Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry：Oral B

Wed. Mar 26, 2025 1:00 PM - 3:20 PM JST | Wed. Mar 26, 2025 4:00 AM - 6:20 AM UTC
[B]A501(A501, Bldg. 1, Area 2 [5F])

[[B]A501-1pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Katsuhiro Isozaki, Yasuhiro Funahashi

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[[B]A501-1pm-01]

Solvent Vapor-Induced Chirality Switching in Luminescent Aluminium(III) Complex

○FUMIYA KOBAYASHI[1], RIUJI ASANO[1], MAKOTO TADOKORO[1] (1. Tokyo Univ. of Sci.)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[[B]A501-1pm-02]

Photoluminescence properties of visible light responsive dinuclear Zn(II) and Cd(II) complexes

○Eri Matsuo[1], Takahiro Maruchi[1], Yoshimasa Wada[1,2], Yusuke Sunada[1,2] (1. Graduate School of Engineering, The University of Tokyo, 2. Institute of Industrial Science, The University of Tokyo)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[[B]A501-1pm-03]

Reactivity and Catalytic Application of Aluminum Complexes with Two Phosphino Groups-Substituted Carbon Ligand

○Hirotaka Okamoto[1], Yoshihiro Nishimoto[1], Makoto Yasuda[1] (1. Graduate School of Engineering, The University of Osaka)

English
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[[B]A501-1pm-04]

Oxidative Cyclization, Insertion and Reductive Elimination on Gallium Complexes Bearing a Phenalenyl-Based Ligand

○Nijito Mukai[1], Takuya Kodama[1,2], Mamoru Tobisu[1,2] (1. Graduate School of Engineering, Osaka University, 2. ICS-OTRI, Osaka University)

English
2:20 PM - 2:40 PM JST | 5:20 AM - 5:40 AM UTC
[[B]A501-1pm-05]

Sm/SmI_2-Induced Reductive Cycloaddition of 1,3-Dienes with Dichlorosilanes

○Zhengwei Chen[1], Tsutomu Mizota[1], Leo Onishi[1], Huiying Mu[1], Koji Miki[1], Akiya Ogawa[2], Kouichi Ohe[1] (1. Kyoto university, 2. Organization for Research Promotion, Osaka Metropolitan University)

English
2:40 PM - 3:00 PM JST | 5:40 AM - 6:00 AM UTC
[[B]A501-1pm-06]

Synthesis, Characterization and Reactivity of NHC adorned Au-Pt Nanoclusters

○Joseph Felix DeJesus[1], Samuel I. Jacob[1], Masakazu Nambo[1,2], Cathleen M. Crudden[1,3] (1. Institute of Transformative Bio-Molecules, 2. Department of Chemistry, Graduate School of

Science, Nagoya University, 3. Department of Chemistry, Queen’s University)

🏷 Japanese

3:00 PM - 3:20 PM JST | 6:00 AM - 6:20 AM UTC

[[B]A501-1pm-07]

Accelerated Catalysis of Gold Nanocluster towards Cyclization of Alkynoic Acids Enabled by Supramolecular Reaction Field

○Kyosuke UEDA[1], Kenta ISERI[1], Masaharu NAKAMURA[1], Katsuhiro ISOZAKI[1] (1. Kyoto University)

溶媒蒸気応答性金属錯体におけるキラル集積化制御と光機能開拓

（東理大理 [1]） ○小林 文也 [1]・浅野 龍樹 [1]・田所 誠 [1]

