Academic Program [Oral B] | 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-：Oral B

Wed. Mar 26, 2025 1:00 PM - 3:40 PM JST | Wed. Mar 26, 2025 4:00 AM - 6:40 AM UTC
[F]2301(2301, Bldg. 2, Area 4 [3F])

[[F]2301-1pm] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Manabu Abe, Yasuharu Yoshimi

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[[F]2301-1pm-01]

Mechanistic Investigation of Halogen Bond-Mediated Photochemical Transformations: An Integrated Experimental and Theoretical Study

〇EIJI Yamaguchi[1], Akichika Itoh[1] (1. Gifu Pharm. Univ.)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[[F]2301-1pm-02]

Optical Properties Based on Intramolecular Charge Transfer of Novel Naphthalene-based π-Electron Conjugated Compounds and Elucidation of Their Mechanisms

〇Yui Manabe[1], Hiroshi Takashima[2], Shoko Yamazaki[3] (1. Graduate School of Human and Science, Nara Women’s University, 2. Faculty of Science, Nara Women’s University, 3. Nara University of Education)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[[F]2301-1pm-03]

Spin-correlated photoabsorption and emission of a carbazole-containing Kekulé-type diradical

〇Yoshika Takewaki[1,2], Asato Mizuno[2], Ryota Matsuoka[2], Shojiro Kimura[3], Tetsuro Kusamoto[2,4,5] (1. SOKENDAI, 2. Osaka Univ., 3. Tohoku Univ., 4. JST-FOREST, 5. OTRI-Spin, Osaka Univ.)

English
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[[F]2301-1pm-04]

Anti-Stokes Emission Utilizing Reverse Intersystem Crossing

〇Shintaro Kohata[1,2], Hajime Nakanotani[1,2,3], Takuya Hosokai[4], Takuma Yasuda[1,5], Youichi Tsuchiya[2], Chihaya Adachi[1,2,3] (1. Grad. Sch, Eng., Kyushu Univ., 2. OPERA, Kyushu Univ., 3. WPI-I2CNER, 4. AIST, 5. IAS, Kyushu Univ.)

Japanese
2:20 PM - 2:40 PM JST | 5:20 AM - 5:40 AM UTC
[[F]2301-1pm-05]

The Double Closed-Ring Isomer of a Diarylethene Fused Dimer

〇Kenji Higashiguchi[1], Kurumi Satake[1], Naoto Ootsuki[1], Kenji Matsuda[1,2] (1. Kyoto Univ., 2. FIFC, Kyoto Univ.)

Japanese
2:40 PM - 3:00 PM JST | 5:40 AM - 6:00 AM UTC
[[F]2301-1pm-06]

Construction and Singlet Fission Properties of Molecular Assemblies Based on Tetracenothiophene Dimers

○Taiga Okamoto[1], Hayato Sakai[1], Taku Hasobe[1] (1. Fac. Sci. Tech., Keio Univ.)

🏷 Japanese

3:00 PM - 3:20 PM JST | 6:00 AM - 6:20 AM UTC

[[F]2301-1pm-07]

Controlled Orientations of Perylene Dimers for Intramolecular Singlet Fission

○Ryoko Shimbo[1], Hayato Sakai[1], Taku Hasobe[1] (1. Fac. Sci. Tech., Keio Univ.)

🏷 Japanese

3:20 PM - 3:40 PM JST | 6:20 AM - 6:40 AM UTC

[[F]2301-1pm-08]

Synthesis and Singlet Fission Properties of Supramolecular Polymers Based on Scissor-Shaped Acene Dimers

○Hayato Sakai[1], Arisa Ino[2], Hiroki Hanayama[3], Hikaru Sotome[4], Shiki Yagai[5], Taku Hasobe[1] (1. Fac. Sci. Tech., Keio Univ., 2. Grad. Sch. of Sci. and Eng., Chiba Univ., 3. Grad. Sch. of Eng., Chiba Univ., 4. Grad. Sch. of Eng. Sci., Osaka Univ, 5. IAAR, Chiba Univ.)

