

JF-SYMPHONIA2013

Aoyama Gakuin University, Kanagawa, Japan
26 April, 2013

Japan-France Bilateral Symposium on Photoresponsive Materials 2013

Supporting: NAIST-AGU-YNU Comprehensive Alliance for the Research of Photoresponsive Materials

Program

- 12:50-13:00 Opening
- 13:00-13:30 Keitaro Nakatani (ENS Cachan)
Photochromic Nanoparticles: Tuning the Properties between Solution and Bulk
- 13:30-14:00 Tsuyoshi Kawai (NAIST)
Efficient Photochromic Molecules Based on 1,2-Dithiazoryl Arylene Structure
- 14:00-14:30 Maylis Orio (Université Lille Nord de France)
Quantum Chemical Investigation of Structural and Spectroscopic Properties of Photochromic Molecules
- 14:30-14:50 Katsuya Mutoh (AGU)
Extremely Slow Valence Isomerization from Biradical State to Quinoid State
- 15:00-15:40 Poster Session A
- 15:40-16:20 Poster Session B
- 16:30-17:00 Remi Métivier (ENS Cachan)
Energy-Transfer-Based Fluorescence Photoswitching at the Nanoscale with Photochromic Materials
- 17:00-17:30 Yasushi Yokoyama (YNU)
Stereoselectivity in Photochromism Based on 6π -Electrocyclization
- 17:30-18:00 Michel Sliwa (Université Lille Nord de France)
The Photodynamic of Complex Photochromic Systems Explored by Chemometrics and Ultrafast Spectroscopy
- 18:00- Closing
- 19:00- Friendly Meeting

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Poster Session Program

Session A (14:30-15:10)

- PA1. Rui Kanazawa, Shigekazu Kawai, Takuya Nakashima, Tsuyoshi Kawai (NAIST)
Syntheses and Photochemical Properties of Terarylene-Tetraoxide Having Ethyl Groups
at Reaction Center Carbon Atoms
- PA2. Kazduhiko Imamura, Kyohei Yamamoto, Takuya Nakashima, Tsuyoshi KAWAI (NAIST)
 α,β -Linked Oligo(2-phenylthiazole)s : Photochrome to Foldamer
- PA3. Hideo Kaichi, Yasushi Yokoyama (YNU)
Photochromism of Diarylethene in Cholesteric Liquid Crystals
- PA4. Tetsuo Yamaguchi, Sayaka Hatano, Jiro Abe (AGU)
Unusual Negative Photochromism of 1,1'-Binaphthyl-Bridged Imidazole Dimers
- PA5. Kentaro Shima, Katsuya Mutoh, Jiro Abe (AGU)
Photochromism of a Naphthalene-Bridged Imidazole Dimer Constrained to the "Anti" Conformation
- PA6. Emi Nakano, Katsuya Mutoh, Jiro Abe (AGU)
Electrochemistry of Photochromic [2.2]Paracyclophane-Bridged Imidazole Dimers

Session B (15:10-15:50)

- PB1. Toshifumi Inouchi, Takuya Nakashima, Tsuyoshi Kawai (NAIST)
Emission Properties of T-Shaped π -Conjugated Molecules Having an Acid-Responsive Benzimidazole Unit
- PB2. Katsutoshi Arai, Katsuya Mutoh, Jiro Abe (AGU)
Peroxide-Bridged O₂ Adducts of Bisphenoxy Radicals
- PB3. Takuya Yamane, Katsuya Mutoh, Jiro Abe (AGU)
Photochromic Properties of a Water-Soluble Naphthopyran
- PB4. Katsuya Mutoh, Jiro Abe (AGU)
Rapid Fluorescence Switching by Using Fast Photochromic Molecules
- PB5. Masayuki Kobayashi, Jiro Abe (AGU)
Mechanism for Optical Motion Control of Maglev Graphite
- PB6. Moemi Samata, Takashi Ubukata (YNU)
Control of Fluorescence Using Photochromic Diarylethene Having Two Carboxylic Acid Groups

Photochromic nanoparticles: tuning the properties between solution and bulk

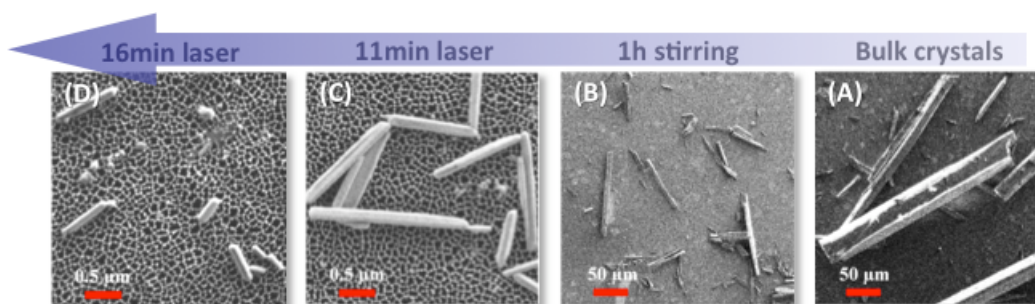
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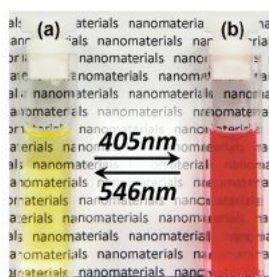
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The presentation will mainly focus on the properties of organic photochromic nanoparticles (NP). Although insoluble in water, optically non-scattering suspensions can be obtained in aqueous solutions, in some cases containing a surfactant. We mainly used the laser ablation (fragmentation) method to get NP from bulk solid.



Fragmentation by laser ablation of an anil (Schiff base) photochromic material (electron microscope images)

For a given molecule, the NP suspensions show different behaviors from the (organic) solution or the bulk solid. Examples taken from diarylethenes and anils (Schiff bases) will be mentioned, where properties such as thermal back reaction rate [1], photoreaction quantum yield, [2] or the two-photon reaction behavior [3] can be modified according to the medium. Also, we will present the possibility to reversibly precipitate and dissolve an organic compound in an aqueous medium, by means of light. [4]



Photoinduced precipitation (405 nm irradiation) and dissolution (546 nm irradiation) of a photochromic diarylethene in an aqueous medium

[1] A. Patra, R. Métivier, J. Piard, K. Nakatani, *Chem. Commun.* **2010**, 46, 6385-7. [2] J. Piard, PhD Thesis, Ecole Normale Supérieure de Cachan, France, **2011**. [3] J. Piard, Y. Ishibashi, H. Saito, R. Métivier, K. Nakatani, G. Gavrel, P. Yu, H. Miyasaka, *J. Photochem. Photobiol.A: Chemistry* **2012**, 234,57-65. [4] A. Patra, R. Métivier, F. Brisset, K. Nakatani, *Chem. Commun.* **2012**, 48, 2489-91.

