

Academic Program [Oral B] | 19. Colloid and Interface Chemistry : Oral B

📅 Tue. Mar 19, 2024 3:55 PM - 5:15 PM JST | Tue. Mar 19, 2024 6:55 AM - 8:15 AM UTC 🏢 A1443(1443, Bldg. 14 [4F])

[A1443-2vn] 19. Colloid and Interface Chemistry

Chair: Erika yoshihara, Kazushi Kinbara

🇯🇵 Japanese

3:55 PM - 4:15 PM JST | 6:55 AM - 7:15 AM UTC

[A1443-2vn-01]

Vesicle Formation of Internal Olefin Sulfonate Induced by Hard Water

○Tadashi Sugahara¹, Haruna Ichihashi¹, Kana Tsumura¹, Atsushi Miyazaki¹, Takaya Sakai¹ (1. Kao Corporation)

🇬🇧 English

4:15 PM - 4:35 PM JST | 7:15 AM - 7:35 AM UTC

[A1443-2vn-02]

Motility of vesicle-type artificial tissues formed by salt bridges

○Tomoya Kojima¹, Yutaro Noguchi¹, Kouichi Asakura¹, Taisuke Banno¹ (1. Keio University)

🇬🇧 English

4:35 PM - 4:55 PM JST | 7:35 AM - 7:55 AM UTC

[A1443-2vn-03]

In situ construction of glycopeptide-based supramolecular hydrogels for medical-related applications

○Shintaro Sugiura¹, Yuki Shintani¹, Sayuri Higashi², Masato Ikeda^{1,3,4} (1. The United Graduate School of Drug Discovery & Medicine Information Sciences, Gifu Univ., 2. GUIAS, Gifu Univ., 3. COMIT, Gifu Univ., 4. iGCORE, Gifu Univ.)

🇬🇧 English

4:55 PM - 5:15 PM JST | 7:55 AM - 8:15 AM UTC

[A1443-2vn-04]

Structural Analyses with Spectroscopic and Computational Studies of Organogels Formed by Liquid-crystalline Phenyl Benzoates

○Kenta Matsumoto¹, Junya Yamaguchi¹, Kotaro Kanetada¹, Yui Endo¹, Yuri Hatsuda¹, Yuki Morita¹, Hiroaki Okamoto¹ (1. Yamaguchi University)

硬水を利用した内部オレフィンスルホン酸塩のベシクル形成

(花王 (株)) ○菅原 規・市橋 春奈・津村 加奈・宮崎 敦史・坂井 隆也

Vesicle Formation of Internal Olefin Sulfonate Induced by Hard Water

(Kao Corporation) ○Tadashi Sugahara, Haruna Ichihashi, Kana Tsumura, Atsushi Miyazaki, Takaya Sakai

Vesicles are known to spontaneously form supported lipid bilayers (SLB) at solid/liquid interface, and cationic surfactants have been mainly used for the SLB formation. On the other hand, anionic surfactants have been used as base agents of detergents because they exhibit superior detergency, foamability and dispersibility of solid particles. However, common anionic surfactants such as sodium dodecyl sulfate, lose their solubilities and functions due to water hardness. Recently, we have developed anionic surfactant, internal olefin sulfonate (IOS)¹⁾. In this study, we investigated self-aggregation behavior of C18HAS, which is one of the main components of IOS with the alkyl chain length of C18 (Fig. 1), in CaCl₂ aqueous solution. The results suggested that formation of the C18HAS vesicles is induced by addition of the water hardness. We also found that the vesicles formed by C18HAS can spontaneously form the supported lipid bilayers (SLB) at solid/liquid interface. These findings lead us to predict that C18HAS can act as surface modifiers, even though it is anionic surfactants.

