropyran (1′,3′-Dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)-indole]) molecule through electrical property measurement by MoS$_2$-FET (Fig 1a shows the illustration of molecular switching on MoS$_2$-FET). Well controlled functionalization of MoS$_2$ by spiropyran (SP) can be possible by the external photon irradiation. The conformational change of the spiropyran between spiropyran and merocyanine (MC) was monitored, shown I Fig 1b. TOF-SIMS measurement confirms the presence of spiropyran over the MoS$_2$ after functionalization. Raman spectroscopy confirms the n-doping of both SP and MC.

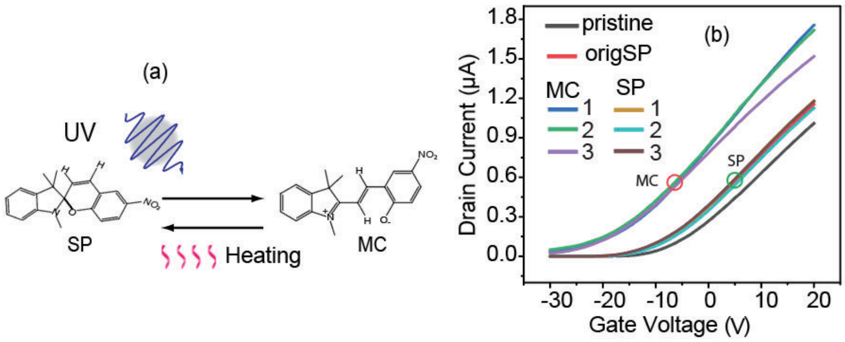

Fig. 1 (a) Illustration of SP/MC isomerization on MoS$_2$-FET, (b) I_d-V_g cycles induced by UV/thermal heat.

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Interfacial "Anchoring Effect" Enables Efficient Blue Perovskite LEDs

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Perovskite light-emitting diodes (PeLEDs) with green and red emissions have made tremendous progress in recent years. However, the realization of efficient and stable blue-emission PeLEDs remains challenging, which greatly limits their potential applications in high-quality full-color displays and solid-state lighting. A delicate control over the entire electroluminescence process is indispensable to overcome the performance limitations of blue PeLEDs. Here, we demonstrate an efficient device architecture to synergistically reduce the energetic losses during electron-photon conversion and boost the extraction of trapped light in the device. A facile and reliable interface engineering scheme for manipulating the crystallization of perovskite films enabled by a multi-functional molecule-triggered anchoring effect at the grain-growth interface via the supplier of heterogeneous nucleation seeds [1]. The crystallization process of highly emissive perovskite nanocrystals is controlled with the suppression of the trap-mediated non-radiative recombination losses due to interfacial hydrogen bonding interactions [2]. This manipulation results in blue perovskite films with large-area uniformity and low trap-states [3]. The synergistical boost in device performance is achieved for large-area sky-blue PeLED with a peak external quantum efficiency (EQE) of 9.2% and small-area device with an EQE of 12.8% emitting at 486 nm, along with the improved spectral stability and operation lifetime [3,4]. In addition, the maximum EQE reaches 16.8% after combining an internal outcoupling structure without spectral distortion, which can be further raised to 27.5% when using a lens-based structure on top of the device [4].

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In-situ Investigations of metal electrodes/Perovskite Interfacial Structures

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$CH_3NH_3PbX_3$ (X = Cl, Br, I) based perovskite solar cells (PVSCs) have recently attracted plenty of attention as they feature excellent properties such as a large extinction coefficient, high carrier mobility and long carrier diffusion length. In the last decade, the power conversion efficiencies (PCEs) of PVSCs have been improved from 3.8 to 25.5%. This is a staggering advancement compared to the rather slow progress achieved for classic silicon solar cells. Nevertheless, the low stability issues of PVSCs are still the largest problem restricting their commercialization, which triggers off a large number of studies for solving the stability problem of PVSCs. It is well-known that the interface structures inside the solar cells strongly affect the performances of the PVSCs. A fundamental understanding of the interface structure between the metal electrode and perovskite is essential to the development of more efficient PVSCs. In this presentation, we will report our recent studies on the interfacial structures of different metals, namely Ag, Al and Cu, on the perovskite thin film samples using in situ synchrotron radiation photoemission spectroscopy (SRPES) and X-ray photoelectron spectroscopy (XPS). The perovskite samples were fabricated by spin-coating the precursor solution (CH_3NH_3I and PbI_2 dissolved in dimethyl formamide and dimethyl sulfoxide) onto the substrate (NiO_x coated on ITO/glass). We found that both Ag and Al can react with the $CH_3NH_3PbI_3$ film, destroying the perovskite structure at the interface, while Cu does not react with perovskite layer. The Cu/$CH_3NH_3PbI_3$ interface is rather stable. Based on these results, we fabricated a proto-type of solar cell with the configuration of Cu/$CH_3NH_3PbI_3$/NiO_x/ITO to verify the device stability. We found that even though Cu is in direct contact with the $CH_3NH_3PbI_3$ film, the PCE of the device equals or even exceeds the initial PCE (9.99 %) after 49 days. The long-term stability of the Cu-$CH_3NH_3PbI_3$ device is attributed to the superb stability of the Cu/$CH_3NH_3PbI_3$ interface, which is further verified with a time dependent XPS. From these detailed interfacial investigations and performance characterizations, we obtained a structure-performance correlation in Cu/$CH_3NH_3PbI_3$ system, which provides a fundamental information guideline for advancing perovskite cell development.

Band engineering in an epitaxial two-dimensional honeycomb $Si_{6-x}Ge_x$ alloy

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Owing to properties finely tunable by means of their composition, alloys are materials of great interest for various applications. This is exemplified by semiconducting alloys, whose band gap can be controlled by the ratio of their components. In this contribution, we demonstrate experimentally that it is possible to form a two-dimensional (2D) silicene-like Si_5Ge compound by replacing the Si atoms occupying on-top sites in the atomic structure of epitaxial silicene on $ZrB_2(0001)$ thin films [1] by Ge atoms [2]. For coverages below 1/6 monolayer, the deposition of Ge atoms on silicene gives rise to a $Si_{6-x}Ge_x$ alloy (with x between 0 and 1) in which the on-top sites of their planar-like structures are randomly occupied by Si or Ge atoms as visible in the scanning tunneling microscopy (STM) image of Figure (a). The progressive increase of the valence band maximum with x resolved by angle-resolved photoemission spectroscopy (ARPES) (Figs. (b) and (c)), was found to originate, according to density functional theory (DFT) calculations, from a charge transfer from Ge atoms to Si atoms.

These achievements provide evidence for the possibility of engineering the band structure in 2D SiGe alloys in a way that is similar for their bulk counterpart and point out the high potential of silicene for keeping scaling down the Si-based technologies.

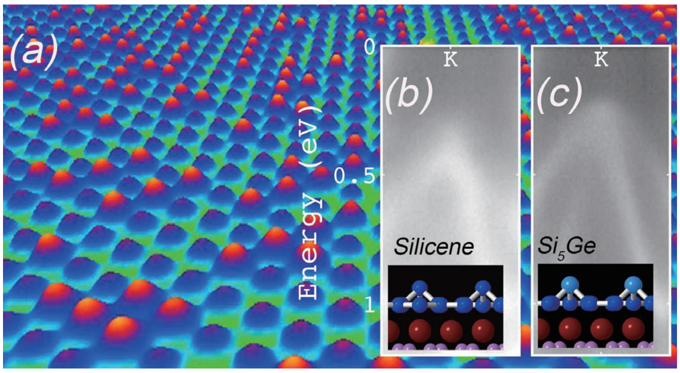

Figure: (a) STM image (V = 1.0 V, I = 100 pA) of $Si_{5.666}Ge_{0.333}$ shown in a perspective view. Tall and small protrusions are Si and Ge atoms respectively. The distance between protrusions is 6.35 Å. (b) and (c) ARPES spectra recorded around the *K* point of unreconstructed Brillouin zone for silicene and Si_5Ge, respectively. The insets show their planar-like structures determined by DFT. Zr, B, Si and Ge atoms are respectively colored in red, pink dark and light blue.

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Spin State of Single Molecule Magnet Adsorbed on Superconducting $NbSe_2$ Surface using Scanning Tunneling Microscopy

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The application of magnetic molecules to the materials of the devices for the quantum information process attracts attentions. It is critical to make the sharp spin state of the molecule coupled efficiently with the electric current and substrate. The double-decker phthalocyanine complex of bis(phthalocyaninato)terbium(III) ($TbPc_2$) molecule shows intriguing single molecule magnet (SMM) behavior and was examined on the substrates Au(111)[1], Ag(111).[2] Here, we studied the $TbPc_2$ molecule adsorbed on the superconducting substrate of $NbSe_2$, in order to demonstrate of the use of the mix states between the SMM spins and the superconducting state.

Experimentally, we show the scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) studies at the sample temperature of 400 mK (Unisoku, Japan) for the system of $TbPc_2$ molecules

We observed Yu-Shiba-Rusinov (YSR) states formed by the two system of the superconductor and the magnetic molecule, which appear in the superconducting gap and. In addition we observed the Kondo resonance of $TbPc_2$ molecule for π-radical of ligand and 4f spin of Tb atom on Co intercalated $NbSe_2$. We assumed that the Co assisted the formation of Kondo resonance where Co spin is responsible to break the Cooper pairs of superconductor substrates and forms itinerary electrons, later these itinerary electrons screened the localized spin to form Kondo resonance for both the π-radical and Tb 4f electrons. Without Co deposition there appears no Kondo resonance We anticipate our results can be contributed towards the utilization of SMM as the building blocks of the future spintronics devices as well as fascinating application to the data storage or quantum computing.

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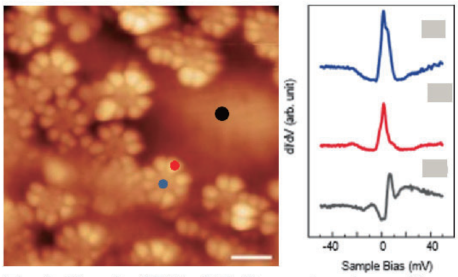

Fig 1: Kondo STS of $TbPc_2$ molecule on Co intercalated $NbSe_2$ substrates

Synthesis and Reactivity of a Model catalyst: isolated Fe_1O_3 sites on Pt(111) and $Cu_2O(100)$

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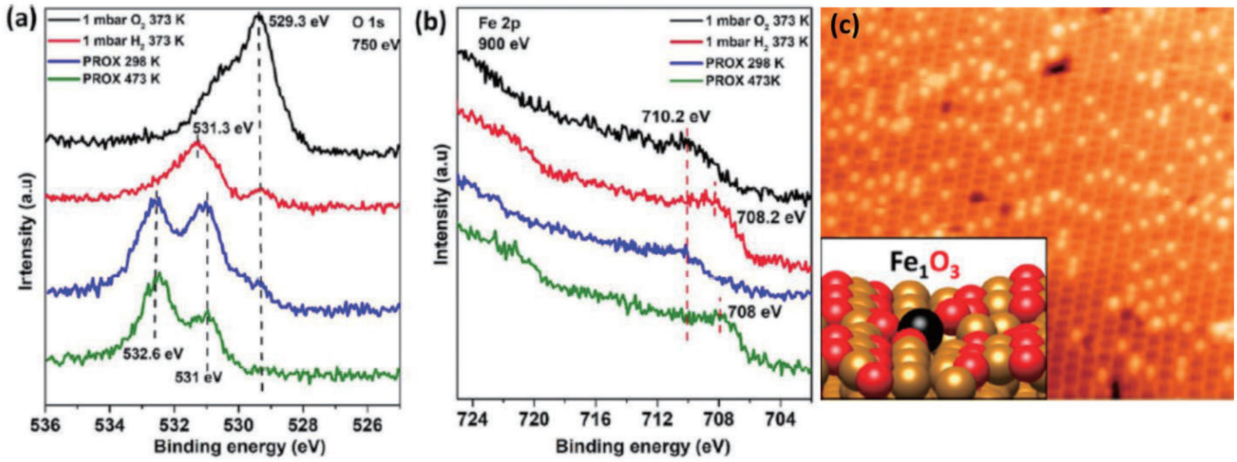
Inverse oxide/metal model systems are frequently used to investigate catalytic structure–function relationships at an atomic level. The reactive centre of the model catalysts presented here is constituted by isolated Fe_1O_x sites on Pt or Cu_2O single crystal surfaces [1-3]. The well-defined structures were prepared through an atomic layer deposition strategy taking advantage of the steric hindrance of the $FeCp_2$. This process allows for formation of single Fe atom sites. We will present structural and chemical analysis at each step of the synthesis process as well as during relevant reaction conditions by primarily scanning tunnelling microscopy and ambient pressure X-ray photoelectron spectroscopy. The analysis allowed us to couple the chemical state of the model catalyst to the reactivity at reaction conditions relevant for preferential oxidation of CO in H_2.



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Role of pyridinic nitrogen in the mechanism of the oxygen reduction reaction on carbon electrocatalysts

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The introduction of pyridinic nitrogen (pyri-N) into carbon-based electrocatalysts for the oxygen reduction reaction is considered to create new active sites.[1] Herein, the role of pyri-N in such catalysts was investigated from a mechanistic viewpoint using carbon black (CB)-supported pyri-N-containing molecules as model catalysts, and the highest activity was observed for 1,10-phenanthroline/CB. X-ray photoemission spectroscopy showed that in acidic electrolytes, both pyri-N atoms of 1,10-phenanthroline could be protonated to form pyridinium ions (pyri-NH$^+$). In O_2-saturated electrolytes, one of the pyri-NH$^+$ species was reduced to pyri-NH upon the application of a potential, whereas no such reduction was observed in N_2-saturated electrolytes (Figure 1). This behavior was ascribed to the electrochemical reduction of pyri-NH$^+$ occurring simultaneously with the thermal adsorption of O_2, as supported by density functional theory calculations(Figure 2). Moreover, according to these calculations, the coupled reduction was promoted by hydrophobic environments.[2]

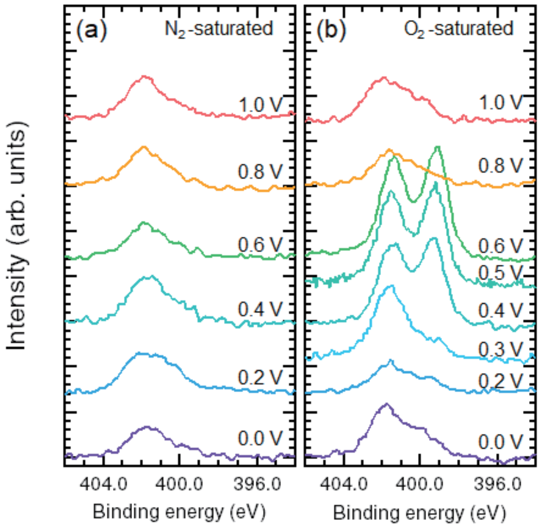

Figure 1. N 1s spectra of 1,10-phenanthroline/CB recorded after the application of different voltages in (a) 1 atm N_2- and (b) 1 atm O_2-saturated 0.1 M H_2SO_4 at 300 K.

