

Mapping the emitting sites within a single conjugated polymer molecule†

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We map the location of emitting sites within a single conjugated polymer molecule poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] with nanometre accuracy by means of a single-molecule imaging technique.

Conjugated polymers are an important class of materials for optoelectronic devices, such as organic light-emitting diodes.¹ Spectroscopic properties of conjugated polymers are determined by the conformation of the polymer chains. A single conjugated polymer can be described structurally as a large number of quasi-independent conjugated segments connected by flexible joints, or chemical defects, which allow for a variety of conformations.^{2,3} Efficient electronic energy transfer is believed to funnel the excitation to the lowest-energy chromophores (exciton traps) during exciton lifetime, resulting in emission from only very localized regions (a few chromophores or even a single chromophore) along the polymer chain.^{4–7} Energy transfer in conjugated polymers has been studied extensively using single-molecule spectroscopic techniques.⁸ Most results,^{9–13} including fluorescence polarization experiments,^{12–15} fluorescence spectral measurements¹⁶ and photon pair-correlation experiments,^{17–19} support a picture of efficient energy funneling to a small number of chromophores within the single conjugated polymer chain.

We have previously reported that a single conjugated polymer molecule, poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) in a polystyrene matrix adopts either folded (oblong defect coil) or open (disc-like defect coil) conformations.¹³ The folded conformation results in a stepwise emission intensity trajectory due to an efficient energy migration within the molecule. On the other hand, the open conformation results in a continuous emission intensity trajectory, because each conjugated segment behaves like an independent chromophore. Here, we map the location of the emitting sites within a single MEH-PPV molecule with nanometre accuracy by means of a single-molecule imaging technique.

A diluted toluene solution of MEH-PPV ($M_n = 200\,000$, $M_w/M_n = 5$) containing 1.5 wt% polystyrene (PS, $M_w = 9,580$, $T_g = 368$ K) was spin-coated on a microscope cover slip.¹³ An aqueous solution of fluorescent microspheres

(60 nm in diameter) was spin-coated on top of the PS/MEH-PPV sample to calibrate stage drifting. The sample was vacuum-dried at 60 °C for 2 h and used immediately for experiments. Fluorescence images were recorded using an inverted microscope with a high N.A. objective lens and an EM-CCD camera. The 488 nm line of an Ar⁺ laser was used for excitation. Centroid positions of the emission obtained from single molecule images were determined by 2D Gaussian fitting.^{20–22} Drift of the microscope stage was corrected by fitting the images of the reference fluorescent beads. The centroid positions obtained by the 2D Gaussian fitting were filtered using an edge preserving the Chung–Kennedy (C–K) algorithm. The resulting experimentally obtained accuracy of the centroid position was dependent on the total photon number, and was in the range of 1–3 nm (for details, see ESI†).

Shown in Fig. 1a is an emission intensity trajectory of a single MEH-PPV molecule which displays two intensity levels (red and blue). Fig. 1b (left) and 1c (left) show the corresponding fluorescence images obtained from the red and blue intensity levels, and Fig. 1b (right) and 1c (right) show images fitted using the 2D Gaussians.^{20–22} The trajectories of the centroid positions (Fig. 1d (open circle), 1e (open circle)) were filtered using the C–K algorithm (Fig. 1d (line), 1e (line)).²³ Fig. 1f shows ratios of the Gaussian widths along the *X* and *Y* axes. The red and blue circles in Fig. 1g are filtered centroid

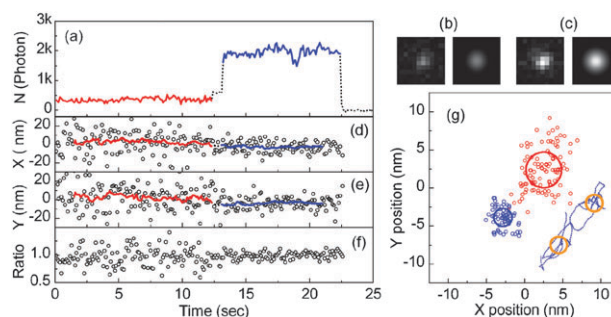


Fig. 1 Analysis of single-molecule fluorescence images of MEH-PPV molecules embedded in a polystyrene matrix. (a) Fluorescence intensity trajectories of a single MEH-PPV molecule. (b, c) (left) Fluorescence images and (right) 2D Gaussian fitting of the images of the (b) dim and (c) bright intensity levels. (d, e) Centroid positions in (d) *X* and (e) *Y* axes obtained from the intensity trajectory. The solid lines show filtered traces using the C–K filter. (f) Ratio of 2D Gaussian width along the *X* and *Y* axes. (g) Filtered Centroid positions obtained from the intensity trajectory. Large circles show positions of emitting sites. The radii of the circles correspond to standard deviations of the centroid positions. (Inset) schematic structures of the molecule. Emitting sites within the molecule are indicated by orange circles.