Keywords : Internal olefin sulfonate, Vesicle, Supported lipid bilayer, Hard water

ベシクルは固液界面に自発的に支持二分子膜(SLB)を形成することが知られており、衣類の柔軟仕上げ剤に用いられている。また、固体表面は水中で負に帯電していることが多いため、SLB 形成には主にカチオン界面活性剤が利用されてきた。一方、アニオン界面活性剤は洗浄力、起泡性、固体粒子の分散性に優れるため、洗浄剤の主基剤として使用されている。しかし、ドデシル硫酸ナトリウムのような汎用のアニオン界面活性剤は、水の硬度(Ca²⁺や Mg²⁺)により溶解性が低下し、機能が失われてしまう。このことは、アニオン界面活性剤の長年の課題であった。近年、我々はアニオン界面活性剤である内部オレフィンスルホン酸塩(IOS)を開発した¹⁾。本研究では、C18 のアルキル鎖長を有する IOS の主要成分の一つである C18HAS(Fig. 1)の CaCl₂ 水溶液中での会合挙動を検討した。その結果、C18HAS は Ca 塩となって高分散なベシクル分散液を形成した。さらに、固体表面への自発的な SLB 形成も確認できた。以上より、C18HAS はアニオン界面活性剤であるにもかかわらず、硬度成分を有効に利用することで、表面改質剤としても機能することが期待される。

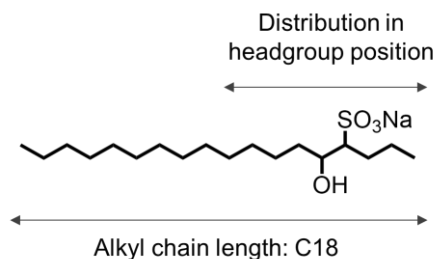


Fig. 1 Typical chemical structure of C18HAS

1) Y. Tabuchi and T. Sakai, RSC Adv. **2021**, *11*, 19836-19843.

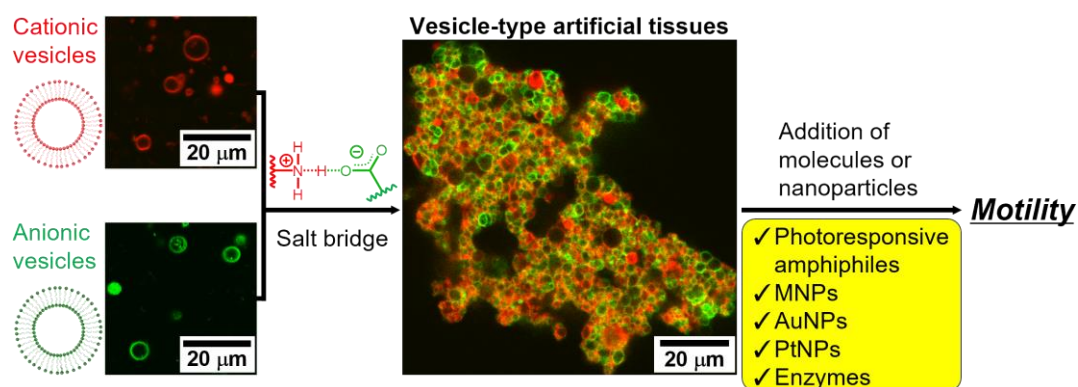
Motility of Vesicle-Type Artificial Tissues Formed by Salt Bridges

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Keywords: Vesicles; Artificial Cells; Artificial Tissues; Motility

Motility is one of the characteristics in life. Reconstitution of such motility functions into synthetic cell-like entities could lead to engineering brand-new biomimetic materials which exhibit manipulation and propulsion. Nowadays, artificial cells are focused on to be engineered as colloidal materials mimicking abilities of biological cells.¹ Among them, vesicles are considered to be artificial cells because they have boundaries between inner and outer phase, which are similar to biomembranes.² Inspired by multicellular organisms where multiple cells assemble into tissues, assembling multiple artificial cells could induce large-scale structures considered to be artificial tissues.³ We previously found a formation of artificial tissues comprising multiple vesicles triggered by salt bridges.⁴ In this presentation, we report how to induce motility of such vesicle-type artificial tissues.

