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

Tue. Mar 19, 2024 1:00 PM - 3:10 PM JST | Tue. Mar 19, 2024 4:00 AM - 6:10 AM UTC E1132(1132, Bldg. 11 [3F])

[E1132-2pm] 13. Organic Chemistry -Reaction Mechanism, Photochemistry, Electrochemistry-

Chair: Ken Onda, Nobuhiro Yanai

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[E1132-2pm-01]
Intramolecular Singlet Fission of Cyclen-Centered Cyclic Pentacene Oligomers

○Hayato Sakai[1], Shion Mizuno[1], Taku Hasobe[1] (1. Keio Univ.)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[E1132-2pm-02]
Emission properties of stable luminescent radicals with two hydrocarbon substituents or radical groups

○Yohei Hattori[1], Ryota Kitajima[2], Atsumi Baba[2], Kohei Yamamoto[2], Kingo Uchida[2] (1. NAIST, 2. Ryukoku Univ.)

Japanese
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[E1132-2pm-03]
Syntheses and Singlet Fission of Tetracenothiophene Dimers

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

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC
Break

English
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[E1132-2pm-04]
C-F Functionalization by Defluorinative Coupling of Trifluoromethyl Compounds

○Chung-Yang Dennis Huang[1], Amit Kumar Jaiswal[1], Priya Saha[1] (1. Hokkaido University)

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[E1132-2pm-05]
Nonradiative Transitions as Phonon Emission and Absorption Processes

○Wataru Ota[1,2], Motoyuki Uejima[3], Naoki Haruta[1,2], Tohru Sato[1,2] (1. Fukui Institute for Fundamental Chemistry, Kyoto University, 2. Graduate School of Engineering, Kyoto University, 3. MOLFEX, Inc.)

Japanese
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[E1132-2pm-06]
Studies on photoexcitaion dynamics in self-organized porphyrin array films by near-infrared femtosecond time-resolved emission spectroscopy

Kenya Shinozaki[1], Minami Nakamura[2], Mitsuhiko Morisue[2], Munetaka Iwamura[1], ○Koichi Nozaki[1] (1. Grad. Sch. Sci. Eng., Univ. of Toyama, 2. Fac. Mol. Chem. Eng., Kyoto Inst. of Tech.)

サイクレン中心環状ペンタセン多量体の分子内一重項分裂

（慶大理工 [1]）○酒井 隼人 [1]・水野 しおん [1]・羽曾部 卓 [1]
Intramolecular Singlet Fission of Cyclen-Centered Cyclic Pentacene Oligomers ([1]*Faculty of Science and Technology, Keio University*) ○Hayato Sakai,[1] Shion Mizuno,[1] Taku Hasobe[1]

Singlet fission (SF) is a photophysical process where two triplet excitons are generated from one-photon absorption in two nearby chromophores. Many examples of SF using dimers and oligomers have been reported, whereas the number of cyclic molecular systems is quite limited. Moreover, the relationship between substituted position and SF properties in cyclic oligomers has not yet been reported. Cyclenes, nitrogen-containing cyclic molecules, are capable of regioselective molecular modification with respect to nitrogen units, and metal insertion allows control of photophysical properties associated with structural changes. In this study, we newly synthesized cyclen-centered pentacene oligomers to examine the SF properties.

Keywords : Pentacene; Cyclene; Singlet Fission; Oligomer

一重項分裂 (SF) は、近接二分子間において一光子吸収により生成した一つの一重項励起子 (S_1) から二つの三重項励起子 (T_1) を生成する多励起子生成過程である。一般に効率的な SF の発現には、隣接する色素間の電子的相互作用の精密な制御が必要である。これまで、SF は色素を共有結合で連結した二量体や直線状多量体で多数観測されているが、環状多量体における色素の修飾位置と SF を関連付けた例はない。一方、含窒素環状分子サイクレンは、窒素に対して位置選択的に分子修飾が可能である。さらに、サイクレンは骨格中心に銀イオンを包接することで分子構造を変化させることもできる。本研究では、サイクレンにペンタセン (TP) を導入した一連の誘導体 [$(TP)_n$-Cy] (Fig. 1) を合成し、置換位置の違いによる SF 特性だけでなく、金属包接に伴う構造変化による SF の制御も検討した。さらに、$(TP)_n$-Cy に対して銀イオンを包接させた錯体 $Ag^+\subset(TP)_n$-Cy も合成し、構造変化による SF の制御も検討した。

