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論文題目

光機能材料を志向した含アクリロニトリル分子結晶工学

英文題目

Acrylonitrile-Containing Molecular Crystal Engineering for Optical Materials

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π-Conjugated molecules exhibit notable optical and electronic properties. Their solid-state functionality, however, is strongly influenced by molecular interactions that arise in aggregated states. When multiple molecules interact and crystallize, densely packed and highly ordered molecular assemblies are formed, providing material platforms suitable for applications such as optical waveguides, laser gain media, and stimulus-responsive sensors. Molecular stacking and orientation further modulate HOMO–LUMO levels, affecting charge transport, exciton diffusion, and overall device efficiency. Aggregation also governs fluorescence behavior, giving rise to phenomena such as aggregation-induced emission, aggregation-induced quenching, and chromic responses triggered by structural reorganization. These chromic properties allow external stimuli to induce distinct optical changes, making such materials promising candidates for highly sensitive sensing applications. Moreover, the precise control of intermolecular arrangements enables the systematic tuning of energy transport efficiency, radiative decay pathways, and energy migration dynamics, offering a bottom-up strategy for designing functional molecular solids. Recent advances in crystal engineering further demonstrate that subtle modifications to molecular shape, substituent patterns, and noncovalent interaction motifs can dramatically alter packing polymorphism and, consequently, the macroscopic optical response. As a result, π-conjugated molecular assemblies have emerged not only as model systems for studying structure–property relationships but also as versatile platforms for developing next-generation photonic and optoelectronic materials.

The structure of a material is closely tied to its function. Therefore, evaluating crystal structures is essential for understanding how specific optical properties emerge. For example, controlling molecular orientation, ensuring the stability of the crystal framework, and elucidating polymorphic processes are all important for the development of optical materials. The Cambridge Structural Database, which contains more than 1.3 million crystal structures, has enabled extensive crystallographic design strategies based on hydrogen bonding, aromatic stacking, halogen bonding, and other molecular interactions. Nevertheless, the intermolecular forces that govern molecular self-assembly are highly complex. As a result, the complete and universal prediction of molecular crystal structures remains a formidable challenge. Approaches that analyze interactions at the functional-group level and rationally combine them to guide packing formation have therefore become increasingly important. Furthermore, the emergence of high-resolution analytical tools, such as micro-focused X-ray diffraction, variable-temperature crystallography, and advanced computational modeling, has made it possible to track subtle structural deformations that directly influence optical responses. These techniques reveal how local packing motifs evolve under external stimuli, offering insights into metastable states, transition pathways, and kinetic control of polymorphs. By integrating such experimental and theoretical approaches, researchers can more precisely map the relationship between molecular interactions and macroscopic functions. This integrated perspective is crucial for the rational design of next-generation luminescent, waveguiding, and stimuli-responsive materials, where targeted control of molecular assembly governs performance.

Acrylonitrile-containing molecules are well known for their excellent solid-state luminescence. For example, cyano-*β*-substituted distyrylbenzene, CDSB, exhibits a much higher photoluminescence quantum yield in the solid state than in solution. These molecular frameworks are also appealing because their emission color can be easily tuned through simple substituent modifications. However, acrylonitrile-containing molecules frequently show polymorphism due to their high conformational flexibility. When *π*-conjugated systems are linked through an acrylonitrile unit, the adjacent single bonds gain increased rotational freedom. This often leads to instability in luminescence properties and variations in excited-state behavior. Therefore, precise control of crystal structure is essential for achieving desirable optical functions. Using molecular interactions as supramolecular synthons provides a systematic approach to rationalizing structure–property relationships in luminescent molecular crystals. In this study, multiple types of molecular interactions were employed as design principles to create distinct opto-functional crystals. The author synthesized such crystals using luminescent molecules, including cross-shaped cyano-β-substituted distyrylbenzene derivatives. Chapters II–IV demonstrate that acrylonitrile-containing molecular crystal engineering enables the construction of high-performance optical waveguides, laser gain media, and stimulus-responsive sensors.

Chapter II demonstrates the noncovalent synthesis of highly one-dimensional, ordered cyano-β-substituted distyrylbenzene-based crystals designed for anisotropic optical waveguiding. Controlling molecular orientation is crucial, as it directly enables the realization of directionally dependent light transport. Optical waveguides confine and guide light through refractive index contrasts, forming the basis of photonic signal propagation in fibers and on-chip circuits. Molecular crystals, with their dense packing and pronounced refractive index anisotropy, can efficiently channel self-emissive light, making them attractive candidates for active optical waveguide materials. Their performance depends strongly on the alignment of the transition dipole moment, and thus one-dimensionally oriented crystals exhibit superior anisotropic waveguiding behavior due to their highly ordered molecular arrangement.

Here, the author presents crystal engineering based on highly directional halogen bonding. The author synthesized two-dimensional platelet-shaped crystals by co-crystallizing a cyano-*β*-substituted distyrylbenzene-based donor–acceptor *π*-conjugated molecule bearing pyridyl groups with a diiodoarene. Single-crystal X-ray diffraction revealed that the pyridyl nitrogens and iodine substituents form highly directional I···N halogen bonds, creating a one-dimensional alternating supramolecular chain. Polarization-dependent photoluminescence experiments demonstrated that the transition dipole moment is oriented horizontally within the 2D crystal plane. This orientation originates from the one-dimensional supramolecular alignment imposed by the halogen-bonded framework. Spatially resolved photoluminescence measurements revealed clear anisotropy in waveguiding. Waveguiding along the long-axis showed only minor optical loss ($\alpha_L = 5.2\times10^1$ dB cm^{-1}). In contrast, propagation along the short-axis experienced severe attenuation ($\alpha_S = 2.1\times103$ dB cm^{-1}). The resulting anisotropy ratio reached 40, greatly exceeding previously reported values for organic molecular crystals. These findings indicate that halogen-bond-directed molecular alignment is highly effective.

