Soft/Hard 2023

10th International Symposium on Functionalization and Applications of Soft/Hard Materials (Soft/Hard 2023)

5th International Symposium on Hetero Structure and Advanced Materials

KAKENHI Grant-in-Aid for Scientific Research (S) Final Symposium

Biwako-Kusatsu Campus
Ritsumeikan University
March 3–5, 2023

Organizer

Research Center for Advanced Materials, Ritsumeikan University

Sponsors

- KAKENHI Grant-in-Aid for Scientific Research (S), JSPS
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10th International Symposium on Functionalization and Applications of Soft/Hard Materials (Soft/Hard 2023)

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Program

March 3rd — Plenary Session

9:55–10:00	Opening remarks

Keynote address (Room R103)

10:00–10:45	Prof. Ganesan Prabu Sankar (Indian Institute of Technology, Hyderabad)
10:45–11:30	Prof. Dmytro Orlov (Lund University)
11:30–12:15	Prof. Pierre Audebert (École Normale Supérieure Paris-Saclay)
12:15–13:30	Lunch break (Room K310, Epoch Ritsumei21)

Invited lecture (Room R103)

13:30–14:00	Prof. Hiroshi Fujiwara (Ritsumeikan University)
14:00–14:30	Prof. Yoichi Kobayashi (Ritsumeikan University)
14:30–15:00	Prof. Benjamin Guennec (Toyama Prefectural University)
15:00–15:30	Dr. Kohsuke Matsumoto (Institute for Molecular Science)

Poster session (Foyer)

15:30–17:30	Poster session
17:30–17:45	Closing remarks and poster award ceremony (R103)
18:00	Banquet (Meeting room, 3rd floor, Rohm Memorial Plaza)

March 4th Sectional meeting

Soft-materials section (Room R103)

10th International Symposium on Functionalization and Applications of Soft/Hard Materials (Soft/Hard 2023)

Invited talk by young scientists (Chair: Prof. Osamu Tsutsumi)

10:00–10:20	Subramaniyam Kalaivanan (Indian Institute of Technology, Hyderabad)
10:20–10:40	Tomoki Shigeyama (Ritsumeikan University)
10:40–11:00	Muduli Gopendra (Indian Institute of Technology, Hyderabad)
11:00–11:20	Satoru Yoshida (Ritsumeikan University)
11:20–11:40	Veerapathiran Sabari (Indian Institute of Technology, Hyderabad)
11:40–12:00	Daisuke Yoshioka (Ritsumeikan University)
12:00–12:20	Nandeshwar Muneshwar Girhari (Indian Institute of Technology, Hyderabad)

12:20	Closing remarks
16:30	Banquet (Meeting room, 3rd floor, Rohm Memorial Plaza)

March 4th Sectional meeting

Hard-materials section (Room R102)

5th International Symposium on Hetero Structure and Advanced Materials
JSPS KAKENHI Grant-in-Aid for Scientific Research (S) Final Symposium
Summary of the JSPS Kakenhi "Harmonic Structure Materials" Project 2018 - 2022

10:00–10:10	Opening remarks
10:10–10:45	Prof. Kei Ameyama (Ritsumeikan University)
10:45–11:00	Coffee break
11:00–11:50	Prof. Yuntian Zhu (City University of Hong Kong)
11:50–13:00	Lunch
13:00–13:50	Prof. Guy Dirras (Université Sorbonne Paris Nord)
13:50–14:05	Coffee break
14:05–14:25	Prof. Yoshikazu Nakai (Kobe University)
14:25–14:45	Prof. Daiki Shiozawa (Kobe University)
14:45–15:05	Prof. Shoichi Kikuchi (Shizuoka University)
15:05–14:20	Coffee break
15:20–15:40	Prof. Tomotsugu Shimokawa (Kanazawa University)
15:40–16:00	Prof. Lei He, Prof. Takamoto Itoh (Ritsumeikan University)
16:00–16:15	Closing remarks (Prof. Kei Ameyama/Prof. Dmytro Orlov)
16:30	Banquet (Meeting room, 3rd floor, Rohm Memorial Plaza)

List of Poster Presentations

March 3rd (15:30–17:30) in Foyer

	Author(s)	Title
P1	Daigo Takeda, Mie Kawabata, Tomoko Kuno, Kei Ameyama, Hiroshi Fujiwara	Microstructure and Mechanical Properties of Ti-Ni/Cu Harmonic structure composite
P2	Ryoga Morozumi, Ryota Honda, Mie Kawabata, Tomoko Kuno, Kei Ameyama, Hiroshi Fujiwara	Microstructure and High Temperature Mechanical Properties of AlCoCrFeNi High Entropy Alloy
P3	Ryosuke Ito, Kosuke Kaneko, Kimiyoshi Kaneko, Tomonori Hanasaki	Synthesis and Characterization of Liquid Crystalline Organic Semiconductor Materials with Benzothiophene Skeleton
P4	Tetsuya Nishide, Daiki Fujioka, Kosuke Kaneko, Kimiyoshi Kaneko, Tomonori Hanasaki	Electrorheological Effect of Pd Nanoparticles Dispersed Nematic Liquid Crystals
P5	Yoshitomo Narita, Satoru Yoshida, Kimiyoshi Kaneko, Kosuke Kaneko, Tomonori Hanasaki	Fluorescence Properties of AIE-Active Perylene Derivatives in the Aggregated State
P6	Kazuma Nagata, Takayuki Menjo, Kosuke Kaneko, Daiki Fujioka, Kiyomi Fuchigami, Kimiyoshi Kaneko, Tomonori Hanasaki	Dynamic Viscoelasticity of Liquid Crystal Elastomer Films Containing Dual Frequency Liquid Crystalline Groups
P7	Tatsuaki Takaoka, Shohei Miyata, Kimiyoshi Kaneko, Kosuke Kaneko, and Tomonori Hanasaki	Liquid Crystalline Property of Dimeric DEME Based Ionic Liquids Doped with Organic Solvents Containing Hydroxy Groups

P8	Masahiro Yasuda, Yuki Ii, Kosuke Kaneko, Daiki Fujioka, Kiyomi Fuchigami, Kimiyoshi Kaneko, Tomonori Hanasaki	Electro Rheological Effects of Dual Frequency Liquid Crystals with Branched Siloxane Cores
P9	Kota Nakano, Fumio Ogawa, Lei He, Hiroshi Fujiwara, Takamoto Itoh	Development of Carbon Nanofiber Reinforced Aluminum Composite with Harmonic Structure Design
P10	Taiki Yamamoto, Yasuhiro Nishida, Lei He, Takamoto Itoh	Development of a creep testing machine with the maximum temperature 1000°C
P11	Takeshi Tanaka	Study of In-Liquid Synthesis of Diamond-Technical Development aimed for Chemical Change/Cut/Precipitation and Self-Assembly/Aggregation
P12	Atsuki Tsuji, Junji Murata	Direct micropatterning of Cu using polymer electrolyte membrane stamp
P13	Yuki Shikata, Kyohei Hisano, Osamu Tsutsumi	Spontaneously Induced Pattern Formation of Liquid Crystal Orientation by Gradient Photopolymerization
P14	Tamon Nakao, Osamu Tsutsumi	Emission Properties of Liquid-Crystalline Trinuclear Gold(I) Complexes with Branched Side Chains
P15	Kazuki Kawai, Tomoki Shigeyama, Osamu Tsutsumi	Preparation of Cross-Linked Liquid-Crystalline Polymer Particles with Precisely Controlled Molecular Orientation

P16	Renzaburo Otani, Yosei Wakasa, Osamu Tsutsumi	Control of Crystal Structure in Discotic Trinuclear Gold(I) Complexes by UV Irradiation
P17	Tatsuya Ishibe, Yuki Shikata, Tsutsumi Osamu	Mechanism of Molecular Orientation Pattern Formation in Liquid-Crystalline Polymers Induced by Gradient Photopolymerization
P18	Mina Matsuda, Osamu Tsutsumi	Mechano-optical Behavior of Multilayered Chiral-Nematic Liquid Crystal Elastomers with Auxetic Structures
P19	Arushi Rawat, Arruri Sathyanarayana, Kumar Siddhant, Masaya Yamane, Kyohei Hisano, Ganesan Prabusankar, Osamu Tsutsumi	Tuning the Au-Au Interactions in Luminescent Linear Polymeric Gold-NHC Complexes
P20	Tomohiro Azumaya, Naoya Fukui, Tomoki Shigeyama, Osamu Tsutsumi	Three-Dimensional Deformation Analysis with Chiral-Nematic Liquid Crystal Polymer Particles
P21	Andriani Furoida, Osamu Tsutsumi	Tunable Emission Color of Polymorphic Gold(I) Isocyanide Complexes
P22	Yurika Kayashima, Osamu Tsutsumi	Monitoring Molecular Orientation Change Induced by Mechanical Stimuli in Chiral-Nematic Liquid Crystal Elastomers with Luminescent Molecules
P23	Tatsuo Sakai, Yuki Nakamura, Akiyoshi Nakagawa, Noriyasu Oguma	Construction of Probabilistic Model on Interior Crack Nucleation and Propagation in Very High Cycle Fatigue of High Strength Steels

P24	Keigo Hori, Daisuke Yoshioka, Yuki Nagai, Yoshinori Okayasu, Yoichi Kobayashi	Excited-State Dynamics of 1-Pyrenecarboxylic Acid-Coordinated ZnS Nanocrystals
P25	Mayu Kimura, Daisuke Yoshioka, Yoshinori Okayasu, Yuki Nagai, Yoichi Kobayashi	Effect of Nanocrystal Surface on Photochromism of Cu-Doped ZnS Nanocrystals
P26	Keisuke Ochiai, Issei Fukunaga, Yoshinori Okayasu, Yuki Nagai, Yoichi Kobayashi	Excited-State Dynamics of a Phenothiazine Derivative Having a Quinoidal Structure
P27	Sota Fujisaki, Yoshinori Okayasu, Yuki Nagai, Yoichi Kobayashi	Spatiotemporal Control of Photochromic Reactions Based on Oxygen Transfer Suppressed in Supramolecular Gel
P28	Yuto Toyota, Yamashita Shohei, Yuki Nagai, Yoshinori Okayasu, Yohei Okada, Yoichi Kobayashi	Controlling Optical Properties of ZnO Nanocrystals by Bulkiness of Alkyl Ligands
P29	Sota Tokuoka, Daisuke Yoshioka, Yoshinori Okayasu, Yuki Nagai, Yoichi Kobayashi	Synthesis and Optical Properties of ZnTe/ZnS Core-Shell Nanocrystals

Abstract

Plenary Session

Light Emitting Gold(I) and Copper(I) N-Heterocyclic Carbene Molecules

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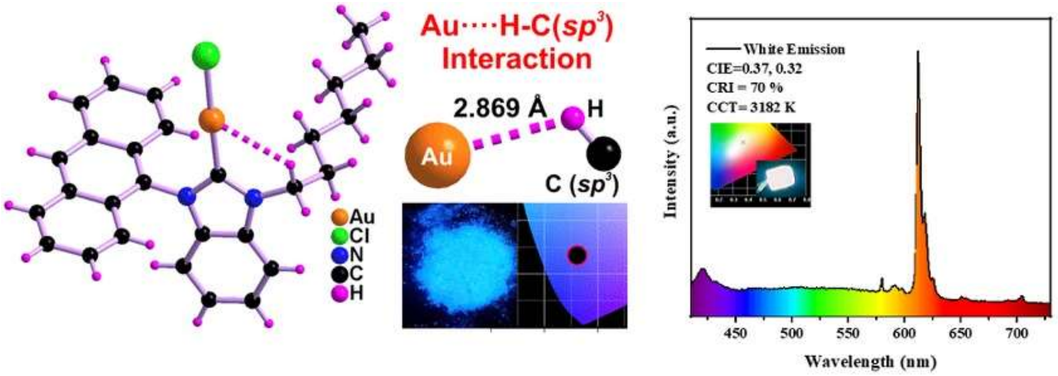
N-heterocyclic carbene (NHC) gold(I) or copper(I) linear complexes have a wide range of applications in materials and medicinal chemistry. Over the past three decades, several NHC complexes of gold(I) and copper(I) have been demonstrated for their robust photophysical properties. The solid-state structural studies of NHC-Au(I) and NHC-Cu(I) complexes unveiled that the structural features are directly related to the unusual photoluminescence property of NHC-Au(I) and NHC-Cu(I) complexes. Some of the influencing factors are the coordination number of metals, metal-metal interaction, π–π interactions, and metal hydrogen bonding. Besides, the molecular aggregations (aggregation-induced emission) can also play a crucial role in the crystalline state of molecules. However, despite the exponential development of the wide range of systems, the rational design of mononuclear gold(I) or copper(I) NHC with tunable emission properties with high quantum yield through the suitable N-substituent is challenging. Indeed, the dearth of reports dealing with the suitable N-substituent of NHC-Au(I) or NHC-Cu(I), urged us to investigate this class of compounds. The relationship between the N-substituent with intramolecular metal hydrogen bonding as well as the luminescence properties in the crystalline state will be addressed.[1-4]



1) M. Vaddamanu, A. Sathyanarayana, Y. Masaya, S. Sugiyama, O. Kazuhisa, K. Velappan, K. Subramaniyam, K. Hisano, O. Tsutsumi, G. Prabusankar, *Organometallics*, **2020,** *39(12)*, 2202.
2) M. Vaddamanu, A. Sathyanarayana, Y. Masaya, S. Sugiyama, O. Kazuhisa, K. Velappan, M. Nandeshwar, K. Hisano, O. Tsutsumi, G. Prabusankar, *Chem. Asian J.,* **2021**, *16(5)*, 521.
3) M. Adinarayana, M. Vaddamanu, A. Sathyanarayana, K. Siddhant, S. Sugiyama, O. Kazuhisa, A.K. Rengan, Kavitha Velappan, Kyohei Hisano, Osamu Tsutsumi and G. Prabusankar, *Dalton Trans.*, **2021**, *50*, 16514.
4) S. Kalaivanan, M. Vaddamanu, K. Siddhant, K. Velappan, K. Hisano, O. Tsutsumi, and G. Prabusankar, *New J. Chem.,* **2022,** *47*, 491.

Use of large-scale research facilities for material science: from basics to recent development trends in Europe

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‘Large-scale research facilities’ is a common name typically used nowadays for describing synchrotrons and neutron sources as well as free-electron lasers and other particle accelerators. Over the last decade, such facilities have been rapidly transforming from use by a limited group of dedicated physicists to the main-stream tool facilitating accelerated development of science and technologies in every field of our activities. For example, Japan operates a synchrotron ‘Spring-8’ and a neutron scattering facility at ‘J-PARC’, while around the World open user programs have 23 synchrotrons and 18 neutron sources including 13 and 8 such facilities, respectively, in Europe. Sweden with a central location in Lund has been emerging as a ‘hot spot’ in this space opening a synchrotron MAX IV Laboratory (MAX IV) in 2016, and a most powerful in the World neutron science facility European Spallation Source ERIC (ESS) scheduled to open for users in 2025.

The large-scale research facilities can be viewed as a natural development of still more common laboratory-scale analytical tools. They can be traced from the development of a first optical compound microscope “Micrographia” in late 17th century where optical lenses were used for condensing photons in a visible spectrum; to electron microscopes where electro-magnetic lenses are used to accelerate electrons, still in a laboratory-scale environment predominantly; to latest facilities where particles that can be charged, e.g. electrons or protons, are accelerated for use as a scattering source generating x-rays, neutrons, *etc.* in a wide range of frequency spectra. Scattering particles are then utilised at beamlines, sometimes having several end stations, for an extremely diverse range of experimental techniques elaborated in the research community by now. One of the strongest sides of such facilities compared to laboratory-scale counterparts is the possibility of setting up experiments in *in situ* and *operando* conditions with very high temporal resolution. These open exceptional opportunities for new discoveries in material science including heterogeneous materials with micro-architected structures.

Nevertheless, it might appear difficult to navigate the environment of large-scale research facilities for material scientists without appropriate background in respective characterisation techniques. Therefore, this talk will clarify similarities, differences and complementarities between laboratory- and large- scale research facility based techniques for materials characterisation. Perspectives on light property control enabled by large-scale facilities as well as brief overview of modern methods of highest interest for crystalline materials including *in situ* techniques will also be given. These will be illustrated by the analysis of hetero-structured materials with examples from our experiments on harmonic-structured pure nickel. Recent trends in the development of characterisation techniques and large-scale research facilities themselves in Europe will also be overviewed.

Heptazines, new promising molecules in photocatalysis and organic photovoltaics; syntheses and first applications.

Pierre Audebert

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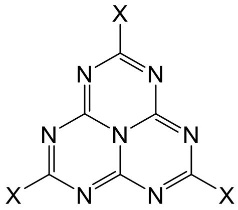
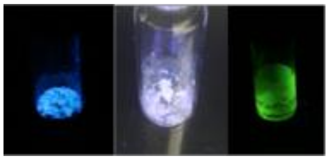
Heptazines, which count very few described examples, are among the most electron deficient high-nitrogen content, stable aromatic heterocycles (Fig. 1) [1]. This peculiarity confers them very original physico-chemical characteristics, including delayed fluorescence, a high electrochemical reduction potential, and a strong potential in organic photocatalysis. In addition, heptazines can trigger enhanced electron transport in OPV devices. However, their synthetic approach, for heptazines, is still in its infancy. We will present and comment on new strategic synthetic procedures involving this family of molecules, insisting in addition on recent results on new heptazines, and new properties.



heptazines



This lecture will therefore first recall new synthetic advances in the field of heptazines. Noticeably, a new synthetic procedure of heptazines using mechanochemistry [2], will be presented, which leads to the second heptazine known with exchangeable leaving groups. In the following, applications of heptazines in photocatalysis and as electron-injecting layers in standard OPV organic cells [3].

1) P. Audebert, E. Kroke, C. Posern and S.-H. Lee,. *Chem. Rev.* **2021**, 121, 2515.
2) L. Galmiche, T. Le, C. Allain and P. Audebert, patent filed, **2018**. P. Audebert, L. Galmiche, C. Allain, R. Guillot, T. Le, *Chem. Sci.*,**2019**, 10 ,5513.
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Wear and Impact Properties of Harmonic Structure Composites with Cemented Carbide/High-Speed Steel

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Dies can mass-produce the same shaped products and are indispensable in modern industries. A high hardness and high toughness metal is used for the die material. The hardness affects to the wear resistance of the die material and the toughness affects to die life. However, the relationship between hardness and toughness is a trade-off. Thus, it is difficult to provide the two properties at the same time. To achieve both high wear resistance and high toughness, a harmonic structure composite that combines cemented carbide with a high hardness and high-speed steel with a high toughness is fabricated by a mechanical milling and spark plasma sintering process. The microstructure of the harmonic structure composite consists of a three-dimensionally network area of a hard material and distributed areas of relatively soft material. In this study, the harmonic structure composite with high-hardness cemented carbide in the network area and high-tough ness high-speed steel in the dispersed area is investigated the microstructure and wear and impact properties in detail.

Cemented carbide powder (WC-13%Co) and high-speed steel powder (Fe-1.27C-4.12Cr-4.92Mo-2.92V-5.89W) were used in this study. These powders were mechanically milled using a planetary ball mill equipment with an SKD11 vessel and cemented carbide balls (ϕ5 mm) in Ar atmosphere at room temperature. Mixed powder consisting of cemented carbide (15 g) and high-speed steel (35 g) was mechanically milled at a ball-to-powder weight ratio of 2 : 1, an MM time of 345.6ks and a rotation speed of 150 rpm. The MM powder was sintered an SPS apparatus at 1223 K and 100 MPa for 0.6 ks. The wear test was performed using a ball-on-disk type friction wear tester under the conditions of a load of 10 N, a rotation radius of 3 mm, a rotation speed of 300 rpm, and a sliding distance of 56.5 m. The wear properties were evaluated by calculating the comparative abrasion quantity. In an impact property evaluation, a split-Hopkinson bar type compression impact test was performed under the condition of an impact bar ejection pressure of 1.0 to 1.5 MPa.

Figure 1 shows an electron micrograph of the cemented carbide/high-speed steel harmonic structure composite. The bright area corresponds to the cemented carbide area with the network connected throughout the microstructure. On the other hand, the dark field corresponds to the high-speed steel area, which is distributed between the cemented carbide networks.

The specific wear amount of the cemented carbide/high-speed steel harmonic structure composite was 3.23×10^{-15} m^3/Nm for the 1223K sintered body and 2.12×10^{-15} m^3/Nm for the compact sintered at 1173K. The specific wear amount at a ratio of 30% carbide shows excellent values from the point of view of the rule of mixture. Also, the impact absorption energy density to fracture of the cemented carbide/high-speed steel harmonic structure composite was about 500 MJ/m^3. It showed a value about twice the impact absorption energy density of a cemented carbide compact. The cemented carbide/high-speed steel harmonic structure composite demonstrates high wear resistance and excellent impact resistance.

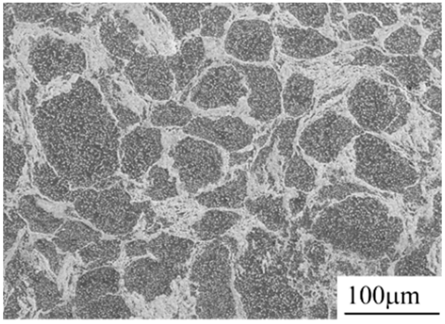

Fig.1 SEM micrograph of the cemented carbide / high speed steel harmonic structure composite.

