アカデミックプログラム［B講演］ | 13. 有機化学—反応機構・光化学・電気化学：口頭B講演

2025年3月28日(金) 15:55 ~ 17:15 [F]2302(第4学舎 2号館 [3階] 2302)

[[F]2302-3vn] 13. 有機化学—反応機構・光化学・電気化学

座長：岡田 洋平、野上 敏材

英語
15:55 ~ 16:15
[[F]2302-3vn-01]
直接的な電極電子移動に基づくポリフルオレンのホスホニル化反応
○谷口 晃平[1]、佐藤 宏亮[1]、稲木 信介[1] (1. 東京科学大学)

英語
16:15 ~ 16:35
[[F]2302-3vn-02]
環状[n]スピロビフルオレニレン誘導体の合成とその一電子酸化体における分子内電子移動
○今井 友也[1]、酒巻 大輔[2]、青柳 忍[1]、雨夜 徹[1] (1. 名古屋市立大学、2. 大阪公立大学)

英語
16:35 ~ 16:55
[[F]2302-3vn-03]
水素結合複合体の電解酸化によるスルホンアミジルラジカル発生を経るスルタムの合成
○奥村 恭之[1]、光藤 耕一[1]、菅 誠治[1] (1. 岡山大院自然)

日本語
16:55 ~ 17:15
[[F]2302-3vn-04]
嵩高いアミノ酸への適用が可能な電気化学的ペプチド合成法の開発
○新城(永原） 紳吾[1]、岡田 洋平[1]、平塚 剛毅[1]、北野 克和[1]、千葉 一裕[1] (1. 東京農工大学)

Phosphonylation of Poly(9,9-dioctylfluorene) via Direct Electron Transfer at Anode

(*School of Materials and Chemical Technology, Institute of Science Tokyo*)
○Kohei Taniguchi, Kosuke Sato, Shinsuke Inagi

Keywords: C–H post-functionalization, electrochemical reaction, anodic phosphonylation, electrode electron transfer, diffusion coefficient

Electrochemical polymer reactions are promising methods for the functionalization of polymers, allowing precise control through electrochemical parameters such as the amount of charge passed and current density. To date, electrochemical reactions of π-conjugated polymers in the film state have been explored.[1,2] However, the range of applicable polymer derivatives is limited to those stable in the film state on the electrode surface without detaching during electrolysis. Given these challenges, electrolysis of polymer solutions has significant potential to improve the versatility of electrochemical polymer functionalization. In this study, we investigated the anodic phosphonylation of π-conjugated polymers such as poly(9,9-dioctylfluorene) (PFO) in solution.

First, we conducted the anodic phosphonylation of PFO, resulting in a high degree of substitution (0.91) at a low current density (Figure 1 (a)). The diffusion coefficient of PFO was 2.5×10^{-7} while that of 2,7-bis[4-(1,1-dimethylethyl)phenyl]-9,9-dimethyl-9*H*-fluorene was 6.5×10^{-6}, indicating that a low current density is required for efficient electron transfer between the polymer and the electrode. Additionally, the degree of substitution could be controlled by tuning the amount of charge passed (Figure 1 (b)). In this presentation, the more detailed results and discussion will be explained.

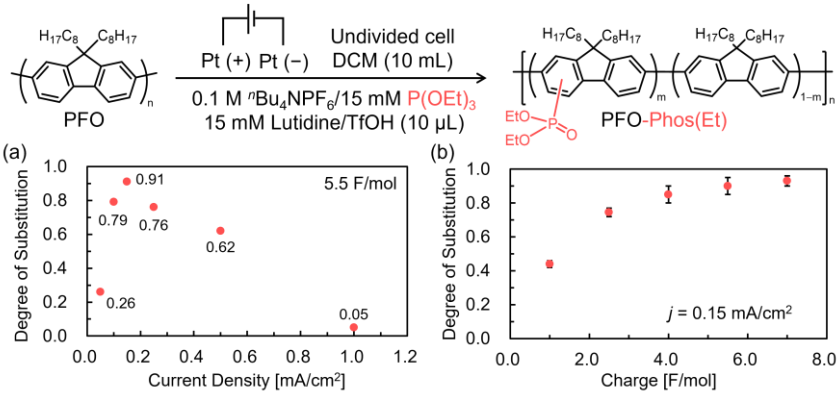


Figure 1. Anodic phosphonylation of PFO. (a) the plot of the degree of substitution vs. current density and (b) the trace of the degree of substitution with various amounts of passed charge.

References

[1] S. Inagi, T. Fuchigami, *Macromol. Rapid Commun.*, **2014**, *35*, 854–867.
[2] T. Kurioka, S. Inagi, *Chem. Rec.*, **2021**, *21*, 2107–2119.