TP 間の配向制御による SF 特性を議論するために、$(TP)_n$-Cy および $Ag^+\subset(TP)_n$-Cy の過渡吸収スペクトルを測定した。一例として(*E*)-$(TP)_2$-Cy では、銀イオンの内包に伴い SF の速度定数が 4.1×10^7 s^{-1} から 1.4×10^8 s^{-1} と一桁加速するだけでなく、独立した T_1 の収率 (Φ_T) も大幅な上昇に成功した。本発表では、導入した TP の置換位置および銀イオンの有無に伴う励起ダイナミクス制御に関して詳細に議論する。

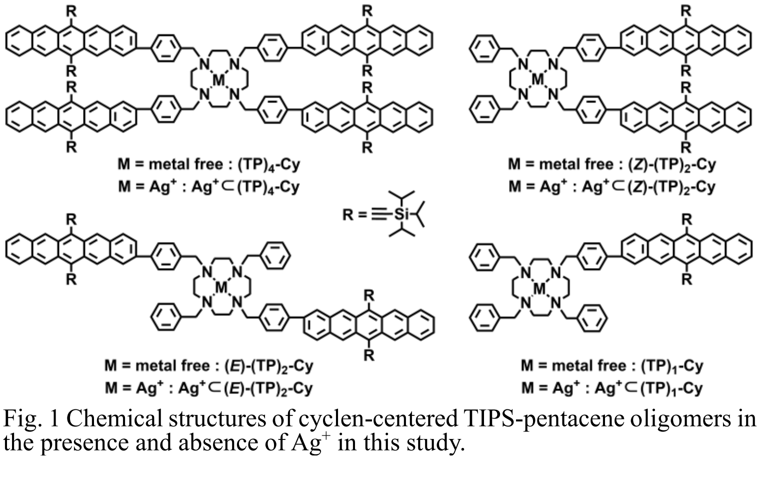


Fig. 1 Chemical structures of cyclen-centered TIPS-pentacene oligomers in the presence and absence of Ag^+ in this study.

二つの炭化水素置換基あるいはラジカル基をもつ安定発光ラジカルの発光特性

（奈良先端大[1]・龍谷大[2]）○服部 陽平[1]・北島 稜大[2]・馬場 温[2]・山本 航平[2]・内田 欣吾[2]

Emission Properties of Stable Luminescent Radicals with Two Hydrocarbon Substituents or Radical Groups

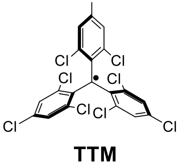
([1]*Nara Institute of Science and Technology*, [2]*Ryukoku University*) ○Yohei Hattori,[1] Ryota Kitajima,[2] Atsumi Baba,[2] Kohei Yamamoto,[2] Kingo Uchida[2]

Stable luminescent radicals have attracted much attention for applications such as highly efficient OLED emitter.1) We study derivatives of PyBTM2) and F_2PyBTM3), which are more photostable than TTM. Suzuki-Miyaura reaction was developed to substitute chlorine atoms at the *para*-position of the benzene rings of PyBTM.4) Especially, when the chlorine atoms were substituted to mesityl groups, photoluminescence quantum yield of the substituted F_2PyBTM in chloroform was as much as 69%.5)

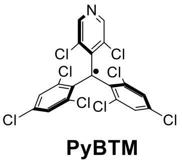
Recently we have prepared stable luminescent radical derivatives with two types of hydrocarbon substituents and diradicals with two radical units bridged by phenylene linker. We will report luminescent properties of these molecules.

Keywords : Fluorescence; Luminescence; Radical; Diradical

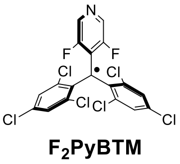
安定発光ラジカルは、高効率有機 EL の発光体等への応用で注目されている 1。我々は、TTM よりも光に強い特長をもつ PyBTM2)や、やや発光効率の良い F_2PyBTM3)の誘導体について研究している。鈴木・宮浦カップリングの応用で、PyBTM や F_2PyBTM のベンゼン環のパラ位の塩素原子をアリール基で置換できるようになり 4)、特にメシチル基で両方の塩素原子を置換したときに、クロロホルム中で 69%と高い蛍光量子収率を示すことがわかった 5)。最近新たに 2 種類の炭化水素芳香族置換基を付けた F_2PyBTM 誘導体や、2 つのラジカルユニットを 1,4-フェニレン基で架橋した発光ジラジカルを開発した。これらの発光特性について考察し、2 つの置換基の影響や、ラジカルユニット同士の影響について考察する。



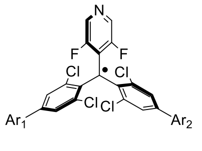
TTM

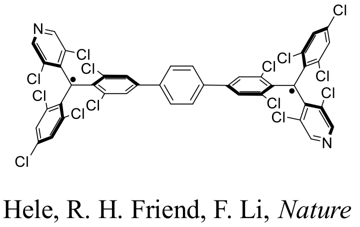


PyBTM



F_2PyBTM





1) X. Ai, E. W. Evans, S. Dong, A. J. Gillett, H. Guo, Y. Chen, T. J. H. Hele, R. H. Friend, F. Li, *Nature* **2018**, *563*, 536.

