アカデミックプログラム［Ｂ講演］｜12. 有機化学—有機結晶・超分子化学：口頭Ｂ講演

2025年3月27日(木) 13:30 ~ 15:40 [F]2106(第4学舎 2号館 [1階] 2106)

[[F]2106-2pm] 12. 有機化学—有機結晶・超分子化学

座長：桶谷 龍成、関 朋宏

英語

13:30 ~ 13:50

[[F]2106-2pm-01]

光誘起融解を示すアシルヒドラゾン結晶の動作温度拡張の試み

○鯉渕 領[1]、吉川 功[1]、北條 博彦[1] (1. 東京大学)

英語

13:50 ~ 14:10

[[F]2106-2pm-02]

ビフェニル基で連結した双頭型シッフ塩基の単結晶-単結晶相転移

○大政 孝一朗[1]、吉川 功[1]、北條 博彦[1] (1. 東大)

英語

14:10 ~ 14:30

[[F]2106-2pm-03]

アミドの水素結合を利用したアントラセンの位置選択的光二量化反応の検討

○倪 汪斌[1]、木原 伸浩[1] (1. 神奈川大学)

14:30 ~ 14:40

休憩

英語

14:40 ~ 15:00

[[F]2106-2pm-04]

ホスト・ゲスト錯体のCH-π相互作用ネットワークが形づくる劈開可能な二次元ハニカム結晶

○小谷 祐希[1]、寺崎 成哉[1]、勝野 亮祐[1]、松野 太輔[1]、福永 隼也[1]、池本 晃喜[1,2]、磯部 寛之[1] (1. 東大院理、2. JSTさきがけ)

英語

15:00 ~ 15:20

[[F]2106-2pm-05]

プロペラ型分子からなる剥離可能な二次元キンヒドロン型複合体の合成、構造および性質

○敦賀 柊太[1,2]、竹原 陵介[1,2,3]、庄子 良晃[1,2,3]、原野 幸治[4]、福島 孝典[1,2,3] (1. 科学大物質理工、2. 科学大化生研、3. 科学大ASMat、4. 物質・材料研究機構CBRM)

英語

15:20 ~ 15:40

[[F]2106-2pm-06]

環修飾したインドールニトロニルニトロキシドラジカル誘導体における強磁性スピン連鎖の形成

○瀧井 優臣[1]、國本 充輝[1]、三浦 洋平[1]、吉岡 直樹[1] (1. 慶應義塾大学)

Extending the Usable Temperature Range of Photo-Induced Melting in Acylhydrazone Crystals

([1]*Institute of Industrial Science, The University of Tokyo*, [2] *Environmental Science Center, The University of Tokyo*) ○Ryo Koibuchi,[1] Isao Yoshikawa,[1] Hirohiko Houjou,[1,2]

Keywords: Photoswitching; Organic crystals; Isomerization; Phase transition

Photoisomerization associated with reversible crystal-to-liquid transitions has become an attractive research field for its potential applications to solar thermal fuels and self-healing materials.[1] Such photo-induced melting typically requires a photoswitching mechanism that leads to meta-stable isomer(s) with lower melting points. The changes in thermal properties associated with such structural transformations are closely related to crystal structures, posing challenges in molecular design for this phase transition. In this work, we aimed to extend the usable temperature range of the photo-induced melting by exploiting the eutectic point, which depends on the transient conformers during photoisomerization.

We synthesized various acylhydrazone derivatives[2] that have structural flexibility around the isomerization site (Figure 1(b)). Owing to the well-separated absorption band and thermal half-lives for as long as several months, both the *E*- and *Z*-isomers were successfully isolated. By mixing these isomers in arbitrary ratios, their eutectic points were determined. Based on this observation, we investigated the temperature dependence of photoinduced melting and found that two critical factors contribute to the extension of the usable temperature range:

1. The transient meta-stable conformer(s) of the *Z*-isomer generated during photoisomerization further lowers the eutectic point of the system.
2. The intramolecular interactions induced by a modifier (R) increase the energy cost of crystallization for the melt *Z*-isomer (Fig. 1(d)).

We will present new molecular designs to achieve low-temperature photoinduced melting utilizing eutectic mixing, together with experimental and theoretical examinations.

