Academic Program [Oral B] | 03. Physical Chemistry -Structure-：Oral B

Thu. Mar 27, 2025 3:55 PM - 5:15 PM JST | Thu. Mar 27, 2025 6:55 AM - 8:15 AM UTC
[C]C204(C204, Bldg. 2, Area 2 [2F])

[[C]C204-2vn] 03. Physical Chemistry -Structure-

Chair: Hikaru Sotome, Hideaki Shirota

Japanese
3:55 PM - 4:15 PM JST | 6:55 AM - 7:15 AM UTC
[[C]C204-2vn-01]

Intermediate in electronic relaxation of aqueous pyrimidine nucleobases

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Japanese
4:15 PM - 4:35 PM JST | 7:15 AM - 7:35 AM UTC
[[C]C204-2vn-02]

Magnetic Circular Dichroism and Magnetic Circularly Polarized Luminescence Specra of Luminescent Triarylmethyl Radicals

○Yohei Hattori[1], Daiya Suzuki[2], Wataru Ota[3], Tohru Sato[3], Gwénaël Rapenne[4], Yoshitane Imai[2] (1. NAIST, 2. Kindai Univ., 3. Kyoto Univ., 4. Univ. of Toulouse)

English
4:35 PM - 4:55 PM JST | 7:35 AM - 7:55 AM UTC
[[C]C204-2vn-03]

Nanostructural Analysis of Thermally Converted Benzoporphyrin Thin Film Using AFM-IR

○Takayuki Oka[1], Nobutaka Shioya[1], So Ueno[1], Mitsuaki Yamauchi[1], Hiroko Yamada[1], Takeshi Hasegawa[1] (1. Kyoto Univ. ICR)

English
4:55 PM - 5:15 PM JST | 7:55 AM - 8:15 AM UTC
[[C]C204-2vn-04]

Intermolecular Dynamics of Lithium Salt-Amide Deep Eutectic Solvents

○Maharoof Koyakkat[1], Hideaki Shirota[1] (1. Chiba University)

ピリミジン核酸塩基水溶液の電子緩和過程における中間体

（京大院理）○鈴木 俊法、小原 祐樹、Srijon Ghosh、神柱 尚汰、足立 俊輔

Intermediate in Electronic Relaxation of Aqueous Pyrimidine Nucleobases

(*Graduate School of Science, Kyoto University*) ○Toshinori Suzuki, Yuki Obara, Srijon Ghosh, Shota Kamibashira, Shunsuke Adachi

Ultrafast electronic relaxation of nucleobases from the $^1\pi\pi^*$ state to the ground electronic state (S_0) is crucial for the photostability of DNA and RNA. However, it has been suggested that electronic relaxation of pyrimidine nucleobases, nucleosides, and nucleotides in an aqueous environment generates an electronically-excited intermediate state with a lifetime of tens to hundreds of picoseconds with a relatively high quantum yield (QY) of 0.2–0.5. The generation of such a long-lived excited state seem to be inconsistent with the photostability of these molecules. A recent extreme ultraviolet time-resolved photoelectron spectroscopy study reinvestigated this problem and revealed that the accurately determined QY for long-lived excited states is much too low to allow an electronically excited reaction intermediate to exist. In the present study, we investigated the nature of the reaction intermediate using ultraviolet and infrared transient absorption spectroscopy, along with quantum chemical calculations to show that the intermediate is in the S0 state, and its infrared spectrum is compatible with a metastable twisted C=C species theoretically predicted by Park et al. [J. Phys. Chem. Lett. (2022) 13, 7072].

Keywords : Nucleobase; Intermediate; Electronic Relaxation; Infrared Spectroscopy

核酸塩基は$^1\pi\pi^*$ 状態から基底状態への高速な内部転換を有し, それがDNAやRNAの光安定性に重要な役割を果たしているとされてきた. 一方で, 水溶液中の核酸塩基・ヌクレオシド・ヌクレオチドの紫外過渡吸収分光によれば，$^1\pi\pi^*$ 状態からは 10−100ピコ秒オーダーの寿命を持つ $^1n\pi^*$状態が生成するとも報告され，光安定性との整合性に疑問が残っていた. 我々は液体マイクロジェットを用いた極端紫外時間分解光電子分光によって，$^1n\pi^*$状態の生成量子収率が従来の報告よりも遙かに低いことを見出し，従来の $^1n\pi^*$状態を経由した緩和説に疑問を呈した．時間分解赤外吸収分光によって，この中間体の赤外スペクトルを観測し量子化学計算とも比較した結果，この中間体は内部転換によって基底電子状態に生成する C5=C6 結合が捻れた過渡種であると結論された．この結果は，核酸塩基の光損傷の反応経路との関係性において注目すべき知見である.