Decomposition of Perfluoroalkyl Substances by Near-UV and Visible Light Irradiation to Semiconductor Nanocrystals

Yoichi Kobayashi,[a,b] Yusuke Sanada,[a] Yuzo Arima,[a] Yoshinori Okayasu,[a] Yuki Nagai[a]
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[b]*PRESTO JST*

Perfluoroalkyl substances (PFAS) such as Teflon and Nafion are practically used in various industries, while their extremely high stability causes serious environmental persistence. Several decomposition methods have been reported: such as heating over 300-400 degree Celsius, strong oxidizing reagents, and irradiation of deep ultraviolet light. However, these methods are too harsh, and technology for decomposing PFAS has not been established to date. Recently, we reported that the powder of Cu-doped zinc sulfide (ZnS) NCs exhibit photochromic reactions by irradiation of 365-nm LED (Fig 1a).[1] The origin of the coloration is the ultralong-lived charge-separated (CS) state. We came up with the idea of using the ultralong-lived state to generate a higher excited state by stepwise two-photon absorption processes.[2]

In this study, we demonstrate that Cu-doped ZnS NCs can efficiently decompose perfluorooctanesulfonic acid (PFOS) by near UV and visible LED light at room temperature and atmospheric pressure (Fig 1b).

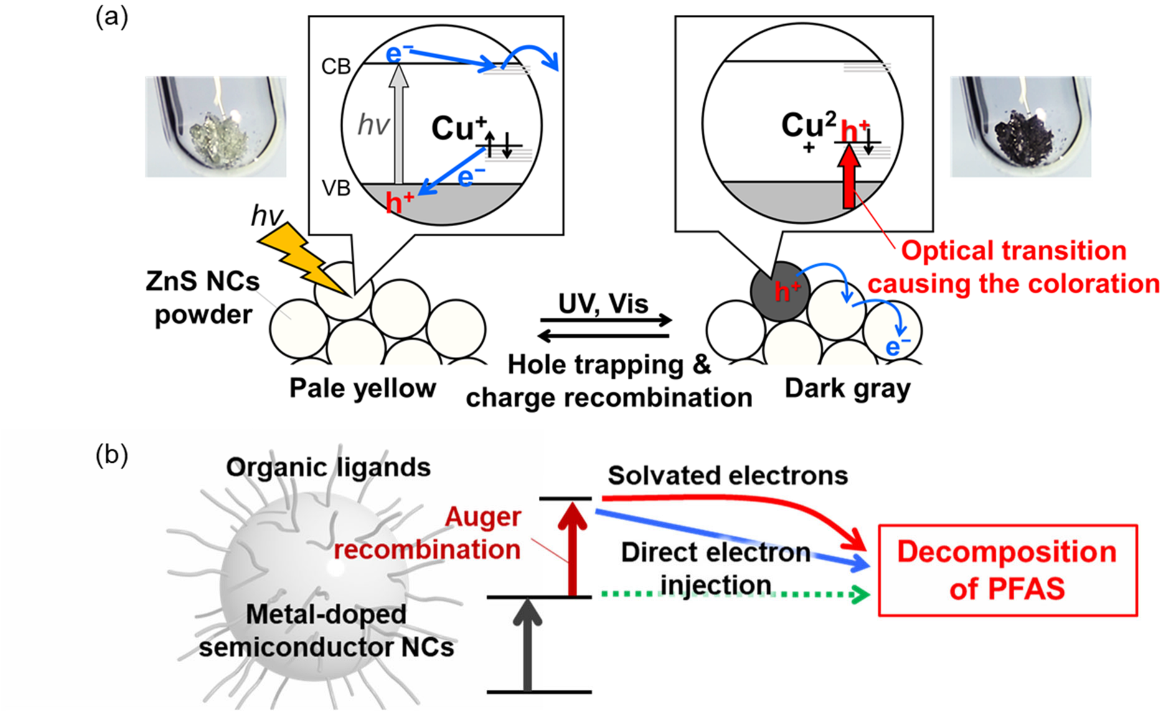

Fig. 1 (a) Photochromic reaction scheme of Cu-doped ZnS NCs and (b) plausible decomposition scheme of PFAS using Cu-doped ZnS NCs by irradiation of near UV and visible light LED light.

1) Y. Han, M. Hamada, I-Y. Chang, K. Hyeon-Deuk, Y. Kobori, Y. Kobayashi, *J. Am. Chem. Soc.* **2021**, *143*, 2239.
2) Y. Kobayashi, J. Abe, *Chem. Soc. Rev.* **2022**, *51*, 2397.

Fatigue Properties of Materials Designed in Harmonic Structure: Summary of Reported Results and Remaining Challenges

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A large spectrum of manufacturing processes has been implemented to improve various properties of materials. This is particularly critical in the case of metallic materials, since their mechanical strengths are intrinsically related to their microstructures. Recently, structures possessing an heterogenous grain size structure are reported to enhance the tensile properties of metallic materials[1]. Based on this concept, Prof. Ameyama has proposed a bimodal grain size microstructure, so-called the "harmonic structure", which presents a grain size gradient in three dimensions. Materials designed in harmonic structure are reported to show higher tensile strength and / or longer elongation at failure[2]. Nevertheless, mechanical responses to complex loading conditions, such as fatigue ones, have to be investigated in order to assure the reliability of this type of materials.

In this context, the investigation of the fatigue behavior of various metallic materials designed in harmonic structure started approximately a decade ago. Among the numerous academic reports published in the literature, numerous experimental conditions related to the material fabrication processing or to the fatigue experimental protocols have been studied. For instance, Guennec et al.3) have underlined an effect of the specimen size on the fatigue strength of Ti-6Al-4V alloy designed in harmonic structure, as represented by the model in Fig. 1. Furthermore, discussions dealing with the investigations on the fatigue crack propagation mechanism has naturally been carried out. As a result, the fatigue properties of such materials are, to some extent, relatively well-understood. Nevertheless, some critical aspects still need to be clarified.

In the present presentation, the major advancement in the overall comprehension of the fatigue behavior of metallic materials designed in harmonic structure will be analyzed from the viewpoints of the fatigue strength and the fatigue crack propagation mechanism. Then, a focus on the remaining challenges related to the comprehension of the fatigue behavior will be introduced.

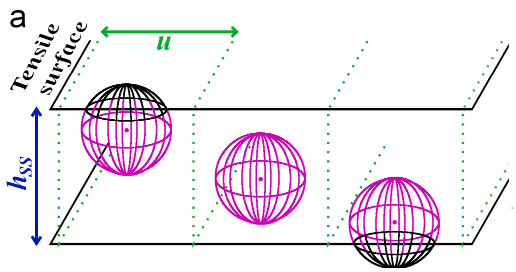

Fig. 1 Analysis of the specimen size effect on the fatigue strength of Ti-6Al-4V alloy designed in harmonic structure. (a) Large-size specimen; and (b) Small size specimen. Spheres represent the interface between coarse and fine grain regions.

1) X. Wu et al., PNAS, **2014**, 111, 7197.
2) M. Ota et al., *Mater. Trans.*, **2015**, 56, 154.
3) B. Guennec at al., *Metals*, 2020, 10, 636.

Effect of light properties on nonlinear molecular reorientation of polymer-stabilized dye-doped liquid crystals

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Liquid crystals (LCs) have both properties of conventional liquids and crystals and exhibit fluidity and optical anisotropy simultaneously. These properties help us control their molecular orientation by application of external stimuli such as an electric field and a laser beam. In particular, adding a small amount of dye to the LCs enhances the sensitivity of their molecular reorientation by irradiation with a linearly polarized laser beam [1]. Such molecular reorientation induces diffraction caused by changing their refractive index. The diffraction occurs by the spatial distribution of the incident light intensity, which is recognized as a typical nonlinear optical effect. Recently, we found that the nonlinear optical response of the oligothiophene dye-doped LCs could be successfully sensitized by adding low-concentration polymers (Polymer-stabilized dye-doped liquid crystals, PSLCs) [2-4]. For applying PSLCs to functional optical devices, it is important to understand the optical response of PSLCs to laser beams with various properties, such as large-beam diameter and different polarization states. In this study, we irradiated the PSLCs with various laser beams. We evaluated the sensitivity of the molecular reorientation and the shape of the diffraction in order to investigate the effect of these incident beam properties on the photoresponsive behavior of PSLCs [5].

A host LC (5CB), acrylate monomer (A4CB), guest dye (TR5), and photopolymerization initiator (Irgacure 651) were mixed and injected into a 100-μm-thick glass cell treated with a silane coupling reagent. The monomers in the glass cell were photopolymerized by irradiation with ultraviolet (UV) light at 365 nm. Polarized optical microscopy and polarized UV-visible absorption spectroscopy revealed that the LC and dye molecule in the cell were homeotropically aligned. We irradiated the PSLCs with a DPSS laser beam at a wavelength of 488 nm and investigated the photoinduced molecular reorientation of PSLCs.

As a result, the irradiation with the large-diameter laser beam decreased the threshold intensity of the molecular reorientation. This enhancement could be explained in terms of the balance of torque; the torque of the bulk elasticity of LCs decreased by the large-area irradiation with the laser beam. Moreover, we revealed that an elliptical diffraction beam appeared on the screen by irradiating the PSLCs with the linearly polarized beam. The torque balance also explains this elliptical diffraction; the addition of polymer increased the anisotropy of the elastic constants of LCs, resulting in the deformation of diffraction.

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2) Y. Aihara, M. Kinoshita, J. Wang, J. Mamiya, A. Priimagi, and A. Shishido, *Adv. Opt. Mater.*, **2013**, *1*, 787.
3) J. Wang, Y. Aihara, M. Kinoshita, J. Mamiya, A. Priimagi, and A. Shishido, *Sci. Rep.*, **2015**, *5*, 9890.
4) K. Usui, K. Matsumoto, E. Katayama, N. Akamatsu, and A. Shishido, *ACS Appl. Mater. Interfaces*, **2021**, *13*, 23049.
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Soft-materials section

Thermally Stable Carbazole Tagged Au(I) Mesoionic *N*-Heterocyclic Carbene Complexes with Diverse Gold–Hydrogen Bonds

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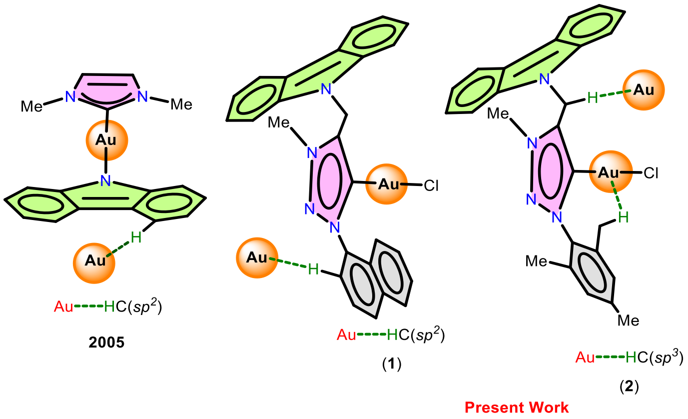
The carbazole-substituted *N*-heterocyclic carbene (NHC) gold molecules have demonstrated diverse structural features and interesting thermal properties. The role of the remotely linked carbazole group to mesoionic carbene in gold(I)-NHC complexes have been addressed in this paper. Thus, we have synthesized and characterized the neutral gold-mesoionic carbene monomers tagged with the carbazole group. The mononuclear gold(I) carbene molecules [($\mathbf{L^1}$)AuCl] (**1**) and [($\mathbf{L^2}$)AuCl] (**2**), where $\mathbf{L^1.HI}$ = 1-(naphth-1-yl)-3-methyl-4-(carbazolylmethyl)-1,2,3-triazolium iodide and $\mathbf{L^2.HI}$ = 1-(mesityl)-3methyl-4-(carbazolylmethyl)-1,2,3-triazolium iodide, have been synthesized and characterized. The new class of complexes depicted interesting gold-hydrogen bonding. In addition, the thermal properties of **1** and **2** were investigated. The Density Functional Theory (DFT) calculation and natural bond orbital analysis (NBO) was accomplished on a model system [(L')AuCl] (**1A**), L'=1-phenyl-4-methyl-carbazole-1,2,3-triazol-ylidene to realize the bonding situations. The calculated metrics agreed reasonably well with the experimental observations.



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Control of Helical Nanostructures of Chiral-Nematic Liquid Crystals in Monodispersed Polymeric Particles

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Liquid crystalline polymers (LCPs) show advanced optical and mechanical functionalities depending on their molecular alignment. For example, chiral-nematic phase forms helical nanostructure of molecular alignment and shows Bragg reflection. The molecular alignment can be reversibly controlled by external stimuli, so LCPs can be used as soft-sensors and actuators. Since these functionalities appear when the LCP is aligned over a relatively long range (> 1 μm), the development of alignment control methods is important for the application of LCPs. In general, low-molecular-weight liquid crystals can be easily aligned over a long range. On the other hand, LCPs easily form very small domains (~ 100 nm) because the alignment is inhibited by the main chain. Therefore, to achieve alignment control of LCPs, polymerization of aligned liquid crystalline monomers have been employed. In this method, the monomers must exhibit liquid crystalline phase. Thus, it is difficult to fabricate an aligned LCPs from monomers that exhibit liquid crystalline phase only after polymerization. Thus, a versatile method to control molecular alignment in LCPs is required.

In this study, we achieved to control molecular alignment in LCPs by dispersion polymerization which is a versatile and simple method to synthesize the polymer particles. In the dispersion polymerization, monomers, a stabilizer, and an initiator are dissolved in the poor solvent for the produced polymer. As a result, the produced polymer precipitates and micro-sized particles can be obtained. We fabricated monodispersed chiral-nematic LCP particles with the size of 2.6 ± 0.1 μm (Figure 1a). Transmission electron microscopy (TEM) observation of the cross-section revealed stripe pattern arising from helical nanostructure of chiral-nematic LCP (Figure 1b). From this uniform stripe pattern, we concluded that LCP was aligned over a long-range during dispersion polymerization. We expect that this alignment was formed during the nucleation-growth process of LCP precipitation. Actually, the growth of molecular alignment can be observed by tracing the particle growth process during dispersion polymerization. This method can be applied to wide range of monomers as long as they are soluble in the polymerization solvent. We expect this method will be a versatile control method of molecular alignment in LCPs.

We also investigated the optical functionality of chiral-nematic LCP particles. Figure 2 shows the characters drawn utilizing the chiral-nematic LCP particle dispersed in resin. Because of the centrally symmetric nanostructures, our chiral-nematic LCP particles showed angular-independent reflection. This result supports that our method has a potential to develop the applications of LCPs, such as reflective coating.

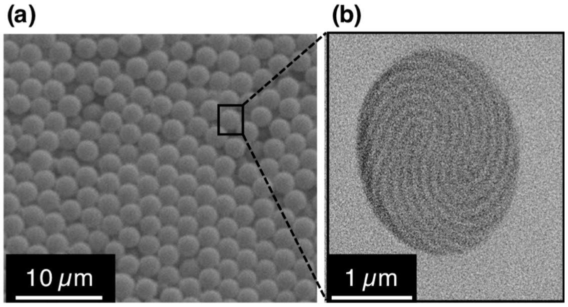

Figure 1. (a) Scanning electron microscope image and (b) TEM image of a chiral-nematic LCP particle of this study.

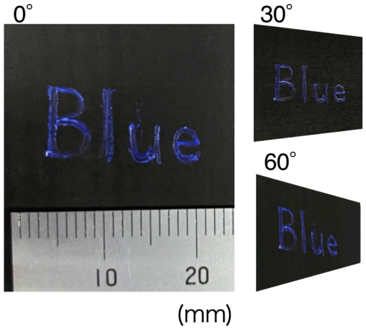

Figure 2. Image of reflective coating patterned with chiral-nematic LCP particles and viewing-angle independence of reflection color.

Light Emitting Copper(I) N-Heterocyclic Carbene Molecule: Synthesis and its photophysical properties

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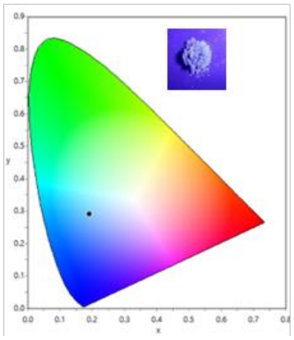
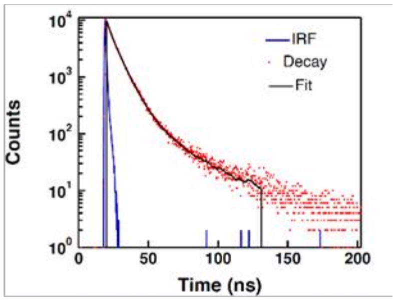
Neutral heteroleptic copper(I) complex have been studied in many fields of catalysis, material science, and medicinal field. The solid-state structure of N-heterocyclic carbene (NHC) complex has attracted the world because of its luminescent materials. The photophysical properties can be tuned by substitution on NHC, metal coordination number, metal-metal interaction, π–π interactions, and metal hydrogenbonding. The crystalline packing in solid state can show the emission in the desired colour range through additional aggregation-induced emission.[1-4] The N-substituted NHC mononuclear copper(I) complex are generally challenging. A new NHC ligand was prepared having a substitution of acridine and butyl chain through multistep synthesis and its complex with copper(I) with neutral mononuclear coordination was isolated and fully characterized by spectroscopic techniques as well as X-ray crystallography. The structural properties of metal-hydrogen bonding and photophysical properties were studied. The blue-emitting copper(I) complex having a lifetime of nanoseconds can be further studied for its wider application in white OLED fabrication.





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Mechanism of Chirality Induction in Photoresponsive Chiral Nematic Liquid Crystals

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We synthesized cyclic chiral compounds by linking a photoresponsive bisbenzothienylethene (BTE) moiety with an axially chiral binaphthyl moiety. The chiral nematic liquid crystals (N*-LCs), prepared by adding the chiral compounds as chiral dopants to host N-LCs, exhibited a reversible chirality inversion in photoisomerization between open and closed forms of the BTE moiety[1]. Herein, the mechanism of chirality inversion in photoresponsive N*-LCs was examined by comparing the helical twisting powers (HTPs) with those of the analogous compounds (**Figure 1**). It was found that the HTPs of these chiral compounds (*R*)-D2s to the host N-LCs are determined by the sum of the right-handed helical sense values of the binaphthyl moiety and the left-handed helical sense values of the BTE moiety. In the chiral dopants with diarylethene (DE) moiety reported previously, the DE moiety is racemic and only the axially chiral binaphthyl moiety induces a helical structure in the host N-LCs[2]. In contrast to the previous chiral compounds, the present (*R*)-D2s have induced chirality of the BTE moiety that is intramolecularly linked with the axially chiral binaphthyl moiety.

In conclusion, we clarified the mechanism of chirality induction occurring in the cyclic chiral compounds including the binaphthyl and BTE moieties through systematic syntheses of various chiral analogues.

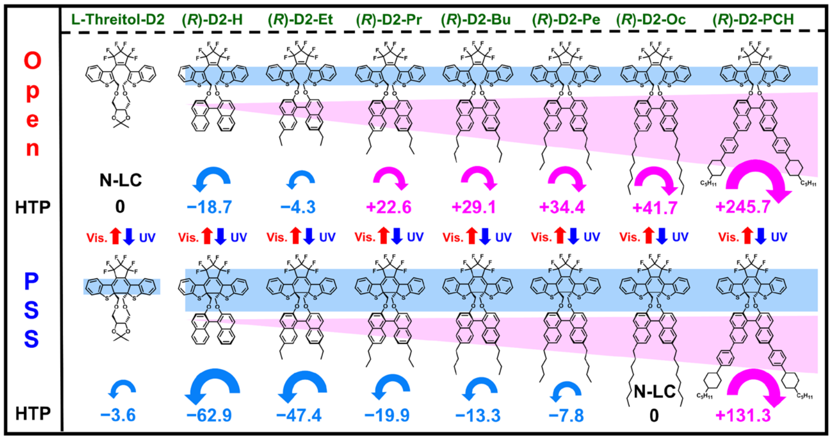

Figure 1. Helical sense and helical twisting powers of the chiral compounds in open and closed states.

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Acknowledgements:

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Acridine and 9-phenyl acridine Based Two Coordinated Luminescent Copper(I) N-Heterocyclic Carbene Complexes

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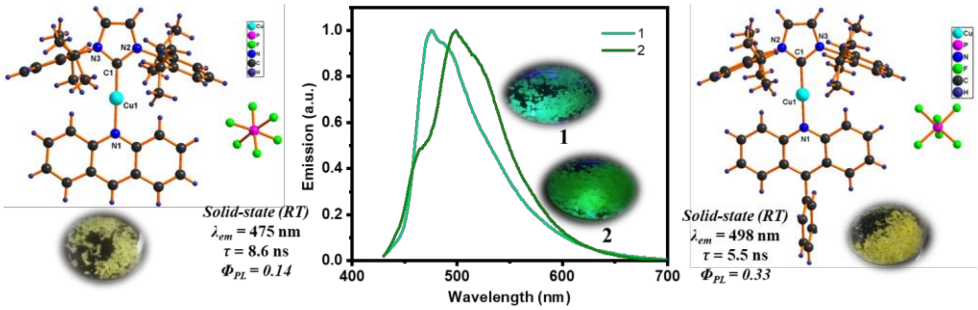
Iridium and platinum-based organometallic compounds are mainly utilised in the field of organic light-emitting diode (OLED) applications. However, several drawbacks of prototypical justify the continuing efforts to explore new avenues of luminescent metal compounds. Their respective d^6 or d^8 electron configuration can lead to the thermal population of metal-centred (MC) d-d* states that foster premature nonradiative decay, a problem which is particularly pronounced for ^{3}MLCT (metal-to-ligand charge transfer) states emitting in the high energy blue region. In addition, only a limited tunability is available due to the fixed octahedral or square-planar geometries, respectively, and not only from an intellectual point of view but also because of sustainability issues concerning mass market use of these rare elements it appears as a wise decision to look for alternatives. Hence, copper(I) complexes have gained increasing attention within the past decade because of the high abundance of this 3d element, MC transitions are absent in their d^{10} electron configuration, and the flexible coordination geometries ranging from tetrahedral to trigonal and linear have led to the discovery of highly interesting photophysical phenomena. Especially N-heterocyclic carbene-based copper complexes have a strong metal-ligand and steric hindrance of N-aryl substituents to provide stability also anionic carbazole derivative and neutral N-heteroaromatic ligands replace the halides in the simple halide coordinated Cu(I)-NHC to form the phosphorescent or thermally activated delayed fluorescence (TADF) Cu(I)-NHC complexes. We have synthesized and characterized acridine and 9-phenyl acridine based on two coordinated Cu(I)-NHC complexes. These two coordinated complexes adopted the linear geometry also imidazole ring co-planar with acridine/9-phenyl acridine derivatives. In the photophysical studies, both compounds show blue emissions in the methanol solution and green emissions in the solid state with a quantum yield of up to 33% in nanosecond lifetime, indicative of singlet states being involved.