Efficient Photochromic Molecules Based on 1,2-Dithiazoryl Arylene Structure

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Photochromic molecules which indicate reversible color change upon photoirradiation of different wavelength have widely been studied from fundamental scientific interest and practical applications such as photon-mode data storage. Some of them show relatively high stability in both colored and bleached state under the dark condition, which provide longterm-photomemory capability. We herein present our recent results on photochromic molecular materials based on 1,2 diaryl-arylene structure with various kinds of central and side aromatic and side groups. Some of them show relatively high photochromic sensitivity, which is generally characterized in term of photochemical quantum yield. We have achieved highly sensitive photochromic compounds showing photochemical quantum yield of almost unity, which is so-called as “photon quantitative reaction”. Photochemical reactivity was controlled with mostly with the ground state geometry which was designed by means of intramolecular non-covalent interaction. Some related molecules shows clear photo-responsibility in their fluorescence emission nature which is potentially applicable for future photo-tunable light emitting materials. Unique electrochemical response of a related compound will also be discussed.

[1] S. Fukumoto, T. Nakashima, T. Kawai, *Angew. Chem., Int. Ed.*, **50**, 1565-1568 (2011)

[2] T. Nakashima, Y. Kajiki, S. Fukumoto, M. Taguchi, S. Nagao, S. Hirota, T. Kawai, *J. Am. Chem. Soc.*, **134**, 19877-19883 (2012)

Quantum chemical investigation of structural and spectroscopic properties of photochromic molecules.

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Nowadays a usual strategy in research groups consists in combining experiment and theoretical calculations for the full characterization of their systems. More particularly, Density Functional Theory (DFT) finds increasing use in applications related to photochromic systems. Advancements in methodology and implementations have reached a point where predicted properties of reasonable to high quality can be obtained. DFT has been established as a valuable research tool because it can serve either to validate the conclusions that have been reached from the analysis of the experiments or to distinguish between those possibilities that were left open. Numerous reviews have already provided an overview of the properties that can be calculated with DFT, such as geometries, energies, reaction mechanisms, and spectroscopic properties. The calculation of a wide range of molecular properties with DFT allows a close connection between theory and experiment and often leads to important clues about the geometric, electronic, and spectroscopic properties of the systems being studied. We will focus here on one family of photochromic molecules: the HexaArylBenzimidazole compounds and its derivatives. In this context, we will show the relevance and the performance of coupling theoretical methods based on Density Functional Theory (DFT) to various elaborated spectroscopic techniques such as Electron Paramagnetic and Nuclear Magnetic Resonances (EPR and NMR) to understand the structure, the properties and the origin of the reactivity of such systems.

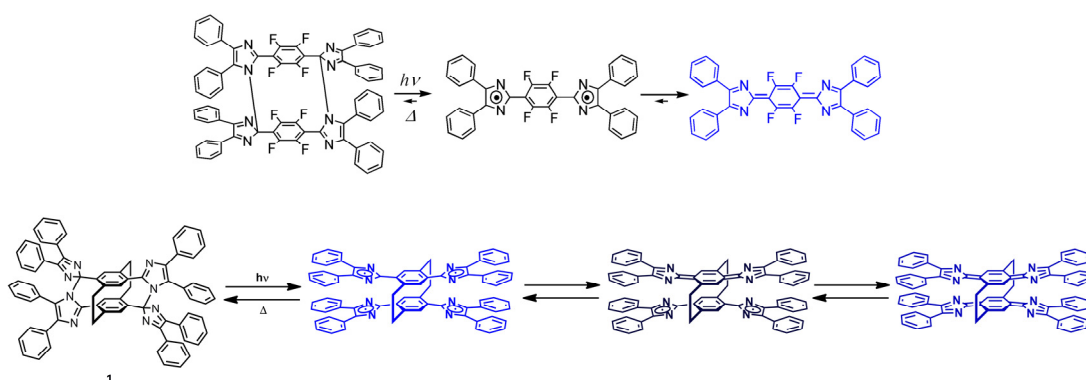
[1] J. Jacq, S. Tsekhanovich, M. Orio, C. Einhorn, J. Einhorn, B. Bessières, D. Jouvenot, F. Loiseau, Structure and dynamics of the excited states of 1,3-diarylisobenzofurans. *Photochem. Photobiol.*, 2012, 88, 633-638.

[2] S. Delbaere, M. Orio, J. Berthet, M. Sliwa, S. Hatano, J. Abe, First ¹³C NMR evidences of dimeric structures of hexaarylbiimidazole derivatives :Experimental and theoretical approaches. 2013, in preparation.

Extremely Slow Valence Isomerization from Biradical State to Quinoid State

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The investigation of the interaction between the radical pair is one of the fundamental studies because it leads to the clarification of the principle of the chemical bond formation. Especially, it has not been revealed whether there is the thermal equilibrium between a diamagnetic-quinoid state and a paramagnetic-biradical state, or whether the two states are described as the resonance structures. The ESR measurements for BDPI-2Y and the derivative, tF-BDPI-2Y, suggest that the thermally excited open-shell state with biradical character is contributing to the ground state.¹ However the definitive evidence for the existence of the thermal equilibrium has not been proved to date. In this study, we have demonstrated the thermal isomerization from biradical state to quinoid state of tF-BDPI-2Y and a novel designed bridged-bisimidazolyl (**1**). The laser flash photolysis measurements of tF-BDPI-2YD and **1** revealed that the biradical state slowly isomerizes to the quinoid state within a few milliseconds at room temperature. Moreover, the quinoid state of **1** goes back to the initial dimer state from a thermally excited tetraradical state via a biradical state.

Scheme 1. Photochromism of tF-BDPI-2YD and **1**.

[1] (a) Y. Sakaino, T. Hayashi, K. Maeda, *Nippon Kagaku kaishi*, **1972**, 100. (b) A. Kikuchi, F. Iwahori, J. Abe, *J. Am. Chem. Soc.*, **2004**, 126, 6526.

Energy-transfer-based fluorescence photoswitching at the nanoscale with photochromic materials

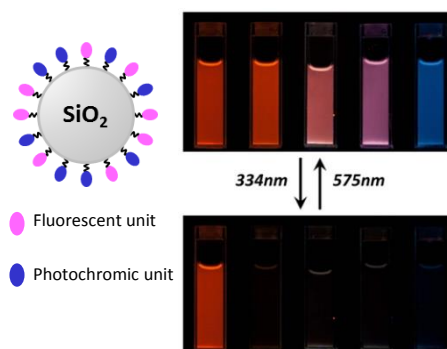
R. Métivier,¹ K. Ouhenia,¹ J. Su,¹ T. Fukaminato,² J. Piard,¹ S. Maisonneuve,¹ A. Brosseau,¹ A. Jacquart,¹ F. Brisset,³ A. Léaustic,³ P. Yu,³ R. Pansu,¹ J. Xie,¹ K. Nakatani¹

