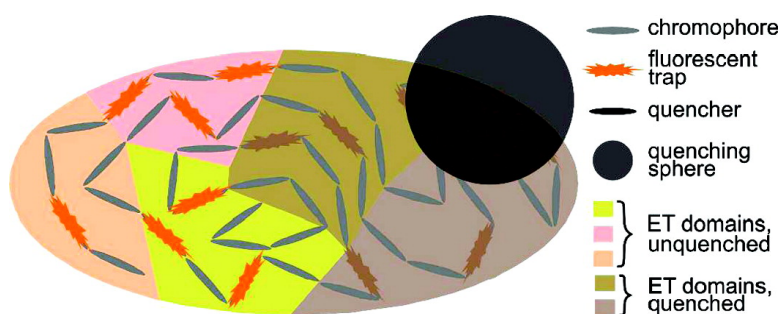Article

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Fluorescence Blinking, Exciton Dynamics, and Energy Transfer Domains in Single Conjugated Polymer Chains

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Abstract: In order to understand exciton migration and fluorescence intensity fluctuation mechanisms in conjugated polymer single molecules, we studied fluorescence decay dynamics at "on" and "off" fluorescence intensity levels with 20 ps time resolution using MEH-PPV [poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] dispersed in PMMA. Two types of intensity fluctuations were distinguished for single chains of conjugated polymers. Abrupt intensity fluctuations (blinking) were found to be always accompanied by corresponding changes in fluorescence lifetime. On the contrary, during "smooth" intensity fluctuations no lifetime change was observed. Time-resolved data in combination with data on fluorescence emission and excitation anisotropy lead to a picture where a single polymer molecule is seen as consisting of several energy transfer domains. Exciton migration is efficient within a domain and not efficient between domains. Each domain can have several emitting low-energy sites over which the exciton continuously migrates until it decays. Emission of individual domains is often highly polarized. Fluorescence from a domain can be strongly quenched by Förster energy transfer to a quencher (hole polaron) if the domain overlaps with the quenching sphere.

1. Introduction

Conjugated polymers (CPs) or so-called organic semiconductors are important materials for organic electronics[1,2] and biodetection.[3–5] Understanding fundamental mechanisms behind their optical and electronic properties[6] is difficult due to complicated intra- and intermolecular interactions in these materials. All these interactions are dependent on material morphology on a nanometer scale,[7] leading to a huge diversity of the properties of individual CP molecules. This diversity is ensemble-averaged in traditional spectroscopy of bulk samples like films and solutions. Therefore, it is important to study conjugated systems at the individual chain/nanoparticle level.[8] Since 1997,[9] conjugated polymers have become the systems intensively studied by single molecule spectroscopy (SMS) techniques.[6,10]

If a polymer chain was ideal and free of defects, the excited state (exciton) would be delocalized over the whole chain regardless of its length at 0 K. For a situation close to that, see ref 11. However, in reality, the presence of static and dynamic disorder (including chemical defects) leads to localization of the excited state.[12] For the poly(phenylene vinylene) (PPV) family of CPs, exciton is localized on 5−10 monomer units (3−6 nm in length). Therefore, a single CP chain with molecular weight of several tens of kilodaltons or more can be seen as an ensemble of hundreds of weakly coupled chromophores.[13] Studying such an ensemble of chromophores by SMS methods may appear futile, since the inevitable averaging over so many chromophores could be expected to make all CP chains behave very similarly. However, it has turned out that CP molecules keep their individuality and behave in many senses in the same way as such classical objects of SMS as organic dyes and quantum dots, showing broadly distributed fluorescence spectra, fluorescence blinking, and fluorescence spectral diffusion, etc.[10,14–22]

A generally accepted model for this "individuality" exploits an idea that the whole ensemble works as an antenna for excitation light, but only very small parts of it (a few chromophores or even a single one) are responsible for the light emission as a result of efficient downhill energy migration (funneling). Such a part is called a "low-energy segment" or

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an "exciton trap".[10,23,24] This idea has been utilized in almost every paper concerning SMS of CPs since 1997.[9] Although in other multichromophoric systems the concept of energy funneling to the chromophore with the lowest energy often works very well,[25] its direct generalization to such "bulky" complex systems of unknown topology as CP isolated chains seems not fully appropriate. It has turned out that the photophysical behavior of a polymer single molecule depends strongly on its particular organization.[26–28] The important factors include molecular weight, the number of chemical defects,[29] the solvent in which the polymer was initially dissolved,[26,27] and whether or not[20] the molecule is embedded in an inert polymer matrix and the type of the matrix.[28]

