Academic Program [Oral B] | 20. Materials Chemistry -Basic and Application-：Oral B

Tue. Mar 19, 2024 3:55 PM - 5:15 PM JST | Tue. Mar 19, 2024 6:55 AM - 8:15 AM UTC C443(443, Bldg. 4 [4F])

[C443-2vn] 20. Materials Chemistry -Basic and Application-

Chair: Katsuya Mutoh, Yousuke Ooyama

Japanese
3:55 PM - 4:15 PM JST | 6:55 AM - 7:15 AM UTC
[C443-2vn-01]

Negative Photochromism of Binaphthyl-Bridged Dibenzo[2,3:6,7]oxepino[4, 5-d]imidazole Dimer

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Japanese
4:15 PM - 4:35 PM JST | 7:15 AM - 7:35 AM UTC
[C443-2vn-02]

Development of a Photochromic Molecule with Characteristics of Hexaarylbiimidazole and Terarylene

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English
4:35 PM - 4:55 PM JST | 7:35 AM - 7:55 AM UTC
[C443-2vn-03]

Photochromic Reaction Behavior of Azadiarylethenes Exhibiting Thermal Cyclization Reaction

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Japanese
4:55 PM - 5:15 PM JST | 7:55 AM - 8:15 AM UTC
[C443-2vn-04]

Influence of Counter Anion of D-A Type Pyridinium Dyes on its Organohalogenochromism

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ビナフチル架橋ジベンゾオキセピノイミダゾール二量体の逆フォトクロミズム

（青山学院大理工 [1]）○八木 詩織 [1]・阿部 二朗 [1]

Negative Photochromism of Binaphthyl-Bridged Dibenzo[2,3:6,7]oxepino[4,5-d]imidazole Dimer

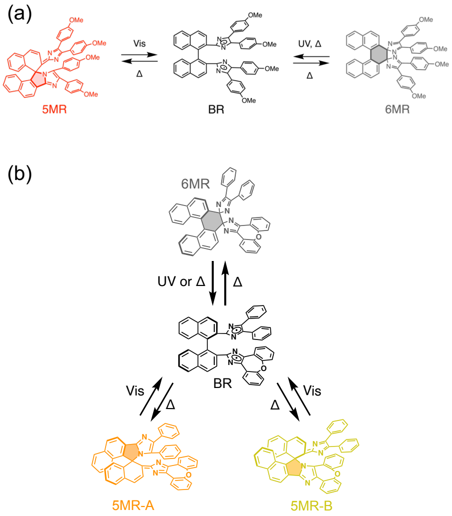
([1] *Dept. Chem., Sch. Sci. Eng., Aoyama Gakuin Univ.*) ○Shiori Yagi,[1] Jiro Abe[1]

Upon exposure of visible light, binaphthyl-bridged imidazole dimers (**BN-ImD**) exhibit negative photochromic reaction from a stable colored isomer to a metastable colorless isomer via a short-lived biradical. In this study, we have successfully synthesized novel binaphthyl-bridged imidazole dimers (**BN-DBOXPImD**) by introducing an imidazole moiety with a dibenzooxepine structure. **BN-DBOXPImD** has two colored isomers, which are isomerized to the colorless isomer upon the irradiation of visible light. This molecule exhibits not only negative photochromism but also bistable photoswitch between two colored isomers.

Keywords : Photochromism; Biradical; Imidazole Dimers

フォトクロミック分子の多くは紫外光照射によって光異性化するが、紫外光はエネルギーが大きく、材料や細胞の光劣化を引き起こすため、エネルギーが小さな可視光や近赤外光に応答するフォトクロミック分子の開発が求められている。当研究室では可視光に応答するビナフチル架橋型イミダゾール二量体（**BN-ImD**）を開発した[1]。**BN-ImD** の安定着色体（5MR）に可視光を照射すると、短寿命ビラジカル（BR）を経由して、準安定体である無色体（6MR）に光異性化する逆フォトクロミズムを示す。本研究では、**BN-ImD** にジベンゾオキセピン構造を有するイミダゾール環を導入することで、新たなビナフチル架橋イミダゾール二量体（**BN-DBOXPImD**）を合成し、その光反応特性の評価を行った。

Scheme 1. Photochromism of (a) **BN-ImD** and (b) **BN-DBOXPImD**.



BN-DBOXPImD はイミダゾール部位が非対称であることから、2 つの着色異性体（5MR-A, 5MR-B）を有する。可視光照射によって、着色異性体は短寿命のビラジカル（BR）を経由して、準安定異性体である 6MR に異性化する。5MR-B は 5MR-A よりも不安定で、熱的に 5MR-A に異性化する。**BN-DBOXPImD** は逆フォトクロミズムだけでなく、5MR-A と 5MR-B 間で双安定なフォトクロミズムを示す。

[1] S. Hatano, T. Horino, A. Tokita, T. Oshima, J. Abe, *J. Am. Chem. Soc.* **2013**, *135*, 3164.