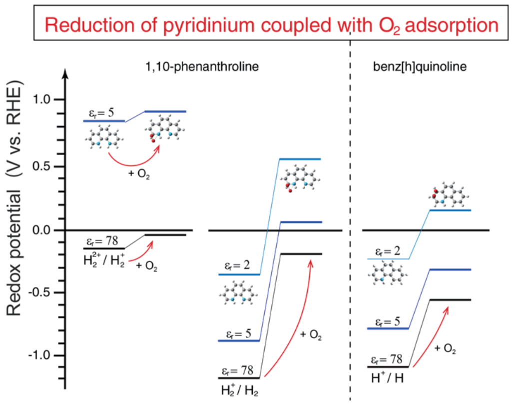

Figure 2. Proposed model for reduction of pyri-NH$^+$ coupled with adsorption of O_2. Calculated redox potentials of pyri-NH$^+$/pyri-NH with and without O_2 adsorption for 1,10-phenanthroline and benz[h]quinoline in water at different relative permittivities.

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Electronic structure of ultrafine water cluster deposited on a hydrophobic surface explored by soft X-ray emission spectroscopy

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In recent years, water clusters called ultrafine water which has several nanometers or less have attracted attention as having a wide range of functions such as humidification, moisture retention, deodorization, air cleaning and sterilization, and static electricity removal. However, little is known about the mechanism of their functional expressions. For example, in moisturizing, penetration into the subcutaneous tissue is considered because the ultrafine water is smaller than the intercellular space on the skin surface. However, this alone cannot explain the moisturizing effect for a long time [1]. Therefore, it is necessary to clarify the physicochemical properties of ultrafine water to understand those macroscopic functions.

In this study, we investigated the electronic structure of ultrafine water deposited on a hydrophobic surface using O 1s X-ray emission spectroscopy (XES). By repeating a heating (by a ceramic heater up to 60 ºC) and fully humidifying cycle on a poly(3,4 - ethylenedioxythiophene) polystyrene sulfonate membrane, ultrafine water of the size of c.a. 1.4 nm was generated. The emitted water molecules were deposited on a CF_3-self assembled monolayer (SAM) coated silicon carbide thin membrane which separates vacuum from the atmosphere and transmits incoming and outgoing soft X-rays. The XES measurement was performed at BL07LSU HORNET station [2] in SPring-8.

The obtained time evolution of the accumulated XES signal implied the presence of OH^- species which were not observed in deposited water by humidification with a regular humidifier. We will discuss a possible mechanism of the generation of ionic species by deposition of ultrafine water clusters and its role on the moisturizing effect.

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Spectra of the photocurrent of CuPc-adsorbed MoS_2-FET

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1. Introduction:

We developed a method to identify the chemical property of the target molecule by combining the MoS_2 field effect transistor (FET) device with monochromatized light. We measured photo-induced drain current generated after monochromatized light is injected onto the channel for the coper phthalocyanine (CuPc) deposited surface, and the FET properties were measured focusing on the photocurrent vs λ spectra.

2. Experimental:

MoS_2 flakes were exfoliated from a natural crystal by using the adhesive tape method on to the 285 nm SiO_2 layer formed on a heavily doped p-type Si substrate. The MoS_2 channel was franked by the electrodes of the source and the drain. The electrodes are formed by the combination of 5 nm-thick Ti and 100-nm-thick Au. We used the light that is emitted from the tungsten-halogen lamp and monochromatized.

3. Results and Discussion:

When monochromatized light are incident for 0.5 s in every 1 s on the surface of the channel part of the FET at the drain voltage of 100 mV, drain current variation can be observed [1]. The increase is named as photocurrent. The photocurrent has a large dependence on the wavelengths of the incident light. Figure 1 show the photo-responsivity, which ia calculaed as photocurrent devided by the light power, as a function of the wavelength of the incident light for the pristine MoS_2, 2 Å CuPc and 10 Å CuPc deposited cases. Experimental data points are plotted as solid dots. The plot for the pristine surface is fitted with three Gaussian peaks with the center wavelength of approximately 550, 610, 650 nm, and an additional peak centered at 705 nm is employed for the sample with CuPc.These results indicate that the peak at 705 nm corresponds to the adsorption of CuPc, and the peak is assigned to the excitation from the HOMO state to the molecule induced state (MIS) formed near the CBM of MoS_2. We consider that the technique can be employed for the molecular sensing with the chemical recognition capability.

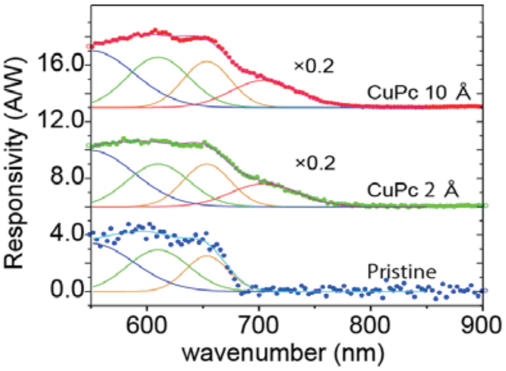

Figure 1 The photo-responsivity as a function of the wavelength of the incident light for (a) the pristine MoS_2, (b) 2 Å CuPc and (c) 10 Å CuPc deposited cases.

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AP-XPS Study of Methane and Carbon Dioxide for Methane Dry Reformation on a Pt(997) Surface

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Methane is a valuable natural resource involved in hydrogen production, and methanol is synthesized from syngas ($CO+H_2$) produced by steam reforming of methane. Syngas is used in the production of various chemical products. Meanwhile, the dry reforming (DRM), which also generates syngas by reacting of methane and carbon dioxide has been focused recently again. The first step in the DRM process is dissociation of methane by metal catalysts. Although a low-cost Ni has been often used, there is a problem that the function of the catalyst is impaired because of coke formation during the process. Since Pt has a lower activation barrier to methane dissociation than Ni and coke formation is less likely to occur on Pt, it is expected as a methane reforming catalyst to replace Ni-based catalysts [1]. The study of the methane dissociation and oxidation reactions of Pt(111) and Pt(211) surfaces by density functional theory (DFT) calculations show that the Pt(211) surface has a lower activation barrier [2]. Therefore, it is important to experimentally identify the adsorption and activation of methane on the stepped surface.

In this study, we investigated the adsorption and thermal process of methane on Pt(997) by infrared reflection absorption spectroscopy (IRAS) and temperature programmed desorption (TPD) in ultra-high vacuum (UHV). Methane was adsorbed at the step site of the Pt (997) surface with higher adsorption energy than at the Pt (111) terrace site. The adsorption and dissociation of methane and carbon dioxide on the Pt (997) surface were also investigated by ambient pressure (AP) -XPS by introducing ~3.6 mbar CH_4 and ~3 mbar CO_2 into the cell as independent experiments. We found dissociated species including CH and CO on the Pt(997) surface at 400 K and room temperature, respectively. These results suggest that DRM could occur on the Pt (997) surface.

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Time-, spin- and angle-resolved photoemission spectroscopy of spin-polarized surface states with the 10.7-eV extreme-ultraviolet at 1-MHz repetition rate

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Spin and angle-resolved photoemission spectroscopy (SARPES) is a powerful technique to reveal various information about the occupied electronic states in solids, including their energy, momentum (k), and spin [1]. In addition to this capability, the combination of SARPES with pump-probe laser techniques makes it possible to image the electron population optically excited into the unoccupied bands in k-space and its ultrafast charge and spin dynamics in the time domain, which is useful for studying novel optical responses of many materials such as topological and spin-valley materials. However, this combination technique is rather very challenging for actual use for research since the spin-detection especially for unoccupied bands has low efficiency.

In my presentation, we introduce our state-of-the-art pump-probe SARPES apparatus recently constructed at ISSP, The University of Tokyo. This apparatus is based on the SARPES system [2] equipped with highly efficient very-low-energy-electron-diffraction (VLEED) spin detectors. We combine this with a high-power pulsed 10.7-eV laser at the high repetition rate (1-MHz), which is driven by the third harmonic generation (347 nm) of a Yb: fiber chirped-pulse amplifier laser [3]. This combination enables us to obtain large photoelectron signals enough to observe the unoccupied spin-polarized bands in various materials and their ultrafast dynamics. We will also report on the observation of unoccupied spin-polarized surface states by using this apparatus.

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Electronic Structure of Borophane, studied by X-ray spectroscopy

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Triggered by discoveries of various exotic phenomena in graphene, varieties of two-dimensional (2D) materials have been theoretically calculated and synthesized to seek for intriguing physical and chemical properties. Recently, an atomic sheet of boron, borophene (B), or of hydrogen boride, borophane (HB) was newly found experimentally. Due to the multi-center-two-electron bonding scheme of boron, the novel material takes various polymorphs with different electronic structures and properties. In 2020, a borophane with a network of the 5-7-membered rings was predicted theoretically to be the Dirac Nodal Line semimetal and it was successfully characterized by a topological variant [1]. A research on such a self-standing film has a huge potential to induce technical innovations in developing nanoscale quantum devices and opens a frontier of novel topological materials.

In the present research, we successfully synthesized the 5-7-membered ring borophane by the ion exchange method. We then studied the electronic structure by X-ray absorption and emission spectroscopies, XAS and XES, at the B K-shell absorption edges. The experiment was made at NewSUBARU. We found spectroscopic features of the gapless electronic states, that are consistent to the electronic structure of the Dirac Nodal Line semimetal. We explain the details and discuss the their electronic characters.

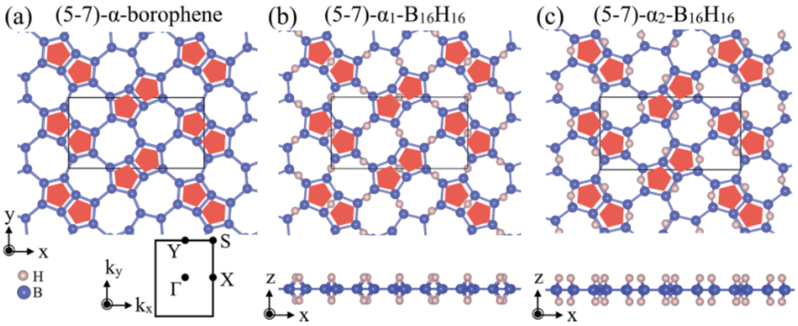

Fig. 1: Structure models of the 5-7-membered ring borophene and borophane (BH). Boron and hydrogen atoms are shown as blue and light pink balls, respectively. [1]

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Interaction between the functionalized MoS_2 basal surface and hydrogen

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Molybdenum disulfide (MoS_2) has been used as catalysts for many years [1]. The basal plane of MoS_2 is known to be inert to molecular adsorption including molecular hydrogen. In order to produce an active site, transition metal atoms have been deposited on the MoS_2 surface [2]. Thus, a functionalized MoS_2 surface gives a reaction field, where various catalytic reactions involving hydrogen dissociation proceed. Therefore, it is very important to understand the interaction between hydrogen molecules / atoms and the functionalized MoS_2 surface. The purpose of this study is to elucidate the interaction between the Pd-deposited MoS_2 surface and hydrogen molecules, where hydrogen dissociation occurs at the Pd site on MoS_2.

Natural mineral MoS_2 crystals were used as the present samples. Ambient-pressure x-ray photoelectron spectroscopy measurements were performed at BL07LSU of SPring-8 on both bare MoS_2 and Pd-deposited MoS_2 surfaces. In addition, the bare MoS_2 exposed to atomic hydrogen was investigated in UHV by XPS at BL-13B of KEK-PF. These XPS spectra were measured using the photon energy of 680 eV at room temperature.

In the Mo 3d and S 2p spectra on the bare MoS_2 surface, the observed peaks show a little shift of 0.03 eV or less toward high binding energy upon the expossure to hydrogen molecules. In contrast, on the Pd-deposited MoS_2 surface, the significant peak shifts of ~0.1 eV were observed toward low binding energy in the Mo 3d and S 2p spectra upon expossure to hydrogen molecules. In the Pd 3d XPS spectra, an increase in the component derived from Pd-H was identified. Note that, in the case of exposure to atomic hydrogen on the bare MoS_2 surface, the lower binding energy shift up to ~1eV was observed. These experimental results suggest that the dissociation of hydrogen molecules at the Pd site and the spillover of hydrogen atoms to the MoS_2 surface occur. We will discuss the band bending due to the spillover of hydrogen atoms on the MoS_2 surface.

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Tuesday

26/Oct./2021

Electronic states at organic-metal interface studied by MAES, UPS, and DFT calculation

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The electronic properties of organic semiconductors in bulk and at interface play an essential role in the characteristic charge transport in soft matter, eventually resulting in performance in advanced organic devices. In this study, we report the local electronic states of the metal surfaces and at the organic-metal interface by ultraviolet photoemission spectroscopy (UPS), metastable atom electron spectroscopy (MAES)[1], and first-principles calculation using the density functional theory (DFT).

The exposure of electron density on metal surfaces is a key factor in understanding of several properties including work function, chemical reactions, charge transport. The DFT calculation of Au(111) shows that electron density decreases exponentially outside the surface,[2] as firstly shown by Lang and Kohn.[3] Also, it reveals that the asymptotic nature strongly depends on the sp/d states and the binding energy, leading to the unusual deexcitation path via Penning ionization on Au(111).[2]

When organic molecules are chemically bound to a metal surface, the so-called chemisorption-induced states may appear across the Fermi level by mixing the molecular orbitals with the metal wave functions. In this case, the chemisorbed molecules are regarded as "metallic" in electronic structure. Our MAES spectra show that alkanethiols, C_{60}, and some π-conjugated organics on Pt(111) are the typical examples, and the resonance states thus formed result in resonance tunneling the relevant molecular junctions.[4]

In the conference, we will address the electronic structure of picene crystalline film on Cu(111), especially the broadening of the HOMO-derived band and the overall structure of π-derived bands.