To explain the blinking effect, it was proposed that the exciton migration is so efficient that an exciton can reach a quencher site from any place in the polymer chain.[24] What is important here is the ratio between the energy migration radius and the size the polymer chain occupies in space. Basically, making the chain more compact results in a more efficient exciton quenching due to facilitating of exciton hopping between more tightly packed segments and shortening of migration distance required to reach the quencher.[27]

In the above description, we have not said anything about the quencher itself. What is the interaction radius between the exciton and the quencher? In other words, how close must the exciton come to the quencher in order to be quenched? In the original works by the group of Barbara,[23] the exciton–quencher interaction was considered to be local, meaning that direct "collision" between the two is required for quenching to occur. Therefore, the exciton migration efficiency alone was responsible for quenching. Later on it was suggested that a charge transfer state like polymer$^+$/O$^-$ (a hole polaron sitting on the chain) is an efficient quencher;[24] however, again the radius of quenching was not discussed.

Already before SMS was applied to CP, a large body of literature concluded that polarons are effective exciton quenchers.[30–32] The quenching itself occurs via a Förster

energy transfer (ET) mechanism because polaron transition possesses large dipole moment and the ET is a spin-allowed process (the same as, for example, singlet–tripet annihilation) (see ref 6 and references therein). Exciton quenching by Förster ET to polarons was suggested to explain the effect of an applied electric field to single PPV nanoclusters (aggregates).[33] Fluorescence blinking of individual MEH-PPV [poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] chains was assigned to long-range ET to photogenerated polarons[18] and confirmed by experiments using an electric field.[34–37]

Therefore, the blinking behavior cannot be considered alone as a solid proof of extraordinary efficient exciton migration over a polymer chain. Indeed, similar blinking effect occurs even at low temperature (77[18] and 15 K[38]) when exciton migration must be substantially suppressed.[39–41] By using the quenching act as a probe of exciton migration, one cannot say how exciton is migrating when the quencher is not there.

Despite the general belief that the quenching act happens on a time scale much shorter than the exciton lifetime (otherwise, the quenching is not efficient), no direct experimental proof has been presented. The only data available in the literature on fluorescence lifetime in the "off" state[24] could not resolve this fast process. The authors proposed that the "irresolvable" part belonged to a component much faster than 50 ps. However, it is known that the fluorescence intensity in some cases can decrease without corresponding lifetime change due to, for example, increasing of generation yield of charged species against single exciton generation[42–44] or reorientation of the emitting transition dipole moment.[45] Therefore, an accurate study of the correlation between fluorescence lifetime and fluorescence intensity of a single polymer molecule is needed. Similar studies have been done to unravel the blinking mechanism in inorganic quantum dots.[46,47]

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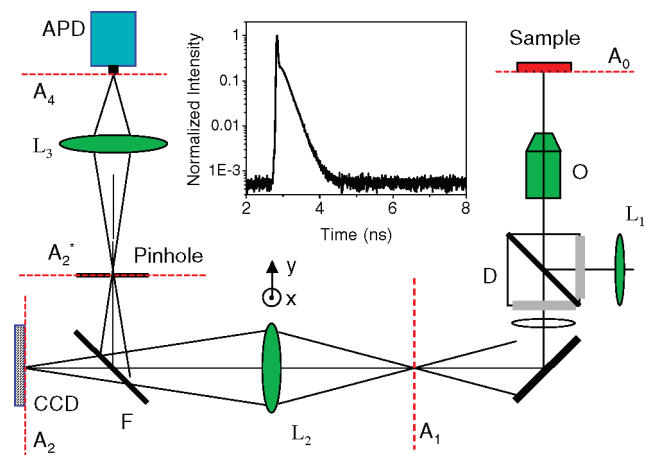(47) Schlegel, G.; Bohnenberger, J.; Potapova, I.; Mews, A. *Phys. Rev. Lett.* **2002**, 88.

Figure 1. Experimental setup for time-resolved measurements. O, objective lens; D, dichroic mirror and filters; F, flipping mirror; L₂, motorized lens. Inset: instrumental response function measured at 460 nm.

In the present contribution, we will present unambiguous data on the fluorescence decay dynamics of single chains of MEH-PPV dispersed in a PMMA matrix measured at different stages of their fluorescence intensity fluctuations. For the first time, anisotropy of absorbing states and emitting states will be compared for the same single molecules of MEH-PPV. Topology of polymer chains will be discussed in relation to observation of the fluorescence polarization changes upon intensity fluctuations. Although it is impossible to explain the properties of all single chains within the framework of one model, we will demonstrate that at very first approximation most of the polymer molecules can be seen as consisting of several independent energy transfer domains.

