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]A307(A307, Bldg. 1, Area 2 [3F])

[[B]A307-1pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Kazuya Ootsubo, Kiyoshi Tsuge

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[[B]A307-1pm-01]

Anion-exchangeable defective UiO-66 and UiO-66-NH_2 for nitrate separation from water

○Aditya Irfan Witono[1], Xin Zheng[1,2], Shin-ichiro Noro[1,2] (1. Graduate School of Environmental Science, Hokkaido Univ., 2. Faculty of Environmental Earth Science, Hokkaido Univ.)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[[B]A307-1pm-02]

Development of a New Structural Transformation Reaction with Cr-based MOFs Induced by Fluoride

○Shintaro Tanaka[1], Takaaki Tsuruoka[2], Kensuke Akamatsu[2], Yohei Takashima[2] (1. Konan graduate school , 2. Konan University)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[[B]A307-1pm-03]

Atomistic simulation of magnetization motion for molecule-based magnets from Landau-Lifshitz-Gilbert approach with thermal fluctuations

○Kenta IMOTO[1], Masamichi NISHINO[2], Seiji MIYASHITA[1], Shin-ichi OHKOSHI[1] (1. The Univ. of Tokyo, 2. NIMS)

English
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[[B]A307-1pm-04]

Optical and magnetic properties of cocrystal based on octacyanidemetallates

○Tatsuya Konishi[1], Kunal Kumar[1], Kazuki Nakamura[1], Yuuki Mineo[1], Koji Nakabayashi[1], Shin-ichi Ohkoshi[1] (1. Department of Chemistry, School of Science, The University of Tokyo)

Japanese
2:20 PM - 2:40 PM JST | 5:20 AM - 5:40 AM UTC
[[B]A307-1pm-05]

Syntheses, Crystal Structures, and Properties of One-Dimensional Assemblies Consisting of Paddlewheel Dimolybdenum Complexes and Copper(I)-Halogenido Complexes

○Atsushi Takamori[1], Kiyoshi Tsuge[1] (1. Graduate School of Science and Engineering, University of Toyama)

English
2:40 PM - 3:00 PM JST | 5:40 AM - 6:00 AM UTC
[[B]A307-1pm-06]

Self-expansion of MOFs to create uniformly cross-linked polymer networks

◯Yuto Osugi[1], Ami Nishijima[1], Takashi Uemura[1] (1. Graduate School of Engineering, The Univ. of Tokyo)

English

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

[[B]A307-1pm-07]

Cooperative binding of polyethylene glycol to alkaline metal ions and the coil–helix phase transition

◯Hongyao Zhou[1], Teppei Yamada[1] (1. The University of Tokyo)

Anion-exchangeable defective UiO-66 and UiO-66-NH_2 for nitrate separation from water

([1]*Graduate School of Environmental Science, Hokkaido University*, [2]*Faculty of Environmental Earth Science, Hokkaido University*) ○Aditya Irfan Witono,[1] Xin Zheng,[1,2] Shin-ichiro Noro,[1,2]

Keywords: Metal-organic framework; Nitrate removal; Defective UiO-66

Nitrate anion is a potential water pollutant because it can harm human health and the environment. Therefore, removing the nitrate anion from water is necessary, and physical separation methods are frequently used due to their simplicity. Metal-organic frameworks (MOFs) are hybrid organic-inorganic polymers with high porosity and structural tunability, which attract much attention for contaminant separation. Recently, we found anion-exchangeable defective Zr-based MOFs, [$Zr_6O_4(OH)_4$(1,4-benzenedicarboxylate)$_6$] (UiO-66) and [$Zr_6O_4(OH)_4$(2-amino-1,4-benzenedicarboxylate)$_6$] (UiO-66-NH_2), with higher nitrate removal capacities and faster nitrate removal rates than a commercially available anion-exchange resin. This study investigates the practical application of anion-exchangeable UiO-66 and UiO-66-NH_2.