Synthesis of Cyclic[*n*]spirobifluorenylene Derivatives and Intramolecular Electron Transfer in One-Electron Oxidized Species

([1]*Graduate School of Science, Nagoya City University*, [2]*Graduate School of Science, Osaka Metropolitan University*) ○Tomoya Imai,[1] Daisuke Sakamaki,[2] Shinobu Aoyagi,[1] Toru Amaya,[1]

Keywords: Spirobifluorene; Redox; Intramolecular Electron Transfer; Spiro-Conjugation

The study of electron delocalization in organic molecules with multiple redox-active units is essential for the development of organic electronics. Organic mixed-valence compounds represent a class of molecules comprising multiple redox units in different valence states. Electron transfer in organic mixed-valence compounds is highly dependent on the molecular structure. A key question in studying electron transfer in molecules with multiple redox units is: "To what extent can electrons delocalize across these units?"

Recently, we reported the synthesis and characterization of macrocyclic compounds **1-[*n*]** (*n* = 3–5) featuring spirobifluorene as a building block (Figure 1a).[1] Cyclic[*n*]spirobifluorene showed small orbital splitting of frontier molecular orbitals due to spiro-conjugation. While orthogonal conformations are generally considered disadvantageous for electron transfer, we hypothesized that, contrary to intuition, electron transfer in their radical cation species could occur due to spatial electronic coupling through spiro-conjugation and the small HOMO-SOMO gap. In this study, we synthesized cyclic[*n*]spirobifluorene derivative **2-[*n*]** with bulky alkyl groups at the terminal positions of each unit. In this presentation, we report the extent of hole delocalization in **2-[*n*]**$^{\bullet+}$ (*n* = 3–5) through electron transfer (Figure 1b).[2]

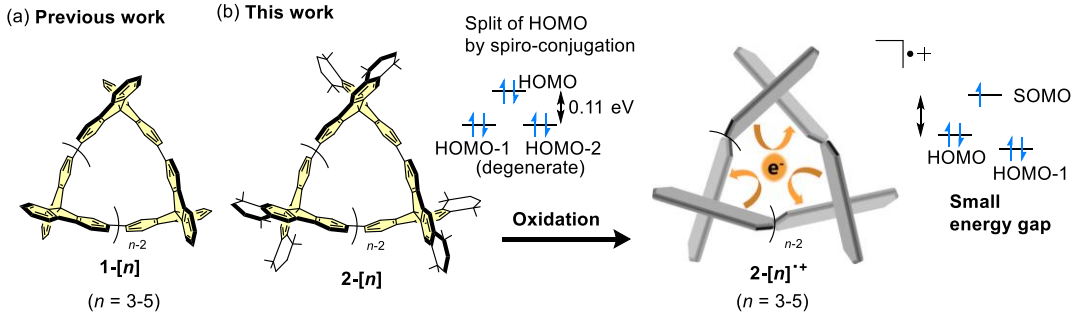


Figure 1: (a) Previous work on cyclic[*n*]spirobifluorenylenes **1-[*n*]**. (b) This work on intramolecular electron transfer in the radical cation of **2-[*n*]**

1) K. Zhu, K. Kamochi, T. Kodama, M. Tobisu, T. Amaya, *Chem. Sci.* **2020**, *11*, 9604.
2) T. Imai, D. Sakamaki, S. Aoyagi, T. Amaya, *Chem. Eur. J.* **2023**, *29*, e202302670.

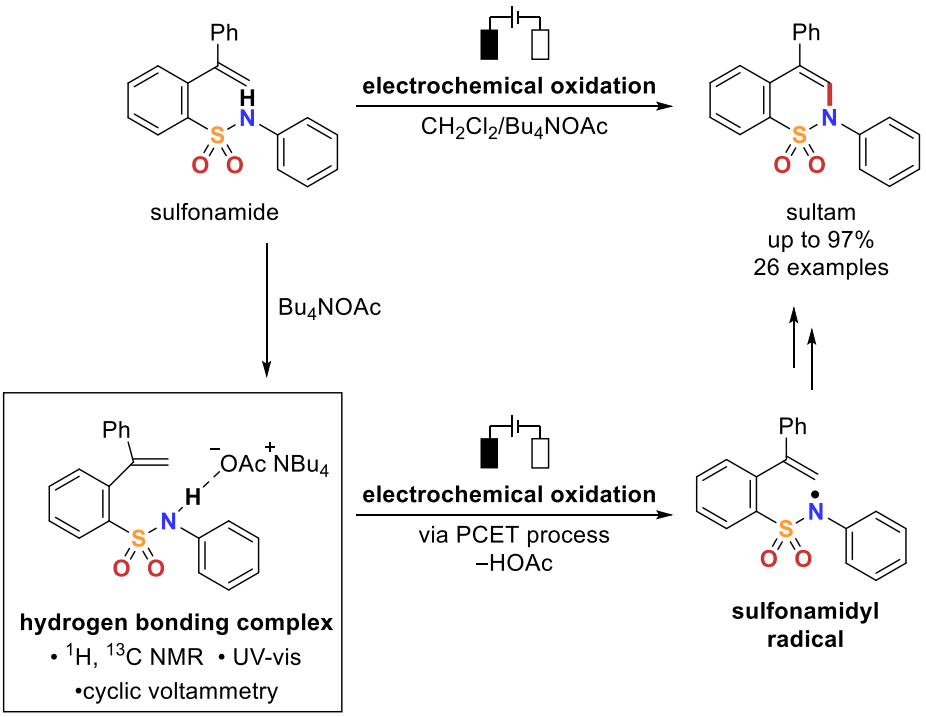
Electrochemical Synthesis of Sultams via Sulfonamidyl Radical Generated by Anodic Oxidation of Hydrogen Bonding Complexes