ヘキサアリールビイミダゾールとターアリーレンの特徴を有する新規フォトクロミック分子の開発

（阪公大院理 [1]）○武藤 克也 [1]・中嶋 琢也 [1]

Development of a Photochromic Molecule with Characteristics of Hexaarylbiimidazole and Terarylene

([1] *Osaka Metropolitan Univ.*)○Katsuya Mutoh,[1] Takuya Nakashima[1]

Multi-state photochromism has been considered more attractive than traditional bistable photochromism because it can offer more versatility and control in photoresponsive systems. One of the attractive designs for the multi-state photochromic molecule is an efficient combination of two photochromic units. In this study, we have designed and synthesized a novel photochromic molecule (1) that consists of a hexaarylbiimidazole unit and a terarylene unit. Compound 1 shows four-state photochromic reaction upon UV light irradiation. We found that the delocalized π-radical on the closed-ring form of the terarylene is efficient to enhance the photosensitivity to the NIR-I and -II region.

Keywords : Photochromism; Hexaarylbiimidazole; Diarylethene; Radical

異種フォトクロミック分子の融合は、単一のフォトクロミック分子では実現できない多彩な光応答性を創出できる。本研究では、ヘキサアリールビイミダゾール [1)]とターアリーレン [2)]の特徴を併せ持つフォトクロミック分子（**1**）を合成し、その光応答性および光学特性を検討した。過渡吸収分光法および量子化学計算より、化合物 1 は紫外光照射により C-N 結合が均等開裂し、発色体としてラジカル（**1OR**）を生成することが明らかとなった。**1OR** に紫外光を照射するとターアリーレンの 6π 閉環反応が進行し **1CR** を生成した。**1CR** は閉環構造にラジカルが非局在化することで近赤外領域まで吸収帯が長波長シフトした。また、1CR は 500 nm を極大吸収波長とする異性体に熱的に変化した。以上のことから、化合物 **1** は 4 つの状態を経由するマルチフォトクロミック反応を示すことを明らかにした。

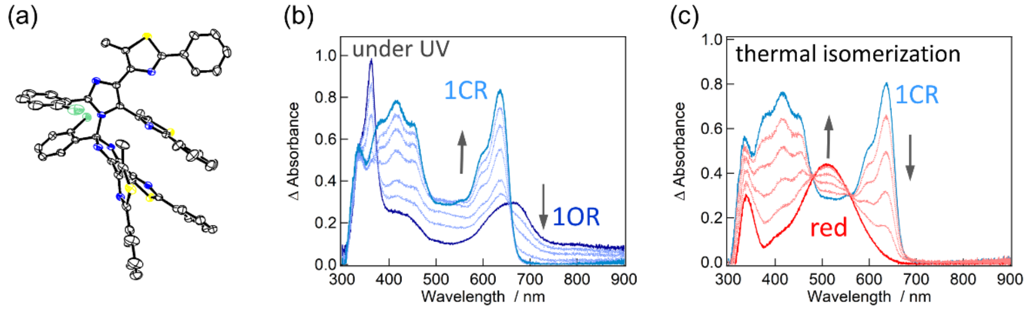


Figure 1. (a) The ORTEP representation of the molecular structure of 1 (thermal ellipsoids at 50% probability). (b, c) The transient absorption spectra of 1OR upon UV light irradiation and the thermal isomerization from 1CR.

1) T. Hayashi, K. Maeda, *Bull. Chem. Soc. Jpn.*, **1960**, *33*, 565.
2) T. Nakashima, M. Goto, S. Kawai, T. Kawai, *J. Am. Chem. Soc.*, **2008**, *130*, 14570.

Photochromic Reaction Behavior of Azadiarylethenes Exhibiting Thermal Cyclization Reaction

(*Graduate School of Engineering, Osaka Metropolitan University*) ○Shota Hamatani, Daichi Kitagawa, Seiya Kobatake

Keywords: Azadiarylethene, Thermal Cyclization, Photochromism

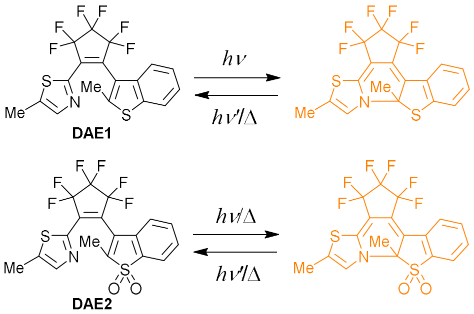


Figure 1. Molecular structure of diarylethene derivatives in this work.

Photochromic compounds are of great interest as light-driven molecular switches in research fields of material and life sciences. Diarylethene is a typical P-type photochromic molecule,[1] and the photochromic reaction is based on a 6π electrocyclic reaction between open-ring and closed-ring isomer. Recently, it has been reported that azadiarylethenes having a nitrogen atom at the reaction site exhibit fast T-type photochromism due to the disrotatory thermal cycloreversion allowed by Woodward-Hoffman rule,[2] and further development of azadiarylethenes is expected. In this work, we synthesized diarylethene derivatives **DAE1** and **DAE2**, in which a benzothiophene ring and a S,S-dioxide benzothiophene ring were introduced into the aryl group, and investigated their photochromic properties (Figure 1).

