

アカデミックプログラム [B講演] | 19. コロイド・界面化学：口頭B講演

2025年3月26日(水) 13:30 ~ 15:20 [C]C506(第2学舎 2号館 [5階] C506)

[[C]C506-1pm] 19. コロイド・界面化学

座長：古賀 智之、伴野 太祐

◆ 日本語

13:30 ~ 13:50

[[C]C506-1pm-01]

金クラスターのナノ結晶化と光学応答

○佐藤 龍磨¹、大郷 和暉¹、中島 捷吾¹、七分 勇勝^{1,2}、小西 克明^{2,1} (1. 北海道大学北大院環境、2. 北海道大学北大院地球環境)

◆ 英語

13:50 ~ 14:10

[[C]C506-1pm-02]

金クラスターからなる多角形ナノ結晶の形成

○HU XIAOYU¹、七分 勇勝¹、小西 克明¹ (1. 北海道大学)

◆ 英語

14:10 ~ 14:30

[[C]C506-1pm-03]

One-dimensional assembly of gold nanodiscs controlled by DNA hybridization for tunable plasmon coupling

○Melda Taspika¹, Yonamine Yusuke², Mitomo Hideyuki², Ijiro Kuniharu² (1. Graduate School of Life Science, Hokkaido University, 2. Research Institute for Electronic Science, Hokkaido University)

14:30 ~ 14:40

休憩

◆ 英語

14:40 ~ 15:00

[[C]C506-1pm-04]

Development of oxidation responsive supramolecular hydrogel based on glucosamine and peptides bearing methylthiophenyl group

○Onaza Ali¹, Yuki Shintani¹, Shintaro Sugiura¹, Chiho Narazaki², Sayuri L. Higashi^{1,4,5}, Masato Ikeda^{1,2,3,4} (1. United Graduate School of Drug Discovery and Medical Information Sciences, Gifu University, 2. Department of Life Science and Chemistry, Graduate School of Natural Science and Technology, Gifu University, 3. Institute for Glyco-core Research (iGCORE), Gifu University, 4. Center for One Medicine Innovative Translational Research (COMIT), Gifu University, 5. Institute for Advanced Study, Gifu University)

◆ 英語

15:00 ~ 15:20

[[C]C506-1pm-05]

オキシムライゲーションによる糖ペプチド超分子ヒドロゲルのワンポット創製および抗菌材料への応用

○杉浦 進太郎¹、東 小百合²、池田 将^{1,3,4} (1. 岐阜大院連合創薬、2. 岐阜大高等研究院、3. 岐阜大 iGCORE、4. 岐阜大COMIT)

金クラスターのナノ結晶化と光学応答

(北大院環境¹・北大院地球環境²) ○佐藤 龍磨¹・大郷 和暉¹・中島 捷吾¹・七分 勇勝^{1,2}・小西 克明^{1,2}

Nanocrystallizations and optical responses of gold clusters (¹*Grad. Sch. of Env. Sci., Hokkaido Univ.*, ²*Fac. of Env. Earth Sci., Hokkaido Univ.*) ○Ryoma Sato,¹ Kazuki Ogo¹, Syogo Nakajima,¹ Yukatsu Shichibu,^{1,2} Katsuaki Konishi^{1,2}

Recently, aggregation-induced emission (AIE) has been drawing the attention from researchers. We previously reported that the aggregation behavior changed the optical properties of Au₈ clusters from fluorescence to phosphorescence and improved AIE properties¹⁾. Additionally, we also found that the clusters could form size-selective nanocrystals upon the addition of sodium-dodecyl-sulfate (SDS) followed by sonication²⁾. Therefore, this study aims to investigate the effects of heating on the optical properties of Au₈ clusters. According to the results, the addition of 0.2 mM SDS to the Au₈ cluster solution at 50°C resulted in the formation of rhombic nanocrystals, which exhibited a significant enhancement in emission intensity.