日本化学会 第105春季年会 (2025)

ハロゲン結合を介した光化学変換反応の機構解析：実験的・理論的アプローチによる統合的研究

○山口 英士[1]、伊藤 彰近[1] (1. 岐阜薬科大学)

Mechanistic Investigation of Halogen Bonding Interaction Mediated Photochemical Transformations: An Integrated Study through Experimental and Theoretical Approaches

Eiji Yamaguchi[1] , Akichika Itoh[1] (1. Gifu Pharmaceutical University)

Halogen bonding, a unique type of non-covalent interaction, is formed through electrostatic interactions between Lewis bases and a positively charged region called a σ-hole on halogen atoms. Recent studies have established that when complexes formed through these halogen bonds are exposed to light irradiation, they undergo photoinduced electron transfer (PET) between the donor and acceptor components of the complex, leading to various photochemical transformations.

In our previous studies, we have discovered that aryl radicals can be efficiently generated via PET in a system utilizing phenol as a halogen bond acceptor and iodobenzene as an electron donor. This finding presents a novel approach to radical generation under mild conditions. However, the detailed reaction mechanism of this process, including the nature of the intermediate species and the role of the halogen bond in facilitating electron transfer, remains insufficiently understood. Elucidation of these mechanistic aspects is essential for further development and optimization of this synthetic methodology.

Against this background, we conducted a comprehensive investigation of the reaction mechanism using complementary experimental and computational approaches. Our experimental studies employed various spectroscopic techniques, while computational analyses provided insights into electronic structures and energy profiles. In this presentation, we will report our findings regarding the characteristic features of halogen bonds in these systems and their influence on photochemical reactivity, with particular emphasis on the factors controlling the efficiency of electron transfer and subsequent radical formation.

Keywords : Halogen-bonding; PET; mechanism; computational chemistry

ハロゲン結合は、ハロゲン原子上に存在するσホールと呼ばれる正電荷を帯びた領域に対し、ルイス塩基が静電相互作用することで形成される。このハロゲン結合により形成された複合体に光を照射すると、ドナーとアクセプター間で光誘起電子移動（PET）が進行することが明らかとなっている。

我々は、ハロゲン結合受容体としてフェノール、電子供与体としてヨードベンゼンを用いた系において、PETを介してアリールラジカルが生成することを見出している。しかしながら、このプロセスの詳細な反応機構については未だ十分な解明がなされておらず、本反応の更なる展開には、その解明が必要不可欠である。

このような背景のもと、我々は実験化学的手法と計算化学的手法を相補的に用いることで、反応機構の解明研究を行った。本発表では、これらの検討から明らかとなったハロゲン結合の特性および反応性について報告する。

1) Halogen-Bonding-Promoted Photoinduced C-X Borylation of Aryl Halide Using Phenol Derivatives K. Matsuo, E. Yamaguchi, A. Itoh *J. Org. Chem.* **2023**, ***88***, 6176-6181.

ナフタレンをベースとした新規縮環系π電子共役化合物の分子内電荷移動に基づく発光特性およびその機構解明

（奈良女大院化学 [1]・奈良女大理 [2]・奈良教育大 [3]）○真鍋 結衣 [1]・高島 弘 [2]・山崎 祥子 [3]

Optical Properties Based on Intramolecular Charge Transfer of Novel Naphthalene-based π-Electron Conjugated Compounds and Elucidation of Their Mechanisms

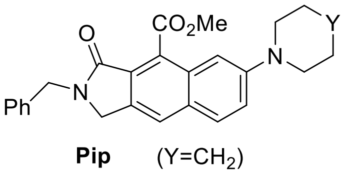
([1]*Graduate School of Human and Science, Nara Women's University,* [2]*Faculty of Science, Nara Women's University,* [3]*Nara University of Education*) ○Yui Manabe,[1] Hiroshi Takashima,[2] Shoko Yamazaki[3]

