HYDROGEN-BONDING NETWORK AND NONRADIATIVE DYNAMICS OF HYDRATED ACRIDINE CLUSTERS

M. MITSUI, Y. OHSHIMA, and O. KAJIMOTO, *Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan*; S. ISHIUCHI, M. SAKAI, and M. FUJII, *Institute for Molecular Sience, Myodaiji, Okazaki 444-8585, Japan*.

Acridine (AD) and its hydrated clusters are studied with the aim at evaluating microscopic correlation between hydrogen-bonding topologies and nonradiative dynamics in the chromophore, whose fluorescence property (*i.e.*, quantum yield) has been well known to depend strongly on solvents. Electronic transitions of AD-$(H_2O)_n$ (n = 1-3) have been observed in 360-380 nm with LIF and two-color resonance-enhanced two-photon ionization (2C-R2PI). Geometries of the hydrated clusters have been established by fluorescence-detected IR spectroscopy with the aid of DFT calculations.[a] The corresponding transition of the monomer cannot be identified with LIF and 2C-R2PI, but it appears clearly as a congested band system in a sensitized phosphorescence spectrum. This observation shows that the proximity effect[b] operates effectively in the monomer, in which strong mixing between the $^1(\pi,\pi^*)$ and $^1(n,\pi^*)$ states mediates fast relaxation process(es) into low-lying triplet (and probably also singlet) state(s). By the solvation with small number of water, the nonradiative processes become much less efficient because of weaker state mixing due to destabilization of $^1(n,\pi^*)$, confirmed by fluorescence-lifetime measurements.

[a] M. Mitsui, Y. Ohshima, S. Ishiuchi, M. Sakai, and M. Fujii, *Chem. Phys. Lett.* **317**, 211 (2000).
[b] E. C. Lim, *J. Chem. Phys.* **90**, 6770 (1986).