RESEARCH ACTIVITIES II
Department of Molecular Structure

II-A Development of Near-Field Dynamic Spectroscopy and Application to Mesophase Systems

There is much demand for the study of local optical properties of molecular assemblies and materials, to understand mesoscopic phenomena and/or to construct optoelectronic devices in nanometric scale. Near-field optical microscopy, which enables spatial resolution beyond the diffraction limit of light, shows remarkable progress in technology in these days. Combination of this advanced optical technology with ultrafast spectroscopic methods may offer a direct probe of molecular dynamical processes in mesoscopic systems. It may bring essential and basic knowledge for analyzing origins of characteristic features and functionalities of mesophase systems. We are constructing apparatus for near-field dynamic spectroscopy with femtosecond temporal resolution and nanometer spatial resolution. Outlines of the construction and some experimental results are summarized here.

II-A-1 Construction of a Scanning Near-Field Optical Microscope with Closed-Loop Operated Stage and an Apparatus for Fluorescence Life-Time Measurement

IMURA, Kohei; NAGAHARA, Tetsuhiko; OKAMOTO, Hiromi

Scanning near-field optical microscope (SNOM) is the only method that can measure local optical properties beyond the diffraction limit of light. Piezo-electric translator, which is used for sample scanning in SNOM, has a large hysteresis and creeping. Thus, reproducible positioning and stability, which are crucial for investigating local properties in detail, is quite poor. We have developed a SNOM apparatus equipped with closed-loop feedback controlled scanning stage, and achieved about 1 nm positioning accuracy.

The developed instrument consists of light source, sample stage, probe head, distance regulation feedback system, and detection systems. Schematic drawing is depicted in Figure 1. Major mechanical parts of the instrument were made of Super Invar steel to ensure thermal stability. Light source is either a laser or a discharge lamp, the latter is used for absorption spectral measurements. Distance between the probe tip and the sample surface is kept within 10 nm by the shear force feedback control. A polychromator equipped with a CCD array detector is used for spectral measurements while an avalanche photodiode or a photomultiplier tube is used for single photon counting measurements. With this apparatus, we have obtained the lateral resolution down to 50 nm, simultaneously measuring topographic image of the sample.

Time-correlated single photon counting system can be also combined with the SNOM apparatus. It consists of photon detectors, time-to-amplitude converter (TAC), and multi-channel buffer (MCB). From time-correlated photon histograms, fluorescence lifetime can be obtained. Temporal response of the system is determined by the response of the avalanche photodiode, ca. 350 ps.

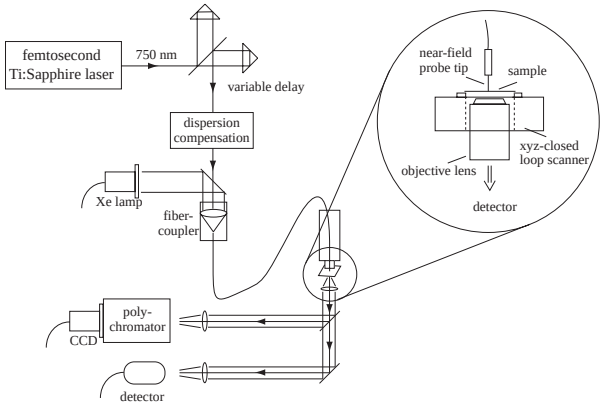

Figure 1. Schematic diagram of experimental set-up. Expansion near the probe is shown at right side.

II-A-2 Near-Field Optical Transmittance Microscopy on the Thin Film of Porphyrin J-Aggregate

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[*Chem. Phys. Lett.* **381**, 368 (2003)]

Mesoscopic structures and photophysical properties of water-insoluble tetrakis(4-methoxyphenyl)porphyrin (TMeOPP) J-aggregate in thin film have been investigated by illumination (transmission) mode SNOM. In the surface topography (Figure 1A), the TMeOPP J-aggregate sample has been found to be composed of planar microcrystalline structures. In the far-field, a broad strong absorption band centered at 760 nm is seen, whereas a narrower band in the 700–800 nm region and several small peaks are observed in the site-specific near-field spectra (Figure 1B). The differences between the far-field and near-field spectra can be ascribed to spatial inhomogeneities, which is related to the *broad* J-bands.

