Symposium | Asian International Symposium：Asian International Symposium - Organic Crystals -

Tue. Mar 19, 2024 1:00 PM - 3:40 PM JST | Tue. Mar 19, 2024 4:00 AM - 6:40 AM UTC A1424(1424, Bldg. 14 [2F])

[A1424-2pm] Asian International Symposium - Organic Crystals -

Chair, Symposium organizer: Ichiro Hisaki, Kenta Kokado, Seiya Kobatake

English Keynote Lecture
1:00 PM - 1:30 PM JST | 4:00 AM - 4:30 AM UTC
[A1424-2pm-01]

Flux Synthesis and Separation Application of Porous Organic Materials

〇Zhenjie Zhang[1] (1. Nankai Unversity)

English Invited Lecture
1:30 PM - 1:50 PM JST | 4:30 AM - 4:50 AM UTC
[A1424-2pm-02]

Photomechanical effect and photochemical reaction kinetics in organic molecular crystals

〇Daichi Kitagawa[1] (1. Osaka Metropolitan University)

English Invited Lecture
1:50 PM - 2:10 PM JST | 4:50 AM - 5:10 AM UTC
[A1424-2pm-03]

Bowl and Butterfly-like Shape Effects on the Formations and the Properties of Molecular Crystals

〇Yumi Yakiyama[1,2] (1. Osaka Univ., 2. ICS-OTRI, Osaka Univ.)

2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC

Break

English Keynote Lecture
2:20 PM - 2:50 PM JST | 5:20 AM - 5:50 AM UTC
[A1424-2pm-04]

Ultra-fast supercritically-solvothermal polymerization for large-sized single-crystalline covalent organic frameworks

〇Dacheng Wei[1] (1. Fudan University)

English Invited Lecture
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC
[A1424-2pm-05]

Flexible Molecular Crystal Photonics

〇Shotaro Hayashi[1] (1. Kochi University of Technology)

English Invited Lecture
3:10 PM - 3:30 PM JST | 6:10 AM - 6:30 AM UTC
[A1424-2pm-06]

Toward Rational Control of Mechanochromic Luminescence by Organic Crystals

〇Suguru Ito[1,2] (1. YOKOHAMA National Univ., 2. PRESTO, JST)

3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC

Closing Remarks

Flux Synthesis and Separation Application of Porous Organic Materials

Zhenjie Zhang[1] (1. Nankai Unversity)

Keywords：covalent organic framework , Flux synthesis, Separation

The synthesis strategy of porous organic materials especially covalent organic frameworks (COFs) mainly employs the solvothermal method which usually results in unscalable powders and environmental pollution that seriously limits their practical applications. We created a new synthesis method based on a green and melt-fluxing synthesis strategy without needing any organic solvent. The generality of melt-fluxing synthesis approaches has been applied in the preparation of various types of COFs, including olefin-linked, imide-linked, Schiff-based COFs on both gram and kilogram scales, and self-shaped neutral COF foams.

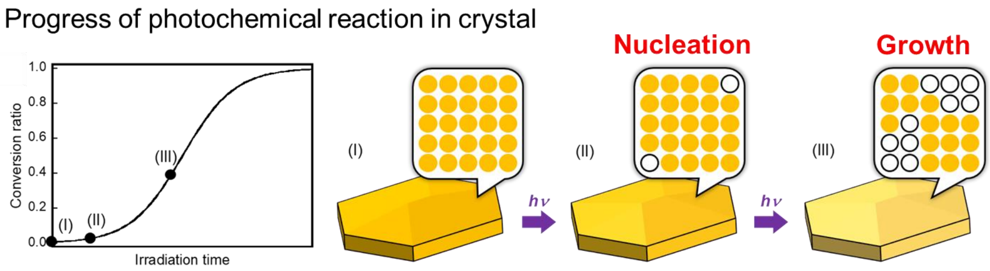
Photomechanical effect and photochemical reaction kinetics in organic molecular crystals

([1]*Graduate School of Engineering, Osaka Metropolitan University*) ○Daichi Kitagawa[1]

Keywords: Organic molecular crystals; Photomechanical response; Photochemical reaction kinetics

Photomechanical materials that directly convert light energy to mechanical energy have been attracting much attention for application to photoactuators.[1] Liquid crystalline polymers and molecular crystals incorporating photoresponsive molecules are known as typical photomechanical materials. Especially, molecular crystals have shown superior actuator performance such as fast response speeds, high energy densities, and photon-to-work conversion efficiencies.[2-4] Therefore, photomechanical molecular crystals are promising candidates for future actuators used in the real world.