2) Y. Hattori, T. Kusamoto, H. Nishihara, *Angew. Chem. Int. Ed.* **2014**, *53*, 11845.

3) Y. Hattori, T. Kusamoto, H. Nishihara, *RSC Adv.* **2015**, *5*, 64802.

4) S. Mattiello, F. Corsini, S. Mecca, M. Sassi, R. Ruffo, G. Mattioli, Y. Hattori, T. Kusamoto, G. Griffini, L. Beverina, *Mater. Adv.* **2021**, *2*, 7369–7378.

5) Y. Hattori, R. Kitajima, W. Ota, R. Matsuoka, T. Kusamoto, T. Sato, K. Uchida, *Chem. Sci.* **2022**, *13*, 13418–13425.

テトラセノチオフェン連結体の合成と一重項分裂

（慶大理工）○岡本 大河・酒井 隼人・羽曾部 卓
Syntheses and Singlet Fission of Tetracenothiophene Dimers (*Faculty of Science and Technology, Keio University*) ○Taiga Okamoto, Hayato Sakai, Taku Hasobe

Singlet fission (SF) is a multi-exciton generation process, in which uncoupled two triplet excitons were generated after one-photon absorption in two nearby molecules. One of the typical chromophores for SF is pentacene and many examples of SF systems utilizing pentacene derivatives were reported, so far. On the other hand, tetracenothiophene (TTh) is one of the pentacene analogs. However, the number of reports regarding singlet fission using TTh is extremely limited as compared to pentacene. In this study, we synthesized a series of TTh dimers linked at the *α* and *β* positions of TTh units and evaluated the detail photophysical properties.

Keywords : Singlet Fission; Dimer; Tetracenothiophene

一重項分裂 (Singlet Fission: SF) とは、一光子吸収により生じた一重項励起子 (S_1) が中間体である三重項対を経由して、2 つの独立した三重項励起子 (T_1) を生じる多励起子生成過程である[1]。そ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 倍以上であることが挙げられる [$E(\mathrm{S}_1) \geq 2E(\mathrm{T}_1)$]。SF を発現可能な代表的な発色団として、ベンゼン環が 5 つ直線状に縮環したペンタセンが知られている [$E(\mathrm{S}_1) = 1.9$ eV, $E(\mathrm{T}_1) = 0.8$ eV]。しかし、ペンタセンは T_1 のエネルギーが低いことから、励起子利用という観点では課題が残る。

一方、アセン骨格にヘテロ環を導入することで、励起エネルギーの制御や構造制御が期待できる。実際、ペンタセン末端をチオフェンに置換したテトラセノチオフェン (TTh) はより高い T_1 のエネルギーを有しており [$E(\mathrm{S}_1) \approx 2$ eV, $E(\mathrm{T}_1) \approx 1$ eV]、二量体中で高速な SF の進行が観測されている[2]。しかしながら、チオフェン末端の連結部位に着目した報告はなされていない。

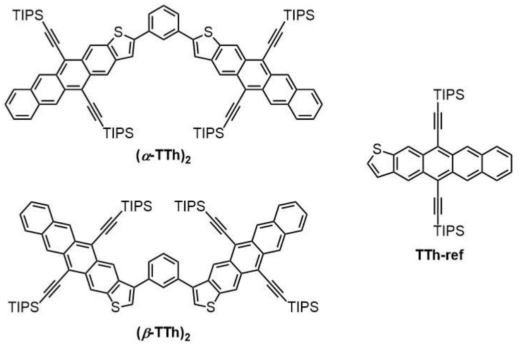


Fig. 1 本研究で用いる化合物の化学構造

本研究では、チオフェンの 2 種類の連結部位でそれぞれ繋いだ TTh 二量体を合成した (Fig. 1)。チオフェンの*α*位および*β*位を用いることで、新たな発色団間のカップリングの制御が期待される。分光測定の結果、いずれの二量体においても良好な SF が進行を観測されたが、SF の反応速度には 2 桁以上の大きな違いがあることが明らかとなった。

