

Flexible Molecular Crystal Photonics

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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.

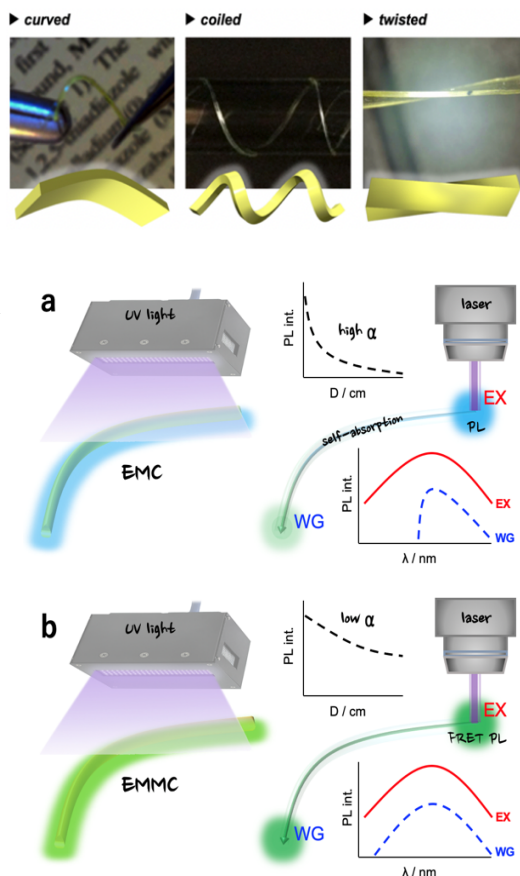
Several phenomena such as chromics, optical waveguides, optical resonators, and lasers can be envisioned as photonics applications of organic molecular crystals. It is preferable that these materials have excellent luminescent properties. Second, the molecular arrangement and orientation in the crystal 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 molecules⁹.

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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