Photomechanical molecular crystals can exhibit a various light induced motions (bending, twisting, coiling, peeling, and hopping) that are driven by a wide range of photochemical reactions, including cis-trans isomerizations, ring opening closing isomerizations, linkage isomerizations, and [2+2] and [4+4] photodimerizations.[5] In most cases, their photomechanical responses have been interpreted by a static method using the unit cell dimension changes revealed by X-ray crystallographic analyses for crystals before and after photochemical reactions. Therefore, it has been difficult to elucidate the dynamic nature of photomechanical responses. In this paper, we introduce our recent research on photomechanical molecular crystals, focusing on the kinetics of photochemical reactions within the crystal.[6-8]


Progress of photochemical reaction in crystal

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Bowl and Butterfly-like Shape Effects on the Formations and the Properties of Molecular Crystals

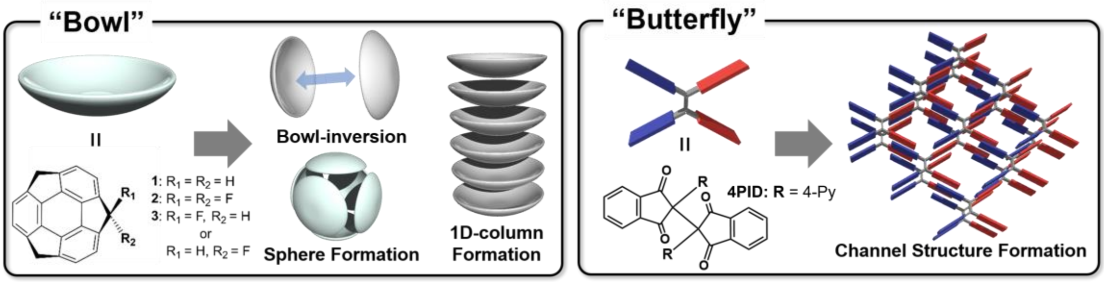
([1]*Graduate School of Engineering, Osaka University*, [2]*ICS-OTRI, Osaka University*) ○ Yumi Yakiyama[1,2]

Keywords: Sumanene; Indanedione; Crystal engineering; Dielectric property; 1D-channel structure

It is quite obvious that the molecular structure largely affects its aggregated structure as well as the resulting physical properties. Especially, some specific structural motifs generate characteristic packing patterns, which cannot be reached by the simple chemical functionalization. In this context, we focused on two types of non-planar molecular shapes, namely, bowl and butterfly-like structures, which possess clear structural features, showing 1D-column formation and 1D-channel construction, respectively, as the main building units of the functional molecular crystals (Figure). Here we show our recent works using bowl shaped sumanene derivative[1] and butterfly-shaped indanedione dimers[2] as well as their structural and physical properties.

"Bowl" shape molecule: Sumanene

Sumanene (**1**) is one of the representative buckybowls and is known to show unique properties such as bowl inversion behaviour derived from its unique bowl shape.[1] Especially **1** affords unidirectionally arraigned π-stacking columns in the solid state.[2] We focused on the possible in-plane motion of **1** in this 1D-stacking column structure and to confirm that we investigated the series of fluorinatedsumanenes via their dielectric properties. The representative one, difluorosumanene (**2**) possesses two fluorine atoms on the same benzylic carbon of pristine sumanene to have a large dipole moment along the in-plane direction. Thermal analyses, variable temperature X-ray diffraction and IR measurements indicated the presence of in-plane motion of **2** although no clear phase transition caused by the bowl flipping was involved.[3a] This thermal property of **2** realized an anisotropic dielectric response with a Debye-type dielectric relaxation in the single crystalline state. This dielectric property was further arranged by making solid solutions with pristine **1** and **2**.[3b]



Meanwhile, mono-substituted molecule, monofluorosumanene **3**, exhibited bowl inversion in the solution state, to be a diastereomeric mixture of the outer (*exo*)- and the inner (*endo*)-side F-substituted derivatives. The population ratio of the two conformers of monofluorinated derivatives in single crystals drastically changed depending on the crystallization solvents and the resulting *exo*/*endo* ratio emerged the significant change in the dielectric properties of the crystalline powder.[4]

“Butterfly” shape molecule: Indanedione dimers

4-pyridylindanedione dimer (**4PID**) is a distorted X-shape, in other words, “butterfly”-like molecule and affords high quality single crystals possessing 1D-channel structure with ca. 5 Å × 7 Å window size under the presence of less-polar solvent such as hexane as well as a tightly-packed structure by the recrystallization with polar solvent selectively. These two structures are interconvertible via guest molecule removal/insertion with keeping crystallinity.[5] The former 1D-channel structure was utilized for the incorporation of various kinds of molecules, such as chain, branched alkanes, simple aromatic compounds, etc. One useful example is the recognition of *p*-xylene from the xylene mixture which can be arranged by the number of N atoms in the hetero ring. This 1D-channel also worked as the space for emergence of unique physical properties such as second harmonic generation (SHG).