Keywords : Self-assembly; Gold cluster; Photochemistry; Surfactant; AIE

近年、分子が分散状態から凝集状態になることで発光特性が変化する凝集誘起型発光 (AIE) が注目されている。当研究室では、[core+exo]型骨格を有し疎水性表面を持つジホスフィン配位 Au₈ クラスター ([Au₈(dppp)₄(CN)₂]²⁺) を凝集させると蛍光から燐光に発光成分が変化し、AIE 挙動を示すことを明らかにした¹⁾。さらに、このクラスターはアニオン性界面活性剤であるドデシル硫酸ナトリウム (SDS) ミセル内包後、超音波照射を行うとサイズ選択的なナノ結晶になることを見出した²⁾。本研究では、SDS 共存下にて加熱を行い Au₈ クラスターの光学特性に与える影響について調べた。

MeCN / water (10 / 90) 混合溶液に Au₈ クラスターを添加したところ、600 nm 付近の蛍光に加えて 740 nm 付近にリン光を示した (Fig. 2 点線)。さらに、この溶液に SDS 0.2 mM を添加し 50°C で加熱すると、SDS の自己組織化によって Au₈ クラスターが内包されたひし形のナノ結晶を得ることができた (Fig. 1)。このナノ結晶は 727 nm 付近に強い燐光を示し、SDS 未添加と比べると約 20 倍発光強度が増加した (Fig. 2 実線)。この結果から、加熱により SDS ミセル中で Au₈ クラスターの結晶化が促進され、その結果著しい発光増大が起こったと考えられる。

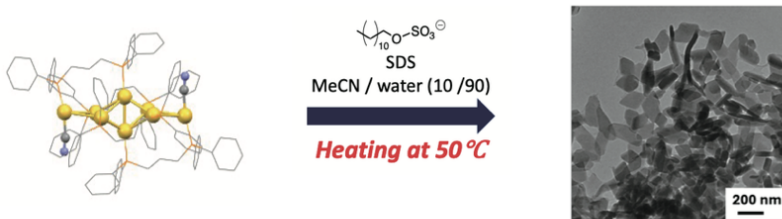


Fig 1. Geometric structure of Au₈ cluster and TEM image of nanocrystals.

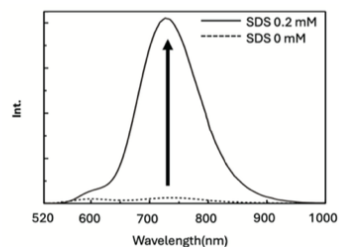


Fig 2. PL spectra of Au₈ cluster with different SDS concentrations.

(1) M. Sugiuchi, *et al.*, *J. Am. Chem. Soc.* **2017**, *139*, 17731. (2) Y. Saito, *et al.* *Chem. Sci.* **2024**, *15*, 11775.

Formation of polygonal nanocrystals composed of gold nanoclusters

(¹Graduate School of Environmental Science and ²Faculty of Environmental Earth Science, Hokkaido University) ○Xiaoyu Hu¹, Yukatsu Shichibu^{1,2}, Katsuaki Konishi^{1,2}

Keywords: PEG modification; amphiphilic; Au clusters

Ligand-protected metal nanoclusters have recently gained increasing attention for self-assembly, which can impart smart nanomaterials with distinctive functions that depend on their structure or morphology.^[1] The simplest strategy to build cluster-based self-assemblies is to use interligand interactions and adjust the assembly conditions. In this study, we extended this approach by introducing amphiphilic ligands (PEG-alkanethiolate) into a thiolate-stabilized Au₂₅ cluster (Fig. 1). And the obtained polygonal nanocrystals by adjusting solution conditions.

The introduction of PEG-alkanethiolate to the surface of the Au₂₅(SR)₁₈ was performed through a conventional ligand exchange reaction between PEG-alkanethiol and hexanethiolate-protected Au₂₅ cluster. The UV-visible absorption spectra of the gold cluster in the THF solution exhibited changes with increased water contents. Dynamic light scattering measurements revealed the growth into larger nanoscale objects as water content increased. Furthermore, transmission electron microscopy (TEM) shows the formation of polygonal nanocrystals (Fig. 2).

