III-I Ultrafast Reaction Dynamics of Photochromism and Related Phenomena

Photochromic reactions of some organic molecules are of considerable interest because of their wide applications including optical information processing, data storage, and nonlinear optics. The photochromism defined as a reversible transformation in chemical species between two forms is based on simple photochemical reactions such as bond cleavage, pericyclic, proton transfer, and isomerization reactions. As a result of different molecular structures between these two forms, the two isomers differ from one another in various properties such as absorption spectra, dipole moments, refractive indices, and so on. To understand the primary processes and functional properties of photochromic systems, we have examined several photochromic compounds by femtosecond and picosecond laser spectroscopic techniques.

III-I-1 Time-Resolved Study on Unconventional Fluorescence of an Azobenzene Liquid Crystal and Its Phase Transition

AZUMA, Jun[1]; TAMAI, Naoto[1,2]; SHISHIDO, Atsushi[3]; IKEDA, Tomiki[3]
([1]Kwansei Gakuin Univ.; [2]IMS; [3]Tokyo Inst. Tech.)

[*Mol. Cryst. Liq. Cryst.* **314**, 83 (1998)]

As far as the luminescence of azobenzene derivatives is concerned, it is well known that azobenzene do not show appreciable emission because of the trans-cis isomerization and the nπ* character of the first-excited singlet state. Fluorescence properties of azobenzene liquid crystal, 4,4'-dioctyloxy-azobenzene (8AB8), were examined by steady-state and picosecond single-photon timing spectroscopy. It was found that the fluorescence from azobenzene aggregate with a peak at ~ 630 nm was observed in the solid phase in addition to the very weak S_2 fluorescence of azobenzene monomer centered at 420 nm. The structure of aggregate was estimated to be J-like structure. The fluorescence lifetimes of both J-aggregate and monomer S_2 state were estimated to be approximately 150 ps and shorter than 2 ps. The fluorescence lifetime of J-aggregate and relative fluorescence intensity of aggregate/monomer were found to be strongly dependent on temperature and liquid crystalline phases. Microscopic aggregate structure of 8AB8 in various liquid crystalline phases was discussed on the basis of these results.

III-I-2 Solvation Dynamics of Excited p-Methoxy-p'-cyanodiphenylacetylene in n-Butanol: Simultaneous Analysis of Time-Resolved Fluorescence Anisotropy and Stokes Shift

TAMAI, Naoto[1,2]; NOMOTO, Takeo[3], TANAKA, Fumio[4]; MATAGA, Noboru[5]
([1]Kwansei Gakuin Univ.; [2]IMS; [3]Mie Univ.; [4]Mie Pref. College of Nursing; [5]Inst. Laser Tech.)

[*Mol. Cryst. Liq. Cryst.* **314**, 131 (1998)]

Solvation dynamics of p-methoxy-p'-cyano-diphenylacetylene in n-butanol was investigated by observing time-resolved fluorescence anisotropy and dynamic Stokes shift in picosecond time domain. Fluorescence spectra of p-methoxy-p'-cyanodiphenylacetylene exhibited a large Stokes shift, depending on the solvent polarity. The observed time-resolved anisotropy and Stokes shift were simultaneously analyzed with the theory based on the continuum model, in which dielectric friction in polar solvent was introduced through rotational motion of solute molecules with non-Markov process according to the framework of Nee and Zwanzig. The both experimental decays satisfactory fit with the theory. The dipole moments in the excited state and the ground state were estimated to be ~ 14 Debye and negligibly small.

III-I-3 A Combined Experimental and Theoretical Study on the Photochromism of Aromatic Anils

MITRA, Sivaprasad[1]; TAMAI, Naoto[1,2]
([1]Kwansei Gakuin Univ.; [2]IMS)

[*Chem. Phys.* **246**, 463 (1999)]

Dynamics of photochromism have been studied in anil compounds using femtosecond transient absorption and picosecond fluorescence spectroscopies. The experimental observations were compared with the theoretical results obtained from AM1-SCF calculations. Excited-state intramolecular proton transfer (ESIPT) and photochromic reactions were found to occur from the S_1 state whereas normal fluorescence appears from the second excited singlet state. The photochromic processes are seen to be very fast which occur within few hundred of femtoseconds. The lifetime of the S_2 state was observed to be relatively long. This slower decay from higher excited singlet state was explained on the basis of the mixed nature of electronic transition comprising this state and relatively weak $S_2 \leftarrow S_1$ internal conversion. Theoretical results predict the ESIPT state to be zwitterionic in character, however, the final product may be a mixture of zwitter-ionic and nonionic in nature.

III-I-4 Photochromism in 2-(2',4'-Dinitrobenzyl)-pyridine Studied by Ultrafast Laser Spectroscopy

MITRA, Sivaprasad[1]; ITO, Hirotsugu[1]; TAMAI, Naoto[1,2]
([1]Kwansei Gakuin Univ.; [2]IMS)

[*Chem. Phys. Lett.* submitted]

Ultrafast transient behavior of photochromic 2-(2',4'-dinitrobenzyl)pyridine have been studied using femtosecond transient absorption spectroscopy. Three different transient signals could be found in the experiment at different time delays. The dynamics of the transient behavior in the short time scale reveal that very fast relaxation (within ~ 400 ± 100 fs) from the initial excited state leads to the formation of a relatively stable intermediate which is the precursor of excited state proton transfer. This intermediate decays to the ground state of proton transferred aci-nitro structure in nanosecond time scale. Solvent hydrogen bonding in ethanol plays an important role in the deactivation of the excited state giving different photophysical behavior.