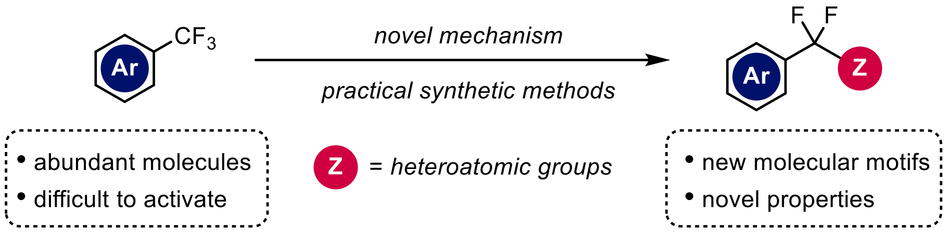
1) M. B. Smith, J. Michl, *Chem. Rev.* **2010**, *110*, 6891.
2) L. M. Campos, M. Y. Sfeir, et al., *J. Am. Chem. Soc.* **2023**, 145, 22058.

C−F Functionalization by Defluorinative Coupling of Trifluoromethyl Compounds

([1]*WPI-ICReDD, Hokkaido University*) ○Amit Kumar Jaiswal,[1] Priya Saha,[1] Dennis Chung-Yang Huang[1]

Keywords: Fluorine Chemistry, Photoredox Catalysis, Hydrogen Atom Transfer, Base Metal Catalysis, C−F Activation

Fluorine-containing compounds represent one of the most important classes of molecules due to their unique properties, where trifluoromethyl group remains as a prestigious motif. Recently, in the effort to expand the available chemical space, attention has been shifted to difluoromethyl moieties. Defluorinative coupling from the abundant trifluoromethyl compounds would be a natural strategy but is currently limited to a small selection of viable mechanisms. Challenges in this approach include strong C−F bonds and product selectivity regarding over-defluorination. Herein, we report two new methodologies for constructing difluoromethyl groups containing C−heteroatom bonds. The first work features a new hydrogen atom transfer (HAT) agent for hydrodefluorination reaction that enables the synthesis of a wide array of molecules containing -CF_2H moieties.[1] Mechanistic studies provided insights on the key role of HAT agent. Secondly, we developed a protocol involving base-metal photoredox catalysis that enables the direct C−F activation to afford C−heteroatom bonds. We proposed that the catalyst serves dual roles in substrate activation and bond-forging cross coupling. Overall, the new mechanism and activation mode point to novel avenue towards general C−F functionalization enabling the expansion of chemical space to unprecedented molecular structures.



1) A. K. Jaiswal, B. B. Skjelstad, S. Maeda, C.-Y. Huang *manuscript in preparation*. 2) P. Saha, C.-Y. Huang *manuscript in preparation*.

日本化学会 第104春季年会 (2024)

フォノンの放出・吸収過程としての無輻射遷移

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Nonradiative Transitions as Phonon Emission and Absorption Processes

([1]*Fukui Institute for Fundamental Chemistry, Kyoto University*, [2]*Graduate School of Engineering, Kyoto University,* [3]*MOLFEX, Inc.*) ○Wataru Ota,[1,2] Motoyuki Uejima,[3] Naoki Haruta,[1,2] Tohru Sato[1,2]

An analytical expression for the nonradiative rate constant is derived based on Fermi's golden rule within the mixed-spin crude adiabatic (CA) approximation. The mixed-spin CA basis is defined by a set of eigenstates for the electronic Hamiltonian that comprises the nonrelativistic electronic Hamiltonian and spin-orbit coupling clumped at the reference nuclear configuration. The mixed-spin basis differs from the pure-spin basis defined by a set of eigenstates for the nonrelativistic electronic Hamiltonian. The mixed-spin CA representation provides a unified view of the nonradiative transitions; both internal conversion and intersystem crossing (ISC) are regarded as vibronically induced phonon emission and absorption processes. The analytical expression enables us to determine important vibrational modes responsible for phonon emission/absorption (promoting modes) and accepting excitation energy (accepting modes) according to the selection rule of vibronic coupling. An advantage of the CA representation is that the spatial distribution of vibronic coupling is elucidated based on its density form, i.e., vibronic coupling density, which can be applied to theoretical molecular design with controlled nonradiative processes. The calculated ISC rate constant for tetracene reproduces the experimental result well.