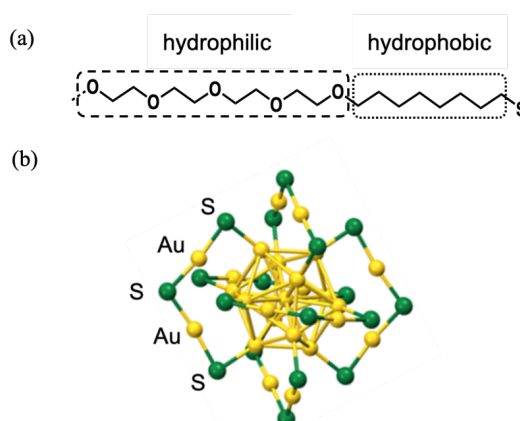


Fig. 1 Structures of (a) PEG-alkanethiolate and (b) Au₂₅(SR)₁₈.

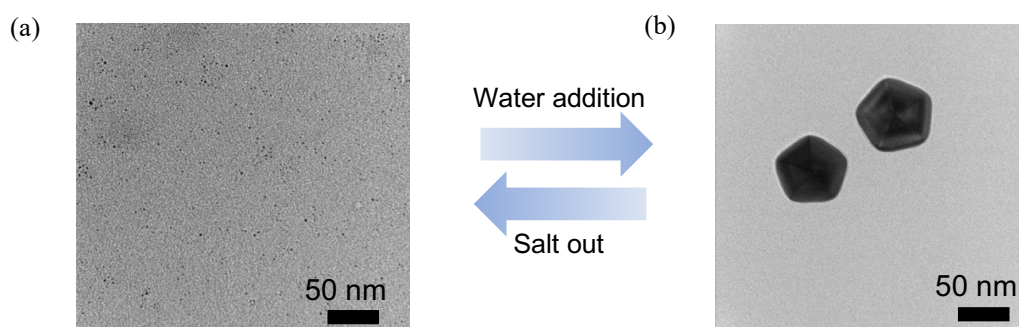


Fig. 2 TEM image of (a) monomer and (b) self-assembly.

1) Y. Saito *et al.*, *Chem. Commun.* **2025**, *in press*.

One-dimensional Assembly of Gold Nanodiscs Controlled by DNA Hybridization for Tunable Plasmon Coupling

(¹Graduate School of Life Science, Hokkaido University, ²Research Institute for Electronic Science, Hokkaido University) ○Melda Taspika,¹ Yusuke Yonamine,² Hideyuki Mitomo,² Kuniharu Ijio²

Keywords: Gold Nanodiscs; Controlled Assembly; Multimerization; Plasmon Coupling; DNA

[Introduction] Gold nanoparticles exhibit localized surface plasmon resonance (LSPR), which is sensitive to the size, shape, and interparticle interactions. Nanoparticle assembly induces plasmon coupling which enhances the electromagnetic fields between nanoparticles. Therefore, controlled assembly, including assembly sizes and interparticle distances, are essential to tune the plasmon coupling. One-dimensional (1D) assembly with large cross-section has advantages in plasmonic wave guiding. Gold nanodiscs (AuNDs) with circular symmetry and large flat surface preferentially assemble into linier structures via face-to-face interaction.¹ In this study, we utilized DNA-modified AuNDs for their assembly formation via DNA hybridization, which allows adjustment of interparticle distances by various DNA lengths and degree of

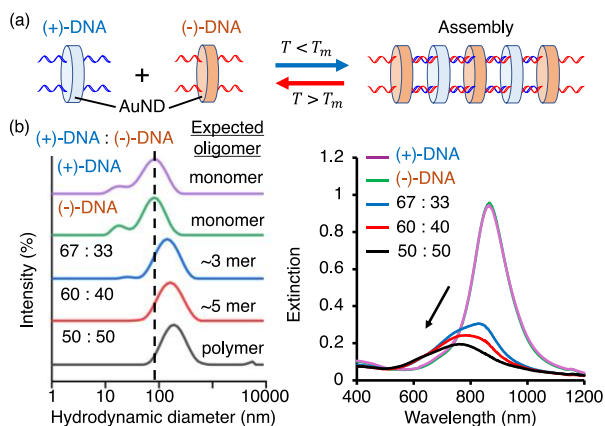


Figure 1. (a) Assembly of DNA-modified AuNDs via hybridization of (+)-DNA and (-)-DNA. (b) Multimerization control by varying the mixing ratios.