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The development of novel optical devices, such as light-driven optical memories or biocompatible nanophotoswitches for super-resolution imaging, attracts considerable interest in the growing field of cutting-edge technologies involving nanomaterials.[1] We report here on the design of photoswitchable fluorescent nanomaterials, based on photochromic and fluorescent molecules, to produce original and highly efficient light-triggered nanodevices. Several recent examples of materials involving fluorescence photoswitching at the nanoscale through efficient (multi)directional excitation energy transfer will be described: non-covalent mixtures of photochromic and fluorescent derivatives in polymeric thin films; fabrication and signal amplification of organic fluorescent nanoparticles; and synthesis of photoswitchable emissive silica nanoparticles based on surface-grafted photoactive molecules (cf. figure). [2]



[1] A. Spangenberg, R. Métivier, J. Gonzalez, K. Nakatani, P. Yu, M. Giraud, A. Léaustic, R. Guillot, T. Uwada, T. Asahi, *Adv. Mater.* **2009**, *21*, 309-13; A. Patra, R. Métivier, J. Piard, K. Nakatani, *Chem. Commun.* **2010**, *46*, 6385-7; A. Patra, R. Métivier, F. Brisset, K. Nakatani, *Chem. Commun.* **2012**, *48*, 2489-91; R. Yasukuni, R. Boubekri, J. Grand, N. Félijdj, F. Maurel, A. Perrier, R. Métivier, K. Nakatani, P. Yu, J. Aubard, *J. Phys. Chem. C* **2012**, *116*, 16063-9.

[2] R. Métivier, S. Badré, P. Yu, R. Pansu, R. Méallet-Renault, K. Nakatani, *J. Phys. Chem. C*, **2009**, *113*, 11916-26; J. Piard, R. Métivier, M. Giraud, A. Léaustic, P. Yu, K. Nakatani, *New J. Chem.* **2009**, *33*, 1420-6; K. Ouhenia-Ouadahi, R. Métivier, S. Maisonneuve, A. Jacquart, J. Xie, A. Léaustic, P. Yu, K. Nakatani, *Photochem. Photobiol. Sci.* **2012**, *11*, 1705-14.

Stereoselectivity in Photochromism based on 6 π -Electrocyclization

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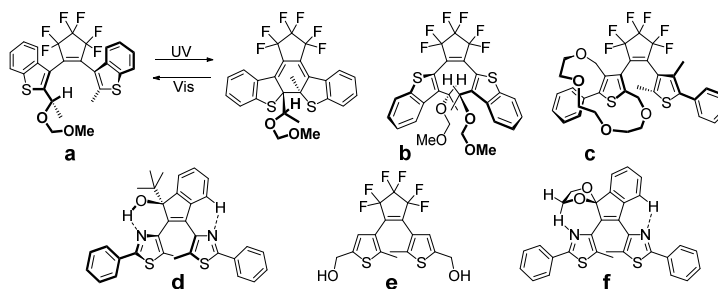
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Control of the stereoselectivity in photochromism is important when it is applied to the field of biology since complications would arise in the system if several enantio- or diastereomeric isomers possessing different functions are produced photochemically and interact independently with the chiral biological molecules.

We first undertook the construction of diastereoselective photochromic systems with diarylethenes. The systems obtained include a chiral helical structure induced by (a) one point-chirality, (b) two point-chirality, (c) one facial-chirality, or (d) one point-chirality and two hydrogen bonds. Construction of several diarylethenes showing 100% diastereoselective ring closure has been achieved.[1] (Scheme: **a – d**)

Recently, we have investigated the enantioselective photochromism carried out in biomolecules such as human serum albumin (HSA). More than 60% enantiomer excess (*ee*) at room temperature and more than 70% *ee* at lower temperature were achieved. (Scheme; **e**)

It is also important to increase the quantum yield values of the photoreactions since less exposure to light is favorable for biological molecules. We have constructed a photochromic



system with >80% cyclization quantum yield with hydrogen bonds by fixation of the conformation in favor of cyclization.[2] Since fixation of the conformation occurred on a chiral compound, diastereoselective photochromic cyclization was also induced.[1g] (Scheme: **f, d**)

[1] a) Y. Yokoyama, H. Shiraishi, Y. Tani, Y. Yokoyama, Y. Yamaguchi, *J. Am. Chem. Soc.*, **2003**, *125*, 7194. b) Y. Yokoyama, *Chem. Eur. J.*, **2004**, *10*, 4388. c) Y. Yokoyama, T. Shiozawa, Y. Tani, T. Ubukata, *Angew. Chem. Int. Ed.*, **2009**, *48*, 4521. d) T. Shiozawa, M. K. Hossain, T. Ubukata, Y. Yokoyama, *Chem. Commun.*, **2010**, 46, 4785. e) Y. Yokoyama, T. Hasegawa, T. Ubukata, *Dyes Pigments*, **2011**, *89*, 223. f) S. Delbaere, J. Berthet, T. Shiozawa, Y. Yokoyama, *J. Org. Chem.*, **2012**, *77*, 1853. g) H. Ogawa, K. Takagi, T. Ubukata, A. Okamoto, N. Yonezawa, S. Delbaere, Y. Yokoyama, *Chem. Commun.*, **2012**, *48*, 11838.

[2] K. Morinaka, T. Ubukata, Y. Yokoyama, *Org. Lett.*, **2009**, *11*, 3890.

The Photodynamic of Complex Photochromic Systems Explored by Chemometrics and Ultrafast Spectroscopy

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New photochromic systems such as metal complexes, nanoparticles and supramolecular systems have attracted increasing attention as new bio-potential materials for optical and electronic devices, photo-drug delivery and high resolution optical imaging. The synthesis, use and performance of these complex photo-systems are limited, mainly due to the fact that the photodynamic scheme involves several pathways dependent of the excitation wavelength, strong influence of the environment, different intermediates and photo-products with kinetic time constants covering the range from femtosecond to several millisecond time scales. We will discuss here several photochromic systems (in different states capsule, nanoparticles, polycrystalline powder...) based on ultrafast proton transfer, electrocyclic reaction and bond cleavage: photochromic nanoparticles based on hexaarylbiimidazole molecules, self-assembled photochromic molecular capsule based on salicylidene-aniline guest and metal complexes with bi-photochromic ligand based on diaryethene and hydroxyphenylthiazole. We will show here how time resolved spectroscopy, from UV-Vis to IR domain, and from nanosecond to femtosecond time scale with the help of advanced data analysis can provide rationalized description of the process investigated.

[1] C. Ruckebusch, M. Sliwa, P. Pernot, A. de Juan, R. Tauler, Comprehensive data analysis of femtosecond transient absorption spectra, *J. Photochem. Photobiol. C*, **2012**, 13, 1.