First, addition of azobenzene-containing amphiphiles induced a contraction of tissues under UV illumination. It was estimated that a deformation of each vesicle due to photoisomerization of the amphiphiles promoted close contacts between vesicles. Second, utilizing magnetic nanoparticles (MNPs) enabled us to manipulate tissues and transport large cargoes by using a magnet. Third, in the presence of gold nanoparticles (AuNPs), phototaxis of the tissues was observed due to a photothermal effect of AuNPs. Fourth, addition of platinum nanoparticles (PtNPs) or catalase caused propulsion at a vertical direction in H₂O₂ solutions, which was due to a buoyancy of oxygen bubbles generated by decomposition of H₂O₂. These results suggest a possibility of engineering biomimetic materials comprising multiple colloids with versatile motility.



1) C. Xu, S. Hu, X. Chen, *Mater. Today* **2016**, *19*, 516. 2) A. J. Dzieciol, S. Mann, *Chem. Soc. Rev.* **2012**, *41*, 79. 3) X. Wang, H. Du, Z. Wang, W. Mu, X. Han, *Adv. Mater.* **2021**, *33*, e2002635. 4) T. Kojima, Y. Noguchi, K. Terasaka, K. Asakura, T. Banno, *under review*.

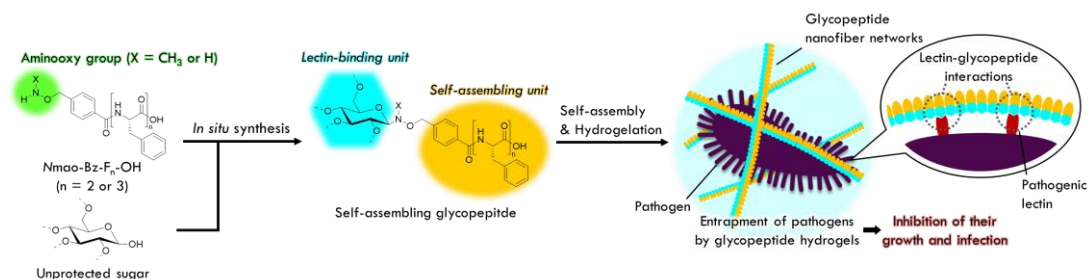
In situ construction of glycopeptide-based supramolecular hydrogels for medical-related applications

(¹United Graduate School of Drug Discovery & Medicine Information Sciences, Gifu University, ²GUiAS, Gifu University, ³COMIT, Gifu University, ⁴iGCORE, Gifu University)
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Keywords: Glycopeptides; Supramolecular hydrogels; Lectin; Antimicrobial nanomaterials

Glycopeptide-based supramolecular materials, serving as a multivalent saccharide ligand toward lectins on the surface of self-assembled structures, can emulate the biological function of polysaccharides and glycans. They thus could lead to exploring a variety of medical-related applications, including regenerative medicine and antimicrobial therapy.^[1] Nevertheless, the chemical complexity of saccharides is a massive barrier to the molecular design and synthesis of self-assembling glycopeptide monomers. Hence, straightforward strategies for developing them are highly desirable. In this study, we applied a one-pot oxyamine ligation^[2] to construct a variety of self-assembling glycopeptide under aqueous conditions, which gives rise to supramolecular hydrogels capable of capturing lectin-bearing pathogens in the hydrogel matrices through lectin-saccharide interactions.

We newly designed and synthesized (*N*-methyl)aminoxy-functionalized peptide derivatives, which gave a supramolecular hydrogel even in the presence of saccharides. ¹H NMR spectroscopic analysis revealed the conjugation of unprotected saccharides toward these peptides. Furthermore, we conducted confocal laser scanning microscopy (CLSM) observations with fluorescent dye-labeled lectins, which revealed their colocalization with fibrous structures of glycopeptides as anticipated. The results indicate the favorable affinity of self-assembled glycopeptide nanostructures toward the lectins and their selectivity. These findings offer opportunities to develop glycopeptide-based supramolecular biomaterials with potential applications in cell culture or vaccine preparation.



- 1) (a) L. Su *et al.*, *Curr. Opin. Chem. Biol.*, **2022**, 69, 102171, (b) A. Brito *et al.*, *Chem*, **2021**, 7, 2943–2964.
- 2) T. Cheewawisuttichai *et al.*, *Org. Biomol. Chem.*, **2021**, 19, 6613–6617.

