

Satoshi HABUCHI Assistant Professor,
Department of Organic and Polymeric Materials

1. Outline of research results in 2009

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 have attempted to visualize excited-state dynamics within a single conjugated polymer molecule (poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV)) by means of single-molecule imaging technique. We have demonstrated that our approach can actually visualize localization of excited energy through intramolecular energy transfer at nanometer scale. Using the technique, we demonstrated that the entire energy migrated into a single trap site when the molecule adopted highly collapsed conformation. On the other hand, multiple trap sites are present within a single molecule when the molecule has more open conformation [1]. Furthermore, we investigated relationship between molecular conformation and excited-state dynamics in detail. We controlled the conformational structure of the molecule by changing polymer matrices and/or the molecular weight of MEH-PPV. Our results demonstrate that our technique would be a powerful tool to study photophysics of nano-size materials.

(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 investigated diffusion processes of ring polymers in a concentrated polymer solution. We measured diffusion of individual fluorescently labeled linear and cyclic poly(THF) dispersed in a highly concentrated (in a semi-dilute regime) linear poly(THF) solution of toluene. Average diffusion coefficients obtained from both the linear and cyclic poly(THF) were nearly identical.

The distribution of diffusion coefficients obtained from the linear poly(THF) matched well with the calculated distribution expected for a homogeneous diffusion. On the other hand, the distribution obtained from the cyclic poly(THF) deviated significantly from the calculated one. Detailed analyses of the experimental data demonstrated the presence of two distinct diffusion mode for the cyclic poly(THF) [2]. Those results suggest partial threading of cyclic poly(THF) by the linear poly(THF), which slows down the diffusion. The unthreaded cyclic poly(THF) should have compacted conformation, which leads to the faster diffusion coefficient.

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

We have developed a single-molecule defocused fluorescence imaging technique which allows determining 3D orientation of individual molecules. Using the method, we tried to determine the distribution of 3D orientation of individual molecules in a polymer thin film. Since the defocused imaging is based on fluorescence measurements under the optical microscope, excitation powers along 3 axes are not equal due to the polarization of light, and thus fluorescence intensity depends on the molecular orientation. This forces us to detect only fraction of the emitting molecules, which leads to bias in the orientation distribution. We calculated the excitation power along three axes, and determined the experimental conditions required for an unbiased experiment. Based on the calculation, we experimentally determined the distribution of 3D orientation of individual molecules, and compared in with the calculation.

(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 which had carbazole unit as an electron donor and benzothiadiazole as an electron acceptor. The molecule has absorption of local states in UV region, and has absorption of the CT state in visible region. Independent of the excitation wavelength, the molecule shows emission from the CT state. We analyzed the emission properties of the CT state at the single-molecule level using polarization measurement as well as defocused fluorescence imaging. We found that emitting sites within the molecule changed over time due to the efficient energy transfer between the CT states. Also, we demonstrated large distribution of the number of emitting sites

within individual molecules. The excited-state photophysical dynamics of the CT conjugated oligomer are significantly different from those observed for energy transfer systems which consist of local electronic states.

2. List of publication

Refereed papers

- 1) Habuchi, S.; Onda, S.; Vacha, M.: **Mapping the emitting sites within a single conjugated polymer molecule.** *Chem. Commun.* **2009**, 4868-4870.
- 2) Habuchi, S.; Satoh, N.; Yamamoto, T.; Tezuka, Y.; Vacha, M.: **Multimode diffusion of ring polymer molecules revealed by a single-molecule study.** *Angew. Chem. Int. Ed.* **2010**, *49*, 1418-1421.
- 3) Hattori, A.; Habuchi, S.; Vacha, M.: **Single-molecule imaging with an inexpensive UV-LED light source.** *Chem. Lett.* **2009**, *38*, 234-235.
- 4) Sekiguchi, Y.; Habuchi, S.; Vacha, M.: **Single-molecule electroluminescence of a phosphorescent organometallic complex.** *ChemPhysChem* **2009**, *10*, 1195-1198.
- 5) Kochaniak, A. B.; Habuchi, S.; Loparo, J. J.; Chang, D. J.; Cimprich, K. A.; Walter, J. C.; van Oijen, A. M.: **Proliferating cell nuclear antigen uses two distinct modes to move along DNA.** *J. Biol. Chem.* **2009**, *284*, 17700-17710.
- 6) Sugimoto, T.; Habuchi, S.; Ogino, K.; Vacha, M.: **Conformation-related exciton localization and charge-pair formation in polythiophenes: ensemble and single-molecule study.** *J. Phys. Chem. B* **2009**, *113*, 12220-12226.
- 7) Sekiguchi, Y.; Habuchi, S.; Vacha, M.: **Nanoscale heterogeneity and light-emitting dynamics is solution-processed phosphorescent organic light-emitting devices.** *Phys. Chem. Chem. Phys.* **2009**, *11*, 8684-8688.
- 8) Ebihara, Y.; Habuchi, S.; Vacha, M.: **Conformation-dependent room-temperature emission spectra of single MEH-PPV chains in different**