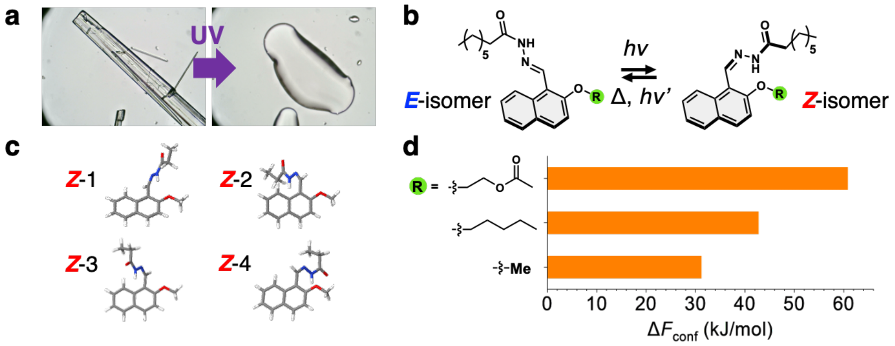


Fig. 1 (a) Microscopy snapshots of photo-induced melting. (b) Molecular structures of *E*/*Z* isomers of acylhydrazones (c) Examples of plausible transient conformers of the *Z*-isomer. (d) Free energy comparison among various R groups.

1) Qiu, et al., *J. Mater. Chem.* *9*(2021)11444. 2) Koibuchi, et al. *J. Phys. Chem. Lett.* *14*(2023)8320.

Single-crystal-to-single-crystal phase transition of biphenyl-type Schiff bases

([1]*Institute of Industrial Science, The University of Tokyo*, [2]*Environmental Science Center, The University of Tokyo*) ○Koichiro Omasa,[1] Isao Yoshikawa,[1] Hirohiko Houjou[1, 2]

Keywords : Single-crystal-to-single-crystal phase transition; Crystal engineering; Polymorphism; Molecular cluster calculations; Salicylideneaniline

We synthesized biphenyl-type disalicylaldehyde Schiff bases, **bis-SAR**s (Fig. 1a), and examined their crystal structures and chromic properties. The fluorine-bearing **bis-SAF** crystal was found in three polymorphs. Form I was prepared via CHCl$_3$/MeOH vapor diffusion, while form III was obtained through CHCl$_2$/Hexane vapor diffusion. Form II was generated through cold crystallization of the melt. The **bis-SAF** crystal exhibited a single-crystal-to-single-crystal (SCSC) phase transition upon heating from form I to form III around 150 °C (Fig. 1b). After the SCSC phase transition, the dihedral angle (θ) of the biphenyl group changed and the crystal packing rearranged (Fig. 1c, d). Differential scanning calorimetry was used to quantify their thermal behavior: form I showed an exothermic phase transition at 146 °C, and forms II and III melted at around 182 °C and 211 °C, respectively. Photoluminescence spectroscopy revealed that form I showed an emission maximum at 592 nm, while form II showed a peak at 594 nm with a shoulder at 631 nm. Under UV irradiation, form III showed no emission and instead an increasing absorbance in the 450–600 nm range, namely photochromism. Quantum chemical calculations using molecular clusters explained the origin of the changes in chromic properties on the basis of their crystal structures.

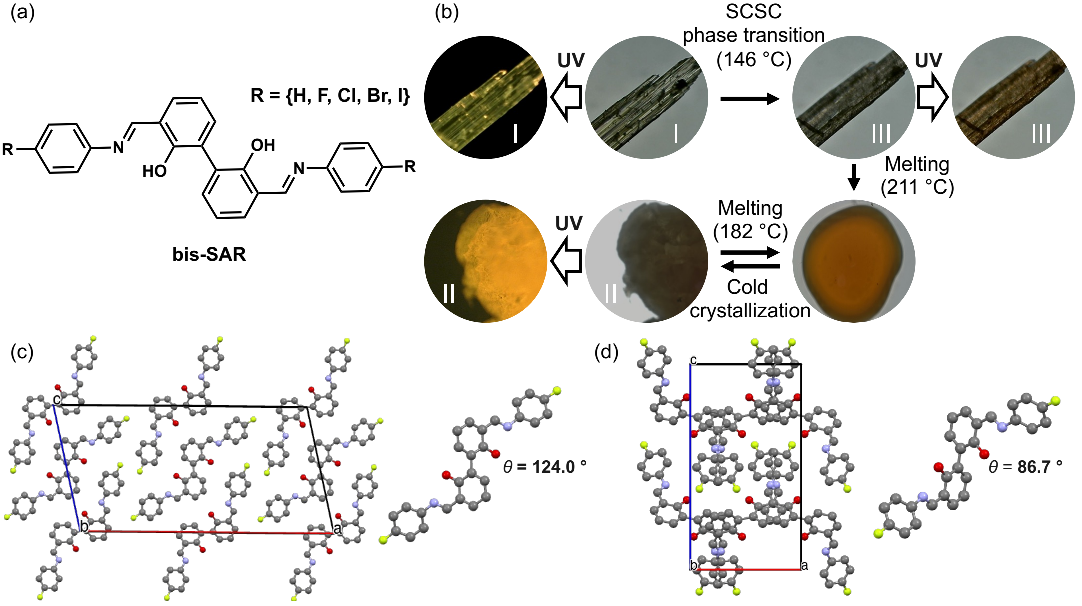


Fig.1 (a) Chemical structure of **bis-SAR**; (b) Microscopy images of **bis-SAF** crystals in form I, II, and III; crystal structures of **bis-SAF** in (c) form I and (d) form III.

