

アカデミックプログラム [B講演] | 18. 高分子：口頭B講演

📅 2025年3月27日(木) 13:00 ~ 15:10 🏢 [F]2404(第4学舎 2号館 [4階] 2404)

**[[F]2404-2pm] 18. 高分子**

座長：小島 崇寛、西島 杏実

## ◆ 英語

13:00 ~ 13:20

[[F]2404-2pm-01]

MOFを利用した2次元架橋高分子の合成

○西島 杏実<sup>1</sup>、北尾 岳史<sup>1</sup>、細野 暢彦<sup>1</sup>、植村 卓史<sup>1</sup> (1. 東大院工)

## ◆ 日本語

13:20 ~ 13:40

[[F]2404-2pm-02]

MOF表面への高分子吸着を用いた位置選択的反応の誘起

○勝谷 祐輔<sup>1</sup>、植村 卓史<sup>1</sup>、細野 暢彦<sup>1</sup> (1. 東大院工)

## ◆ 英語

13:40 ~ 14:00

[[F]2404-2pm-03]

Vectorial On-Surface Synthesis of Polar 2D Graphene Nanoribbon Crystals

○Cong Xie<sup>1</sup>, Takahiro Kojima<sup>1</sup>, Shunpei Nobusue<sup>1</sup>, Shigeki Kawai<sup>2</sup>, Kazuhiro Fukami<sup>1</sup>, Takahiro Nakae<sup>3</sup>, Hiroshi Sakaguchi<sup>1</sup> (1. Kyoto University, 2. National Institute for Materials Science, 3. KRI Inc.)

14:00 ~ 14:10

休憩

## ◆ 英語

14:10 ~ 14:30

[[F]2404-2pm-04]

Electrochemical on-surface synthesis of a strong electron-donating graphene nanoribbon catalyst

○Yingbo Cheng<sup>1</sup>, Takahiro Kojima<sup>1</sup>, Shunpei Nobusue<sup>1</sup>, Kazuhiro Fukami<sup>1</sup>, Hiroshi Sakaguchi<sup>1</sup> (1. Kyoto University)

## ◆ 英語

14:30 ~ 14:50

[[F]2404-2pm-05]

メチルケトン側鎖または鎖内ケトン基を有する高密度ポリエチレンのUV分解性の比較

○袁 浩波<sup>1</sup>、高橋 講平<sup>1</sup>、Nontarin Roopsung<sup>1</sup>、中川 慎太郎<sup>1</sup>、吉江 尚子<sup>1</sup>、野崎 京子<sup>1</sup> (1. 東大)

## ◆ 英語

14:50 ~ 15:10

[[F]2404-2pm-06]

電子供与性基を有するトリアリールスルホニウム塩の合成と優れた耐アルカリ特性をもつカチオン官能基としての応用

○今井 智大<sup>1</sup>、一二三 遼祐<sup>1</sup>、稲木 信介<sup>1</sup>、富田 育義<sup>1</sup> (1. 東京科学大学)

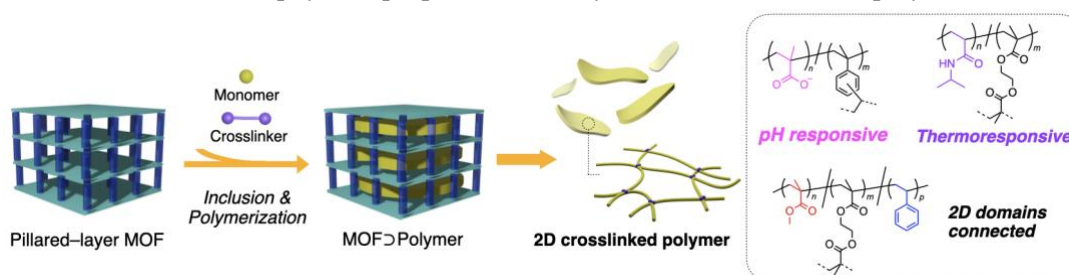
## Synthesis of 2D crosslinked polymers using MOF templates

(<sup>1</sup>Graduate School of Engineering, the University of Tokyo) ○Ami Nishijima,<sup>1</sup> Takashi Kitao,<sup>1</sup> Nobuhiko Hosono,<sup>1</sup> Takashi Uemura<sup>1</sup>