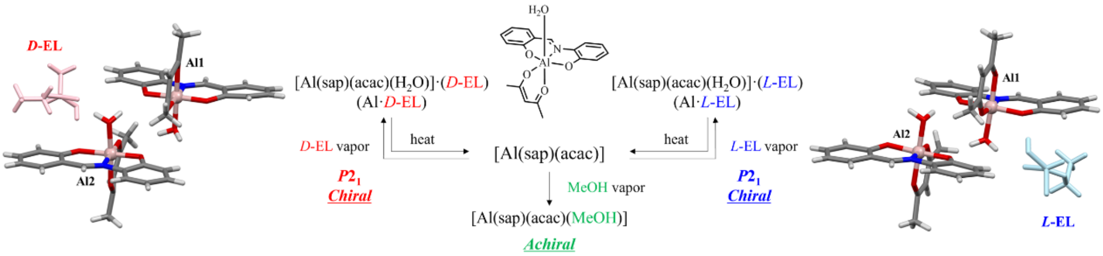
Solvent Vapor-Induced Chirality Switching in Luminescent Aluminium(III) Complex

([1]*Department of Chemistry, Faculty of Science, Tokyo University of Science*) ○ Fumiya Kobayashi,[1] Riuji Asano,[1] Makoto Tadokoro[1]

Vapor-induced functional switching systems, which exhibit facile structural transformations in response to specific vapor stimuli, have been reported; such transformations include changes in magnetic properties and luminescence properties. In our previous study, we demonstrated that mononuclear complexes, incorporating a substitution-prone coordination site, could switch dielectric behavior and polarity, which was attributed to the structural transformations triggered by exposure to solvent vapor.[1-3] The study provided a novel example of vapor-induced polarity switching systems, wherein coordinated solvent substitution was the ‘trigger' for the corresponding structural rearrangements. Thus, expanding the scope of application of the above system to other type compounds is highly desirable for the development of multifunctional molecular materials. Herein, we report the achievement of solvent vapor-induced chiral molecular arrangement switching in luminescent crystals of the type $[Al(sap)(acac)(H_2O)]\cdot(EL)$ (EL = Ethyl Lactate).

Keywords : Aluminium(III) Complex; Chiral Molecular Arrangement; Luminescence Property; Solvent-Vapor Responsive

ゲスト分子などの外部刺激に応答する分子性化合物はセンシング技術などへの応用の観点から注目を集めている。当研究室ではこれまでに、溶媒蒸気曝露による配位溶媒の置換反応を駆動力とした集積構造制御が可能な六配位八面体型単核錯体 $[M^{III}(sap)(acac)(solvent)]$ (M = Fe, Al; H_2sap = 2-salicylidenenaminophenol; acac = acetylacetonate) を用いた集積構造変換システムを報告している。[1-3] 本研究では、円偏光発光（CPL）などの特異的なキラル物性を示すキラル化合物群へと展開することによって、キラル集積化の制御を目指した。キラル溶媒である (*D*, *L*)-Ethyl Lactate を使用することによって、溶媒蒸気曝露による可逆的なキラル集積化制御が可能な高発光性アルミニウム(III)錯体の開発に成功した。



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1) F. Kobayashi, *et al*., *Chem. Commun*., **2020**, 56, 10509-10512. 2) F. Kobayashi, *et al*., *Chem. Eur. J*., **2023**, 29, e202203937. 3) F. Kobayashi, *et al*., *Dalton Trans*., **2024**, 53, 11689-11696.

日本化学会 第105春季年会 (2025)

可視光吸収性 Zn および Cd 二核錯体の発光特性評価

（東大院工 [1]・東大生研 [2]）○松尾　絵理 [1]・丸地　貴大 [1]・和田　啓幹 [1,2]・砂田　祐輔 [1,2]

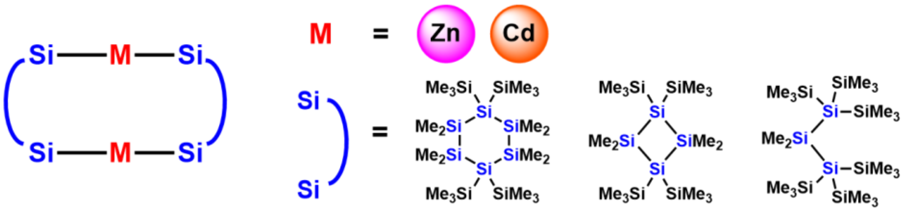
Photoluminescence properties of visible light responsive dinuclear Zn(II) and Cd(II) complexes.