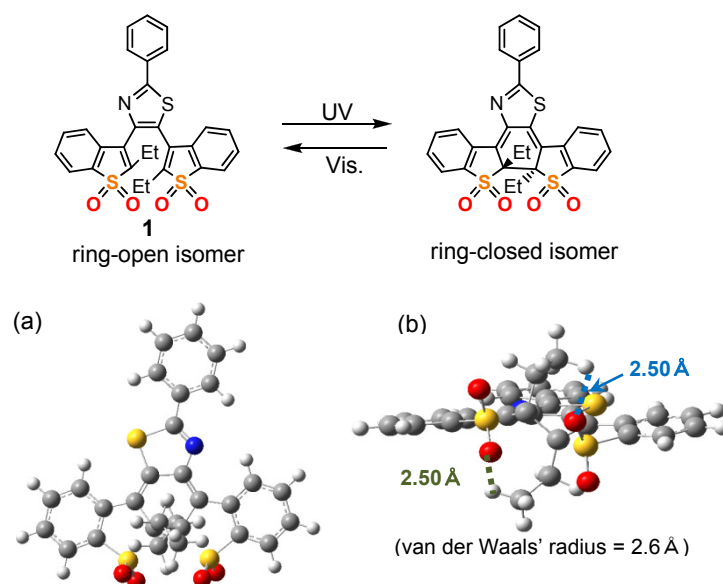
[2] M. Sliwa, P. Naumov, H. Choi, Q. Nguyen, B. Debus, S. Delbaere, C. Ruckebusch, Effects of a self-assembled molecular capsule on the ultrafast photodynamics of a photochromic salicylideneaniline guest, *Chem. Phys. Chem.*, **2011**, 12, 1669.

Synthesis and Photochemical Properties of Terarylene-tetraoxide Having Ethyl Groups at Reaction Center Atoms

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Controlling the photoswitching properties based on the modulation of terarylene structures has received considerable attention for future molecular memory and display systems.¹ Although, oxidized terarylenes with SO₂ units showing irreversible photo-coloration reaction have been proposed to be used in photopattern formation, the relationship between molecular structures and photoreactivities have not yet been fully understood. In this study, terarylene-tetraoxide **1** was synthesized, and their photochromic and fluorescent properties are studied. Moreover, density functional theory (DFT) and time-dependent density functional theory (TDDFT) have been performed to investigate the effect of molecular structures for their photoreaction properties. Ethyl groups are introduced at reaction center atoms to enhance the CH/OS hydrogen bonding interactions (**Scheme 1**).



Scheme 1. Photochromic reaction of **1** and its optimized structure (ring-closed isomer) calculated at the B3LYP/6-31G(d,p); (a) the front view and (b) the edge view

- [1] (a) T. Nakashima, K. Atsumi, S. Kawai, T. Nakagawa, Y. Hasegawa and T. Kawai, *Eur. J. Org. Chem.*, **2007**, 3212–3218. (b) M. Taguchi, T. Nakagawa, T. Nakashima and T. Kawai, *J. Mater. Chem.*, **2011**, 17425-17432. (c) K. Uno, H. Niikura, M. Morimoto, Y. Ishibashi, H. Miyasaka, and M. Irie, *J. Am. Chem. Soc.*, **2011**, 133, 13558–13564. (d) Jeong, Y.-C.; Yang, S. I.; Kim, E.; Ahn, K.-H. *Tetrahedron* **2006**, 62, 5855-5861.

α , β -Linked Oligo(2-phenylthiazole)s : Photochrome to Foldamer

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In the past decade, various organic π -conjugated compounds with controlled conformation have been extensively studied, since their optical and electric properties rely on spatial distribution of π -systems. Recently, we have reported photochromic terarylenes^[1,2] with controlled conformations, which are stabilized by multiple weak intramolecular interactions involving heteroatoms. Thiazole is one of the representative heteroaromatic compounds, which possesses two heteroatoms, sulfur and nitrogen. Therefore, a variety of combinations of thiazoles with α,β -connections lead to various arrangements of heteroatom interactions in a molecule to control its geometry. We herein report on the development of helical foldamers based on oligo(2-phenylthiazole)s, in which S-N heteroatom interactions between vicinal thiazole units operate to harness the interunit dihedral angles. Figure 1 shows chemical and X-ray crystallographic structures of oligo(2-phenylthiazole)s from trimer to hexamer with head-to-tail connections. A number of intramolecular nonbonding interactions including S-N interheteroatom, CH/heteroatom, CH/ π and π - π stacking interactions were found to stabilize the helix conformations.

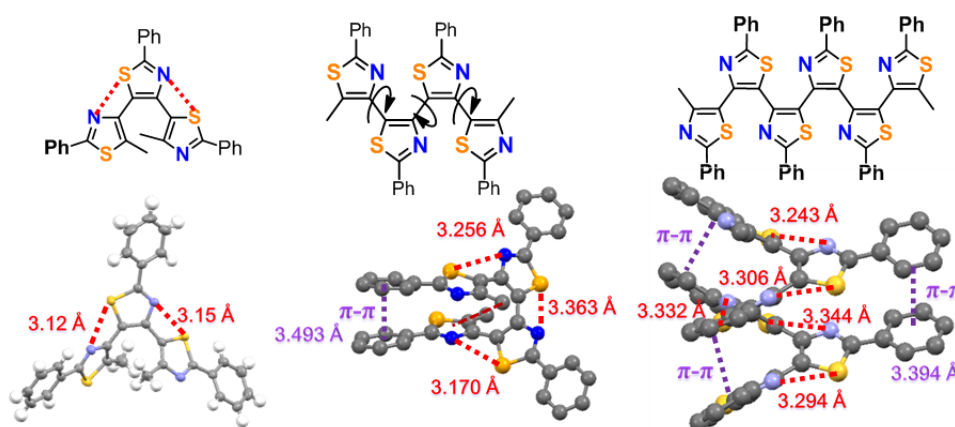


Figure 1. Chemical structures and X-ray crystal structures of oligo(2-phenylthiazole)s.

[1] T. Nakashima, K. Atsumi, S. Kawai, T. Nakagawa, Y. Hasegawa and T. Kawai, *Eur. J. Org. Chem.*, **2007**, 3212-3218.

[2] S. Fukumoto, T. Nakashima, T. Kawai, *Angew. Chem., Int. Ed.*, **50**, 1565-1568 (2011)

Photochromism of Diarylethene in Cholesteric Liquid Crystals

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Photochromism of diarylethenes such as **10** produces two enantiomeric closed form (**1C**) upon photocyclization. When the diarylethene is placed in a chiral environment, the ratio of enantiomers may not be 50/50. In this research the mutual interactions of diarylethenes having no chiral unit and the cholesteric liquid crystals which have the chiral helical alignment of the liquid crystalline molecules.

Two chiral dopants **2** or **3** were added to a nematic liquid crystal, **5CB**, to generate cholesteric liquid crystals. Addition of **10** followed by 365-nm light irradiation resulted in the change in cholesteric pitch and the slight enantioselective ring closure of **10**.

To know the effect of photochromism on the nature of cholesteric liquid crystals, the dopants **2** or **3** was added to **5CB** containing **10**, and the mixture was irradiated with 365-nm light at the temperature where the mixture exhibits the liquid crystalline state.

The change in pitch length was measured by the Cano's method, and the results are summarized in Table 1.