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Ultra-fast supercritically-solvothermal polymerization for large-sized single-crystalline covalent organic frameworks

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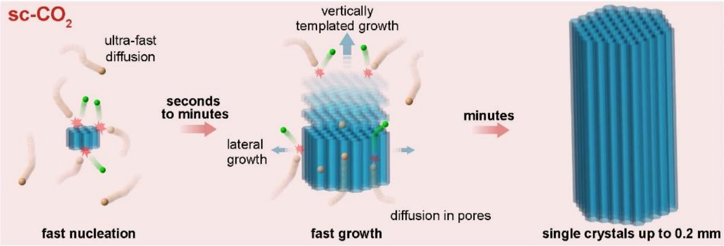
Keywords: covalent organic framework; single crystal; supercritical fluid; solvothermal polymerization

Crystalline polymer materials, e.g., hyper-crosslinked polystyrene, conjugate microporous polymers and covalent organic frameworks are used for catalyst carrier, organic electronic device and molecular sieve. Their properties and applications are highly dependent on their crystallinity. An efficient polymerization strategy for the rapid preparation of highly or single-crystalline materials is beneficial to not only structure-property studies but also practical applications. However, polymerization usually leads to the formation of amorphous or poorly crystalline products with small grain sizes. It has been a challenging task to efficiently and precisely assemble organic molecules into a single crystal through polymerization.

To address this issue, we developed a supercritically-solvothermal method that uses supercritical carbon dioxide (sc-CO2) as the reaction medium for polymerization. sc-CO2 accelerates crystal growth due to its high diffusivity and low viscosity compared with traditional organic solvents. Six covalent organic frameworks with different topologies, linkages and crystal structures are synthesized by this method. Sub-mm-sized single crystals are synthesized within 1~5 min, including 6 covalent organic frameworks with different topologies, linkages or crystal structures. The crystal growth rate reaches 40 μm min−1, at least 6,000 times faster than state-of-the-art results of other ultra-fast polymerization technologies. The as-synthesized products feature polarized photoluminescence and second harmonic generation, indicating their high-quality single-crystal nature. This method holds advantages such as rapid growth rate, high productivity, easy accessibility, industrial compatibility and environmental friendliness.



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Flexible Molecular Crystal Photonics

([1]*School of Engineering Science, Kochi University of Technology*) ○Shotaro Hayashi [1]

Keywords: Flexible Molecular Crystals; Elasticity; π-Conjugated Systems; Resonators; Waveguides

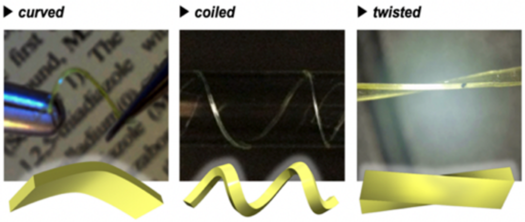
Organic molecular crystals are attractive because of the wide variety of unique properties based on the diversity of their molecular structures.[1] The design of π-conjugated molecules is one of the attractive topics for light-emitting and semiconducting performances. Controlling band-gap through expansion and combination of molecular systems is by no means a difficult task in recent years. On the other hand, improving functionality and performance based on design to improve quantum efficiency, molecular arrangement in crystals, and crystal shape control is a difficult challenge. In the design of molecular crystals, a method of treating a combination of interacting functional groups as a synthon is called a supramolecular synthon.[2] We have focused on this synthon and have been developing crystal-specific physical properties and creating functions. This idea is extremely useful in photonics applications that require the aforementioned quantum efficiency improvement design, molecular arrangement in crystals, and crystal shape control.

