アカデミックプログラム［Ｂ講演］｜18. 高分子：口頭Ｂ講演

2024年3月18日(月) 13:00 ~ 14:40 D341(3号館 [4階] 341)

[D341-1pm] 18. 高分子

座長：稲木 信介、相見 順子

日本語

13:00 ~ 13:20

[D341-1pm-01]

共有結合性有機構造体の電極表面への間接電解合成とその応用

○佐藤 宏亮[1]、白倉 智基[1]、稲木 信介[1] (1. 東京工業大学)

日本語

13:20 ~ 13:40

[D341-1pm-02]

電荷蓄積高分子を用いて溶液プロセスで作製する有機トランジスタメモリ

○相見 順子[1] (1. 物質・材料研究機構)

英語

13:40 ~ 14:00

[D341-1pm-03]

Tailoring Electrochromic Properties through Ru-Carbon Covalent Bonds: Design and Synthesis of Metallosupramolecular Polymers

○BANCHHANIDHI PRUSTI[1], Takasi Sato[1], Ritsuko Nagahata[2], Masayoshi Higuchi[1] (1. National Institute for Materials Science, 2. National Institute of Advanced Industrial Science and Technology)

英語

14:00 ~ 14:20

[D341-1pm-04]

Image Data Analysis of Electrochromic Display Devices for Improvement of the Durability

○Shifa Sarkar[1,2], Masayoshi Higuchi[1,2] (1. National Institute for Materials Science, 2. Osaka University)

英語

14:20 ~ 14:40

[D341-1pm-05]

大気安定性の高いn型化学ドーピングによる高分子半導体ダイオードの電子注入特性向上

○山下 侑[1,2]、刑部 永祥[2]、田嶋 陽子[2]、Stephen Barlow[3]、Seth Marder[3]、渡邉 峻一郎[2]、竹谷 純一[1,2] (1. 物材機構、2. 東大、3. コロラド大ボルダー校)

共有結合性有機構造体の電極表面への間接電解合成とその応用

（東工大物質理工 [1]）　○佐藤宏亮 [1]・白倉智基 [1]・稲木信介 [1]

Indirect Electrochemical Synthesis of Covalent Organic Frameworks on Electrode Surface and Its Application

([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology*)
○Kosuke Sato[1], Tomoki Shirokura[1], Shinsuke Inagi[1]

Covalent organic framework (COF) is known as a functional polymer material with stability and porosity. In our previous work, we have reported an indirect electrolytic method to form imine-base COFs by using electrochemically generated acid (EGA). However, the practical application of the resultant COF film was unexplored. In this study, we attempted to control the morphology of the COF thin films by controlling the amount of EGA. Under the coexistence of monomers, the COF film was synthesized by electrochemical oxidation of diphenylhydrazine, a precursor of EGA, in the DMF electrolyte (Fig. 1a). The thickness of the film was controllable within a range of 1 to 10 μm, depending on the conditions. Furthermore, under low EGA source concentration conditions, we effectively controlled the coating thickness of the COFs on carbon nanotubes, achieving a range between 6 and 32 nm. (Fig. 1b). We applied the EGA-assisted synthesis method to various carbon materials and evaluated them as electrocatalysts related to water spiriting reaction. *Keywords : Covalent Organic Frameworks; Electrochemical Synthesis; Composite Materials; Thin Film; Electrocatalyst*

共有結合性有機構造体(COF)は、分子構造に基づく機能と安定性・多孔性とを両立した材料であり、合成法に依存して形態や特性が左右される。COFの合成法として、当研究室では電解発生酸(EGA)でイミン結合を形成させる間接電解法を報告している[1]。しかし、本手法はCOF粒子凝集体を得るに留まっており、COFの機能を活かした応用は達成されていない。本研究では、EGA発生量すなわちCOF生成の駆動力を電解条件によりコントロールすることで、COFの形態制御とその応用を検討した。

モノマーの共存下、EGA源であるジフェニルヒドラジンをDMF中で電解酸化することでCOFの合成を行った(Fig. 1a)。EGA源濃度20 mMのとき、膜厚は電解条件に依存し1–10 μmの範囲で変化した。EGA源濃度2 mMの条件下、電解時間を10–90 secの間で変化させると、多層カーボンナノチューブ上に形成されるCOF層の厚さを6–32 nmの範囲で制御可能であった(Fig. 1b)。種々のカーボンに本手法を適用し得られた複合体を、電極触媒として評価しその形状と電極触媒活性について考察した。