The effect of chirality of the cholesteric liquid crystalline media on the enantioselectivity of the ring closure of **10** was examined by an HPLC apparatus equipped with a chiral column. The results are summarized in Table 2.

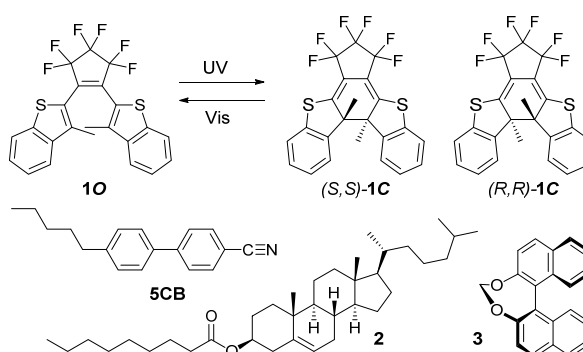


Table 1. Pitch change of cholesteric LC by photochromism.

Dopant in 5CB	Conc. of 10 / mol dm ⁻³	Pitch length / μm		
		10	PSS at 365 nm	PSS at 450 nm
2 ¹⁾	5.18×10 ⁻³	53.7	54.7	53.9
	9.71×10 ⁻³	52.6	55.0	52.8
3 ²⁾	5.00×10 ⁻³	41.3	39.4	39.8
	8.91×10 ⁻³	25.6	24.4	25.0

1) Conc. of **2**: 7.39 × 10⁻³ mol dm⁻³.

2) Conc. of **3**: 2.83 × 10⁻³ mol dm⁻³.

Table 2. Enantioselectivity.

Dopant in 5CB	Conc. of 10 / mol dm ⁻³	Pitch / μm	ee / %
2 ³⁾	9.71 × 10 ⁻³	52.6 ⁵⁾	0
3 ⁴⁾	3.88 × 10 ⁻³	0.67 ⁵⁾	1.8
2 only	5.25 × 10 ⁻³	0.27 ⁵⁾	2.6

3) Conc. of **2**: 7.39 × 10⁻³ mol dm⁻³.

4) Conc. of **3**: 7.71 × 10⁻² mol dm⁻³.

5) Before irradiation.

As shown in Table 1, the pitch change is reversible. With the dopant **2** in **5CB**, the pitch is longer at the photostationary state (pss) of UV irradiation than that before UV irradiation. On the other hand, the pitch is shorter at the UV pss than that before UV irradiation when the dopant **3** was used.

Although the enantioselectivity was not remarkable, it showed 2.6 % of enantiomer excess (ee) when pure **3** was used as the cholesteric liquid crystal.

Unusual Negative Photochromism of 1,1'-Binaphthyl-Bridged Imidazole Dimers

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Hexaarylbiimidazole (HABI) shows instantaneous coloration from pale yellow to purple by UV light irradiation. This photochromic behavior is attributed to hemolytic cleavage of the C–N bond between the nitrogen atom of the 1-position of an imidazole ring and the carbon atom of the 2-position of another imidazole ring. The decoloration reaction of HABI proceeds only thermally and this reaction takes several minutes at room temperature. Bridged imidazole dimers were developed to accelerate the thermal back-reaction of HABI. [2.2]Paracyclophane-bridged imidazole dimer shows instantaneous coloration and rapid fading in the dark. The photochromic behavior of [2.2]paracyclophane-bridged imidazole dimer is explained by the similar bond cleavage of that of HABI. The thermal back-reactions of [2.2]paracyclophane-bridged imidazole dimers are completed within several seconds.

Recently, a new type of bridged imidazole dimer, 1,1'-binaphthyl-bridged imidazole dimer, is synthesized.¹ Although, general HABI derivatives can be obtained in a colorless species by oxidizing lophine precursor, 1,1'-binaphthyl-bridged imidazole dimer can be obtained in deep-red-colored species. The discoloration of the colored species from deep red to colorless by visible light irradiation was observed (**Fig. 1**). The photochromic behavior is attributed to the photogeneration of the 2,2'-isomer via short-live radical species and the 2,2'-isomer thermally returns to colored species within 20 min at room temperature.

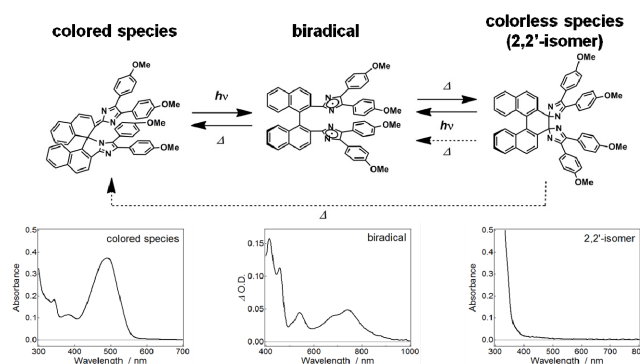


Fig. 1 Photochromism of 1,1'-binaphthyl-bridged imidazole dimer.

[1] S. Hatano, J. Abe, Unusual negative photochromism via a short-lived imidazolyl radical of 1,1'-binaphthyl-bridged imidazole dimer, *J. Am. Chem. Soc.* **2013**, *135*, 3164.

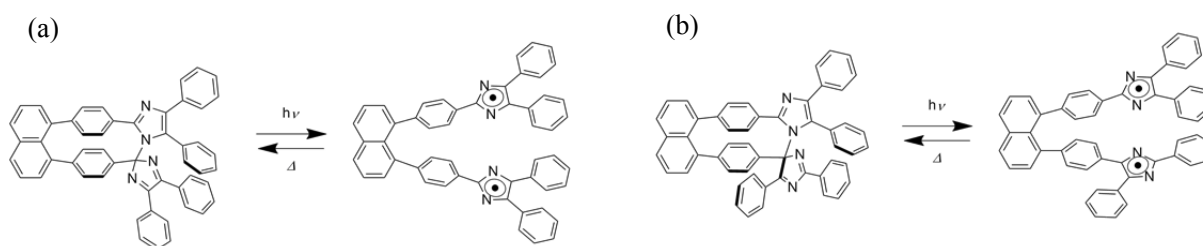
Photochromism of A Naphthalene-Bridged Imidazole Dimer Constrained to the “*Anti*” Conformation

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Naphthalene-bridged imidazole dimers show instantaneous coloration upon irradiation with UV light and rapid fading in the dark, which have received considerable attention because of their potential for applications to the optical storages, optical lenses and the other photo-responsive materials. Conventionally, two imidazole rings of naphthalene-bridged imidazole dimers are constrained to *syn*-arrangement and the two imidazole rings are connected with the C–N bond between N1 and C2' of each imidazole rings. In this study, we have designed and synthesized a novel naphthalene-bridged imidazole dimer, *anti*-1,8-bisTPI-naphthalene, which two imidazole rings are constrained to the “*anti*” conformation. The NIR absorption intensity of the radical species generated from *anti*-1,8-bisTPI-naphthalene upon UV light irradiation diminishes due to the weak orbital overlap between two triphenylimidazole rings. Besides, the specific bond-formation between two imidazole rings is observed owing to the “*anti*” conformation.