The anion-exchangeable UiO-66 and UiO-66-NH_2 were synthesized via solid-state synthesis,[1] resulting in the chloride-included defective structure. The maximum nitrate removal capacities of UiO-66 and UiO-66-NH_2 were 1.16 and 1.97 mmol/g, respectively, higher than that of the commercial anion exchange resin (1.03 mmol/g). The release of chloride anions was found simultaneously with nitrate anion removal. Thus, the nitrate removal mechanism was an anion exchange between the nitrate and chloride anion (Figure). On the day, we will discuss the structures and the application of nitrate removal for these MOFs.

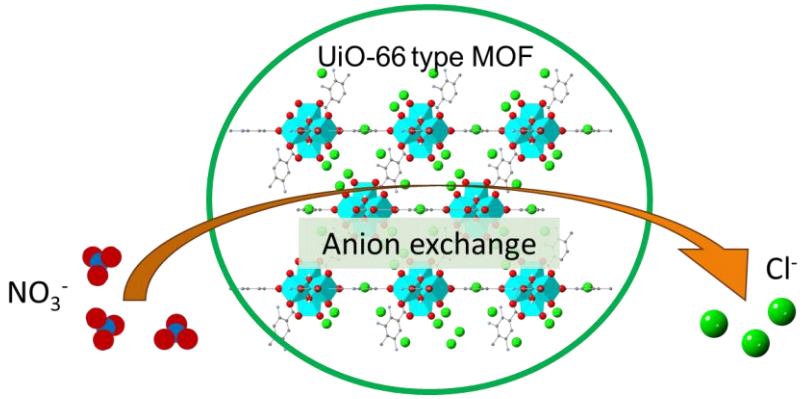

Figure. The nitrate removal by anion exchange in Cl-included defective UiO-66.

1) G., Ye, D., Zhang, X., Li, K., Leng, W., Zhang, J., Ma, Y., Sun, W., Xu, S., Ma, *ACS Appl. mater. interfaces* **2017**, *9*, 34937.

Development of a New Structural Transformation Reaction with Cr-based MOFs Induced by Fluoride

(Graduate School of Frontiers of Innovative Research in Science and Technology (FIRST), Konan University) ○ Shintaro Tanaka, Takaaki Tsuruoka, Kensuke Akamatsu, Yohei Takashima

Keywords: Metal-organic frameworks; Structural transformation; Fluoride

Metal-organic frameworks (MOFs), composed of metal ions and organic linkers, possess well-defined structures with permanent porosity, high specific surface areas and notable flexibility. These properties position MOFs as promising candidates for various applications. A distinguishing feature of MOFs is their ability to form various structures using the same metal ions and organic ligands and it is noteworthy that some MOFs could transform to other MOFs. However, the transformable MOFs were still very few especially in the case of kinetically inert MOFs, though they are promising for future sustainable applications. In this work, we focused on kinetically inter Cr-based MOFs, MIL-101(Cr) and MIL-53(Cr) to develop new structural transformation system. Both MOFs are composed of Cr^{3+} ions and terephthalate and have the same Cr^{3+}/terephthalate ratio, indicating that MIL-101(Cr) could be completely consumed to form MIL-53(Cr). In addition, we used fluoride as an additive to weaken the coordination bond between Cr^{3+} and terephthalate, inducting the structural transformation reaction. (**Figure a**).

By heating MIL-101(Cr) in 60 mM CsF (aq), MIL-53(Cr) was successfully obtained. From time-course TEM observations, the number of sphere-like MIL-101(Cr) crystals decreased while the number of large cubic-like MIL-53(Cr) increased. Additionally, the size of MIL-101(Cr) crystals has become gradually smaller as the transformation proceeded, indicating that the nucleation reaction of MIL-53(Cr) initiated from partially eluted metal ions and organic linkers (**Figure b**). These results suggest that the structural transformation reaction proceeded through a partial dissolution-recrystallization process. In addition, XPS measurements showed that the resulting MIL-53(Cr) has fewer defects than the one directly synthesized from Cr^{3+} ions and terephthalic acid, indicating that this transformation reaction is useful to generate highly crystalline MIL-53(Cr).

