doi:10.1246/cl.2010.780

Dependence of Single-photon Emission from Single Conjugated Polymer Chains on Their Spatial Size as Determined by Photon-correlation Measurements in Fluid Solution

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Photon-correlation measurements were applied to single chains of poly[2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylene vinylene] of various molecular weights in a fluid solvent in order to investigate the relationship between the probability of single-photon emission and spatial size of the chains. We clearly observed that polymer chains with faster translational diffusion time exhibited a high probability of single-photon emission. This result indicates that the photon antibunching behavior of single conjugated polymer chains is strongly correlated with their spatial size, and that the polymer chains can be made to behave as single-photon sources by controlling the size.

Conjugated polymers are widely used as active materials in a broad range of electronic devices including organic light emitting diodes, photovoltaic devices, field effect transistors, and chemical sensors. One interesting emission property of the conjugated polymers is single-photon emission from a single chain.[1] In recent years, single-photon sources which can emit only one photon at any point in time have been intensively investigated for quantum-information-processing applications. Single-photon emission has generally been observed from single-quantum systems such as single atoms[2] and ions,[3] and single fluorescent molecules.[4] In addition to the single-quantum systems, some multiquantum systems, including multichromophoric dendrimers,[5] molecular assemblies consisting of organic dyes,[6] and quantum dots,[7] have been induced to emit single photons by controlling their size on a nanometer scale. A single conjugated polymer chain is also a multiquantum system because it consists of a number of segments, called chromophores, each of which can absorb and emit photons. Recently, we demonstrated that the probability of single-photon emission from single poly[2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV) chains embedded in host polymer matrices increases with a decrease in the molecular weight (MW) of the chains and on formation of a compact collapsed conformation.[8] These results most probably indicate that the probability of single-photon emission from single chains increases with a decrease in the spatial size of the chains. However, the direct relationship between the probability of single-photon emission and the spatial size of the chains has not yet been determined because the above-mentioned experiments were performed on single MEH-PPV chains embedded in polymer matrices.

In order to reveal the direct relationship, in this present study, we apply simultaneous photon-correlation measurements, namely fluorescence correlation spectroscopy (FCS)[9] and the Hanbury-Brown and Twiss type photon-correlation measurement,[10] to MEH-PPVs with three different MWs dissolved in a good solvent. We demonstrate that the probability of single-photon emission increases with a decrease in the translational diffusion time obtained from FCS measurement. This result indicates that the probability of single-photon emission from single MEH-PPV chains is directly correlated with their spatial size.

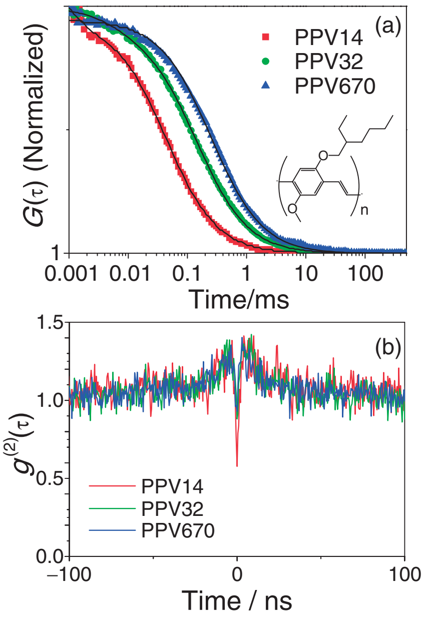

Figure 1. (a) Normalized autocorrelation functions, $G(\tau)$, obtained from chloroform solutions of PPV14 (squares), PPV32 (circles), and PPV670 (triangles). An excitation laser power of 10 μW was applied. Each $G(\tau)$ was calculated from data integrated over 5 min. Solid lines are fitting curves based on eq 1. (b) The autocorrelation function, $g^{(2)}(\tau)$, (i.e., the cross-correlation between two APDs) obtained from the same sample solutions as in (a). Each $g^{(2)}(\tau)$ was determined from a 180 min-integration on the TCSPC module. An excitation laser power of 150 μW was applied. Inset in (a) shows the chemical structure of MEH-PPV.

Three different MEH-PPVs (number average molecular weight $M_n = 5000\,\mathrm{g\,mol^{-1}}$, polydispersity $M_w/M_n \approx 4$, SIGMA-ALDRICH; $M_n = 125000\,\mathrm{g\,mol^{-1}}$, $M_w/M_n = 2.3$, SIGMA-ALDRICH; and $M_n = 2600000\,\mathrm{g\,mol^{-1}}$, $M_w/M_n = 1.5$, Polymer Source; structure shown in Figure 1) were used without further purification. It was estimated that each chain of the above-mentioned MEH-PPVs contained an average 14, 32, and 670 chromophores, respectively, assuming that a single chromophore consists of 15 monomer units.[11] Hereafter, these polymers are referred to as PPV14, PPV32, and PPV670, respectively. Each MEH-PPV was dissolved in chloroform, which is a good solvent for MEH-PPVs, with very dilute concentrations of 10^{-11}–

10^{-12} M in order to observe single polymer chains, and the solutions were injected into homemade glass-bottom petri dishes for measurement.

