アカデミックプログラム［B講演］ | 11. 有機化学—構造有機化学：口頭B講演

2025年3月28日(金) 9:00 ~ 11:30 [F]2205(第4学舎 2号館 [2階] 2205)

[[F]2205-3am] 11. 有機化学—構造有機化学

座長：羽村 季之、清水 大貴

英語
9:00 ~ 9:20
[[F]2205-3am-01]
炭素がなす究極的共有結合の探求

○島尻 拓哉[1] (1. 東京大学大学院理学系研究科)

日本語
9:20 ~ 9:40
[[F]2205-3am-02]
電気化学的構造変換を利用した多様な分子構造の創出

張本 尚[1,2]、菊池 モト[1]、鈴木 孝紀[1]、○石垣 侑祐[1] (1. 北大院理、2. 分子研)

日本語
9:40 ~ 10:00
[[F]2205-3am-03]
キュバン異性化反応におけるJahn–Teller効果

○杉村 潤輝[1,2]、春田 直毅[1,2]、竹邊 日和[1]、松原 誠二郎[1]、佐藤 徹[1,2] (1. 京大院工、2. 京大福井セ)

日本語
10:00 ~ 10:20
[[F]2205-3am-04]
酢酸エステルにおける枝分かれ構造及び環構造の変化と匂いの関係について

○井上 翔也[1] (1. 早稲田中学高等学校)

10:20 ~ 10:30
休憩

英語
10:30 ~ 10:50
[[F]2205-3am-05]
超原子価ケイ素化合物の幾何構造を用いたπ共役系のエネルギー変調

○権 正行[1]、田中 一生[1] (1. 京都大学)

日本語
10:50 ~ 11:10
[[F]2205-3am-06]
ビフェニレンとジエチニレンを構成単位としたマクロサイクルの合成と性質：大環状骨格におけるビフェニレン部位を介したπ電子共役系の形成

長山 祥子[1]、川勝 宏樹[1]、浅井 大輔[1]、○田原 一邦[1] (1. 明治大学)

英語
11:10 ~ 11:30
[[F]2205-3am-07]
Self-assembly-induced luminescence of pyrene derivatives driven by anionic surfactants

○Jamuna Kannan[1], Rasel Ahmed[1], Yuna Kim[1], Ken-ichi Iimura[1] (1. Utsunomiya University)

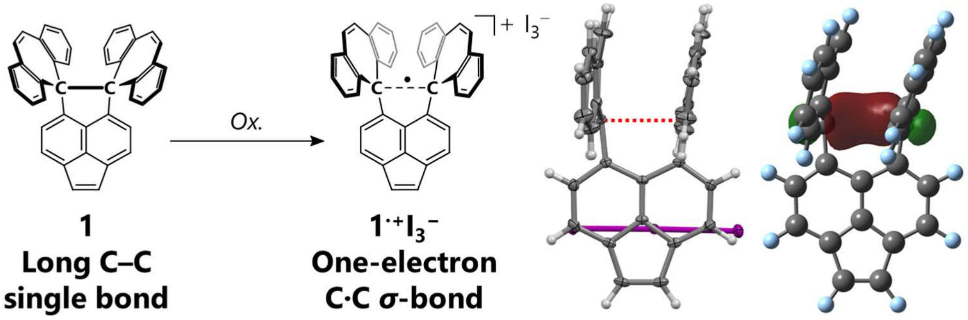
Exploring the ultimate covalent bond based on carbon

(*Graduate School of Science, The University of Tokyo*) ○Takuya Shimajiri

Keywords: One-electron C•C *σ*-bond; X-ray analysis; Raman spectroscopy; Near-infrared absorption

Covalent bonds share electron pairs between two atoms and make up the skeletons of most organic compounds in single, double and triple bonds. Meanwhile, Pauling proposed a concept of covalent bonds with one unpaired electron (‘one-electron *σ*-bonds’) in 1931, which is shared between two atoms.[1] In striking contrast to the large body of work on electron-pair bonds, the paucity of examples with one-electron bonds is remarkable, which is most likely due to their intrinsic weakness. So far, merely five studies have reported on the subject of one-electron bonds between atoms other than carbon.[2-5] Importantly, since Pauling’s postulation almost a century ago, direct evidence (*e.g.*, X-ray structural analysis) that would corroborate the presence of such one-electron bonds between carbon atoms, which is arguably the most prevalent element in organic chemistry, has remained recalcitrantly elusive. Although several attempts have been made to directly prove the presence of a one-electron bond, in almost all cases these one-electron bonded species were only detected transiently using methods such as electron-spin-resonance.

