2-6-7. Aggregation-Induced Emission

Overview

Conventional organic luminescent dyes exhibit aggregation-caused quenching (ACQ) in the solid state, while aggregation-induced emission (AIE)-active molecules (AIEgens) can exhibit enhanced luminescence only in the aggregated state. In 2001, Tang *et al.* reported AIE from the multiple-benzene-substituted siloles, and a series of AIEgens, including tetraphenylethene (TPE), have been discovered. Several mechanisms, depending on the differences in the degree of molecular motions between solution and the aggregated state and the formation of J-aggregation have been reported. More recently, a process known as unconventional luminescence was also focused. AIEgens and AIE materials have been applied as bioprobes for visualizing aggregates *in vivo* and luminescent components in organic light-emitting devices.

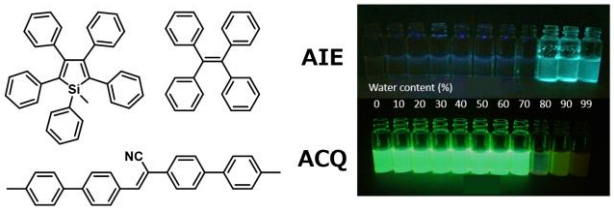

Figure 1. Conventional AIEgens and typical AIE behavior (*Mater. Chem. Front.*, **1**, 1573–1579 (2017)).

Current Status and Frontiers

Aggregation-induced emission enhancement (AIEE) is sometimes used to distinguish between cases where a certain degree of luminescence is present in solution. AIE generally refers to the phenomenon of luminescence enhancement in poor solvents such as water, and the luminescence mechanisms are diverse. For example, based on fluorescent boron diketonates, by replacing the oxygen bonded to the boron atom with nitrogen, the skeletal rigidity of the complex can be lowered. As a result, in solution, similar to TPE, deactivation due to molecular motion occurs, resulting in quenching. On the other hand, luminescence is recovered in aggregate through the suppression of molecular motions, and subsequently AIE behaviors can be obtained. This is the first example of converting a luminescent complex exhibiting ACQ into an AIEgen. (Chujo, Tanaka *et al.*). AIEgens can be also obtained by connecting aromatic hydrocarbons with boron cluster molecules known as carboranes (Chujo, Tanaka *et al.*). In the excited state, the carboranes can work as an electron acceptor, and intramolecular charge transfer (ICT) state can be realized. In solution, quenching occurs due to the opening of the carbon-carbon bond in the carboranes, meanwhile in the aggregated state, this motion is suppressed, resulting in AIE. By changing the type of aryl moieties, emission color can be tuned. Moreover, since some of aryl-modified carboranes, morphology changes in the solid state, such as the transition from amorphous to crystal, can induce luminescent color change. As a result, they exhibit mechanochromic, vapochromic and thermochromic luminescence, potentially enabling their application as paint-type sensors.

Konishi *et al.* demonstrated that it is possible to control the expression of AIE properties by

regulating the potential difference leading to a conical intersection in the excited state through the substituent effect based on anthracene derivatives.

Owing to advances in computational chemistry, the accuracy in the prediction of molecular structures in excited states has been improved. These developments contribute to the establishment of molecular designs. When intense emission can be observed only in the crystalline state, this behavior is called crystallization-induced emission (CIE). Compared to AIEgens, there are few examples to offer CIE properties, and molecular design was yet to be established. Tanaka *et al*. compared the most stable structures in the ground and excited states estimated by density functional theory (DFT) and time-dependent DFT, respectively. It was shown that the boron complexes with large degree of structural differences between ground and excited states can exhibit CIE. Furthermore, when these complexes were polymerized, luminescent films were obtained. Especially, some of these exhibited stimuli-responsive luminochromic properties originating from morphology changes of polymer chains. These materials are expected to be used as film-type sensors.

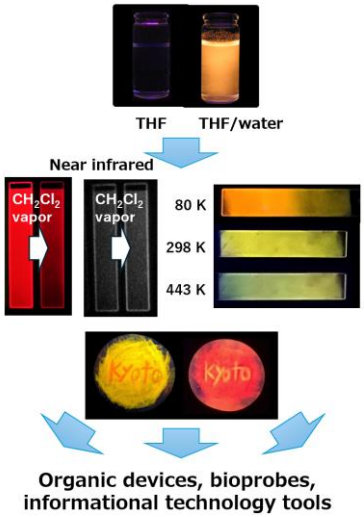

Figure 2. Outline of progress of AIE research.

The design guideline for AIEgens is to introduce multiple benzene rings to a conjugated core, and the luminescent color can be tuned from visible to near-infrared region by modulating the length of the conjugated system. Recently, it has been reported that luminescence (unconventional luminescence) can also be observed from non-conjugated molecules through aggregation. This phenomenon is called cluster-triggered emission (CTE) and is said to result from interactions such as through-space conjugation. In recent years, it was accomplished to modulate luminescent color from visible to near-infrared region, as with conjugated molecules. These CTE materials have been applied in the information technology field, such as encryption media and security inks.

References

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Future Perspectives and Directions

Issues that are expected to be resolved or realized within the next 10 years: application to theranostic drugs that combine photothermal therapy and molecular imaging, use in encrypted communication technology, and molecular environmental sensors.

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