Academic Program [Oral B] | 12. Organic Chemistry -Organic Crystals, Supramolecular Chemistry-：Oral B

Wed. Mar 18, 2026 1:00 PM - 3:20 PM JST | Wed. Mar 18, 2026 4:00 AM - 6:20 AM UTC | E1132 (1132, Bldg. 11 [3F])

[E1132-2pm] Oral B

Chair: Toshikazu Ono, Tomoya Fukui

English

1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC

[E1132-2pm-01] Solvato-Magnetic Effect Observed in Nitronyl Nitroxide Crystals

○Masaomi Takii[1], Naoki Yoshioka[1] (1. Keio University)

English

1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC

[E1132-2pm-02] Single Crystal-Single Crystal Transformation of Monomeric Distyrylbenzene Derivative to Polymer Showing Photo-salient Behaviour with Colour-tunability

○Sandipa Bhandari[1], Masatoshi Ishida[1] (1. Tokyo Metropolitan University)

Japanese

1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC

[E1132-2pm-03] Development of photochemical cold energy storage based on photodimerization of anthracene derivatives

○Yuki Nagai[1], Keita Ishiba[3], Nobuo Kimizuka[4], Yoichi Kobayashi[1,2] (1. College of Life Sciences, Ritsumeikan University, 2. PRESTO, JST, 3. Graduate School of Engineering, Kyushu University, 4. K-NETs, Kyushu University)

2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC

Break

Japanese

2:20 PM - 2:40 PM JST | 5:20 AM - 5:40 AM UTC

[E1132-2pm-04] Topotactic Metal Ion Exchange in Two-Dimensional Organic-Inorganic Hybrid Perovskite Crystals

○Tomoya Fukui[1,2,3], Naoya Mita[1,2], Takanori Fukushima[1,2,3] (1. CLS, Science Tokyo, 2. Sch. Mater. Chem. Tech., Science Tokyo, 3. ASMat, Science Tokyo)

Japanese

2:40 PM - 3:00 PM JST | 5:40 AM - 6:00 AM UTC

[E1132-2pm-05] Arrangement-Dependent Magnetic Properties of Heteroporphyrin-Based Ion-Pairing Assemblies

○Masaki Fujita[1], Ko Furukawa[2], Hiromitsu Maeda[1] (1. Ritsumeikan Univ, 2. Niigata University)

Japanese

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

[E1132-2pm-06] Single-crystal-to-single-crystal structural transition accompanied by chiral symmetry breaking and circularly polarized luminescence properties

○Ryusei Oketani[1], Musashi Okada[1], Saki Ikeda[1], Ken-ichi Yuyama[2], Takuya Nakashima[2], Ichiro Hisaki[1] (1. The University of Osaka, 2. Osaka Metropolitan University)

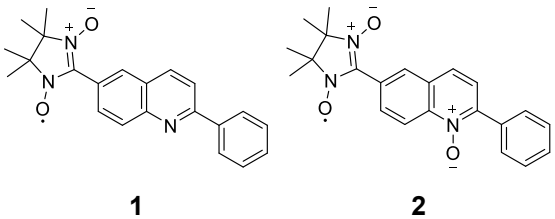
Solvatomagnetic Effect Observed in Nitronyl Nitroxide Crystals

(*Faculty of Science and Technology, Keio University*) ○Masaomi Takii, Naoki Yoshioka
Keywords: Organic Crystal, Stable Radical, Nitroxyl Radical, Molecule-Based Magnetism, Solvatomagnetic Effect

Nitronyl nitroxide(NN) is widely used as spin center in molecule-based magnetic materials due to their stability and synthetic versatility. In particular, their delocalized spin densities are suitable for inducing ferromagnetic couplings. Since magnetic properties in periodic structures highly correlate with the mode of intermolecular close contacts, fine-tuning through chemical modification is feasible. The *N*-oxide group functions as a supramolecular synthon in the crystal and mainly offers O···H or O···heteroatom interactions. Even minor chemical modifications can lead to significant structural changes accompanied by different magnetic properties. Moreover, bulky substituents adjacent to the supramolecular synthon enable them to control over the direction of intermolecular interactions. In the present study, a novel quinoline-based NN derivative with bulky phenyl group and *N*-oxide, **2** and a control molecule **1** were designed and synthesized to compare their crystal structures and magnetic properties (**Scheme 1**).