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Quasi-reversible photoinduced displacement of functional organic ligands from colloidal semiconductor nanocrystals

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Organic-inorganic hybrid semiconductor nanocrystals (NCs) coordinated with functional organic ligands have been attractive and widely studied in various fields for optoelectronic materials, such as solar cells, photocatalysis, and photon upconversion. In these materials, coordination bonds of ligand molecules are usually assumed to be stable during or even after optical processes. However, this assumption is not always valid. Surprisingly, even though it is very important to consider the coordination state of surface organic ligand molecules to control photoreactions, there have been very few studies of the coordination environment dynamics of ligands molecules on photoexcitation state.

In this study, we synthesized perylenebisimide-Zinc sulfide nanocrystals (PBI-ZnS, PBI is on Figure 1b inset) and demonstrate that the coordination bonds between ligand molecules and NCs by carboxyl groups are displaced quasi-reversibly by light irradiation (Figure 1a).

The optical properties of PBI-ZnS were analyzed by wide time range spectroscopy (femtosecond to several seconds) and density functional theory (DFT) calculations. Time-resolved transient absorption, and Raman spectroscopy and (DFT) calculations show that the photoinduced ligand displacement is driven by ultrafast hole transfer from PBI to ZnS NCs. Interestingly, the PBI is displaced from NCs surface as a radical anion after light irradiation, and the PBI radical anion survives over the second timescale (Figure 1b). Moreover, DFT calculation suggests that PBI radical anion displace involved the neighbor Zn atom. The long-lived charge-separated state can be generated repeatedly without any degradations.

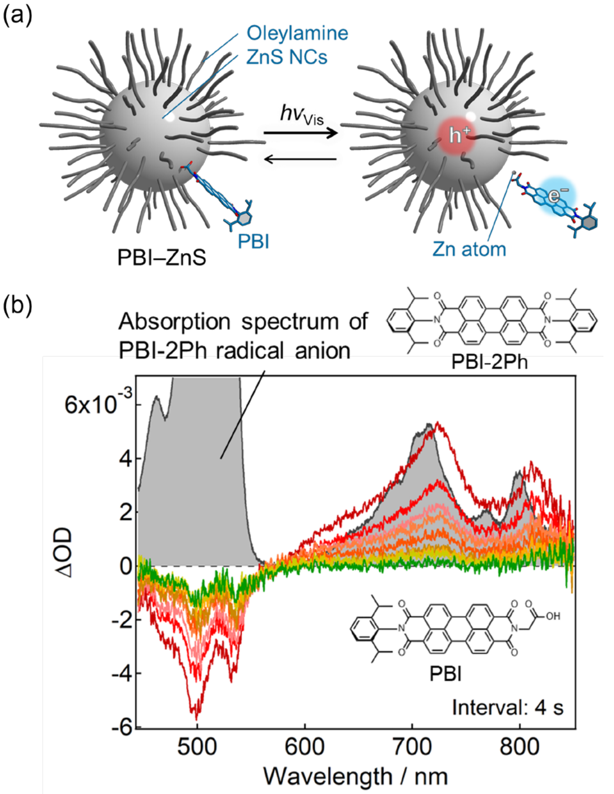

Figure 1. (a) Molecular structure of PBI and (b) schematic of the quasi-reversible photoinduced displacement of PBI coordinated to the surface of ZnS NCs.

Acridine *N*-Heterocyclic Carbene Gold(I) Compounds: Turning from Yellow to Blue Luminescence

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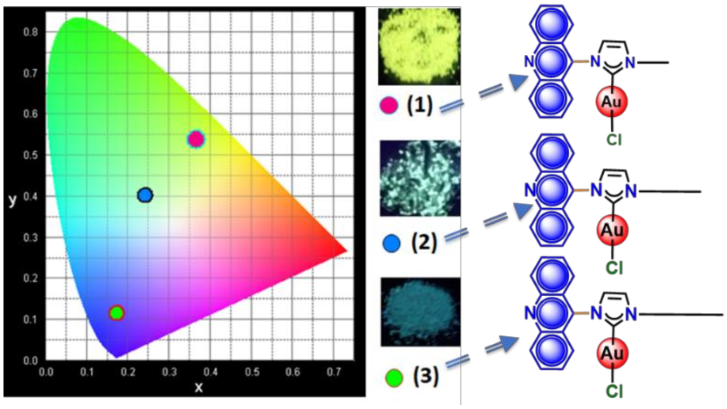
The synthesis of *N*-heterocyclic carbene (NHC) gold complexes has recently attracted wide attention due to their considerable range of applications, in areas such as luminescent materials and medicinal chemistry, as well as their potential role as new catalysts in gold-catalyzed processes. For several years, NHC-gold materials have found many applications in the field of organic light-emitting diode. In the case of gold–NHC complexes two types of luminescent complexes could be distinguished: molecules showing native luminescence and enhancing luminescent after addition of organic chromophores. Thus we sought to extend our approach to non-chromophoric N-substituent, mainly alkyl chains. In fact, due to their flexible carbon-carbon rotation we expected them to promote unusual solid packing and hence add a novel property to this kind of compound relative to the rigid N substituents. As a result of our investigations, we have synthesized the new acridine substituted NHC-gold complexes with different N-alkyl chains to understand the photophysical and thermal properties, which will be discussed in detail.[1]



1) M. Vaddamanu, A. Sathyanarayana, Y. Masaya, S. Sugiyama, O. Kazuhisa, K. Velappan, M. Nandeshwar, K. Hisano, O. Tsutsumi, G. Prabusankar, *Chem. Asian J.*, **2021**, *16(5),* 521.

Hard-materials section

【Grant-in-Aid for Scientific Research (S)】

Clarification of innovative deformation mechanism in harmonic structure materials and creation of design principle for structure materials for next generation

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For many years, ultra-fine grained (UFG) metals have proven to be attractive structural materials due to their superior strength, especially when compared to their coarse-grained (CG) counterparts. However, the disadvantage of homogeneous UFG materials is typically low elongation due to plastic instability in the early stages of deformation. Therefore, producing materials with superior combinations of high strength and high elongation remains a hot topic in materials engineering. Harmonic Structure (HS) design can be a candidate material design that combines high strength with high ductility at the same time. Figure 1 shows a concept of HS design. In contrast to a "Homogeneous UFG" material, the "HS" material has a unique heterogeneous "Three-dimensional (3D) Gradient Microstructure" in which the UFG regions form an interconnected three-dimensional network surrounding the CG regions, and the CG and UFG regions are periodically arranged in all directions. The HS materials exhibit various anomalous deformation behaviors, such as "preferential recrystallization", "preferential stress-induced transformation", and so on. Therefore, the purpose of the present research project is to reveal these unique deformation behaviors and create an innovative structural metallic materials design concept.

The first step of the research is to develop an efficient process to produce the HS materials via multiple severe plastic deformation powder metallurgy processes. The HS materials will be subjected to deformation behavior analysis not only by an in-situ SEM deformation analysis facilities, but also the Spring-8 synchrotron facility. Simulation techniques such as MD and FEM modeling will also be applied to clarify the deformation mechanism from the atomic scale.

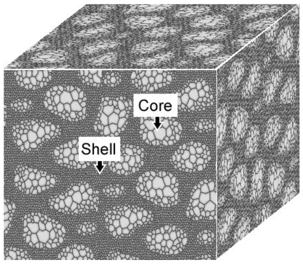

Figure 1
Concept of the HS design

This research project is expected to resolve the strength-ductility paradox. Understanding the micro- and macro-scale deformation mechanisms will guide the development of innovative structural materials. From the engineering point of view, the HS materials can be produced by combining the classical industrial methods based on the powder metallurgy processes. It is worth noting that this research project will be very useful in practical applications.

Publications related to the project: ~ 50 publications

1) Kei Ameyama, Fabien Cazes, Hervé Couque, Guy Dirras, Shoichi Kikuchi, Jia Li, Frédéric Mompiou, K. Mondal, Dmytro Orlov, Bhupendra Sharma, David Tingaud, Sanjay K. Vajpai: *Materials Research Letters*, Vol.10(2022), 440-471.
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3) Tomotsugu Shimokawa, Tatsuya Hasegawa, Keito Kiyota, Tomoaki Niiyama, Kei Ameyama: *Acta Materiala*, Vol.226(2022), 17679
4) Shoichi Kikuchi, Yuhei Nukui, Yuta Nakatsuka, Yoshikazu Nakai, Masashi Nakatani, Mie O Kawabata, Kei Ameyama: *International Journal of Fatigue*, Vol.127(2019), 222-228.
And so on.

Progress in Heterostructured Materials

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Strong and tough materials are desired for light-weight applications such as electric cars and aerospace applications. Recently, heterostructures are found to produce unprecedented strength and ductility that are considered impossible from our textbook knowledge and materials history [1]. Heterostructured materials consist of heterogeneous zones with dramatic (>100%) variations in mechanical and/or physical properties [2-4]. The interaction in these hetero-zones produces a synergistic effect where the integrated property exceeds the prediction by the rule-of-mixtures. Importantly, HS materials can be produced by current industrial facilities at large scale and low cost. There are many scientific issues with such materials that challenge the communities of experimental materials science and computational material mechanics. Heterostructured materials is quickly becoming a hot research field. In this talk I'll present the progress in heterostructured materials as well as future challenges and issues.

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4) 4. YT Zhu: Metall. Mater. Trans. A, 2021, vol. 52, pp. 4715-4726.

Heterostructure materials are the new Uranium!

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Structural materials (i.e., designed primarily to transmit forces), given their wide variety and importance in many industrial sectors, give rise to numerous research programs worldwide, often carried out in partnership between academic and industrial laboratories. Two types of research can be carried out: (i) research on "traditional" materials (metal alloys, composite materials, etc.), for which it is a question of optimizing the properties for a given application, and the industrial sectors mainly concerned are then those of energy, transport, aeronautics, civil engineering, mechanics, ... and (ii) research on new materials (foams, metallic glasses, nanostructured materials, multi-materials. ..) for which the structural function is no longer necessarily the only primary function sought and for which industrial applications are still marginal or affect other sectors such as microelectronics or biomaterials.

In this context, the main goal of the design of new materials ("materials by design") is to adapt to the new societal demand, which includes both growing needs and improved performance, and increased recyclability. For example, in the field of structural materials, the need to lighten structures in the areas of transport and aeronautics has generated a great deal of research on the optimization of the transformation processes of traditional metal alloys (Fe, Al, Ti…in particular) or the optimization of their microstructure and chemical composition by adding alloying elements. Alongside these relatively conventional methods, which already allow significant gains in terms of lightening and mechanical properties, new ways are being developed which make it possible to further increase the gains in terms of energy saving and recycling while at the same time working from the most easily accessible materials. These methods favor the optimization of microstructures rather than the addition of expensive alloying elements.

In this presentation, we illustrate the approach implemented for several years at the laboratory of process and materials sciences of Sorbonne Paris Nord University. This approach thus aims to develop a methodology for generating innovative microstructures (multimodal, multi-structured materials), taking advantage of the properties linked to the different types of contrasts (mechanical, chemical, morphological) induced by heterogeneous microstructures[1]. Powder metallurgy, but not only, proved to be an optimal and very versatile method for such an objective. The example of the *HighS-Ti*[2] project funded by the French National Research Agency (ANR) carried out in collaboration with the group of Prof. K. Ameyama at Ritsumeikan University will be presented.

1) Yuntian Zhu, Xiaolei Wu, *Progress in Materials Science*, **2023**, *131*,101019.
2) High Strength Titanium with Harmonic Microstructure: Processing, properties, and multi-scale modelling. **ANR-14-CE07-003**.

Effect of Grain Size and Force Ratio on Fatigue Crack Propagation of Commercially Pure Titanium with Harmonic Structure

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Fatigue crack propagation tests were conducted on cold rolled commercially pure titanium with a bimodal harmonic structure to clarify the effects of the grain size and force ratio.[1] As shown in Fig. 1, the threshold stress intensity factor range ΔK_{th} for the L-T orientation was always lower than that for the T-L orientation, and ΔK_{th} was lower for a higher force ratio and a higher rolling reduction for either rolling reduction. Crack closure resulting from the roughness of the fracture surface can be partially explained by the above effects, and the effective threshold stress intensity factor range $\Delta K_{\mathrm{eff,th}}$ also depended on the same factors, whereas the effects were smaller than those for ΔK_{th}. As shown in Fig. 2, the crack opening stress intensity factor $K_{\mathrm{op,th}}$ and effective threshold stress intensity factor range $\Delta K_{\mathrm{eff,th}}$ linearly increased with the square root of the average grain size in the Shell region, which decreased with rolling reduction. Thus, the threshold condition of the harmonic structured material is considered to be determined by the average grain size in the Shell region.

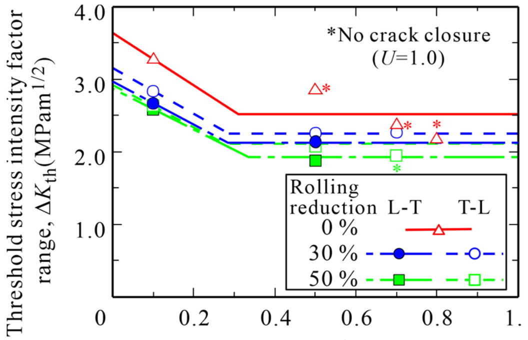
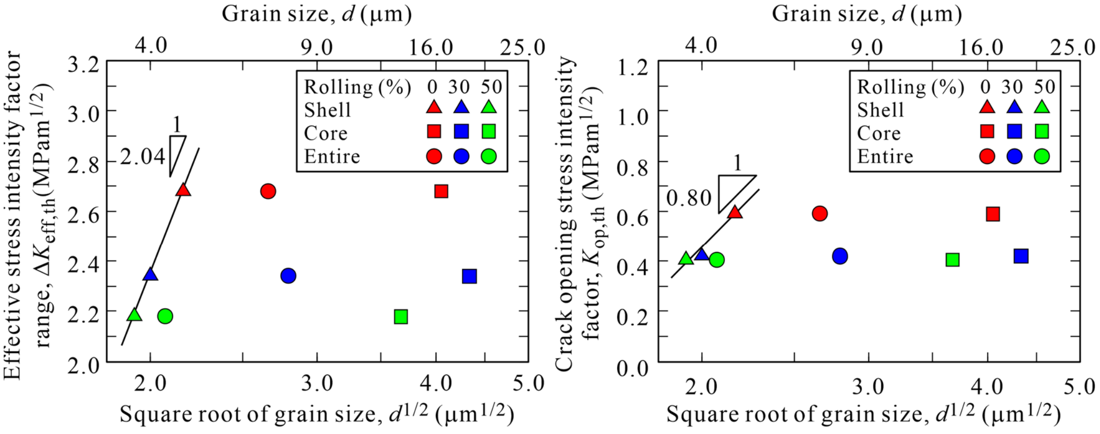


Figure 1. Effect of force ratio on threshold stress intensity factor range.

References:

1) Y. Nakai , S. Kikuchi, K. Osaki, M.O. Kawabata, K. Ameyama, *Int. J. Fatigue*. **2021**, *143*, 106018.



(a) $\Delta K_{\mathrm{eff,th}}$ (b) $K_{\mathrm{op,th}}$

Figure 2. Effect of grain size on threshold stress intensity factors at R = 0.1.

Observation of Misoriantation Behavior in SUS304 and SUS316L with Harmonic Structure by Synchrotron DCT under Tensile and Cyclic loading

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A bimodal harmonic structure is a structure in which fine grain structures (shell) are arranged around coarse grains structure (core). Metallic materials with a bimodal harmonic structure have both high ductility and high strength. However, the role of these each two structures in tensile deformation and fatigue on strength and ductility is not clear. In this study, X-ray diffraction contrast tomography (DCT) was used to investigate the role of the two structures under tensile and fatigue tests.

DCT is a 3D particle mapping technique for polycrystalline materials using ultra-bright synchrotron X-rays. When the sample is irradiated with X-rays, diffraction occurs at the grains that satisfy the Bragg condition. Diffraction spots appear in the direction of the diffraction angle, and dark extinction spots appear behind the sample. The diffraction spot appears in the grain over the rotation range $\Delta\omega_{\mathrm{diff}}$ that satisfies the Bragg condition. Since this corresponds to the misorientation in the grains, the misorientation β is calculated by $\Delta\omega_{\mathrm{diff}}$, diffraction angle θ, and Debye–Scherrer ring angle ψ. Furthermore, the excess dislocation density ρ was calculated from the grain size D which measured from result of DCT and Burger's vector b.

DCT imaging was performed using the BL46XU beamline of the synchrotron radiation facility of Super Photon ring 8(SPring-8). Grains as small as 10 μm or less cannot be reconstructed by DCT. A sample in which the grain size was increased while maintaining the grain size ratio of the shell and core was prepared. The average grain size of core is 77μm and that of shell is 15μm. Fig. 2 shows the results of tensile test for the specimens with the harmonic and normal homogeneous structure. It was found that the tensile strength and elongation of harmonic structure specimen are higher than those of the homogeneous structure specimen. The prepared samples with coarsened grains also had the characteristics of the harmonic structure.

DCT measurements were performed during the tensile tests. The reconstructed grains were classified by size, and the misorientation and dislocation density of each grain were investigated. Fig. 3 shows the change in the excess dislocation density. The change in dislocation density ρ is small for grains with a size of 20-80μm, on the other hand, it is large for grains with a size of less than 20μm and more than 80μm. It was found that the change in dislocation density differs between the core and shell structures.

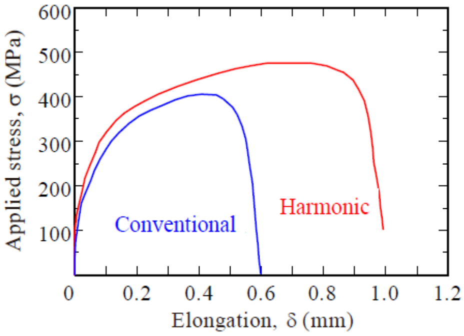

Fig. 1 Stress-elongation relationships

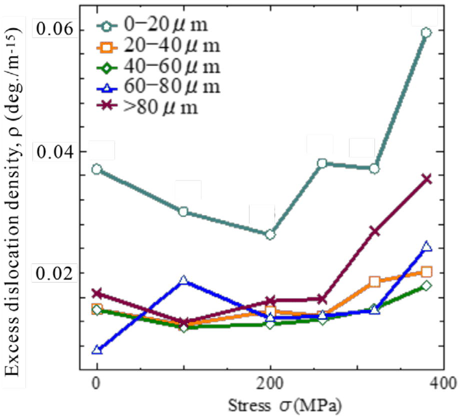

Fig. 2 Change of excess dislocation density in tensile test.

Fatigue Properties of Notched Austenitic Stainless Steel with Harmonic Structure

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Austenitic stainless steel (JIS-SUS304L) with a bimodal harmonic structure, which is defined as a coarse-grained structure surrounded by a network structure of fine grains, was fabricated using powder metallurgy to improve both the strength and ductility. The present authors have examined the fatigue properties of harmonic structured materials to achieve sufficient performance for practical applications in the engineering fields.[1-3] Axial fatigue tests were conducted for smooth and notched specimens (Fig.1(a)) at stress ratio of 0.1 at room temperature in a laboratory atmosphere. The fatigue limits of the notched specimens with a homogeneous microstructure were lower than those of the smooth one (Fig.1(b)). In contrast, the fatigue limit of the notched harmonic structured specimen showed almost the same as the smooth one (Fig.1(c)). The fracture surfaces and specimen surfaces were observed using scanning electron microscopy (SEM) to elucidate the mechanism of fatigue fracture in SUS304L with harmonic structure. The fatigue crack was initiated from the coarse-grained structure in the smooth specimen with harmonic structure, whereas the fatigue crack was initiated from the fine-grained structure, which shows high resistance of fatigue crack initiation, in the notched specimen with harmonic structure due to the stress partitioning. Thus, a notch effect disappeared by the harmonic structure design.

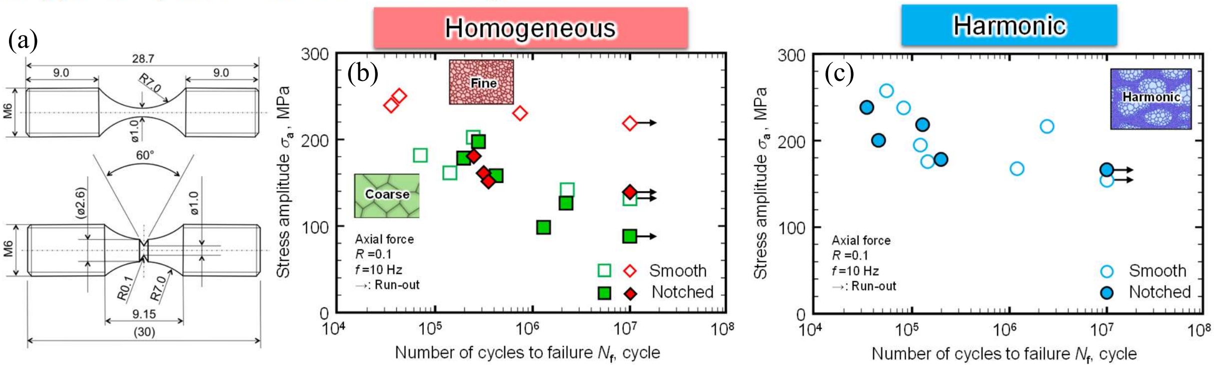

Figure 1 (a) Specimen configuration and results of fatigue tests for specimens with (b) homogeneous microstructure and (c) harmonic structure.