DAE1 and **DAE2** were synthesized, their properties were investigated. When **DAE1** in *n*-hexane was irradiated with ultraviolet (UV) light, it became to color yellow. When UV light irradiation was stopped, it quickly returned to its original colorless state, exhibiting fast T-type photochromism. This fast thermal cycloreversion reaction is based on a disrotatory pathway. **DAE2** in *n*-hexane was pale yellow. When irradiated with UV light, it turned a deep yellow color. When UV light irradiation was stopped, it returned to its original color. These color changes are based on photocyclization and thermal cycloreversion. Furthermore, when the solution was irradiated with visible light, it became colorless. Without visible light irradiation, it gradually returned to its original pale yellow. These results suggested that open-ring and closed-ring isomer exist in thermal equilibrium, and thermal cyclization can proceed. Thus, it was found that the cyclization reaction of azadiarylethene derivatives with S,S-dioxide benzothiophene ring proceeds not only by photochemical reactions but also by thermal reactions.

1) M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, *Chem. Rev.* **2014**, *114*, 12174–12277.
2) S. Hamatani, D. Kitagawa, S. Kobatake, *J. Phys. Chem. Lett.* **2023**, *14*, 8277–8280.

D-A 型ピリジニウム色素のオルガノハロゲノクロミズムに及ぼすカウンターアニオンの影響

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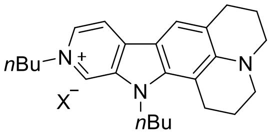
Influence of Counter Anion of D-A Type Pyridinium Dyes on its Organohalogenochromism

(*Grad. Sch. of Adv. Sci. and Eng., Hiroshima Univ.*) ○Kumpei Kozuka, Keiichi Imato, Yousuke Ooyama

Organohalogenochromism (OHC) is a photophysical phenomenon that induces a significant bathochromic or hypsochromic shift of the photoabsorption bands of organic dyes in halogenated solvents compared with those in non-halogenated solvents 1)-3). Thus, OHC is a specific solvatochromism observed only in halogenated solvents that is different from a common solvatochromism depending on the Solvent polarity. However, there is little published research on OHC although the phenomenon is of great scientific interest and practical importance, such as the development of optical sensing technology for the detection of toxic organohalogen compounds. In this work, in order to establish new molecular design strategies for OHC dyes and elucidate the mechanism of OHC, we designed and synthesized D-A type pyridinium dyes **KK1**–**KK4** bearing various counter anions. Indeed, **KK2** bearing chloride ion as a counter anion showed bathochromic shifts of the photoabsorption band in halogenated solvents by about 20 nm compared with those in non-halogenated solvents. In this presentation, we will report the optical properties of **KK1–KK4** in various halogenated or non-halogenated solvents.

Keywords : Organohalogenochromism, Pyridinium dye, Counter anion, Photoabsorption property, Oraganic halogenated solvent.

オルガノハロゲノクロミズ（OHC）とは、ハロゲン溶媒中における有機色素の光吸収帯が非ハロゲン溶媒中のものと比べて長波長シフトあるいは短波長シフトする現象である 1)-3)。OHC はハロゲン溶媒中でのみ観測される特異的なクロミズムであり、溶媒極性の増加に伴い色素の光吸収帯がシフトするソルバトクロミズムとは異なる。OHC は学術的に興味深いだけではなく、有毒な有機ハロゲン化合物を検出するための光学センサーへの応用など実用的にも重要であるにも関わらず、OHC に関する研究はほとんど行われていない。そこで本研究では、OHC 色素の新たな分子設計指針の確立と OHC のメカニズムの解明を目的とし、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を分子設計及び合成した（Fig. 1）。その結果、塩化物イオンをカウンターアニオンとして有する **KK2** の光吸収帯はハロゲン溶媒中において長波長シフトしており、OHC を発現することが観察された（Fig. 2）。本発表では、**KK1–KK4** の様々なハロゲンまたは非ハロゲン溶媒中における光学特性を評価した結果について報告する。



KK1 : X = Cl, **KK2** : X = Br
KK3 : X = I, **KK4** : X =BPh$_4$

Fig. 1 Chemical structures of **KK1**–**KK4**.

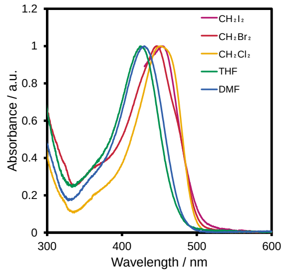


Fig. 2 Photoasorption spectra of **KK2** in various solvents.

1) Y. Ooyama, Y. Oda, T. Mizuno, J. Ohshita, *Tetrahedron*, 2013, **69**, 1755.
2) T. Higashino, Y. Ooyama, *Chem. Lett.*, 2021, **50**, 1530.
3) K. Kozuka, K. Imato, Y. Ooyama, *Mater. Adv.,* 2023, DOI: 10.1039/D3MA00671A.