polymer matrices. *Chem. Lett.* **2009**, *38*, 1094-1095.

- 9) Furumaki, S.; Habuchi, S.; Vacha, M.: **Fluorescence-detected three-dimensional linear dichroism: a method to determine absorption anisotropy in single sub-wavelength size nanoparticles.** *Chem. Phys. Lett.* **2010**, *487*, 312-314.

Review

- 1) Habuchi, S.: **Single-molecule studies on DNA-protein interaction.** *Bunseki* **2009**, *4*, 198-199.

4. Conferences

International

- 2) Habuchi, S.: **Single-molecule view of DNA-protein interaction (invited).** 4th Asian and Pacific Rim Symposium on Biophotonics. May 27 – 29, 2009, Jeju, Korea
- 3) Vacha, M.; Ebihara, Y.; Sugumoto, T.; Onda, S.; Habuchi, S.: **Relationship between conformation and optical/electrical properties of single conjugated polymer chains: MEH-PPV and polythiophene** (oral). 10th International Conference on Hole Burning and Single Molecule Spectroscopies, June 22-27, 2009, Palm Cove, Australia.
- 4) Vacha, M.; Sekiguchi, Y.; Habuchi, S.: **Single molecule electroluminescence of a phosphorescent organometallic complex** (poster). 10th International Conference on Hole Burning and Single Molecule Spectroscopies, June 22-27, 2009, Palm Cove, Australia.
- 5) Habuchi, S.; Onda, S.; Sugimoto, T.; Ebihara, Y.; Vacha, M.: **Relationship between conformation and optical/electrical properties of single conjugated polymer molecules** (oral). XXIV International Conference on Photochemistry. July 19 – 24, 2009, Toledo, Spain

- 6) Onda, S.; Habuchi, S.; Vacha, M.: **Mapping the emitting sites within a single conjugated polymer molecule** (poster). XXIV International Conference on Photochemistry. July 19 – 24, 2009, Toledo, Spain
- 7) Habuchi, S.; Vacha, M.: **Mapping the emitting sites within a single conjugated polymer molecule (invited)**. 4th International Symposium on Integrated Molecular/Materials Engineering. October 28 – 29, 2009, Chendu, China
- 8) Vacha, M.; Habuchi, S.: **Nanoscale heterogeneity and light-emission dynamics in solution-processed organic light-emitting devices: Single-molecule study (invited)**. 4th International Symposium on Integrated Molecular/Materials Engineering, October 28 – 29, 2009, Chendu, China.

Domestic

- 1) Vacha, M.; Habuchi, S.: **Relationship between conformation and photophysical and electrical properties of single conjugated polymer chains** (oral). 58th Autumn Meeting of the Society of Polymer Science, September 16-18, 2009, Kumamoto.
- 2) Habuchi, S.; Yabiku, Y.; Vacha, M.: **Towards single-molecule chiroptical responses (oral)**. 2009 Annual Meeting on Photochemistry, September 16 – 18, 2008, Kiryu, Gunma.
- 3) Vacha, M.; Sekiguchi, Y.; Habuchi, S.: **Nanoscale heterogeneity and dynamics of organic EL devices: single-molecule study (oral)**. 2009 Annual Meeting on Photochemistry, September 16 – 18, 2008, Kiryu, Gunma.
- 4) Onda, S.; Habuchi, S.; Vacha, M.: **Mapping the emitting sites within a single conjugated polymer molecule (poster)**. 2009 Annual Meeting on Photochemistry, September 16 – 18, 2008, Kiryu, Gunma.