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著者(和文)	岩井梨輝
Author(English)	Riki Iwai
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博士論文要約

**Design of bridged stilbenes
for aggregation-induced emission luminogen and liquid crystal**

Riki Iwai

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**School of Materials and Chemical Technology
Department of Chemical Science and Engineering
Tokyo Institute of Technology**

I have designed bridged stilbenes with a skeleton in which the 2- and β -positions of the styrene moiety are bridged by an alkyl chain to develop superior aggregation-induced emission (AIE) luminogens (AIEgens) and π -conjugated calamitic molecules with a nematic phase at low temperature, and have evaluated their photophysical properties and liquid crystalline properties. In the studies of AIEgens, the theoretical calculation and the experimental measurements of photophysical properties indicated that rigid-bridged stilbenes with a short alkyl chain, i.e., forming a five- or six-membered ring structure, exhibited higher energy in the CI and strong fluorescence in solution, while loose-bridged stilbenes with a long alkyl chain, i.e., forming a seven- or eight-membered ring structure, exhibited lower energy in the CI and very weak fluorescence in solution. This result displays the validity of the control of conical intersection accessibility (CCIA) strategy for the development of AIEgens. I have also designed bridged α -methylstilbenes, in which a methyl group is substituted for a hydrogen atom on the olefinic carbon atom of the bridged stilbenes. A π -extended bridged α -methylstilbene forming the seven-membered ring structure exhibited almost no light emission in solution and excellent AIE properties. The study of the non-radiative decay process concerned with the bridged α -methylstilbene using time-resolved spectroscopy and theoretical calculations revealed that ultrafast non-radiative decay occurs due to the two factors (1) the large energy difference between the Franck-Condon (FC) excited state and the local minimum near the FC excited state ($S_{1\min}$), (2) the closer geometry between the $S_{1\min}$ and the CI, even if the energy barrier between the $S_{1\min}$ and the CI is not zero. The solid-state fluorescence of bridged stilbenes is also interesting. Although bridged stilbenes with the seven-membered ring exhibited the behavior of H-like aggregate in a process of light absorption, the bridged stilbenes exhibited relatively high radiative decay rate constant such as J-like aggregate. This result suggests that the seven-membered ring structure disrupts H-like aggregate in the excited state due to molecular motions of the ring structure. In addition, the bridged stilbenes with a seven-membered ring structure exhibited different solid-state fluorescence depending on the different positions of the substituted *tert*-butyl group due to the twist of the conjugated π -systems.

In the study of liquid crystals, the π -extended bridged stilbene analogs with a seven-membered ring structure exhibited nematic phase near room temperature, whereas the π -extended bridged stilbene analogs with a six-membered ring structure exhibited a high-ordered smectic phase near room temperature. The existence of a low-temperature nematic phase is attributed to the conformational changes of the seven-membered ring structure in the ground state, i.e., intramolecular entropy. Finally, the combination of the solid-state fluorescence and

liquid crystalline properties resulted in an electric-field-responsive light-emitting switch device. The device consists entirely of luminescent mesogens, which are expected to lead to the development of ultrafast switchable luminescent materials. The molecular design with moderate strain and flexibility in bridged stilbenes leads to several conformational changes in the ground state and specific intramolecular motions in the excited state, in contrast to rigid molecular skeletons, which can contribute to the development of environmentally switchable fluorescent materials such as AIEgens and molecular rotor, and organic semiconductors applying for features of liquid crystals.