発光性トリアリールメチルラジカルの MCD 及び MCPL スペクトル

(奈良先端大[1]・近大[2]・京大[3]・トゥールーズ大[4]) ○服部 陽平[1]・鈴木 太哉[2]・大田 航[3]・佐藤 徹[3]・ゲナエル ラッペン[4]・今井 喜胤[2]

Magnetic Circular Dichroism and Magnetic Circularly Polarized Luminescence Specra of Luminescent Triarylmethyl Radicals ([1]*Division of Materials Science, Nara Institute of Science and Technology*, [2]*Department of Applied Chemistry, Faculty of Science and Engineering, Kindai University*, [3]*Fukui Institute for Fundamental Chemistry, Kyoto University*, [4]*CEMES-CNRS, Université de Toulouse*) ○Yohei Hattori,[1] Daiya Suzuki,[2] Wataru Ota,[3] Tohru Sato,[3] Gwénaël Rapenne,[4] Yoshitane Imai[2]

Stable triarylmethyl have recently attracted much attention for their luminescent properties. However, magnetic circular dichroism (MCD) and magnetic circularly polarized luminescence (MCPL) have not been observed for simple triarylmethyl radicals, probably due to their photodegradability. We have reported the first observation of MCD and MCPL of triarylmethyl radicals in solution using racemic mixtures of (3,5-dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (PyBTM)1) and (3,5-difluoro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (F_2PyBTM),2) which are much more photostable than simple triphenylmethyl radical derivatives. Faraday B terms, which are at the origin of magnetic dichroism in nondegenerate systems, were calculated using TD-DFT, and the line shape of MCD spectra was well reproduced. 3)

Keywords : Stable Radicals; Magnetic Circular Dichroism; Magnetic Circularly Polarized Luminescence; DFT Calculations; Photostability

近年安定トリアリールメチルラジカルの発光性が着目されているが、その光分解性のため単純なトリアリールメチルラジカルの磁気円偏光二色性(MCD)及び磁気円偏向発光(MCPL)はこれまで観測されてこなかった。我々はトリアリールメチルラジカルの中では光安定性が高い (3,5-ジクロロ-4-ピリジル)ビス(2,4,6-トリクロロフェニル)メチルラジカル(PyBTM) 1)と(3,5-フルオロ-4-ピリジル)ビス(2,4,6-トリクロロフェニル)メチルラジカル(F_2PyBTM)2)を用いて、溶液中のトリアリールメチルラジカルの MCD 及び MCPL を初めて観測した。さらに TD-DFT を用いて Faraday B 項を計算し、MCD スペクトルの線形の再現を行った。3)

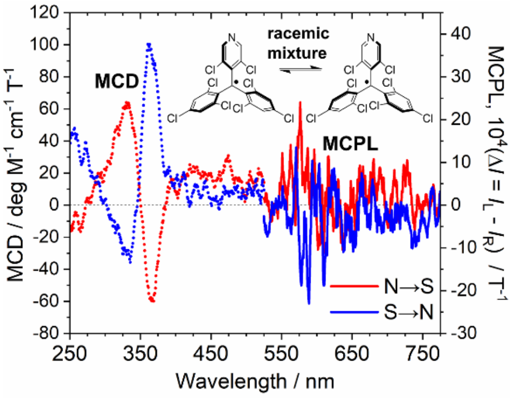

図 PyBTM の MCD 及び MCPL スペクトル 3)

1) Y. Hattori, T. Kusamoto, H. Nishihara, *Angew. Chem. Int. Ed.* **2014**, *53*, 11845–11848.
2) Y. Hattori, T. Kusamoto, H. Nishihara, *RSC Adv.* **2015**, *5*, 64802–64805.
3) Y. Hattori, D. Suzuki, W. Ota, T. Sato, G. Rapenne, Y. Imai, *J. Phys. Chem. Lett.* **2024**, *15*, 11696–11700.

AFM-IR によるベンゾポルフィリン前駆体薄膜の熱転化反応のナノ構造解析

（京大化研 [1]）○岡 昂徹 [1], 塩谷 暢貴 [1], 上野 創 [1], 山内 光陽 [1], 山田 容子 [1], 長谷川 健 [1]

Nanostructural Analysis of Thermally Converted Benzoporphyrin Thin Film Using AFM-IR.

([1] *Kyoto Univ. ICR.*) ○Takayuki Oka[1], Nobutaka Shioya[1], So Ueno[1], Mitsuaki Yamauchi[1], Hiroko Yamada[1], Takeshi Hasegawa[1]

Benzoporphyrins (BP) are excellent organic semiconductor materials, and BP thin films are formed from precursor thin films through thermal conversion reactions. Although many previous studies have already investigated the reaction processes of the precursor materials of BP, few focuses on the structural distribution within the thin films. In this study, the distribution of reaction intermediates has been investigated by AFM-IR, which measures infrared (IR) spectra in microscopic regions of atomic force microscope (AFM) images. As a result, the structural distribution of complex thin films containing intermediates are revealed at the nanoscale for the first time.