**Keywords:** Metal–Organic Frameworks; Crosslinking; 2D polymer; Network polymer

Two-dimensional (2D) network polymers, characterized by their unique topology, are expected to exhibit distinct properties compared to conventional linear polymers. These materials hold promise for applications such as gas separation membranes, anisotropic thermal conductive materials, and coating materials.<sup>1</sup> However, the synthetic methods for polymers with 2D structures are not yet well-established. To date, various approaches such as topochemical polymerization, interfacial synthesis, and synthesis using the interlayer spaces of inorganic layered compounds have been reported.<sup>2</sup> Despite these efforts, a versatile and scalable synthesis method for 2D polymers remains elusive.

In our research, we utilize metal–organic frameworks (MOFs) as templates for polymerization reactions. MOFs are porous materials whose pore sizes and channel dimensions can be precisely designed by the combination of metal ions and organic ligands. Among the diverse types of MOFs, we identified that pillared-layer MOFs with 2D nanopores (thickness 0.7 ~ 1.2 nm) are particularly suitable as templates to synthesize 2D polymers.<sup>3</sup> By polymerizing various monomers and crosslinkers within these MOFs, we successfully synthesized unimolecularly thick 2D network polymers in a simple and scalable manner. The resulting 2D network polymers exhibit unique thermal and mechanical properties distinct from conventional linear polymers, attributed to their 2D molecular structure. Furthermore, our method is applicable to a wide range of vinyl monomers such as styrene,<sup>3</sup> methyl methacrylate,<sup>3,4</sup> acrylonitrile,<sup>5</sup> *N*-isopropylacrylamide, and their copolymers (**Figure**).<sup>6</sup> We discuss the advancements in synthetic methodology and the common chemical and physical properties of the synthesized 2D network polymers.



**Figure.** Schematic illustration of the synthesis of 2D polymer networks.

- 1) A. D. Schlüter *et al.*, *Chem. Commun.* **2016**, 52, 18–34.
- 2) W. R. Dichtel *et al.*, *Chem. Rev.* **2022**, 122, 442.
- 3) N. Hosono, T. Uemura, S. Mochizuki, Y. Hayashi, *Nat. Commun.* **2020**, 11, 3573.
- 4) A. Nishijima, Y. Hayashi, K. Mayumi, N. Hosono, T. Uemura, *Macromolecules* **2023**, 56, 3141–3148.
- 5) X. Zhang, T. Kitao, A. Nishijima, T. Uemura, *ACS Macro Lett.* **2023**, 12, 415–420.
- 6) A. Nishijima, M. Ximenis, S. Qiao, N. Hosono, T. Uemura, *Chem. Eur. J.* **2025**, e202404169.

## MOF 表面への高分子吸着を用いた位置選択的反応の誘起

(東大院工<sup>1</sup>) ○勝谷 祐輔<sup>1</sup>・植村 卓史<sup>1</sup>・細野 暢彦<sup>1</sup>

Regioselective Reaction Induced by Polymer Adsorption on MOF surfaces (<sup>1</sup>Graduate School of Engineering, Tokyo University) ○Yusuke Katsutani,<sup>1</sup> Takashi Uemura,<sup>1</sup> Nobuhiko Hosono<sup>1</sup>

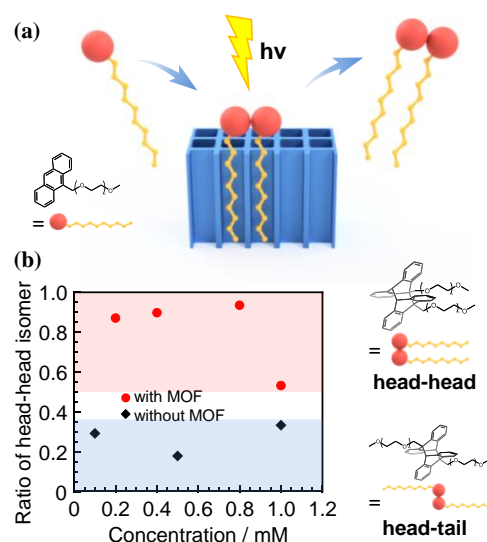
Reactions between polymers are generally subject to substantial steric congestions, making it difficult to achieve both high conversion and controlled regioselectivity. In this study, we successfully realized efficient and highly regioselective polymer reactions by exploiting the surfaces of a metal–organic framework (MOF) as the reaction platform. We investigated the photodimerization of polyethylene glycol modified at one terminus with an anthracene group. Under conventional homogeneous conditions, the head-tail product predominated, exhibiting over 80% selectivity due to steric effects of the chain. In contrast, in the presence of MOF particles, the head-head isomer was formed with over 90% selectivity. This result highlights the promising potential of MOF surfaces as a catalyst for polymer reactions.