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Photoelectron Spectroscopy Reveals Inversion Layers in Hybrid Organic-Silicon Heterojunctions

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Dopant-free heterocontacts involving the conductive polymer PEDOT:PSS are frequently utilized as charge-carrier selective contacts of hybrid silicon solar cells with high power conversion efficiencies. Although these interfaces are well characterized from a device perspective, the physics and chemistry of contact formation mechanisms are still not well understood. We use X-ray photoelectron spectroscopy (XPS) to track core-level shifts upon contact formation and to access the built-in potential. Furthermore, vacuum-level shifts are measured by ultraviolet photoelectron spectroscopy (UPS). By spin-coating ultrathin PEDOT:PSS layers on hydrogen-terminated n-Si we can track the Si core-levels upon contact formation and get direct evidence for inversion layer formation. In addition, our XPS and UPS data allows us to speculate that PEDOT passivates Si surface states [1]. Furthermore, we demonstrate that the built-in potential measured with XPS correlates well with the open-circuit voltage of model solar cells. The same holds for devices with dopant-free MoOx/n-Si or LiF/p-Si heterocontacts as main building blocks [2]. Strikingly, the insulator LiF forms a Schottky contact with p-Si and facilitates an ohmic contact in n-Si [3]. Furthermore, we demonstrate the impact of substrate hydrophobicity on the layer composition and work function of PEDOT:PSS thin films [4].

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Theory of core-level photoelectron spectroscopy

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X-ray photoemission spectroscopy (XPS) is one of the most commonly used experimental techniques to investigate the elemental composition, structure, and electronic state of materials. Since the absolute binding energy of the core level electron is determined for each element, it can be used as a fingerprint of the element to analyze the elemental composition near the surface. In addition, the binding energy of the core level electrons changes sensitively depending on the chemical environment in which the atom is placed, and by measuring the slight difference in binding energy, we can trace the structure near the surface and its change over time. Thus, it has become an indispensable experimental tool for analyzing the structure of surfaces and two-dimensional materials and the reaction mechanism of catalysts at the atomic level. On the other hand, in spite of its long history and importance in materials science, a first-principles method to calculate the absolute binding energy of core electrons, which is the most fundamental measured quantity, based on density functional theories (DFT) with high accuracy, had not been developed until recently. We have recently developed a new method [1] to calculate the absolute binding energy of core electrons in solids (metals, semiconductors, and insulators) based on DFT together with the Gunnarsson-Lundqvist theorem [2]. The fundamental basis of the method enables us to treat not only XPS but also X-ray absorption near edge structure (XANES) in a single framework including the spin-orbit interaction, magnetic exchange interaction, and many body screening effect.

In this tutorial talk, I will discuss the details of the theory and introduce a series of collaborative researches including silicene on ZrB_2 [3], borophene on Ag (111) [4], single atom dispersion of Pt on graphene [5], and bitriangular Ge structure on ZrB_2 [6].

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Hybrid image potential states in lead phthalocyanine on graphene

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Image potential states (IPSs) are peculiar unoccupied states characterized by a Rydberg series that is composed of parabolic bands with effective mass m^* close to the electron mass m_e. The properties of IPSs are modified by molecular adsorption, whose impact appears most significantly in the change in m^*. Angle-resolved two-photo photoemission measurements have revealed the increase of $m^* = 2.2\ m_e$ for the lowest IPS of a lead phthalocyanine (PbPc) monolayer on graphite [1]. Although the increase in m^* has been explained by an effective periodic potential due to the PbPc molecules, the detail of the modified IPS is yet to be clarified. Here, we theoretically investigate the IPSs of PbPc on graphene and demonstrate that the mechanism we proposed in Ref. [2] also applies to the present system, i.e., an IPS-like state emerges on the PbPc monolayer, hybridizing with the lowest IPS of graphene to form bonding and antibonding states. Our results not only indicate that the antibonding IPS has increased m^* comparable to the experimental value, but also predicts that the bonding IPS exhibits anisotropic and much larger m^* as a result of further hybridization with PbPc molecular orbitals.

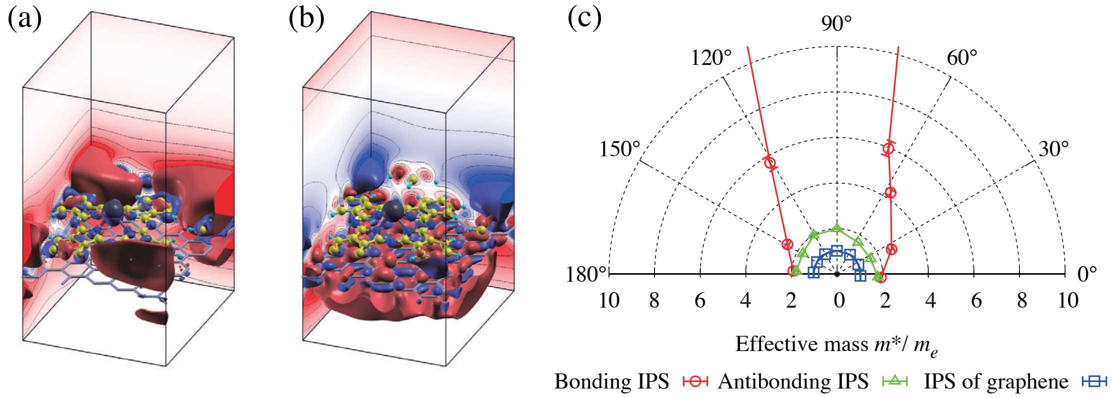

Figure: Bonding and antibonding IPSs (a, b) and azimuthal dependence of m^* (c)

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Confined Hot Electron Relaxation at the Molecular Heterointerface of the Size-Selected Plasmonic Noble Metal Nanocluster and Layered C_{60}

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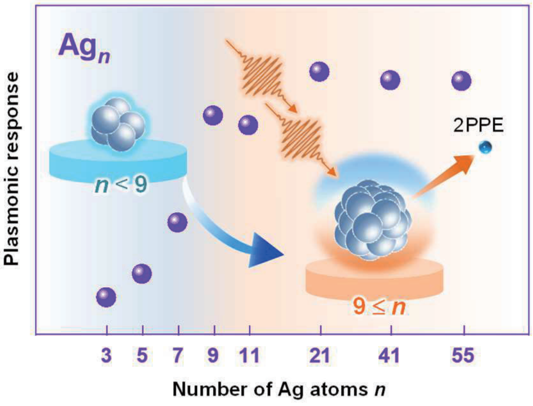
The plasmonic response of metallic nanostructures plays a key role in amplifying photoelectric conversion in organic devices. Since the plasmonic behavior of noble metal nanoparticles is known to generate energetic charge carriers such as hot electrons, it is expected that the hot electrons can enhance photoconversion efficiency if they are transferred into an active organic layer.

Herein, we fabricated a molecularly well-defined heterointerface between the size-selected plasmonic noble-metal nanoclusters (NCs) of Ag_n (n = 3−55)/Au_n (n = 21) and the organic C_{60} film to investigate hot electron generation and relaxation dynamics using time-resolved two-photon photoemission (2PPE) spectroscopy. [1] By tuning the NC size and the polarization of the femtosecond excitation photons, the plasmonic behavior is characterized by 2PPE intensity enhancement by 10−100 times magnitude, which emerge at $n \geq 9$ for Ag_n NCs. Furthermore, the time-resolved measurements demonstrate that plasmon dephasing generates hot electrons which undergo electron-electron scattering. The present 2PPE study reveals the mechanism of ultrafast confined hot electron relaxation within plasmonic Ag_n NCs at the molecular heterointerface.



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Toward accurate description of organic semiconductors and organic/metal interfaces from first principles

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Precise description of geometric structures of organic semiconductors and organic/metal interfaces is a prerequisite for detailed understanding of their spectroscopic properties. Density functional theory (DFT) calculations may play a complementary role to the experimental structural determination, but widely used semilocal DFT, such as generalized gradient approximation, fails to accurately describe the long-range dispersion interaction, which is essential in intermolecular and molecule-metal interactions. Recent developments of dispersion correction methods [1] and van der Waals density functionals (vdW-DF) [2] have led to improved description of structures of organic semiconductor and organic/metal interfaces. In this talk, I will give a brief overview of vdW-DF and one of the variants, rev-vdW-DF2 [3,4], and discuss its application to a wide range of systems relevant to organic/metal interfaces. I will also discuss applicability and limitation of vdW-DF to study the electronic properties of organic semiconductors and organic/metal interfaces [5-9], and how to overcome by using the many-body perturbation theory approach [8,9].

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Energy band dispersion modified by phonon and vibronic couplings

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Understanding the impacts of weak electronic interaction on the electron delocalization is required to discuss the rich functionalities of organic molecular materials. Moreover, effects of the strong coupling of phonon (collective lattice vibration) and/or local molecular vibration to the electron must be unveiled. Angle-resolved UPS (ARUPS) is known to be a powerful technique to study the electronic structure. The HOMO-band features can offer a wide variety of key information, that is essential to comprehend charge-hopping transport (small-polaron related transport) in the ordered monolayer film [1] as well as to coherent band transport in the molecular single crystal [2,3]. However, the experimental study of fine features in the HOMO state has not been progressed till recently due to difficulty in the sample preparation, damages upon irradiation, and so on. We present recent findings regarding on the precise measurements of electronic fine features found for rubrene ($C_{42}H_{28}$) single crystal by using low-energy-excited and high-resolution ARUPS [4,5]. We concluded that the HOMO band consists of a single MO in which Γ point is a saddle point against the previous theory [6-8] for the orthorhombic crystal structure (*Cmca*). The precise experiments of the 2D momentum scan in the ARUPS would provide a perspective of designing the organic semiconductor devices.

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Fermi level pinned molecular donor/acceptor junctions: reduction of induced carrier density by interfacial charge transfer complexes

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Increased hole density in an electron donor-type organic semiconductor can be achieved by deposition of a strong acceptor-type molecular layer on top, as has been shown to enable adjusting the carrier density in organic field effect transistors (OFETs). This interfacial charge transfer is due to simultaneous Fermi level (E_F) pinning of the donor's highest occupied level and the acceptor's lowest unoccupied level. Here, we investigate the electrical properties of such an E_F-pinned junction formed by diindenoperylene (DIP, as donor) and hexafluoro-tetracyano-naphthoquinodimethane (F6, as acceptor) in OFETs, as well as its electronic properties by photoelectron spectroscopy and electrostatic modelling. We find that, in addition to the E_F-pinning induced integer charge transfer across the interface, DIP and F6 form charge transfer complexes (CPXs) at their junction. The molecularly thin CPX interlayer acts as insulator and significantly reduces the density of carriers induced on either side of the junction, compared to a scenario without such an interlayer. CPX formation is thus unfavorable for the effectiveness of controlling carrier density at molecular donor/acceptor junctions by E_F-pinning. [1]

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Studies of Organic Heterostructures on Coinage Metal Substrates

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Heteromolecular bilayers of π-conjugated organic molecules on metals, considered as model systems for more complex thin film heterostructures, are investigated with respect to their structural and electronic properties, by ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED) and normal-incidence X-ray standing wave (NIXSW) techniques.

We have studied the organic-metal interaction strength with 6,13-pentacenequinone (P2O) and 5,7,12,14-pentacenetetrone (P4O) due to their different molecular structures. On Ag(111), copper-phthalocyanine (CuPc) forms a bilayer when deposited on a monolayer P4O/Ag(111) but molecular exchange takes place with P2O as the templating layer. [1] To further explore the influence of the organic-metal interaction strength in bilayer systems, we determine the molecular arrangement in the physisorptive regime for copper-hexadecafluorophthalocyanine (F_{16}CuPc) on Au(111) with intermediate layers of P4O and perylene-3,4,9,10-tetracarboxylic diimide (PTCDI), which present the ordered bilayer growth mode. [2] In the next, a study of the properties on a simplified model system of a donor-acceptor (D-A) bilayer structure is presented, pentacene (PEN) as donor and perfluoropentacene (PFP) as acceptor material are chosen to produce bilayer structures on Au(111) and Cu(111) by sequential monolayer deposition of the two materials. [3] Furthermore, titanyl-phthalocyanine (TiOPc) molecule grown on Ag(111), which form an up-down bilayer with **0** net dipole, is considered to provide different templating effect on the heterostructure system. Therefore, we have studied the valence state and adsorption of molecular thin films deposited onto mono- and bi-TiOPc layers. [4]

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Insights into the collective electronic losses at surfaces with momentum resolution

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Investigating the dispersion of phonons and collective charge modes with high surface sensitivity is best achieved with high-resolution electron energy loss spectroscopy (HREELS) [1]. However, a systematic dispersion measurement over the whole Brillouin zone can takes weeks with standard instruments, which measure the electron intensity sequentially, i.e., at one specific loss energy and one scattering angle at a time. Therefore, we have modified a high-resolution electron source to meet the requirements of commercial hemispherical electron analyzers with E(k) imaging capabilities [2]. This allows the parallel detection of electrons in a broad range of momenta without sample movement. In this contribution I will show application examples of this new development for phonon, plasmon and exciton dispersion on 2D materials, quantum materials and organic single crystals.

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Exciton energy-momentum dispersion in the single crystal pentacene probed by low-energy angle-resolved electron energy-loss spectroscopy

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Fundamental properties and behaviors of excitons in molecular crystals are long-standing targets in the research fields of molecular science. The exciton characters in molecular solids are often explained as hydrogen atom-like pairs of localized electrons and holes confined into a single molecule or an adjacent pair of molecules. However, inter-molecular delocalization of electron and/or hole states has been demonstrated in a number of organic semiconductor materials [1]; single crystal pentacene is one prominent example for which the energy-momentum (E-$\boldsymbol{K}$) dispersion of the electronic states was experimentally confirmed [2]. This situation may also alter the exciton characters from those of the textbook Frenkel-type ones. In this study, we attempted to measure E-$\boldsymbol{K}$ dispersion relations of the excitons in the single crystal pentacene by angle-resolved electron energy-loss spectroscopy (AR-EELS) [3].