Optical properties based on intramolecular charge transfer (ICT) were investigated for various novel naphthalene-based π-electron conjugated compounds with electron-donating amino or electron-withdrawing carbonyl groups. UV-visible absorption spectra, emission spectra, absolute quantum yields, and fluorescence lifetimes were measured in six solvents with different polarities. As a result, it was found that the solvatofluorochromism shows significantly different behavior depending on the substituents. In particular, significant differences were observed in the properties of compounds with methyl ester groups and those with carboxy groups. To consider the mechanisms of them, DFT and TD-DFT calculations were conducted.

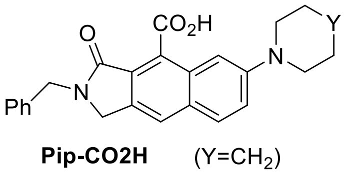
Keywords :Solvatofluorochromism; Solvatochromism; Intramolecular Charge Transfer; Fluorescence; DFT Calculation

溶媒の種類（極性）によって，発光色が変化する現象をソルバトフルオロクロミズムという．これを示す蛍光分子は，周囲の環境によって発光特性が変わることから，系の状態を把握することが可能であり，化学センサーや蛍光プローブ等への応用が期待される．

本研究では，電子供与性のアミノ基や電子求引性のカルボニル基などを導入した，さまざまな新規縮環系π電子共役化合物[1,2]について，その分子内電荷移動（ICT）に基づく発光特性を調べた．6 種類の溶媒中における紫外可視吸収スペクトル，蛍光スペクトル，絶対蛍光量子収率および蛍光寿命を測定したところ，置換基の種類によって大きく異なるソルバトフルオロクロミズムを示すことが分かった．特に，エステル基を有する化合物とカルボキシ基を有する化合物では大きな違いが見られた．また，その機構を理論化学計算（DFT および TD-DFT 計算）から検討した．



Pip (Y=CH$_2$)
Molph (Y=O)



Pip-CO2H (Y=CH$_2$)
Molph-CO2H (Y=O)

[1] Z. Wang, S. Yamazaki, Y. Mikata, M. Oba, H. Takashima, T. Morimoto, A. Ogawa, *J. Org. Chem.*, **2022**, *87*, 11148–11164. [2] Z. Wang, S. Yamazaki, T. Morimoto, H. Takashima, A. Nakaoku, M. Shimizu, A. Ogawa, *Org. Biomol. Chem.*, **2023**, *21*, 2172–2187.

Spin-correlated photoabsorption and emission of a carbazole-containing Kekulé-type diradical

([1]*Sokendai,* [2]*Grad. Sch. of Eng. Sci., Osaka Univ.*, [3]*IMR, Tohoku Univ.*, [4]*JST-FOREST*, [5]*OTRI-Spin, Osaka Univ.*) ○ Yoshika Takewaki,[1,2] Asato Mizuno,[2] Ryota Matsuoka,[2] Shojiro Kimura,[3] Tetsuro Kusamoto[2,4,5]

Keywords: Luminescent Radical, Diradical

Diradicals have electronic ground and excited states with both singlet and triplet spin multiplicities, which differ from those of organic closed-shell molecules and monoradicals. This unique electronic structure enables thermal equilibrium between the singlet and triplet electronic ground states, leading to spin-correlated photofunctions. An example of such photofunction is spin-state-dependent absorption reported particularly in Kekulé-type diradicals, which could realize selective excitation of the singlet or triplet state. As another example, we have reported spin-correlated emission of non-Kekulé-type diradicals.[1,2] We envisioned that a combination of spin-state-dependent absorption and emission allows a more comprehensive understanding of the relationship between the molecular structure and the spin-correlated photofunctions. In this study, Kekulé-type diradical **27R$_2$** was synthesized, and its magnetic and photophysical properties were compared with those of the non-Kekulé-type counterpart **36R$_2$**, which was previously reported to exhibit triplet-specific emission (Fig. 1a).[2]