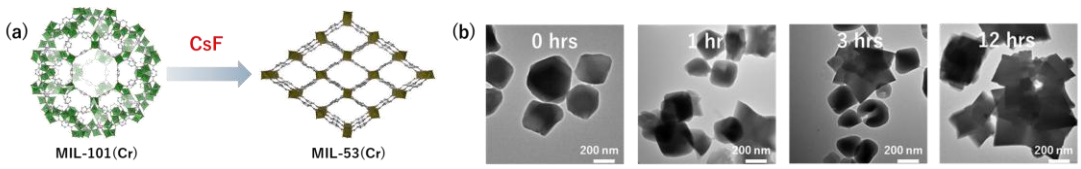

Figure. (a) Schematic of structural transformation from MIL-101(Cr) to MIL-53(Cr).
(b) TEM images of the samples obtained with 60 mM CsF (aq) over different reaction times.

Atomistic simulation of magnetization motion for molecule-based magnets from Landau-Lifshitz-Gilbert approach with thermal fluctuations

([1]*Graduate School of Science, The University of Tokyo*, [2]*National Institute for Materials Science*) ○ Kenta IMOTO[1], Masamichi NISHINO[2], Seiji MIYASHITA[1], Shin-ichi OHKOSHI[1]

Keywords: simulating magnetic properties; molecule based magnet; stochastic LLG equation

Molecule-based magnets are extensively investigated due to their fascinating functionalities such as pressure-induced phase transition and magnetic designability.[1–3] In the present work, we performed spin dynamic simulations of 3-dimensional cyanido-bridged molecule-based magnets using stochastic Landau-Lifshitz-Gilbert equation,

$\frac{d}{dt}\boldsymbol{M_i} = -\frac{\gamma}{1+\alpha_i^2}\boldsymbol{M_i} \times \left(\boldsymbol{H_i^{eff}} + \xi_i\right) - \frac{\alpha_i \gamma}{(1+\alpha_i^2)M_i}\boldsymbol{M_i} \times [\boldsymbol{M_i} \times \left(\boldsymbol{H_i^{eff}} + \xi_i\right)]$, where $\boldsymbol{M_i}$, α_i, γ, ξ_i, and H_i^{eff} are magnetization, damping factor, gyromagnetic constant, noise, and the effective field calculated from the Hamiltonian, including magnetic interactions, single ion anisotropy, magnetic field.[4]

Calculations of 3-dimensional cyanido-bridged molecule-based magnets using the crystallographic data and magnetic interactions of Ni–[Cr(CN)$_6$] ferromagnet and Mn–[Cr(CN)$_6$] ferrimagnet for 125000 sites reproduced the experimental magnetic phase transition temperatures of 90 K (Fig. 1). Additionally, the magnetization vs temperature plot for the unit cell at the corners, the sides, and the center showed that the magnetization was larger at the center than the sides, and was larger at the sides than the corners (Fig. 1b). The reason for the difference in magnetization can be explained by the difference in the number of superexchange pathways from 6, 5, to 3 at center, surface, and corner, respectively.

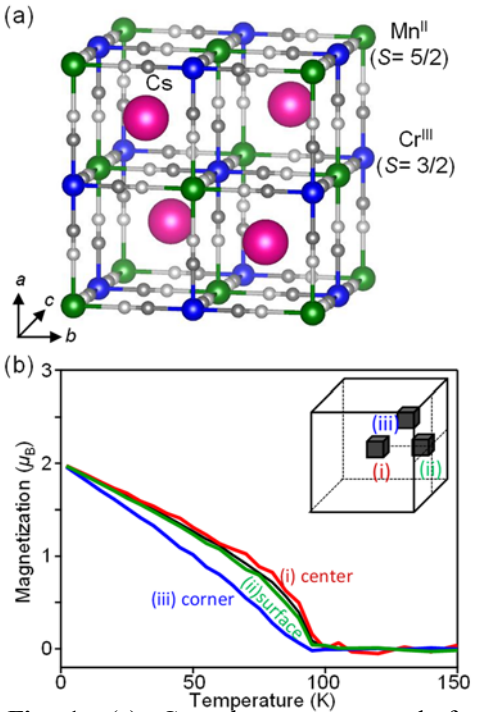

Fig 1. (a) Crystal structure used for calculations. (b) Magnetization vs temperature of the unit cell at the corner, the side, and the center.