**Keywords :** Metal-Organic Framework; Polymer Adsorption; Regioselectivity

高分子化合物同士の反応は、一般に高分子鎖の排除体積効果による強い制約を受ける。そのため、通常の溶液系反応では、高い反応率および反応の位置選択性を達成することは困難を伴う。本研究では、規則的に並んだ細孔を有する多孔性金属錯体 (MOF) の表面を反応場として用いる新しいアプローチにより、高分子化合物の高効率かつ高位置選択的反応の実現に成功した。

分子量 5000 のポリエチレングリコール (PEG) について MOF ( $[\text{Zn}_2(\text{ndc})_2(\text{ted})]_n$ ,  $\text{ndc} = 1,4\text{-naphthalenedicarboxylate}$ ,  $\text{ted} = \text{tetraethylenediamine}$ ) の単結晶表面における吸着現象を原子間力顕微鏡 (AFM) により観察したところ、PEG のドメイン形成が観察され、複数の PEG 鎖が互いに隣接した細孔へ優先的に取り込まれることが示唆された。

AFM 観察による結果を踏まえ、MOF 表面の特殊な吸着様式を利用してアントラセンを片末端に修飾した PEG の光二量化反応について検討した。MOF 表面において PEG 鎖が隣接した細孔へ導入され、アントラセン部位が近接した結果、光二量化反応の位置選択性 (head-head, head-tail) が変化すると期待した (Fig. 1a)。結果、通常の均一系反応では高分子の立体的要因により head-tail 体が 80% 以上の選択性で得られたのに対し、系中へ MOF 粒子 (1 mg/mL) を加えて同様の反応を行ったところ、90% 以上の選択性で head-head 体が得られることがわかった (Fig. 1b)。これらの結果から、MOF 表面が高分子反応の触媒として作用するという極めて興味深い現象が示された。



**Fig. 1.** (a) Schematic illustration of the reaction on the MOF surface. (b) Concentration dependence of dimerization regioselectivity with and without MOF.

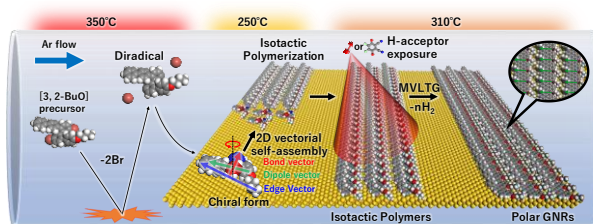
## Vectorial On-Surface Synthesis of Polar 2D Graphene Nanoribbon Crystals

(<sup>1</sup>Kyoto University, <sup>2</sup>National Institute for Materials Science, <sup>3</sup>KRI Inc.) ○ Cong Xie<sup>1</sup>, Takahiro Kojima<sup>1</sup>, Shunpei Nobusue<sup>1</sup>, Shigeki Kawai<sup>2</sup>, Kazuhiro Fukami<sup>1</sup>, Takahiro Nakae<sup>3</sup>, Hiroshi Sakaguchi<sup>1</sup>

**Keywords:** Graphene nanoribbons; Stereoregular polymerization; On-surface synthesis

The asymmetric introduction of functional groups into graphene nanoribbons (GNRs) is promising due to its potential to provide novel electronic and magnetic properties as theoretically predicted. Though traditional on-surface bottom-up synthesis has succeeded in creating various types of GNRs, it struggles to realize this concept due to the difficulty of stereoregular polymerization, degradation of the thermally sensitive functional groups during prepolymer dehydrogenation and the tendency for overall polarity cancellation during agglomeration.<sup>1</sup>