To analyze further the spatial inhomogeneity, we have assumed that there exists a sharp spectral component, and calculated the correlation between this spectral component and the observed spectra. The mapped

correlation images (Figures 1C and D) show structures that have some correlations with the topography. The finer structures (black arrows) seem to show a tendency to be oriented to the polarization directions, indicating a large transition moment parallel to their long crystalline axes. The results suggest that the assumed sharp spectral component is relevant to a substance that is buried in the inhomogeneously broadened spectrum.

Reference

1) S. Okada and H. Segawa, *J. Am. Chem. Soc.* **125**, 2792–2796 (2003).

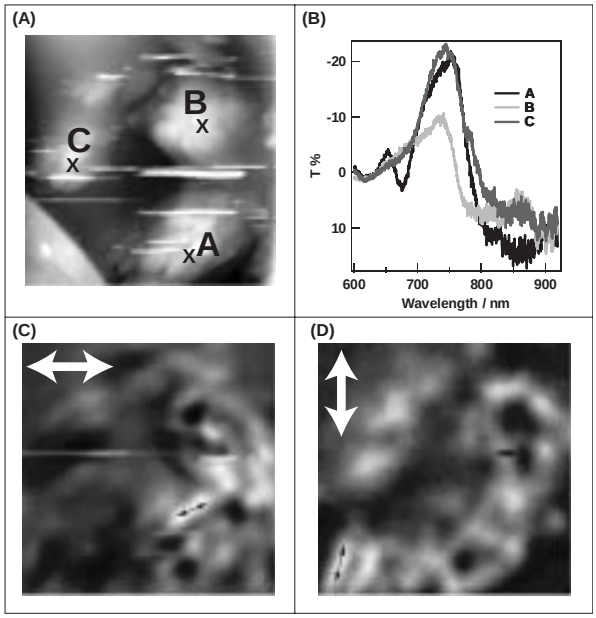

Figure 1. (A) Surface topography of the sample. (B) Transmittance difference spectra in the near-field at positions indicated in (A). (C),(D) Spatial distribution of an assumed spectral component of J-aggregate. Scan range: 5 μm × 5 μm. Arrows in (C) and (D) indicate the directions of the observing polarization.

II-A-3 Time-Resolved Near-Field Spectroscopy of Porphyrin J-Aggregates

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[*Chem. Phys. Lett.* **381**, 368 (2003)]

We have measured the time-resolved equal-pulse transmission correlation (EPC) of porphyrin (TMeOPP) J-aggregate in the near-field, and tried to elucidate site-specific optical features in mesoscopic scales. In Figure 1B, typical pump-probe EPC signal of TMeOPP observed at position "X" indicated in the topography (Figure 1A) is shown. Time and spatial resolutions, and wavelength of our femtosecond pump-probe SNOM apparatus were 100 fs, 100 nm, and 780 nm, respectively. The observed decay may be ascribed to population decrease in the excited-state. Similar exponential decays are also observed at various positions, but not at a bare glass surface. The lifetimes are raging from 10 to 50 ps, that are of the same order as the reported lifetime (50 ps) of J-aggregate of tetrakis(4-sulfonatophenyl)-porphyrin/H_2O in the far-field, and are distinct from that of monomer (3.87 ns).[1] The scatter of the obtained lifetimes may be ascribed either to site-specificity or experimental errors. Further detailed investigations, to clarify the origin of the variations of the excited-state lifetimes may be needed. More precise lifetime measurements by using moderately lower repetition-rate and higher peak power laser pulses are under way.

Reference

1) N. C. Maiti *et al.*, *J. Phys. Chem.* **99**, 17192–17197 (1995).

