アカデミックプログラム［Ｂ講演］｜20. 材料化学―基礎と応用：口頭Ｂ講演

2025年3月26日(水) 13:30 ~ 15:40 [G]3401(第4学舎 3号館 [4階] 3401)

[[G]3401-1pm] 20. 材料化学―基礎と応用

座長：山田 美穂子、相良 剛光

日本語

13:30 ~ 13:50

[[G]3401-1pm-01]

湾曲状コラニュレン骨格を有するジアリールエテン誘導体の反応性および光学特性

○今井 隆太[1]、山田 美穂子[1]、河合 壯[1] (1. 奈良先端大)

日本語

13:50 ~ 14:10

[[G]3401-1pm-02]

CPL特性変化を示すロタキサン型超分子メカノフォアの開発

○野中 慧悟[1]、黒田 拓海[1]、榎戸 雅基[2]、鶴井 真[2]、北川 裕一[3,4]、長谷川 靖哉[3,4]、中野 幸司[5]、相良 剛光[1] (1. 東京科学大物質理工、2. 北大院総化、3. 北大院工、4. 北大WPI-ICReDD、5. 東農工大院工)

日本語

14:10 ~ 14:30

[[G]3401-1pm-03]

不均一構造に由来した特異な蛍光特性を示すサリチル酸メチル誘導体

○小林 圭[1]、坂井 賢一[1]、中西 尚志[2] (1. 公立千歳科学技術大学、2. 物質・材料研究機構)

14:30 ~ 14:40

休憩

英語

14:40 ~ 15:00

[[G]3401-1pm-04]

キラリティによって制御される過冷却アルキル－カルバゾールゲルの相転移挙動

○竪山 瑛人[1,2]、松下 能孝[2]、木村 真也[3]、中西 尚志[1,2] (1. 北大院生命、2. 物質・材料研究機構、3. 明治薬大)

英語

15:00 ~ 15:20

[[G]3401-1pm-05]

二状態蛍光発光性フッ素化ピリミド[5,4-h]キナゾリン： 合成、構造,光物理学的およびハロクロミック特性

○kirti kirti[1,3]、Taro Udagawa[1]、Masahiro Ebihara[1]、Yasuhiro Kubota[1]、Toshiyasu Inuzuka[2]、G Krishnamoorthy[3]、Kazumasa Funabiki[1] (1. Gifu University、2. Gifu University Institute for advanced study、3. Indian Institute of Technology Guwahati, India)

英語

15:20 ~ 15:40

[[G]3401-1pm-06]

種々のカウンターアニオンを有するD-A型ピリジニウム色素のオルガノハロゲノクロミック特性

○小塚 訓平[1]、今任 景一[1]、大山 陽介[1] (1. 広島大学)

湾曲状コラニュレン骨格を有するジアリールエテン誘導体の反応性および光学特性

（奈良先端大物質[1]）○今井 隆太[1]・山田 美穂子[1]・河合 壯[1]

Reactivity and Photochemical Properties of Diarylethene Derivatives with Curved Corannulene Skeletons

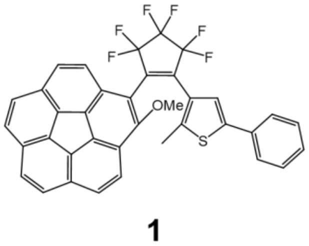
([1]*Division of Materials Science, Nara Institute of Science and Technology*) ○Ryuta Imai,[1] Mihoko Yamada,[1] Tsuyoshi Kawai[1]

In diarylethene, the aromaticity and geometrical structure of side aryl moieties affect the physical properties such as photoreactivity and thermal stability.[1] Corannulene is a curved aromatic compound with 20π-electrons and exhibits some properties different from typical planar aromatic compounds, such as bowl-to-bowl inversion. In this study, we designed and synthesized diarylethene derivatives having curved corannulene moieties as one side or both side aryl units, aiming for revealing the impact of curved skeletons on photochromic behavior.