Chapter III presents the design and synthesis of pyridyl-appended cyano-*β*-substituted distyrylbenzene derivatives aimed at achieving thermally robust laser gain media. A stable crystal framework is essential for constructing efficient laser materials, as single crystals minimize optical scattering, reduce propagation losses, and lower oscillation thresholds owing to their structural uniformity. However, in densely packed crystalline environments, aggregation-caused quenching can severely compromise emission efficiency. To address this challenge, crystal structures that suppress deleterious π–π interactions are highly desirable. Moreover, the extraction of amplified spontaneous emission under intense photoexcitation requires irradiation at high power densities, which inevitably generates localized heating within the crystal. Thus, maintaining structural integrity at elevated temperatures becomes crucial for ensuring consistent optical performance. The incorporation of pyridyl groups reinforces molecular interactions and enhances lattice rigidity, enabling the crystal to withstand thermal perturbations without degrading its emissive properties. This chapter demonstrates how combining molecular design with crystallographic control provides a viable strategy for creating thermally durable, high-performance laser gain media.

In this Chapter, the author focused on molecular interactions associated with the electrostatic potential of pyridine. Pyridyl–pyridyl interactions impart significant thermal robustness to the crystal lattice. Therefore, cross-shaped cyano-*β*-substituted distyrylbenzene derivatives bearing either pyridyl or phenyl groups were crystallized, and their optical properties together with their thermal stability were thoroughly evaluated. In the pyridyl-containing crystal, three types of double hydrogen bonds, including characteristic pyridyl–pyridyl contacts, generated a rigid and translationally symmetric framework. Differential scanning calorimetry revealed that this pyridyl-based lattice exhibited markedly higher thermal stability owing to the strengthened molecular interactions. Under pulsed-laser excitation, both crystals displayed amplified spontaneous emission; however, the pyridyl crystal required a higher threshold, consistent with its shorter excited-state lifetime. Importantly, the pyridyl crystal continued to exhibit stable amplified spontaneous emission even at high fluence, a performance attributed to its mechanically and thermally robust framework. These findings highlight that lattice rigidity and thermal stability are indispensable design parameters for achieving reliable amplified spontaneous emission in organic single-crystal laser media.

Chapter IV presents the design of multifunctional cyano-β-substituted distyrylbenzene derivatives that enable dramatic structure–property changes in the solid state. This chapter demonstrates molecular crystals capable of undergoing polymorphic phase transitions triggered by subtle chemical modifications. In luminescent crystals, such transitions often result in pronounced emission color changes, as even minor variations in molecular conformation or packing can significantly alter photophysical behavior. Consequently, molecular crystals that undergo stimulus-responsive phase transitions are attracting increasing attention as next-generation sensing materials. Multifunctionalized molecules, which can participate in diverse and competing molecular interactions, are particularly suitable for generating rich polymorphism and achieving tunable, stimulus-dependent optical responses. By intentionally incorporating groups that modulate dipolar, halogen-bonding, and other weak interactions, the resulting crystals exhibit multiple accessible phases with distinct optical signatures. This chapter highlights how the deliberate integration of multiple interaction motifs provides a powerful strategy for engineering responsive luminescent materials with controllable and reversible switching properties.

Designing molecules capable of forming multiple crystalline phases is an effective strategy for developing responsive materials. Herein, screening molecular crystals bearing multiple methoxy and bromo substituents leads to polymorphs. These crystals differ in both morphology and emission color, indicating that they adopt distinct molecular packing arrangements. X-ray analysis showed that one form is stabilized primarily by methoxy–methoxy dipole interactions, leading to a one-dimensional columnar architecture. In contrast, the other form incorporates additional Br···O halogen bonding, resulting in a more robust three-dimensional packing network. Computational studies suggest that the former structure is kinetically favored, whereas the latter represents the thermodynamically more stable phase. Heating the metastable crystal induced a single-crystal-to-single-crystal phase transition into a more stable form, accompanied by a yellow-to-green emission shift. Mechanical grinding also converted the metastable crystal, but via an amorphous intermediate, producing phases that showed orange-to-green emission switching. These thermally and mechanically driven transformations arise from changes in molecular torsion and from shifts in the balance between dipole–dipole interactions and halogen bonding. Furthermore, the crystalline powders exhibited reversible mechanochromic and thermochromic behavior when deposited on paper, demonstrating potential utility as a security material.

This thesis studies a series of luminescent molecular crystals based on cross-shaped cyano-β-substituted distyrylbenzene derivatives, whose structures and properties were elucidated using X-ray diffraction, spectroscopy, and thermal analysis. The details of these findings and underlying design principles are presented in the following chapters. Each optical functionality arises directly from the corresponding crystal structure. In other words, the results demonstrate that controlling molecular orientation through supramolecular synthons, ensuring the stability of the crystal framework, and elucidating polymorphic processes are all crucial for achieving targeted optical properties. These insights provide a new design strategy for the development of advanced opto-functional materials. Furthermore, by integrating crystallographic analysis with photophysical evaluation, this work establishes a clear structure–function correlation across multiple length scales, from molecular conformation to macroscopic optical behavior. The comparative studies of anisotropic waveguiding, thermally durable gain media, and stimulus-responsive polymorphs highlight how subtle variations in packing motifs can dictate excitonic coupling, emission efficiency, and response to external stimuli. Collectively, the results underscore the importance of precise supramolecular control when designing next-generation organic photonic materials. This thesis therefore offers not only specific molecular design guidelines but also a generalizable framework for engineering functional crystals with predictable and tunable optical properties.