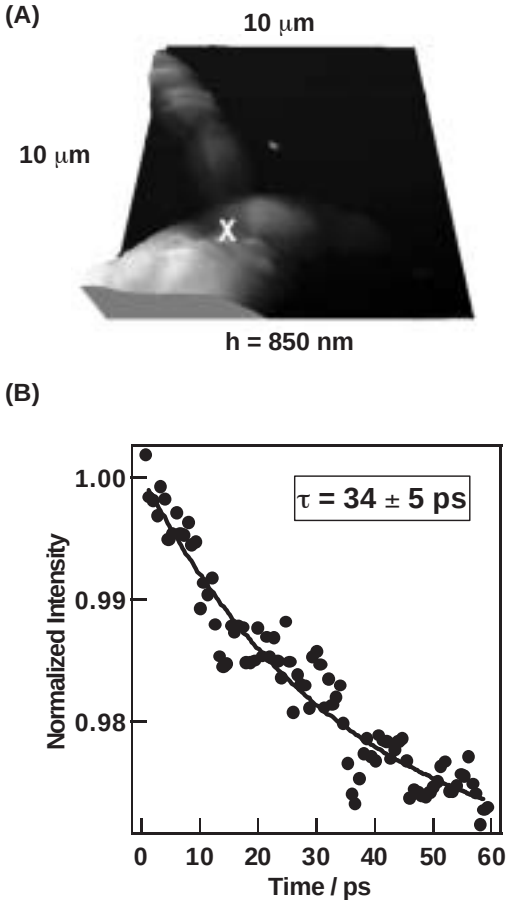

Figure 1. (A) Surface topography of the sample. (B) Equal-pulse transmission correlation signal intensity as a function of delay time, together with that of the least-squares fit.

II-A-4 Near-Field Optical Observation of Gold Nanoparticles

IMURA, Kohei; NAGAHARA, Tetsuhiko; OKAMOTO, Hiromi

For past decades, the surface plasmons (SP) due to collective oscillation of electrons have been widely investigated, for the purpose of understanding physical mechanism in surface enhanced Raman scattering (SERS), and for potential applications in industry as well. Local electric field enhancement near the particle has been recognized as one of the enhancement sources in SERS. Although evidence of local field enhancement has been easily observed after near-field effect translat-

ed into the far-field, little observation in near-field has been reported. In order to understand interaction of photons and the particle in near-field, we have measured near-field transmission spectrum of the particles by a scanning near-field optical microscope (SNOM).

Sample was prepared by spin-coating of 100 nm diameter gold spheres followed by spin-coating with polymer in order to attain flat surface of the sample. Figure 1 shows typical transmission spectrum of a gold particle measured in near-field. Positive and negative signs correspond to enhancement and reduction of the transmission, respectively. We ascribe the enhanced transmission to the antenna effect of the particle. The evanescent wave emerging from the aperture probe first couples into the surface mode of the particle, followed by re-radiation into the far-field. SNOM probe is a source not only of non-propagating evanescent wave but also of propagating wave. Thus, propagating wave also contributes to the observed signal. Absorptive part of the spectrum can be attributed to scattering and absorption, on the gold particle, of the propagating wave from the aperture probe. These considerations imply that spectral profile consists of two different contributions of evanescent and propagating waves.

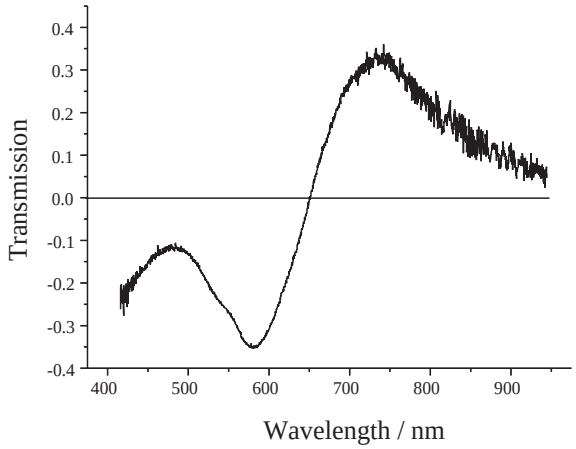

Figure 1. Transmission spectrum of gold sphere (100 nm diameter) measured in near-field.