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positions obtained from the red and blue intensity levels of the trajectory in Fig. 1a. The large circles in Fig. 1g show the average positions of the red and blue centroids and their radii correspond to standard deviations of the centroid positions. The figure clearly shows that the average position of the emission jumps about 7 nm from the red location to the blue location when the emission intensity jumps up from the red to the blue intensity levels.

It is known that the intensity distribution of an emitting molecule depends on its three dimensional orientation.²⁴ In our experimental conditions (N.A. 1.3, pixel size 100 nm), a change of the emitter's 3D orientation would result in a maximum apparent change of the centroid position of about 5 nm.²⁴ However, a change in the dipole orientation would lead to a change in the symmetry of the fluorescence image of the molecule,²⁴ which is not seen here (Fig. 1b, 1c). Furthermore, a change in the dipole orientation would lead to a change in the ratio of the 2D Gaussian width along the *X* and *Y* axes.²⁴ In our experiment, the ratio is nearly constant (Fig. 1f). These results strongly suggest that the observed jumps of the centroid positions are the result of spatial shifts of emitting sites rather than due to changes of the dipole orientation.

The trajectory in Fig. 1a shows two intensity levels, which are indicative of two emitting sites within the molecule. A schematic structure and emitting sites in the molecule are shown as inset in Fig. 1g. Initially, the molecule shows a dim emission. This suggests that one of the emitting sites is temporally photooxidized and acts as a quencher. At about 12–13 s, sudden intensity (Fig. 1a) and position (Fig. 1g) jumps occur simultaneously. This could be interpreted as a recovery of the temporally photooxidized (quenching) site which becomes bright. The net result is a spatial shift of the centroid position of the emission. Those results suggest the presence of two independently emitting sites within the molecule. The high-resolution imaging method visualizes the excited state photodynamics occurring within a single conjugated polymer molecule.

Fig. 2 shows other examples of intensity trajectories. The trajectory displayed in Fig. 2a shows only one emission intensity level that indicates the presence of only one emitting site, probably due to a highly folded conformation of the molecule. Centroid positions obtained from the molecule (Fig. 2c) are localized within a few nanometers and the average position does not show any detectable spatial jump (the schematic structure of the molecule and an emitting site within the molecule are shown in the inset of Fig. 2c).

The intensity trajectory displayed in Fig. 2d shows six intensity levels. The intensity jumps are accompanied by spatial jumps in the average centroid positions. (Fig. 2f). The molecule shows neither changes in the symmetry of the images (see ESI†) nor changes in the ratio of the 2D Gaussian widths along the two axis (Fig. 2e), demonstrating that the jumps of the centroid positions are related to spatial shift of emitting sites. Compared to Fig. 1g, the spatial jumps of the average positions are more ambiguous. The observed multiple emission intensity levels suggest that the molecule has several independently emitting sites, probably due to relatively open conformation (see inset of Fig. 2f for a schematic structure and