1) S. Kikuchi, Y. Nakatsuka, Y. Nakai, M. Nakatani, M.O. Kawabata, K. Ameyama, *Frattura ed Integrità Strutturale* **2019**, *48* 545.
2) S. Kikuchi, Y. Nukui, Y. Nakatsuka, Y. Nakai, M. Nakatani, M.O. Kawabata, K. Ameyama, *Int. J. Fatigue* **2019**, *127* 222.
3) H. Zhou, Z. Liu, S. Kikuchi, K. Shibanuma, *Mater. Des.* **2023**, *226* 111657.

Lattice defect dynamics in harmonic structure metals through atomic simulations

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Core–shell harmonic structure materials, in which coarse grains (core regions) are surrounded by many fine grains (shell region), have excellent mechanical properties, particularly, the coexistence of high strength and ductility. In order to investigate the mechanism of the excellent mechanical properties, we use atomic and dislocation simulations. The harmonic structures are modeled simply while maintaining the three main characteristics of harmonic structure materials as shown in Fig. 1: heterogeneous distributed strength, interfaces between the core and shell regions, and shell region network. The results of the simulations(1) show many synergistic effects of the coexistence of core and shell regions in the harmonic structure models as following: 1) Because the core region has lower strength than the shell region, the atomic simulations show that plastic deformation starts in the core region before the shell region. 2) The core–shell interface provides a strong resistance to dislocation transmission across the interface from the core region to the shell region. The dislocation simulations explain this resistance as a direct consequence of the back stress from the dislocations in the shell region. 3) Compared with the homogeneous structure model consisting of coarse grains with the same size of the core regions, the dislocation density of a portion of the core regions in contact with the core–shell interface increases, thus, the strength of the core region increases. 4) Compared with the homogeneous structure model with fine grains with the same size of the shell region, the strength of a portion of the shell network region in contact with the core–shell interface decreases. This weakening of the part of the shell network region is assumed to be due to the activation of plastic deformation by the stress concentration caused by dislocation pile-up in the core region.

The above results lead to a possible mechanism providing high strength and ductility in harmonic structure materials: 1) The high strength of the harmonic structure materials is provided by dislocation strengthening due to the core–shell interface in the core regions, which is sufficient to compensate for the weakening in the shell region. 2) The high ductility of the harmonic structure materials results from the suppression of plastic instability in the shell region, which is caused by the weakening of the shell region and the increased work-hardening rate of the core region because of the highly accumulated dislocations at the core–shell interface.

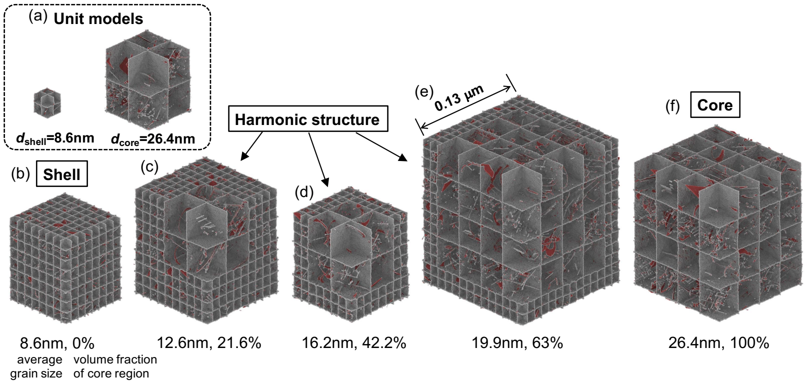

Fig. 1: Harmonic structure models constructed by two types of unit models with the grain sizes of 8.8 nm and 26.4 nm which correspond to shell and core regions.

1) T. Shimokawa, T. Hasegawa, K. Kiyota, T. Niiyama, K. Ameyama, *Acta Mater.* **2022**, *226*, 117679.

Multiaxial creep-fatigue deformation modeling and damage evaluation considering non-proportional loading effect

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In recent years, carbon neutral is one of the most significant measures for improving environment of the earth. To achieve the objective, using clear energy such as nuclear power generation to replace traditional power such as coal-fired power generation is essential. It is well known that components of nuclear power generation are subjected to complex loading conditions at elevated temperature, thermal stress induced by temperature vibration and mechanical loading may cause non-proportional loading in which the directions of principal stress or strain rotate in one cycle, non-proportional loading can reduce fatigue life of materials, significantly. Numerous of articles have been published on the abovementioned issue[1]. However, during service period, creep damage also exists which leads to components are borne to non-proportional creep-fatigue loading condition. Fatigue life prediction method under aforementioned condition is an open issue. Thus, to ensure safe operation of nuclear power generation, the relative research on investigating fatigue life prediction method and damage mechanism of materials under non-proportional creep-fatigue loading is significant.

In the current study, to propose fatigue life prediction method, non-proportional creep-fatigue tests using SUS 304 were performed. Moreover, to clarify the damage mechanism, SEM, EBSD and TEM observation were also carried out.

The multiaxial constitutive modeling combining the proposed unified viscoplasiticty model and an energy-based damage parameter[2] was established for life prediction. Fig. 1 shows the comparison between experimental and predicted results using the proposed constitutive modeling. All plots distribute within 1.5 factor band-line. Thus, it could be concluded that the established method could evaluate fatigue life under non-proportional loading condition for SUS 304 with high accuracy. Moreover, dislocation configurations are displayed in Fig. 2. The domination of slip type is switched from single slip to multi-slip under axial and axial creep-fatigue loading. Under non-proportional loading conditions, deformation mechanism is changed to wavy slip, as manifested by cell structure, which is the main reason for additional hardening.

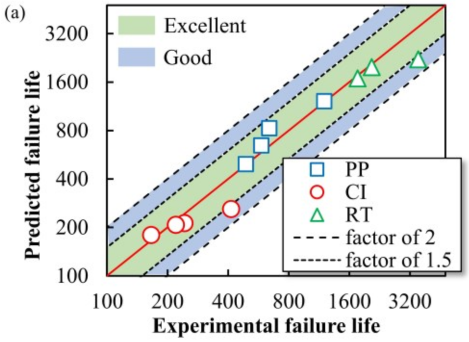

Fig. 1 Comparison between experimental and predicted results

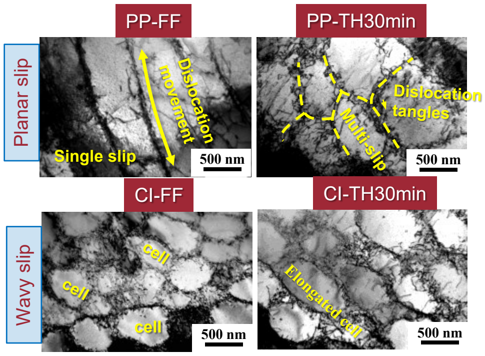

Fig. 2 Dislocation configuration under various loading condition

1) T. Itoh, M. Sakane, M. Ohnami, D.F. Socie, *J Eng Mater-T Asme*. **1995**, 285.
2) R.-Z. Wang, X.-C. Zhang, S.-T. Tu, S.-P. Zhu, C.-C. Zhang, *Int J Fatigue*. **2016**, *90*, 12.

Poster session

Poster Presentation Guidelines

- Poster presentations will be held in the first-floor foyer of "L’Arcadia".
- Please check your poster number in the program and post your poster to the corresponding poster board.
- Please post your poster by noon on March 3rd.
- Poster sessions will take place from 3:30 pm to 5:30 pm on March 3rd.
- Poster awards will be given to outstanding presentations. The award will be announced in room R103 at 5:45 pm on March 3rd.
- Please remove your poster by noon on March 4th after the session. Posters left after that time will be disposed of by the organizing committee.

Microstructure and Mechanical Properties of Ti-Ni/Cu Harmonic Structure Composite

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Grain refinement is well known to improve the mechanical properties of materials. The nano grain structure materials show very high strength but a limited ductility because of the early plastic instability. On the other hand, harmonic structured materials with fine and coarse grain areas demonstrate high strength and sufficient ductility simultaneously. The harmonic microstructure consists of fine-grained network and disperses coarse grained areas. The fine-grained network area has a role of the strength increase and the dispersed coarse grained area has a role of maintaining the elongation. The harmonic structure can achieve the trade-off mechanical properties simultaneously. In addition, the harmonic structured composites consist of a low fraction metal region like network and a dispersed another major metal region like island by using deferent metals. The harmonic structure composite also improves various trade-off mechanical properties. For example, the Mo/Cu harmonic structure composites demonstrate low coefficient of linear expansion and enough thermal conductivity despite the trade-off relationship between low thermal expansion and high thermal conductivity. In this study, the microstructure and mechanical properties of the Ti-Ni/Cu harmonic structured composites fabricated by mechanical milling (MM) and spark plasma sintering (SPS) processes are investigated in detail.

Ti-Ni alloy powder (approximately 184 μm) and pure Cu powder (approximately 122 μm) were used in this study. These powders were mechanically milled using planetary ball mill equipment with an SKD11 container and SUJ2 steel balls in Ar atmosphere for 21.6 to 86.4 ks at cryogenic temperature. The MM powder consists of the Ti-Ni alloy of the surface and Cu of the middle. Such as MM powder was sintered by using the SPS apparatus at 1073 K for 1.8 ks. The microstructure of the SPS compacts was characterized using scanning electron microscopy (SEM) / energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The mechanical properties of SPS compacts were evaluated based on the tensile tests at 373 K.

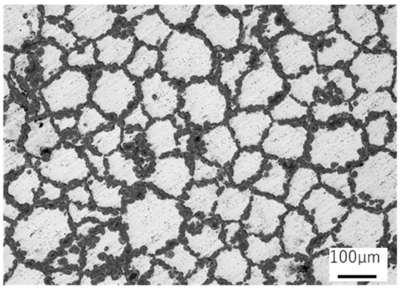

Fig.1 SEM micrograph of harmonic structure of SPS compact of the MM powder for 43.2 ks.

The sintered compacts of MM powders produced by each milling time demonstrate the harmonic structure with the network and dispersive areas as shown in Fig. 1. The XRD results reveal that network and dispersive areas correspond to Cu-Ni-Ti alloy and Cu, respectively. This reason is the Cu diffusion during sintering. The MM time increase leads to decreasing the grain size in the network area without change the network area fraction. Fig.2 shows the tensile test results of Ti-Ni/Cu harmonic structure composite produced by each MM time and Cu compact. The MM time increase leads to increase the tensile strength and to decrease the elongation. The grain refinement of network area without increasing network area fraction is effective to improve the mechanical properties of the harmonic structure composite.

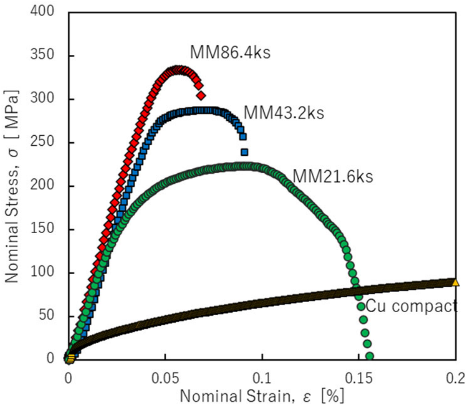

Fig.2 Tensile test results of SPS compact of Cu powder and the MM powder for 21.6 to 86.4 ks.

Microstructure and High Temperature Mechanical Properties of AlCoCrFeNi High Entropy Alloy

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High entropy alloys (HEA) have attracted much attention in recent years because of their interesting microstructure and excellent mechanical properties. AlCoCrFeNi is one of the most extensively studied alloy systems of HEA. In this study, sintered compacts of AlCoCrFeNi HEA powder are produced by the spark plasma sintering (SPS); furthermore, its microstructure and mechanical properties at elevated temperature are investigated in detail. Their microstructure of the SPS compacts was characterized using scanning electron microscopy /energy dispersive X-ray spectroscopy / electron back scatter diffraction. Their mechanical properties of SPS compacts were evaluated based on the compression tests at room temperature (RT) and 673 K, 873K and 1073 K. Fig.1 demonstrates the microstructure for compacts sintered at 1173K (a), 1273K (b), and 1373K (c). These microstructure for compacts sintered at 1173K, 1273K, and 1373K is composed of FCC, BCC, and B2 phases, but each compact exhibits a different microstructure morphology as shown in Fig. 1. The FCC phase precipitates in B2 grain boundary and BCC phase precipitates in the B2 matrices. The compositions for FCC, BCC and B2 phases are Co-Cr-Fe rich, Cr-Fe rich, and Al-Ni rich, respectively. The FCC phase fraction decreases and the BCC phase is finer dispersed in B2 matrices with sintering temperature increases. Fig. 2 shows the mechanical properties by the compression test. The compact sintered at 1273K exhibits the highest compressive strength at room temperature, but the compacts sintered at 1373K have the highest compressive strength at each elevated temperature. The higher the compression test temperature, the lower the strength of compact sintered at each temperature.

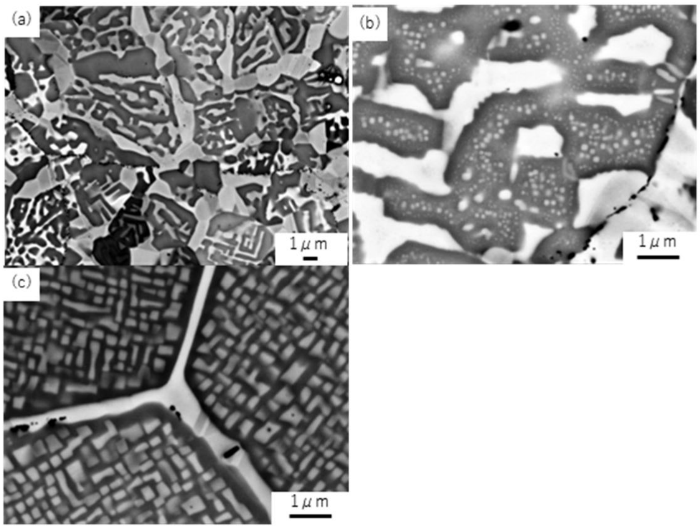

Fig.1 SEM micrographs sintered at 1123 K (a), 1223 K (b) and 1323 K (c).

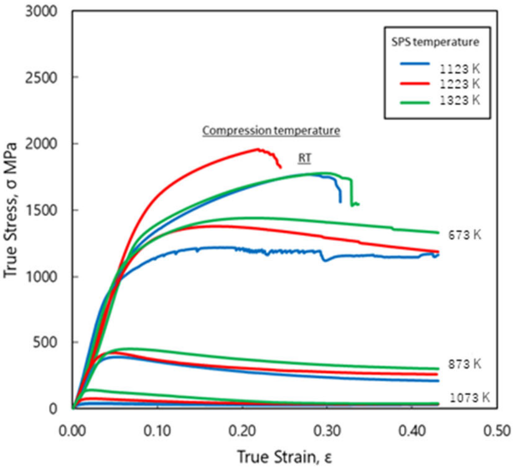

Fig.2 Compression test results for the sintered compacts at 1123 to 1323 K at ambient temperature of RT to 1073 K.

Synthesis and characterization of liquid crystalline organic semiconductor materials with benzothiophene skeleton

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【Introduction】 Organic thin-film transistors are made with organic compounds with semiconductor characteristics and can be fabricated in a large area on thin substrates at low temperatures. However, the field-effect mobility indicative of transistor performance is low. One of the factors related to the low field-effect mobility is the crystal grain boundaries created during the fabrication of thin films for semiconductor devices. It has been reported that the self-organization of liquid crystal (LC) molecules can be used to improve this problem by suppressing the crystal grain boundaries[1)]. In this study, we focused on benzodithiophene (BDT) which has a planar conjugated structure expected to show high field-effect mobility[2)]. The objective of this study is to synthesize LC organic semiconducting polymers with high field-effect mobility at low temperatures by introducing polymerizable parts into organic semiconducting molecules with BDT cores and polymerizing them while retaining an LC order.

【Experiment】 The target compound, 6-(6-(thiophen-3-yl-ethynyl)benzo[1,2-b:4,5-*b*']dithiophen-2-yl)hexa-5-yn-1-yl acrylate (PE-BDT-AA), was synthesized through the synthetic routes as shown in Figure 1 and was subjected to ^{1}H NMR (JEOL ECS-400) measurements to identify its structure.

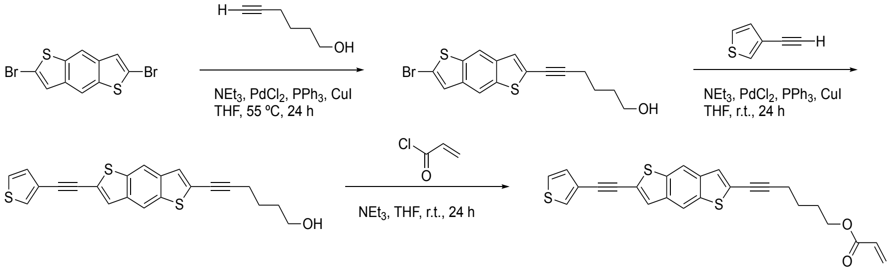

Figure 1 Synthetic pathway of PE-BDT-AA.

【Results and Discussion】 The results of differential scanning calorimetry (DSC) and powder X-ray diffraction (XRD) measurements of the obtained PE-BDT-AA are shown in Figures 2 and 3, respectively. As shown in Figure 2, an endothermic peak was observed at around 170 °C in the heating process. A fan-shaped texture was observed under a polarizing optical microscope around this temperature, suggesting the presence of the LC phase. Based on the results of XRD measurement at 160 °C as shown in Figure 3, this phase was determined to be a smectic E phase which is a higher-order LC phase.

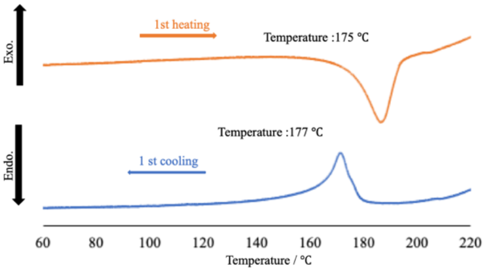

Figure 2 DSC curves of PE-BDT-AA.

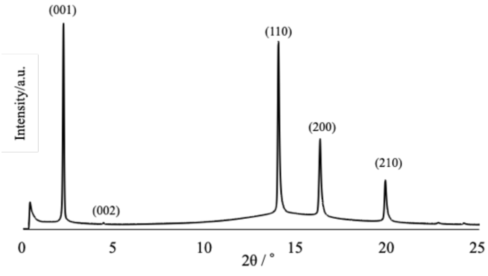

Figure 3 XRD pattern of PE-BDT-AA (160 ºC).

【Reference】

1) W. Pisula, M. Zorn, and J. Y. Chang, *Macromol. Rapid Commun.*, **2009**, *30*, 1179.
2) H. Wu, H. Iino, and J. Hanna, *Chem. Lett.*, **2018**, *47*, 510.

Electrorheological Effect of Pd Nanoparticles Dispersed Nematic Liquid Crystals

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The electrorheological (ER) effect denotes a reversible change in the apparent viscosity of certain fluids, such as a colloidal suspension, under an external electric field. The ER properties of composite materials consisting of a nematic liquid crystal (LC) and nanoparticles (NPs) have been studied in our laboratory. For example, the composite material consisting of a nematic LC (4'-pentyl-4-biphenylcarbonitrile, 5CB) and gold nanoparticles (GNPs) with alkyl chains and mesogenic groups showed a higher enhancement in shear stress under an application of electric fields.1) However, the detailed mechanism for viscosity increasing in such composite materials is not known. In order to understand the detailed mechanism of ER effect in composite materials, the correlation between the particle size and the viscosity increasing in such composite materials has been studied. Specifically, we synthesized nanoparticles of different sizes, dispersing in liquid crystals and decided to clarify the correlations by measuring their viscosity. Palladium nanoparticles (PdNPs) with various sizes were synthesized in this study, because Pd NPs has better dispersibility than GNPs. The PdNPs were synthesized using an aqueous approach and the sizes were controlled in the range of 6–18 nm by adjusting the rate of reduction of Pd^{2+} ions.2) The transmission electron microscope (TEM) image of synthesized 18 nm PdNPs were shown in Figure 1. The dispersity of the PdNPs in the nematic LC was investigated by a polarizing optical microscopy (POM). In the previous study, the presence of the GNPs in the nematic LC led to a slightly enhanced ER effect compared to that observed for only the nematic LC. However, the presence of the PdNPs in the nematic LC led to a reduced ER effect compared to that observed for only the nematic LC as shown in Figure 2.