Figure 1 shows AR-EELS spectra of a pentacene single crystal sample taken in its Γ-X direction, where the primary electron energy (E_p) was set at 10.183 eV. The excitonic loss peak at the electron kinetic energy of 8.2 - 8.4 eV exhibited an energy shift depending on the electron scattering angle, suggesting that the low-energy AR-EELS measurements are applicable for the pursuit of the excitonic E-$\boldsymbol{K}$ dispersion relations in single crystal organic semiconductor materials.

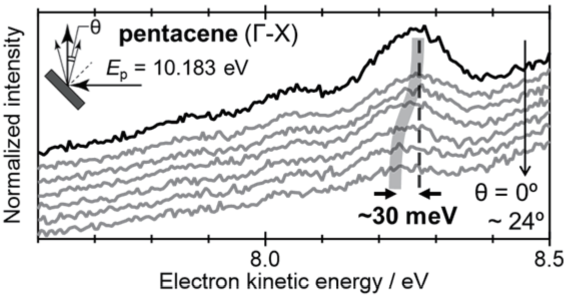

Fig. 1: Low-energy AR-EELS spectra of the pentacne single crystal (001) surface taken in the Γ-X direction.

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Electronic Properties of Interfaces with N-Heteropolycyclic Molecules

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For improvement and optimization of the performance of organic molecule-based devices, such as photovoltaic cells and thin-film transistors comprehensive insight into the physical and chemical properties of the organic molecules at surfaces is necessary.

N-heteropolycyclic aromatic compounds are promising candidates for n-channel semiconductors. The introduction of nitrogen atoms into the π-backbone of the polycyclic aromatic hydrocarbons stabilizes the frontier orbitals and increases the electron affinity, while the size of the HOMO−LUMO (optical) gap is nearly unaffected. By using two-photon photoemission spectroscopy (2PPE) and high resolution electron energy loss spectroscopy (HREELS) we determined quantitatively transport, singlet and triplet states as well as electronic spectra of serval N-heteropolycyclic molecules adsorbed on Au(111) [1-5]. Using angle-resolved 2PPE we identified strongly dispersing occupied and unoccupied electronic states, which result from hybridization between localized molecular states and delocalized metal bands at the metal/organic interface [4, 5].

We acknowledge funding by the German Research Foundation through the SFB 1249 (N-Heteropolycycles as Functional Materials) and the Cluster of Excellence (3D Matter Made to Order).

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Correlation between Superstructure, Photoluminescence, and Excited-State Dynamics of Polyaromatic Hydrocarbon Thin films on Graphite

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A molecular-level understanding of the photoluminescent properties at the organic/electrode interface is a key to understand organic optoelectronic thin film devices. However, due to the dominant ultrafast non-radiative decay to the electrode substrate, it was difficult to assess experimentally thus has not been thoroughly explored so far. Here, we investigated the correlation between superstructures, photoluminescent (PL) properties, and excited-state dynamics of ultrathin films on graphite. As a typical polyaromatic hydrocarbon (PAH), perylene ($C_{20}H_{12}$, Fig 1(a) [1]) and pyrene ($C_{16}H_{10}$, Fig. 1(b)) were adopted as basic chromophore units that compose two-dimensional films. The superstructures were investigated using a combination of LEED and STM. In the case of pyrene deposited on the graphite(0001) surface at room temperature, flat-lying adsorption was observed as shown in Fig. 1(c). Further deposition of pyrene on low temperature substrate (90 K) resulted in amorphous film growth as shown in Fig. 1(d). From this amorphous film, blue PL emission was observed as shown in the inset in Fig. 1(d), which is originated from the excited state of the dimer (excimer). To discuss the de-excitation mechanism upon photoluminescence, occupied and unoccupied states in the vicinity of the Fermi level were measured by two-photon photoemission (2PPE) spectroscopy. It is elucidated that the excited state (EX) in the unoccupied region is responsible for the visible light emission. The EX state was observed on the amorphous film shown in Fig. 1(d) but *not* on the ordered $(4\sqrt{3}\times 4\sqrt{3})$R30° phase. The flat-lying adsorption style in Fig. 1(c) is not suitable for the formation of excimer, because it is difficult to achieve the co-facial molecular arrangement.[2]

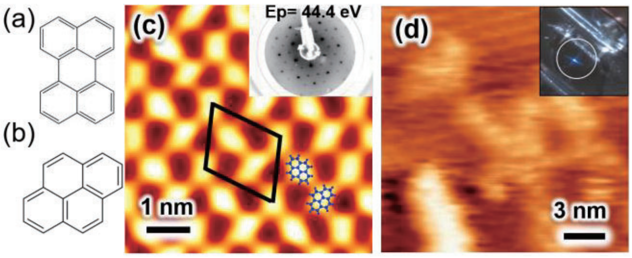

Fig.1 Molecular structures of (a) perylene and (b) pyrene. (c) $(4\sqrt{3}\times 4\sqrt{3})$R30° structure of pyrene on graphite. (d) Amorphous growth of pyrene islands formed on (c). The inset photo shows PL emitted from the film.

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Impact of weak electronic coupling on the electronic structure at the molecule/graphite interface

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We clarify the impacts of the formation of oriented organic/inorganic interface stabilized by weak van der Waals force on the electronic structure. For the pentacene (PEN) monolayer prepared on graphite which is a typical system of physisorption, the valence band is modified unexpectedly despite the weak interaction at the interface [1, 2]. The modification of electronic states is to appear clearly in the unoccupied states by a larger spread of the wave functions [3]. In this study, we fabricated oriented-monolayer film of PEN on graphite (HOPG or single crystal) and measured the electronic structure utilizing low-energy excitation angle-resolved photoelectron spectroscopy (LE-ARPES) at BL7U in UVSOR. Fig. 1(a) shows hν-dependence of LE-ARPES of PEN/HOPG taken at 14 K. The dispersive “convex” band appears in the kinetic energy range of 1 to 3 eV as a constant final state (CFS) feature overlapping to the non-dispersive HOMO with vibronic coupling fine features (denoted 01 and 02), while those features are absent in pristine substrate. In Fig. 1(b), the LE-ARPES maps are averaged as a CFS image taken for various photon energies. Three convex CFS bands are found and two types of band dispersion with positive or negative intensity profiles are observed, which could be originated from Fano resonance due to the coupling of discrete and continuum states [4], indicating that the CFS band could demonstrate the weak hybridization of the wavefunction connection to a newly-formed conduction band.

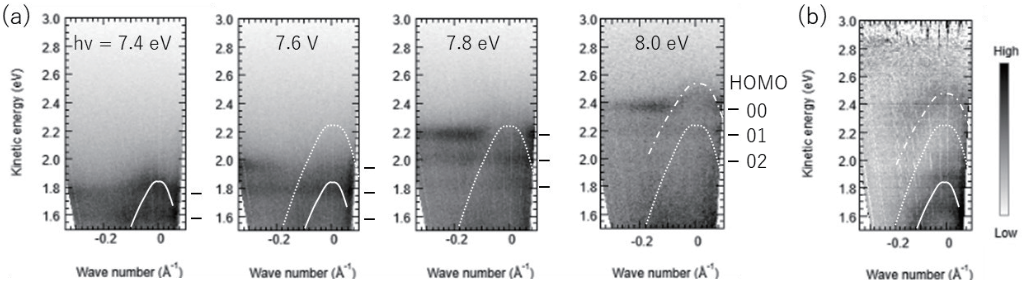

Fig.1 (a) LE-ARPES maps of PEN/HOPG taken at hν = 7.4, 7.6, 7.8, and 8.0 eV and (b) the average of maps using hν = 7.2 ~ 8.0 eV normalized by the horizontally and vertically integrated profiles.

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Measurement of LUMO Band Structure in Organic Semiconductor

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Highest occupied molecular orbital (HOMO) band and lowest unoccupied molecular orbital (LUMO) band are responsible for the charge transport of holes and electrons in organic semiconductors, respectively. Until now, HOMO band structures have been measured in many organic semiconductors [1]. Whereas, the LUMO band structures have never been reported so far due to a lack of suitable experimental method.

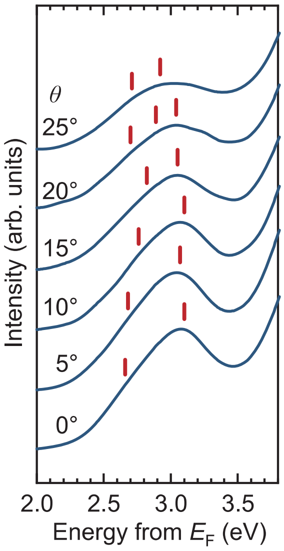

Fig. 1 ARLEIPS spectra of pentacene thin film.

In this work, we report the first measurement of the LUMO band structure of organic semiconductor. For this purpose, we have developed angle-resolved low-energy inverse photoelectron spectroscopy (ARLEIPS) by improving LEIPS [2] to enable the angle-resolved measurement. For the organic system, we chose the thin film phase of pentacene. The observed ARLEIPS spectra are shown in Fig. 1. The red bars indicate the peak positions determined from the minima of the second derivatives of the spectra. The LUMO band structure obtained is shown in Fig. 2 (open circles). Clear energy dispersion was observed despite the uniaxially-oriented polycrystalline film. To interpret this result, we simulated the band structure of the pentacene polycrystalline film by integrating the intensities of bands around the azimuth direction; the experimental band structure is well reproduced. Assuming the tight-binding approximation, we optimized the transfer integrals to best reproduce the experimental band structure (Fig. 2, heat map). We also computed the electron effective mass.

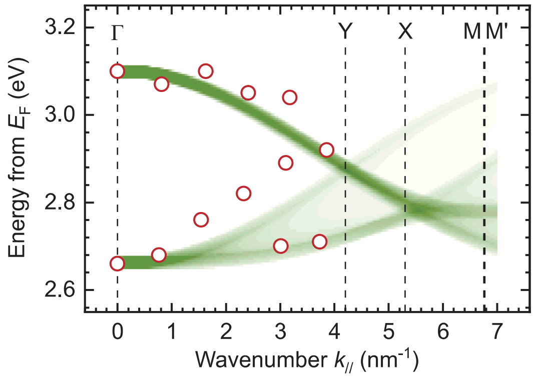

Fig. 2 Experimentally observed LUMO band structure of pentacene by ARLEIPS (open circles) together with the simulated azimuth-angle integrated band structure (heat map).

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Evidence of Polaron Formation in Organic Semiconductor from Temperature-Dependent HOMO/LUMO Bandwidth

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The charge carriers (electrons and holes) in organic semiconductors strongly couple with phonon (intra/intermolecular vibrations), which may result in the formation of polaron. The polaron formation could be proved by the bandwidth narrowing which depend on temperature. However, the earlier attempt to observe the highest occupied molecular orbital (HOMO) bandwidth was failed because the bandwidth was also affected by the thermal expansion [1]. In this study, we demonstrate the polaron formation in high-mobility organic semiconductor, pentacene, by comparing the bandwidths of HOMO and lowest unoccupied molecular orbital (LUMO) bands using ultraviolet photoelectron (UPS) and low-energy inverse photoelectron (LEIPS) [2] spectroscopies.

Figure 1 shows HOMO and LUMO region of UPS/LEIPS spectra at the Γ point. Each peak contains two components corresponding to 2 sub-bands splitting due to the two inequivalent molecules in a unit cell. The band structure calculation shows that the difference in the sub-band energy at the Γ point of the present pentacene film corresponds to the respective HOMO/LUMO total bandwidth [3]. Thus, we examined temperature dependence of the HOMO/LUMO bandwidths from the spectra shown in Figure 1. We found that the HOMO and LUMO bandwidths are broadened about 0.069 and 0.24 meV K^{-1} upon cooling, respectively. This observation is explained by the fact that the low-frequency vibrational mode (about 254 cm^{-1}, comparable to the thermal energy) mode strongly couples only with LUMO. The observed temperature dependences quantitatively supported by a theoretical calculation confirming the formation of the polaron in pentacene.

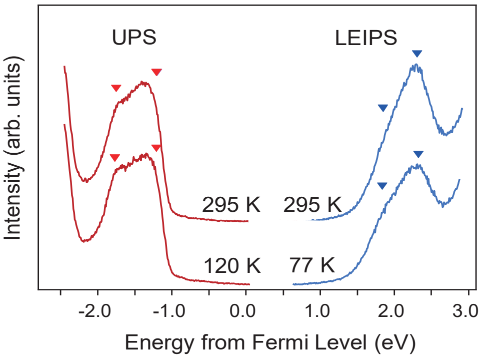

Figure 1. Temperature dependent UPS/LEIPS spectra of pentacene film at Γ point. The sub band indicated by the triangles were obtained as the minima of the 2nd derivatives of the spectral line shape.

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Momentum microscopy of highly oriented organic thin films on Ag(110)

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Introduction

While devices based on [1]benzothieno[3,2-b] [1]benzothiophene (BTBT) derivatives have achieved mobility in excess of 30 cm^2/Vs, the origin of their efficient conduction is still not fully understood. Although the mobility of many organic semiconductors has been understood by the energy and the spatial distribution of HOMO, a recent study has shown that the contribution of HOMO-1 is significant in BTBT derivatives [1]. In this study, we investigated the Photoelectron Momentum Maps (PMM) of Dph-BTBT and Picene to compare the electronic structure of their frontier orbitals.

Experiment

Molecular films were fabricated by supplying 10 nm of molecules on clean Ag(110). The molecular structure of the films were examined using a scanning tunneling microscope (STM) and low energy electron diffraction (LEED). The PMM measurements were performed using momentum microscope at BL6U of UVSOR.

Result & Discussion

Fig.1(a, c) shows the STM images of Dph-BTBT and Picene films on Ag(110). On both films, the molecular long axis is almost along with the [1-10] direction of the substrate, indicating the formation of nearly one-dimensional structure. Although they were not a single-domain structure, they are suitable samples for the measurement of PMM.