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*institute of Industrial Science, The University of Tokyo*) ○Eri Matsuo,[1] Takahiro Maruchi,[1] Yoshimasa Wada,[1, 2] Yusuke Sunada[1, 2]

Complexes based on group 12 elements are known to be less responsive to visible light than those of other d-block elements. Recently, we have developed a dinuclear Zn(II) complex capable of absorbing visible light, leveraging intermetallic interactions between two Zn(II) centers in close proximity. Additionally, we expanded the molecular design by synthesizing visible light responsive dinuclear Zn(II) complexes with various organosilyl ligands, as well as dinuclear Cd(II) complexes. Based on analyses from single crystal X-ray diffraction measurements and photophysical measurements, we derived that the twisted spatial arrangement of the metal centers together with the coordinated ligands is important as well as the short metal-metal atom distance, to develop visible light-absorbing dinuclear complexes featuring group 12 elements. In this study, we report the effect of metal centers on photoluminescence performance of these dinuclear Zn(II) and Cd(II) complexes, supported by a series of photophysical measurements and theoretical calculations.

Keywords : zinc; cadmium; intermetallic interaction; visible light absorption/emission

周期表第 12 族の亜鉛(Zn)族元素を中心金属に有する錯体は、他の d ブロック元素である第 3-11 族元素の場合と比較し、可視光応答性に乏しいことが知られている。一方で、当研究室では、2 つの Zn 原子間に働く軌道相互作用の利用により、ケイ素配位子により架橋された可視光応答性 Zn 二核錯体が創出可能であることを見出した [1)]。また、上記手法が類似の有機ケイ素配位子および同族の Cd に拡張できることも見出し、多様な可視光吸収を示す Zn および Cd 二核錯体を合成した。単結晶 X 線構造解析および光物性測定による解析から、12 族元素を中心金属に有する二核錯体において、効果的な可視光吸収には、短い金属原子間距離に加え、配位子を含めた金属中心のねじれた空間配置が重要であることがわかった。本研究では、それらの Zn および Cd 二核錯体に対し、種々の光物性測定および量子化学計算による解析から、中心金属が錯体の発光物性に与える影響を考察したので報告する。



1) Wada, Y.; Maruchi, T.; Ishii, R.; Sunada, Y. *Angew. Chem. Int. Ed.*, **2023**, *62*, e202310571.

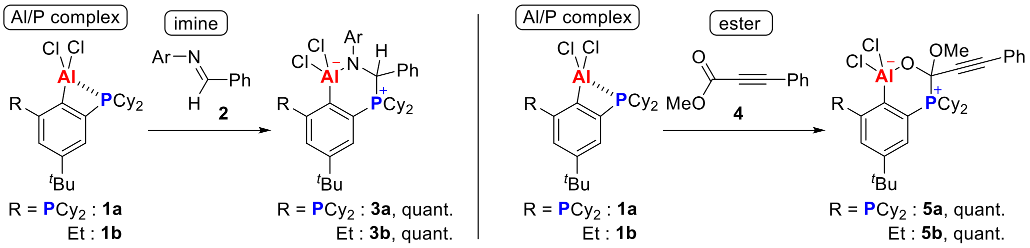
Reactivity and Catalytic Application of Aluminum Complexes with Two Phosphino Groups-Substituted Carbon Ligand

(*Graduate School of Engineering, Osaka University*) ○Hirotaka Okamoto, Yoshihiro Nishimoto, Makoto Yasuda

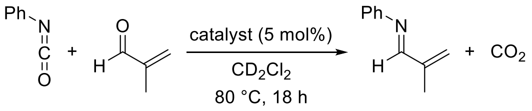
Keywords: Lewis acid/Lewis base catalysts; Aluminum; Phosphino group