1) S. Ohkoshi, K. Nakagawa, M. Yoshikiyo, A. Namai, K. Imoto, Y. Nagane, F. Jia, O. Stefanczyk, H. Tokoro, J. Wang, T. Sugahara, K. Chiba, K. Motodohi, K. Isogai, K. Nishioka, T. Momiki, R. Hatano, *Nat. Commun.*, **2023**, 14, 8466. 2) S. Ohkoshi, et al. *Phys. Rev. B*,**1997**, *56*, 11642–11652. 3) S.Ohkoshi, et al. *Phys. Rev. Lett.*, **1999**, *82*, 1285–1288. 4) M.Nishino, S.Miyashita. *Phys.Rev.B* , **2015**, *91*, 134411.

Optical and magnetic properties of cocrystal based on octacyanidemetallates

([1]*Graduate School of Science, The university of Tokyo*) ○Tatsuya Konishi,[1] Kunal Kumar,[1] Kazuki Nakamura,[1] Yuuki Mineo,[1] Koji Nakabayashi,[1] Shin-ichi Ohkoshi,[1]

Keywords: cyanide complex, antiferromagnetic ordering, near-infrared emission, nonlinear optical effects

Many molecule-based magnetic materials have been reported due to high structural controllability providing various structures and functionalities. Among them, cyanido-bridged metal assemblies in which cyanidemetallates and transition/lanthanide metal ions are connected via cyanides show versatile magnetic and optical properties such as photomagnetism[1], and luminescence[2]. Nevertheless, the physical properties of the cyanidemetallates themselves have received little attention. Herein, we report cocrystals $A_3[M^V(CN)_8]$(glycine), **AM(gly)** (A = Cs, M = W, **CsW(gly)**; A = Rb, M = W, **RbW(gly)**; A = Cs, M = Mo, **CsMo(gly)**; A = Rb, M = Mo, **RbMo(gly)**) and discuss the optical and magnetic properties.

All cocrystals were isostructural, belonged to the tetragonal space group of *P*4*bm* with spontaneous polarization in the *c*-axis direction (Figure 1a). In the UV-vis spectra, **CsW(gly)** and **CsMo(gly)** showed broad peaks at 484 nm and around 450 nm, respectively (Figure 1b). The peak around 485 nm corresponds to a ligand-to-metal charge transfer (LMCT) transition. When irradiated with 470 nm light, **CsW(gly)** and **CsMo(gly)** showed emission with a peak at 788 nm and 724 nm, respectively (Figure 1c). The Rb analogues also showed similar absorption and emission spectra. Quantum chemical calculations revealed that these emissions are from the ^{2}LMCT state. Magnetization measurements revealed that these cocrystals have a one-dimensional antiferromagnetic chain of Heisenberg spins due to the overlapping of the π-spin orbitals on the cyano group of octacyanidemetallate. They showed strong antiferromagnetic interactions among the cyanidemetallate moieties along the *c*-axis.

1) K. Nakamura, S. Ohkoshi, et al., *Inorg. Chem. Front.* **2024**, *11*, 2752. 2) J. Rzepiela, S. Ohkoshi, et al., *Inorg. Chem. Front.* **2024**, 11 1366.