Fig.1(b, d) shows the energy distribution curves (EDC) and PMMs of Dph-BTBT and Picene film on Ag(110). It is found that HOMO and HOMO-1 are energetically overlapped in both molecules. Especially in Dph-BTBT, each orbital can be fitted with two Gaussian functions, suggesting that orbital splitting due to the overlap of neighboring molecules. In PMM, the HOMO and HOMO-1 of picene showed a strong distribution in the opposite direction, while Dph-BTBT showed an intensity distribution in the similar positions. These results suggest that HOMO and HOMO-1 overlap spatially and energetically in the Dph-BTBT film, which may lead to efficient conduction of Dph-BTBT contributed by HOMO-1.

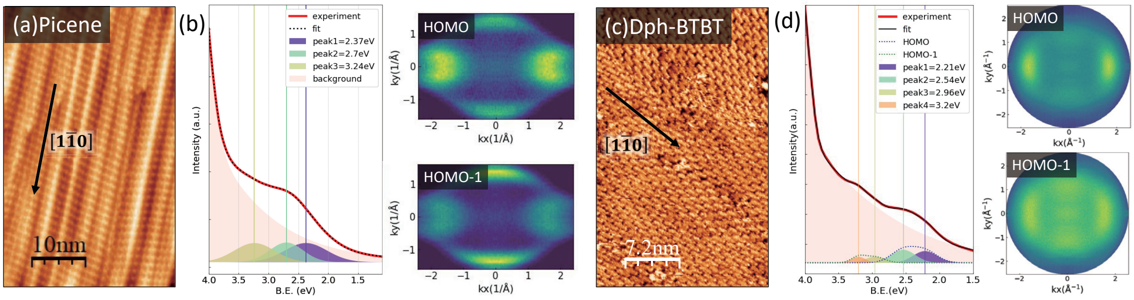

Fig.1 (a, c) The STM images of Picene and Dph-BTBT films on Ag(110).
(b, d) The EDC and PMM of Picene and Dph-BTBT

Interface structures and electronic states of tetraaza-acenes on single crystal pentacene

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Acenes are one of the most important classes of organic semiconductor materials. Among them, pentacene has been a subject of many researches because of its particularly high charge carrier mobility. In addition, the occurrences of the epitaxial growth and the energy-momentum dispersion of the intermolecular electronic bands were observed for heteroepitaxial perfluoropentacene, which has a similar molecular shape to pentacene, stacked on the pentacene single crystal (PnSC) [1]. Therefore, the stacking of n-type acene derivatives on PnSC can realize crystalline p-n heterojunctions with excellent transport properties. In this study, we focused on p-n heterojunctions of tetraaza-acenes stacked on PnSC substrates. The structural and electronic properties of p-n heterojunctions formed by stacking 5,6,11,12-tetraazanaphthacene (TANC, Fig.1(a) inset) or 5,6,13,14-tetraazapentacene (BTANC, Fig. 1(b) inset) [2] on the PnSC surfaces were investigated by X-ray diffraction and photoelectron spectroscopy.

Figures 1(a) and (b) show the ultraviolet photoelectron spectroscopy (UPS) spectra depending on the thickness of TANC and BTANC on PnSCs, respectively. Full-width-at-half-maximum (FWHM) of the HOMO-derived peak in TANC was estimated to be 0.4 (±0.1) eV, while that of BTANC was wider at 1.0 (±0.2) eV. This implies a possibility of strong inter-molecular coupling leading to wide HOMO band dispersion for BTANC.

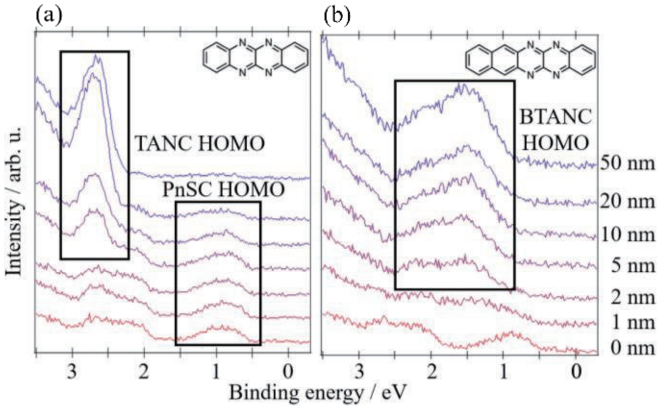

Fig. 1: Evolution of the UPS spectra in the valence regions depending on the thickness of (a) TANC and (b) BTANC on the PnSCs

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Wednesday

27/Oct./2021

Study on the electronic structure of van der Waals heterointerfaces: 2D semiconductor with functional organic molecules

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Recent Van der Waals heterointerfaces consist of two-dimensional (2D) materials, the organic molecules of which have been intensively studied to enable the enhancement of their excellent optoelectrical properties. For instance, if the organic molecules are properly designed, it enables manipulation of the electronic structure of 2D materials, as well as their energy level alignment. The type of energy level alignment, which generally can be classified as straddling type-I and staggered type-II, can significantly impact the optical behavior at the heterointerfaces. In conventional materials, this energy level alignment can be predicted using their ionization energies, i.e. the rule of vacuum level alignment. However, this rule is sometimes no longer valid without the consideration of unique 2D properties stemming from the atomical thin thickness. Furthermore, the mechanism of the aforementioned electronic structure turning is not properly understood so far. In this contribution, first, we demonstrate the controlling of the electronic structure of 2D materials itself using the model functional (acceptor for 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane) and (donor for Dichloro[hexamethylbenzene] ruthenium[II] dimer] organic molecules. Those are evidenced by the measurement of the angle-resolved and X-ray photoelectron spectroscopy. In the same manner, the turning of energy level alignment between heterointerfaces was also discussed. The impact of the surrounding environment i.e. the substrate effect on its control and their mechanism will be addressed. In line with that, how the type of energy level alignment influences the optical properties were investigated by time-resolved PL and transient absorption spectroscopy. Our findings reveal that the type of energy level alignment at the heterointerfaces determines interface carrier dynamics: (1) type-I for the "resonance energy transfer, i.e., electron–hole pair transfer" and (2) type-II for the "direct excited charge transfer." These results help not only to understand interfacial physical phenomena, but also helps design optimized optoelectrical applications.

Tailoring the Optical and Electronic Response in 2D Materials

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Van der Waals layered materials such as the transition metal dichalcogenides have opened unprecedented opportunities to investigate the physics of quantum confinement, correlated phases and quantum phase transitions. To take full advantage of these opportunities, new ways of tailoring the electronic structure of the van der Waals materials need to be developed. The ability to prepare layered heterostructures has already expanded the range of accessible architectures and compositions considerably, though many challenges exist to fully enable the kind of materials by design capabilities available e.g. for organic semiconductors.

Here, I will discuss how atomic and molecular adsorbates offer an alternative for designing new kinds of van der Waals and 2D heterostructures with radically different optical and electronic properties.

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Ultrahigh resolution laser photoelectron spectroscopy

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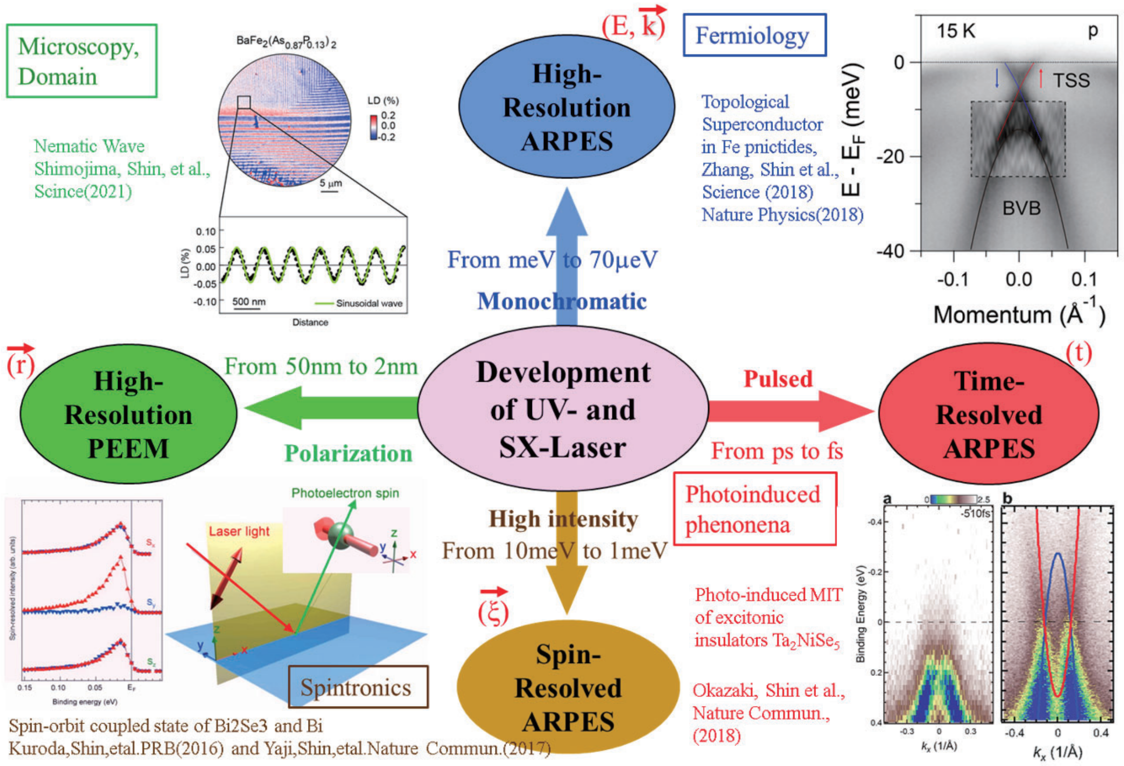
Angle resolved photoemission spectroscopy (ARPES) is very powerful to know the solid-state properties, because we can know the electrons in the materials directly. ARPES has been studied by synchrotron radiation or noble-gas-discharge lamp. Recently, ultra-violet(UV)- and soft-X-ray(SX)-lasers have been developed very rapidly, and have proven to be powerful new light sources for the photoemission spectroscopy. Lasers have excellent properties, such as coherence, monochromaticity, polarization, ultra-short pulse, very high intensity, and so on. Each excellent property of laser will give us the fruitful results to see the deep insights into the various nature of the materials. I would like to introduce various laser-photoemission spectroscopy, such as high resolution ARPES, spin-resolved ARPES, time-resolved ARPES, and photoemission microscopy (PEEM), based on the recent experimental results.



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Spin-orbit coupled state of Bi2Se3 and Bi
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Photo-induced MIT of excitonic insulators Ta$_2$NiSe$_5$

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Adsorption of toxic gases on borophene: surface deformation links to chemisorptions

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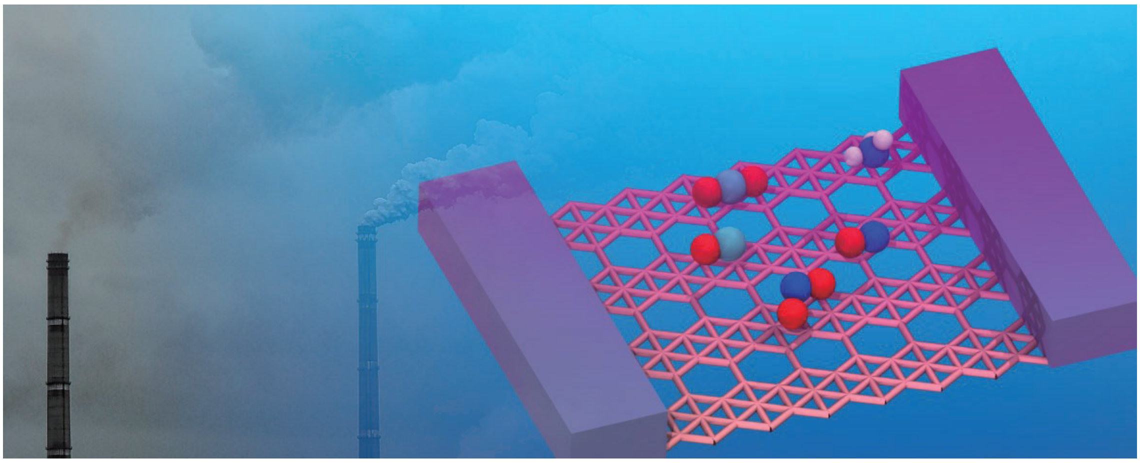
β_{12} borophene has received great attention because of its intriguing mechanical and electronic properties. One of the possible applications of borophene is gas sensing. However, the interaction between common gases and β_{12} borophene remains to be clarified. In this work, we study the interactions of β_{12} borophene towards five hazardous gases, namely, CO, NO, NH_3, NO_2, and CO_2 using various non-empirical van der Waals density functionals and provide an insight into the adsorption behavior of borophene. Adsorption mechanism and molecular vibration are discussed in great detail. Among the gases considered, CO_2 is physisorbed while other gases are chemically bonded to β_{12} borophene. We also demonstrate that the deformation at the ridge of borophene enables its active p_z orbital to strongly hybridize with frontier orbitals of the studied polar gases. Consequently, borophene is predicted to interact strongly with CO, NO, NH_3, and especially NO_2, making it a sensitive sensing material to toxic gases. [1]



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Multipole plasmon excitation at a multilayer structure of Cs/graphene/Cs on Ir(111)

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We have investigated a multipole plasmon (MP) at a multilayer structure of Cs/graphene(Gr)/Cs/Ir(111) using both steady-state reflectivity measurement and time-resolved reflectivity measurement. Gr on Ir(111) was prepared by the chemical vapor deposition [1], using C_2H_4, under an ultrahigh vacuum condition ($< 4\times10^{-8}$ Pa). Cs atoms were deposited from a well-degassed source on the Gr covered Ir(111) surface. After the complete intercalation of Cs atoms between the Gr and Ir substrate, the Cs second layer grows on top of the Gr. Thus, Gr was sandwiched by Cs atom layers on an Ir(111) substrate. The MP spectrum was measured *in situ* during the Cs deposition process by a halogen lamp. We further measured the ultrafast dynamics of the MP of Cs/Gr/Cs/Ir by using femtosecond pump-probe spectroscopy with a reflection geometry.