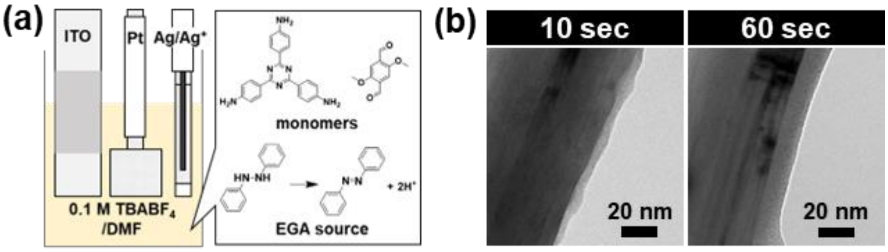


Fig. 1 (a) Electrochemical cell setup in this work (b)TEM images of the COF/carbon nanotube

1) S. Inagi, *et al. Angew. Chem. Int. Ed.*, **2023**, *62*, e202307343.

電荷蓄積高分子を用いて溶液プロセスで作成する有機トランジスタメモリ

（物質・材料研究機構[1]）○相見順子[1]

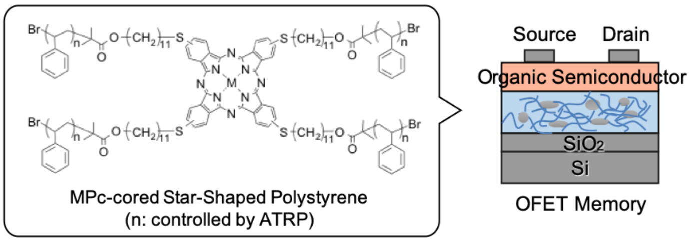
Solution-processable OFET memory devices based on star-shaped polymers with a phthalocyanine core

([1]*National Institute for Materials Science* (NIMS)) ○Junko Aimi[1]

Non-volatile organic filed-effect transistor (OFET) memory is an emerging and promising technology for possible use in wearable data storage. We have developed charge-trapping materials for the organic memory based on a metallophthalocyanine (MPc)-cored star-shaped polystyrene (MSP). The MPc cores form self-assembled nano-sized aggregates dispersed in and isolated by the surrounding polystyrene arms, permitting them to store or release hole charges in a manner similar to a nano-floating gate. In this study, we prepared OFET memory devices by a one-pot solution process via polymer-matrix assisted phase separation of MSP and a soluble organic semiconductor.

Keywords ：OFET Memory Device; Star polymer; Phthalocyanine, Phase Separation

多様化する市場ニーズに伴い、有機材料を用いる有機不揮発性メモリが近年注目されている。我々は、金属フタロシアニンをコアに持つスターポリマー（MSP）を有機トランジスタメモリの記録層（ナノフローティングゲート）材料に用いて、高性能有機フラッシュメモリを開発した。このスターポリマーは、電荷蓄積部位である金属フタロシアニンコアが絶縁体のポリスチレンに囲まれた構造を持ち、有機トランジスタ素子中で有機半導体との電荷の授受により安定な電荷蓄積材料として機能する1)。ポリスチレン鎖を精密重合することで、ナノフローティングゲート構造を調節することができ、最終的なデバイス性能を向上させることができる2)。また、可溶性有機半導体とスターポリマーの相分離を利用することで、基板上に有機半導体・メモリ層を一度に成膜することが可能である3)。本研究では、成膜条件の検討により、有機半導体の真空蒸着プロセスを必要とせずに OFET メモリを作製するプロセス技術を開発した。



1) J. Aimi, C. T. Lo, H. C. Wu, C. F. Huang, T. Nakanishi, M. Takeuchi, W. C. Chen, *Adv. Electron. Mater.*, **2016**, *2*, 1500300. 2) J. Aimi, P. H. Wang, C. C. Shih, C. F. Huang, T. Nakanishi, M. Takeuchi, H. Y. Hsueh, W. C. Chen, *J. Mater. Chem. C.* **2018**, 6, 2724. 3) J. Aimi, T. Yasuda, C. F. Huang, M. Yoshio, W. C. Chen, *Mater. Adv.*, **2022**, 3, 3128.