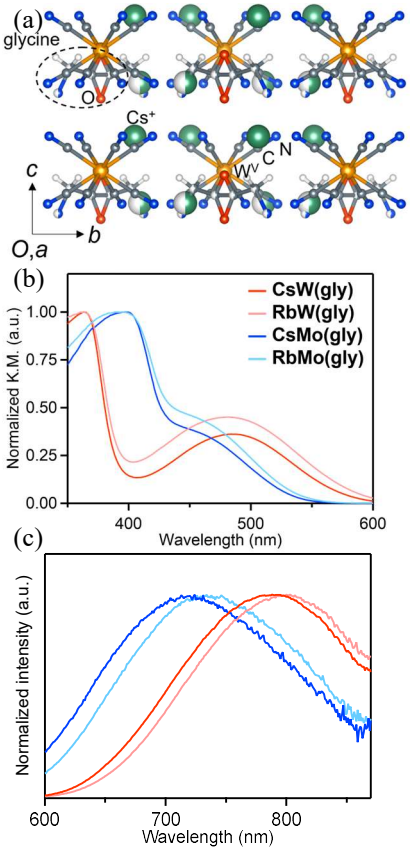

Figure 1 (a) Crystal structure of **CsW(gly)** viewed from the *a*-axis. (b) UV-vis spectra of **AM(gly)**. (c) Emission spectra of **AM(gly)**.

パドルホイール型モリブデン複核錯体と銅(I)ハロゲノ錯体からなる一次元集積体の構造と性質

（富大院理工）○高森 敦志・柘植 清志

Syntheses, Crystal Structures, and Properties of One-Dimensional Assemblies Consisting of Paddlewheel Dimolybdenum Complexes and Copper(I)-Halogenido Complexes (*Graduate School of Science and Engineering, University of Toyama*) ○Atsushi Takamori, Kiyoshi Tsuge

Paddlewheel dimolybdenum complexes with bridging pyridine carboxylate are useful metalloligand by their pyridine rings. Here, we prepared novel one-dimensional chain complexes, consisting of paddlewheel dimolybdenum metalloligand and copper(I)-halogenido complex unit $\{Cu_2I_2(PPh_3)_2\}$, with $-[Cu_2]-[Mo_2]-$ alternating arrangement.
Keywords: *One-dimensional Chain; Coordination Polymer; Metalloligand; Quadruple Bond*

パドルホイール型錯体は集積型金属錯体のモジュールとして広く利用されている。最近、この構造をもつ錯体として、ピリジンカルボン酸架橋モリブデン複核錯体 $[Mo_2(4\text{-pyca})_4]$ (pyca = pyridine carboxylate)が報告された[1]。この複核錯体はエカトリアル方向に配位フリーのピリジン窒素をもち、第二金属種や金属錯体に連結する錯体配位子となりえる。本研究では、パドルホイール型錯体配位子を利用した新しい集積体構築を目標に、$[Mo_2(n\text{-pyca})_4]$ (= $[Mo_2]$)と $\{Cu_2I_2(PPh_3)_2\}$ (= $[Cu_2]$)の集積体を合成した。

既報を参考に、$[Mo_2(O_2CCH_3)_4]$と過剰量のピリジンカルボン酸を THF 中で混合し、$[Mo_2(n\text{-pyca})_4]$ ($n = 3, 4$)を合成した。これと CuI、PPh_3 を、それぞれ、DMSO 中または MeCN/DMSO 混合溶媒中で混合することで、赤色結晶の $[\{Cu_2I_2(PPh_3)_2\}\{Mo_2(3\text{-pyca})_4(DMSO)_2\}]_n$ (**1**)と、暗赤色結晶の $[\{Cu_2I_2(PPh_3)_2\}\{Mo_2(4\text{-pyca})_4(DMSO)_2\}]_n \cdot 2n$MeCN (**2**)を得た。単結晶 X 線構造解析の結果、いずれも、モリブデン複核錯体中の 4 つのピリジン窒素のうち、トランス位に位置する 2 つの N 原子のみが Cu 中心に配位し、$-[Cu_2]-[Mo_2]-$と並んだ一次元鎖錯体であることがわかった（図 1）。**1** と **2** の一次元鎖中の Mo−Mo 間距離は 2.1218(11) Å (**1**)および、2.1261(4) Å (**2**)であり、出発化合物中の 2.1193(4) Å ($[Mo_2(3\text{-pyca})_4]$)、2.1210(14), 2.1242(14) Å ($[Mo_2(4\text{-pyca})_4]$)とほぼ同じ距離であった。結合長および組成から、それぞれの一次元鎖中の Mo の金属酸化数は+2 であり、4 重結合を保持していると考えられる。

1) F.J. Claire *et al.*, *J. Am. Chem. Soc.* **2018**, *140*, 10673.

