2-6-6. Supramolecular Luminescent Materials

Overview

Supramolecular luminescent materials are functional systems whose emission originates from assemblies formed via noncovalent interactions. With structural tunability and environmental responsiveness, they have attracted significant attention as smart materials since the early 2000s. π-Conjugated molecules and metal complexes can self-organize into one-dimensional fibrous or two-dimensional sheet-like architectures—often termed supramolecular polymers—which hierarchically organize into macroscopic soft materials such as gels and films. These assemblies harness collective photophysical processes, such as exciton diffusion and energy transfer, for organic optoelectronic devices and biomedical imaging. Their luminescence properties are governed not only by the intrinsic nature of the constituent molecules but also by the mode of intermolecular interactions and the nano-to-mesoscale assembly structures. Consequently, phenomena such as stimuli-responsive emission color/intensity changes triggered by temperature, solvent, light, pH, or mechanical inputs, as well as multicolor emission from single-component systems, become possible—making them an exceptionally intriguing subject from the standpoint of fundamental science.

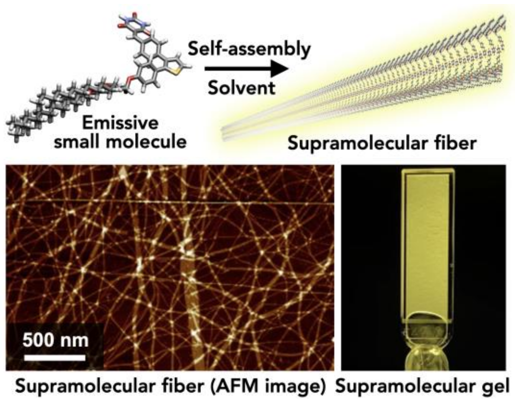

Figure 1. Supramolecular fiber and gel.

Current Status and Frontiers

Research into luminescence properties of supramolecular assemblies traces its origins to the 1930s discovery of emission arising from J-aggregates of cyanine dyes. Since then, the luminescence of supramolecular assemblies has become an important focus in organic materials science. In recent years, the introduction of the aggregation-induced emission (AIE) concept has further accelerated the development of diverse supramolecular luminophores. In such systems, elucidating exciton diffusion dynamics within the assemblies is key to advancing applications in organic optoelectronic devices. Importantly, emission can serve as a direct probe to visualize exciton migration distances and diffusion mechanisms, providing unique insight into photofunctions.

In Japan, systematic studies on luminescent supramolecular assemblies have progressed since around 2000 (Aida). Recent advances include chiral assemblies exhibiting circularly polarized luminescence (CPL) (Kawai, Nakashima), and studies inspired by natural photosynthetic systems focusing on collective behavior of dyes, such as exciton transport and light-harvesting functions. Supramolecular polymers—poised as next-generation macromolecules—are also under active investigation, with design strategies employing functional molecules containing hydrogen-bonding sites to construct noncovalently linked supramolecular polymers (Yagai). This has enabled simultaneous achievement of processability into flexible gels and retention of luminescent function, exemplified by photon-upconversion-emitting gels based on triplet–triplet annihilation (TTA-UC) (Yanai, Kimizuka). Moreover, the impact of topologies in one-dimensional assemblies on emission properties has gained attention. For instance, open-ended assemblies with structural defects and closed-toroidal assemblies devoid of defects exhibit significant differences in emission quantum yield, wavelength, and exciton diffusion length (Yagai). Elucidating such structure–property correlations is highly valuable for device material design.

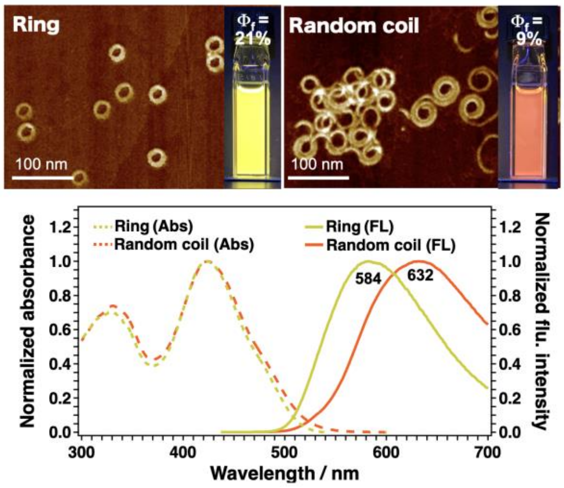

Figure 2. AFM images and fluorescence properties of supramolecular ring and random coil.

References

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Future Perspectives and Directions

Key challenges and targets for the coming decade include: the development of technologies capable of performing multiscale simulations from molecular design to supramolecular assembly and prediction of photophysical properties; the creation of smart luminescent materials whose emission color, CPL, and lifetime can be switched instantaneously by external stimuli; the introduction of supramolecular luminescent devices into the fields of biology, energy, and quantum optics; and the development of biodegradable and recyclable sustainable supramolecular luminescent materials.

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