The photon-correlation measurements were performed using a homemade confocal microscope system consisting of an oil-immersion objective lens (NA: 1.4; UPLSAPO100XO, Olympus). As the excitation light, a circularly polarized beam from a continuous wave (CW) Ar^+ laser (LGK7872M, LASOS) with a wavelength of 488 nm or a picosecond-pulsed diode laser (10 MHz, ca. 100 ps fwhm, LDH-P-C-470B, PicoQuant) of 465 nm was introduced into the microscope. Photons emitted from the single MEH-PPV chains inside the confocal (sampling) volume were passed through a dichroic mirror (FF495-Di02, Semrock) and a 30 μm-pinhole. After passing through a long-pass filter (LP02-514RU, Semrock), the photons were divided into two equal beam paths by a 50/50 beam splitter, and were then detected by two avalanche single-photon counting modules (APDs) (SPCM-AQR-14, Perkin-Elmer). The signals from the two APDs were connected to a time-correlated single-photon counting (TCSPC) module (SPC630, Becker & Hickl) and a digital correlator (ALV-7004/fast, ALV) in order to obtain the cross-correlation between the two APDs and the autocorrelation function. In all the measurements, the focusing point of the excitation laser was located 30 μm above the bottom of the dishes. All experiments were performed at room temperature (22 ± 0.5 °C).

Figure 1a shows the autocorrelation functions, $G(\tau)$, obtained from chloroform solutions of PPV14, PPV32, and PPV670. The obtained $G(\tau)$ shifts to a longer correlation time with an increase in the molecular weight (MW) of the MEH-PPV chain. This indicates that the diffusion times of the MEH-PPV chains (i.e., the hydrodynamic radii of the chains) increases with MW. Generally, $G(\tau)$ is expressed by:[9]

$$G(\tau) = 1 + \frac{1}{N}\left(1 + \frac{p}{1-p}\exp\left(-\frac{\tau}{\tau_T}\right)\right) \times \left(1 + \frac{\tau}{\tau_D}\right)^{-1}\left(1 + \frac{\tau}{w^2\tau_D}\right)^{-1/2} \tag{1}$$

where N is the average number of molecules in the confocal volume, V_{conf}; p and τ_T are the fractional contribution of the off-state (for example, the triplet state in organic molecular systems) and its lifetime respectively; and w is the structure parameter defined by $w = w_z/w_{xy}$. Here, w_z and w_{xy} are the axial length and radius of the cylindrical confocal volume ($V_{\mathrm{conf}} = 2\pi w_z w_{xy}{}^2$), respectively. In our set-up, w_{xy} was determined to be 180 nm on the basis of the diffusion constants of rhodamine 6G ($2.8 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$)[12] and rhodamine 123 ($3.0 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$)[13] measured in water. τ_D is the diffusion time, which is related to the translational diffusion coefficient, D, by

$$\tau_D = \frac{w_{xy}{}^2}{4D} \tag{2}$$

Equation 1 shows that $G(\tau)$ is influenced by the contribution of the off-states. It was demonstrated for colloidal quantum dots that the shape of $G(\tau)$ depends on the excitation laser power,[14] and that the $G(\tau)$ obtained by applying high excitation laser power could not be fitted by eq 1 because of strong blinking behavior that exhibits a power-law distribution in the off-times. The present MEH-PPVs have a similar dependences on excitation power; hence, the $G(\tau)$ shown in Figure 1a were measured by applying a low excitation power (10 μW) to ensure that there was not a large contribution from the off-states. The fitting curves based on eq 1 are good agreement to the experimental data. By analyzing $G(\tau)$ using eqs 1 and 2, D of 58.3 ± 19.1, 25.4 ± 3.0, and 13.8 ± 3.1 $\mathrm{\mu m^2\,s^{-1}}$ were estimated for PPV14, PPV32, and PPV670, respectively. The hydrodynamic radius (R_H) of each MEH-PPV chain was calculated to be 7.3 ± 2.9, 15.1 ± 1.6, and 28.7 ± 2.6 nm for PPV14, PPV32, and PPV670, respectively, from the obtained D on the basis of the Stokes–Einstein model (eq 3).

$$D = \frac{kT}{6\pi\eta R_H} \tag{3}$$

Here, k is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of solution. Because of very diluted solution, the viscosity of solvent was used as η for the calculation.