In this work, the isolation of a compound with a one-electron *σ*-bond between carbon atoms is reported by means of the one-electron oxidation of a HPE-type hydrocarbon with an elongated C–C single bond.[6] The presence of the C•C one-electron *σ*-bond (2.921(3) Å at 100 K) was confirmed experimentally by single-crystal X-ray diffraction analysis and Raman spectroscopy for the single crystals of the obtained salt, and theoretically by density functional theory calculations.



1
Long C–C single bond

$1^{\cdot+}I_3^-$
One-electron C·C *σ*-bond

1) L. Pauling, *J. Am. Chem. Soc.* **1931**, *53*, 3225.; 2) G. Bertrand *et al., Science* **1998**, *279*, 2080.; 3) J. C. Peters *et al., J. Am. Chem. Soc.* **2013**, *135*, 3792.; 4) M. Wagner *et al., Angew. Chem. Int. Ed.* **2014**, *53,* 4832. 5) J. Xie, J.-H. Su, X.-J. Yang *et al., J. Am. Chem. Soc.* **2024**, *146*, 2333–2338.; 6) T. Shimajiri, S. Kawaguchi, T.Suzuki, Y. Ishigaki, *Nature* **2024**, *634*, 347‑351.

電気化学的構造変換を利用した多様な分子構造の創出

（北大院理[1]・分子研[2]）張本 尚[1,2]・菊池 モト[1]・鈴木 孝紀[1]・○石垣 侑祐[1]

Electrochemical Transformations to Realize Diverse Structures of Linked Quinodimethanes

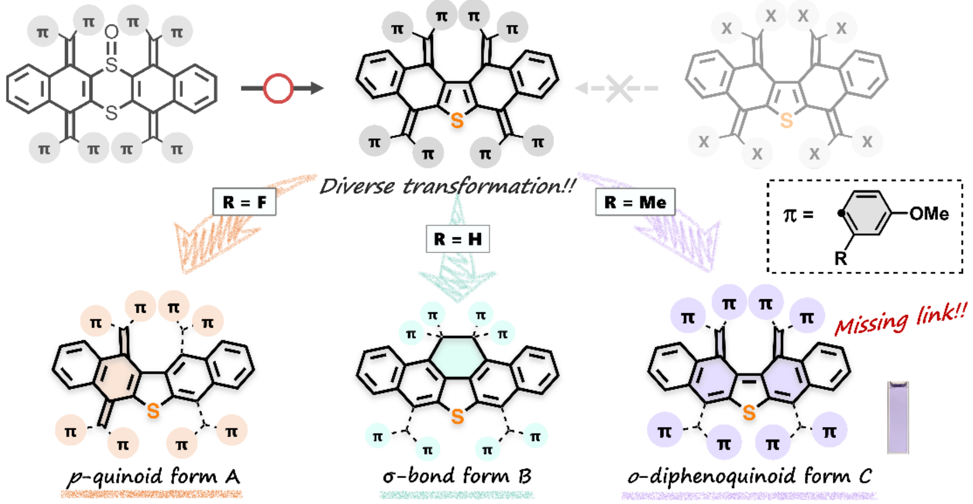
([1]*Faculty of Science, Hokkaido University*, [2]*Institute for Molecular Science*)
Takashi Harimoto,[1,2] Moto Kikuchi,[1] Takanori Suzuki,[1] ○Yusuke Ishigaki[1]

Covalently linked quinodimethane derivatives were designed as unprecedented redox-active motifs that can be converted into three different geometries via electrochemical stimulation. Based on the isolation and X-ray analysis, we demonstrate that the favored geometry of the corresponding redox states of each derivative can be precisely controlled by adjusting the steric bulk of the *ortho* substituents of the aryl group to change the proximity of the quinodimethane units. This redox-mediated strategy also led to the isolation and structural determination of the missing link with an *o*-diphenoquinoid structure, a diphenoquinoid isomer whose isolation had remained elusive for almost a century.

