

## **1. Outline of research results in 2010**

We have studied nanoscale structure and optical properties of organic and polymeric materials using single-molecule spectroscopic techniques. We have also developed single-molecule detection techniques for materials research.

### ***1) Direct visualization of nanoscale photophysical dynamics using single-molecule imaging***

We investigated exciton migration, trapping and emission processes occurring within a single conjugated polymer molecule by means of superresolution fluorescence localization microscopy. This methodology allowed us to locate the spatial distribution of emitting sites within single chains with nanometer precision. The study was done on individual poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) molecules with average molecular weights ranging from 215,000 to 1,440,000 and with narrow weight distributions. We found that mean emission intensity increases proportionally to the polymer molecular weight. The localization experiments suggest that the emitting sites are distributed nearly uniformly within a single chain and that the sites are on average 10 nm apart, irrespective of the molecular weight of the polymer. Furthermore, spatial contours formed by all the combined emitting sites within one chain show elongated shapes, in agreement with a rod-like structure of MEH-PPV in a collapsed state. [ref. 3]

### ***2) Multimode diffusion of ring polymer molecules revealed by a single-molecule study***

In collaboration with Prof. Yasuyuki Tezuka in the Department of Organic and Polymeric Materials, Tokyo Institute Technology, we have been investigating diffusion processes of ring and linear polymers in a concentrated linear polymer solution. The study demonstrated a multimode diffusion of the ring polymer, in contrast to a single-mode diffusion of the linear polymers. These results suggested the threading of the ring polymer with the linear matrix polymer. In order to analyze the threading of the polymer chains based on polymer physics theory, we investigated diffusion of single polymer chains in a polymer melt. In order to make it possible to conduct measurements on melt samples, we implemented improvement of the equipment. We first introduced a temperature control for the microscope, and also optimized experimental conditions for

conducting single-molecule fluorescence imaging experiments at a temperature higher than room temperature. Those modifications allowed us to prepare nearly identical melt samples of poly(THF) constantly, and allowed us to obtain single-molecule diffusion trajectories of the ring polymer in the melts.

### ***3) Developing new imaging method for determining distribution of 3D orientation of single molecules***

We developed a method to determine full three-dimensional orientation distribution of individual molecules based on wide-field defocused fluorescence imaging. Excitation efficiencies of out-of-plane oriented molecules were improved dramatically by illuminating molecules with multiple laser beams. Our high throughput approach allowed us to obtain unbiased statistical distributions of orientations of doped molecules in spin-coated polymer thin films. We found thickness- and glass transition temperature-dependent distributions of the molecular orientations which reflect local chain orientations and relaxation in the polymer thin films. [ref. 5]

### ***4) Single-molecule characterization of photophysical properties of charge-transfer conjugated polymer molecule***

We investigated excited-state photophysical dynamics occurring within a charge-transfer (CT) conjugated oligomer, CzBT which consisted of carbazole (Cz) and benzothiadiazole (BT) by means of various single-molecule spectroscopic methods as well as DFT calculation. The single-molecule experiments demonstrated that the dimer structure was a spectroscopic unit in the oligomer. This result agreed well with the theoretical calculation. Single-molecule fluorescence spectra and lifetime of CzBT showed broad distributions, which indicated that each molecule has different twist angle of the Cz and BT unit. The twist angle dependent electron delocalization in CzBT was also supported by the theoretical calculation. These results suggest that the excited-state photophysical dynamics of CzBT is dominated by the twist angle between two moieties.

### ***5) Single-molecule optical switching for researches on material science***

While super-resolution fluorescence imaging based on single-molecule optical switching has been recognized as a powerful means in the field of life science, the methodology is not well recognized in the field of material science yet. In order to

establish a super-resolution fluorescence imaging technique which is applicable for material science researches, we investigated and characterized optical switching behavior of a versatile fluorescence dye, Atto655, at the single-molecule level.

## 2. List of publication

### *Refereed papers*

- 1) Mudalige, K.; Habuchi, S.; Goodwin, P. M.; Pai, R. K.; De Schryver, F.; Cotlet, M. **Photophysics of the red chromophore of HcRed: Evidence for cis-trans isomerization and protonation-state changes.** *J. Phys. Chem. B* **2010**, *114*, 4678-4685.
- 2) Yardimci, H.; Loveland, A. B.; Habuchi, S.; van Oijen, A. M.; Walter, J. C. **Uncoupling of sister replisomes during eukaryotic DNA replication.** *Mol. Cell* **2010**, *40*, 834-840.
- 3) Habuchi, S.; Onda, S.; Vacha, M. **Molecular weight dependence of emission intensity and emitting sites distribution within single conjugated polymer molecules.** *Phys. Chem. Chem. Phys.* **2011**, *13*, 1743-1753.
- 4) Suzuki, K.; Habuchi, S.; Vacha, M. **Blinking of single dye molecules in a polymer matrix is correlated with free volume in polymers.** *Chem. Phys. Lett.* **2011**, *505*, 157-160.
- 5) Habuchi, S.; Oba, T.; Vacha, M. **Multi-beam single-molecule defocused fluorescence imaging reveals local anisotropic nature of polymer thin films.** *Phys. Chem. Chem. Phys.* **2011**, *13*, 6970-6976.
- 6) Furumaki, S.; Vacha, F.; Habuchi, S.; Tsukatani, Y.; Bryant, D. A.; Vacha, M. **Absorption linear dichroism measured directly on a single light-harvesting system: the role of disorder in chlorosomes of green photosynthetic bacteria.** *J. Am. Chem. Soc.* *In press.*

### *Review*

- 1) Habuchi, S.; Vacha, M. **Structural conformation and photophysical properties of conjugated polymer molecules.** *Kobunshi* **2011**, *60*, 58-61.
- 2) Vacha, M.; Habuchi, S. **Conformation and physics of polymer chains: a single-molecule perspective.** *NPG Asia Mater.* **2010**, *2*, 134-142.