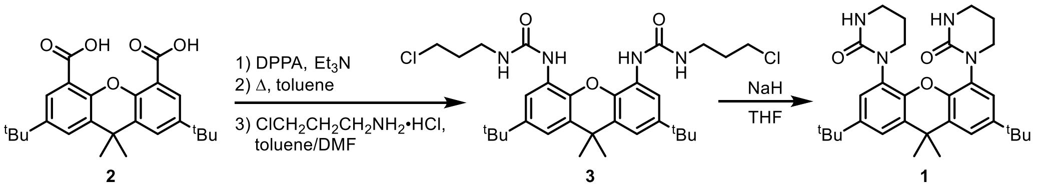
Regioselective photodimerization using hydrogen bonding of amides

(*Graduate School of Science, Kanagawa University*) ○Wang-Bin Ni, Nobuhiro Kihara

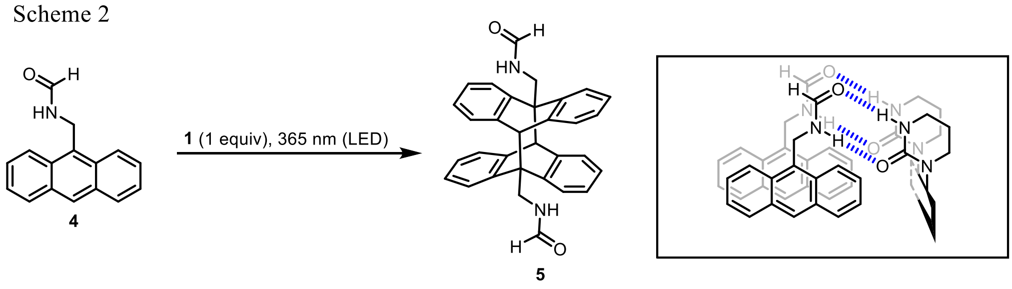
Keywords*:* molecular recognition, photodimerization, regioselectivity, amide, hydrogen bonding

In the photodimerization of anthracene derivatives, head-to-tail regio-isomer is formed selectively because of the steric hindrance of the substituents. Therefore, the preparation of head-to-head dimer is difficult. Photodimerization of amide-substituted anthracene **4** was carried out in the presence of cyclic amide-substituted xanthene **1**, by which regioselective formation of head-to-head regio-isomer was expected because of the alignment of the amide group in anthracene **4** on xanthene **1** by the hydrogen bonding between amides. However, the formation of head-to-head dimer was not observed. To avoid the free rotation of sp^3-sp^3 bonds to fix the conformation of hydrogen bonding complex, photodimerization of anthracene derivatives **6** and **7** and naphthalene derivatives **8** and **9** in the presence of **1** are under investigation.

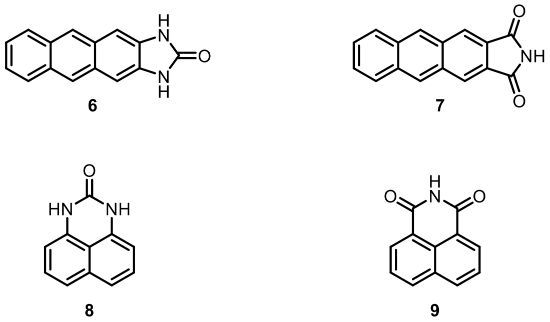
Scheme 1



Scheme 2



Scheme 3



Exfoliatable Layered 2D Honeycomb Crystals of Host-guest Complexes Networked by CH-π Hydrogen Bonds

([1]*Department of Chemistry, The University of Tokyo*) ○Yuki Kotani,[1] Seiya Terasaki,[1] Ryosuke Katsuno,[1] Taisuke Matsuno,[1] Toshiya M. Fukunaga,[1] Koki Ikemoto,[1] Hiroyuki Isobe[1]

Keywords: Honeycomb Structure; Nanotubes; Supramolecular Chemistry; Two-dimensional Crystal