Keywords : redox systems; para-quinodimethanes; long C−C bonds; ortho-diphenoquinoid; NIR absorption

パラキノジメタン（*p*-QD）は代表的な交差共役系骨格であり，可逆的なレドックス挙動を示すモチーフとして利用されてきた。分子内に複数の *p*-QD ユニットを導入することで，多電子移動を駆動可能な応答系が報告されているが，各レドックス状態における構造は母体となる *p*-QD 骨格の性質を引き継ぐのみである。

本研究では，従来にない構造変換を実現するため，共有結合で *p*-QD ユニットを連結した誘導体を設計・合成した。その結果，周辺 π 骨格上のオルト位置換基の嵩高さを調整することで，レドックス活性な *p*-QD ユニット間の σ／π 結合の組み換えの精密制御が可能となり，対応するレドックス状態で発現する分子構造の多様化を実現した。この戦略により，複数構造の発現のみならず，これまで単離例のないオルトジフェノキノイド構造をもつ分子の単離と構造決定に成功した。



Jahn–Teller Effect in Isomerization of Cubane

([1]*Graduate School of Engineering, Kyoto University*, [2]*Fukui Institute for Fundamental Chemistry, Kyoto University*) ○Junki Sugimura,[1,2] Naoki Haruta,[1,2] Hiyori Takebe,[1] Seijiro Matsubara,[1] Tohru Sato[1,2]

Keywords: *DFT; Symmetry; Substitution Effect; Point Group Theory; Reaction Path*

Cubane has been experimentally reported to isomerize to cuneane in the presence of Ag(I) Lewis acid catalysts. A substituted cubane yields product isomers, and their formation ratio depends on the introduced substituents. The reason for such a substituent effect has been veiled. In the present study, we determine a reaction path of the isomerization using density functional theory calculations and analyze the obtained reaction mode. Cubane becomes cationic by charge transfer to Ag(I), resulting in the Jahn–Teller effect. The cationic cubane can be thermally transformed between some stable equivalent structures on the Jahn–Teller potential energy surface (JTPES), and such a transformation (pseudo-rotation) gives rise to various patterns of C–C cleavages. Further coupling of a skeleton-twisting mode to the C–C cleavages results in the formation of cuneane. This result implies that introducing substituents asymmetrically warps the JTPES and makes the stable structures energetically non-equivalent, consequently making a difference in the formation ratio of isomers.

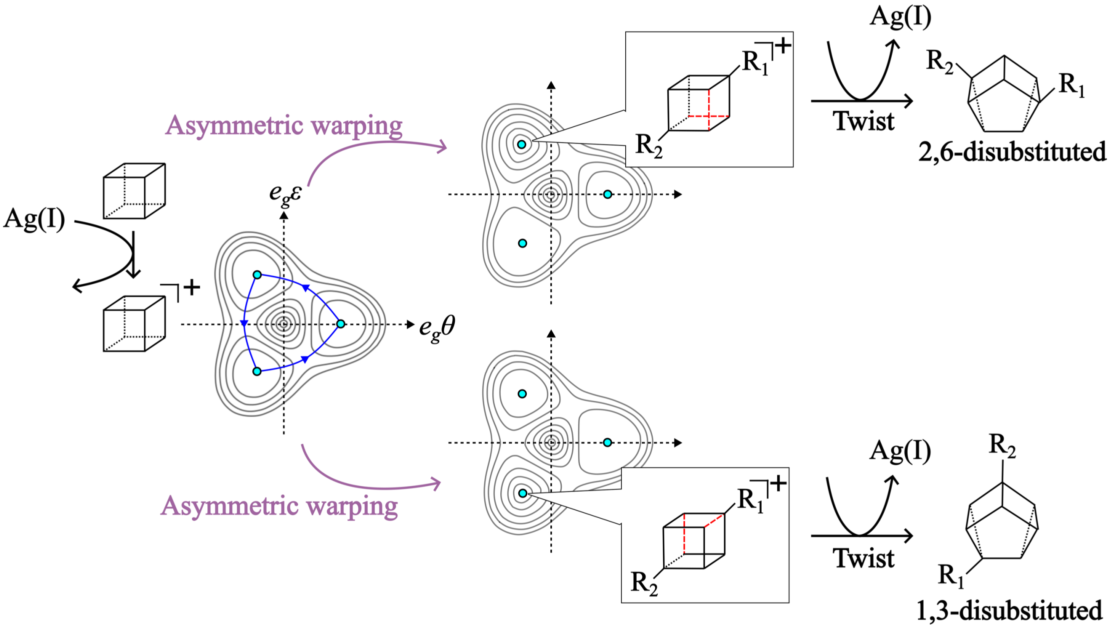


Fig. 1. The schematic diagram of isomerization reaction paths.

1) H. Takebe and S. Matsubara, Eur. J. Org. Chem. **27**, e202300891 (2024).