Keywords : Diarylethene; Corannulene; Photochromism; Aromaticity; Photoreaction

ジアリールエテンは繰り返し耐久性や熱安定性が高いフォトクロミック分子として知られており、そのサイドアリール部位の芳香族性や立体構造は光反応性や熱安定性に大きく影響する[1)]。コラニュレンは20π電子を有する湾曲状芳香族化合物で、曲面の反転挙動など平面芳香族化合物とは異なる性質を示す。本研究では、湾曲骨格がフォトクロミック特性に与える影響について明らかにすることを目的とし、湾曲状のコラニュレンを片側または両側のサイドアリール部位として導入したジアリールエテン誘導体を合成し、これらの光反応性や光学特性について評価した。

コラニュレンを片側または両側に導入したジアリールエテン誘導体 **1** および **2**[2)]はトルエン溶液中で紫外光照射により着色し、さらに可視光照射により消色する可逆フォトクロミズムを示した。化合物 **2** は光閉環量子収率が 0.64、光開環量子収率が 0.49 であり、両方向で高効率なフォトクロミズムを示すことが明らかとなった。本発表では、**1** のチオフェン環を酸化した **3** の光学特性についても報告し、これらの熱安定性や光反応性を曲面由来の異性体などを考慮して詳細に議論する。



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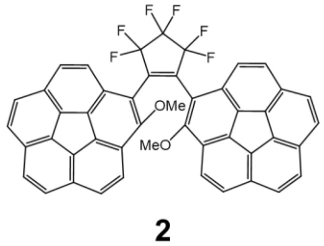

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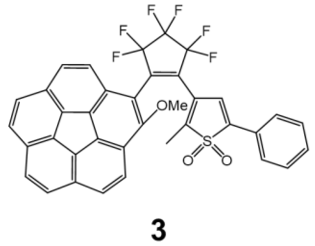


3

1) M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, *Chem. Rev.*, **2014**, *114*, 12174.
2) R. Imai, S. Katao, F. Asanoma, T. Kawai, M. Yamada, *J. Mater. Chem. C*, **2024**, *12*, 15654.

CPL 特性変化を示すロタキサン型超分子メカノフォアの開発

（東京科学大物質理工[1]・北大院総化[2]・北大院工[3]・北大 WPI-ICReDD[4]・東農工大院工[5]）○野中 慧悟[1]・黒田 拓海[1]・榎戸 雅基[2]・鶴井 真[2]・北川 裕一[3,4]・長谷川 靖哉[3,4]・中野 幸司[5]・相良 剛光[1]

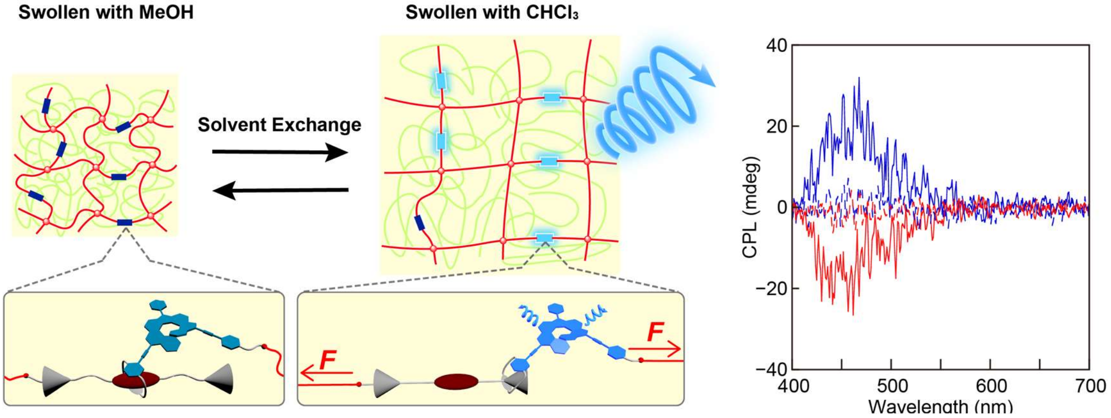
Development of A Rotaxane-based Supramolecular Mechanophore Changing CPL Property