The MP spectrum for the multilayer structure exhibited remarkable features: a significant linewidth narrowing from that of alkali monolayer directly deposited on a metal surface [2]. A numerical simulation by time-dependent density functional theory with a jellium model revealed that the spectral narrowing of the MP of the multilayer was ensured by decoupling of the outermost Cs layer from the Ir bulk with graphene. In addition, we found unique ultrafast responses of the MP of the multilayer structure compared to that of a Cs thick film: a transient response within several tens of femtoseconds and spectral modulation with coherent surface phonons of the composite in the THz frequency range [3].

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Imaging Excitonic States with Time-Resolved Photoemission Spectroscopy in 2D Semiconductor Heterostructures

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About a decade ago, the discovery of monolayers of transition metal dichalcogenides opened a new frontier in the study of optically excited states in semiconductors. These materials exhibit a plethora of robust excitonic states – bound quasiparticle pairs of electrons and holes, such as bright excitons, momentum- and spin-forbidden dark excitons, and hot excitons. Optics-based experiments, that have largely been used to study these systems, cannot resolve the momentum degrees of freedom of an exciton, and hence only access the bright excitons. Utilizing angle-resolved photoemission (ARPES) based techniques to resolve the momentum coordinates of excitons, and thereby access the dark excitons, or the internal electron-hole wavefunction, has been a decades-old grand challenge. Understandably, such experiments come with significant technical and conceptual challenges. For example, one needs to apply time-resolved ARPES techniques to micron-scale samples of 2D materials, using XUV photons.

In today's talk, I will discuss the progress in my lab towards resolving the momentum-coordinate of excitons in 2D semiconductor heterostructures [1, 2, 3] utilizing ultrafast photoemission techniques that we have developed and applied to other semiconducting systems over the past few years [4, 5, 6, 7]

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Environmental effects in layer-dependent dynamics of Dirac Fermions in quasi-crystalline bilayer graphene

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Dynamical behavior of carriers in graphene has attracted academic interests to investigate temporal evolutions of the massless Dirac Fermions and also technical needs to develop the next-generation optoelectronic devices. The comprehensive understanding has been conducted by direct observations of the electronic states by time- and angle-resolved photoemission spectroscopy (TARPES). Using optical pulses, photo-excited carriers in graphene layers were traced in *real time* and the dynamics was described by various elementary processes[1]. Recently, a TARPES experiment on the epitaxial quasi-crystalline bilayer graphene (QCBG)[2] discovered the transient voltage between the two layers that were not expected theoretically[3]. The experimental reasoning has required contributions from the substrate but the detailed scenario has remained unknown.

In the present research, we preformed TARPES measurements on various systems of single and bilayer graphene on the Si-face SiC substrates to extensively study the carrier dynamics. In QCBG, we observed temporal evolutions of photo-excited carriers in Dirac cones that were asymmetric between the upper and lower layers and quantitatively described by the transient doping from the interface. Experimental comparisons of TARPES results between the graphene layers on a flat SiC substrate and the one on a stepped one indicated that the doped carriers in the epitaxial graphene are originated from Si or C states at the interface that are not covered by the buffer layer.

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Tracing orbital images at surfaces and interfaces on ultrafast time scales by photoemission tomography

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Photoemission orbital tomography (POT) is a powerful technique to image the electron distribution in molecular orbitals in momentum space. However, unoccupied molecular orbitals have not been accessible until recently. We combined time-resolved photoemission using high laser harmonics and a momentum microscope to establish a tomographic, femtosecond pump-probe experiment of unoccupied molecular orbitals[1]. For demonstration purposes we examined PTCDA/Cu(001)-2O where the unit cell of the monolayer consists of two flat lying molecules rotated by 90° with respect to each other.

The excited state-state momentum maps clearly correspond to the LUMO of PTCDA which is found to decay with a time constant if 250 fs. The experiment also allowed us to clearly link the excited-state dynamics to real-space excitation pathways. Depending on the polarization of the visible pump pulses, the LUMO is either populated from the HOMO by an intramolecular excitation or by electron transfer from the substrate. Both processes can be clearly distinguished by their signature in the time evolution of the respective momentum maps. Our results highlight the potential of time-resolved photoemission orbital tomography (tr-POT) to identify electron excitation and transfer processes at molecular surfaces and interfaces.

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On-surface construction of host-guest molecular system: absorption of guest atom / molecule on host crown ether array

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Molecular machines or motors provide mechanical motion triggered by external energy such as light or heat. In our previous work [1], we successfully demonstrated heat induced mechanical motion using host-guest molecular system. Crown ether has been used as a host molecule since its ring has an ability to trap a guest atom or molecule.

In this study, we directly visualized how guest atoms or molecules absorb on a well-ordered host molecular array. Absorption and electronic structures were investigated by means of low-temperature scanning tunneling microscopy (STM) / spectroscopy (STS), and ultraviolet photoelectron spectroscopy (UPS), respectively. All experiments were performed in ultrahigh vacuum.

The host molecular array was grown on an atomically flat and clean Cu(111) surface by deposting 4,4’5,5’-teterabromodibenzo [18]crown-6 ether (Br-CR) at 300 K, which forms a (7×4) super lattice [2]. Cobalt atoms [3] and [ferrocenylmethyl(methy) ammonium]$^+$ $(PF_6)^-$ (Fc-ammonium salt) molecules were absorbed as guest materials on the (7×4) Br-CR super lattice. A precise control of deposition amounts provided host-guest inclusion complexes without breaking the well-ordered host molecular array.

Especially, the Fc-ammonium salt structure on the Br-CR super lattice indicated a voltage-induced mechanical rotation.

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Resolving dynamics in real world complexes with time-resolved x-ray spectroscopy

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With the recent advances in the development, performance and availability of ultra-short x-rays pulses it has become possible to use element selective spectroscopy as a regular tool in sample characterization. In the field of light sensitization and light activated catalysis these tools are increasingly used to study model complexes and learn the principles behind the observed dynamics. Understanding these principles in turn has led to the development of extraordinary new complexes capable of harvesting and using solar energy. During recent years the experimental conditions have improved and now allow the study of realistic complexes that are active as catalysts and/or drive light harvesting in dye sensitized solar cells. We will show a number of examples in which we used x-ray spectroscopy to understand the light induced dynamics in complex molecular systems. First a series of iron carbene sensitizers that allow the construction of dye sensitized solar cells based on earth abundant materials. We will discuss the electronic and vibrational dynamics studied with x-ray emission spectroscopy and x-ray scattering including some hot electron dynamics critical for future applications. Second we discuss the dynamics at the catalytic reaction center of several light activated hydrogen evolving Ru-Pt catalysts studied with XAS at the reaction center. We found beside the expected electron transfer clear evidence for a chemical reaction triggered by light that consumed two electrons after the activation with a single absorbed photon and thus a potential pathway to avoid the usual requirement of multi photon processes for hydrogenase in molecular systems. We will finish by presenting a series of table top systems producing ultrafast pulses of x-rays from a laser between 1mJ and 100mJ now enabling groups to perform similar measurements in the laboratory.

Beyond the Ligand Exchange Model: Time-Resolved APXPS studies of the atomic layer deposition of HfO_2 on InAs

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Atomic layer deposition (ALD) is a powerful technique for the highly controlled deposition of thin-film materials. While its parent techniques, chemical and physical vapor deposition, have been popular for a long time, the importance of ALD has increased first since the turn of the new century. Today, it is, however, central to a wide range of material technologies, including e.g. solar cells, transistors, and quantum materials.

The ideal ALD scheme is based on the sequential self-limiting adsorption and reaction of two gaseous precursors with a substrate. The exposure of the substrate leads to the formation of not more than a monolayer of material. This is the origin of the excellent thickness control of ALD. However, ALD in general and the ALD of high-κ dielectrics still suffer from that the involved surface reaction mechanisms and kinetics are largely unknown [1]. The postulated ideal ligand exchange reaction path for high-κ dielectric deposition and the passive role of the substrate need to be revisited.

This study presents new insight into the ALD of HfO_2 on InAs(100) from TDMAHf and water obtained by *in situ* ambient pressure XPS (APXPS). InAs is an optimal material for the generation of future high-speed metal-oxide semiconductor devices due to it high electron mobility and small band gap, but it suffers from a high defect density at the interface between the semiconductor and its native oxide surface. The ALD of HfO_2 on InAs may help to improve the performance of InAs significantly due to the "self-cleaning effect" that occurs during the early stage of ALD. From APXPS we find that the unwanted oxide is entirely substituted by the desired high-κ oxide already in the first ALD half-cycle. This initial reaction stops first once all oxygen is consumed.

Further, our APXPS results shows that the initial ALD reaction, which, surprisingly, proceeds in the absence of surface hydroxyls, does not follow the standard ligand exchange mechanism. Instead, a bimolecular β-hydride elimination reaction is found to take place.

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Aromatic molecules decoupled from metals via modern 2D materials beyond graphene

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The interfaces between organic molecules and metal contacts play a crucial role in the design of new molecular electronic devices since they affect the charge carrier injection and therefore the device efficiency. The interaction of the molecular frontier orbitals with the bands of the metal substrate results in changes of the intrinsic optical and electronic properties of the adsorbed molecule. This process is referred to as hybridization. Some applications, however, require to preserve the intrinsic properties of the molecules such as the typically rather narrow optical absorption and/or emission bands. To achieve this, one needs to electronically decouple the molecules from the substrate, which can be achieved through, e.g., two-dimensional (2D) interlayers. Therefore, 2D materials beyond graphene are increasingly drawing attention, giving rise to rapid progress in the synthesis and characterization across diverse chemical categories. It is especially intriguing to assess the formation of the interfaces between a 2D material/metal substrate and a molecular adlayer, which can be readily motivated by the semiconducting properties of many organic materials.

In my contribution I will focus on two different 2D materials, namely hexagonal boron nitride (h-BN) and blue phosphorene (BlueP) as an example of phosphorus-based 2D materials which have recently moved into the focus. I will discuss how the underlying metal, either its chemical nature or its surface orientation, influences the properties of the 2D layer [1,2]. Finally, I will discuss the properties of an organic adlayer deposited on each of the two 2D materials on the examples of DBP on h-BN, deposited either on Ni(111) or Pt(111) [1], and PTCDA, deposited on BlueP/Au(111) [3].

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Competition between adsorbate-adsorbate coupling and adsorbate-substrate interaction in the superstructure formation of molecular layers

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In the organic crystals and films consisting of organic halogen molecules, "hydrogen bond" (between halogen and a hydrogen atom) and "halogen bond" (between a halogen atom and a Lewis base) are key ingredients to determine their crystal structures. Covalently-bonded halogens have polar regions of positive electrostatic potential along the extensions of the covalent bonds. On the other hand, the potentials on the equatorial sides of these halogens are negative. The regions of positive potential are called "σ-holes", and then the region can couple with Lewis bases molecules as halogen bond.

In the case of the organic thin films, their structures are determined by the competition between molecule-molecule halogen bond, hydrogen bond and the molecule-substrate interaction. In this study, we carried out STM measurements for 1, 3, 5-tris(4-bromophenyl)benzene (TBB) molecules on the Ag films on Si(111), and the mechanisms to form the molecular layer on Si(111) $\sqrt{3} \times \sqrt{3}$-Ag, Ag multi-layer and TBB layer have been explored.

On the $\sqrt{3} \times \sqrt{3}$-Ag surface, two types of molecular layers are observed. One is commensurate with the substrate, and hydrogen bonds between molecules are expected in the film. The other structure shows almost random distribution, and the molecule-molecule coupling by hydrogen and halogen bond is more preferable than the molecule-substrate interaction. On the Ag multi-layer where its surface is Ag(111), a hexagonal molecular lattice is observed, and thus the triple-halogen bonds between three molecules are expected. To unveil the molecule-molecule coupling, we have carried out DFT calculations and the results are shown in the presentation.

Direct Visualization of Nearly-Free-Electron States Formed by Superatom Molecular Orbitals in Li@C_{60} Monolayer

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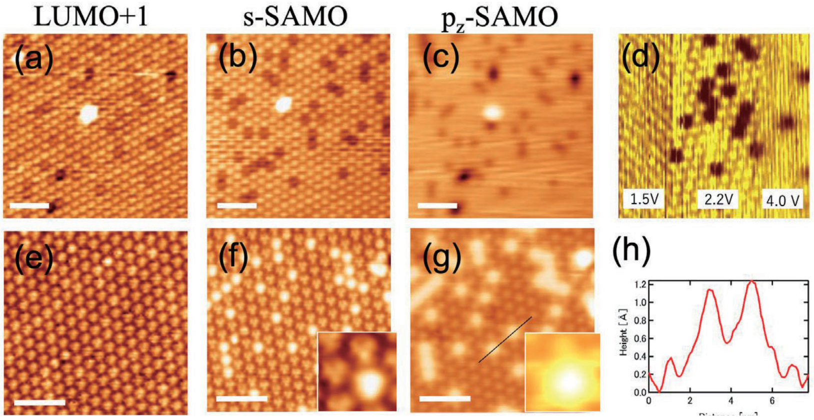
Using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, we directly determine the spatial and energetic distributions of superatom molecular orbitals (SAMOs) of an Li@C_{60} monolayer adsorbed on a Cu(111) surface. Utilizing a weakly-bonded [Li^{+}@C_{60}] NTf_2^{-} (NTf_2^{-}: bis(trifluoromethanesulfonyl)imide) salt makes it possible to produce a Li@C_{60} monolayer with high concentration of Li@C_{60} molecules. Due to the very uniform adsorption geometry of Li@C_{60} on Cu(111), the p_z-SAMO, populated *above* the upper hemisphere of the molecule, exhibits an isotropic and delocalized nature, with an energy that is significantly lower compared to that of C_{60}. The isotropic overlapping of p_z-SAMOs in the condensed monolayer of Li@C_{60} results in a laterally homogeneous STM image contributing the formation of a free-electron-like band[1]. These findings make an important step toward further basic research and applicative utilization of SAMOs of Li@C_{60}.