Utilization of aluminum complexes as Lewis acid catalysts is significant in organic synthesis due to the abundance and low toxicity of aluminum. The properties of organoaluminum complexes can be electronically and sterically controlled by modifying their hydrocarbyl ligands.[1] In this study, we synthesized organoaluminum complexes **1a** and **1b** with one or two phosphino groups at the ortho positions of the aryl substituent.[2,3]

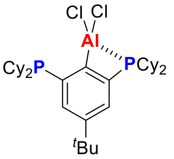
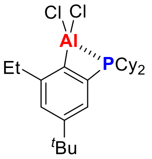
Complexes **1a** and **1b** reacted with imine **2** to give the addition product **3a** and **3b**, respectively. The addition reaction with ester **4** also proceeded to afford **5a** and **5b**, respectively. In these reactions, the aluminum center and the phosphino group act as a Lewis acid and a Lewis base, respectively. Thanks to high Lewis acidity of the dichloroaluminum moiety, complexes **1a** and **1b** can activate imines and esters in contrast to previously reported Al/P complexes.[3]



On the other hand, we observed differences in the following catalytic reaction with complexes **1a** and **1b**. In the reaction of isocyanates with unsaturated aldehydes to give imines, complex **1a** having two phosphino groups was found to be more efficient than complex **1b** having one phosphino group.



The catalyst with two phosphino groups enhanced the yield.

catalyst		
	1a	**1b**
yield	64%	3%

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1) a) H. Yamamoto *et al.*, *J. Am. Chem. Soc.* **1985**, *107*, 4573. b) Y. Nishimoto, S. Nakao, S. Machinaka, F. Hidaka, M. Yasuda, *Chem. Eur. J.* **2019**, *25*, 10792. c) S. Nakao, Y. Nishimoto, M. Yasuda, *Chem. Lett.* **2021**, *50*, 538.
2) a) K. Lammertsma, W. Uhl *et al.*, *Angew. Chem. Int. Ed.* **2011**, *50*, 3925. b) F. -G. Fontaine *et al.*, *Organometallics* **2013**, *32*, 6804. c) C. Limberg *et al.*, *Chem. Commun.* **2022**, *58*, 13451. d) N. W. Mitzel *et al.*, *Chem. Sci.* **2022**, *13*, 8088.
3) a) W. Uhl *et al.*, Chem. Eur. J. **2018**, *24*, 12856. b) Y. Mizuhara, N. Tokitoh *et al.*, *ChemPlusChem* **2020**, *85*, 933.

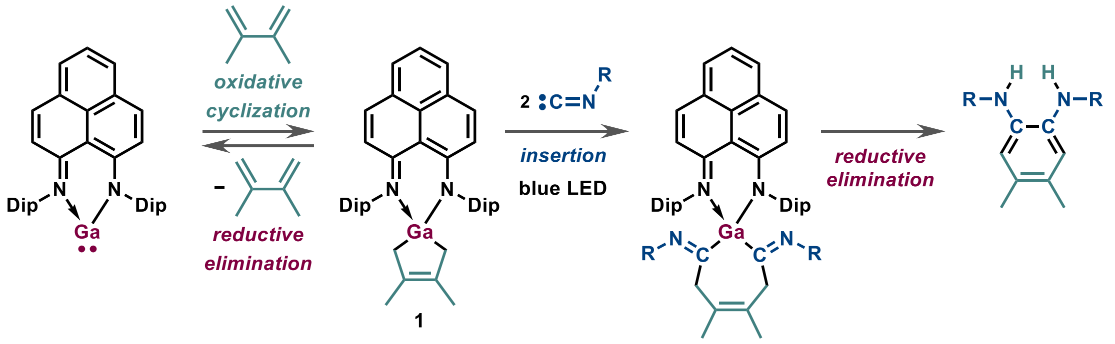
Oxidative Cyclization, Insertion and Reductive Elimination on Gallium Complexes Bearing a Phenalenyl-Based Ligand