([1] *Sch. Mater. and Chem. Tech., Science Tokyo,* [2]*Grad. Sch. Chem. Sci. Eng., Hokkaido Univ.,* [3]*Fac. Eng., Hokkaido Univ.,* [4]*WPI-ICReDD, Hokkaido Univ.,* [5] *Grad. Sch. Eng., Tokyo Univ. of A&T*) ○ Keigo Nonaka,[1] Takumi Kuroda,[1] Masaki Enokido,[2] Makoto Tsurui,[2] Yuichi Kitagawa,[3,4] Yasuchika Hasegawa,[3,4] Koji Nakano,[5] Yoshimitsu Sagara[1]

We have developed rotaxane-based supramolecular mechanophores that exhibit rapid and reversible changes in fluorescence intensity.1) Other photofunctions, such as FRET, could also be controlled at the single-molecule level.2) In this study, we introduced rotaxane mechanophores featuring a CPL-active helicene fluorophore into the first network of the DN gel as crosslinkers. The mechanophores were activated by swelling the DN gel and exhibited turn-on of CPL signals. The swelling ratios of DN gels were different for methanol and chloroform. The CPL properties were reversibly changed upon solvent exchanges between the two solvents.

Keywords : Mechanophore; Rotaxane; Helicene; Circularly polarized luminescence; Double network gel

当研究室では機械的刺激に対して瞬時かつ可逆的な蛍光の on/off スイッチングを示すロタキサン型超分子メカノフォアを開発してきた 1)。FRET などの光機能を一分子レベルで制御できることも見出している 2)。本研究では、蛍光団に円偏光発光（CPL）を示すヘリセン誘導体を用いたロタキサン型超分子メカノフォアをダブルネットワーク（DN）ゲルのファーストネットワークにクロスリンカーとして導入した。DN ゲルを膨潤するとメカノフォアがアクティベートされ、一分子レベルでの力による CPL 特性の制御が達成された。また、メタノールとクロロホルムで DN ゲルの膨潤率が異なるため、これらの溶媒を置換することにより、可逆的な CPL 強度変化も達成した。



1) Y. Sagara et al., *J. Am. Chem. Soc.* **2018**, *140*, 1584. 2) T. Muramatsu et al., *ACS Appl. Mater. Interfaces* **2023**, *15*, 8502.

不均一構造に由来した特異な蛍光特性を示すサリチル酸メチル誘導体

（公立千歳科技大院 [1]・物質·材料研究機構 [2]）○小林圭 [1]・坂井賢一 [1]・中西尚志 [2]

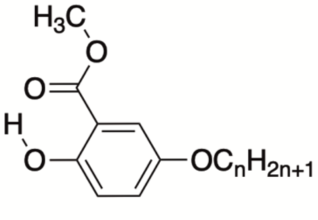
Unique fluorescence properties of methyl salicylate-based molecular liquids incorporating inhomogeneous structures

([1]*Chitose Institute of Science and Technology*, [2]*National Institute for Materials Science*)○Kei Kobayashi,[1] Ken-ichi Sakai,[1] Takashi Nakanishi[2]

Functional molecular liquids (FMLs) have attracted attention as fundamental materials for mechanically flexible devices. Conventionally, it has been considered better to design FMLs by isolating π-conjugated systems that exhibit electronic and optical functions. In this study, we synthesized molecules consisting of methyl salicylate (MS) linked to alkoxy chains of different lengths, obtaining fluorescent powder or liquid samples depending on the length of the carbon chain. The liquid samples were found to exhibit characteristic optical properties derived from the self-assembled structure of overlapping π-conjugated systems. Furthermore, the melted powder samples at room temperature exhibited optical properties very similar to those of the liquid samples at room temperature. We systematically investigated the differences in the self-assembled structures of molecular liquids by measuring DSC, XRD, IR spectra, and fluorescence lifetimes of the obtained samples.