27R$_2$ was shown to exhibit both spin-correlated absorption and emission. **27R$_2$** displayed emission at 701 nm in cyclohexane (Fig. 1b). A noteworthy observation is the difference between the absorption and the excitation spectra of **27R$_2$**, whereas those of **36R$_2$** show no such discrepancy. By measuring the absorption, emission, and excitation spectra at various temperatures (i.e. at various singlet-triplet ratios), **27R$_2$** was suggested to show spin-state-dependent absorption and triplet-specific emission. This was also supported by theoretical calculations and the magnetic-field effect on the luminescence. The detailed comparison of **27R$_2$** and **36R$_2$** revealed the impact of substitution position on their photofunctions.

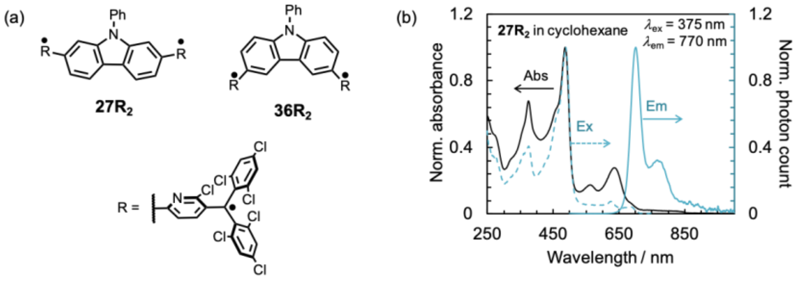


Fig. 1 (a) Chemical structures of **27R$_2$** and **36R$_2$**. (b) Absorption, emission, and excitation spectra of **27R$_2$** in cyclohexane (λ_{ex} = 375 nm, λ_{em} = 770 nm).

(1) R. Matsuoka *et al.*, *J. Am. Chem. Soc.*, **2023**, *145*, 13615. (2) A. Mizuno *et al.*, *J. Am. Chem. Soc.*, **2024**, *146*, 18470.

Anti-Stokes Emission Utilizing Reverse Intersystem Crossing

([1]*Grad. Sch, Eng., Kyushu Univ.*, [2]*OPERA, Kyushu Univ.*, [3]*WPI-I2CNER*, [4]*AIST*, [5]*IAS, Kyushu Univ.*) ○Shintaro Kohata,[1,2] Hajime Nakanotani,[1,2,3] Takuya Hosokai,[4] Takuma Yasuda,[1,5] Youichi Tsuchiya[2], and Chihaya Adachi[1,2,3]

Keywords: Photon-upconversion, Anti-Stokes emission, Thermally activated delayed fluorescence, Dexter-type energy transfer, Förster-type energy transfer

Photon-upconversion (PUC) processes in organic molecular systems, such as triplet-triplet upconversion, two-photon absorption, and hot-band absorption, are promising technologies for future energy harvesting. One of the unique applications utilizing PUC processes is thermal energy harvesting, leading to optical cooling in matters.[1] Although these processes can generate high-energy excitons compared to excitation energy, a PUC process with a high yield and no energy loss has not been established and, therefore, is highly desired.

Here, we propose an alternative PUC mechanism that uses reverse intersystem crossing on thermally activated delayed fluorescence (TADF) molecules.[2] This process combines a triplet sensitizer and a TADF molecule, generating a triplet in the former and transferring it to the latter. Specifically, the triplet energy transfer from **Ir(ppy)₃** (sensitizer) to **CzBSe** (TADF) results in anti-Stokes emission with an anti-Stokes energy of 0.18 eV. We found that the triplet energy transfer rate strongly depends on the triplet radiative decay rate of the TADF molecules and the difference in the Gibbs energy between the energy acceptor and donor. Our findings will contribute to understanding triplet energy transfer dynamics in organic energy donor-acceptor systems and will lead to various applications, such as future optical cooling systems.