The molecules were successfully crystallized, and magnetic properties and magneto-structural correlations were investigated. Compound **1** exhibited antiferromagnetic π-stacked dimers and N–O···N–O close contacts. The results were experimentally and theoretically confirmed. In contrast, compound **2** yielded two types of crystals: a crystal with two independent molecules in asymmetric unit **2**, and a crystal of methanol adduct **2·MeOH**. Pristine **2** exhibited two-step antiferromagnetic interactions following the sum of the Bleaney-Bowers two-spin models, arising from its layered structure. Contrary to this, **2·MeOH** exhibited ferromagnetic interactions, the result supported by computational analysis (**Fig. 1**). Furthermore, these two types of crystals were reversibly interconverted by heating and vapor exposure.

Detailed solvatomagnetism related to solvent sorption/desorption phenomena will also be discussed in connection with magneto-structural correlation.



1 **2**

Scheme 1

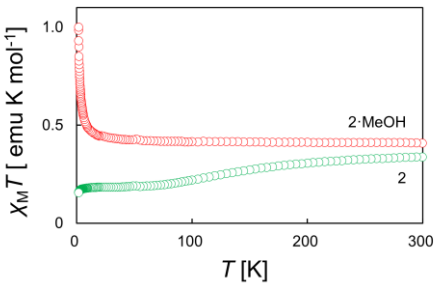


Fig. 1 Temperature dependence of $\chi_M T$ for **2** (green) and **2·MeOH** (red).

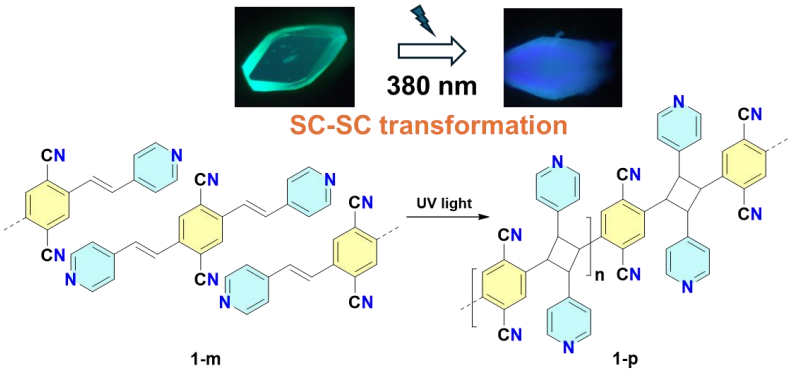
Single Crystal-Single Crystal Transformation of Monomeric Distyryl-benzene Derivative to Polymer Showing Photo-salient Behaviour with Colour-tunability

([1]*Graduate School of Science, Tokyo Metropolitan University*) ○ Sandipa Bhandari,[1] Masatoshi Ishida[1]

Keywords: Fluorescence; Photocycloaddition; Topochemical reaction; Photo-salient; Reversible

Photoactive materials have garnered considerable interest due to their potential applications in sensing, actuators, flexible electronics, and soft robotics.[1] DSB derivatives with electron-withdrawing groups exhibited unique photochemical reactivity: their lower LUMO energies led to enhanced intramolecular charge transfer, longer-lived excited states, and favourable solid-state packing via intermolecular interactions. As a result, these systems channel excitation energy into reactive pathways rather than radiative ones.