Layered Two-dimensional (2D) crystals have been extensively studied since the discovery of graphene.[1] Although layered molecular crystals are of particular interest for diversification, the weak intermolecular interactions and the diverse structure have hampered the facile construction of layered molecular crystals. In this work, a D_3-symmetrical tubular molecule, (*P*)-(9,6)-[3]cyclo-3,11-dibenzochrysenylene with substituents [(*P*)-$\mathbf{[3]C^{db}C}$-R],[2] was found to readily construct layered 2D crystals via CH-π hydrogen bonds with various combinations for structural diversification (Figure 1a).[3]

The single crystal of (*P*)-$\mathbf{[3]C^{db}C}$-C_6⊃adamantane was found to grow into a large, 1-centimeter crystal, with a layered hexagonal honeycomb structure (Figure 1b). Atoms-in-molecule (AIM) analyses and Hirshfeld analyses showed that the honeycomb structure was constructed by the network of CH-π hydrogen bonds of the host molecules. This system can accept 32 guest molecules in the hexagonal networks. The structures were further diversified with six substituents on the tube, two intercalants and three stereochemistries, which should give 32 × 6 × 2 × 3 structural combinations. Furthermore, the exfoliation of the crystal surface with tape revealed a one-layer step structure (Figure 1c), which showed the exfoliatability of the diverse layered host-guest 2D crystals.

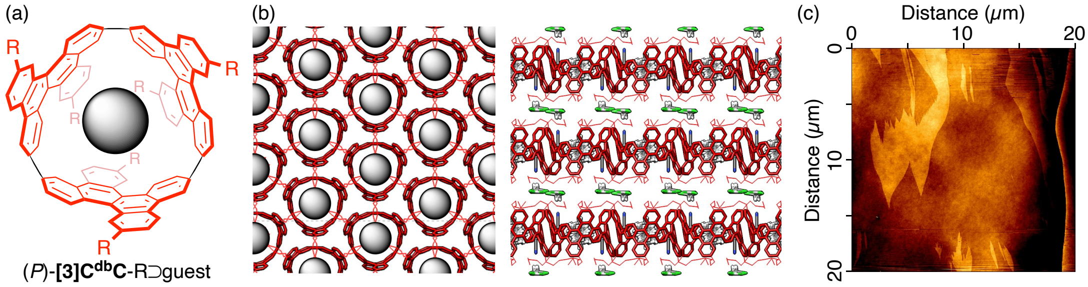


Figure 1. (a) Molecular structure and (b) schematic crystal structure of (*P*)-$\mathbf{[3]C^{db}C}$-R⊃guest. (c) AFM image of the exfoliated crystal surface of (*P*)-$\mathbf{[3]C^{db}C}$-C_6⊃adamantane.

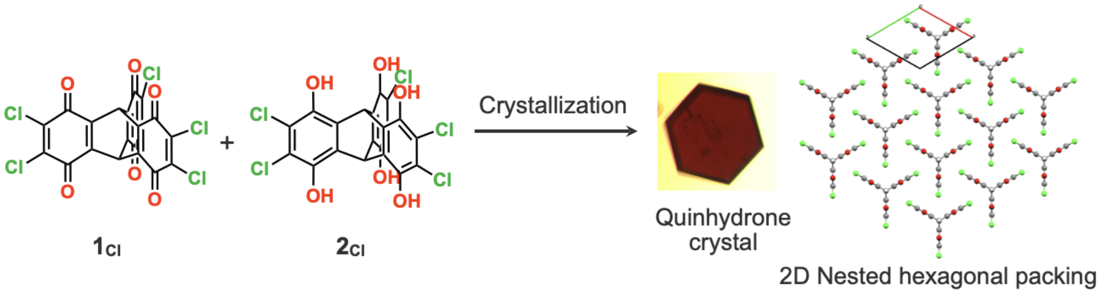
1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* **2004**, *306*, 666-669. 2) Kogashi, K.; Matsuno, T.; Sato, S.; Isobe, H. *Angew. Chem. Int. Ed.* **2019**, *58*, 7385-7389. 3) Terasaki, S.; Kotani, Y.; Katsuno, R.; Matsuno, T.; Fukunaga, T. M.; Ikemoto, K.; Isobe, H. *Angew. Chem. Int. Ed.* **2024**, *63*, e202406502.