In this study, we designed a ‘compass’ precursor possessing three independent vectors: a vector for bonding, an edge vector for inducing intermolecular forces in one direction, and a dipole vector for electronic asymmetry by asymmetrically introducing a butoxy functional group to Z-type polyphenylene precursors. Our developed ‘two-zone chemical vapor deposition’ enabled isotactic polymerization of these precursors under 250°C via the vectorial self-assembly of chiral precursor diradicals.<sup>2</sup> The isotactic prepolymers were then successfully converted into polar GNRs via newly developed ‘molecular-vapor assisted low temperature growth (MVLTG)’ technique (exposed to oxygen at a pressure of 0.8 kPa for 5 min at 310°C), which was capable of promoting the dehydrogenation reactions by exposure to hydrogen-accepting molecular vapor successfully forming polar 2D crystalline structures.<sup>3</sup> Additionally, we recently demonstrated Janus GNR, which has an asymmetric edge structure, zigzag and coved edge, resulting in ferromagnetic with the asymmetric Z-type precursor.<sup>4</sup>



1) T. Kojima, C. Xie, H. Sakaguchi, *ChemPlusChem* **2024**, 89, e202300775. 2) T. Kojima, K. Patel, S. Nobusue, A. Mahmoud, C. Xie, T. Nakae, S. Kawai, K. Fukami, H. Sakaguchi, *Adv. Mater. Interfaces* **2023**, 10, 2300214. 3) T. Kojima, C. Xie, K. Patel, S. Nobusue, K. Fukami, H. Sakaguchi, *J. Phys. Chem. C* **2023**, 127, 10541. 4) S. Song, Y. Teng, W. Tang, Z. Xu, Y. He, J. Ruan, T. Kojima, W. Hu, F. J. Giessibl, H. Sakaguchi, S. G. Louie, J. Lu, *Nature*, **2025**, DOI: <https://doi.org/10.1038/s41586-024-08296-x>.

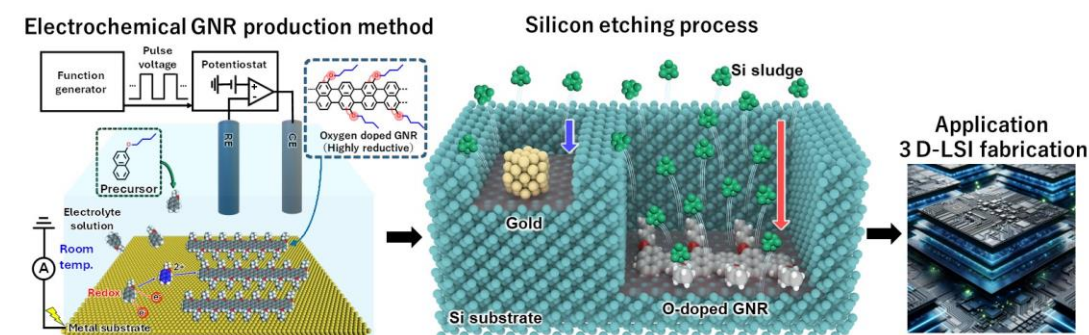
## Electrochemical on-surface synthesis of a strong electron-donating graphene nanoribbon catalyst

(<sup>1</sup>*Institute of Advanced Energy, Kyoto University*, <sup>2</sup>*Department of Materials Science and Engineering, Kyoto University*) ○ Yingbo Cheng<sup>1</sup>, Takahiro Kojima<sup>1</sup>, Shunpei Nobusue<sup>1</sup>, Kazuhiro Fukami<sup>2</sup>, Hiroshi Sakaguchi<sup>1</sup>

**Keywords:** Graphene nanoribbon (GNR), Electric double layer (EDL), Si etching, On-Surface Synthesis

Edge functionalization of graphene nanoribbons (GNRs) by introducing electron-donating or withdrawing substituents into their backbones is crucial for their applications in electronic, magnetic, and energy fields. However, edge-functionalization through the on-surface synthesis can be challenging. This is mainly due to the decomposition of functional groups at temperatures ranging from 300 to 500°C and limited monolayer GNR growth based on metal catalysis. To solve the problem, we developed an electrochemical technique for on-surface GNR synthesis that overcomes these limitations to produce edge-functional GNRs. Our approach involves regioselective ionic polymerization and oxidation-based dehydrogenation, which occur at the electric double layer (EDL), liquid-solid interface. Our technique allows GNR growth at <80°C and layer-by-layer growth, which was previously impossible.