酢酸エステルおける枝分かれ構造及び環構造の変化と匂いの関係について

（早稲田中学高等学校 [1]）○井上 翔也 [1]

Relationship between changes in branching and ring structure and smell in acetate esters

([1]*Waseda junior and senior high school*) ○Shoya Inoue[1]

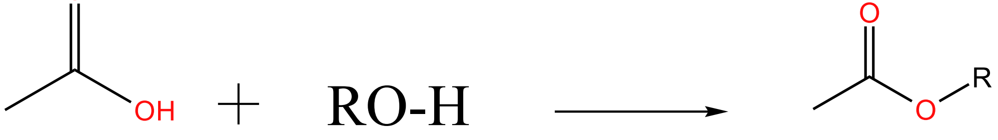
Acetate esters are a group of substances known as naturally occurring smell compounds. Last year, we synthesized acetate esters with 2-4 carbons in the side chain and published our findings on the relationship between odor, carbon number and branching structure. This time, we expanded the scope of our study to 8 carbons in the side chain and discussed esters with linear and branched structures at the same number of carbons, based on literature 2). At the same time, esters containing a ring structure were also discussed and reported. Acetate esters were synthesized using Fisher's ester synthesis.

The results of the investigation showed that there are combinations in which the odor changes depending on the position of the branching structure, and combinations in which there is no change. At the same time, it was also confirmed that the smell of acetate esters can be significantly changed by changing the type of ring structure, even at the same carbon number. These results, including those from last year, are discussed in terms of the physical properties of the molecule and the olfactory mechanism.

Keywords : Acetate esters, Smells, Branching structure, Structural Organic Chemistry.

酢酸エステルは、天然由来の香気成分として知られる物質群である。昨年、我々は側鎖の炭素数が 2~4 の酢酸エステルを合成し、その匂いと炭素数や枝分かれ構造との関係を見出し発表した 1)。今回は昨年より検討対象を拡大し、側鎖の炭素数を 8 まで増やして、文献 2)を基にしながら同一炭素数における直鎖構造を持つエステルと枝分かれ構造を持つエステルについての議論を行った。同時に環構造を含むエステルについても検討を行ったので報告する。酢酸エステルは Fisher のエステル合成を用いて合成した。

調査の結果、枝分かれ構造の位置によって匂いが変化する組み合わせと変化のない組み合わせがあることが分かった。同時に酢酸エステルにおいても、同一の炭素数でも環構造の種類を変えることによって匂いが大きく変わることも確かめられた。この結果について昨年の結果も含めて分子の物性と嗅覚メカニズムから考察する。



1) 井上翔也 酢酸エステルの匂いと炭素数および分子構造との関係について 日本化学会春記年会（2024）

2) Y. Oosuga; T.Hasegawa; E.Kuraya., Structure and Aroma of γ-Lactones Journal of Japan Association on Odor Environment vol. 51 issue 3 (2020) pp: 205-208

Energy Modulation of π-Conjugated System Based on Geometry of Five-Coordinated Hypervalent Silicon Compounds

(*Graduate School of Engineering, Kyoto University*)
○Masayuki Gon, Kazuo Tanaka

Keywords: Silicon; Hypervalent; Luminescence; Chromism; π-Conjugated system

A hypervalent compound is a class of molecules in which a main-group element has more than 8 electrons in its valence shell beyond the limits of the Lewis octet rule. We recently found a unique electronic effect of hypervalent bonds on the linked π-conjugated system originating from polarized three-center four-electron (3c-4e) bonds (Figure 1A).[1,2] In the five-coordinated structure, there are two geometries called square pyramidal (SP) and trigonal bipyramidal (TBP) geometries. Since the contribution of the 3c-4e bonds to the formation of SP and TBP geometries is different, it is expected that the energy modulation of π-conjugated systems depending on the geometries should be achieved. Herein, we investigated the optical properties through five-coordinated hypervalent silicon compounds with the SP and TBP geometries.

Hypervalent silicon compounds (**SAmPh** and **SAmMes**) with tridentate azomethine ligands were synthesized (Figure 1B). From the single crystal X-ray diffraction analysis, it is revealed that two different crystal polymorphs were obtained in **SAmPh**. The yellow and red crystals (**SAmPh-Y** and **SAmPh-R**) formed the SP ($\tau_5 = 0.207$, τ_5: degree of trigonality) and TBP ($\tau_5 = 0.830$) geometries, respectively. On the other hand, **SAmMes** was obtained as only one type of red crystal with the TBP ($\tau_5 = 0.797$) geometry. From these results, it was proved that geometrical control should be a novel strategy for energy modulation of the π-conjugated systems.