Keywords : Functional Molecular Liquids, Aggregate, Fluorescence, Thermochromism

機能性分子液体(FMLs)は，機械的に柔軟なデバイスの基盤材料として注目されている。これまで，FMLs の設計においては，有機分子の電子・光機能を担う π 共役部分が互いに接触しないようにすることが有効とされてきた。本研究では，サリチル酸メチル(MS)に長さの異なるアルコキシ鎖を連結した分子(**Scheme 1**)を合成し，炭素数が 4～7 の鎖を連結した場合に液体状の蛍光性サンプル(**4**～**7**)を得た(**Fig. 1**)。これらのサンプルでは，分子の π 共役系部分が重なった集積構造に由来する特異な光学特性が発現することが示唆された。一方，サンプル **2** および **3** は常温で固体粉末として得られたが，加熱して融解させた後には，液体サンプル **4**～**7** と同様の光学特性を示した。



1 ~ 10 : n = 1 ~ 10

Scheme. 1 Molecular structures of methyl salicylates with different alkoxy chain lengths.

得られたサンプルについて，DSC 測定，XRD 測定，IR スペクトル解析，蛍光寿命測定を行い，均一な液体状態の中に不均一な会合体構造が存在することを確認した。

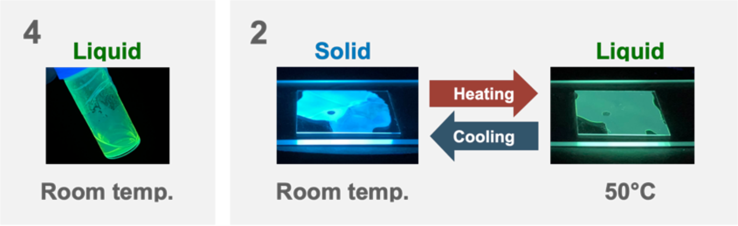


Fig. 1 Photographs of **2** and **4** under 365 nm UV irradiation.

Phase transition behavior of supercooled alkyl–carbazole gels controlled by chirality

([1]*Graduate School of Life Science, Hokkaido University*, [2]*National Institute for Materials Science,* [3]*Meiji Pharmaceutical University*) ○Akito Tateyama,[1,2] Yoshitaka Matsushita,[2] Shinya Kimura,[3] Takashi Nakanishi[1,2]

Keywords: Gel; Functional Molecular Liquid; Chirality; Supercooling; Phase Transition

Solvent-free functional liquids obtained by modifying a π-conjugated moiety with bulky yet flexible branched alkyl chains (alkyl–π liquids) are promising materials toward next generation soft electronics.[1] Physical properties of alkyl–π liquids such as elastic modulus and electret performance can be controlled by gelation (alkyl–π gels).[2] The effect of the chirality on the physicochemical properties of alkyl–π liquids and their gels remains largely unexplored. This study focuses on the effect of chirality of both an alkyl–π liquid and gelators concerning their physical properties, particularly phase transition behavior.

In this study, we utilized a liquid carbazole bearing an (*R*)-isomeric branched alkyl chain (**_R_-CZL**, Fig. 1a) as a gel medium. 1 wt% low-molecular-weight gelators containing amide units for intermolecular hydrogen bonding (**_RR_-GA** or **_SS_-GA**, Fig. 1b)[3] were added to **_R_-CZL** to form blue luminescent chiral alkyl–carbazole gels (Fig. 1c). Interestingly, these gels were supercooled state stable for over 6 months at r.t. (21 ± 2 °C). Therefore, long-term stable supercooled π-gels were developed for the first time in this study. **_R_-CZL** exhibited 2 types of crystal structure defined as crystal α (m.p.: 25 °C) and β (m.p.: 34 °C). When heated from −40 °C at 0.5 °C min^{-1}, 1 wt% **_R_-CZL**/**_RR_-GA** gel formed crystal α by cold crystallization at −20 °C firstly, and then exhibited notable solid-solid phase transition to crystal β at 25 °C (Fig. 1d). In contrast, 1 wt% **_R_-CZL**/**_SS_-GA** gel formed only crystal α under the same condition. This indicates that the phase transition behavior of supercooled gels based on **_R_-CZL** can be regulated by combining the chirality of the gel medium and gelators. This finding leads to the development of novel stimuli-responsive gels.