([1]*Graduate School of Engineering, Osaka University*, [2]*ICS-OTRI, Osaka Univ.*)
○Nijito Mukai,[1] Takuya Kodama,[1,2] Mamoru Tobisu[1,2]

Keywords: Gallium, Low-Valent Complex, Visible Light, Oxidative Cyclization, Reductive Elimination

The transition metal-like reactivity of p-block elements, particularly involving two-electron redox processes at the central element, has garnered significant attention as a promising next-generation catalytic platform.[1] Recent advances have demonstrated E^{n}/E^{n+2} redox processes for group 14 and 15 elements in catalysis.[2,3] However, such redox behavior on group 13 elements remains unexplored, primarily due to the inherent instability of the reduced E^{I} species.

Our group recently reported on Ga^{I} complexes bearing a phenalenyl-type bidentate ligand, which undergoes oxidative cyclization with 1,3-diene to yield complex **1**.[4] Herein, we demonstrate that complex **1** undergoes visible-light-induced reductive elimination via C–Ga bond cleavage to regenerate the initial Ga^{I} complex. When photo-irradiated in the presence of isocyanide, the two isocyanides insert into the C–Ga bond, forming a seven-membered gallacycle. Furthermore, we achieved reductive elimination from the double-inserted complexes to yield phenylenediamines.



1) P. P. Power, *Nature* **2010**, *463*, 171.
2) Selected example for 14 group elements: T. Sugahara, J. Guo, T. Sasamori, S. Nagase, N. Tokitoh, *Angew. Chem. Int. Ed.* **2018**, *57*, 3499.
3) Selected example for 15 group elements: N. L. Dunn, M. Ha, A. T. Radosevich, *J. Am. Chem. Soc.* **2012**, *134*, 11330.
4) T. Kodama, N. Mukai, M. Tobisu, *Inorg. Chem.* **2023**, *62*, 6554.

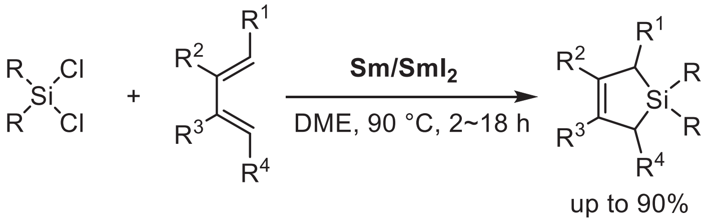
Sm/SmI$_2$-Induced Reductive Cycloaddition of 1,3-Dienes with Dichlorosilanes

([1]*Graduate School of Engineering, Kyoto University*, [2]*Organization for Research Promotion, Osaka Metropolitan University*) ○Zhengwei Chen,[1] Tsutomu Mizota,[1] Leo Onishi,[1] Huiying Mu,[1] Koji Miki,[1] Akiya Ogawa,[2] Kouichi Ohe[1]

Keywords: Dichlorosilane; SiR$_2$ Transfer Reaction; Samarium; Conjugated Diene; [1+4]-cyclization

As one of the most attractive methods, a direct transfer of silylene (SiR$_2$) moieties to unsaturated organic compounds is desired in construction of silacarbocycles. Representative protocols have been established using well-defined precursors as SiR$_2$ synthons.[1] However, the limited availability of silylene precursors has prompted us to explore the use of easily accessible raw materials as silylene equivalents. Dichlorosilanes are commercially available reagents for reductive silylene transfer reactions, basically achieved by harsh conditions like alkali metals. It was only recently that chemists explored a mild catalytic SiR$_2$ transfer to unsaturated compounds using dichlorosilanes, which still requires specific ligands synthesized from multistep procedures.[2]

Samarium reagents find extensive use in organic synthesis, yet their utility in organosilicon chemistry remain underexplored. Although the reductive polymerization of dichlorosilane induced by Sm/SmI$_2$ has been reported, there have been no reports on Si-C bond formation to date.[3] We envisioned that samarium reagents could achieve reductive SiR$_2$ transfer reactions under mild conditions. Herein, we have developed a facile and efficient SiR$_2$ transfer reaction to 1,3-dienes using Sm/SmI$_2$ and readily obtainable dichlorosilanes. This reaction can be applied to a variety of dienes and dichlorosilanes, affording 1,4-dihydrosiloles in good yields with high diastereoselectivity.