In this work, a novel photo-induced single crystal-single crystal (SC-SC) transformation of distyryl-benzene (DSB) monomer (**1-m**) to polymer (**1-p**) has been studied. The intermolecular interactions, such as hydrogen bonds and π-interactions, in the crystalline **1-m** facilitate [2+2] photocycloaddition under 365 nm irradiation, resulting in distinct fluorescence switching from green to blue while maintaining single crystallinity in **1-p** (photopolymer). During this transformation, the crystals **1-m'** prepared by sublimation under ambient atmosphere undergo mechanical motions such as jumping, bending, peeling, and curling. The detailed molecular structures, packing arrangements, and structural evolution during the SC-SC transformation process have been successfully examined by X-ray diffraction and microED analysis. Noticeably, upon heating, the **1-p** single crystals undergo covalent bond cleavage and are deposited as monomer single crystals (**1-m'**), maintaining their photophysical properties. A new type of polymer synthesis via topochemical polymerization in a solvent-free process, with good reversibility, rapid response, and high sensitivity will be discussed.



1) J. Usuba, Z. Sun, H. P. Q. Nguyen, C. Raju, K. Schmidt-Rohr, G. G. D. Han, *Commun. Mater.* **2024**, *5*, 98.

アントラセン誘導体の光二量化に基づく光蓄冷現象の創出

(立命館大生命科学[1]・九大院工[2]・九大 K-NETs[3]・JST さきがけ[4]) ○永井 邑樹[1]・石場 啓太[2]・君塚 信夫[3]・小林 洋一[1,4]
Development of photochemical cold energy storage based on photodimerization of anthracene derivatives ([1]*College of Life Sciences, Ritsumeikan University*, [2]*Graduate School of Engineering, Kyushu University*, [3]*K-NETs, Kyushu University*, [4]*PRESTO, JST*) ○Yuki Nagai,[1] Keita Ishiba,[2] Nobuo Kimizuka,[3] Yoichi Kobayashi[1,4]

To realize a sustainable society, cooling technologies based on renewable light energy are desired. In this study, we propose a novel concept of photochemical cold energy storage, based on the photoinduced liquid-to-solid phase transition upon photodimerization of anthracene derivatives (Fig. 1). In this system, the photogenerated dimer solid returns to the monomer liquid as the thermal dissociation proceeds over time. If the melting heat of the dimer is larger than the dissociation heat, it is expected that an endothermic behavior will be obtained.

We observed that the Ant-AcO-C_6 dimer had a melting heat greater than its dissociation heat, and that the dimer crystals underwent melting even below its melting point as the thermal dissociation proceeded. These results indicate the potential for photochemical cold-energy storage phenomena.

Keywords : Photochromic reaction; Photoinduced phase transition; Photochemical reaction; Enthalpy; Entropy

持続可能な社会の実現に向け、再生可能な光エネルギーに基づく冷却技術が求められる。本研究では、アントラセン誘導体の光二量化 (Fig. 1a) による光誘起液ー固相転移に基づき、光活性化された状態から徐々に吸熱を示す「光蓄冷」という新しい概念を提案する (Fig. 1b)。具体的には、光生成した二量体固体が熱解離反応の進行に伴い経時的に単量体液体に戻る際、二量体の融解熱が解離熱の寄与を上回れば、全体として吸熱的挙動を示すことが期待される。

実際に Ant-AcO-C_6 二量体において、融解熱が解離熱を上回ること、二量体融点以下において熱解離反応の進行に伴って融解が進行することが確認されており、光蓄冷現象の実現が示唆される。