## **4. Conferences**

### *International*

- 1) Vacha, M.; Furumaki, S.; Vacha, F.; Psencik, J.; Habuchi, S. **Absorption linear dichroism directly measured on a single light-harvesting complex of photosynthetic bacteria** (oral). 17<sup>th</sup> International Conference on Dynamical Processes in Excited States of Solids, June 20-25, 2010, Argonne, USA.
- 2) Habuchi, S.; Onda, S.; Sugimoto, T.; Vacha, M. **Relationship between conformation and optical properties of single conjugated polymer molecules** (oral). 17<sup>th</sup> International Conference on Dynamical Processes in Excited States of Solids, June 20-25, 2010, Argonne, USA.
- 3) Habuchi, S.; Yamamoto, T.; Tezuka, Y.; Vacha, M. **Multimode diffusion of ring polymer molecules revealed by a single-molecule study** (invited). 5<sup>th</sup> International Symposium on Integrated Molecular/Materials Engineering, September 20 – 22, 2010, Changzhou, China.
- 4) Vacha, M.; Habuchi, S. **Single-molecule approach to nanoscale structure and dynamics of molecular complexes: from conjugated polymers to photosynthetic light harvesting** (invited). 5<sup>th</sup> International Symposium on Integrated Molecular/Materials Engineering, September 20 – 22, 2010, Changzhou, China.
- 5) Habuchi, S.; Yamamoto, T.; Tezuka, Y.; Vacha, M. **Multimode diffusion of ring polymer molecules revealed by a single-molecule study** (poster). The 16<sup>th</sup> Takeda Science Foundation Symposium on Bioscience, December 1 – 2, 2010, Tokyo,

Japan.

- 6) Habuchi, S. **Single-molecule studies on polymer science** (oral). TokyoTech-EPFL workshop on Materials, March 13-16, 2011, Château-d'Oex, Switzerland

### *Domestic*

- 1) Vacha, M.; Furumaki, S.; Habuchi, S. **Structure of chlorosomal antennae of photosynthetic bacteria studied by single-molecule absorption spectroscopy** (oral). 2010 Annual Meeting on Photochemistry, September 8 – 10, 2010, Chiba.
- 2) Habuchi, S.; Yamamoto, T.; Tezuka, Y.; Vacha, M. **Multimode diffusion of ring polymer molecules revealed by a single-molecule study** (oral). 2010 Annual Meeting on Photochemistry, September 8 – 10, 2010, Chiba.
- 3) Oba, T.; Habuchi, S.; Vacha, M. **Full three dimensional orientational distribution of single molecules determined by simultaneous multiple beam illumination** (poster). 2010 Annual Meeting on Photochemistry, September 8 – 10, 2010, Chiba.
- 4) Hatano, T.; Habuchi, S.; Vacha, M. **Nanoscale characterization of conjugated polymer light emitting diodes by fluorescence micro-spectroscopy** (poster). 2010 Annual Meeting on Photochemistry, September 8 – 10, 2010, Chiba.
- 5) Osawa, Y.; Vacha, M.; Habuchi, S.; Iyoda, T.; Komiyama, H. **Development of efficient optoelectronic materials using nanocylinders of a block copolymer as a template** (poster). 2010 Annual Meeting on Photochemistry, September 8 – 10, 2010, Chiba.
- 6) Onda, S.; Habuchi, S.; Vacha, M.: **Dependence of spatial jump size of emitting sites within a single conjugated polymer chain on the polymer molecular weight** (ポスター). 2010 Annual Meeting on Photochemistry, September 8 – 10, 2010, Chiba.
- 7) Habuchi, S.; Michinobu, T.; Vacha, M. **A single-molecule study on the donor-acceptor type conjugated polymer** (poster). 2010 Annual Meeting on

Photochemistry, September 8 – 10, 2010, Chiba.

- 8) Nozue, S.; Habuchi, S.; Vacha, M. **Development of simultaneous AFM and fluorescence confocal microscopy with single molecule sensitivity for the study of nanoscale properties of organic materials** (poster). 2010 Annual Meeting on Photochemistry, September 8 – 10, 2010, Chiba.
- 9) Furumaki, S.; Habuchi, S.; Vacha, M. **Development of new microscopic methods using absorption anisotropy for the study of the properties of antenna complexes of green sulfur bacteria** (poster). 2010 Annual Meeting on Photochemistry, September 8 – 10, 2010, Chiba.
- 10) Habuchi, S. **Single-molecule studies on optical and physical properties of polymers** (invited). 2010 Forum of Polymer/Hybrid Materials Research Center for Young Scientists, December 6, 2010, Sendai.