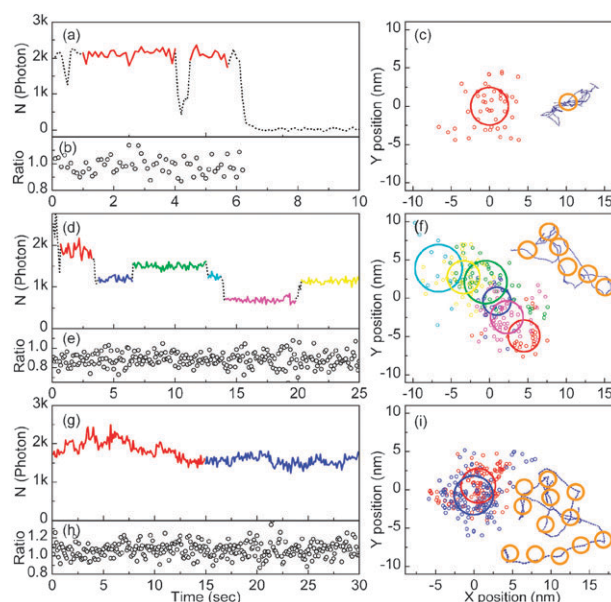


Fig. 2 Relationship between the structure and photophysics of individual MEH-PPV molecules. (a, d, g) Fluorescence intensity trajectories of individual molecules. (c, f, i) Centroid positions obtained from trajectory (a), (d), and (g), respectively. Large circles show positions of emitting sites. The radii of the circles correspond to standard deviations of the centroid positions. (Inset) Schematic structures of the molecule. Emitting sites within the molecule are indicated by orange circles. (b, e, h) Ratio of 2D Gaussian width along *X* and *Y* axis.

emitting sites of the molecule). Thus, temporal photooxidation of one or a few sites has a smaller effect on the overall spatial distribution of the emitting sites compared to a molecule which has only a few emitting sites.

More than a half (131 out of 236) of intensity jumps observed on 91 molecules were accompanied by spatial jumps of the average positions. Since the observed position jumps are the projection of three dimensional distributions of the emitting sites to the *X–Y* plane, the spatial jumps perpendicular to the sample plane can not be detected in the experiments. These results suggest statistically significant correlation between the intensity and position jumps.

An extreme case of this type of a molecule is shown in Fig. 2g. The molecule displays a continuous change in the emission intensity. This type of trajectory was assigned to an open conformation containing a large number of independently emitting sites (see ESI†).¹³ Centroid positions obtained from the molecule do not show any significant spatial jumps (Fig. 2i). The first and second part of the intensity trajectory and the centroid positions are shown in red and blue. The centroid positions of the red and blue data points largely overlap, demonstrating the random distribution of the centroids in time. The nearly constant centroid positions of this type of molecule suggest that there is minimum effect of temporal and/or permanent photooxidation of the chromophores on the spatial distribution of the emitters. This is consistent with previous findings, which suggest the presence of large number of independently emitting chromophores in the molecules.^{12,14,15,17}

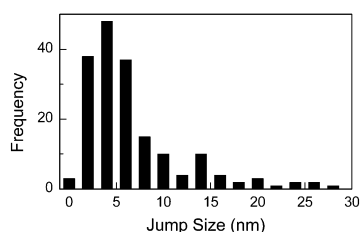


Fig. 3 Frequency histogram of the jump size distribution calculated from the centroid positions.

Previous studies suggested that interchain energy migration is more efficient than the intrachain process. The trap sites are believed to be generated by π - π interaction of the chains.⁸ However, much less is known about the size of the domains in which the efficient energy migration occurs. A temporal quenching of the entire emission of a single conjugated polymer, as well as antibunching behavior¹⁸ indicate energy migration to a single trap site. Those findings together with a gyration radius of MEH-PPV simulated in a good solvent (20 to 40 nm, see ESI†)¹³ indicate that efficient energy funneling occurs on the order of tens of nanometres. On the other hand, other experimental evidence indicates that the energy funneling occurs within a few nanometres.⁵ We analyzed statistically the jump size of the average centroid positions. A histogram of the jump sizes (Fig. 3) shows a peak at around 5 nm. While most of the data points are distributed below 10 nm, a small number of larger jumps (> 20 nm) were also observed. We could not determine the number of emitters in each molecule. This limitation makes it difficult to discuss the jump size quantitatively. Nevertheless, our results clearly demonstrate large distribution of the jump sizes, indicating large distribution of the distances energy can migrate due to the conformational distribution of the polymer, and making the excited state dynamics of conjugated polymers more complicated than expected.²⁵

So far, the ultra-high resolution single-molecule imaging technique has been mainly applied for studying movement of individual, especially protein, molecules.²⁶ Our results demonstrate that the technique is also a powerful tool to study photophysics of synthetic macromolecules which have dimensions of nanometres to tens of nanometres.²⁷ The ultra-high resolution imaging method can be combined with other single-molecule techniques such as fluorescence polarization microscopy and defocused fluorescence imaging,²⁸ and will provide detailed views of photophysics of conjugated polymers as well as physical and chemical properties of polymers.²⁹

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