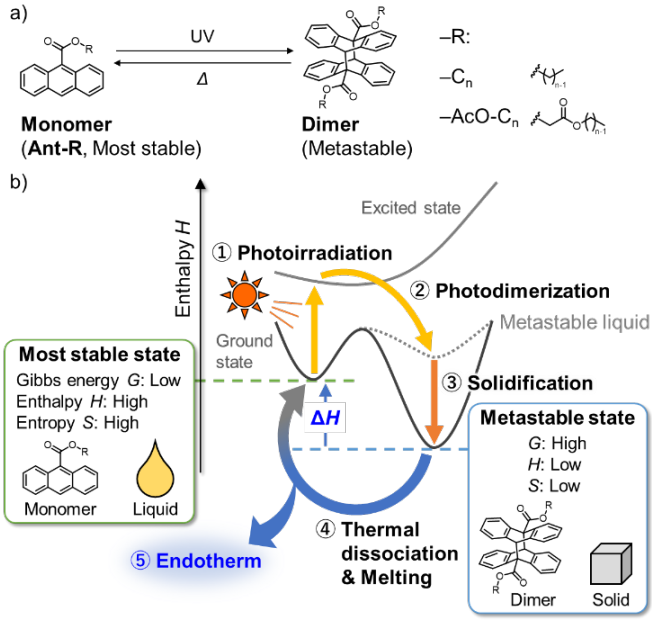


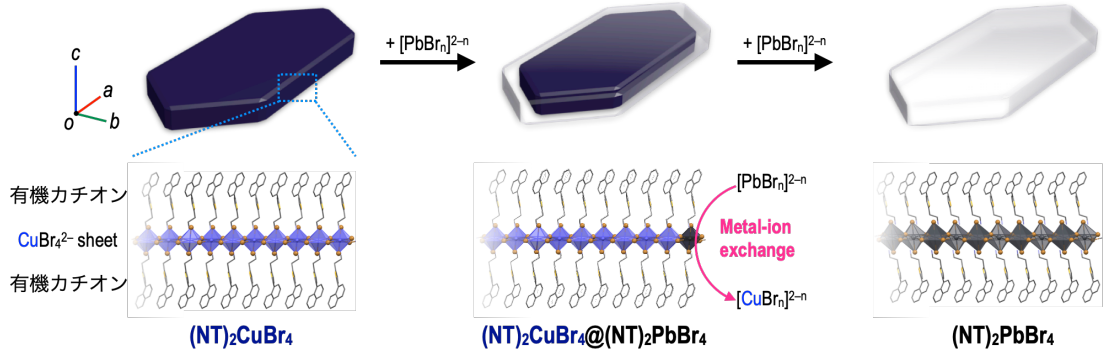
Fig. 1 (a) Molecular structure of anthracene derivatives (Ant-R) and their photodimerization. (b) Schematic image of photochemical cold-energy storage based on photodimerization of anthracene.

二次元有機無機ハイブリッドペロブスカイト結晶におけるトポタクティック金属イオン交換

（科学大化生研[1]・科学大物質理工[2]・科学大 ASMat[3]）○福井 智也[1,2,3]・三田 尚哉[1,2]・福島 孝典[1,2,3]
Topotactic Metal Ion Exchange in Two-Dimensional Organic-Inorganic Hybrid Perovskite Crystals ([1]*CLS, Science Tokyo*, [2] *Sch. Mater. Chem. Tech., Science Tokyo,* [3]*ASMat, Science Tokyo*) ○Tomoya Fukui,[1,2,3] Naoya Mita,[1,2] Takanori Fukushima[1,2,3]

We have been developing block-type heterostructures composed of different molecular crystals, aiming to realize new functions arising from lattice strain generated at the heterojunction interface.[1)] In this study, we examined the construction of block structures using two-dimensional organic-inorganic hybrid perovskite crystals. Unexpectedly, we found that when a certain type of two-dimensional perovskite single crystal is immersed in a solution containing different metal ions, the metal ions inside the crystal undergo topotactic exchange while its crystal structure is preserved.
Keywords : Organic-inorganic hybrid perovskites; Organic cations; Crystal; Block structure; Seeded crystallization

我々は、異種分子結晶を接合したブロック構造体を創製し、ヘテロ界面で生じる格子歪みを利用した機能発現を目指す研究を展開している[1)]。最近、二次元ハイブリッドペロブスカイトの結晶を構成要素とするブロック構造体の作製を検討したところ、予期せぬことに、ある種のペロブスカイト単結晶を、異種金属イオンを含む溶液に浸すと、結晶構造を保持したまま内部の金属イオンが定量的に交換される興味深い現象を発見したので報告する。