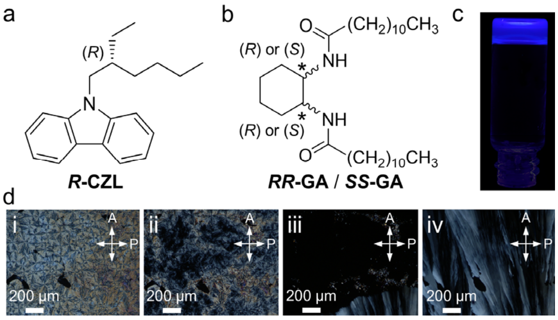


Figure 1 Molecular structures of (a) **_R_-CZL** and (b) **_RR_-GA** ((*R*,*R*)-isomer), **_SS_-GA** ((*S*,*S*)-isomer). (c) Photo of 1 wt% **_R_-CZL**/**_RR_-GA** gel under 365 nm UV irradiation. (d) Polarized optical microscopy images of 1 wt% **_R_-CZL**/**_RR_-GA** gel taken at i) −10 °C, ii) 25 °C, iii) 26 °C, and iv) 27 °C at fixed point during solid-solid phase transition when heated from −40 °C.

1) A. Tateyama, T. Nakanishi, *Responsive Mater.* **2023**, *1*, e20230001. 2) A. Tateyama, T. Nakanishi, et al., *Angew. Chem. Int. Ed.*, **2024**, *63*, e202402874. 3) K. Hanabusa, et al., *Angew. Chem. Int. Ed.*, **1996**, *35*, 1949.

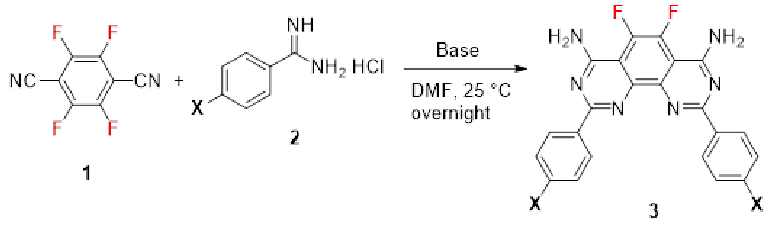
Dual State Fluorescence Emissive Fluorinated Pyrimido[5,4-*h*]quinazolines: Synthesis, Structure, and Photophysical and Halochromic Properties

([1]*Department of Chemistry and Biomolecular Science, Gifu University,* [2]*Gifu University institute of advanced research,* [3]*Indian Institute of Technology Guwahati, India*) ○Kirti,[1,3] Taro Udagawa,[1] Yasuhiro Kubota,[1] Toshiyasu Inuzuka,[2] and G.Krishnamoorthy,[3] Kazumasa Funabiki[1]

Keywords: pyrimido[5,4-*h*]quinazoline; spectroscopic measurements; aggregates; Halochromism; chelation

A series of the novel tricyclic fluorophore with the core moiety pyrimido[5,4-*h*]quinazoline (**3**), has been designed and synthesized via the condensation reaction of tetrafluoroterephthalonitrile and derivatives of benzimidamine hydrochloride in presence of base. To address the need for a fluorophore with enhanced stability, selectivity, and versatility across various applications, this new compound incorporates additional nitrogen atoms, offering superior performance to traditional fluorophores like 1,10-phenanthroline. Mechanistic insights emphasized the importance of selecting a suitable base to guarantee its efficiency and success.

NMR and single-crystal X-ray studies confirmed the structure of **3**, while spectroscopic measurements showed that these fluorophores are dual-state (solution and solid-state) emissive under UV-visible light. Photophysical studies highlighted the red-shifted fluorescence spectra in the solid state rather than the solution state. Further investigation revealed the formation of aggregates in the solid state. DFT calculations showed that the electron-withdrawing capability of **3** stabilized the energy levels. Electrochemical properties were also investigated, which were in good agreement with the results of DFT calculations. High decomposition temperature in the TG-DTA experiment proved the thermal stability of **3** at elevated temperatures. Due to the presence of protonable protons in **3**, it gave the positive Halochromism.[1] These fluorophores are anticipated to have enhanced chelation, leading to more stable metal complexes, which will increase their potential applications for further studies in future.



1) S Kothavale, N. Sekar, *Dyes and Pigments*. **2017**, *136*, 31-45.

