

Martin Vacha, Associate Prof.

Department of Organic and Polymeric Materials

1. Outline of research results in 2009

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 π -conjugated polymers

In this ongoing research project we concentrated on the physical control of the conjugated polymer structure (conformation). In contrast with previous approaches where we controlled the conformation by solvent quality or by chemical composition of the polymer side-chains, this time we chose to limit the range of possible conformations by using physical restriction imposed by a periodic template. The template is a phase-separated non-conjugated block-copolymer thin film consisting of a regular array of vertical columns a few nm in diameter. In the first phase of this research we concentrated on exploring methods to incorporate a single conjugated polymer chain into such column. The most promising method appears to be a post-doping process where a chemical force (concentration gradient) at an interface formed by the free-standing block-copolymer film is used to incorporate water-soluble PPV derivative, MPS-PPV, into the film columns. Restrictions on the PPV conformation due to the column are expected to significantly affect the conjugated polymer photophysical properties and increase its emission quantum efficiency in solid state.

In a related research, super-resolution microscopy was used to study nanoscale light-emission domains in single chains of the conjugated polymer MEH-PPV.

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

We found previously that in non-conjugated polymer-based organic light-emitting devices doped with organometallic phosphorescent complexes the charge recombination and electroluminescence (EL) processes occur in discrete sites with a diameter of a few hundreds of nanometers. These high-efficiency 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. To investigate further this phenomenon we extended the study to devices which use conjugated polymers as the charge transporting/light emitting layer. We compared

devices with two different cathode structures, a low electron injection efficiency Al cathode and high-efficiency LiF/Al cathode. The conjugated polymers were commercially available derivatives of the PPV family, MEH-PPV and a polymer with commercial name Super Yellow. We found that the phenomena observed on the non-conjugated polymer devices are not unique to dye-doped systems and that the same trends can be found in the conjugated systems as well. These are, namely, driving-voltage dependent nanoscale spatial and temporal heterogeneities in the devices. The appearance and magnitude of these heterogeneities are directly related to the electron-injection efficiency from the cathode, but also to the chemical composition of the PPV compound.

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

In this ongoing research we measured and analyzed absorption anisotropy (linear dichroism, LD) of individual chlorosomes, the light-harvesting complexes of green photosynthetic bacteria, using two newly developed microscopic methods, single-molecule fluorescence-monitored three-dimensional LD and single-molecule absorption LD. The results show that the inner structure of each chlorosome is affected (to a varying extent) by local structural disorder along the chlorosome long axis, and that excitonic disorder is not manifested in the LD observables. Using a simple structural model, the LD observed on single chlorosomes provided limits for the angles at which excitonic transition dipole moments of the bacteriochlorophyll aggregates can be oriented within the chlorosome.

(4) Study on nanoscale dynamics in polymer thin films near glass transition

Dynamics of polymers and glasses near glass transition temperature T_g is an important yet little understood phenomenon. Here, we used a single-molecule approach to get insight into the nanoscale nature of the glass transition. We explored the potential of the phenomenon of fluorescence blinking of a cyanine dye molecule embedded in a polymer film as a probe of the nanoscale structural dynamics. We found that the ratio of blinking molecules depends linearly on temperature and reflects the increase of free volume associated with each dye molecule. At the same time, the rate of the blinking is insensitive to temperature because the cyanine dye conformational change which is associated with the blinking occurs at rates that are orders of magnitude faster than the rates of the relaxation of the surrounding polymer main chains (alpha relaxations). The blinking of single cyanine dyes can thus serve as an alternative probe to measure temperature changes of local free volume in polymers.