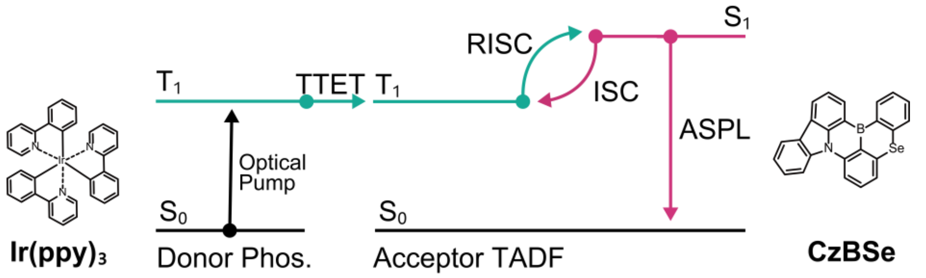


Fig. 1: Schematic illustration of the proposed ASPL mechanism utilizing the RISC process on the TADF molecules, and the chemical structures of energy donor and accept molecule used in this study.

[1] M. P. Hehlen, *J. Lumin.* **2022**, *252*, 119270.

[2] S. Kohata, H. Nakanotani, T. Hosokai, T. Yasuda, Y. Tsuchiya, and C. Adachi, *Angew. Chem. Int. Ed.* **2024**, e202419323.

ジアリールエテン縮環二量体の二重閉環体

（京大院工 [1]・京大福井セ [2]）○東口 顕士 [1]・佐竹 来実 [1]・大月 直人 [1]・松田 建児 [1,2]
The Double Closed-Ring Isomer of a Diarylethene Fused Dimer ([1]*Graduate School of Engineering, Kyoto University*, [2] *Fukui Institute for Fundamental Chemistry, Kyoto University*)
○Kenji Higashiguchi,[1] Kurumi Satake,[1] Naoto Ootsuki,[1] Kenji Matsuda [2]

Diarylethene dimers with a long spacer connecting the units can form the double closed-ring isomer, of which both the units are the closed-ring structure. However, the photochemical properties are estimated to be similar to the sum of comprising units due to the small electronic correlation. In this study, we discuss the near-infrared absorption character and its photoinduced ring-opening reaction of the double ring-closed product, which is a fused dimer in which two diarylethene units are connected by a conjugated structure.
Keywords : Diarylethene; Photochromism; Electrochromism; NIR absorption; Quantum yield

ジアリールエテン二量体を光異性化させる場合、ユニット間を繋ぐスペーサーが短ければエネルギー移動により二つ目の閉環が起こらず、長ければ両ユニットが共に閉環した状態をとり得るものの二重閉環体の長波長化は起こらない。本研究では、二つのジアリールエテンユニット同士の共役構造が繋がっている縮環型二量体 **1** (Fig. 1, R: N(tBu$_2$Ph)$_2$)の二重閉環体の近赤外吸収と光開環反応を評価した。[1)]

二重閉環体 **1-cc** は、**1-oo** 溶液への UV 照射による **1-co** への異性化、その後酸化剤 (magic blue) および還元剤 (FeCp*$_2$) の添加により得られ、逆相 HPLC により精製した。二重閉環体 **1-cc** は NIR 吸収を示した (Fig. 2, λ_{max} = 945 nm)。量子収率は、まず絶対法により **1-co** の開環量子収率を求め ($\Phi_{\mathbf{oo\text{-}co,580}}$ = 0.0062)、それを基準とした相対法により **1-cc** から **1-co** への開環量子収率 $\Phi_{\mathbf{cc\text{-}co,1064}}$ ~ 10^{-8} を得た。得られた **1-co** は通常のフォトクロミズムを示した。

