【1】 Lewis acid catalysts in aqueous media

Catalytic reactions in aqueous media are drawing much attention as a type of green chemistry for the next generation. Though the first report on the aqueous reaction catalyzed by Ln complex, called the Kobayashi-modification of the Mukaiyama-Aldol (MA) reaction, was published 20 years before, there are unsolved questions concerning the role of the water. One question is why the stereoselectivity of this reaction depends on the solvent. In the case of conventional catalytic systems, which have rigid structures, only a few TSs of stereo-determining step need to be computed to solve this question. In the case of Ln catalytic systems, however, the coordination structure around Ln is very flexible and there could be a large number of TSs. To overcome this problem, an exhaustive structural sampling of TSs of stereo-determining step was efficiently performed using the artificial force induced reaction (AFIR) method. As a result, I found more than 150 TSs, in which coordination structure around Ln and orientation between two substrates are slightly different. By considering all the obtained TSs, I succeeded in reproducing the stereo ratio quantitatively. This is the first study that demonstrated that the AFIR can efficiently sample all the TSs that may contribute to the stereoselectivity of a flexible reaction system. This report was highlighted in Spotlights on Recent JACS Publications.

【2】 Luminescent thermometers

Another attractive application of Ln complex is the luminescent materials originating from intra $4f^N$ transitions (f-f transitions). To design the luminescent materials with appropriate functions, the energy levels of LMs and crossing points on and between the ground and excited states need to be controlled. However, as mentioned above, ab initio calculations of Ln excited states are too demanding. To overcome this problem, I have proposed the energy shift method, a reasonable approximation to describe the potential energy surfaces (PESs) and to find the LMs and crossing points related to the emission and quenching. The basic idea of this approximation is that the PESs of $4f^N$ excited states have nearly identical shapes to that of the ground state, and the excitation energies are independent of the surroundings. Thus, the PES of $4f^N$ excited states can be described by that of the ground state corrected by an "energy shift". By using this idea, all the states related to the quenching process can be evaluated by a conventional ground state calculation method, instead of highly demanding ab initio excited state calculations.

By using this approximation, I succeeded in clarifying the origin of the thermosensitivity of emission color and intensity. Moreover, I proposed a new idea to control the thermosensitivity of a polymer including more than two Ln cations, which was validated via experimental measurements.

It should be also emphasized that this approximation is the only one way to predict the structural change during the emission and quenching. This approximation could open the door to the rational design of various Ln luminescent materials.