multimerization by varying the mixing ratios, enabling to tune the plasmon coupling (Fig. 1a). **[Results and discussion]** AuNDs were assembled by mixing at the same ratio (50:50) of (+)-DNA-AuND and (-)-DNA-AuND in a buffer solution including 150 mM NaCl. Upon gradual cooling from 80 to 25 °C, AuNDs assembled into one-dimensional cylindrical multimers with face-to-face interactions driven by DNA hybridization. Specifically, interparticle distances of assembled AuNDs were adjusted by various DNA lengths. The strength of plasmonic interactions highly depended on the interparticle distances (8, 11, and 20 bp DNA). Plasmonic shifting became larger by reducing DNA lengths due to the stronger plasmonic coupling. Besides, the degree of multimerization was controlled by varying the mixing ratios of (+)-DNA-AuND and (-)-DNA-AuND (67:33, 60:40, and 50:50), enabling to tune the assembly sizes and plasmon coupling (Figure 1b). Large multimers were formed at the equal molar ratio (50:50), whereas smaller oligomers were obtained when the ratio was lower.

[Reference] 1) J. Chidiebere Mba, H. Mitomo, Y. Yonamine, G. Wang, Y. Matsuo, K. Ijio, *Nanomaterials*. **2022**, 12, 1421.

Development of oxidation responsive supramolecular hydrogel based on glucosamine and peptides bearing methylthiophenyl group

(¹United Graduate School of Drug Discovery and Medicinal Information Sciences, Gifu University, ²Department of Life Science and Chemistry, Graduate School of Natural Science and Technology, Gifu University, ³iGCORE, Gifu University, ⁴COMIT, Gifu University, ⁵Institute for Advanced Study, Gifu University) ○ Onaza Ali¹, Yuki Shintani¹, Shintaro Sugiura¹, Chiho Narazaki², Sayuri L. Higashi^{1,4,5}, Masato Ikeda^{1,2,3,4}

Keywords: Supramolecular hydrogels; Oxidation response; Biomolecules; Sulfide; Aqueous self-assembly

Supramolecular hydrogels capable of showing stimuli responsiveness (e.g., pH, light, enzyme, redox, etc.) have attracted growing attention. Saccharide^{1,2,3} and peptide⁴ derivatives are considered as ideal candidates for the development of stimuli-responsive supramolecular hydrogel-based materials, due to their potential biocompatibility and relative facile chemical synthesis. Reactive oxygen species (ROSs) are reported to be utilized for cell signaling and for nanomedicine. In aqueous media, oxidation of sulfide to sulfoxide could result in the disruption of self-assembled structure^{2,4}. These oxidation responsive supramolecular hydrogels can be exploited for several types of biomedical applications, including cell encapsulation, drug delivery, etc.

In this study, we design and develop oxidation stimuli-responsive supramolecular hydrogels based on glucosamine and peptide derivatives. As shown in **Figure 1**, the glucosamine and peptide derivatives bearing sulfide moieties (e.g., -SCH₃) were newly synthesized. After investigating their aqueous self-assembly property, we found that **GlcN-CX₃SPmoc** (X = H and F) and **CH₃SPmoc-X-OH** (X = F and FF) can form hydrogels. Moreover, hydrogen peroxide (H₂O₂) as a typical oxidant or ROS, induced gel-to-sol transition (gel degradation) of these hydrogels. The details will be presented.

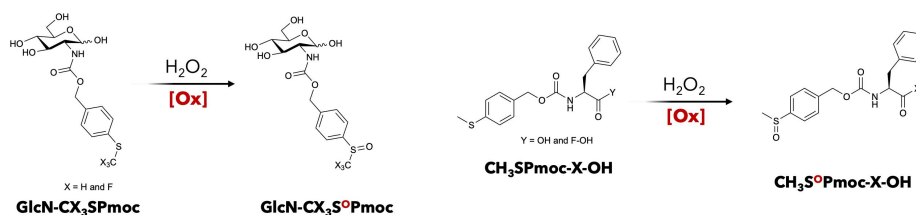


Figure 1 Chemical structures of **GlcN-CX₃SPmoc** (X = H and F) and **CH₃SPmoc-X-OH** (X = F and FF).