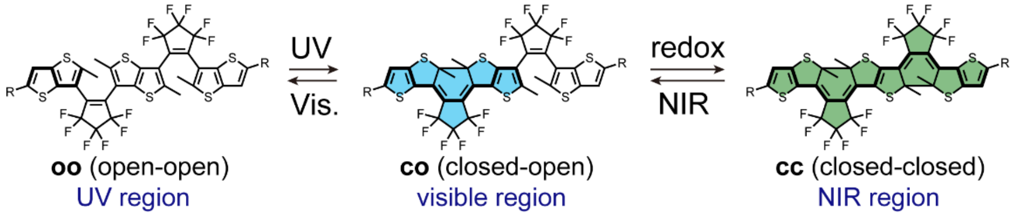


Fig. 1. Diarylethene fused dimer and the isomerization upon photo- and redox stimuli.

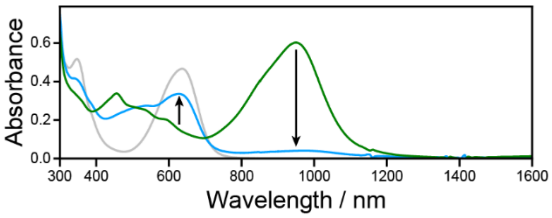


Fig. 2. An NIR-induced back reaction from the isolated **1-cc** to **1-co** in CH$_2$Cl$_2$.

1) K. Satake, K. Higashiguchi *et al.*, *under revision*.

テトラセノチオフェン二量体を基盤とした分子集合体の構築と一重項分裂

（慶大理工）○岡本 大河・酒井 隼人・羽曾部 卓

Construction and Singlet Fission Properties of Molecular Assemblies Based on Tetracenothiophene Dimers

(Faculty of Science and Technology, Keio University) ○Taiga Okamoto, Hayato Sakai, Taku Hasobe

Singlet fission (SF) is a photophysical process, in which one singlet excited state is converted into two triplet excited states. One of the typical chromophores for SF is a pentacene and intramolecular singlet fission was observed in its dimeric and oligomeric forms. On the other hand, tetracenothiophene (TTh) is one of the pentacene analogs, which has a higher energy of the triplet excited state, and the unique linker positions derived from the terminal thiophene unit. However, there are only a few reports on SF using TTh. We newly synthesized a series of TTh dimers and oligomers to evaluate the detailed structural and photophysical properties.

Keywords : Singlet Fission; Tetracenothiophene; Molecular Assembly

一重項分裂 (Singlet Fission: SF) とは、近接二分子間において 1 つの一重項励起子 (S_1) が 2 つの三重項励起子 (T_1) へと変換される多励起子生成反応である。SF の発現条件として、S_1 と T_1 の間でエネルギー保存則を満たすことが挙げられ [$E(S_1) \geq 2E(T_1)$]、ベンゼン環が 5 つ直線状に縮環したペンタセンはその代表的な材料である。これまでに二量体におけるペンタセンの SF は多数報告されており、さらには多量体への展開もなされている。しかしながら、ペンタセンは T_1 のエネルギーが低いため [$E(S_1) = 1.9$ eV, $E(T_1) = 0.8$ eV]、励起子の利用という観点では課題が残る材料である。

一方で、アセン骨格の一部を複素環に置換することにより、励起状態の制御や新たな構造制御が期待できる。中でも、ペンタセン末端のベンゼン環を 1 つチオフェンに置換したテトラセノチオフェン (TTh) は、ペンタセンより高い T_1 のエネルギーを有し [$E(S_1) \approx 2$ eV, $E(T_1) \approx 1$ eV] 、アセンとは異なる末端五員環由来の連結位置を活用できる。しかしながら、二量体の分子内 SF は報告されているものの、末端五員環の連結位置依存性や多量化に関連した報告は皆無である [1]。

