1. Main Research Results

In our research we use single-molecule spectroscopy to study nanoscale structure and optical/electrical properties of organic and polymeric materials.

1) Relationship between structure and optical/electrical properties of $\pi$-conjugated polymers

Single-molecule spectroscopy was used to study conformation and related photophysical and electrical properties of the conjugated polymers MEH-PPV and polythiophene (PT). In the case of MEH-PPV, the chain conformation is controlled by the solvent quality of the matrix polymer, and is measured via the single chain 3D absorption ellipsoid and reconstructed using a coarse-grain molecular dynamics (MD) simulation. The different conformations are correlated with qualitatively different types of emission fluctuations (blinking) and with different spectral characteristics. In the case of polythiophene, the chain conformation is controlled by its chemical composition using long grafted side-chains, and reconstructed using MD simulations. The simulation results show that a PT chain without the grafted side-chains attains a compact conformation where distances between any two conjugated segments (chromophores) are within the Forster range of efficient energy transfer, while the PT with the side chains retains an extended PT backbone with reduced inter-segment interactions. Single chain emission anisotropy and fluorescence blinking confirm the conformation-dependent differences in exciton localization.

2) Microscopy and single molecule study of the process of electroluminescence in organic light-emitting devices

We studied microscopy of a polymer-based organic light-emitting device and succeeded in the detection of electroluminescence (EL) from single small organic molecules. The emitting molecule is a red organometallic phosphorescent complex (Ir(btp)$_2$acac) dispersed at low concentrations in a hole conducting non-conjugated polymer, poly(vinylcarbazole). Microscopic imaging reveals that charge recombination and EL in the neat undoped host polymer occurs in discrete sites with a diameter of a few hundreds of nanometers. The sites are randomly distributed in the device and show strong driving-voltage-dependent emission fluctuations on timescales of tens of seconds. The origin of the sites lies in favorable local conformation of the host polymer that enables efficient charge injection and/or transport. The emission dynamics is likely caused by conformational changes due to high local current densities. The single-molecule EL detection was made possible by the fact that the onset voltage for EL of the dopant molecules is lower than that for the host. The guest molecules could thus be separated from the host EL background both spectrally and by the applied voltage. The dynamics of single-molecule electroluminescence originates from the dynamics of the charge-recombination sites of the host polymer.
rather than from the photophysical behavior of the molecule itself. Bias-dependent electroluminescence spectra show a non-linear mechanism where the iridium complex dopant molecules are excited preferentially at low bias voltages and saturate quickly, revealing differences in the electroluminescence mechanism between the host and the dopant.

3) Microscopic study on the inner structure of individual light-harvesting complexes of photosynthetic bacteria

Single-molecule detection method was used to study the microscopic inner structure of chlorosomes, the light-harvesting complexes of green photosynthetic bacteria. Chlorosomes are formed by large aggregates of bacteriochlorophyll molecules and are able to efficiently collect sunlight in dim or dark conditions. This property makes them ideal model systems for efficient light collection in photovoltaic devices. We have developed theoretically and experimentally a method to investigate the inner structure of individual chlorosomes based on the measurement of fluorescence-monitored 3D linear dichroism. We have also succeeded for the first time in direct measurement of absorption anisotropy of individual light-harvesting complexes and correlated the results with fluorescence experiments. We found a large distribution of absorption anisotropy values both among different chlorosomes, as well as among different dimensions within one chlorosome. These results support the idea that the bacteriochlorophyll aggregates from two-dimensional sheets, or lamellae, within the chlorosome, and the complex folding of the lamellae gives rise to the observed distributions.

2. List of Publication (original article, comment/book)

1) Original Paper


3. Invited/Plenary Talks in Conference

1) International Conference or Workshop

(1) M. Vacha, Y. Ebihara: Conjugated polymer conformations and related photophysics in thin-film matrices: a single molecule study (invited). Joint 2nd International Conference on Science and
Technology for Advanced Ceramics and 1st International Conference on Science and Technology of Solid Surface and Interface. May 30 - June 1, 2008, Chiba, Japan


2) Domestic Conferences


(5) M. Vacha: Relationship between conformation and photophysics of single conjugated polymer chains (oral). 2008 Autumn Meeting of the Physical Society of Japan, September 20 – 23, 2008, Iwate University, Morioka