Figure 1b shows the autocorrelation function, $g^{(2)}(\tau)$, (i.e., the cross-correlation between the two APDs) obtained from the same sample solutions as those used for the FCS measurement. An excitation laser power of 150 μW was applied to generate multiple excitons in the single MEH-PPV chains. In this correlation function, a decrease in the correlation function minimum at time 0, $g^{(2)}(0)$, indicates an increase in the probability of single-photon emission. The dip at time 0 for PPV14 is clearly deeper than those of the other two MEH-PPVs. $g^{(2)}(0)$ for PPV14, PPV32, and PPV670 in Figure 1b were estimated to be 0.58, 0.88, and 0.93, respectively. These results clearly indicate that the probability of single-photon emission from PPV14, which has the lowest MW, is higher than those from the other two MEH-PPVs, and that the probability strongly depends on the spatial size of the MEH-PPV chains. It should be noted that $g^{(2)}(0)$ for mobile single chromophores in solution is larger than that from fixed single chromophores because of the very large contribution of background counts. In fact, $g^{(2)}(0)$ obtained from single rhodamine 123 molecules in water (10^{-10} M) under the same experimental conditions was 0.34. Hence, it is considered that the actual probability of single-photon emission is higher than the $g^{(2)}(0)$ obtained in the present fluid solvent. In addition, each $g^{(2)}(\tau)$ was measured with a time resolution of 0.49 ns (a time window of 500 ns per 1024 channels of the TCSPC module, and the time resolution is limited to several hundreds of picoseconds by the time jitter of APDs). The emission lifetime of the MEH-PPVs in chloroform (10^{-8} M) was measured by a streak scope in conjunction with femtosecond pulsed laser excitation and was found to be ca. 0.3 ns for three MEH-PPVs. Therefore, some antibunching events were lost in the obtained $g^{(2)}(\tau)$, but this should not affect the trend of single-photon emission on MW because the lifetimes of these MEH-PPVs are almost the same.

In addition to the above CW excitation measurements, $g^{(2)}(\tau)$ of these MEH-PPVs were measured under pulsed laser excitation. Figure 2 shows the photon correlation histograms. It shows that coincidence events at time 0 clearly decrease with decreasing MW. $g^{(2)}(0)$ (which here is the ratio of the number of detection events around time 0 to that around other times) was calculated to be 0.41, 0.80, and 1.0 for PPV14, PPV32, and PPV670, respectively. These results clearly indicate again that the probability of single-photon emission from PPV14 is higher than those from the other MEH-PPVs. In other words, the

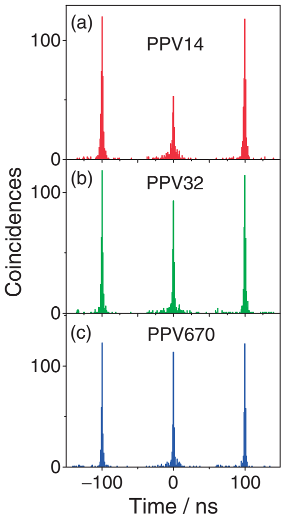

Figure 2. Photon correlation histograms obtained from chloroform solutions of (a) PPV14, (b) PPV32, and (c) PPV670 under pulsed laser excitation. The sample solutions are same as those used in the CW excitation measurements. An excitation laser power of 100 µW was applied. Each histogram was determined from a 60 min-integration time on TCSPC module.

probability of single-photon emission increases with a decrease in the spatial size of the MEH-PPV chains.

The present results indicate that even if MEH-PPV chains adopt extended conformation in a good solvent, only the polymer chains of PPV14 with the lowest MW exhibit single-photon emission behavior because of the small spatial size. This trend is similar to that for single MEH-PPV chains embedded in a host polymer matrix of polystyrene (PS), which was reported previously by us.[8] When MEH-PPV chains were embedded in PS and in poly(methyl methacrylate) (PMMA), only PPV14 exhibited single-photon behavior, whereas PPV32 exhibited single-photon behavior only in PMMA, but not in PS. In the previous report, we attributed this difference to chain conformation. For single-photon emission behavior of multiquantum systems including conjugated polymers, efficient exciton–exciton annihilation processes are important,[15] because the sequential annihilation processes give one exciton in the single chain. MEH-PPV chains adopt a more extended conformation in PS than in PMMA judging from solubility parameters. In the extended conformation, exciton migration and exciton–exciton annihilation along the polymer backbone are dominant, while three-dimensional intrachain exciton processes (not only along the polymer backbone but also between closely stacked segments in a same polymer chain) is possible in the collapsed conformation. Therefore, since exciton–exciton annihilation is less efficient in the extended conformation than in the collapsed conformation, polymer chains with the extended conformation tend to decrease in the probability of single-photon emission with increasing MW. That is, a decrease in the spatial size of the MEH-PPV chains results in an increase in the probability of single-photon emission. The present results support this explanation.

In summary, photon-correlation measurements were applied to MEH-PPV chains with different MWs in chloroform. The translational diffusion time decreased with an increase in the MW of the MEH-PPV, indicating that the spatial size of the chains increases with MW. The MEH-PPV chains with a small spatial size exhibited a high probability of single-photon emission. These results clearly indicate that the multiquantum systems consisting of a large number of chromophores can be made to behave as single-photon sources by appropriately controlling their size.

This work was partly supported by a Grant-in-Aid for Young Scientists (B) (No. 20710086) and a Grant-in-Aid for Scientific Research in the Priority Area "Super-Hierarchical Structures" from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT); and by PRESTO from Japan Science and Technology Agency (JST).

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