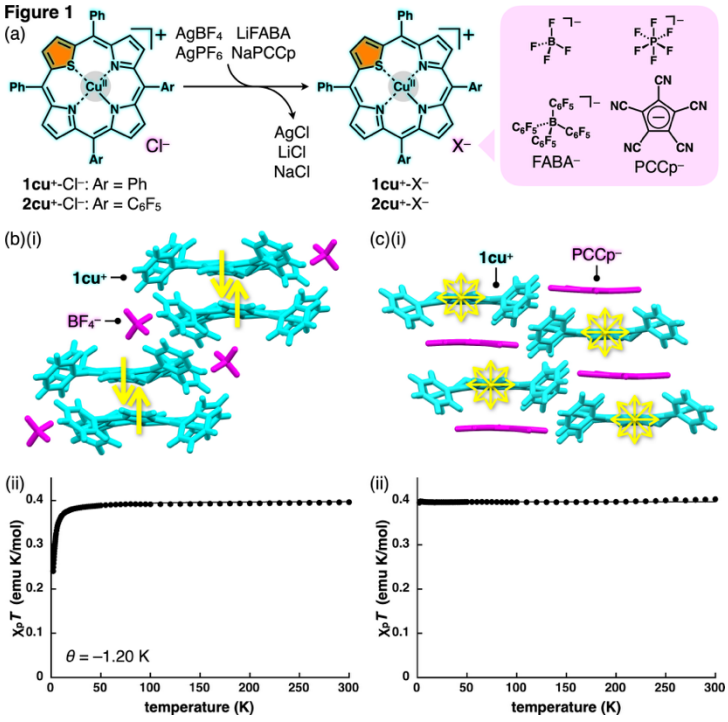
1) T. Fukui, M. Tsuchiya, N. Mita, T. Fukushima, *Chem. Sci.* **2025**, *16*, 22387.

ヘテロポルフィリンイオンペア集合体の配列様式による磁性制御

（立命館大生命科学[1]・新潟大研究統括機構[2]）○藤田 雅輝[1]・古川 貢[2]・前田 大光[1]
Arrangement-Dependent Magnetic Properties of Heteroporphyrin-Based Ion-Pairing Assemblies ([1]*College of Life Sciences, Ritsumeikan University*, [2]*Institute for Research Administration, Niigata University*)○Masaki Fujita,[1] Ko Furukawa,[2] Hiromitsu Maeda[1]

Thiaporphyrin M^{II} complexes act as π-electronic cations that form ion-pairing assemblies. Crystal-state assembly modes and electric conductivity and solution-state spectroscopic behavior were modulated by the metal center, substituents, and counteranions. In this study, ion-pairing assemblies of Cu^{II} complex paramagnetic cations were constructed to investigate the magnetic properties that depend on the ordered arrangements.
Keywords : ion-pairing assemblies; charged π-electronic systems; thiaporphyrin cations; Cu^{II} complexes

チアポルフィリン+2 価金属錯体はπ電子系カチオンとしてふるまい、イオンペア集合体[1)]を構成する。[2)] 今回、d^9 配置を有する Cu^{II} 錯体常磁性カチオン **1cu**$^+$, **2cu**$^+$ と多彩な対アニオンからなるイオンペアを HSAB 則に基づいたイオンペアメタセシスにより合成し（Figure 1a）、磁性イオンペア集合体の規則配列様式に起因した磁気特性発現と機能化を検討した。**1cu**$^+$-BF_4^- は **1cu**$^+$の分散力により積層 2 量体からなり、電荷種分離配置型の寄与を示す集合体を形成した（Figure 1b(i)）。結晶性粉末の SQUID 磁化率測定において、2 量体内でのスピン–スピン相互作用に起因した低温での反強磁性が観察された（Figure 1b(ii)）。一方で **1cu**$^+$-$PCCp^-$は電荷積層型集合体を構築し、低温でも常磁性を保持したことから、イオンペアリングによる集合体の磁性制御が可能であることを見出した（Figure 1c）。[3)]