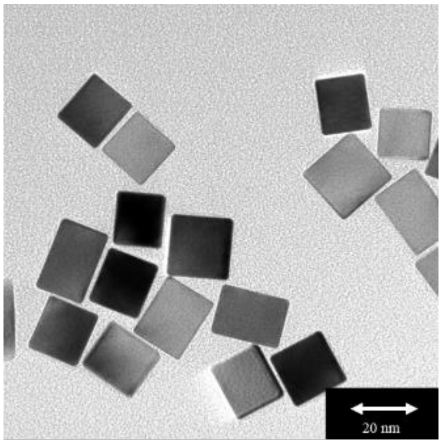

Figure 1. The TEM image of Pd nanoparticles

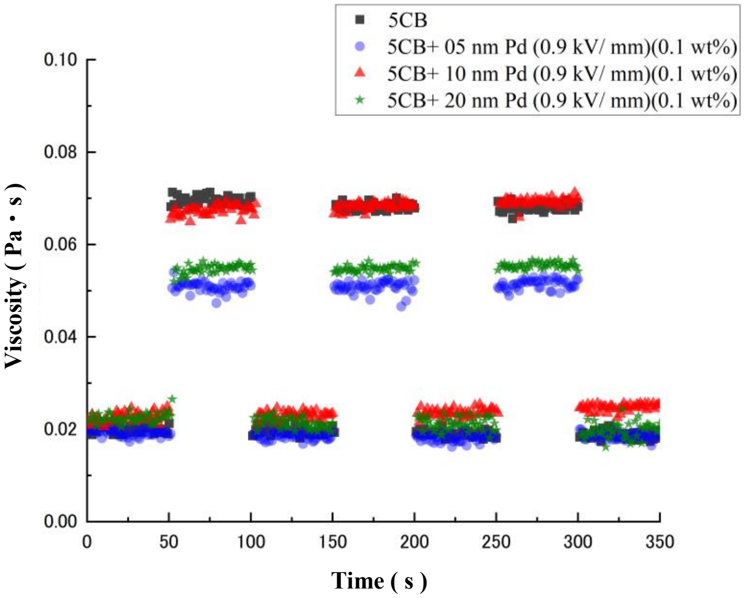

Figure 2. The results of viscosity measurements

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2) M. Jin, H. Liu, H. Zhang, Z. Xie, J. Liu and Y. Xia, *Nano Res*.**2011**, *4*, 83

Fluorescence Properties of AIE-Active Perylene Derivatives in the Aggregated State

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【Introduction】

Perylene derivatives have attracted attention as excellent fluorescent materials because of their high quantum yields. The perylene core aggregates easily to form a stacked organization due to its strong π-π interaction, therefore many reports have shown the appearance of discotic columnar liquid crystal phases in this series. In recent years, by controlling the aggregated structure with the highly ordered structure like liquid crystals, circularly polarized luminescence (CPL) materials have been developed. However, their quantum yields in the aggregated state are significantly reduced.

We have therefore aimed to improve the quantum yield in the aggregated state by introducing tetraphenylethene (TPE) cores, which is known as an aggregation-induced emission (AIE) molecule, into a perylene derivative. In this study, we synthesized disk-shaped PT-Dn (n=18, 12, 8, 6, 0) by introducing TPE moieties with alkyl chains into a perylene core (Fig.1), and investigated the luminescence behavior of each compound in the aggregated states.

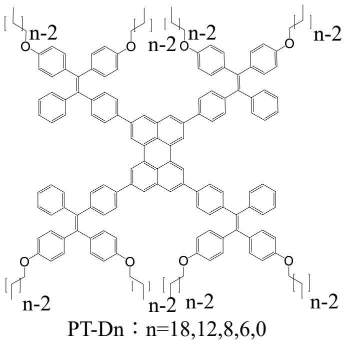

Fig.1 The structure of PT-Dn

【Result & Discussion】

PT-Dn (n=18, 12, 8, 6, 0) were characterized by ^{1}H NMR, and the POM images and the DSC curves showed that they had no liquid crystallinity. The optical properties were characterized by UV-vis and photoluminescence (PL) spectroscopy. From the results of PL measurements, the fluorescence quantum yields of PT-Dn (n=18, 12, 8, 0) in the aggregated states were lower than that in the dilute solution (Table 1).) However, the quantum yield of PT-D6 in the aggregated state was higher than that in the dilute solution. This property is a typical AIE behavior.

In addition, the PL intensity changed depending on the alkoxy chain length (Fig.2). These results suggest that the aggregation structure changes with the length of the alkoxy chain.

Table 1. The Quantum Yield of PT-Dn

	PT-0	**PT-D6**	**PT-D8**	**PT-D12**	**PT-D18**
solution	74%	2%	23%	35%	41%
aggregation	4%	**30%**	2%	6%	22%

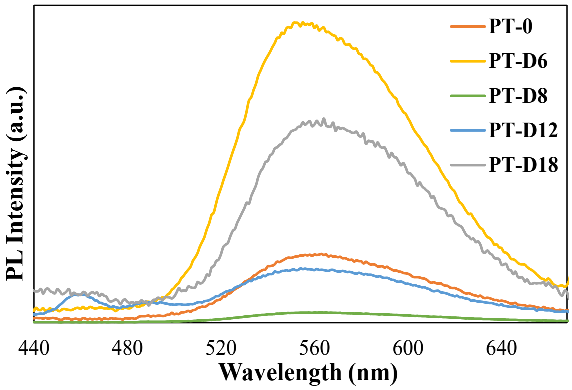

Fig.2 The PL Intensity of PT-Dn

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2） X.-F. Duan *et al.*, *Synthesis,* **2007**, *5*, 713.

Dynamic Viscoelasticity of Liquid Crystal Elastomer Films Containing Dual Frequency Liquid Crystalline Groups

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Liquid Crystal Elastomers (LCEs) are responsive to external stimuli such as heat and light. There are few reports on change in viscoelasticity due to the phase transition of the LCEs, and only the small amount of the change has been observed. In addition, the practical application using the LCEs is still difficult because the thermal stimulation is used to cause the phase transition with shape change.[1] In this study, we developed the dual frequency LCE film in which the orientation of LC molecules is controlled by the frequency of the applied AC electric field to provide a switching function of an increase or decrease in viscoelasticity. (Fig. 1)

The desired LCE film was obtained by the procedure shown in Fig. 2.

Fig. 3 shows the dynamic viscoelastic behavior of the LCE films when an electric field was applied. The measurement was performed in the following condition:

-20 ºC, strain 2 %, strain frequency 1 Hz, and voltage 6 kV / mm.

It was found that the storage modulus of the LCE film can be changed by the application of an electric field. The details of the mechanism of the viscoelasticity change will be discussed in the poster session.

[References]

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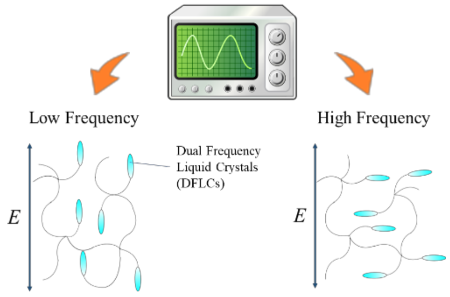

Fig. 1 Orientation change of DFLCs inside the liquid crystal elastomer film due to different frequency of applied AC electric field.

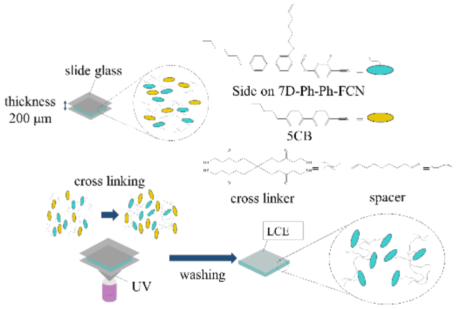

Fig. 2 Preparation of the LCE film.

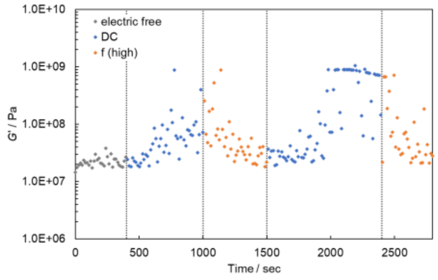

Fig. 3 Dynamic viscoelasticity of the LCE film.

Liquid Crystalline Property of Dimeric DEME Based Ionic Liquids Doped with Organic Solvents Containing Hydroxy Groups

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【Introduction】

Ionic liquids (ILs) are defined as "salts having a melting point below 100 °C" and consisting of organic ions as either or both anions and cations[1]. ILs have non-volatility, a wide potential window, high conductivity, and chemical stability, therefore it is expected to be applied as lubricants and electrolytes for electrical devices. Among them, ILs with *N*,*N*-diethyl-methyl-*N*-(2-methoxyethyl)ammonium (DEME) cations have been reported to exhibit relatively high electrochemical stability, because the cations have no π-conjugated system which shows relatively low stability to redox reactions [2]. In this study, we synthesized dimeric ILs (In-diDEME-X-14 (X = I, Br, Cl)) with two cationic moieties. In our previous study, it was revealed that the addition of water or organic solvents such as ethylene glycol to In-diDEME-I-14 induced the development of liquid crystalline phases. It has been considered that a hydrogen bonding between the nonionic moieties and the OH groups of the solvents affected the formation of liquid crystalline structures. However, the details have not been clarified. Therefore, we investigate the mechanism of the development of liquid crystalline phases when various solvents with OH groups are added.

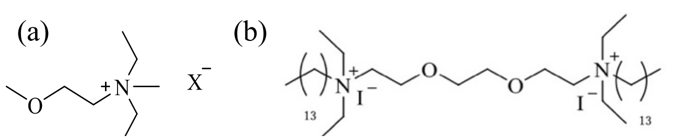

Fig.1 Structural formulas of (a) [DEME][X] and (b) In-diDEME-I-14

【Experiments】

In-diDEME-X-14 was synthesized. The samples were prepared by adding Ethylene Glycol, 1,2-Propanediol, 1,2-Butanediol, and 1,3-Butanediol to In-diDEME-I-14, respectively. The samples of In-diDEME-Br-14 and In-diDEME-Cl-14 with Ethylene Glycol were also prepared. The phase transition behavior of these samples was measured by using a polarized optical microscope (POM) and a differential scanning calorimeter (DSC). In addition, the liquid crystal structures of these samples were identified by X-ray diffraction (XRD) measurements. Moreover, the moisture contents in these samples were measured using a Karl Fischer moisture meter.

【Results】

According to the results of the POM observations and the DSC measurements, a liquid crystalline phase appeared in In-diDEME-X-14 with the addition of the solvent. The XRD results suggest that the different liquid crystalline phases are observed depending on the anion species.

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Synthesis and Electro Rheological Effects of Dual Frequency Liquid Crystals with Branched Siloxane Cores

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【Introduction】

The phenomenon in which the viscosity of a fluid reversibly changes when an external electric field is applied or removed is called the electro-rheological (ER) effect, and fluids exhibiting this phenomenon are called ER fluids. Liquid crystals (LCs) composed of rod-shape molecules are known as a homogeneous ER fluids, and it is believed that the applying an electric field increases flow resistance occurs and developing viscosity by aligning the LC molecules perpendicular to the shear direction.[1] However, there is basically no driving force acting on the LC molecules after the removal of the electric field, resulting in a slow response speed.[1] For this reason, we focused on dual-frequency liquid crystals[2] that exhibit different dielectric anisotropy depending on the frequency of the applied AC electric field and aimed to obtain the ER fluid with an excellent response by changing the frequency for controlling the molecular orientation of the LC molecules. In this study, oligomeric LCs with siloxane cores are synthesized in order to obtain ER fluids possessing both a large increase in viscosity and a good response, and their ER effect is evaluated. [3] The molecular structures of the target compounds (Tetrahedral 5-Cl-5, Cube 5-Cl-5) are shown in Figure 1.

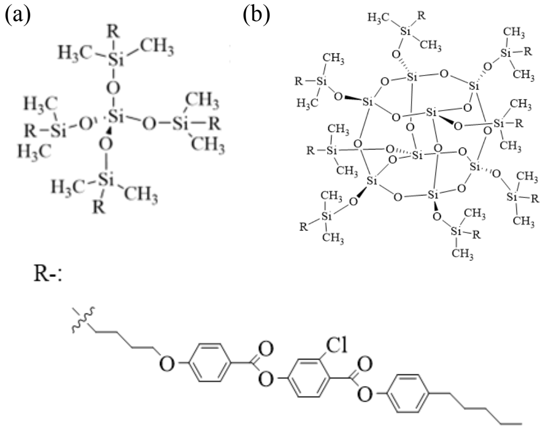

Figure.1 Molecular structures of (a)Tetrahedral 5-Cl-5 and (b)Cube 5-Cl-5.

【Experiment and Result】

The target compounds were synthesized, and the phase transition behavior was determined by differential scanning calorimetry (DSC) measurements and polarization microscope (POM) observations. The ER effect was measured using the rotational viscometer. The shear rate dependence and temperature dependence of the ER effect in Tetrahedral 5-Cl-5 and Cube 5-Cl-5 were measured, and the ER effect results are shown in Figure 2. As shown in Figure 2(a), it is found that Tetrahedral 5-Cl-5 exhibits a reversible viscosity change with frequency switching. But the orientational change of the mesogenic groups leading to a large increase in viscosity could not be realized. Figure 2(b) reveals that Cube 5-Cl-5 showed a significant decrease in viscosity when the applied frequency was high. On the other hand, the viscosity was comparable with that without the AC field when the applied frequency was low.

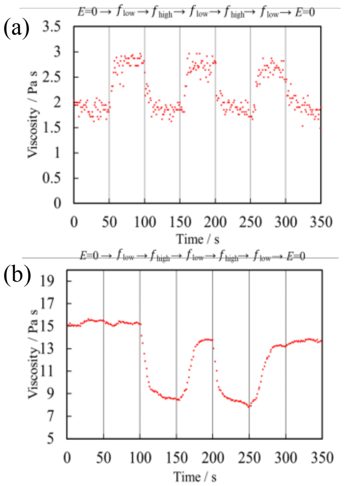

Figure.2 ER effect of (a)Tetrahedral 5-Cl-5 (70°C) and (b)Cube 5-Cl-5 (80°C).

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2） H. Xianyu, S. T. Wu, and C. L. Lin, *Liq. Cryst.*, **2009**, *36*, 717.
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Development of Carbon Nanofiber Reinforced Aluminum Composite with Harmonic Structure Design

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Aluminum has excellent properties, such as specific strength, electrical conductivity, thermal conductivity, and workability, etc. In recent years, developing aluminum with more functional has gathered attention. One way to improve the functionality of aluminum is to composite it with carbon nanofibers. After adding carbon nanofiber into matrix materials, the dispersed carbon nanofiber can improve the strength, electrical conductivity, and thermal conductivity of the metal[1,2].

It is well known that strength and ductility trade-offs exists. Similarly, carbon nanofibers increase strength, while decreasing ductility and processability. In addition, carbon nanofibers are easily attracted to each other and form aggregates in which voids contained in aggregate and can cause the deteriorating workability of the composite materials.

To solve the issue, in this study, a method that dispersing carbon nanofibers using a ball mill and introducing harmonic structures into aluminum was proposed. Harmonized structure is a structure that coarse grained regions are arranged between fine-grained regions arranged in a three-dimensional network. Harmonic structure has a good balance between strength and ductility[3].

The process are as follows. First, fine Al powder (3 μm) and spherical Al powder (45-75 μm) were combined to produce a spherical Al powder surrounded by fine Al powder with carbon nanofibers. The mechanical milled powders were plasma sintered to produce a carbon nanofiber reinforced aluminum composite with harmonic structure. The mechanical properties of the composite material were investigated by conducting tensile tests and microstructure observations.

According to microstructure observation, harmonic structure was obtained (Fig. 1). In addition, based on the tensile test results, it is observed that the material fractured in elastic region. Fracture surface observation results (Fig. 2) indicate that, it fractured at the powder interface.

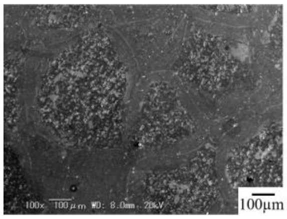

Fig.1 Microstructure of Al-CNF composite with harmonic structure

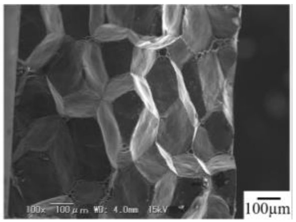

Fig.2 Fracture surface of Al-CNF composite with harmonic structure

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3) Kei Ameyama, Mie Ohta, *Powder and Powder Metallurgy.* **2017**, 64, 3

Development of a creep testing machine with the maximum temperature 1000℃ for utilizing miniature specimens and evaluation of creep strength for IN713C-MIM

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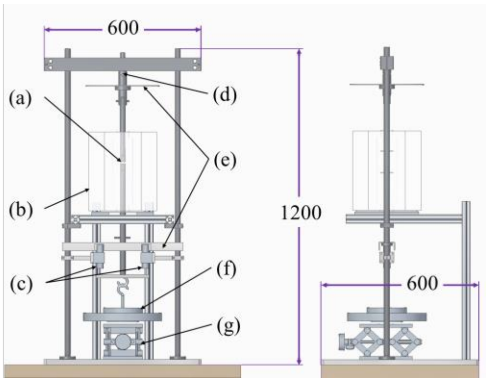
In the current study the development of a creep testing machine with a maximum temperature 1000 degrees for utilizing miniature specimens and evaluation of creep strength for IN713C-MIM were conducted. The remaining creep life could be predicted by destructive evaluation method with high accuracy. The method is that a specimen sampled from the actual high temperature machine is tested under on a stress level which is identical to the actual loading. However, when sampling from the actual high temperature machine with large size, which will damage the actual machine and the sampling component cannot be reused. The remaining creep life assessment of actual devices using the miniature specimens is expected as the better method because it can decrease the damage to sampling component. Moreover, the creep strength of MIM materials is lower than that of cast or forged materials. A few studies focus on investigating creep strength of MIM materials, it is necessary to survey the creep behavior of the materials.

This research aims at solving the abovementioned needs and developing a superalloy with excellent creep-strength.

Fig.1 shows a schematic diagram of the developed test equipment. This is capable of creep testing in air with a maximum temperature of 1200°C and a maximum load of 200kgf. The loading mode is axial loading type.Fig.2 show the shape and dimension of specimen used in this study. Creep tests were performed on the IN713C-MIM material at 982°C and 40MPa.The tested results are rupture time of 3.5h, creep strain of 23 %, minimum strain rate of 1.7 %/h. It is suggested that the test equipment can measure rupture time, creep strain and minimum strain rate. However, more detailed evaluating of the strength is also necessary.



(a) Specimen
(b) Electric furnace
(c) LVDT
(d) Hole of cooling water
(e) Heat shield plate
(f) Weight
(g) Lab jack

Fig.1 Schematic showing of creep testing machine (mm).

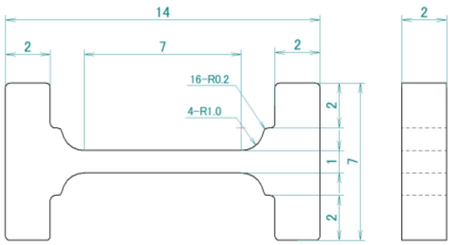


Fig.2 Shape and dimensions of specimen (mm).

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Study of In-Liquid Synthesis of Diamond

Technical development aimed for chemical change/cut/precipitation and self-assembly/aggregation

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1. Introduction

The investigated test results are described for establishing the new technology of diamond thin film synthesis that coexists with the traditional manufacturing methods of HPHT, CVD and Detonation. The most important subjects of this paper are to form diamond thin film, to verify the synthesis phenomena and to clarify the success of in-liquid synthesized diamond for recognizing a synthesis establishment[1].

2. Construction and hypothesis concept of synthesis principle

The active carbon species and organic compounds are generated in an organic sol by the chemical change. The cut of these substances using an ultraviolet lead to generate the free carbons (atomic carbons of sp^2 and sp^3) in the organic sol. The self-assembly precipitates amorphous from monomer. The aggregation forms diamond on the substrate where these amorphous and monomer precipitate.

3. Experimental procedures

Figure 1 shows the schematic diagram of synthesis method. It appears that the combined bridges of most organic polymers are cut by irradiating an ultraviolet bellow about 400 nm wave length. We use the reaction vessel that made from quart glass, or the combinations of soda glass and polypropylene resin. The closed reaction vessel respectively leaves the one bottle that contains Liquid A, and the other bottle that contains Liquid B or Liquid D.

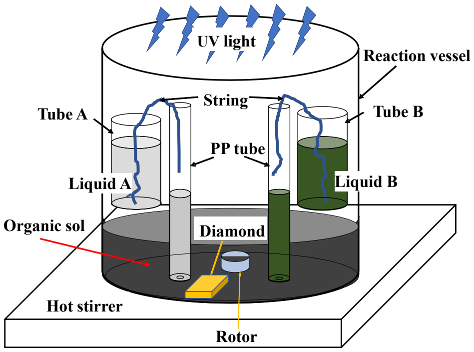

Fig.1 Schematic diagram of in-liquid synthesis method

4. Results and discussion

Figure 2 shows XAFS result of the synthesis that carried using PCD. Pre-synthesis substrate (Origin PCD) clearly has an intensity valley at around 302 eV, but not a spectrum at around 350 eV. Three kinds of PCD that synthesized under each condition have an intensity valley at around 302 eV and a spectrum at around 350 eV. In other words, it appears that the film formed over PCD is diamond which a little contains organic polymer included with Ca. On the other hand, pre-synthesis substrate (Origin PCD) clearly had a spectrum of Co, since PCD is sintered using Co. However, three kinds of PCD that synthesized under each condition have not a spectrum of Co. The synthesized film is different from the substrate of origin PCD.

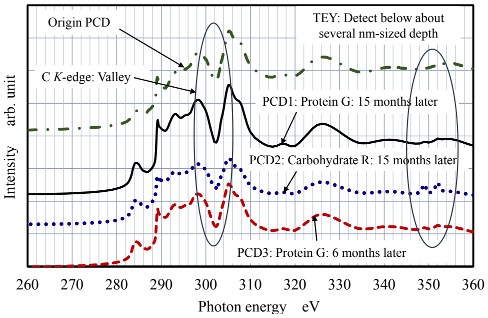

Fig.2 XAFS TEY analysis of thin film formed in liquid

5. Conclusions

Acetone/KOH aqueous solution resolve/hydrolyze a polystyrene and a gelatin/cocoon/rice. Chemical change between them leads to make organic sol black, and generates active carbon species and organic compounds. Diamond is synthesized on PCD and natural diamond by self-assembly/aggregation of carbons.