Structural Analyses with Spectroscopic and Computational Studies of Organogels Formed by Liquid-crystalline Phenyl Benzoates

(¹Graduate School of Sciences and Technology for Innovation, Yamaguchi University, ²Advanced Technology Institute, Yamaguchi University) ○ Kenta Matsumoto,¹ Junya Yamaguchi,¹ Korato Kaetada,¹ Yui Endo,¹ Yuri Hatsuda,¹ Yuki Morita,² Hiroaki Okamoto¹

Keywords: Liquid Crystal; Low-molecular Gel; Phenyl Benzoate; Fluoroalkyl Group; Coumarin

In our previous works, it has been found that some liquid-crystalline phenyl benzoates with several organic solvents can form physical gels.^{1,2} While the correlation between molecular structures and gelation is not elucidated. Meanwhile, it has been reported in our publication² that 2-oxochromene-6-yl 4-alkoxybenzoates (Compounds **3-n**, Figure 1) with organic solvents were self-assembled by electrostatic interaction between coumarin skeletons, supporting in UV-Vis and TD-DFT.

In this work, self-assembly phenomena of gelation in organic solvents with phenyl benzoates containing a fluoroalkyl group (Compounds **1-n** and **2-n**, Figure 1) or a coumarin skeleton (Compounds **3-n**) were analyzed by spectroscopic and computational studies.

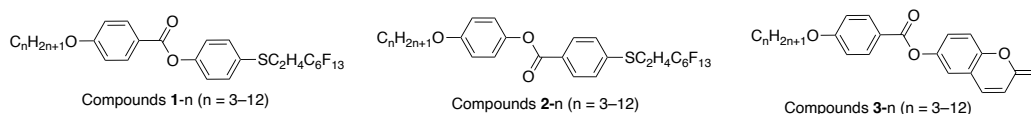


Figure 1. Chemical structures of compounds **1-n**, **2-n**, and **3-n**.

Optimized structures as a dimer for compounds **1-8** and **2-8**, and each formation enthalpies (ΔH_f) are shown in Figure 2. The gel-sol transition enthalpies for propylene carbonate gels ($\Delta H_{\text{gel-sol}}$) with compounds **1-8** and **2-8** at room temperature estimated 36.6 kJ mol⁻¹ and 12.5 kJ mol⁻¹, respectively. self-assembly phenomena for gelation with compounds **1-8** and **2-8** may be driven by π - π interaction and fluorophilic effect, respectively, since absolute value of $\Delta H_{\text{gel-sol}}$ $\Delta_f H$ are similar values.

In this presentation, effect of polar functional group on gelation, which compared with compounds **1-n** and **3-n**, analyzed by XRD and IR will be reported.

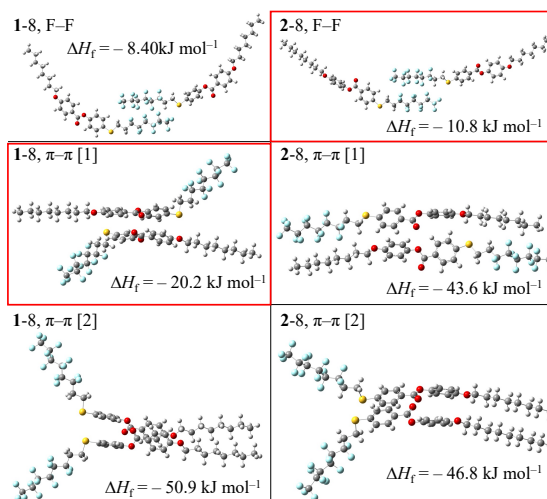


Figure 2. Optimized geometries of compounds **1-n** and **2-n** as a dimer and DFT-calculated formation enthalpy ($\Delta_f H$) using the M06/6-311G (d) level.

1) B-P. Cao, *et al.*, *J. Fluorine Chem.*, **2019**, 226, 109348. 2) Y. Endo *et al*, *Chem. Lett.* **2023**, 52, 337.