This study demonstrated the successful use of electrochemical on-surface synthesis to produce oxygen-doped GNRs with 5-AGNR widths and butoxy substituents using the asymmetric precursor, 2-butoxynaphthalene. We discovered a unique nonlinear growth mechanism for GNR synthesis. The di-cation form of the asymmetric precursor, produced through a two-electron oxidation process via high voltage application, becomes an active intermediate for GNR growth, suggesting a previously unknown heterochiral di-cationic polymerization mechanism. This research demonstrates that electrochemically synthesized GNRs are highly effective catalysts for silicon chemical etching in the semiconductor industry, surpassing the efficiency of previously used noble metal catalysts.



1) H. Sakaguchi, T. Kojima, Y. Cheng, S. Nobusue, K. Fukami, *Nat. Commun.*, **2024**, 15, 5972.



## Comparison of UV degradation of high-density polyethylene-like polymers with methyl ketone side chains or in-chain ketone groups

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Polyethylene (PE) has been widely applied because of its unique mechanical properties and chemical resistance. On the other hand, its high stability (or low degradability) endowed by its non-polar all-carbon main chain makes it one of the main waste sources for white pollution. Efforts have been made to make HDPE degradable or recyclable by inserting functional groups into or on the main chain. For example, the HDPE with ester or peptide groups in main chains can be recycled by fragmentation and repolymerization.<sup>1-2</sup> HDPE with carboxylic acid groups can be degraded under blue light through radical process.<sup>3</sup>

Efforts have also been made for making ethylene/CO copolymers (poly(E/CO)) with CO contents, high in dispersion but low in amount, and with high molecular weights. Such polymers can degrade under UV light by cutting the ketone groups through Norrish reactions. Previously, our group has synthesized high density polyethylene bearing isolated in-chain carbonyls, that degrades under UV-light irradiation (Fig. 1).<sup>4</sup>

In this work, HDPE-like polymer with methyl ketone side chains were synthesized by copolymerization of ethylene and methyl vinyl ketone (poly(E/MVK)) and its UV degradability was compared with poly(E/CO)<sup>4</sup> (Fig. 1). By tracing the molecular weight by size-exclusion chromatography, Poly(E/MVK) showed higher degradation efficiency than the corresponding poly(E/CO). By an NMR study, rapid consumption of the ketone moiety via both Norrish type I and II scissions were suggested for the degradation of poly(E/MVK), while mainly type II is responsible for poly(E/CO). Such difference could be associated with preferable location of ketone group in the amorphous phase or conformationally flexible to undergo the type II reaction in poly(E/MVK). By the precise control of the ketone content of poly(E/MVK), the ones with low MVK content were found to have physical properties comparable to HDPE yet photodegradable.

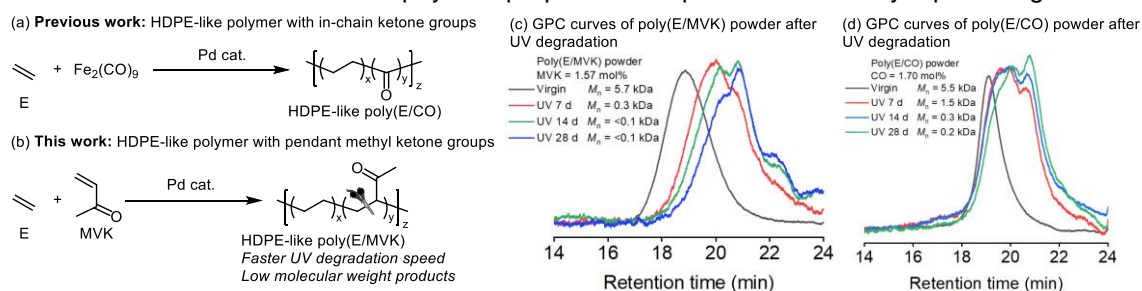


Fig. 1 HDPE-like polymers with methyl ketone side chains or in-chain ketone groups.