Scheme 1. Photochromism of (a) 1,8-bisTPI-naphthalene, (b) *anti*-1,8-bisTPI-naphthalene.

[1] F. Iwahori, S. Hatano, J. Abe, Rational design of a new class of diffusion-inhibited HABI with fast back-reaction, *J. Phys. Org. Chem.*, **2007**, *20*, 857-863.

[2] K. Fujita, S. Hatano, D. Kato, J. Abe, Photochromism of a radical diffusion-inhibited hexaarylbiimidazole derivative with intense coloration and fast decoloration performance, *Org. Lett.*, **2008**, *10*, 3105-3108.

Electrochemistry of Photochromic [2.2]Paracyclophane-Bridged Imidazole Dimers

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The photochromic behavior of hexaarylbiimidazole (HABI) derivatives can be attributed to the photoinduced homolytic cleavage of the C–N bond between the two imidazole rings. On the other hand, although the simultaneous formation of the imidazolyl radical and imidazole anion by the one-electron reduction of a HABI derivative was reported, no definitive evidence has been demonstrated¹. We have reported the first direct evidence for the electrochemical generation of the imidazolyl radical from the radical anion of the imidazole dimer by conducting the UV–vis–NIR spectroelectrochemical analysis of the [2.2]paracyclophane-bridged imidazole dimer². We have recently developed a series of photochromic [2.2]PC-bridged imidazole dimer with electron donating or accepting substituents. In this study, we have revealed the electronic structures of the [2.2]PC-bridged imidazole dimer derivatives in detail by investigating the substituent effect with electrochemistry and DFT calculation.

It is clearly shown that the HOMO and LUMO of the imidazole dimers are localized over only one of the imidazole ring by the electrochemistry and DFT calculation of the [2.2]PC-bridged imidazole dimer. Hence, the HOMO and LUMO energy levels of the imidazole dimers can be controlled by the introduction of the appropriate substituents to the 4 π or 6 π electron system imidazole rings.

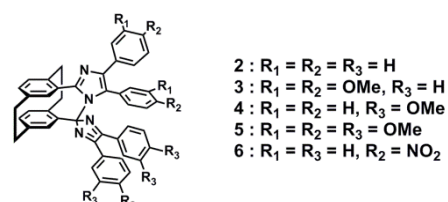
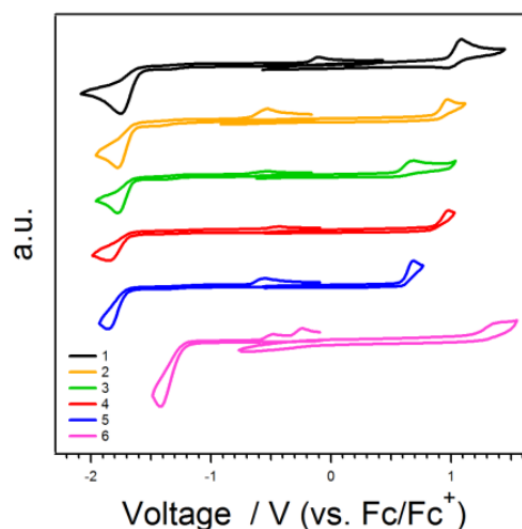


Chart 1. Chemical structures of 2-6.

Figure 1. Cyclic voltammograms of 1-6 in acetonitrile containing TBAPF₆.[1] Edward, W. O. Dennis, H. E. *J. Electroanal. Chem.* **1997**, 432, 145.[2] Nakano, E. Mutoh, K. Abe, *J. J. Phys. Chem. A*, **2012**, 116, 6792.

Emission Properties of T-Shaped π -Conjugated Molecules having an Acid-responsive Benzimidazole Unit

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Recent interest has been focused onto synthesis and characterization of various π -conjugated linker units of specific topological feature. We here synthesized T-shaped π -conjugated molecules with an *N*-methyl-benzimidazole junction and their acid-responsive photophysical properties owing to the change in the π -conjugation system were discussed. T-shaped π -conjugated molecules consist of two orthogonal π -conjugated systems including a phenyl thiophene extended from the 2-position and alkyl phenylenes connected via various π -spacers from the 4,7-positions of the central *N*-methyl-benzimidazole junction (Fig.1). The π -spacers such as thiophene, ethyne and ethene should affect on their acid-response nature in terms of changes in conformation, excited state energy and charge-transfer (CT) characteristics. In particular, the π -conjugated molecule with ethynyl spacers (**EBIm**) exhibited a marked red-shift in fluorescent wavelength with a large Stokes shift upon addition of acid, whereas the other molecules showed substantial quenching in fluorescence emission. The red-shift in emission was studied in detail as a function of temperature, which indicated specific transition to a twisted intramolecular charge-transfer (TICT) state over a finite activation energy at the excited state. The photophysical properties, especially the emission properties, have also been compared for T-shaped crossconjugated and linear conjugated molecules. X-ray crystal structures and optimized structures based on DFT calculations suggested a planar conformation of the 2-thienyl-*N*-benzimidazole structure even after protonation, where intramolecular S–N and NH–S interactions, respectively, are responsible for the stabilization of planar structures. Despite the planarity in the ground state, the T-shaped cross-conjugated molecules exhibit the TICT emission in response to protonation, whereas the corresponding linear conjugated molecule without a horizontal π -system does not have a charge transfer state. The differences in the separation of the HOMO and LUMO and the energy barrier of the rotation about the thienyl ring predicted by the DFT calculations are responsible to the different decay processes of the linear and cross-conjugated molecules with a protonated benzimidazole unit.

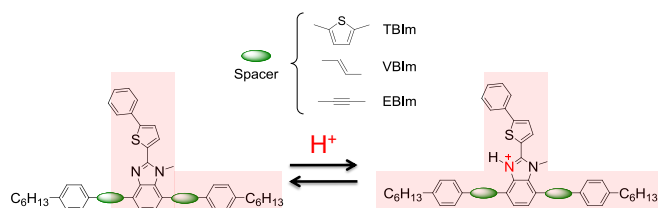


Fig.1 Structures of T-shaped π -conjugated molecules and their acid-responsivity.

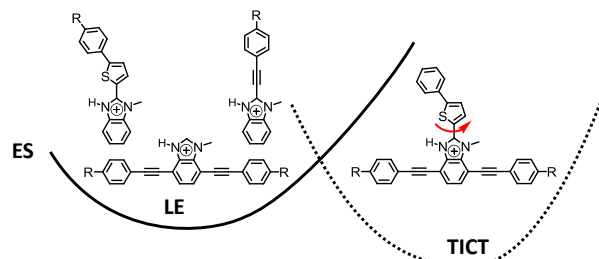


Fig.2 Potential energy surfaces for the S_1 state of T-shaped, orthogonal, and vertical molecules.