III-J Photophysics and Photochemistry in Interface Layers and Mesoscopic Systems

Photochemical and photophysical processes in thin films, liquid/electrode interface layers, and some confined systems are considerable interest because of their characteristic properties different from those in the bulk. For analyzing the dynamics in these systems, we have applied various ultrafast spectroscopic techniques such as femtosecond transient grating spectroscopy, picosecond single-photon timing spectroscopy, and scanning probe microscopy (SPM). The development of time-resolved scanning near-field optical microscopy (SNOM) and STM are indispensable for these studies. The mesoscopic structures and dynamics of molecular aggregates on solid surfaces have been examined by time-resolved SPM. The photoelectrochemistry is an another important subject to analyze the role of interface layers. The characteristic properties of carrier and electron transfer dynamics in liquid/electrode interface layers have been also examined by femtosecond laser spectroscopy.

III-J-1 Time-Resolved and Near-Field Scanning Optical Microscopy Study on Porphyrin J-Aggregate

MIURA, Atsushi[1]; MATSUMURA, Kazuo[1]; SU, Xingguang[1]; TAMAI, Naoto[1,2]
([1]Kwansei Gakuin Univ.; [2]IMS)

[*Acta Phys. Pol.* **94**, 835 (1998)]

Water-soluble porphyrin, 5,10,15,20-tetraphenyl-21H,23H-porphinetetrasulfonic acid (TPPS), forms J-aggregate in aqueous solution depending on experimental conditions such as pH, dye concentration, and/or ionic strength. The steady-state fluorescence and picosecond single-photon timing spectroscopy were applied for protonated monomer and J-aggregate in aqueous solution and in thin films to reveal the dynamics in the S_2 and S_1 states. The S_2 fluorescence spectra from the protonated monomer and J-aggregate were observed in addition to the normal S_1 fluorescence. The lifetime of the S_2 state was estimated to be shorter than a few ps for J-aggregate. The mesoscopic structures of J-aggregate in thin film with and without polymer on the glass surface were examined by scanning near-field optical microscopy (SNOM). With the surface topography and SNOM transmission images, TPPS J-aggregate was found to form a long and narrow tube-like structure which has a few µm length, 0.2~0.5 µm width, and 5~30 nm height. An unidirectional orientation of the structure was also found, which may be originated from the spin-coating process.

III-J-2 Excitation Energy Transfer in Langmuir-Blodgett Films of 5-(4-N-Octadecylpyridyl)-10,15,20-tri-p-tolylporphyrin on Gold-Evaporated Glass Substrates Studied by Time-resolved Fluorescence Spectroscopy

ZHANG, Zhijun[1]; VERMA, Atul[1]; TAMAI, Naoto[1,2]; NAKASHIMA, Kenichi[3]; YONEYAMA, Michio[4]; IRIYAMA, Keiji[5]; OZAKI, Yukihiro[1]
([1]Kwansei Gakuin Univ.; [2]IMS; [3]Saga Univ.; [4]Mitsubishi Chem. Co.; [5]Jikei Univ.)

[*Thin Solid Films* **333**, 1 (1998)]

The fluorescence decays in mono- and multilayer Langmuir-Blodgett (LB) films of 3-(4-N-octadecyl-pyridil)-10,15,20-tri-p-tolylporphyrin (porphyrin338a) deposited on gold evaporated glass substrates were measured to explore various cannels for excitation energy transfer processes. The decays in the 1-layer LB films of porphyrin 338a separated from gold surface by LB film of arachidic acid were also measured as a function of the thickness of spacer, *i.e.* the thickness of the LB films of arachidic acid. Consistent with our previous steady-state fluorescence study, the expectation values of the lifetime obtained by fitting the decay curves indicate that at the short separation distance, the energy transfer from the porphyrin molecules to the gold surface overshadows other processes, including intra- and interlayer energy transfers. The deviation of energy transfer rate from Chance *et al.* (CPS) prediction of inverse distance cubed in our case may be interpreted by assuming the presence of additional excitation energy decay pathways in the LB films of porphyrin 338a on the gold evaporated glass substrates.

III-J-3 Carrier Dynamics on Titanium Dioxide Single Crystals by Femtosecond Transient Grating Spectroscopy

YANG, Xiujuan[1]; TAMAI, Naoto[1,2]; NAKATO, Yoshihiro[3]
([1]Kwansei Gakuin Univ.; [2]IMS; [3]Osaka Univ.)

The photogenerated carrier dynamics in bare titanium dioxide (TiO_2) single crystals with (100), (110), and (001) faces was examined by femtosecond transient grating spectroscopy. The dynamics of transient grating signal at low excitation intensity was found to be very similar to that of the luminescence observed at ~ 430 nm, suggesting that the same species were probed by both time-resolved spectroscopies existing in the surface layer of TiO_2 single crystals. The decay curves of transient grating were strongly dependent on the excitation intensity but independent on the types of crystal faces. The rate of the formation of Γ-state or electron trapping in TiO_2 single crystal was found to be faster than 50 fs. The subsequent intensity-dependent relaxation was analyzed in terms of electron-hole recombination kinetics, and the recombination rate constants in single crystals were compared with that of TiO_2 nanoparticles.