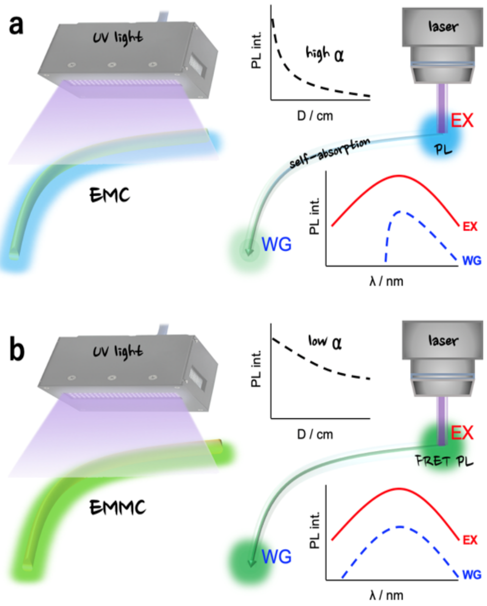
Several phenomena such as chromics, optical waveguides, optical resonators, and lasers can be envisioned as photonics applications of organic molecular crystals. It is preferable that these materials have excellent luminescent properties. Second, the molecular arrangement and orientation in the crystal becomes important. Thirdly, the crystal shape has a large effect on the optical oscillation efficiency. Since laser oscillation can be caused by a resonator with a well-arranged crystal shape, the quantum efficiency, molecular arrangement, and shape that enable stimulated emission are important factors.[3]

Optical waveguide properties of various luminescent microcrystals have been reported. Since isotropic diffusion of light is observed from a two-dimensional crystal compared to a one-dimensional crystal, we can understand its importance in crystal shape. The anisotropic optical waveguide crystal by Yong Shen Zhao et al.[4] is noteworthy in that it controls the diffusion of a two-dimensional crystal anisotropically. Since light traveling perpendicular to the transition dipole moment of molecules is strongly reabsorbed, the two-dimensional light diffusion direction is limited to one dimension by the molecular arrangement. We have achieved a two-dimensional crystal with extremely high anisotropic diffusivity by appropriately arranging functional groups on luminescent molecules and designing an alternating supramolecular polymer structure based on angle-specific attraction. [5] These results also demonstrate that crystal structure design has an important position in photonics applications.

Organic molecular crystals are brittle and have poor mechanical deformability. Therefore, it is difficult to realize flexible devices that directly utilize molecular crystals. On the other hand, we realized elastic flexibility of molecular crystals for the first time by focusing on the repulsion between molecules in a π-conjugated system.[6] This crystal design approach combines mechanical deformability with low bandgap (and its control) performance, making it directly applicable to flexible photonics.[7] We have realized the following new potential in this crystal. Elastic molecular crystals are based on changes in the π-π stacking structure upon deformation, and upon crystal deformation, changes in the molecular packing structure induce luminescence changes.[8] In addition, since optical waveguide can be carried out even when the crystal is deformed, it has been possible to develop it into a flexible waveguide. On the other hand, we have developed an efficient optical waveguide by doping the crystal with acceptor-like light-emitting molecules[9].

Furthermore, we showed that it is possible to function as an optical resonator by optimizing the crystal shape, and that the resonator operates reversibly based on deformation.[10]





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Toward Rational Control of Mechanochromic Luminescence by Organic Crystals

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Keywords: Organic Crystals; Solid-state Emission; Mechanochromism; Intermolecular Interaction; Energy Transfer

In recent years, there has been increasing interest in mechanochromic luminescence (MCL) of organic crystals, where the emission color of fluorescence or phosphorescence changes in response to mechanical stimuli.[1,2] The MCL exhibited by organic crystals often originates from alterations in molecular arrangement and conformation induced by amorphization or phase transition to another polymorphic crystal upon mechanical stimulation. However, the design of organic crystals that manifest the desired MCL properties remains a challenging task. This presentation will discuss the current research progress toward the rational control of MCL.

1. Control of MCL properties through the two-component segregated crystals

The mechanoresponsive shift of the maximum emission wavelength could be extended by preparing two-component segregated crystals of pyrene derivatives with other fluorophores. Significant shifts in emission wavelength were achieved by mechanical stimulation-induced amorphization of the segregated crystals, resulting in energy transfer from the excimer of pyrene to the other fluorophore.[3,4] This method could be applied to the bispyrene derivative **1**, which exhibited MCL between the monomer and excimer emission of the pyrene moieties (Figure 1).[5] When **1** was mixed with 3,4,9,10-perylenetetracarboxylic diimide (**PTCDI**), a wide-range MCL exhibiting the MCL shift of 340 nm was realized. In addition, when mixed with 9,10-anthraquinone (**AQ**), a two-step MCL from blue to blue-green and orange was achieved in response to the intensity of mechanical stimulation.