Acknowledgements

The author is deeply indebted to Prof. M. Takisawa and Mr. D. Yamasaki for their helps and suggestions.

Reference

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Direct micropatterning of Cu using polymer electrolyte membrane stamp

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Cu is widely used in the fabrication of metal interconnects for electronic devices such as integrated circuits and printed-circuit boards because of its low resistivity and good thermal stability[1]. Furthermore, Cu can be used as a substrate for graphene growth, and graphene nanostructures have been achieved using patterned Cu substrate[2]. Due to superior pattern resolution to other direct patterning processes, photolithography is generally used to prepare patterned Cu surfaces. However, photolithography is complex and has a high environmental impact because of the multistep process with the need for resists and harsh chemicals. To avoid this problem, we establish a direct electrochemical imprinting process that generates micropatterns on the Cu surface in a single step without the need for resists and harsh chemicals. In this process, a polymer electrolyte membrane (PEM), which is an ion-conductive polymer material, is used instead of the liquid electrolyte. A Cu/PEM/cathode electrochemical system is proposed to form the pattern on the Cu surface by the selective electrochemical etching that occurred at an interface between PEM stamp and Cu (Fig. 1(a)). PEM stamps with various patterns such as sharklet, lattice, and line-and-space structures were prepared via hot embossing. Patterning characteristics were investigated on the surface of Cu thin film deposited on a glass substrate. Scanning electron microscopy and atomic force microscopy indicate that the Cu surface in contact with the PEM stamp is selectively etched to form the pattern structure (Fig. 1(b)). The depth of the resulting pattern structure matches the thickness of the Cu film, indicating that etching by the electrolysis automatically stopped when it reaches the glass substrate. The proposed electrochemical treatment is an environment-friendly and cost-effective approach because it is a simple direct imprinting process that does not employ resists and harsh chemicals. Furthermore, it is expected to increase the efficiency of microfabrication such as metal interconnects because the micropatterns can be formed on the Cu surface in a single step without the need for a complex multistep.

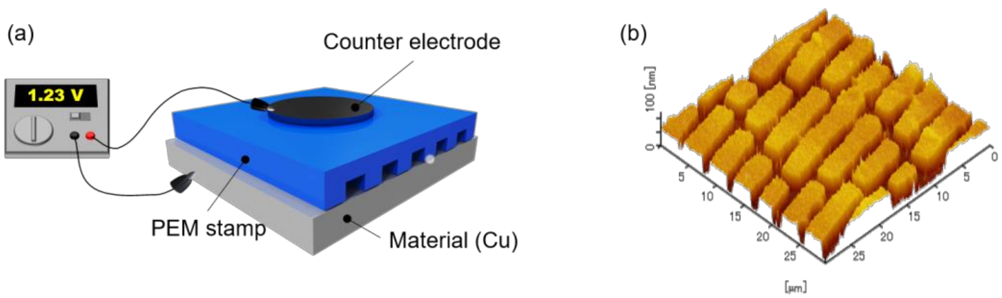

Fig. 1 (a) Schematics of the proposed patterning process, (b) atomic force microscopy image of micropattern formed on the Cu surface by the proposed process.

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Spontaneously Induced Pattern Formation of Liquid Crystal Orientation by Gradient Photopolymerization

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Since liquid crystals show the birefringence, liquid crystalline materials have been applied to various optical materials such as diffractive gratings, lens, reflective devices. The key to those materials is the controlled pattern of molecular orientation, which bring about the distribution of refractive index. Thus, technologies for controlling molecular orientation in one- or multi dimensions have been desired. The current methods achieve the control of one-dimensional molecular orientation by applying uniform external fields along one direction such as surface rubbing treatment and mechanical stress. Recently, light-driven orientation control methods achieve the control of two-dimensional molecular orientation[1, 2]. However, to date, the arbitrary control of molecular orientation with a periodicity below a few micrometers over large area is still challenging. Previously, we have found that the periodic molecular orientation patterns were spontaneously formed by photopolymerization with intensity-gradient patterned light (gradient photopolymerization). In this study, we discussed the mechanism of the formation of molecular orientation pattern.

The chemical structures of a monomer mixture used for gradient photopolymerization are shown in Figure 1. We irradiated monomer mixture in handmaid grass cell (thickness: 4 μm) with UV light (λ = 365 nm) using a photomask. Light intensity was continuously changed by a photomask using black gradation pattern. In resultant polymer film, the stripe patterns were observed with polarized optical microscopy (POM), as shown in Figure 2A. White line shows the spatial light intensity profile in observation area. To evaluate the molecular orientation in the stripe pattern, we performed the POM observation with a retardation plate (R = 137 nm), as shown in Figure 2B. Blue dotted arrow shows the optical axis of a retardation plate. In the bright area of stripe pattern, liquid-crystalline molecules (mesogen) oriented perpendicular to optical axis. In the dark area, mesogen oriented parallel or perpendicular to optical axis. Thus, periodic molecular orientation pattern was induced by gradient photopolymerization, as shown in Figure 2C.

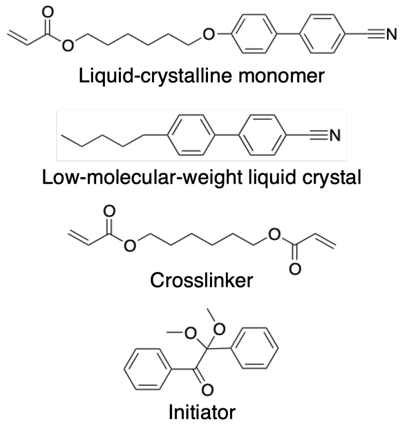

Figure 1. Chemical structures of a monomer mixture used in this study

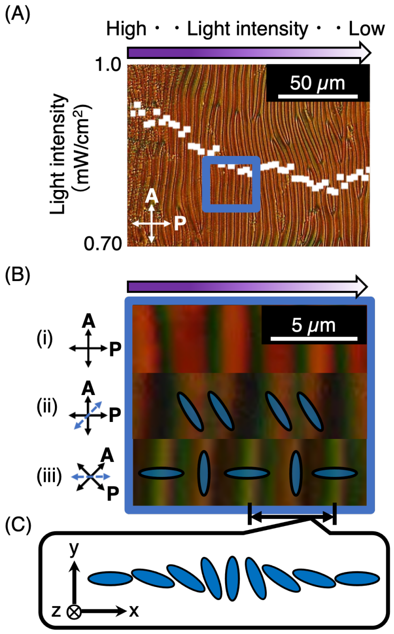

Figure 2. (A) POM observation of polymer film. The spatial profile of light intensity is plotted in the figure. (B) Enlarged view (i) without a retardation plate with offset 0°, (ii) with a retardation plate with offset 0°, (iii) with offset 45°. (C) Schematic illustration of molecular orientation pattern in the polymer film

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Emission Properties of Liquid-Crystalline Trinuclear Gold(I) Complexes with Branched Side Chains

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Aggregation-induced emission (AIE) materials exhibit strong luminescence in the solid state. The AIE materials are of interest for potential applications in OLED and bio-imaging. Our research focuses on using Au(I) complexes with AIE properties. These complexes demonstrate aurophilic interaction, which leads to highly efficient luminescence. The luminescence behavior of these complexes depends on their aggregated structure, meaning that it can be adjusted by controlling the aggregation structure. We have reported that by using liquid crystallinity of the Au complexes their aggregated structure and luminescence properties can be controlled. Au complexes with liquid crystalline properties can be oriented with external stimuli like electric field and mechanical force. Thus, we can expect that this enables us to control the aggregated structure and luminescence behavior.

In this study, we synthesized trinuclear Au complexes with pyrazole ligands bearing branched side chains (Figure 1a). Here, we explore how the branched structure affects the thermodynamic and photophysical properties of these complexes. We found that the branched structure significantly lowers their melting point. For instance, the melting point of **E-H** without branched structure was 132 °C, while that of **E-Hex** with long branching chains was –15 °C. As a result, **E-Hex** exhibiting a discotic nematic phase (N_D) over an extensive temperature range from -15 °C to its thermal decomposition temperature (285 °C). All complexes synthesized emitted room-temperature phosphorescence with the emission maximum at ~740 nm. Effects of the branched structure and phase structure of complexes on the photophysical properties will be discussed.

1) Y. Kuroda, *et al., Commun Chem.* **2020**, 3, 139.

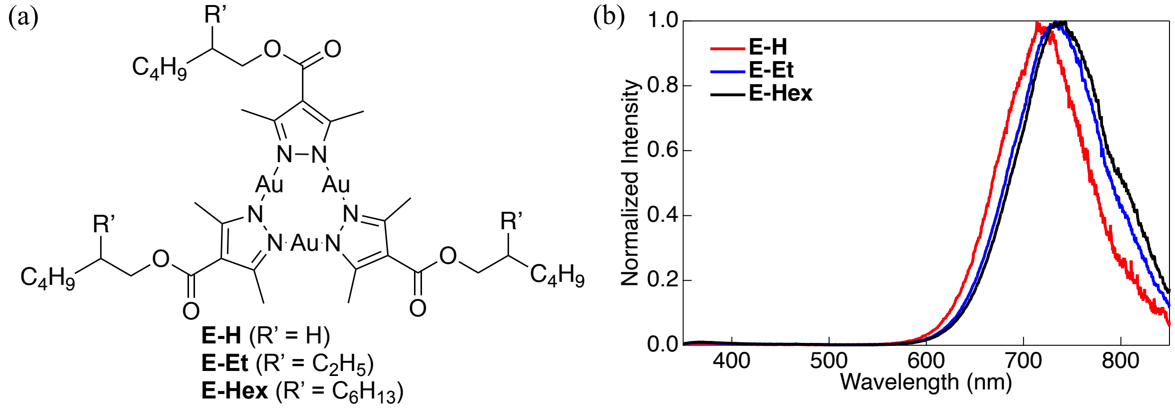

Figure 1. (a) Molecular structure of Au complexes used in this study. (b) Photoluminescence spectra of each Au complexes at room temperature (λ_{ex} = 300 nm).

Preparation of Cross-Linked Liquid-Crystalline Polymer Particles with Precisely Controlled Molecular Orientation

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Monodispersed liquid-crystalline (LC) polymer microparticles which exhibit unique optical properties have been developed. The introduction of crosslinking structures in the LC polymer microparticles can enhance their environmental stability against heat and solvents. In this study, we developed a new hetero-bifunctional crosslinker showing liquid crystallinity that can crosslink the LC polymers with an arbitrary crosslinking density.

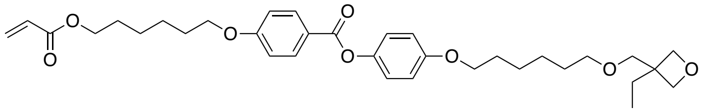

Figure 1. Molecular design of LC crosslinker

Non-crosslinked microparticles were obtained by dispersion polymerization of the LC crosslinker in a DMF/MeOH mixture. The non-crosslinked microparticles were then redispersed in MeOH containing a photoacid generator and irradiated with UV light at 65 nm to induce ring-opening polymerization of the oxetane ring to introduce a crosslinked structure. The resulting microparticles showed a cross-shaped dark field inside the particles, indicating that the LC molecules were radially oriented. The crosslinked particles did not dissolve in dichloromethane. This indicates that a crosslinked structure was successfully introduced into the microparticles, and highly crosslinked liquid crystalline polymer microparticles were synthesized.

The average size of the particles was estimated to be 3.6 ± 0.2 µm by image analysis. POM observation revealed a cross-shaped optical texture, suggesting that the molecules are oriented radially inside the particles. Although the non-crosslinked particles were dissolved in a good solvent for the polymer (dichloromethane), the crosslinked particles did not dissolve in the solvent (Figure 2e,f). Thus, we can conclude that we successfully introduced a cross-linked structure into the microparticles.

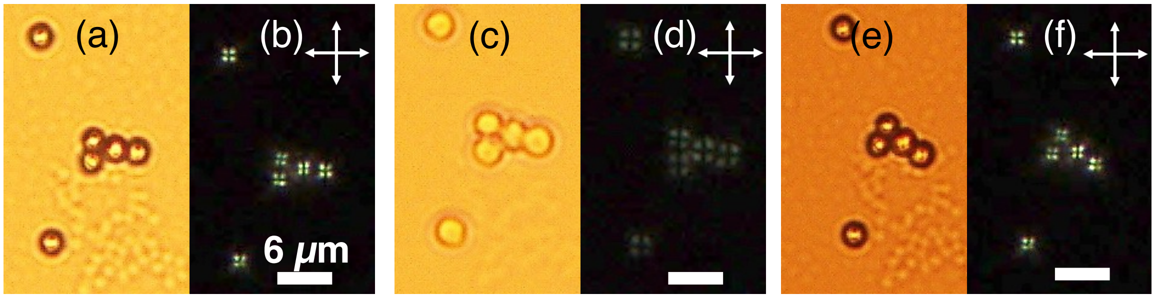

Figure 2. Optical and crossed nicol micrographs of the crosslinked particles: (a, b) in air, (c,d) in CH_2Cl_2, (e, f) in air after of evaporation CH_2Cl_2.

Control of Crystal Structure in Discotic Trinuclear Gold(I) Complexes by UV Irradiation

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Gold complexes in aggregates exhibit strong luminescence due to aurophilic interactions. It has been reported so far that this interaction was amplified in excited states. We have reported the photophysical properties of discotic trinuclear Au(I) complexes (Figure 1), and that their emission colors varied depending on the aggregated structure. Considering that the aurophilic interaction is enhanced in the excited state, we can expect that the crystal structure can be controlled by photoexcitation.

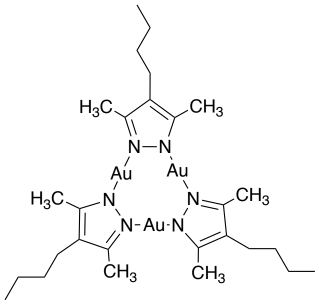

Figure 1. Chemical structure of discotic trinuclear gold(I) complexes.

In this study, we investigated crystal structure of Au complexes formed under photoexcitation to understand the mechanism behind it. We prepared single crystals of the complexes by recrystallization from THF under UV irradiation at 254 nm. The crystals obtained under UV irradiation exhibited different luminescence behavior from those obtained in the dark. The single-crystal X-ray structural analysis revealed that both crystals showed the completely different structure (Figure 2). We found an increase in the number of the sites of aurophilic interaction in the crystals obtained under UV light irradiation. Based on these results, we conclude that crystallization under UV light irradiation to enhance the aurophilic interaction induced the different crystal structure.

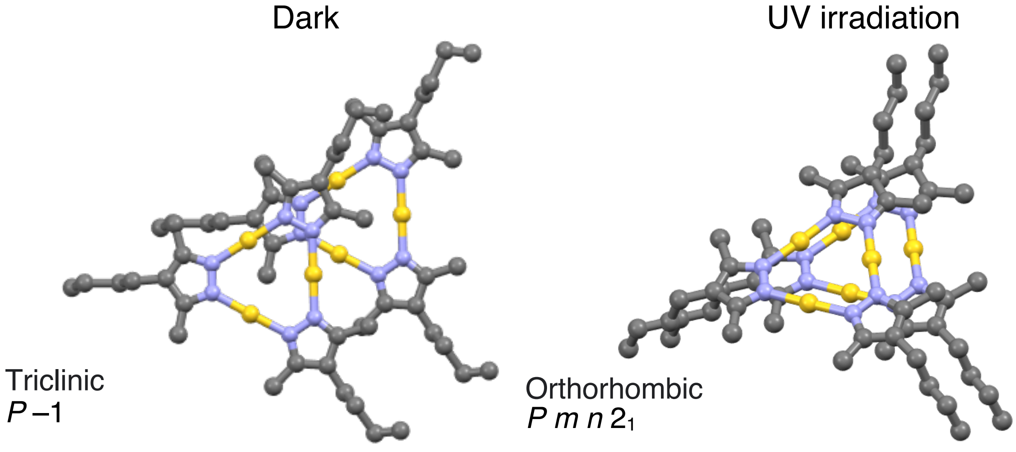

Figure 2. Structure of Au-complex crystals obtained by recrystallization under dark and UV irradiation.

1) Seki, T.; Sakurada, K.; Muromoto, M.; Ito, H. *Chem. Sci.* **2015**, *6*, 1491.
2) Y. Kuroda, *et al.*, *Commun. Chem.*, **2020**, *3*, 139.

Mechanism of Molecular Orientation Pattern Formation in Liquid-Crystalline Polymers Induced by Gradient Photopolymerization

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We have recently found a new phenomenon that the periodic pattern of the molecular orientation of liquid crystal (LC) can be spontaneously formed by gradient photopolymerization of LC monomers. Since LCs show optical anisotropy, the LC polymers with the periodic orientation pattern can be useful for the highly functional optical materials. However, the mechanism of the periodic pattern of the molecular orientation formation has not been still unclear. So far, we found that the orientational pattern formation occurs simultaneously with the formation of the dissipative structures of polymer, and that the interdiffusion of monomers and non-polymerizable molecules is the key to this phenomenon. In this study, we discussed the mechanism of the orientational pattern formation in details.

Two types of monomer mixtures were prepared with LC/non-LC monomers and non-polymerizable molecules. Sample 1 were prepared using LC monomers and non-LC non-polymerizable molecules (Figure 1A). Sample 2 were prepared using non-LC monomers and LC non-polymerizable molecules (Figure 1B). Monomer mixtures were sealed in glass cells (cell gap: 4 μm) and irradiated with UV light (365 nm) for photopolymerization. In this process, a photomask with a gradient pattern was used to provide a spatial gradient with respect to the intensity of the irradiated light. Polarized light microscopy of polymerized Sample 1 reveal formation of the periodic pattern of the molecular orientation (Figure 2A). However, the periodic pattern of the molecular orientation was not formed by photopolymerization of Sample 2 (Figure 2B). We will discuss the mechanism of this difference.

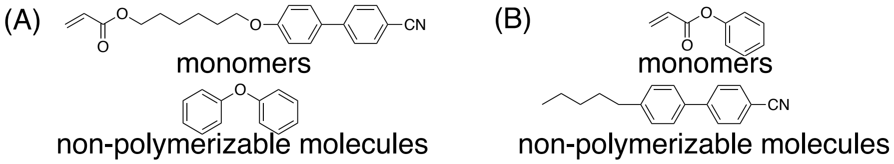

Figure 1 Molecular structures used in monomer mixtures (A) Sample 1 (B) Sample 2

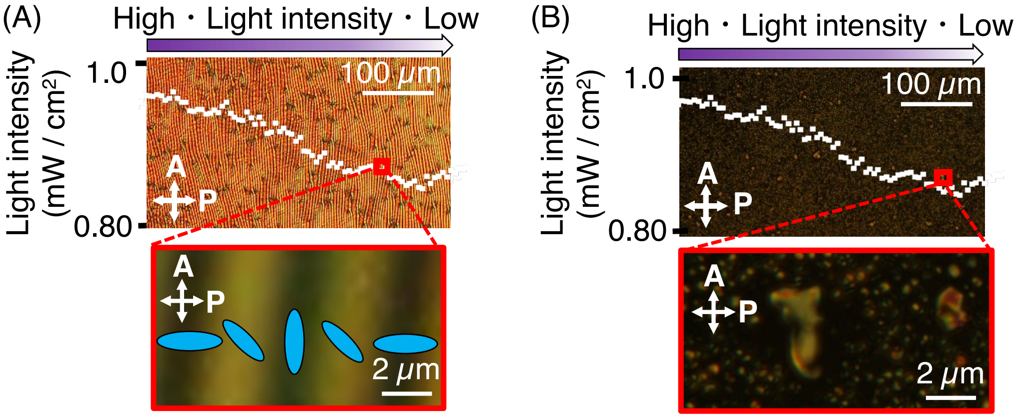

Figure 2 POM observation of polymer films. (A) Sample 1(B) Sample 2 The spatial profile of light intensity is plotted in the figure.

Mechano-optical Behavior of Multilayered Chiral-Nematic Liquid Crystal Elastomers with Auxetic Structures

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Chiral-nematic liquid crystal elastomers (N*LCEs) show selective reflection derived from the helical orientation of the liquid crystal molecules. N*LCEs can respond to applied strain as a change in the selective reflection wavelength, they are expected to be applied to stress/strain sensors. We have previously developed N*LCEs stacked with different materials and reported that the mechanical-optical response behavior of N*LCEs can be controlled by the mechanical properties of the outer layer materials1). In this study, we focus on the auxetic structure and consider that the optical response behavior can be controlled more sensitively by changing the structure of the outer layer. Auxetic structures have the property of elongation perpendicular to the axial direction as shown in Figure 1. In this study, we fabricated stacked N*LCEs incorporating various forms of auxetic structures and developed materials that show sensitive optical response to strain.

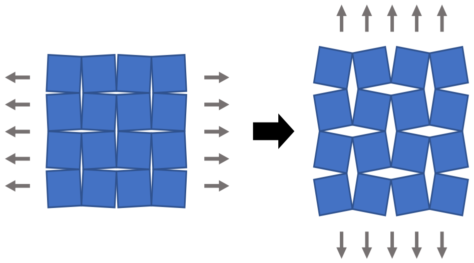

Figure 1. Image of Auxetic structure.

The liquid crystal monomers, chiral agents, cross-linking agents, plasticizers, and initiators shown in Figure 2 were mixed and permeated into cells made of glass substrates to which polydimethylsiloxane (PDMS) films were attached, and photo-polymerization was applied to obtain stacked N*LCEs. Auxetic structures were fabricated by cutting PET film and double-sided tape using a laser cutting machine, and then affixed to the N*LCE to fabricate a film incorporating the Auxetic structure. The tensile behavior of the film was observed and reflectance spectra were measured.