([1]*Okayama University*) ○Yasuyuki Okumura,[1] Koichi Mitsudo,[1] Seiji Suga[1]

Keywords: sulfonamidyl radical, electrochemical oxidation, hydrogen bonding complex, proton coupled electron transfer, sultam

Amidyl radicals and sulfonamidyl radicals are widely used in the field of organic synthesis.[1] In particular, electrochemical oxidation of amides in the presence of bases is one of the most practical methods for generating amidyl radicals. However, it is often difficult to observe "true" radical precursor, such as an amide or a hydrogen bonding complex with an amide and a base.[2,3]

We reveal that the sulfonamides and Bu_4NOAc form the 1:1 hydrogen bonding complex by several spectroscopic experiments. Cyclic voltammetry suggests that the complexes would be oxidized more easily than sulfonamides and Bu_4NOAc, and sulfonamidyl radical would be generated via proton-coupled electron transfer process (PCET) by the electrochemical oxidation of the complexes. Thus-generated sulfonamidyl radicals could be applied for the electrochemical synthesis of a variety of sultams.



1) Roisen, J. L. et al. *Chem. Rev.* **2022**, *122*, 2353. 2) Moeller, K. D. et al. *J. Am. Chem. Soc.* **2008**, *130*, 13542. 3) Lei, A. et al. *ACS Catal.* **2018**, *8*, 9370.

嵩高いアミノ酸への適用が可能な電気化学的ペプチド合成法の開発

（東農工大院農）新城（永原）紳吾・岡田洋平・平塚剛毅・北野克和・千葉一裕
Electrochemical peptide synthesis applicable to sterically hindered amino acids using electron-rich phosphines ([1]*Graduate School of Agricultutre, Tokyo University of Agriculture and Technology)* Shingo Shinjo-Nagahara, Yohei Okada, Goki Hiratsuka, Yoshikazu Kitano, Kazuhiro Chiba

While peptides have been regarded as one of the candidates for medium molecular medicine, a problem that the large amount of waste is produced in the conventional peptide synthesis have been unresolved. One of the causes is use of coupling reagents. In every peptide bond formation, these reagents are used stoichiometrically, and byproducts accumulate as waste.

In this context, we have developed electrochemical peptide synthesis using triphenylphosphine as a recyclable coupling reagent. We confirmed that this reaction is applicable to all canonical amino acids, and demonstrated that producing waste from the coupling reagent can be avoided.

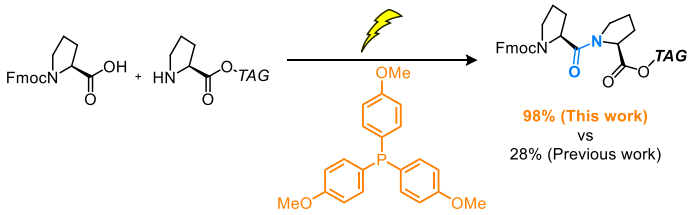
Yet, there was room for improvement in the viewpoint of reaction efficiency, especially when sterically hindered amino acids were employed. In this work, we found that tris(4-methoxyphenyl)phosphine improves the reaction efficiency. We also succeeded in synthesizing oligopeptides difficult for our previous method.

Keywords：electrochemical synthesis, peptide synthesis, phosphine

ペプチドは，中分子医薬品開発において注目を集めているが，合成時に大量の廃棄物が排出される課題がある．その一因として，縮合剤の使用が挙げられる．縮合剤は，アミノ酸を 1 残基伸長するごとに化学量論量を要し，同当量の副生成物が生じて廃棄物の蓄積につながっている．

この問題に対し，我々はトリフェニルホスフィンをリサイクル可能な縮合剤として用いた電気化学的ペプチド合成法を開発した [1)]．本合成法は，基本的なアミノ酸 20 種すべてに適用可能であることに加え，縮合剤由来の廃棄物を削減できる．

一方，嵩高いアミノ酸を縮合する際には反応が完結せず，通電後に原料が残存する課題があった．本研究において，我々は tris(4-methoxyphenyl)phosphine を用いた際に反応効率が向上することを見出し，以前の方法では合成困難なオリゴペプチドの合成にも成功した [2)]．



1) S. Nagahara, Y. Okada, Y. Kitano, K. Chiba, *Chem. Sci.*, **2021**, *12*, 12911-12917; 2) S. Shinjo-Nagahara, Y. Okada, G. Hiratsuka, Y. Kitano, K. Chiba, *Chem. Eur. J.* **2024**, *30*, e202402552.