1) a) Cirakovic, J.; Driver, T. G; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 9370. b) Ohmura, T.; Masuda, K.; Takase, I.; Suginome, M. *J. Am. Chem. Soc.* **2009**, *131*, 16624. 2) Qi, L.; Pan, Q.-Q.; Wei, X.-X.; Pang, X.; Liu, Z.; Shu, X.-Z. *J. Am. Chem. Soc.* **2023**, *145*, 13008. 3) Li, Z.; Iida, K.; Tomisaka, Y.; Yoshimura, A.; Hirao, T.; Nomoto, A.; Ogawa, A. *Organometallics* **2007**, *26*, 1212.

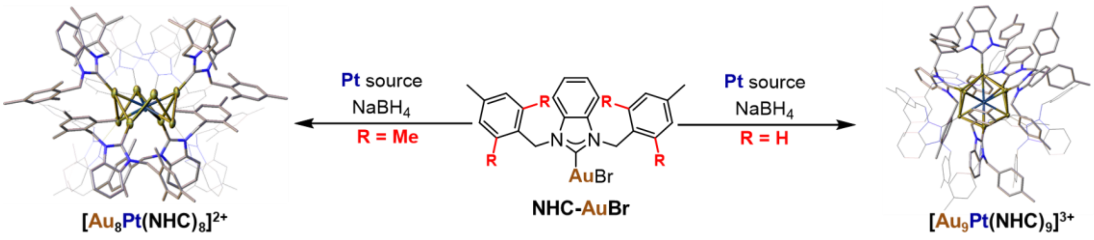
Synthesis, Characterization and Reactivity of NHC Adorned Au-Pt Nanoclusters

(*[1]Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, [2]Department of Chemistry, Graduate School of Science, Nagoya University, [3]Department of Chemistry, Queen's University)* ○Joseph F. DeJesus,[1] Samuel I. Jacob,[1] Masakazu Nambo,[1,2] Cathleen M. Crudden[1,3]

Keywords: gold, platinum, NHC, nanocluster

N-heterocyclic carbenes (NHCs) have increasingly received attention in recent years as a ligand platform for nanomaterials, due to their enhanced thermal and oxidative stability conferred by the NHCs over phosphine and thiolate ligands. Our group[1-3] and others[4-6] have recently utilized Au-NHC complexes to synthesize atomically precise nanoclusters (NCs) that possess greatly enhanced thermal stability and photophysical properties. However, beyond gold, there are very few examples of heterometallic Au NHC clusters.[7,8] Heterometallic nanoclusters are promising nanomaterials for catalysis as they provide opportunities for understanding cooperative reactivity of multiple different metal centers with precise molecular formula.

This presentation details the disparate synthesis of Au-Pt NHC nanoclusters by adjusting the choice of the initial NHC-AuBr complex. We recently reported the first example of Au-Pt NHC nanocluster: $[Au_8Pt(NHC)_8]^{2+}$ through the use of an NHC with CH_2Mes wingtips.[9] This was accomplished by the addition of a 1/8th molar equivalent of a Pt source in the reaction of the reduction of NHC-AuBr with $NaBH_4$. This was possible with both electron rich and poor NHCs, and the cluster was able to electrocatalytically reduce CO_2 to CO. Continuing from the initial report, we have determined conditions to generate a new $[Au_9Pt(NHC)_9]^{3+}$ cluster by using a less sterically encumbered NHC ligand. Both types of Au-Pt NHC clusters, and their derivatives, are fully characterized through multinuclear NMR, ESI-MS, UV-Vis, and SCXRD. The investigation of reactivities through electrochemical and stoichiometric experiments, and formation pathways of each unique nanoclusters will be discussed.