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Fano interference in electron transport through individual CuPc molecules on Cu(100)

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Copper-phthalocyanine (CuPc) is a prototypical molecule for the study of the interaction between π-conjugated orbital and metal surfaces. The LUMO (e_g) is interacted with the metallic continuous bands to be broadened and shift down to the Fermi level, which is associated with electron transport properties at the metal-organic interface. Here, we study the interaction of CuPc, F_8CuPc, and F_{16}CuPc molecules on Cu(100) by means of STM/STS. While the fluorination causes ~ 1eV downshift of LUMO for free molecule, it is found that it is distributed around the Fermi level for all species on the surface. This apparent contradiction is ascribed to the difference in the interaction with the surface. The filled F 2p orbital is repelled by the surface via Pauli mechanism, causing the equilibrium distance from the surface to be larger for the fluorinated species [1]. As a result, the adsorption-induced reduction of the local work function and thus the downshift of LUMO is smallest for F_{16}CuPc, compensating for the original energy difference. Thus, the fluorination has little effect on the electronic state of the molecules (position of LUMO with respect to the Fermi level) on the surface. On the other hand, we observe remarkable effect of the fluorination on the conductance properties at the Fermi level. We suggest that the adsorption height plays a critical role in the interference between the conductance paths and is therefore an important factor in determining the conduction characteristics.

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Crystal Structure of C_{70} Fullerene on Organic Single Crystals

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In organic semiconductor, the function is expressed at the pn hetero junctions. Therefore, these structure are important for the improvement of device performance. In order to control the structure of the pn hetero-junction, we have been investigating the organic-organic epitaxial growth. We have shown that epitaxial growth of n-type semiconductor materials on a p-type organic semiconductor single crystal surface can be achieved, and that the crystallite size can be controlled by the deposition conditions [1]. Recently, we have focused on C_{70} fullerenes to clarify the effect of molecular symmetry on the crystal structure. On a pentacene single crystal (PnSC), C_{70} fullerene has a (111) surface as in the bulk, and epitaxial growth with the $[1\bar{1}0]$ orientation of the PnSC (001) surface. We also found that the crystal structure of C_{70} epitaxially grown on PnSCs changes depending on the deposition conditions. In this presentation, we report the change in the crystal structure of C_{70} depending on the substrate temperature and deposition rate during the deposition.

PnSC were prepared by gas phase recrystallization by physical vapor transport (PVT). These single crystals were introduced into an ultrahigh vacuum to evaporate C_{70} fullerene up to 20 nm thickness, and used as a sample. The deposition rate was set at 0.05 Å/s, 0.2 Å/s, and 1 Å/s, and the substrate temperature was arbitrarily set between 123 K and 363 K. These samples were subjected to grazing incidence X-ray diffraction measurements (GIXD) at SPring-8 BL19B2 to determine the interface structure.

Fig. 1 shows the variation of GIXD peaks of C_{70} in out-of-plane and in-plane orientations at high temperatures. As the temperature increased, the out-of-plane peak shifted to the high-angle side. On the other hand, the peak in the in-plane orientation shifts to the low angle side. The estimated surface spacing is consistent with the reported temperature variation of the bulk structure [2]. In the presentation, we will also report the change in crystal structure with deposition at low temperatures.

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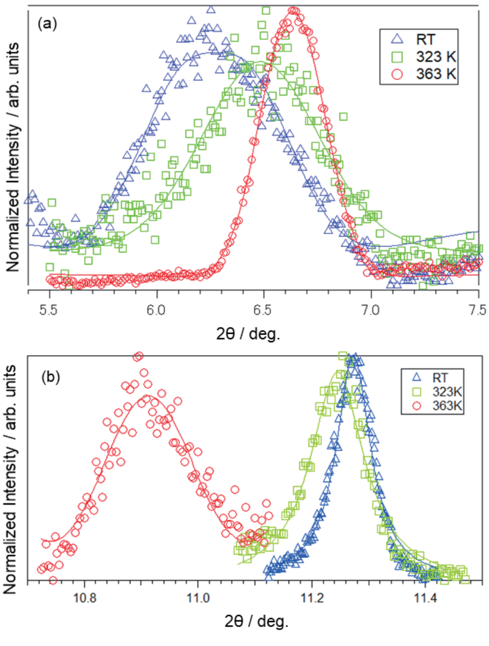

Fig.1 Temperature dependence of GIXD peak of C_{70} on PnSC (a)out-of-plane (b)in-plane.

Crystal structures of pentacene thin films grown on the epitaxial C_{60} on the single crystal rubrene

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Highly ordered arrangements of organic semiconductor molecules are one possible route to achieve improved device efficiency through imoroved charge carrier mobility. Recentely, organic solar cells of a device structure with alternately-stacked crystal thin films of donor and acceptor molecules were proposed [1]. On the other hand, our group has been focusing on the epitaxial growth of molecules as a method for obtaining stacked organic semiconductor crystals. For instance, (111)-oriented C_{60} of good crystalline qualities can be obtained on the pentacene (Pn) single crystal (001) surface [2]. The purpose of this study is to verify the possibility of epitaxial growth for the reverse structure; that is, Pn on C_{60}(111). In this work, the crystal structure of Pn thin films formed on C_{60} epitaxially grown in the (111) orientation over rubrene single crystals (Rub-SC) was studied by two-dimensional grazing-incidence X-ray diffraction (2D-GIXD).

Rub-SCs as the base substrates were prepared by a physical vapor transport method. We used a vacuum vapor deposition method to epitaxially grow C_{60} to a film thickness of 20 nm on the Rub-SCs, and subsequently Pn was deposited up to 20 nm to prepare the samples. 2D-GIXD measurements were performed on the Pn / C_{60} / Rub-SC samples at BL46XU and BL19B2 of SPring-8.

2D-GIXD results revealed that Pn took the thin film phase in the (001) orientation on the (111)-oriented C_{60}. From variation of the 2D-GIXD patterns depending on the sample azimuthal angle, two-types of crystalline domains of Pn in different in-plane orientations were identified as shown in Fig. 1; in either domain, Pn aligned its 100 or 1-30 axis along one of molecular nearest-neigbour directions of C_{60}.

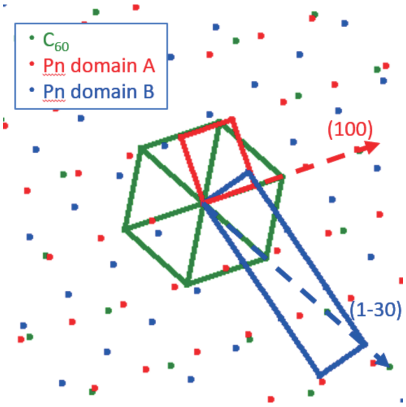

Fig. 1: Inter-lattice relationships of the epitaxial Pn on the (111)-oriented C_{60}.

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H_2O-iduced Crystallization of Organic Luminescent Thin Films by Direct Film Storage in a High Vacuum

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Atmospheric gas molecules, such as H_2O and O_2, are well-known to crucially affect the performance of various organic devices and are practically avoided by device fabrications in a vacuum followed by device encapsulation in a glovebox filled with inert gases. However, it is often unclear whether the post-growth films can retain their intrinsic properties without any gas exposure and post-growth time under high-vacuum conditions (10^{-3}–10^{-5} Pa), where residual H_2O is postulated to absorb on the device components and degrade device performance. H_2O-induced crystallization was observed microscopy for thin films of tris(2-phenylpyridinato)iridium(III) ($Ir(ppy)_3$), an organic luminescent material, grown on various silicon oxide surfaces [1]. Surface observation by atomic force microscopy revealed the crystallization. The crystallization occurred not only by ambient air or H_2O vapor exposure but also by just maintaining the films under high-vacuum conditions directly after the film fabrication. We developed an in-situ photoluminescence measurement apparatus and adopted it to organic luminescent thin films. H_2O-induced crystallization was also accompanied by spectral changes (Fig.1). Furthermore, we investigated substrate dependence, H_2O exposure and so on for other organic luminescent films to understand the crystallization phenomenon. Based on our findings, the crystallization phenomenon is correlated with the surface roughness of the underlying substrates and the chemical nature of the molecules. Our results provide a comprehensive understanding of the deviations that can potentially occur during the photophysical characterization of organic thin films and the performance of organic devices fabricated under different vacuum environments, thus enable the improved performance of the organic devices.

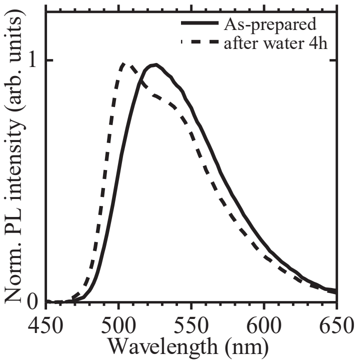

Fig.1. PL spectra of the Ir(ppy)3 thin film on glass. Solid line: in-situ. Dashed line: after water exposure.

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Thursday

28/Oct./2021

In-situ/operando soft x-ray spectroscopy study charge transfer and structural formation of electrochemical interfaces

Jinghua Guo (ALS, LBNL)

The energy materials and devices have been largely limited in a framework of thermodynamic and kinetic concepts or atomic and nanoscale. Soft x-ray spectroscopy characterization offers unique characterization in many important energy materials of energy conversion, energy storage and catalysis in regards to the functionality, complexity of material architecture, chemistry and interactions among constituents within.

It has been found that the microstructure and composition of materials as well as the microstructure have a great influence on performances of energy conversion and energy storage materials, chemical and catalytic processes. However, it is challenging to reveal the real mechanism of the chemical processes. In-situ/operando x-ray spectra characterization technique offers an opportunity to uncover the phase conversion, chemical speciation at the solid/gas and solid/liquid interfaces and devices in real time.

I will give some basics on in situ/operando soft x-ray spectroscopy characterization of interfacial phenomena in energy materials and devices, and how to use the powerful in-situ/operando characterization techniques, e.g. soft x-ray absorption spectroscopy (XAS) and resonant inelastic soft x-ray scattering (RIXS) to investigate the real electrochemical mechanism during the operation. A number of electrochemical liquid cells will be presented with success in revealing the catalytic and electrochemical reaction at real time.

Time-resolved XPS study of the effect of stacking order on exciton dissociation in a bilayer photovoltaic system

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Organic photovoltaic cells are one of ubiquitous renewable energy generators. A bilayer-type photovoltaic has the simplest structure and is suitable for studying fundamental phenomena that the photovoltaics exhibit. The present study has devoted to elucidate the effect of the stacking structure of electron donor and acceptor layers in a model bilayer organic photovoltaic. A special attention was paid to the carrier recombination process studied by laser-pump and synchrotron-radiation-probe time-resolved soft X-ray photoelectron spectroscopy (TR-XPS) [1]. We employed copper phthalocyanine (CuPc) and C_{60} fullerene as electron donor and acceptor molecules, respectively. Monolayer-thick films of these molecules were grown *in situ* on a model electrode, rutile TiO_2(110), with sequences of CuPc/C_{60}/TiO_2(110) and C_{60}/CuPc/TiO_2(110), which were subjected to TR-XPS measurements at BL07LSU of SPring-8.

Irradiation of the ultraviolet laser pulses is found to induce a shift of C 1s peaks of both C_{60} and CuPc towards higher binding energies irrespective of the stacking order. This implies that both C_{60} and CuPc are cationized by transferring the electrons excited to unoccupied states the molecules to the TiO_2 substrate. The C_{60} C 1s peak shifts as large as 10−15 meV, which is diminished monotonically over time from 0.1 ns to >4 µs after laser pulse irradiation in the CuPc/C_{60}/TiO_2 system. On the other hand, a slight increase from 6 to 10−15 meV is observed below 1 ns in the C_{60}/CuPc/TiO_2 system. We speculate that delayed dissociation of excitons within the C_{60} layer should be responsible for this peculiar behavior. Details of this phenomenon will be discussed [2].

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Electronic signature of a “breathing” transition in a metal-organic framework by resonant inelastic x-ray scattering (RIXS)

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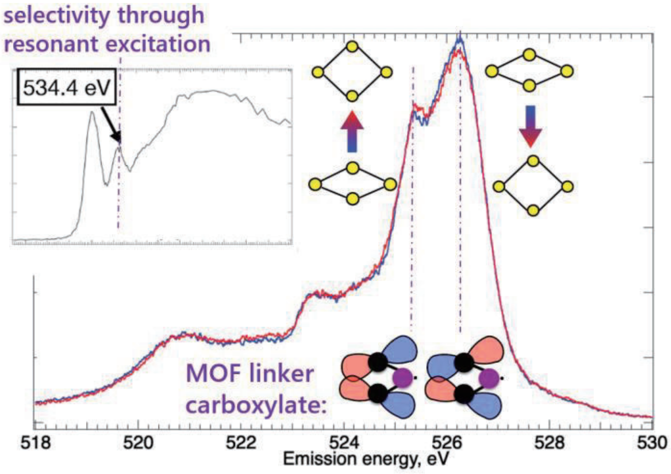
Structural flexibility in metal-organic frameworks (MOFs) illustrate the role of dynamics in the stability and function of these nanoporous materials. A key demonstration is the “breathing transition” between narrow-pore and large-pore phases of the MOF MIL-53(Al) [1,2]. Temperature and guest adsorption were observed to influence this phase transition, with high temperatures and empty guest loadings preferring the large-pore over the narrow-pore phase [2]. In this work, modulation of electronic structure accompanying the breathing transition was selectively probed at the carboxylate moiety, the site of metal-ligand interaction, by oxygen *K* edge resonant inelastic x-ray scattering (RIXS). Measurements on MIL-53(Al) both in vacuum and in ambient conditions were performed using the high-resolution soft x-ray emission spectrometer [3] housed in SPring-8 beamline BL07LSU. In vacuum conditions, the temperature-induced phase transition only involves a modulation of the occupancy of the carboxylate oxygen lone pair orbitals. In turn, water adsorption under ambient humidity involves an additional perturbation of deep-lying π states not observed for the phase transition solely driven by temperature.



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Present status and future of organic device

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Electronic devices in the expected sustainable societies require maximum function with minimum amount of constituent materials and energy cost for production. Noting that electronic functions for information technology, which our future society further relies on, are mostly originated from two-dimensional material properties, such integrated devices of large area (more function) and small thickness (less material consumption) are desired. This presentation introduces only nanometer thick semiconductor crystals of organic molecules, which grow to the size of 30 cm with a low-energy process near room temperature. Applications for recently developed large-area low-cost integrated circuits and flexible displays are proposed to add on the present infrastructure utilizing existing surfaces without deformation.