- [1] T. Inouchi, T. Nakashima, M. Toba, and T. Kawai, *Chem. Asian J.* **2011**, 6, 3020–3027
 [2] T. Inouchi, T. Nakashima, and T. Kawai, *Asian J. Org. Chem.* **2013**, 2, 230–238

Peroxide-Bridged O₂ Adducts of Bisphenoxy RadicalsKatsutoshi Arai¹, Katsuya Mutoh¹, Jiro Abe^{1,2}¹ Department of Chemistry, School of Science and Engineering, Aoyama Gakuin University, Kanagawa, Japan² CREST, Japan Science and Technology Agency, Tokyo, Japan

Challenging of the formation of the extremely long C–C single bond has attracted great attention because it has small bond dissociation energy and dissociates easily. The longest C–C single bond length reported to date is estimated to be 1.77 Å,¹ which is extremely long compared with the C–C bond length of ethane (1.54 Å). Previously, we have developed naphthalene-bridged phenoxy radical dimer which forms a new C–C bond between two 2,5-cyclohexadienone.

The bond length is found to be 1.637 Å due to the steric repulsion between the tert-butyl groups. Accordingly, we have newly designed a phenoxy radical dimer derivative (**2**) to achieve the formation of the longest C–C single bond by expanding the distance between the phenoxy radicals. The C–C bond length of **2** between phenoxy radicals is estimated to be 1.788 Å from the DFT calculation (B3LYP/6-31G(d)). Therefore, it would be expected that the phenoxy radical dimer forms the long C–C bond which has never been reported to date. The X-ray crystallography revealed that naphthalene-bridged phenoxy radicals generate unique structural O₂ adducts (**3**, **4**) at room temperature. We revealed that **4** releases oxygen thermally in solution and solid state. On the other hand, because **2** is unstable at room temperature, it is expected that the formation of an extremely long C–C single bond would be achieved at low temperature.

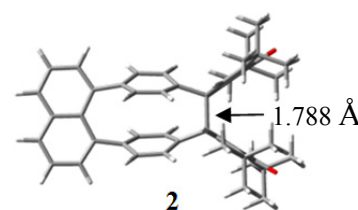


Figure 1. The molecular structure of **2** optimized at the B3LYP/6-31G(d) level of theory.

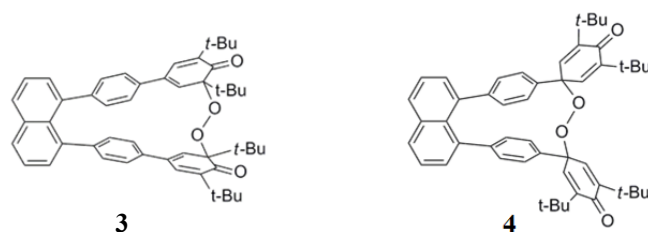


Figure 2. The molecular structures of two peroxide-bridged O₂ adducts (**3** and **4**).

[1] Suzuki, T.; Takeda, T.; Kawai, H.; Fujiwara, K. *Pure Appl. Chem.* **2008**, *80*, 547-553.

Photochromic Properties of a Water-Soluble Naphthopyran

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Photochromic molecules play important roles as a photo-switchable trigger that regulates various functions in nature. Thus, controllable photoresponsive molecules to mimic the biological systems, such as photoregulation of the ion channel and the electron transport, have been extensively studied. Sialic acids have been known as a stop sign of the sugar chain elongation and are transferred to the non-reducing end of the sugar chain. Regulation of the sialyltransferase function can be expected to lead to the development of a simple tool in biochemical experiments, such as control and breakthroughs of various life phenomena, because the sialylation catalyzed by the sialyltransferase is involved in a number of life phenomena. Naphthopyran is one of the photochromic molecules, which generates two colored photoisomers (TC and TT isomer) on UV light irradiation. Because of the good fatigue resistance and relatively fast thermal back-reaction, the application of naphthopyrans to the ophthalmic plastic lenses is expected. However, few applications such as photo switching in aqueous environment towards the biological use are reported. Therefore, in this study, we have synthesized a photochromic sialyltransferase inhibitor based on naphthopyran (STI). Figure 1 shows the photochromic behavior of STI in water at 289 K. STI changes the color from colorless to orange upon UV light irradiation, and the colored form slowly goes back to the initial closed form in water, compared with that in ethanol. The thermal back reaction of colored species can be accelerated under visible light irradiation (470 nm). Therefore, the application of STI to the light trigger of sialylation would be expected.

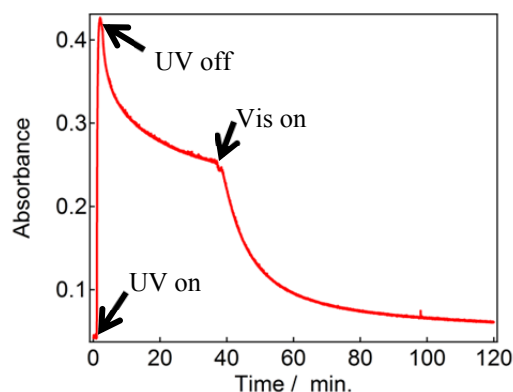


Figure 1. The photochromic behavior of STI in water at 289 K (5.22×10^{-5} M).

[1] Banghart, R. M.; Mourot, A.; Fortin, L. D.; Yao, Z. J.; Kramer, H. R.; Trauner, D. *Angew. Chem. Int. Ed.* **2009**, *48*, 9097.

[2] Al-Atar, U.; Fernandes, R.; Johnsen, B.; Baillie, D.; Branda, R. N. *J. Am. Chem. Soc.* **2009**, *131*, 15966.

Rapid Fluorescence Switching by Using Fast Photochromic Molecules

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Recently, we have developed a series of fast photochromic imidazole dimers bridged by a [2.2]paracyclophane (PC) moiety, and succeeded the acceleration of the thermal decoloration rate.¹ The colorless [2.2]PC-bridged imidazole dimers show a photoinduced homolytic bond cleavage of the C–N bond between the imidazole rings to give a pair of colored imidazolyl radicals upon UV light irradiation, followed by the radical–radical coupling reaction to form the initial C–N bond between the imidazole rings. The high quantum yield close to unity of the photochromic reaction and the large extinction coefficient of the radical achieves both the high optical density at photostationary state and rapid switching speed. The application to rapid fluorescence switching has been investigated to develop a new type of photochromic fluorescence switching molecule applicable to super-resolution microscopy.² We successfully developed a [2.2]PC-bridged imidazole dimer possessing a perylene bisimide (PBI) moiety as a fluorescence unit. This photochromic dye shows fast photochromism to give a pair of imidazolyl radicals that quench the fluorescence from the fluorescent unit by the FRET mechanism. The fluorescence intensity can be switched rapidly with the fast photochromism.