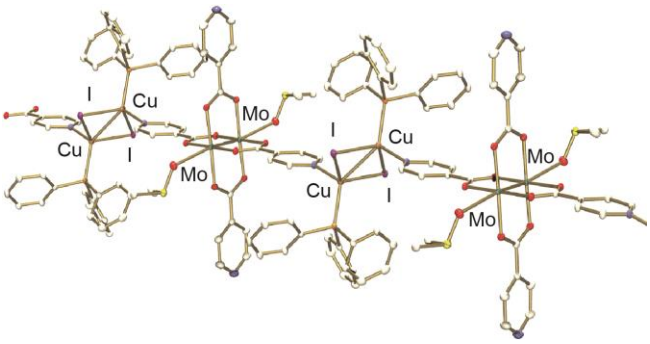

図 1. $[\{Cu_2I_2(PPh_3)_2\}\{Mo_2(4\text{-pyca})_4(DMSO)_2\}]_n \cdot 2n$MeCN (**2**)の結晶構造

Self-expansion of MOFs to create uniformly cross-linked polymer networks

([1]*Graduate School of Engineering, The University of Tokyo*) ○Yuto Osugi,[1] Ami Nishijima,[1] Takashi Uemura[1]

Keywords: Metal-Organic Framework (MOF), Cross-linking polymer, Gel, Ozonolysis, Precisely designed network polymer

Regularity of network structure in polymer gels strongly influences their mechanical properties.[1] Although various approaches have been explored to improve the network regularity, preparation of polymer gel with crystalline-level uniformity remains difficult. To address this challenge, metal–organic frameworks (MOFs), crystalline compounds formed by self-assembly of metal ions and organic ligands is employed as precursors to directly transform their organic ligands into polymeric linkers. In this work, we demonstrate a self-expansion approach of MOFs using ring-openable ligands, affording uniformly cross-linked polymeric materials (Figure).[2]

We designed the ligand (**L**) with stilbene moiety tethering flexible oligomeric chains (Figure b). Using **L** and $ZrCl_4$, we obtained a Zr-MOF ($[Zr_6O_4(OH)_4(\mathbf{L})_6]_n$) with 3D network structure.[3] Similarly, an Al-MOF ($[Al(OH)(\mathbf{L})]_n$) with 1D nanochannels was prepared using L and $AlCl_3$.[4] Formation of these MOFs was confirmed by X-ray and electron diffraction analyses, and scanning electron microscopy. N_2 adsorption analysis indicated that oligomeric chains filled the MOF pores. The self-expansion of the MOFs was performed via ozonolysis to cleave the C=C double bond in the stilbene moiety (Figure b). Ozonolysis of the MOFs was carried out by bubbling ozone through the dispersion of MOF particles in methanol, followed by treatment with dimethyl sulfide. As a result, the C=C double bonds in the MOFs were efficiently converted into two aldehydes with the coordination bonds retained, giving regular network structures with expanded pores.

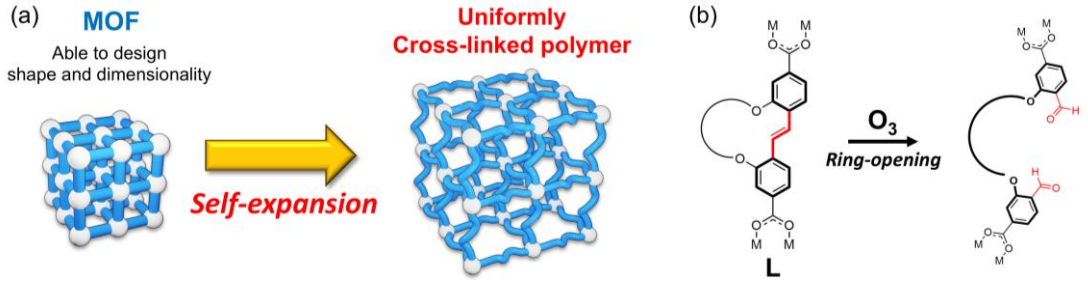

Figure. (a) The schematic illustration of this research. (b) The design of a ring-openable ligand (**L**).