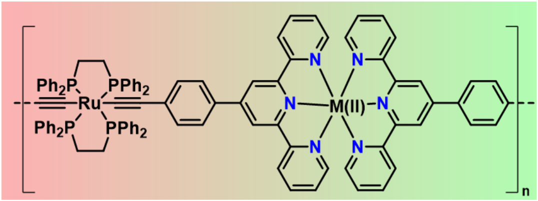
Tailoring Electrochromic Properties through Ru-Carbon Covalent Bonds: Design and Synthesis of Metallosupramolecular Polymers

([1]*National Institute for Materials Science*, [2]*National Institute of Advanced Industrial Science and Technology*) ○ Banchhanidhi Prusti,[1] Takasi Sato,[1] Ritsuko Nagahata,[2] Masayoshi Higuchi[1]

Keywords: Metallosupramolecular Polymer; Electrochromism; Near-Infrared Absorption; Device Fabrication; Ru-Based Polymer

Electrochromism refers to the phenomenon of color alteration when an electrical voltage is applied. Its application is extensive, finding relevance in practical, real-world scenarios.[1-3] The incorporation of metal species into the organic framework introduces color to these systems. Consequently, the control of the metal-to-ligand charge transfer phenomenon can be achieved through the application of an external potential. Metallosupramolecular polymers (MSPs), belonging to the category of amorphous materials, exhibit rapid color changes, robust durability, and facile fabrication. Therefore, there is a need to explore these materials for various applications. Recently, there has been a notable focus on investigating near-infrared (NIR) electrochromism, particularly due to its promising applications in the development of smart windows designed for heat-shading.

Our research group has been dedicated to the development of metallosupramolecular polymers (MSPs). This report outlines the synthesis of a series of organometallic-bonded MSPs, namely **PolyRuRu**, **PolyRuFe**, and **PolyRuZn**. Characterization was carried out using ^{1}H NMR, revealing an average molecular weight on the order of 10^4. Among these polymers, **PolyRuZn** demonstrated NIR absorption (1100 nm) under the influence of voltage, attributed to intervalence charge transfer, whereas **PolyRuFe** and **PolyRuRu** did not exhibit NIR switching. Notably, **PolyRuZn** exhibited outstanding features, including a high contrast ratio ($\Delta T > 60\%$), impressive color efficiency ($\eta = 333$ cm^2/C), and a rapid response rate (within 3 seconds) in the NIR spectrum. Consequently, a device incorporating PolyRuZn was crafted for UV-vis and NIR absorption studies.



❑ Organometallic-Bonded MSPs ❑ UV-Vis to NIR Switching

1) Y. Wang, R. Shen, S. Wang, Y. -M. Zhang, S. X. -A. Zhang, *Adv. Mater.* **2021**, *34*, 2104413. 2) X. Liu, J. Wu, Z. Tang, J. Wu, Z.. Huang, X. Yin, J. Du, X. Lin, W. Lin, G. Yi, *ACS Appl. Mater. Interfaces.* **2022**, *14*, 33829. 3) a) G. Cai, J. Wang, P. S. Lee, *Acc. Chem. Res.* **2016**, *49*, 1469.

Image Data Analysis of Electrochromic Display Devices for Improvement of the Durability

([1]*Graduate School of Information Science and Technology*, *Osaka University*, [2]*National Institute for Materials Science*) ○Shifa Sarkar,[1,2] Masayoshi Higuchi[1,2]

Keywords: Electrochromic Devices; Metallo-Supramolecular Polymer; Degradation Analysis; Image Data; Durability

Electrochromic devices (ECDs) are cutting-edge technologies for their applications ranging from smart windows to electronic paper that change optical properties in response to an applied voltage. Among the various electrochromic (EC) materials, metallo-supramolecular polymers (MSPs), specifically Fe(II)-based MSP (polyFe), have received much attention for their unique properties. However, the long-term performance and stability of these devices are critical factors for practical applications. These devices might degrade over time, which would decrease their effectiveness and functionality. It becomes essential to conduct a detailed analysis of the degradation patterns in electrochromic devices to address this problem. This work employs the Python OpenCV library to perform advanced grayscale image processing techniques for the degradation analysis of polyFe-based ECDs.

Here, a solid-state polyFe-based ECD was fabricated by a spray coating method. Then chronoamperometric technique was used to understand the EC properties of the device for each cycle by taking movies and images. The device changed its color from purple to colorless at a low voltage of 1.0V. For the 1st cycle, the images showed a colorless state of the device but in the case 1000th cycle, the device was not able to show a completely bleached state. Besides during the cyclic test, for image data analysis, movies were taken to record the degradation performance phenomenon of the device. Python OpenCV was used to extract images from movies which were then cropped and converted into grayscale images from where pixel values were extracted. By using the pixel values time vs. contrast graphs were plotted for 1st to every 100th cycle till the 1000th cycle. The time vs. contrast graph for the 1st cycle exhibited a sharp change of purple color to a colorless state in the device; on the other hand, the graph for the 1000th cycle didn't show a sharp color change which indicates, the performance of the device becomes slower as the cycle number increases.