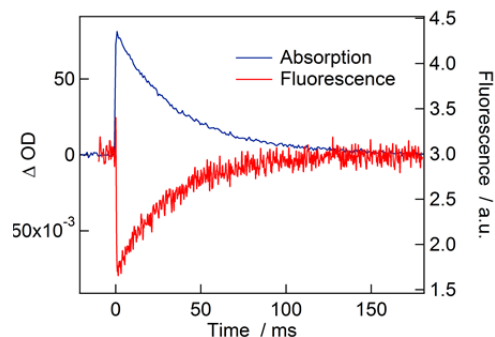


Fig. 1 Fluorescence switching with fast photochromism.

[1] (a) Y. Kishimoto, J. Abe, *J. Am. Chem. Soc.*, **2009**, *131*, 4227. (b) Y. Harada, S. Hatano, A. Kimoto, J. Abe, *J. Phys. Chem. Lett.*, **2010**, *1*, 1112. (c) K. Mutoh, J. Abe, *J. Phys. Chem. A*, **2011**, *115*, 4650.

[2] K. Mutoh, M. Sliwa, J. Abe, *J. Phys. Chem. C*, **2013**, *117*, 4808.

Mechanism for Optical Motion Control of Maglev Graphite

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Graphite has been known as a typical diamagnetic material and can be levitated in the strong magnetic field. Since a magnetically levitating diamagnetic material without any contact can be effectively manipulated by weak forces, the passive maglev has attracted interest for its potential applications for actuator and transport systems. However, so far no practicable maglev-based actuator systems have been developed because of some problems that include low responsivity and the inefficient displacement. Here we show that the magnetically levitating pyrolytic graphite (PG) can be moved in the arbitrary place by simple photoirradiation. It is notable that the optical motion control system described here requires only NdFeB permanent magnets and light source. Firstly, we attempted to drive a 25 μm thick PG disk ($\phi = 10\text{ mm}$) levitating on 457 mT NdFeB magnets arranged to face in alternate directions by direct irradiation with the laser light of 405 nm to the PG disk. In the case of moving the light source in any direction, the levitating PG disk can be driven in the same direction as the light beam (Figure 1, left). In this case, the maximum velocity was estimated to be around 45 mm s^{-1} . On the other hand, the levitating PG disk above cylinder type NdFeB magnets begins to rotate during light irradiation at the edge of the PG disk (Figure 1, right). Such a behavior was also observed under sunlight, it was revealed that the maximum rotational speed of the PG disk was reached over 200 rpm, indicating that it is possible to develop a new class of light energy conversion system. In this poster, we will also discuss the possible mechanism of the optical motion control system.

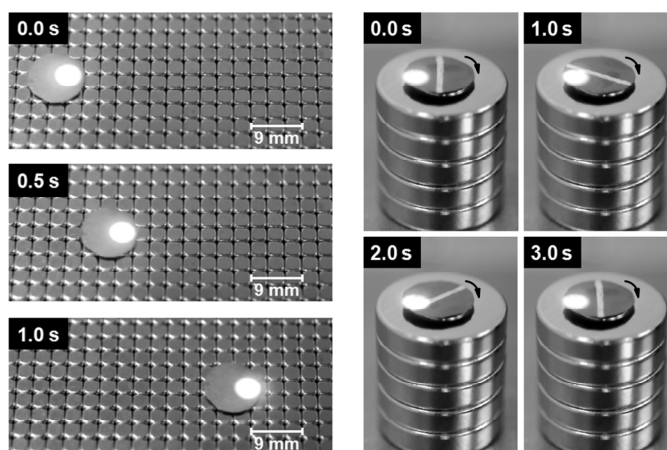


Figure 1. Arbitrary motion control of the magnetically levitating PG disk by a laser.

[1] M. Kobayashi, J. Abe, Optical motion control of maglev graphite, *J. Am. Chem. Soc.*, **2012**, *134*, 20593.

Control of Fluorescence Using Photochromic Diarylethene Having Two Carboxylic Acid Groups

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Fluorescence switching of photochromic compounds has attracted much attention, because of applications for biological probe, optical recording and so on.[1] For the former use, photochromic compounds should function in aqueous solution. In this research, we synthesized a diarylethene **1-O**, which has two carboxylic acid groups, and investigated its photochromic and fluorescence behavior aiming at multiple switching system responding to light and pH in aqueous solution.

Photochromic and fluorescence behavior of **1-O** was first investigated in dichloromethane. **1-O** showed good photochromism upon irradiation with 366-nm light and subsequent 436-nm light (Fig. 1a). When **1-O** was excited with 345-nm light, fluorescence was observed at around 500 nm. The fluorescence intensity of **1-O** decreased by photochromic ring closure upon irradiation with 366-nm light (Fig. 1b). Reversible fluorescence intensity change was also observed along with the photochromic reaction. Fig. 1c shows the change in the fluorescence spectra when 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added to the dichloromethane solution of **1-O** to generate the carboxylate anion **1-O⁻**. The fluorescence intensity was dramatically increased, and the fluorescence maximum was shifted from 504 nm to 451 nm upon addition of DBU. The fluorescence intensity was recovered when trifluoroacetic acid was added to the solution. Thus, we have succeeded in multiple switching of fluorescence using **1-O** in dichloromethane. Fluorescence behavior of **1-O** in aqueous solution is now investigated.

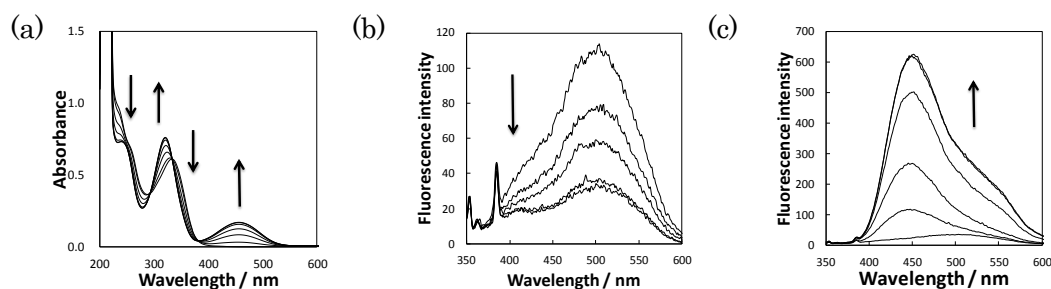
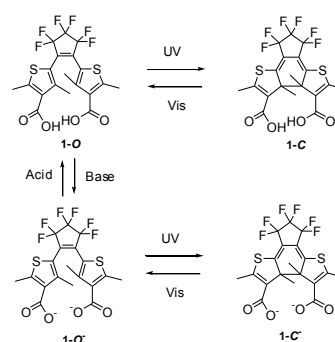


Fig. 1 (a) Absorption spectral change of **1-O** upon irradiation with 366-nm light in CH_2Cl_2 .
(b) Fluorescence spectral change of **1-O** upon irradiation with 366-nm light in CH_2Cl_2 .
(c) Fluorescence spectral change of **1-O** upon addition of DBU in CH_2Cl_2 .

[1] K. Suzuki, T. Ubukata, Y. Yokoyama, *Chem. Commun.*, **2012**, 48, 765-767.