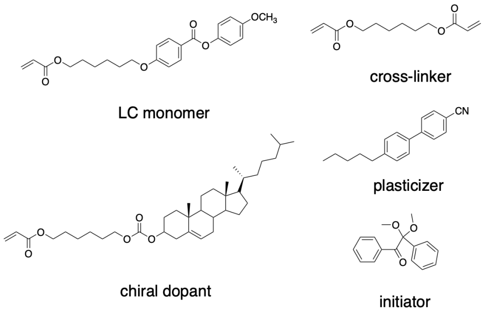

Figure 2. Chemical structures of a monomer mixture used in this study.

When the laminated N*LCE with the paper cut structure was elongated and deformed, only the reflectance color of the cut area changed (Figure 3). Compared to the N*LCE without the paper cut structure, the reflectance color changed more sensitively to strain. This result was attributed to the increased strain in the film thickness direction caused by the Auxetic structure.

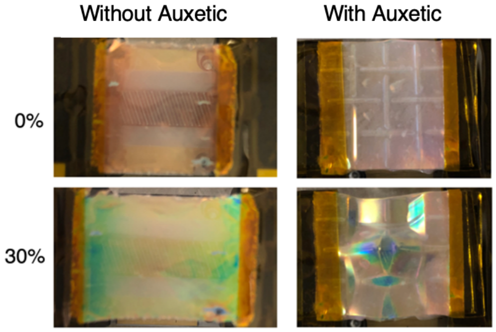

Figure 3. Picture of N*LCE at each applied strain.

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1) Hisano, K.; Kimura, S.; Ku, K.; Shigeyama, T.; Akamatsu, N.; Shishido, A.; Tsutsumi, O. *Adv. Funct. Mater.* **2021,** 31, 2104702.

Tuning the Au-Au Interactions in Luminescent Linear Polymeric Gold-NHC Complexes

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Luminescent organic molecules play a crucial role in the field of material science and life science. However, their application in industrial field has been limited because they suffer from the phenomenon known as ‘Aggregation Caused Quenching’ in condensed phases. Contrary to this, Tang *et.al.* reported the phenomenon called ‘Aggregation Induced Emission’ which opened the door towards the practical application of luminescent organic molecules in solid phases, for instance, in organic light emitting diodes (OLEDs), and has henceforth this phenomenon has played an important role in industrial applications. Among numerous other molecules, gold complexes have also been identified as promising AIEgens, due to their ability to show metalophilic d^{10}-d^{10} interactions in condensed phases, which deeply influences the luminescence behavior depending on the extent of these interactions. Changes in the molecular aggregates can be brought upon by application of external stimuli, therefore altering the aurophilic interactions, which is known as Aggregation Controlled Emission (ACE)[2]. For such fine tuning of the aggregated structures, a suitable choice of ligand is an important parameter, in which context N-heterocyclic carbenes (NHCs) have proven to be a good choice. In this context, polymers possess various desirable properties, like tunable structural morphology and mechanical strength.

Combining the properties of gold-NHC complexes with polymer science can lead to the development of materials that can show enhanced behavior and tunable properties with applications in plethora of fields. However, this field has attained less attention owing to the difficulties in the synthesis to control the degree of polymerization, purification methods and limited solubility of polymers. To overcome these challenges, in this work the authors report the synthesis of linear polymeric Au-NHC complexes, with benzimidazole moiety as the luminophore and alkyl/alkoxy spacers between the benzimidazole units. Their luminescence behavior depending on the degree of polymerization were reported along with comparative studies with the monomeric core structures.

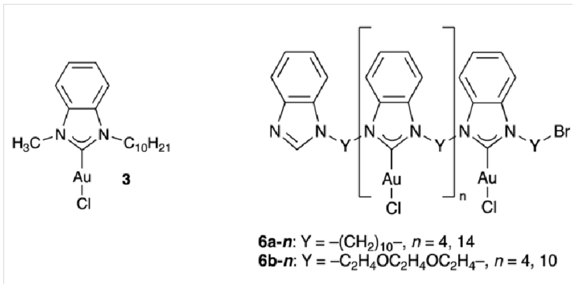

Figure 1. Molecular design of the monomer **3** and the polymeric complexes with alkyl spacer **6a-n** and alkoxy spacers **6b-n**.

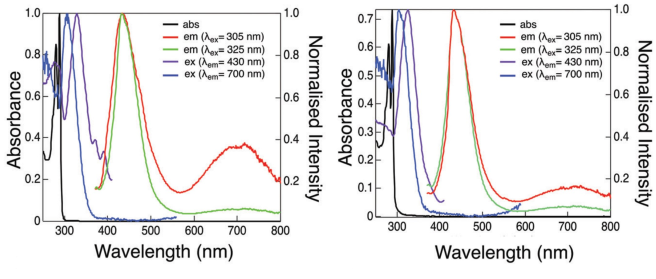

Figure 2. Absorption and photoluminescence spectra for the monomer **3** and the polymeric complexes **6a-4** and **6a-14**.

1) J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, *Chem. Commun.*, **2001**, 1740.

2) K. Fujisawa, S. Yamada, Y. Yanagi, Y. Yoshioka, A. Kiyohara and O. Tsutsumi, *Sci. Rep.*, **2015**, 5, 7934.

Three-Dimensional Deformation Analysis with Chiral-Nematic Liquid Crystal Polymer Particles

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Liquid crystal (LC) is a material that blends the anisotropy of crystals with the fluidity of liquids. Some types of LCs are capable of modifying their optical properties by altering the molecular orientation in response to external stimuli. One particular type, known as chiral nematic LC (N* LC) in which the molecules arranged helically, selectively reflects circularly polarized light at a specific wavelength depending on the helical pitch. When a tensile strain is exerted on a N* LC film, the film thickness as well as the helical pitch is compressed, leading to a change in reflection color. By utilizing this phenomenon, we have developed a strain sensor that measures the change in film thickness caused by elongation deformation.The digital image correlation (DIC) method that utilizes micro-particles as probes is a technique used to visualize strains within 2D surfaces. In this method, micro-particles are applied onto the specimen as probes, and the displacement of the particles by deformation is measured by image analysis to visualiz the 2D strain distribution. Here we proposde the method to visualize 3D strain distribution with the N*LC particles as the strain sensor.

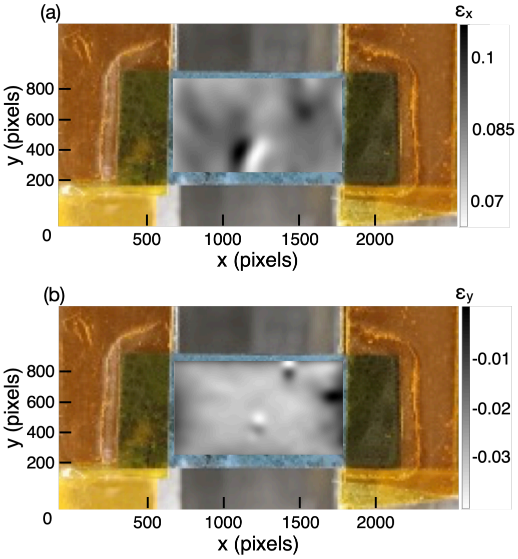

Figure 1. DIC measurement using N*LC probe. (a) Tensile strain, (b) compressive strain.

We prepared laminated materials using N* LC micro-particles as analytical probes, and conducted DIC analysis (Figure 1). We observed the color change of reflection from the micro-particles induced by the strain (Figure 2). This color change was occurred by the deformation of the particles corresponding to the applied strain, which resulted in hte compression of the helical pitch. By successfully visualizing the strain distribution within the 2D surface and quantifying the strain direction in the film thickness, we have demonstrated the possibility of conducting 3D deformation analysis.

References

1) Hisano, K.; Kimura, S.; Ku, K.; Shigeyama, T.; Akamatsu, N.; Shishido, A.; Tsutsumi, O. *Adv. Funct. Mater*. **2021**, *31*, 210472.

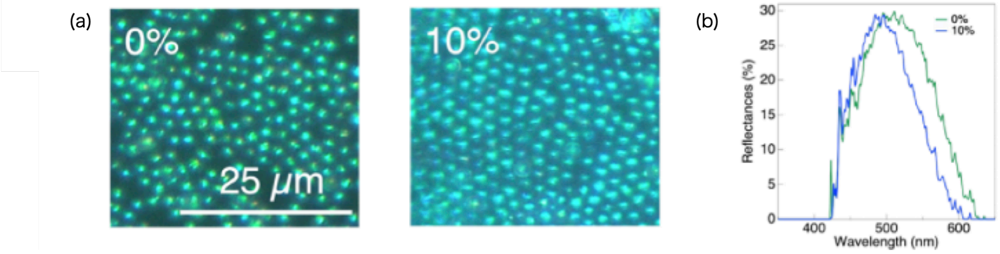

Figure 2. (a) Microscopy image of N*LC microparticles before and after deformation. (b) Reflection spectra of N*LC microparticles before and after deformation.

Tunable Emission Color of Polymorphic Gold(I) Isocyanide Complexes

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Organic materials with aggregation-induced emission (AIE) are demonstrated to be promising as optoelectronic devices. Generally, single molecule organic luminescent material only exhibits one emission color according to Kasha's rule, which cause a limitation for multifunctional material. Since the luminescence properties is strongly dependent on the aggregated structure, it is desirable to control the aggregated structure to obtain the desired luminescence properties. Polymorphic material which possesses more than one crystalline phase, can be utilized to obtain multi-color emission from one chromophore. Another method to tune the emission color is by applying external stimuli (e.g., mechanical force, heat, pressure) which also related to the change in aggregated structure. Such mechano-responsive materials can endow various applicability in sensors, probes, and memory devices.[1] Gold complex is a promising material to induce both efficient luminescence in aggregated states and stimuli-responsive luminescence behavior owing to the unique Au–Au (aurophilic) system. Indeed, numerous studies have reported various gold complexes with luminescence color sensitivity toward external stimuli.[2]

In this study, we designed and synthesized gold complexes having biphenyl or cyclohexylphenyl and isocyanide ligands (Figure 1a). This type of complexes having ligand with less steric hindrance around Au atoms is favorable to manifest aurophilic interaction. Photophysical behaviors of the gold complexes in various states were discussed based on not only their primary structures but also aggregated structure. Both complexes are AIE-active where strong room-temperature phosphorescence (RTP) was observed in the crystal. Interestingly, **CP** exhibited intriguing stimuli-responsive luminescence by having both polymorphism and mechanochromic luminescence properties. High-contrast luminescence color tuning was observed in **CP** by simply controlling the recrystallization conditions (Figure 1b). Such polymorphism-dependent emission color is likely to attribute to the change in the aggregated structure between crystal polymorphs as well as the ground crystal.

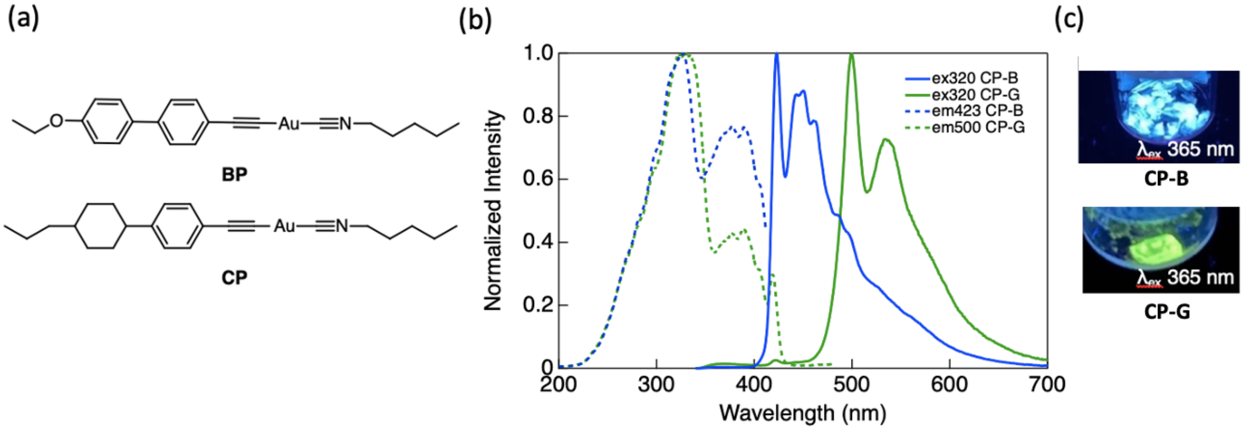

Figure 1. (a) Molecular structures of **BP** and **CP** gold(I) complexes. (b) Excitation and emission spectra of **CP** crystal polymorphs (**CP-B** and **CP-G**). Solid line, emission spectra (λ_{ex} = 320 nm); dashed line, excitation spectra. (c) Photographs of **CP-B** and **CP-G** bulk crystal under UV irradiation (λ_{ex} = 365 nm).

1) Hajime Ito *et al.*, *Angew. Chem. Int. Ed.*, **2013**, 52, 12828.
2) Kaori Fujisawa et al., *Sci Rep.*, **2015**, 5, 7934

Monitoring Molecular Orientation Change Induced by Mechanical Stimuli in Chiral-Nematic Liquid Crystal Elastomers with Luminescent Molecules

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Liquid crystal materials are highly responsive to external stimuli, such as heat and electric fields. Chiral nematic liquid crystals are characterized by a helical structure, which results in a periodic distribution of refractive index. In aqddition, the chiral nematic liquid crystals reflect circularly polarized light at a specific wavelength with the same chirality as the helix. When these materials have luminescent properties, circularly polarized luminescence is observed. Previously, it has been reported that the wavelength of the selctive reflecrion is changed by strain owing to change in the molecular orientation. However, it has not yet been clarified how the molecular orientation is affected by the application of strain. Thus, this study aimed to investigate the changes in molecular orientation induced by mechanical stimuli in chiral nematic liquid crystal elastomers with a luminescent moleculra probve.

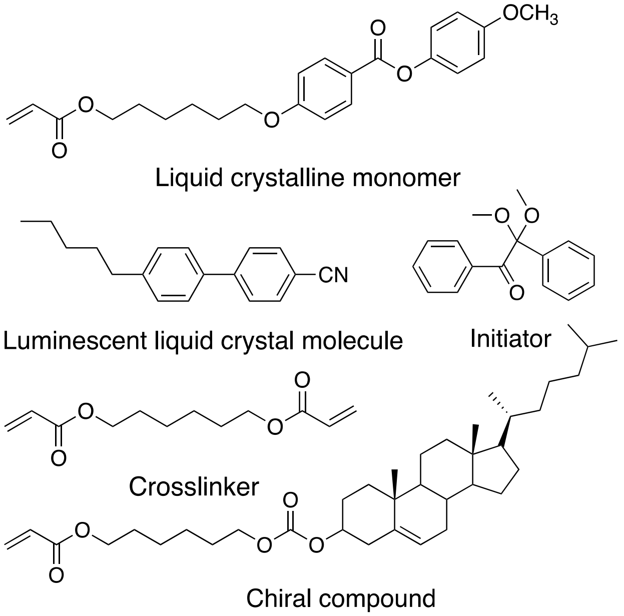

Figure 1. Chemical structures of a monomer mixture used in this study.

The chemical structures of materials used in this study are shown in Figure 1. To produce the film, we utilized photopolymerization by exposing the monomer mixture to UV light with at 365 nm in a glass cell. The resulting film and its reflectance spectra are shown in Figure 2. We observed the emission spectrum of the film using a circularly polarized light filter, as shown in Figure 3. We found that at 0% tensile strain, the reflection band and emission peak of the film coincided at 410 nm. We also confirmed that the film showed left-handed circular polarized emission with a *g* value of approximately 10^{-1} at 410 nm.

1) K. Hisano, O. Tsutsumi, *et al.*, *Adv. Funct. Mater,* **2021**, 2104702.

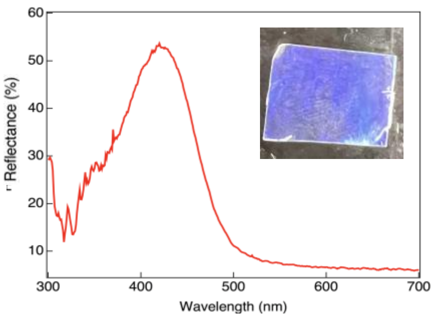

Figure 2. The image of the film and its reflectance spectra

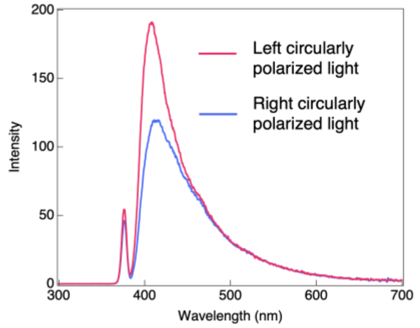

Figure 3. The luminescent spectra of the film

Construction of Probabilistic Model on Interior Crack Nucleation and Propagation in Very High Cycle Fatigue of High Strength Steels

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Introduction

In very high cycle regime, the fatigue crack of high strength steels tends to occur around the interior inclusion, and fine granular area (FGA) is formed around the inclusion. The fatigue crack growth rate in the FGA is less than the Bergur's vector and lattice constant of the steel. How can we interpret such a low rate of the fatigue crack growth? This question is the fundamental motivation of the present study.

Fractography of fatigue crack growth inside the material and its probabilistic model

The authors have carried out fatigue tests for the bearing steel (SUJ2) in rotating bending toward the very high cycle regime of 10^9 cycles. Fig.1 indicates the SEM observation of the fracture surface around inclusion, in which a clear FGA is found around the inclusion[1]. Fig2(a) represents the FGA replaced by a number of fine cells, whereas Fig.2(b) indicates the definition of the crack length *a* (radius of penny-shape crack).

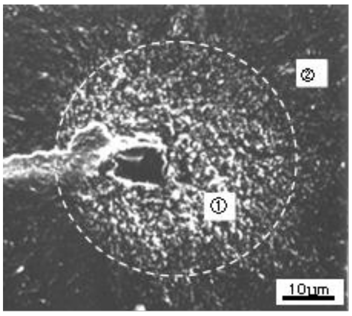
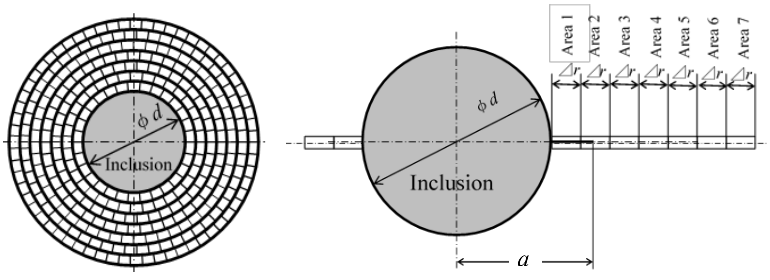


Fig.1 FGA formed around inclusion



(a) Cell division (b) Definition of virtual crack length within FGA

Fig.2 Cell division and definition of crack length within fine granular area (FGA)

Then, the crack length is given as follows;

$$a = \frac{d}{2} + 7\Delta r \frac{n_c}{n_t} = \frac{d}{2} + 7\Delta r P(N) \qquad (1)$$

where n_t is total number of cells inside the FGA, n_c is the number of debonded cells and *P(N)* denotes the debonding probability, respectively. Thus, we obtain the crack growth rate by Eq.(2).

$$\frac{da}{dN} = 7\Delta r \frac{dP(N)}{dN} \qquad (2)$$

Accepting the intermittent and discrete cell debonding together with an appropriate function as *P(N)*, the crack growth law indicated by thick line in Fig.3 is obtained through numerical analysis. The analytical result is in good agreement with the experimental results by some researchers.

Conclusion

The crack growth behavior within FGA is well interpreted by introducing the intermittent and discrete debonding model combined with an appropriate function of *P(N)*.

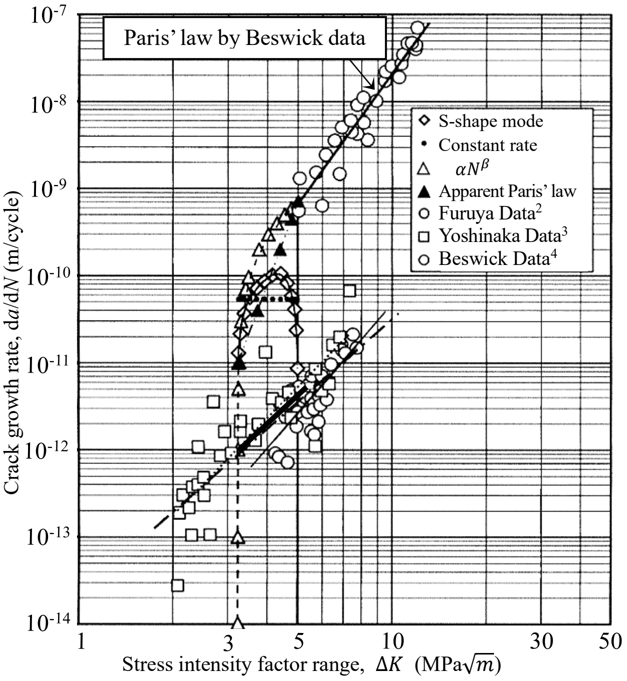


Fig.3 Relationship between da/dN and ΔK

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3) F. Yoshinaka et al., *J Soc Mat Sci, Japan*, Vol.66, **2017**, p.928. 4) J. M. Beswick, *Metal. Trans.*, Vol.20A, **1989**, p.1961.