The ultrathin organic semiconductor single crystalline films of a p-type organic semiconductor alkyl-naftobenzodithiophene (Cn-DNBDT) are easily grown from solution to the size up to 30 cm X 30 cm at temperatures around 80 ºC either on a film or glass substrates. A 30-cm-long blade continuously supplies solution on the substrate sliding slowly with appropriately controlled speed, so that the thickness is tuned by the conditions [1]. The molecule is designed to diminish molecular fluctuation at room temperature so that holes are less scattered by lattice vibration. Therefore, hole mobility of the single-crystal transistors exceeds 10 cm^2/Vs, achieving intermolecular charge coherence. N-type organic single-crystal transistors with electron of 3 cm^2/Vs are recently developed for Phenyl-alkyl-benzo[de]isoquinolino[1,8gh]quinolinediimide (Ph-C2-BQQDI) [2]. With excellent chemical and thermal stability in such materials, integrated devices are developed based on organic CMOS processing technologies. The cut-off frequency of the p-type transistors exceed 40 MHz so that small-scale integrated circuits are practically meaningful. Successful rectification and RF identification are demonstrated at 13.56 MHz with printed organic CMOS circuits.

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Energy Band Structure of the Lowest Unoccupied Molecular Orbital and Polaron Formation in High-Mobility Organic Semiconductors

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Energy band structure is a fundamental material property that contains crucial information on charge carrier transport in semiconductors such as effective mass, transfer integral and electron-phonon coupling. In organic semiconductors, the valence (highest occupied molecular orbital; HOMO) band structure has been observed using photoelectron spectroscopy since 1990s, whereas the conduction (lowest unoccupied molecular orbital; LUMO) band structure has never been observed. In this presentation, we report the first observation of LUMO energy band structure of organic semiconductor. At first, we developed a new technique, angle-resolved low-energy inverse photoelectron spectroscopy (AR-LEIPS, Fig. 1a). Then, we show observed LUMO energy band structure of a prototypical high-mobility organic semiconductor, pentacene (Fig. 1b). We found that the observed LUMO bandwidth is substantially narrower than that predicted by DFT calculation, indicating polaron formation owing to the strong electron-phonon coupling in organic semiconductors. To confirm it, we examined the temperature dependence of LUMO and HOMO bandwidths. The bandwidths are quantitatively reproduced by the polaron model. The present result establishes the existence of polaron in high-mobility organic semiconductors.

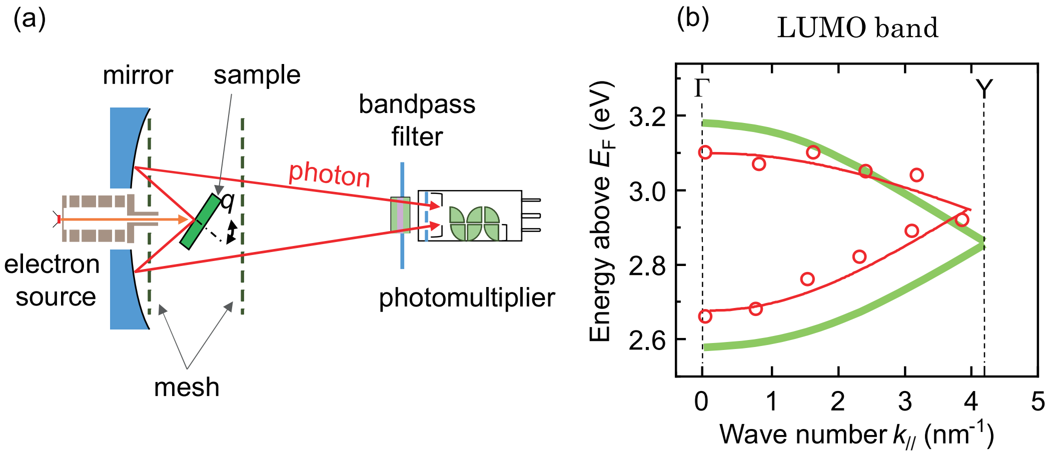

Figure 1. (a) AR-LEIPS apparatus. (b) The observed LUMO band of pentacene (red circles and lines) compared with the DFT calculation (green lines) along Γ-Y direction.

Impact of Small Polaron with Low-Frequency Molecular Vibration on Electron Mobility of Organic Semiconductors

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Intrinsic charge transport in crystalline organic semiconductors is strongly influenced by the charge-phonon interaction because energy of intermolecular electronic couplings (transfer integral $t \approx 0.1$eV) are comparable to the molecular vibrations (energy $\hbar\omega$). The high-frequency vibrations ($\hbar\omega > t$) have the effect of dressing the charge with molecular/lattice distortion cloud ("polaron"). The slow vibrations ($\hbar\omega < t$) mainly modulates intermolecular electronic coupling and scatter the Bloch waves ("dynamic disorder"). The both effects decrease the charge carrier mobility. To calculate the charge carrier mobilities taking the both effects into consideration, we have been developed the time-dependent wave-packet diffusion (TD-WPD) method. The method predicts hole mobilities satisfactory [1] but electron ones insufficient.

In this presentation, we discuss the electron mobility by reconsidering the polaron-formation mechanism. Previous studies consider only an arbitrary chosen high-frequency mode ($\hbar\omega > t$) for the polaron formation. Many organic semiconductors, however, possesses a low frequency mode which couples weakly with hole but strongly with electron. Thus, we modify the polaron model by taking all the vibrational modes into account; low-frequency modes with $\hbar\omega \approx t$ which were ignored in the earlier studies may couple partially with the charge carrier; we include this partial contribution based on the Debye relaxation. The calculated valence and conduction band structures of pentacene (Figs. 1a and b) quantitatively reproduce the experimental photoelectron and inverse photoelectron spectra. Using these findings, we modified the TD-WPD method and evaluated the hole and electron mobilities for several organic semiconductors (Fig 1c for pentacene). The calculated electron mobilities and its temperature dependence satisfactorily agree with the experimental values.

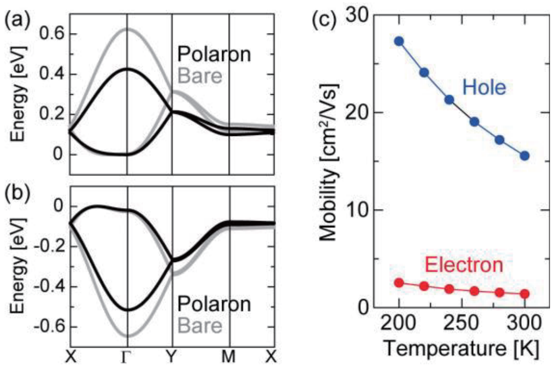

Fig.1. (a) Calculated conduction and (b) valence band structures for pentacene. (c) Calculated mobilities.

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Time- and angle-resolved photoemission study on quantum materials

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Time- and angle-resolved photoemission spectroscopy (TARPES) has played an important role in revealing the non-equilibrium electronic structures of solid-state materials. The implementation of high harmonic generation (HHG) to obtain a higher photon energy also allows us to investigate the wide Brillouin zone on a time scale below 100 fs.

In this presentation, I will talk about our recent studies on quantum materials using HHG-laser-based TARPES [1]. I will first highlight iron-based superconductors, namely $BaFe_2As_2$ [2] and FeSe [3]. We found significant time-dependent oscillations of photoemission intensities, which result from generations of coherent phonons. I will discuss the relation of this observation to lattice modulations and the possibility of photo-induced superconductivities. Then, I will move on to the ultrafast carrier dynamics of a quasi-crystalline 30° twisted bilayer graphene [4]. We found unbalanced electron distributions between the upper-layer and lower-layer Dirac cones in the ultrafast time scale. I will show the calculation results by solving rate equations to explain the observed dynamics, and discuss the possible mechanisms. Lastly, I will talk about Ta_2NiSe_5, which is regarded as a unique candidate for an excitonic insulator. We successfully revealed the dynamical behavior characteristic of an excitonic insulator, and the unexpected emergence of the photo-induced semimetallic state [5]. Furthermore, we investigated the underpinned mechanisms of this photo-induced insulator-to-metal transition by developing a novel analysis method, which we call frequency-domain ARPES (FDARPES) [6].

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Surface-doping induced Mott breakdown in Ca_2RuO_4

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Mott physics lies at the heart of emergent phenomena such as high-temperature superconductivity and colossal magnetoresistance. Controllability is an important aspect of Mott transitions not only for exploring new quantum phenomena or tackling the controversial mechanism of the Mott state but also for a possible application purpose. In this regard, the Mott insulator Ca_2RuO_4 serves as a model system. It displays huge susceptibilities to various kinds of external perturbations, such as chemical/physical pressure [1,2] and electric field [3], and turns into different metallic states.

In recent years, alkali-metal deposition is being recognized as a promising candidate to trigger an insulator-to-metal transition. Upon dosed, Alkali metals form ionic bonds at the surface to supply electrons to the sample. This method is particularly of high value when the sample of interest does not allow chemical substitutions for doping carriers. Mott-insulating Sr_2IrO_4, where electron doping was impossible via chemical substitutions, was demonstrated by angle-resolved photoemission spectroscopy (ARPES) to undergo a surface Mott transition by K dosing and form a metallic surface state with a putative signature of superconductivity [4].

Motivated by such successful applications to Mott insulators, we have attempted alkali-metal dosing to Ca_2RuO_4 and tracked electronic-structure changes using ARPES. We found that initial changes can be characterized by the downward shift of bands by electron doping, which is accompanied by a modest decrease of lower-Hubbard-band intensity. Upon dosing more, the lower Hubbard band further loses its intensity, and an in-gap state grows up in the low-energy region that eventually reaches the Fermi level. This observation suggests that the Mott breakdown and the emergence of a metallic state on the Ca_2RuO_4 surface is caused by the interplay with dosed alkali metals. The changes cannot be understood within a simple carrier-doping picture, and hence a framework specific to the alkali-metal dosed surface is required.

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Exploring Effective Surface Passivation of CdS QD's with Gallic Acid: From Green Synthesis to Highly Fluorescent Molecular Probe

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Abstract:

Surface functionalization of nanoparticles is the only way to eliminate gaps, dangling bonds, and non-stoichiometry on the surface, as well as serve as the source of trap states for electrons, holes, and excitons, significantly modifying their optical properties. Gallic acid has been discovered for the first time as a unique surface passivating agent for CdS QDs that produces a considerable increase in photoluminescence intensity. At 75°C, highly soluble surface functionalized CdS was generated in an aqueous media. The interaction of CdS with gallic acid through head groups is shown to be very good using Fourier transform infrared spectroscopy (FTIR). The generation of cubic CdS (zinc blende structure) is confirmed by X-ray diffraction. Scanning electron microscopy (SEM) images shows that surface passivation has a significant impact on nanocrystal size and shape. The size and shape-dependent quantum confinement effect in gallic acid functionalized CdS nanoparticles is well confirmed by UV-visible and photoluminescence spectroscopy. Significant hypsochromic shifting of absorption peak to lower wavelength have been recorded in aqueous solution. Commendable reports have been made on effect of surface functionalization on microstructural parameters like crystallite size, average strain and dislocation density. Systematic data analysis concludes that gallic acid functionalization results in effective surface passivation leading to potential alteration in optical and textural properties.

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Charge Transfer Interaction of Citric Acid Passivated CdS QD’s with Natural Dyes Under Visible Light Irradiation

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Abstract

The use of various plant extracts for the green synthesis of CdS nanoparticles has recently attracted a lot of attention across the world. The chemical and biological qualities of the components found in antioxidant-rich fruits which contain citric acid have gotten a lot of attention in recent times. Until now citric acid has not been used as a surface passivating agent for the synthesis of CdS nanoparticles. So, in this study we are reporting Citric Acid (CA) as a new surface functionalizing agent for the synthesis of colloidal CdS quantum dots. The interaction of CA passivated colloidal CdS quantum dots with natural dyes was probed using photo induced interaction. Adsorption of dye molecules on the CdS surface occurs effectively which causes dye molecules to emit less light. UV–Visible spectroscopy experiments clearly show that the photo-induced charge transfer interaction of CdS quantum dots with natural dyes indicating H-aggregation of dyes on CdS surface. Photo-induced quenching of both dyes is attributed to electron transfer from the excited state of the dyes to the conduction band of CdS which has been confirmed from the density calculations (DFT) performed using ORCA.

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Investigating excited-state dynamics in molecules with quantum light

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Quantum light, such as entangled photons, is a key resource for promoting cutting-edge quantum technology. One class of this technology aims to improve the precision of optical measurements via non-classical photon correlations, and quantum metrology has rapidly gained widespread attention due to its ability to make measurements with sensitivity and resolution beyond the limits imposed by the laws of classical physics. In this light, it is hoped that quantum light will also open new avenues for optical spectroscopy using the parameters of quantum states of light [1].

In this presentation, we discuss quantum light spectroscopy for probing exciton and charge dynamics in complex molecules. Specifically, we address transmission measurement of frequency-entangled broadband photon pairs generated via parametric down-conversion with a monochromatic laser. It is observed that state-to-state dynamics in the system under study are temporally resolved by adjusting the path difference between the entangled twin beams when the entanglement time is sufficiently short. The non-classical photon correlation enables time-resolved spectroscopy with monochromatic pumping instead of a pulsed laser. It is further demonstrated that the signal corresponds to the spectral information along anti-diagonal lines of, for example, two-dimensional Fourier-transformed photon echo spectra [2]. This correspondence inspires us to anticipate that more elaborately engineered photon states would broaden the availability of quantum light spectroscopy [3].

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Unraveling structural and dynamical properties of (quantum) nuclei in diverse materials

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The inclusion of nuclear motion, including quantum effects like zero-point-energy and tunneling in high-dimensional anharmonic systems, represents a considerable challenge in atomistic simulations. I will discuss methodology based on the combination of electronic structure theory and the path integral formalism that is fully applicable to systems where a high number of anharmonic degrees of freedom are relevant. As paradigmatic examples, I will discuss effects of nuclear motion on the charge transfer at hybrid material interfaces [1] and the intramolecular hydrogen transfer dynamics of the porphycene molecule. We discovered that surface fluctuations can enhance the intramolecular hydrogen tunnelling rate by orders of magnitude when these molecules are adsorbed on metallic surfaces [2]. I will finish with considerations about the impact of electronic friction on hydrogen tunnelling reactions in metallic environments, providing physical insight on the effects of this non-adiabatic process in tunnelling events.

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