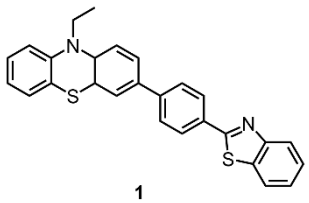


1) Haketa, Y.; Yamasumi, K.; Maeda, H. *Chem. Soc. Rev.* **2023**, *52*, 7170.
2) (a) Fujita, M.; Haketa, Y.; Tanaka, H.; Yasuda, N.; Maeda, H. *Chem. Commun.* **2022**, *58*, 9870. (b) Fujita, M.; Haketa, Y.; Seki, S.; Maeda, H. *Chem. Commun.* **2024**, *60*, 4190.
3) Fujita, M.; Furukawa, K.; Okazawa, K.; Shigeta, Y.; Horita, H.; Maeda, H. to be submitted.

キラル対称性の破れを伴う単結晶ー単結晶構造転移と円偏光発光特性

（阪大院基礎工[1]・阪公大院理[2]）○桶谷 龍成[1]・岡田 武蔵[1]・池田 紗希[1]・柚山 健一[2]・中嶋 琢也[2]・久木 一朗[1]

Single-Crystal-to-Single-Crystal Structural Transition accompanied with Chiral Symmetry Breaking and Circular Polarized Light Emission ([1]*Graduate School of Engineering Science, The University of Osaka*, [2]*Graduate School of Science, Osaka Metropolitan University*) ○ Ryusei Oketani,[1] Musashi Okada,[1] Saki Ikeda,[1] Ken-ichi Yuyama,[2] Takuya Nakashima,[2] Ichiro Hisaki[1]



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Chiral symmetry breaking (CSB) is recognized as a key phenomenon for understanding the origin of homochirality in living systems. Preferential enrichment and Viedma ripening are known CSB phenomena in chemistry. However, these phenomena occur during crystallization from solutions, making it difficult to elucidate their mechanisms at the molecular level. In this context, we have discovered a molecular crystal that undergoes a single-crystal-to-single-crystal transition from a racemic compound to a conglomerate.[1] A phenothiazine derivative **1**, was synthesized according to reported procedures, and racemic compound and conglomerate crystals were selectively prepared by crystallization from ethyl acetate or chloroform/heptane mixture. Under polarized optical microscopy, heating a single crystal of the racemic compound to 160 °C induced a propagative change in interference colors across the entire crystal. SCXRD of the transformed sample revealed that the crystal retained its crystallinity while undergoing transition to a conglomerate. In this presentation, we will discuss the structural features of this transition and the control of chirality after the transformation in detail.

Keywords : Chirality; Chiral Symmetry Breaking; Structural Transition; Organic Crystal

キラル対称性の破れは生命のホモキラリティの起源の理解の鍵として認識されている。化学分野では、結晶化に伴うキラル対称性の破れ現象として、優先富化やビエドマ熟成が知られている。これらはいずれも溶液からの結晶化における現象であり、その全容を分子レベルで理解することは困難である。これに対し、我々は分子性結晶のラセミ化合物がコングロメレートに構造転移する化合物を見出した[1]。

フェノチアジン誘導体 **1** を既報に従い合成し、酢酸エチルまたはクロロホルムとヘプタンの混合溶媒から結晶化することにより、ラセミ化合物とコングロメレートを選択的に調製した。偏光顕微鏡観察下において、ラセミ化合物の単結晶を 160 °C に加熱すると、結晶全体の干渉色が伝搬するように変化した。転移後の試料の単結晶 X 線構造解析を行ったところ、単結晶性を維持したまま空間群が $P2_1$ のコングロメレートに転移したことが明らかになった。本発表では構造解析や転移後のキラリティの制御、結晶の円偏光発光特性について詳細に議論する。

1) R. Oketani *et al. Chem. Sci.* **2025**, *16*, 17621-17629.