本研究では、まずフェニレンリンカーを用いて TTh の末端五員環を連結した二量体を合成した。その後、図 1 に示した TTh 六量体などを新たに合成し、二量体を基盤とした多量体の合成へと展開した。分光測定の結果、いずれの系においても良好な SF の進行が観測された。本発表では、材料合成および励起ダイナミクスの詳細について報告する。

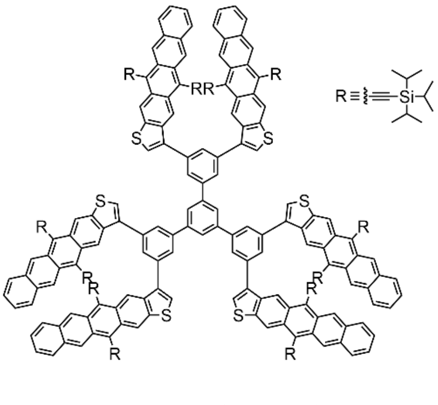


図 1 TTh 六量体の化学構造

1) L. M. Campos, M. Y. Sfeir, et al. *J. Am. Chem. Soc.* **2023**, *145*, 22058.

配向を制御したペリレン二量体の合成と分子内一重項分裂

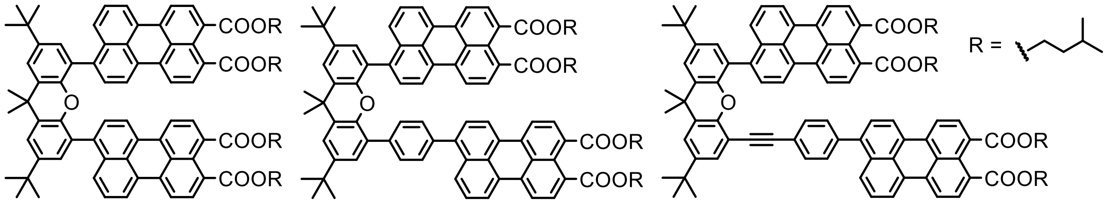
（慶大理工[1]）○真保 遼子[1]・酒井 隼人[1]・羽曾部 卓[1]
Controlled Orientations of Perylene Dimers for Intramolecular Singlet Fission ([1]*Fuculty of science and Technology, Keio University*) ○Ryoko Shimbo,[1] Hayato Sakai,[1] Taku Hasobe[1]

Singlet Fission (SF) is a multi-exciton generation process that produces two individual triplet excitons from one-photon absorption in two nearby chromophores. SF has been widely studied using acenes, whereas one of the serious issues includes the extremely weak reduction properties of the triplet excited states due to the small excitation energies. In contrast, perylene has the relatively higher excitation energies and the stronger reduction properties of the triplet excited states. In this study, we synthesized a series of cofacial perylene dimers through xanthene linker with different electronic coupling and conformational flexibility between chromophores for intramolecular SF and evaluated intramolecular singlet fission properties.

Keywords : Intramolecular Singlet Fission; Perylene

一重項分裂 (Singlet Fission) とは、最低一重項励起状態 (S_1) の分子が近接する基底状態の分子と相互作用し、二つの最低三重項励起状態 (T_1) が生成する多励起子生成過程である 1)。SF 発現のエネルギー条件として、S_1 のエネルギーが T_1 のエネルギーの 2 倍と同程度もしくはそれ以上であることが挙げられる。複数のベンゼン環が直線状に縮環したアセン系分子はエネルギー条件をよく満たし、高効率な SF の発現が多数報告されている。しかしながら、縮環数の増加に伴って T_1 のエネルギーは低下し、その後の化学反応への利用が困難になる。一方、ベンゼン環が非直線状に縮環したペリレンはアセン系分子よりも高い T_1 のエネルギーを有し、T_1 における還元力も高い。SF 発現に必須のエネルギー条件をおおむね満たすものの、競合するエキシマーの発現によって一重項分裂の報告例は数例に限られ、その収率も極めて低い 2)。