1) M. Shibayama, *Macromol. Chem. Phys.*, **1998**, *199*, 1. 2) T. Uemura, et al, *Angew. Chem. Int. Ed.*, **2024**, 63, e202404155. 3) R. S. Forgan, et al., *J. Mater. Chem. A.*, **2016**, 4, 6955. 4) C. H. Lin, et al., *J. Mater. Chem. A,* **2013**,1, 324.

Cooperative binding of polyethylene glycol to alkaline metal ions and the coil–helix phase transition

(*Graduate School of Science, The University of Tokyo*) ○Hongyao Zhou, Teppei Yamada
Keywords: Statistical mechanics; Guest-induced phase transition; Polymer

Cooperative binding is often observed in biological systems, showing that a binding of the initial guest molecule changes structure of the host macromolecule to increase its binding affinity to another guest molecule. Cooperative binding is known to drastically enhance the catalytic or adsorption activity of the host macromolecule. On the other hand, very few example has been reported on synthetic polymers showing the cooperative host–guest binding, and their mechanistic study is scarcely carried out. Recently, we reported that polyethylene glycol (PEG) transforms into a helical structure and crystallizes upon coordination to alkaline metal cations in the presence of triiodide ion in water.[1] This crystallization is promoted with increasing length of PEG chain. However, the binding mechanism of PEG to those ions remained unknown.

Herein, we study the binding model of PEG to the alkaline metal cation by statistical mechanical approach and report that PEG shows cooperative binding to the alkaline metal cation in the presence of triiodide. The statistical model is built based on Zimm–Bragg model,[2] which was developed to model the coil–helix transition of protein alpha helix. The partition function Q of PEG is expressed in Equation (1):

$$Q = (1 \quad 1)\begin{pmatrix} 1 & 1 \\ n & w \end{pmatrix}^{N-1}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \text{(Eq. 1)}$$

N is the total number of ethylene oxide mer unit in the single PEG chain, and n and w are the statistical weight of nucleation and propagation of the helix, respectively (Figure 1). Typically, $n \ll 1$ and $w > 1$, so that the nucleation is more difficult than the propagation of the helix. The simulation curve calculated from this model agreed with the experimental result. This study shows that the coil–helix transition of PEG takes place in cooperative way and can be explained by Zimm–Bragg model.

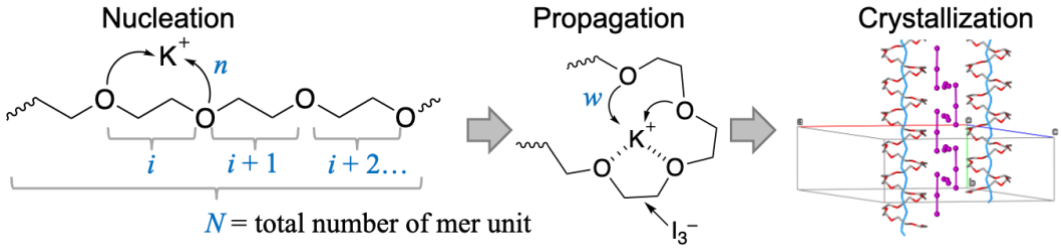

Figure 1. Zimm–Bragg model showing cooperative binding of PEG to potassium cation, starting from the nucleation to the propagation and finally the crystallization of the helix.

1) Patent pending to H. Zhou, R. Matsuno, T. Yamada, Japanese Patent Application No. 2022-004709, January 14, 2022. 2) B. Zimm and J. Bragg, *J. Chem. Phys.* 31, 526, 1959