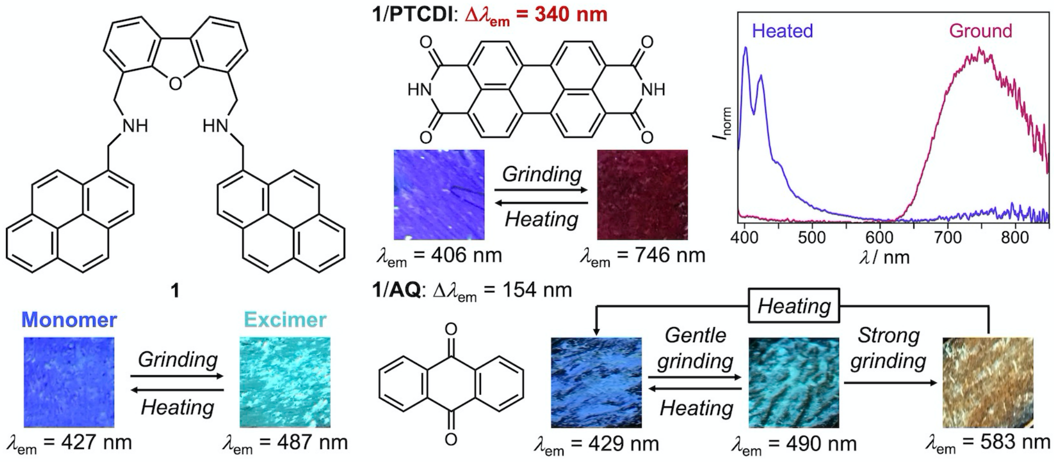

Figure 1. Wide-range MCL of **1**/**PTCDI** and two-step MCL of **1**/**AQ**.

2. Extension of the mechanoresponsive luminescence shift via formation of doped crystal

Crystalline benzothiadiazole derivatives substituted with electron-rich heteroaromatic rings exhibit versatile MCL properties.[6–9] While substituted thienylbenzothiadiazole derivatives showed significant hypsochromic shifts of luminescence upon grinding, the mechanoresponsive luminescence shift of the unsubstituted derivative **2** was only 10 nm.[10] However, by doping with a trace amount of dithienylbenzothiadiazole **3**, the mechanoresponsive shift could be extended to 69 nm (Figure 2).[11] Specifically, the emission color of crystalline **2** was changed from green (λ_{em} = 502 nm) to yellow (λ_{em} = 559 nm) by doping with 250 ppm of **3**. Mechanistic studies revealed that the yellow emission from the doped crystal **2·3** was due to Förster resonance energy transfer (FRET) from **2** to **3**. When a mechanical stimulus was applied to crystalline **2·3**, the emission color shifted in the hypsochromic direction to light blue (λ_{em} = 490 nm). The fluorescence spectrum of ground **2·3** was in good agreement with that of ground **2**, indicating the significant decrease in FRET efficiency in ground **2·3**. This doping strategy represents a new design principle to rationally control the mechanoresponsive properties of luminescent organic crystals.

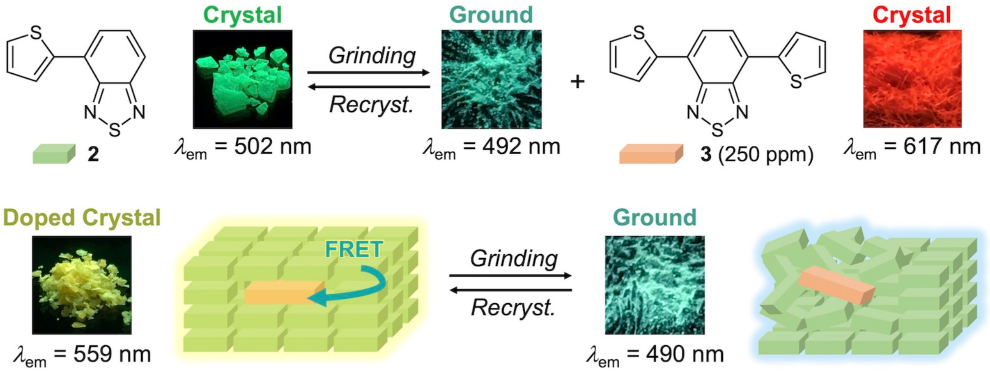

Figure 2. Extension of mechanoresponsive luminescence shift of **2** by doping with **3**.

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