そこで、本研究ではキサンテンをリンカーとしたペリレン同士が向かい合う配向が可能なペリレン二量体に注目した。特に、エチニル基とフェニル基を基盤としたスペーサーを非対称に導入することでペリレン間の相互作用や立体柔軟性を系統的に変化させ、分子内 SF の評価を行った。



Xan-(0,0)-(PDE)$_2$ **Xan-(0,Ph)-(PDE)$_2$** **Xan-(0,EPh)-(PDE)$_2$**

Fig. 1 本研究で合成したペリレン二量体

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ハサミ型アセン二量体を基盤とする超分子ポリマーの合成と一重項分裂

（慶大理工[1]・千葉大院融合理工[2]・千葉大工学研究院[3]・阪大院基礎工[4]・千葉大国際高等研究基幹[5]）○酒井 隼人[1]・井野 有彩[2]・花山 博紀[3]・五月女 光[4]・矢貝 史樹[5]・羽曾部 卓[1]

Synthesis and Singlet Fission Properties of Supramolecular Polymers Based on Scissor-Shaped Acene Dimers

([1]*Fac. Sci. Tech., Keio Univ.*, [2]*Grad. Sch. of Sci. and Eng., Chiba Univ.*, [3]*Grad. Sch. of Eng., Chiba Univ.*, [4]*Grad. Sch. of Eng. Sci., Osaka Univ.*, [5]*IAAR, Chiba Univ.*) ○Hayato Sakai,[1] Arisa Ino,[2] Hiroki Hanayama,[3] Hikaru Sotome,[4] Shiki Yagai,[5] Taku Hasobe[1]

We have been exploring supramolecular polymers with unique structural and functional properties based on scissor-shaped chromophoric dimers. On the other hand, acene derivatives such as tetracene and pentacene are one of typical chromophores for occurrence of singlet fission (SF), and various molecular systems on covalently linked acene dimers with high triplet quantum yields have already been reported. However, little attention has been drawn to SF in acene-based supramolecular polymers. In this study, we newly synthesized supramolecular polymers based on scissors-shaped acene dimers and evaluated their triplet exciton generation and migration processes through SF.

Keywords : Acene; Dimer; Supramolecular Polymer; Singlet Fission

非共有結合によって連結した超分子ポリマーは、多様な機能を持った分子を簡単に高分子化することができ、分解が容易で自己修復が可能であるなど、従来のポリマーにはない性質を有する。我々は最近、可溶性部位を介して色素分子を連結したハサミ型二量体が有する自己組織化特性を利用することで多様な超分子ポリマーを形成することを見出している 1)。一方、一重項分裂 (SF) は一光子吸収から二つの三重項励起子を生成する光物理過程で、アセン二量体で盛んに検討されているが 2)、超分子ポリマーの SF に関する例は非常に限られる 3)。 本研究では、超分子ポリマーにおける SF 特性の制御を目指し、π共役部位としてテトラセンを側鎖として異なるアルキル鎖を導入したハサミ型二量体を合成した (Fig. 1)。このテトラセン二量体からなる超分子ポリマーを調製し、過渡吸収測定を行ったところ、SF を示唆する結果が得られた。この結果に関して詳細に報告する。

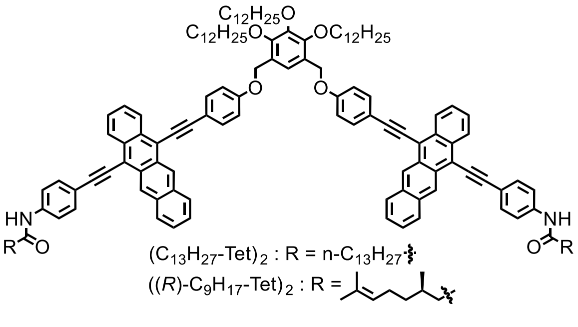

Fig. 1 Chemical structures of scissors-shaped tetracene dimers in this study.

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