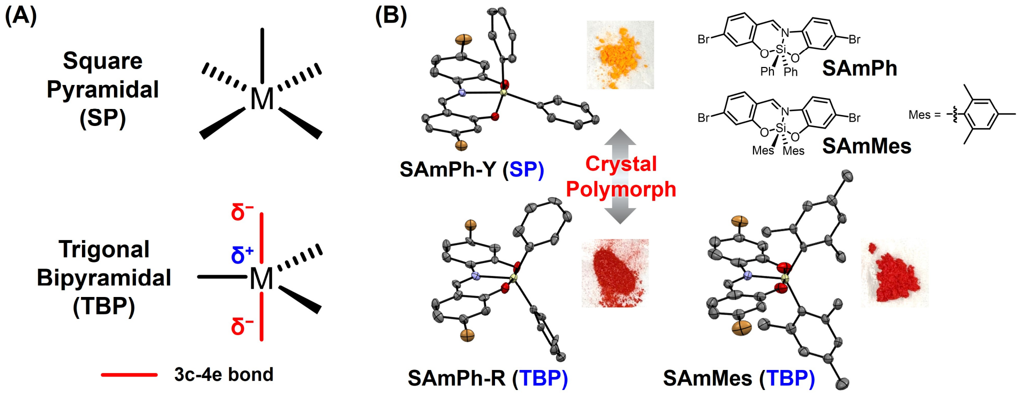


Figure 1. (A) Illustration of SP and TBP geometries. (B) ORTEP drawings and chemical structures of **SAmPh** and **SAmMes**. Hydrogen atoms are omitted for clarity.

1) Gon, M.; Tanaka, K. *Eur. J. Org. Chem.* **2024**, *27*, e202400738.
2) Gon, M.; Tanaka, K.; Chujo, Y. *Chem. Eur. J.* **2021**, *27*, 7561.

ビフェニレンとジエチニレンを構成単位としたマクロサイクルの合成と性質：大環状骨格におけるビフェニレン部位を介したπ電子共役系の形成

（明大院理工 [1]・明大理工 [2]）長山祥子 [1]・川勝宏樹 [1]・浅井大輔 [1]・○田原一邦 [2]

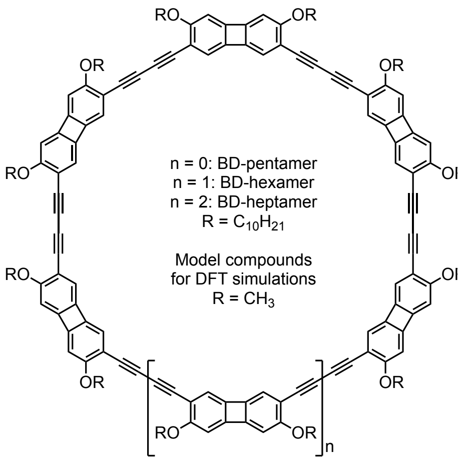
Synthesis and Properties of Macrocycles Comprising Biphenylene and Diethynylene Units: π-Electron Conjugation through Biphenylene Units

([1]*Graduate School of Science and Technology, Meiji University*, [2]*School of Science and Technology, Meiji University*) Shoko Nagayama,[1] Hiroki Kawakatsu,[1] Daisuke Asai,[1] ○Kazukuni Tahara[2]

We herein report the production of novel macrocycles consisting of biphenylene and diethynylene units. Comparison to arylene-diethynylene macrocycles and other reference compounds in their optoelectronic properties with the aid of sophisticated DFT calculations conclude that the biphenylene unit act as a linker with the connection angle of 120° maintaining π-electron conjugation. The macrocyclic π-electron conjugation pathway is established through a quinoidal electronic structure at the biphenylene units which enhances the local antiaromatic character of the 4MRs, leading to significant impacts on their electronic properties. The macrocycles form self-assembled molecular networks at the liquid-solid interfaces. The present knowledge is useful not only for designing the fully π-electron conjugated macrocycles but also for tuning their properties.