### References

- (1) Arroyave, A.; Cui, S.; Lopez, J. C.; Kocen, A. L.; LaPointe, A. M.; Delferro, M.; Coates, G. W., *J. Am. Chem. Soc.* **2022**, *144* (51), 23280-23285.
- (2) Lu, Y.; Takahashi, K.; Zhou, J.; Nontarin, R.; Nakagawa, S.; Yoshie, N.; Nozaki, K., *Angew. Chem. Int. Ed. Engl.* **2024**, *63* (43), e202410849.
- (3) Lu, B.; Takahashi, K.; Zhou, J.; Nakagawa, S.; Yamamoto, Y.; Katashima, T.; Yoshie, N.; Nozaki, K., *J. Am. Chem. Soc.* **2024**, *146* (28), 19599-19608.
- (4) Tang, S.; Seidel, F. W.; Nozaki, K., *Angew. Chem. Int. Ed. Engl.* **2021**, *60* (51), 26506-26510.

## Synthesis of triarylsulfoniums containing electron-donating groups and their applications to cationic functional groups with excellent alkaline-resistant performance

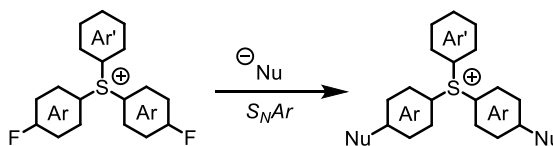
(<sup>1</sup>*School of Materials and Chemical Engineering, Institute of Science Tokyo*)

○Tomohiro Imai<sup>1</sup>, Ryoyu Hifumi<sup>1</sup>, Shinsuke Inagi<sup>1</sup>, Ikuyoshi Tomita<sup>1</sup>

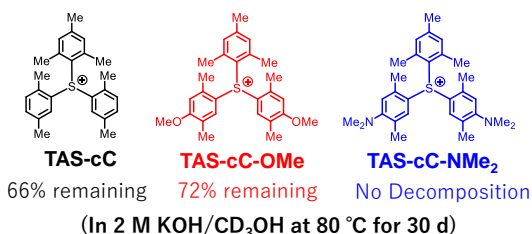
**Keywords:** Triarylsulfonium Salts; Cationic Functional Groups; Electron-donating Groups; Alkaline Resistance

To realize the low-cost hydrogen production system, the water splitting module that operates under alkaline conditions is paid much attention since it does not require noble metals such as Pt for electrodes. However, due to the low chemical stability of the anion-exchange membrane (AEM) which consists of polymers possessing cationic functional groups, modules that exhibit sufficient durability have scarcely been realized yet.

We have been working on the development of alkaline-tolerant triarylsulfonium (**TAS**) structures that are potentially applicable to cationic functional groups in robust AEM materials. Based on the synthetic methods including the Friedel-Crafts reaction using diaryl sulfoxides, **TASs** with excellent alkaline stability were developed by introducing sterically demanding substituents.<sup>1)</sup> For example, **TAS-cC** exhibits 25 times higher stability compared to benzyltrimethylammonium (BTMA), the commonly used cationic functional group for AEM materials. To develop further cations with much excellent alkaline-resistant properties, **TASs** with electron-donating groups such as -NMe<sub>2</sub> and -OMe (**TAS-cC-NMe<sub>2</sub>** and **TAS-cC-OMe**, respectively) were prepared by the post-functionalization of a fluorine-substituted reactive precursor (**Fig.1**). Especially, in the case of **TAS-cC-NMe<sub>2</sub>**, it was surprising that no decomposition occurred even after 30 d in 2 M KOH/CD<sub>3</sub>OH at 80 °C (**Fig. 2**). The synthesis of polymers containing alkaline-tolerant **TAS** units will also be described.



**Fig. 1** Post-functionalization of **TAS**.



**Fig. 2** Alkaline stability of functionalized **TAS** cations

1) T. Imai, R. Hifumi, S. Inagi, I. Tomita, *72nd SPSJ Symp. Macromol.*, **2023**, 2B18.