Keywords : AFM-IR, Nanostructural analysis, Benzoporphyrin, Atomic force microscopy, Infrared spectroscopy

近年，有機エレクトロニクス材料の大面積加工を実現するための様々な製膜技術が開発されている．この目的のためには，溶液プロセスによる製膜が最適であるが，実用的な半導体材料の中には有機溶媒に対して難溶性を示すものも少なくない．この場合には，薄膜中での前駆体の転化反応を利用する前駆体法は有用である [1]．例えば，溶液プロセスによって塗布製膜されたビシクロポルフィリン（CP）を熱アニールすることで，溶解性の低いベンゾポルフフィリン（BP）の薄膜を得ることができる（Fig. 1a）[2]．この反応は複数の中間体を経由することが計算化学や熱分析によって示唆されているが，薄膜中での中間体の存在を示す証拠は得られていない．この手法を実用化させるためには，薄膜中での反応メカニズムの解明が求められる．

本研究では，AFM 画像中のナノスケール領域の赤外スペクトルを測定する AFM-IR を用いることで，中間体が薄膜中で局所的に存在することを捉えた（Fig. 1b, c）．一方，転化生成物である BP は，プレート状のドメインを形成することを明らかにした．このように，本研究では中間体の存在を解明しただけでなく，それぞれの化学成分の構造分布をナノメートルオーダーで初めて解明した．

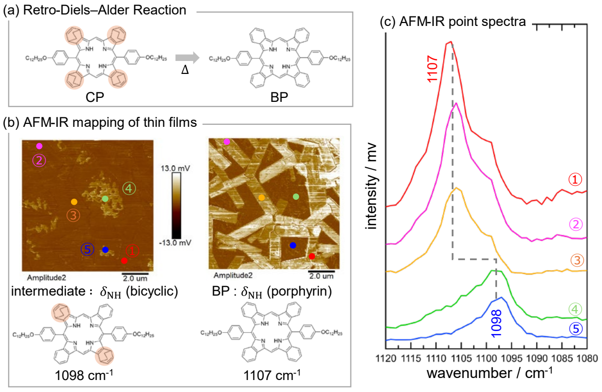

Fig. 1 (a) Retro-Diels–Alder Reaction, (b) AFM-IR mapping, and (c) point spectra

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(2) Uno, H., et al., *Eur. J. Org. Chem.* **2008**, *2008* (1), 87.

Intermolecular Dynamics of Lithium Salt-Amide Deep Eutectic Solvents

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Keywords: Intermolecular Vibration; Orientational Dynamics; Deep Eutectic Solvents; Dynamic Kerr Effect Spectroscopy

Deep eutectic solvents (DESs) are mixtures of two or more solids that exhibit a melting point far lower than their individual components, making them a liquid at room temperature. Here, we have investigated the intermolecular dynamics, including intermolecular vibration and orientational dynamics, of five DESs based on lithium bis(trifluoromethylsulfonyl)amide ($Li[NTf_2]$) and organic amides, using dynamic Kerr effect spectroscopy: femtosecond Raman-induced Kerr effect spectroscopy (fs-RIKES)[1] and subpicosecond optical Kerr effect spectroscopy (ps-OKES).[2] The former one was used for the intermolecular vibrations and the latter one was used for the collective orientational dynamics. The five organic amides were acetamide (AcAm), propanamide (PrAm), *N*-methylacetamide (NMAc), butyramide (BuAm), and urea. The DESs were prepared by mixing $Li[NTf_2]$ and organic amides at a 1:3 molar ratio. In addition, liquid properties such as density, surface tension, and viscosity were measured and compared with the spectroscopic results.

The low-frequency spectra obtained from the fs-RIKES measurements of different DES systems exhibited differences in the line shape and peak frequency. For example, $Li[NTf_2]$/NMAc showed a trapezoidal spectrum, while other DESs exhibited a bimodal one. In the bimodal spectrum, the shoulder peak at ~20 cm^{-1} was mainly due to the cross-term and anion, and the high-frequency band at ~60 or 70 cm^{-1} was attributed to the intermolecular amide hydrogen bonding (N–H···O=C). The peak frequency of the higher frequency bands of $Li[NTf_2]$/urea and $Li[NTf_2]$/AcAm were 71.0 and 69.2 cm^{-1}, respectively, whereas $Li[NTf_2]$/PrAm and $Li[NTf_2]$/BuAm showed peaks at ~60 cm^{-1}. The first moments of the low-frequency spectral band of $Li[NTf_2]$/urea and $Li[NTf_2]$/AcAm were also higher than those of the other three DESs. These findings suggest that the microscopic intermolecular interactions in the urea- and acetamide-based DESs are comparatively stronger than the other three DES systems. The surface tension values of the present DESs were also correlated with this tendency. Furthermore, the analysis of intramolecular vibrational bands of $[NTf_2]^-$ anion showed that the population of transoid $[NTf_2]^-$ was slightly higher in $Li[NTf_2]$/urea. This indicates that the lithium cation solvation via hydrogen bonds is larger in $Li[NTf_2]$/urea than in the other four DESs. Regarding the collective orientational dynamics, the ps-OKES results revealed that the slow relaxation dynamics depend on organic amides. However, the slow relaxation time did not exhibit a linear correlation with viscosity and thus did not follow the Stokes-Einstein-Debye hydrodynamic model.

1) H. Shirota, J. Phys. Chem. A **2011**, *115*, 14262.

2) H. Shirota, M. Koyakkat, J. Rajbangshi, R. Biswas, *J. Phys. Chem. B*, in press