Excited-State Dynamics of 1-Pyrenecarboxylic Acid-Coordinated ZnS Nanocrystals

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Organic-inorganic hybrid nanomaterials have attracted much attention in recent years for their applications in photocatalysis and photon upconversion. While efficient electron transfer and long-lived charge-separated states often play important roles in such hybrid nanomaterials, their fundamental understanding is still insufficient because of the lack of the variety of these hybrid nanomaterials. In this study, we report on the synthesis of 1-pyrenecarboxylic-acid-coordinated zinc sulfide (ZnS) NCs (PCA-ZnS) as a model system and investigated their optical properties (Fig. 1a).

PCA-ZnS was prepared simply by mixing PCA and ZnS NCs in chloroform. The absorption spectra of PCA-ZnS in chloroform at low concentrations of PCA and ZnS NCs (9.1×10^{-7} and 4.2×10^{-8} M for PCA and ZnS NCs, respectively) are almost identical to the superposition of the absorption spectra of PCA and ZnS NCs, suggesting that there is no electronic interaction, i.e., PCA is not coordinated to the surface of ZnS NCs under the condition. On the other hand, the absorption spectrum of PCA-ZnS with the concentration of (2.1×10^{-4} and 9.6×10^{-6} M for PCA and ZnS NCs, respectively) is different from those of the superposition of PCA and ZnS NCs, suggesting that PCA is coordinated to the surface of ZnS NCs. (Fig. 1b) The weak coordination of PCA may be due to the direct substitution of the carboxy group on pyrene for PCA.

To reveal the excited-state dynamics of PCA-ZnS, transient absorption spectra were measured using a 360-nm femtosecond pulse as the excitation light. In PCA-ZnS in chloroform, additional small transient absorption band in addition to the excited-state absorption of the S1 at 510 nm was observed at 450 nm. Considering the potentials of PCA and ZnS NCs, selective excitation of pyrene at 360 nm is expected to induce electron transfer from the lowest unoccupied molecular orbital (LUMO) of pyrene to the conduction band (CB) of ZnS. Since the cation radical of pyrene is reported to be observed around 450 nm, this result suggests that a fast electron transfer has occurred in PCA-ZnS.

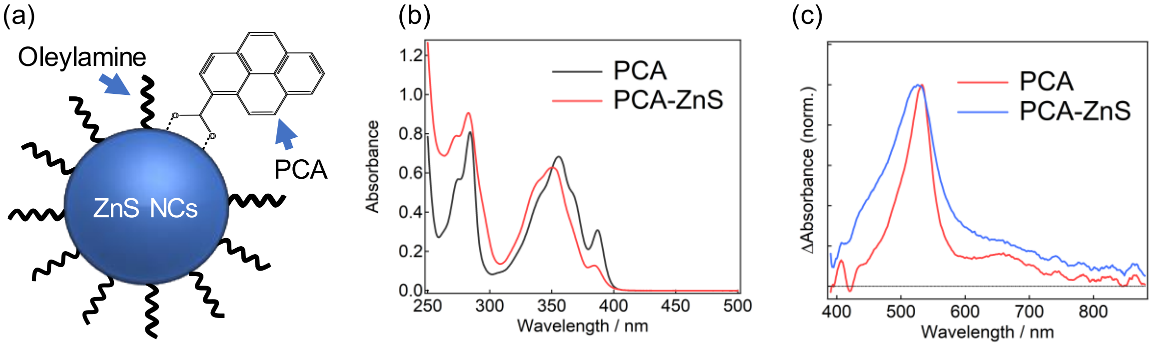

Fig. 1 (a) Schematic of PCA-ZnS and (b) The absorption spectra of PCA and PCA-ZnS (PCA/ZnS = 22) in chloroform; 2.1×10^{-4} M PCA in the 1-mm cuvette. (c) The transient absorption spectra at 30 ps of PCA and PCA-ZnS exited with a 360 nm femtosecond laser pulse (20 nJ/pulse).

Effect on Nanocrystal Surface on Photochromism of Cu-Doped ZnS Nanocrystals

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Doping of metal ions to semiconductors is an effective way to modify the electrical, optical, and magnetic properties of semiconductor nanocrystals (NCs). For example, the introduction of transition-metal dopants such as Cu and Mn ions forms midgap states between the valence and conduction bands of host semiconductor NCs, which largely alter optoelectrical properties of NCs. Recently, our group reported that hydrophilic Cu-doped ZnS NCs exhibit relatively fast T-type photochromism, which is brought by hole trapping in the Cu level and interparticle electron hopping.[1] The NCs show more efficient photosensitivity than other inorganic photochromic materials and exhibit temperature-insensitive color fading at around room temperature.[2] In addition, Cu-doped ZnS NCs are composed of earth-abundant atoms and are easy to synthesize in large quantities. Therefore, this material is promising for large-scale industrial applications. For industrial use such as paint materials, however, solubility in organic solvents is strongly desired. In this study, we synthesized organic solvent-soluble Cu-doped ZnS NCs and investigated the photochromic properties.

Hydrophobic Cu-doped ZnS NCs were synthesized by the hot-injection method using oleylamine (OLA) as surface ligand. The color of Cu-doped ZnS NCs in chloroform reversibly changes from pale yellow to dark brown by UV light irradiation. A broad absorption band is observed in the visible light region (Fig. 1 (a)). Because the observed absorption spectra are very similar to that of phidrophic Cu-doped ZnS NCs, it suggests that the origin of coloration is the same mechanism as the previous study: the electronic transition from the valence band to the Cu^{2+} level (Fig. 1 (b)).[1] It takes several minutes in the color fading reaction, and it is relatively longer than the hydrophilic Cu-doped ZnS NCs in the previous report.

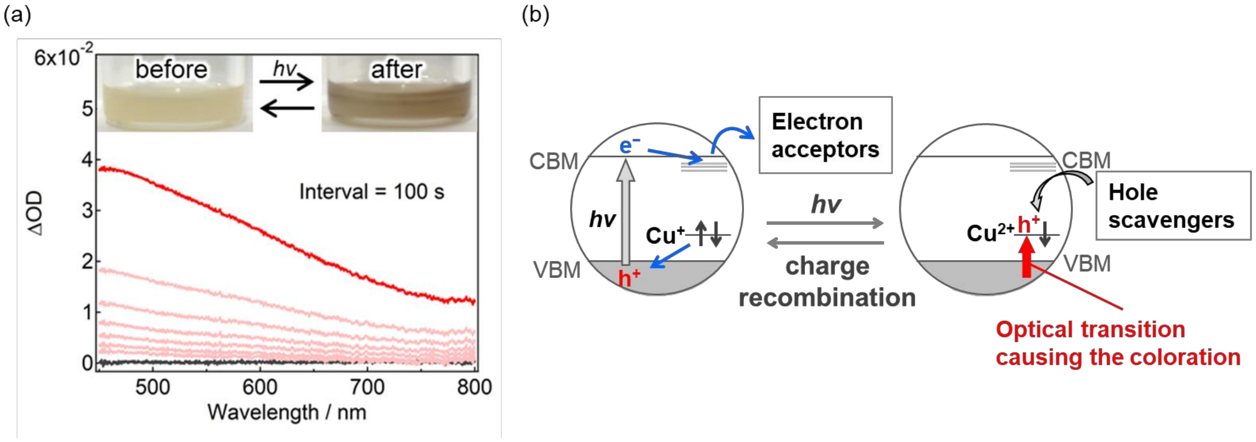

Fig. 1 (a) Photographs and time evolution of the differential absorption spectrum of the Cu-doped ZnS NCs in chloroform after continuous-wave UV irradiation (365 nm, 150 mW cm^{-2}) for 30 s and (b) plausible coloration scheme of Cu-doped ZnS NCs in organic solvents after 365 nm UV irradiation.

1) Y. Han, M. Hamada, I.Y. Chang, K. Hyeon-Deuk, Y. Kobori, Y. Kobayashi, *J. Am. Chem. Soc.* **2021**, *143*, 2239.
2) Y. Sanada, D. Yoshioka, Y. Kobayashi, *J. Phys. Chem. Lett.* **2021**, *12*, 8129.

Excited-State Dynamics of Phenothiazine Derivative Having a Quinoidal Structure

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Organic dyes that responses to the longer wavelength are important for dye-sensitized solar cells, triplet sensitizers, and photopharmacology because long-wavelength light is low phototoxicity, higher transmittance of matter, and higher selectivity for excitation. Organic molecules that have quinoidal structures are one of the efficient molecular frameworks to increase the absorptive properties in longer wavelength light. However, the lifetimes of the excited states of these compounds are generally extremely short due to nonradiative relaxations, which limit the potentials of their applications. In this study, we synthesized a phenothiazine derivative with quinoid structure **1** (Fig.1a) and investigated the excited-state dynamics.

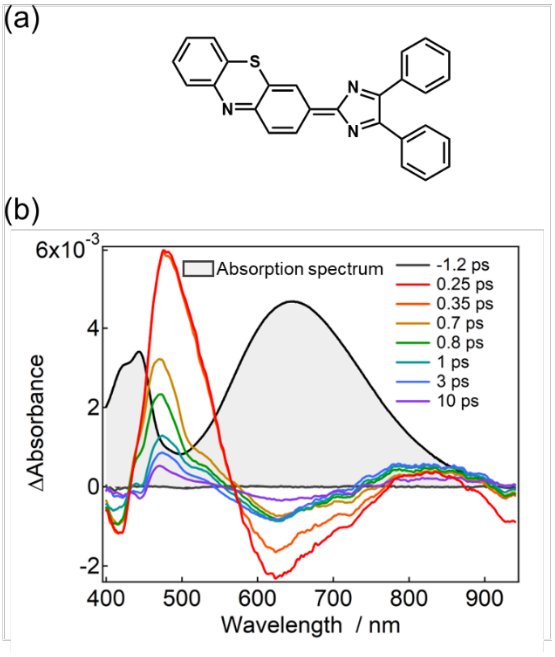

Fig.1 (a) Molecular structure, and (b) the steady-state and transient absorption spectra of **1** in acetonitrile (9.0×10^{-5} M) excited with a 650-nm femtosecond laser pulse (20 nJ/pulse) at room temperature.

Fig.1b shows the steady-state absorption spectrum and the transient absorption spectra of **1** in acetonitrile excited with a 650-nm femtosecond laser pulse. After the excitation of **1** in acetonitrile with a 650-nm laser pulse at 360 K (Fig.1b), ground-state bleach signals were observed at 410 nm and 620 nm, and an excited- state absorption signal was observed at 480 nm. Because **1** does not have any absorption at >900 nm, the negative signal at 950 nm is ascribed to the stimulated emission. The transient absorption signal at ~480 nm was blue-shifted, and the spectral shape also changed slightly. Subsequently, a component showing a broad absorption gradually appeared at 800 nm, and it decayed to the ground state with a time constant of 10 ps. These results suggest the deactivation process involves the conical intersection because the deactivation rate is extremely fast.

Spatiotemporal Control of Photochromic Reactions Based on Oxygen Transfer Suppressed in Supramolecular Gel

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In photofunctional materials utilizing triplet excitons, preventing triplet quenching by molecular oxygen (O_2) is an important issue. On the other hand, if the triplet quenching process can be arbitrarily controlled rather than simply prevented, it will lead to the development of unique photoresponsivity. In this study, we focus on the photochromic reaction of anthraquinone (AQ, Fig. 1a) as a model reaction.[1] The colorless and nonemissive AQ form is converted to the yellow and emissive AQH_2 form via photoexcitation to the S_1 state and subsequent intersystem crossing to the T_1 state, while the AQH_2 form is reversibly oxidized to AQ by O_2. We achieved spatiotemporal control of this photochromic reaction based on O_2 transfer suppressed in a supramolecular gel.[2]

A supramolecular gel was prepared by adding a gelator to a methanol solution of AQ containing triethylamine as a singlet oxygen scavenger. When this gel was irradiated with 365-nm light, a new absorption peak at around 400 nm was produced due to the photoreduction to AOH_2 (Fig. 1b). Interestingly, the absorbance at 400 nm remained unchanged for the initial stage of the photoirradiation and began to increase several tens of seconds after starting the irradiation. This unique behavior is explained as follows; At first, the photogenerated T_1 state of AQ is quenched by O_2 dissolved in the gel to produce singlet oxygen and then the singlet oxygen is consumed mainly by reaction with triethylamine. Because O_2 supply from the air through diffusion and convection is efficiently suppressed due to the supramolecular gel network, the O_2 concentration in the gel is gradually decreased, which finally triggers the photoreduction of AQ via the T_1 state. In addition, while the AQH_2 showed a lifetime of over 1 hour in the gel state, the decoloration was completed instantly upon the gel-to-sol transition by heating. This is because the sol state allows quick O_2 supply from the air in contrast to the gel state. Moreover, spatiotemporal patterning and on-demand erasing of the photochromic reaction were conducted to demonstrate the potential in application to cryptography and display devices.

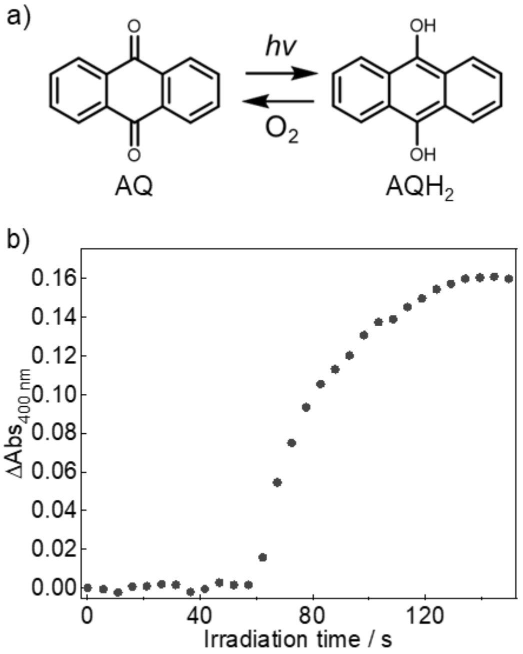

Fig.1 a) Photochromic reaction of AQ, b) Absorbance change of the MeOH gel of AQ under 365-nm light irradiation.

1) K. Hamanoue, T. Nakayama, Y. Yamamoto, K. Sawada, Y. Yuhara, H. Teranishi., *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1121.
2) P. Duan, N. Yanai, H. Nagatomi, N. Kimizuka, *J. Am. Chem. Soc.* **2015**, *137*, 1887.

Controlling Optical Properties of ZnO Nanocrystals by Bulkiness of Alkyl Ligands

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Organic ligands on the surface of semiconductor nanocrystals (NCs) are important for the chemical stability and dispersibility of colloidal NCs. Aliphatic ligands are generally used as ligands to enhance the dispersion of NCs, and in terms of electronic interactions, they do not seem to affect the photophysical properties of NCs. On the other hand, insufficient coverage of the surface ligands leads to the formation of structural defects on the NC surface, which have a significant impact on the optoelectrical properties of NCs. Therefore, systematic investigation of the effect of the molecular structures of ligands on the optical properties of NCs is indispensable even in aliphatic ligands. In this study, we synthesized a series of alkylphosphonic-acid-capped zinc oxide (ZnO) NCs (L1S-L3 in Fig. 1a) as a model system and investigated their photophysical properties.

The as-synthesized ZnO NCs have acetic acid as the surface ligand, and then the ligands are replaced with each type of phosphonic acids. Fourier transformed infrared absorption (FT-IR) spectra show that both acetic acid and phosphonic acid were coordinated on the NCs as the ligand. The average diameter of ZnO NCs was 6.45 nm.

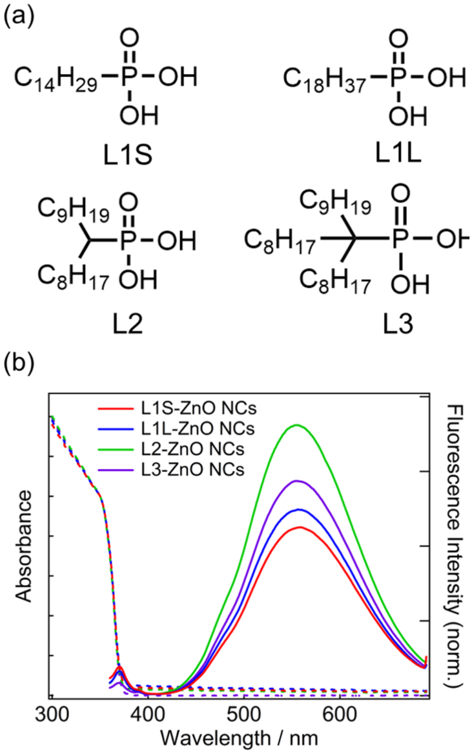

Fig 1. (a) Molecular structures of phosphonate ligands and (b) the absorption and fluorescence spectra of phosphonate-capped ZnO NCs in chloroform (λ_{ex} = 350 nm)

The absorption edge of ZnO NCs dispersed in chloroform is 371 nm (3.34 eV), which is slightly larger than the bandgap of bulk ZnO (3.3 eV) due to the quantum size effect.[1] When excited by UV light (350 nm), two emission bands were observed at around 370 and 550 nm. The emission band at the shorter wavelength is ascribed to the band-edge excitonic emission, and that at the longer wavelength is ascribed to the emission from oxygen defects.[2] Structural defects mostly emerge around the surface than inside of NCs. Therefore, it is expected that the bulky ligands increase the number of defects on surface of NCs and the photoluminescence quantum yield (PLQY) increases because the bulky ligands decrease the density of the ligands on the surface of NCs and results in the insufficient surface coverage. The PLQY of L1L-, L2-, and L3-ZnO NCs were 3.5, 4.9, and 4.0%, respectively. The reason why the lower PLQY of ZnO NCs covered with tertiary ligands is probably because L3 is too bulky to be exchanged with acetic acid, which effectively coordinated to the surface of NCs. The larger amount of acetic acid in L3-ZnO is supported by the Fourier-transformed infrared spectroscopy.

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Synthesis and Optical Properties of ZnTe/ZnS Core-Shell Nanocrystals

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ZnTe is a visible-light-responsive semiconductor with a direct transition band gap of 2.26 eV. Because of this feature, it is expected to be used for green LEDs and solar cells. In general, semiconductor nanocrystals (NCs) are expected to improve luminescence quantum yield and high reactivity as photocatalysts compared to the bulk state. However, ZnTe NCs are easily decomposed by light irradiation, which has been a serious challenge in their application. Although covering ZnS layers around ZnTe NCs to confine excitons has been reported as a useful method to improve the photostability,[1] the detail such as excitation dynamics is unclear. In this study, we synthesized ZnTe/ZnS core-shell NCs and compared the stability and excited-state dynamics with those of ZnTe NCs. Understanding the excited-state dynamics will provide additional insight into their use as photofunctional materials.

ZnTe NCs were synthesized by hot injection using oleic acid as ligands.[2] The ZnS shell was grown on the ZnTe core using the successive ionic layer adsorption and reaction (SILAR) method in octadecene. ZnTe NCs and ZnTe/ZnS NCs were characterized by X-ray diffraction (XRD) measurements, X-ray fluorescence analysis, and transmission electron microscopy. The crystal structure of the ZnTe NCs was zincblende and the average particle diameter was 5.4 nm (Fig. 1a,b). The average diameter increases to 6.9 nm by the shell growth process. Because the length of the monolayer of ZnS shell is estimated to be 0.32 nm from the crystal structure, the change of the diameter from 5.3 to 6.9 nm by the shell growth process indicates that the 2.5 monolayers of ZnS were grown on the surface of ZnTe NCs. Furthermore, the absorption spectrum of ZnTe/ZnS NCs exhibited red-shifted band-edge absorption compared to ZnTe NCs (Fig. 1c, solid lines), which indicates that the bandgap was decreased due to the quantum size effect, i.e. the increase in the particle size by shell formation.

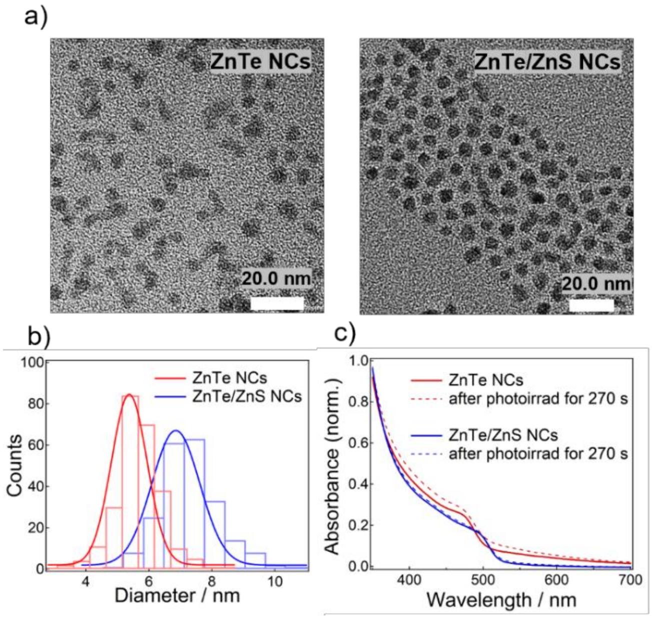

Fig. 1 a) TEM images of ZnTe and ZnTe/ZnS NCs. b) Particle size distribution of ZnTe and ZnTe/ZnS NCs. c) Absorption changes of ZnTe/ZnS and ZnTe NCs under light irradiation (360 nm, 72 mW/cm^2)

Air- and photo-stability of the NCs in hexane were evaluated from the UV-Vis spectral changes. Both in the air-saturated solution in the dark and in the N_2-atmosphere solution under UV light (365 nm, 72 mW cm^{-2}), the spectral change of ZnTe/ZnS NCs was small compared to that of ZnTe NCs (Fig. 1c). This result shows that the formation of ZnS layer enhanced the air- and photo-stability. In addition, transient absorption spectroscopy was conducted to compare the excited state dynamics. A positive broad signal, which may originate from surface defects, was observed in both samples. This signal intensity was weaker in the ZnTe/ZnS NCs, which suggests that some surface defects on the ZnTe core were removed by the ZnS layer formation.

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