Keywords： Internal Conversion; Intersystem Crossing; Vibronic Coupling

混合スピン粗断熱表現を用いたフェルミの黄金律に基づき、分子の全振動モードを考慮した無輻射速度定数の解析的表式を導出した[1)]。混合スピン状態は非相対論的電子ハミルトニアンにスピン軌道相互作用を加えたハミルトニアンの固有状態で定義される。これは、非相対論的電子ハミルトニアンの固有状態で定義される純粋スピン状態[2)]とは異なる。混合スピン粗断熱表現では、無輻射遷移を振電相互作用を駆動力としたフォノン放出、吸収過程とみなせ、内部転換と系間交差を統一的に扱うことができる。得られた解析的表式により、振電相互作用の選択則に基づきながら、振動モードをフォノン放出・吸収に関与するモード（促進モード）と電子励起エネルギーを受け取るモード（受容モード）に分類することができる。また、粗断熱表現を用いることで、振電相互作用の起源を振電相互作用密度[3)]により明らかにし、系間交差を制御した分子設計に応用することが可能である。計算によって得られたテトラセンの系間交差速度定数は実験値を良く再現した。

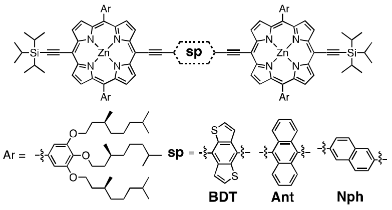
1) W. Ota, M. Uejima, N. Haruta, T. Sato, *Bull. Chem. Soc. Jpn.* in press.
2) B. R. Henry and W. Siebrand, *J. Chem. Phys.* **1971**, *54*, 1072.
3) T. Kato, N. Haruta, and T. Sato, *Vibronic Coupling Density: Understanding Molecular Deformation* (Springer, 2021).

Studies on photoexcitation dynamics in self-organized porphyrin array films by near-infrared femtosecond time-resolved emission spectroscopy

(*Grad. Sch. Sci. Eng., Univ. of Toyama,*[1] *Fac. Mol. Chem. Eng., Kyoto Inst. of Tech.*[2]) Kenya Shinozaki[1], Minami Nakamura[2], Mitsuhiko Morisue[2], Munetaka Iwamura[1], ○Koichi Nozaki[1]

Keywords: porphyrin, aggregate, near-infrared luminescence, bar-coated thin film

Arylene-linked porphyrin arrays bearing elastic 3,4,5-tri((S)-3,7-dimethyl-octyloxy)phenyl groups (Scheme 1) form amorphous molecular glasses containing a partial crystalline arrangement due to self-organization[1]. Neat films of the porphyrin arrays display a large split of the B (Soret) band at 400-500 nm and a bathochromic shift of the Q band at around 700 nm due to exciton coupling in the J-type aggregates (Figure 2). Bar-coated films of the arrays exhibit fluorescence from the Q states at 700-800 nm. Furthermore, near-infrared (NIR) emissions with maxima at 795, 895, and 960 nm were observed for the **Nph**, **BDT**, and **Ant** films, respectively. The emission quantum yields of the films were 5.8×10^{-2} (**Nph**), 1.6×10^{-4} (**BDT**), and 1.0×10^{-3} (**Ant**).



Scheme 1. Arylene-linked porphyrin arrays.

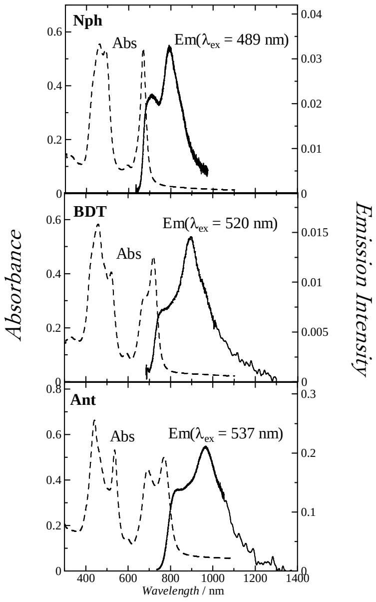


Figure 2. Absorption and emission spectra of bar-coated films of arylene-linked porphyrin arrays.

To understand the photoexcitation dynamics in the self-organized porphyrin glasses, femtosecond fluorescence up-conversion measurements were carried out for the **BDT** bar-coated films. Upon excitation into the B band at 420 nm, ultrafast B→Q internal conversion ($\tau < 0.05$ ps) was followed by relaxation within the Q states with 0.1 ps. The Q-band emission at 740 nm decayed with lifetimes of 0.1 ps(29%) and 0.55ps(55%). The NIR emission at 920 nm appeared within 0.1 ps immediately after the excitation, suggesting that the NIR-luminescent species are ascribed to excimers resulting from self-trapping of the excitons in the aggregates. The NIR emission then decayed with lifetimes of 1 ps (27%), 24 ps(59%), and 400 ps (13%).

1) M. Morisue *et al., RSC Adv.*, **2017**, *7*, 22679.