Luminescent Chromism with Reversible Coordination Number of Hypervalent Tin(IV) Complexes

(*Graduate School of Engineering, Kyoto University*)
○Masayuki Gon, Kazuo Tanaka, Yoshiki Chujo
Keywords: tin; hypervalent bond; luminescence; chromism; π-conjugated system

Luminescent chromism can be applied to highly sensitive chemical sensor. To achieve clear responsiveness of luminescent π-conjugated molecules, it is significant to keep the π-conjugated systems before and after sensing. However, that is difficult because the luminescent color change induced by external stimuli often accompanies structural distortion or alteration. Herein, we found that hypervalent bonds were effective in controlling energy levels of π-conjugated systems preserving the shape of the frontier molecular orbitals (FMOs). Concretely, stable luminescent chromisms both in solution and solid states were realized by using reversible coordination-number control of hypervalent tin(IV)-fused azobenzene complexes.[1)]

Figure 1 shows the chemical structures and luminescent chromism of **TAz-F** with five- and six-coordination forms in solution and solid states. In non-coordinating solvent such as toluene, **TAz-F** had the five-coordinate geometry showing orange emission. Meanwhile, in DMSO, the oxygen atom of DMSO molecule was attached to the tin atom of **TAz-F** and the resulted six-coordinate complex exhibited yellow emission. In solid state, reversible crystal–crystal transition between five- and six-coordinate structures occurred by heating and exposure of DMSO vapor, and the resulted solids showed deep-red and orange emissions, respectively. We confirmed preservation of the shape of FMOs during reversible coordination-number change of tin atom by theoretical calculation. Those chromisms were attributed to variation of electronic states of the π-conjugated systems constructed by azobenzene and hypervalent bonds around the tin atom.

Our findings propose that the hypervalent system is expected to open the field of clear sensing system with color-tunable π-conjugated system.

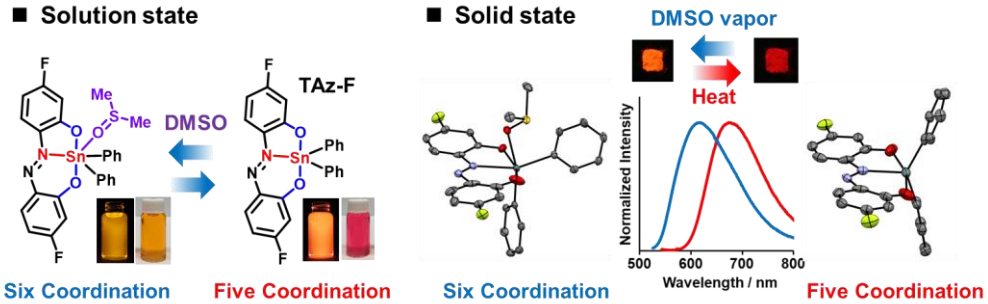

Figure 1. The luminescent chromism of **TAz-F** with DMSO in solution and solid states.

1) Gon, M.; Tanaka, K.; Chujo, Y. *Chem. Eur. J.* **2021**, *27*, 7561.