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アルキン酸の金ナノクラスター触媒的環化における超分子反応場による反応加速効果

（京大化研・京大院工）○上田 恭輔・井芹 建太・中村 正治・磯﨑 勝弘

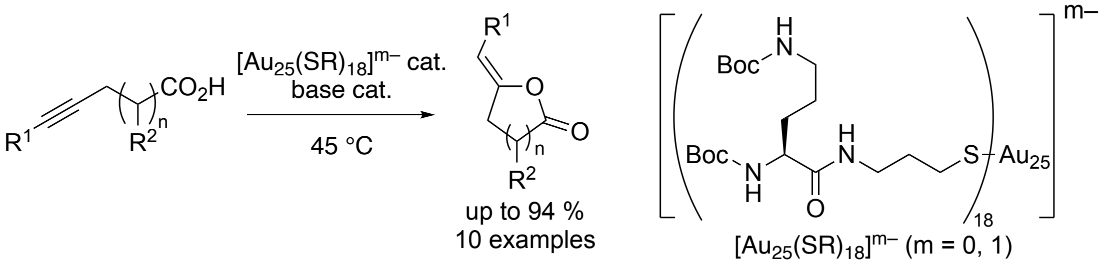
Accelerated Catalysis of Gold Nanoclusters towards Cyclization of Alkynoic Acids Enabled by Supramolecular Reaction Field. *(Institute for Chemical Research, Kyoto University, Graduate School of Engineering, Kyoto University)* ○Kyosuke Ueda, Kenta Iseri, Masaharu Nakamura, Katsuhiro Isozaki

Peptide dendron thiolate ligands serve as a hydrogen bonding supramolecular reaction field thereby accelerating the cyclization reaction of alkynoic acids to alkylidene lactones in the presence of a catalytic amount of catalyzed by $[Au_{25}(SR)_{18}]^-$ nanoclusters. The present study elucidates the screening of ligands, the scope of substrates, and the reaction acceleration effect of the hydrogen bonding reaction field.

Keywords: Gold Nanocluster; Catalyst; Supramolecular Reaction Fields; Cyclization Reaction; Reaction Field.

チオラート保護金ナノクラスターは, 特異な物性と化学反応性を示すことに加えて単一組成の分子として調製できることから, 触媒利用研究が盛んに行われてきた。しかし, 強固な金－チオラート結合が反応基質とクラスター表面との相互作用を阻害するため, 触媒活性が低いことが課題とされてきた。我々は多数の水素結合点を有するペプチドデンドロンチオラート配位子を用いることで, Au_{25}ナノクラスター（Au_{25}NC）上に水素結合性超分子反応場が構築され, Au_{13}超原子コアの光増感作用に基づく光触媒反応[1]が効率よく進行することを見出している。本研究ではAu_{25}NCを触媒としたアルキン酸環化反応における, 水素結合性超分子反応場による反応加速効果について検討を行った。

4-ペンチン酸のクロロホルム溶液に対しそれぞれ触媒量の塩基およびAu_{25}NCを添加し, 45 °Cに加熱することで対応する環化生成物が94%の収率で得られた。また, ペプチドデンドロン配位子の世代数検討により, 水素結合性超分子反応場による反応加速効果を明らかにした。更に, Au_{25}NCとアルキン酸－アミン塩の会合実験により, 配位子－基質間の水素結合が反応速度向上に寄与していることが強く示唆された。本講演では, Au_{25}NCの配位子検討, 基質適用範囲ならびに, 水素結合性超分子反応場の効果について報告する。



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[1] (a) Isozaki, K.; Nakamura, M. et al. *ACS Catal.* **2021,** *11,* 13180–13187. (b) Isozaki, K.; Nakamura, M. et al. *Angew. Chem. Int. Ed.* **2024,** *63,* e202312135.