1) S. L. Higashi et al., *JACS Au* 2021, **1**, 1639. 2) O. Ali et al., *ChemBioChem* 2024, **17**, e202400459. 3) L. S. Birchall et al., *Chem. Sci.* 2011, **2**, 1349. 4) I. Piergentili et al., *Biomacromolecules* 2023, **24**, 3184.

One-pot construction of glycopeptide-based antimicrobial supramolecular hydrogels via oxime ligation

(¹UGS-DDMIS, Gifu Univ., ²GUiAS, Gifu Univ., ³iGCORE, Gifu Univ., ⁴COMIT, Gifu Univ.)
 ○Shintaro Sugiura¹, Sayuri Higashi^{1,2,4}, Masato Ikeda^{1,3,4}

Keywords: Glycopeptide; Supramolecular hydrogel; Oxime ligation; Antimicrobial material

Recently, one-pot construction of supramolecular materials under aqueous conditions has been extensively explored owing to the facile accessibility for preparing supramolecular assemblies^[1] and potential bioapplications such as drug loading and cell culture. Moreover, *in situ* synthesis of self-assembling building blocks is an attractive approach to construct supramolecular materials and modulate their functions.

In this study, we developed the one-pot facile preparation method of glycopeptide-based supramolecular hydrogels through *in situ* oxime ligation. Oxime ligation is a classical but valuable bioorthogonal reaction that occurs under aqueous conditions.^[2] We envisaged that oxime bond formation between benzaldehyde-tethered saccharides (α -ManBz/ β -GalBz) and aminooxy-functionalized peptides (Ao-Bz-F₃-OH) would give rise to glycopeptides capable of assembling into supramolecular fibrous networks, which could entrap pathogens through multivalent lectin-saccharide interactions (Fig. 1).

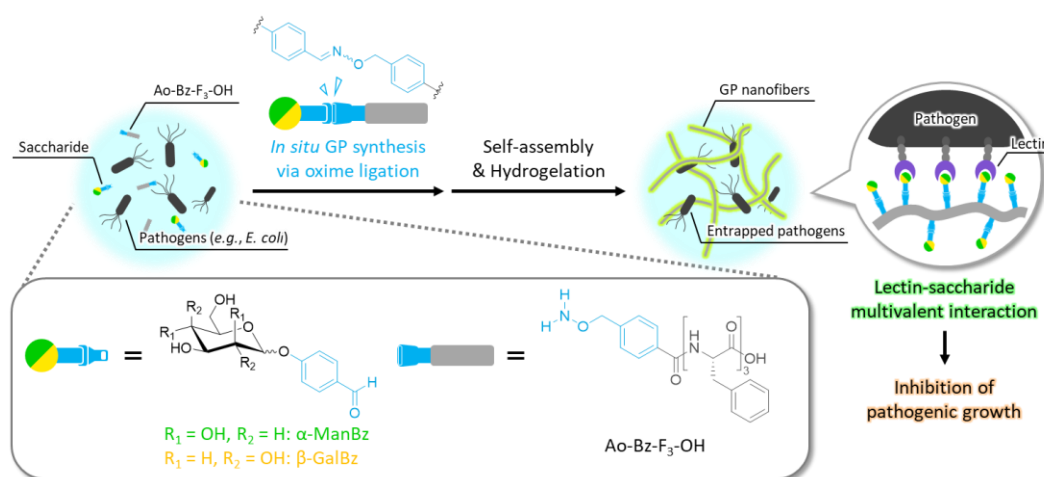


Fig. 1 One-pot construction of glycopeptide (GP)-based supramolecular hydrogels via oxime ligation, which could exhibit antimicrobial activity through multivalent lectin-saccharide interactions.

1) (a) S. L. Higashi *et al.*, *ACS Appl. Bio Mater.*, **2020**, 3, 9082–9092. (b) Y. Shintani *et al.*, *Chem. Eur. J.*, **2022**, e202104421. (c) S. Sugiura *et al.*, *Nanoscale*, **2023**, 15, 1024–1031. 2) S. Ulrich *et al.*, *Chem. Eur. J.*, **2014**, 20, 34–41.