Keywords : Macrocycles; Biphenylene; Antiaromaticity; Self-Assembly; Liquid-Solid Interface

π共役した剛直な大環状化合物は、光電子材料への応用、様々な環境下での自己組織化による集合体の構築、分子内空孔でのゲスト分子認識などから多大な関心を集めている。今回我々は、ビフェニレンとジエチニレンを構成単位とした新たな大環状化合物（BD-macrocycle）を合成してそれらの性質を調べた。また、参照化合物として合成したアリールとジエチニレンを構成単位とする大環状化合物（AD-macrocycle）の性質と比較したので報告する。BD-macrocycle と AD-macrocycle の溶液中における可視光吸収を調べたところ、BD-macrocycle では吸収帯が長波長側に大きくシフトすることが分かった。また、外部磁場に対するビフェニレン部位の四員環における常磁性環電流効果が、未環化体と比べて強まることが分かった。これらは量子化学計算による予測からも支持された。BD-macrocycle では、キノイド型の電子構造の寄与を伴うビフェニレン部位を介した効率的なπ電子共役系の拡張が起こるためだと考えられる。加えて、合成した BD-macrocycle は、固液界面において溶質濃度に依存して単分子膜から積層膜を形成することが分かった。



Self-assembly-induced Luminescence of Pyrene Derivatives Driven by Anionic Surfactants

([1]*Center for Innovation Support, Institute for Social Innovation and Cooperation, Utsunomiya University*, [2]*Graduate School of Regional Development and Creativity, Utsunomiya University*)
○ Jamuna Kannan[1], Rasel Ahmed[2], Yuna Kim[2], Ken-ichi-Iimura[2]

Keywords: Pyrene-imidazole derivatives; Nano-aggregates; Anionic surfactants; Aggregation-induced emission, Fluorescence

Pyrene is a classic molecule for constructing self-assembled aggregates with diverse luminescence properties across different phases. In a dilute state, it primarily exhibits monomer emission, while in an aggregated state, it tends to form excimer emissions via π-π interactions. The molecular packing and fluorescence characteristics are controllable and tunable in a self-assembled state. However, the application of pyrene derivatives is somewhat limited due to their shorter emission wavelength and aggregation-caused quenching. To overcome these limitations, in this work, functionalized pyrene derivatives have been synthesized through covalent modification (Fig. 1(a)). Then, fluorophore/surfactant assemblies have been developed in aqueous solutions to enhance fluorescence stability and quantum yield (Fig. 1(b) and (c)).

Motivated by the significant advances in surfactant-assembly systems over recent years[1-3], we have designed organic amphiphiles and fabricated luminescent, ordered self-assemblies through interactions between these amphiphiles and anionic surfactants in an aqueous medium. This approach produces pyrene amphiphiles exhibiting diverse aggregation behaviors characteristic of surfactants, along with enhanced fluorescence properties. Initially, these amphiphilic compounds form disordered assemblies in water due to unstable hydrophobic interactions, leading to a mixture of monomeric emissions. However, in the presence of surfactants, the fluorescence behavior and self-assembly stability are significantly enhanced. This work highlights a novel luminescent self-assembled nanomaterial derived from aggregation-induced emission active pyrene amphiphiles.

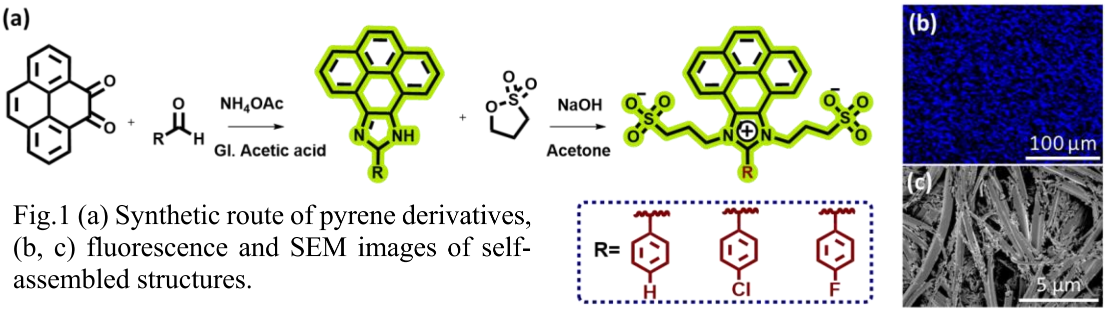


Fig.1 (a) Synthetic route of pyrene derivatives, (b, c) fluorescence and SEM images of self-assembled structures.

Acknowledgment: This work is supported by 3C fund of Utsunomiya University.

1) Ba-Salem, A.O. *et al.*, *Langmuir*, 2022, 38,7484-7495. 2) He, P.P. *et al.*, *Acc. Chem. Res*, 2019, 52, 367-378. 3) Hayashi, K. *et al.*, *J. Phys. Chem. B*, 2021, 125, 6192-6200.