2. List of publications

Refereed papers

- 1) S. Furumaki, S. Habuchi and M. Vacha: Fluorescence-detected three-dimensional linear dichroism: A method to determine absorption anisotropy in single sub-wavelength size nanoparticles. *Chem. Phys. Lett.* 487 (2010) 312-314
- 2) S. Habuchi, N. Sato, T. Yamamoto, Y. Tezuka and M. Vacha: Multimode Diffusion of Ring Polymer Molecules Revealed by a Single-Molecule Study. *Angew. Chem. Int. Ed.* 49 (2010) 1418-1421
- 3) J. Taguchi, T. Yano, S. Habuchi, M. Vacha and S. Shibata: Control of orientation of Rhodamine 6G in organic-inorganic hybrid film by capillary electrophoresis doping technique. *Thin Solid Films*, accepted
- 4) Y. Ebihara, S. Habuchi and M. Vacha: Conformation-dependent room-temperature emission spectra of single MEH-PPV chains in different polymer matrices. *Chem. Lett.* 38 (2009) 1094-1095
- 5) Y. Sekiguchi, S. Habuchi and M. Vacha: Nanoscale heterogeneity and light-emission dynamics in solution-processed phosphorescent organic light-emitting devices. *Phys. Chem. Chem. Phys.* 11 (2009) 8684-8688
- 6) T. Sugimoto, S. Habuchi, K. Ogino and M. Vacha: Conformation related exciton localization and charge-pair formation in polythiophenes: Ensemble and single-molecule study. *J. Phys. Chem. B* 113 (2009) 12220-12226
- 7) Y. Sekiguchi, S. Habuchi and M. Vacha: Single Molecule Electroluminescence of a Phosphorescent Organometallic Complex. *ChemPhysChem* 10 (2009) 1195-1198
- 8) S. Habuchi, S. Onda and M. Vacha: Mapping the emitting sites within a single conjugated polymer molecule. *Chem. Commun.* 2009, 4868-4870
- 9) A. Hattori, S. Habuchi and M. Vacha: Single-Molecule Imaging with an Inexpensive UV-LED Light Source. *Chem. Lett.* 38 (2009) 234-235

3. Books

T. Tsurumi, H. Hirayama, M. Vacha, T. Taniyama: *Nanoscale Physics for Materials Science*. Textbook, CRC Press (2009)

4. Conferences

International

- 1) M. Vacha, Y. Ebihara, T. Sugimoto, S. Onda, S. Habuchi: 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.

- 2) M. Vacha, Y. Sekiguchi, S. Habuchi: 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.
- 3) M. Vacha: Introducing NPG Asia Materials: A new journal for materials research in Asia-Pacific region (Opening Plenary). 3rd AEARU workshop on Advanced Materials, November 2009, Pohang, Korea.
- 4) M. Vacha, S. Habuchi: Nanoscale heterogeneity and light-emission dynamics in solution-processed organic light-emitting devices: Single-molecule study (Invited). 4th
- 5) International Symposium on Integrated Molecular/Materials Engineering, October 28 – 29, 2009, Chendu, China.
- 6) S. Habuchi, S. Onda, T. Sugimoto, Y. Ebihara, M. Vacha: Relationship between conformation and optical/electrical properties of single conjugated polymer molecules (Oral). XXIV International Conference on Photochemistry. July 19 – 24, 2009, Toledo, Spain.
- 7) S. Onda, S. Habuchi, M. Vacha: Mapping the emitting sites within a single conjugated polymer molecule (Poster). XXIV International Conference on Photochemistry. July 19 – 24, 2009, Toledo, Spain
- 8) S. Habuchi, M. Vacha: 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.

Domestic

- 1) M. Vacha, S. Habuchi: 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) S. Habuchi, Y. Yabiku, M. Vacha: Towards single-molecule chiroptical responses (Oral). 2009 Annual Meeting on Photochemistry, September 16 – 18, 2009, Kiryu, Gunma.

- 3) M. Vacha, Y. Sekiguchi, S. Habuchi: Nanoscale heterogeneity and dynamics of organic EL devices: single-molecule study (Oral). 2009 Annual Meeting on Photochemistry, September 16 – 18, 2009, Kiryu, Gunma.

- 4) S. Onda, S. Habuchi, M. Vacha: Mapping the emitting sites within a single conjugated polymer molecule (Poster). 2009 Annual Meeting on Photochemistry, September 16 – 18, 2009, Kiryu, Gunma.