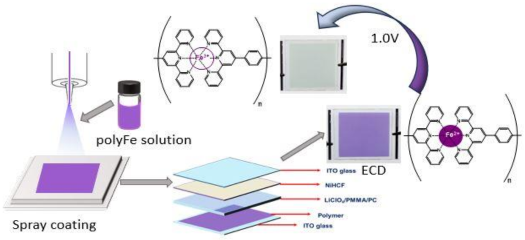


Fig.1: Fabrication and EC properties of a polyFe-based ECD

1) Monk, P. M. S.; ECM and Devices; John Wiley & Sons, **2015**. 2) Gustavsen, A; Sol. Energy Mater. Sol. Cells, **2010**, *94*, 105.

Highly air-stable n-type chemical doping improving electron injection properties in polymeric semiconductor diodes

([1]NIMS, [2]The Univ. of Tokyo, [3]CU-Boulder) ○Yu Yamashita[1,2], Nobutaka Osakabe[2], Akiko Tajima[2], Stephen Barlow[3], Seth R. Marder[3], Shun Watanabe[2], Jun Takeya[1,2]

Keywords: organic semiconductor, chemical doping, diode

Chemical doping using redox reactions has been used to control the electronic properties of organic semiconductors[1]. Redox reactions between effective n-type dopants and organic semiconductors introduce electrons and cationic dopants into the semiconductors. However, owing to the reactivity and diffusivity of dopant molecules, a doping process that is stable and selective to certain parts of devices has been challenging. Recently, we reported novel doping processes that achieve moderately ambient-stable n-type doping[2,3]. The dimer of metal complexes $(RuCp^*Mes)_2$ shown in Fig. a is a strong reducing agent that forms a cationic monomer through dimer cleavage and redox reactions. The use of this dopant dramatically improves the stability of n-type doping compared with the conventionally employed cobaltocene, where the former can maintain a stable 18-electron cationic state[2].

We have developed a method to selectively introduce this stable dopant material at the electrode/semiconductor interface in diodes, which improve injection characteristics and enable GHz operation of the fabricated diodes. In this method (Fig. a), the Au electrode was treated with $(RuCp^*Mes)_2$ to introduce electrons and dopant cations on the electrode surface, which dramatically shifts the work function to 3.7 eV (Fig. b). Following this process, a polymer semiconductor thin film and a top electrode were fabricated. The selective introduction of dopant cations at the electrode/semiconductor interface without diffusion was evident from electrical conduction measurements of the diode and X-ray photoelectron spectroscopy. The mechanisms for the adsorption of dopant molecules through redox reactions and the suppression of their diffusion will be discussed in this talk.

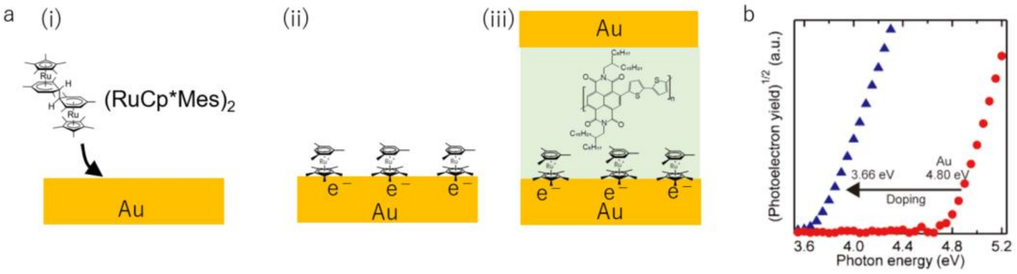


Figure a. The processes and materials to fabricate diodes. (b) Photoelectron yield spectroscopy of Au electrode before (red) and after (blue) the treatment with $(RuCp^*Mes)_2$.

(1) Y. Yamashita, J. Takeya, S. Watanabe et al., Nature 572, 634 (2019). (2) Y. Yamashita, S. R. Marder, J. Takeya et al., J. Mater. Chem. C, 9 4105 (2021). (3) Y. Yamashita, S. R. Marder, S. Watanabe *et al.*, preprint DOI: 10.21203/rs.3.rs-3484432/v1.