Synthesis, Structure, and Properties of Exfoliable 2D Quinhydrone -Type Complexes Consisting of Propeller-Shaped Molecules

([1] *MCT*, *Science Tokyo* [2]*CLS*, *Science Tokyo*, [3]*ASMat*, *Science Tokyo*, [4]*CBRM*, *NIMS*) ○Shuta Tsuruga,[1,2] Ryosuke Takehara,[1,2,3] Yoshiaki Shoji,[1,2,3] Koji Harano,[4] Takanori Fukushima[1,2,3]

Keywords: Organic two-dimensional material; Triptycene tribenzoquinone; Electron acceptor; Hydroquinone; Quinhydrone

The construction of two-dimensional organic materials by molecular self-assembly remains a big challenge. Recently, we have reported that a perchlorinated triptycene-tribenzoquinone[1] (**1**$_{\mathrm{Cl}}$), when mixed with its hydroquinone derivative (**2**$_{\mathrm{Cl}}$), can form a crystalline assembly consisting of layered nanosheets that feature a nested hexagonal packing structure.[2] Dielectric measurements show that the crystals exhibit anisotropic dielectric responses in the in-plane direction. We also examined the exfoliation of these layered crystals and found suitable conditions to obtain micrometer-scale monolayer and a few-layered films. In this presentation, we will report details of the above experimental results, as well as the structure and properties of the resulting nanosheets.



[1] Y. Shoji, S. Yamamoto, T. Fukushima, *Chem. Lett.* **2021**, *50*, 1240.

[2] S. Tsuruga, S. Yamamoto, R. Takehara, Y. Shoji, T. Fukushima, The 34th Symposium on Physical Organic Chemistry, 1A07.

Formation of Ferromagnetic Spin Chain Observed in Indole Nitronyl Nitroxide Derivatives and Effect of Ring Modification

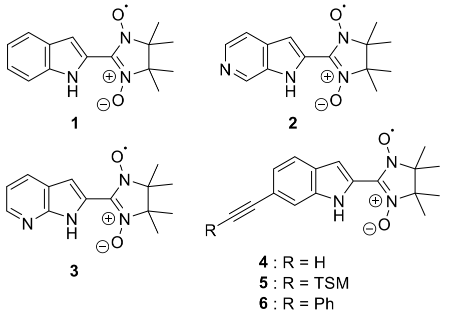
(*Faculty of Science and Technology, Keio University*) ○Masaomi Takii, Mitsuki Kunimoto, Youhei Miura, Naoki Yoshioka

Keywords: Hydrogen Bond, Self-Assembly, Nitroxyl Radical, Molecule-Based Magnetic Material, Magneto-Structural Correlation

Nitronyl nitroxide is widely used as spin source of molecule-based magnetic materials due to ease of introduction. Especially, indol-2-yl nitronyl nitroxide (In-NN, **1**) derivatives forms 1-D hydrogen-bonded columnar structures with strong intracolumn ferromagnetic interactions[1,2]. To control intercolumnar interactions in In-NN crystal, optimization of peripheral substituents is essentially important because 1-D columnar structures and the other stable crystal phases are competitively observed depending on substituents. According to past examples, 6- substituted In-NN with small dipole moment have tendency to form 1-D columnar structures. In the present study, another N atom and ethynyl group on indole ring are introduced for inducing supramolecular self-assembly. Indoles of additional N atom on indole ring and ethynyl substitution at 6-position with various terminal group on magneto-structural correlation will be discussed to control intercolumnar magnetic interaction.

According to the strategy, 6- substituted and aza- In-NN derivatives **2**-**6** were synthesized (**Scheme 1**). Small spin density distributions were observed on ethynyl group from DFT calculation. A single crystal of **6** was obtained by recrystallization from benzene/hexane. Single crystal X-ray analysis revealed that **6** formed 1-D columnar structure with vacancy including benzene molecules. SQUID measurement for **6** suggested J = 6.5 cm^{-1} of ferromagnetic interactions following Heisenberg 1-D ferromagnetic chain (**Fig. 1**).

Detailed magneto-structural correlation of other derivatives will be discussed.



Scheme 1

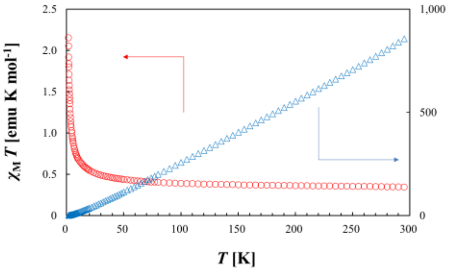


Fig. 1 Temperature dependence of $\chi_m T$ (○) and χ_m^{-1}(△) for **6**.

1) H. Nagashima, N. Yoshioka, *et. al.*, *New J. Chem.*, 2003, ***27***, 805–810.
2) H. Nagashima, N. Yoshioka, *et. al.*, *Cryst. Growth. Des.*, 2004, ***4***, 1, 19–21.