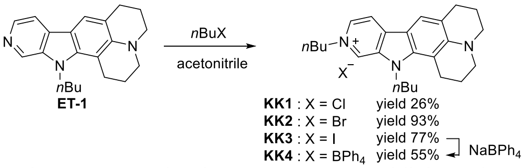
Organohalogenochromic Characteristics of D-A Type Pyridinium Dyes Bearing Various Counter Anions

(*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Kumpei Kozuka, Keiichi Imato, Yousuke Ooyama

Keywords: Organohalogenochromism, Halogen bond, Pyridinium dye, Halogenated organic solvent

Organohalogenochromism (OHC) is a photophysical phenomenon causing significant bathochromic or hypsochromic shifts of the photoabsorption bands of organic dyes in halogenated organic solvents compared with those in non-halogenated solvents[1–4]. Such specific solvatochromism in halogenated organic solvents has been previously observed in some donor–π–acceptor (D–π–A) type cationic dyes. However, there have been a few reports for OHC, although the phenomenon is of great scientific interest and practical importance such as the development of optical sensor materials for detecting toxic organohalogen compounds. Thus, in this study, to elucidate the OHC mechanism from the viewpoint of halogen bond between the halogen atoms of halogenated solvents and the counter anion of the dye, we designed and synthesized D–A type pyridinium dyes **KK1–4** bearing various counter anions (Cl^-, Br^-, I^-, BPh_4^-) (Scheme 1).

The photoabsorption spectra of **KK2** bearing Br^- as a counter anion are shown in Fig 1, and the photoabsorption maximum wavelength (λ_{max}^{abs}) of **KK2** are summarized in Table 1. In all the solvents, the photoabsorption bands appeared at around 420–470 nm, which are attributed to intramolecular charge transfer (ICT) excitation of the julolidine unit as donor moiety to a pyrido[3,4-*b*]indolium unit as acceptor moiety. In particular, the λ_{max}^{abs} of **KK2** shows a significant bathochromic shift of ca. 10–30 nm in halogenated solvents compared with those in non-halogenated solvents. The HOMO and LUMO energy levels of **KK2** in CH_3CN and CH_2Cl_2 were evaluated from cyclic voltammetry (CV) and photoabsorption properties (Table 2). It was suggested that the HOMO-LUMO band gap in CH_2Cl_2 is reduced compared with that in CH_3CN due to a significant destabilization of the HOMO energy level. In this presentation, we will report the effect of halogen bond formation on the electronic structure of the dye based on the photoabsorption properties of **KK1–4** and the single-crystal X-ray structural analyses and discuss the mechanism for the expression of OHC.



Scheme 1 Synthesis of D-A type pyridinium dyes **KK1–4** bearing various counter anions.

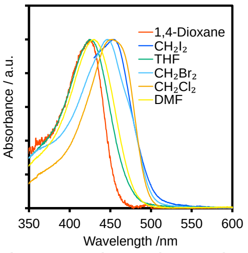


Fig. 1 Photoabsorption spectra of **KK2** in various solvents.

Table 1 Photoabsorption maximum wavelength of **KK2** in various solvents.

solvent	λ_{max}^{abs} /nm
1, 4-Dioxane	424
PhI	454
CH_2I_2	453
PhBr	443
PhF	436
PhCl	440
THF	425
CH_2Br_2	446
CH_2Cl_2	452
DMF	430

Table 2 The onset potentials (E^{ox}_{onset}) of the oxidationwaves, optical energy gap (E^{opt}_{g}), and HOMO and LUMO energy levels of **KK2** in CH_3CN and CH_2Cl_2.

Solvent	E^{ox}_{onset} / V	E^{opt}_{g} / V	HOMO / eV	LUMO / eV
CH_3CN	0.35	2.58	-5.15	-2.57
CH_2Cl_2	0.06	2.50	-4.86	-2.36

1) Y. Ooyama *et al.*, *Tetrahedron*, 2013, **69**, 1755–1760; 2) T. Higashino *et al.*, *Chem. Lett.*, 2021, **50**, 1530–1533; 3) K. Kozuka *et al.*, *Mater. Adv.*, 2024, **5**, 2218–2229; 4) K. Kozuka *et al.*, *ChemPhotoChem*, 2025, **9**, e202400187.