2. Experimental Section

MEH-PPV (M_n = 150 000–250 000) was purchased from Sigma-Aldrich and the polydispersity index was determined to be 5.0 by GPC. MEH-PPV solutions of appropriate concentration (~3 × 10⁻⁷ g/L) were prepared by dissolving the polymer in a solution of 10% PMMA [poly(methyl methacrylate), M_w = 996 000, Sigma-Aldrich] in toluene. The solution was spin-cast onto a quartz or silicon/silicon oxide substrate to yield a uniform film with a thickness of about 200 nm.

A home-built wide-field fluorescence microscope setup based on an Olympus IX-71 inverted microscope and a CCD camera with on-chip multiplication gain (Photometrics, Cascade 512B) was used to study MEH-PPV at single molecule level. For steady state measurements the sample was excited by CW Ar ion laser at 458 or 514 nm. For time-resolved measurements, we used excitation by the second harmonic of a 150 fs pulse from a Ti-Sapphire laser (Tsunami, 80 MHz repetition rate) with spectral maximum at 916 nm. The light of the second harmonic (spectral maximum at 458 nm) was passing through the same set of filters ("filter cube") as the light of the 458 nm Ar ion laser line, resulting in excitation spectrum with maximum at 458 nm and ≈10 nm spectral width.

A long working distance objective lens (Olympus LUCPlanFl 40×, NA 0.6) allowed imaging of the sample through a 1 mm thick window of a vacuum chamber (10⁻² Torr) in which the sample was always situated for room-temperature experiments. Low-temperature experiments were carried out using a Janis ST-500 microscopy cryostat. Lens L₁ (Figure 1) was used to defocus the excitation beam, giving an excitation spot of ~30 μm in diameter at the sample plane. Typical excitation power was 80 W/cm² or less. Lens L₂ imaged the sample to the CCD camera (image plane A₂). The total magnification of the system was 80×.

By flipping the mirror (Figure 1) the image could be obtained at the pinhole plane (A₂*). By adjusting the position of the lens L₂ in the plane perpendicular to the optical axis the image XY position could be tuned so that the fluorescence light from a molecule of interest passed through the 100 μm pinhole. The fluorescence photons were then detected by a fast avalanche photodiode (APD, Micro Photon Devices, crystal size 100 μm, 250 cps dark counts) and counted by a PicoHarp 300 (PicoQuant GmbH) photon counting system. This system operating in time-correlated single photon counting regime had a response function of about 50 ps [see Figure 1 inset for the instrumental response function (IRF) measured at 460 nm]. Unfortunately, the shape of the IRF depends on the wavelength of the photons detected by the photodiode (stronger tail for shorter wavelengths). Therefore, the IRF shown in the figure could not be used directly to fit the fluorescence decays of single molecules emitting in a different spectral range. The IRF was corrected (its tail was partly suppressed) to give satisfactory monoexponential fits to fluorescence kinetics of dye solutions, which are known from literature to decay monoexponentially.[48] Due to the tail of the IRF, a monoexponential decay with a time constant longer than 300–400 ps has a maximum at ca. 50–100 ps after the start pulse, a purely numerical effect. Time-tagged time-resolved (TTTR) mode was used to detect absolute arrival times of all photons together with synchronization pulses from the laser in order to obtain fluorescence decay kinetics and fluorescence intensity at any given time of the fluorescence transient measurement.

To perform polarization-sensitive experiments, a λ/2 waveplate was placed into the linearly polarized excitation beam and a polarization filter (analyzer) was set in front of the CCD camera. A Berek polarization compensator was used to maintain the linear polarization of the excitation light at the sample plane after it passed the dichroic mirror and filters. By rotating the λ/2 plate with a step motor (rotation frequency ≈ 0.125 Hz) the polarization angle of the excitation light (φ_{ex}) was rotated in the sample plane. The analyzer angle (φ_{fl}) was also rotated by another motor with approximately 10 times lower frequency. As a result, fluorescence intensity as a function of angles φ_{ex} and φ_{fl} was measured. To the best of our knowledge, such a technique of continuous polarization rotation both in excitation and fluorescence paths has not been used in single molecule spectroscopy earlier. More details about the technique will be reported elsewhere. This two-dimensional function, $I(\varphi_{ex}, \varphi_{fl})$, contains all the information about polarization properties of an investigated molecule. For example, we can extract information about polarization anisotropy in excitation of a molecule by averaging $I(\varphi_{ex}, \varphi_{fl})$ over φ_{fl}: $I_E(\varphi_{ex}) = \frac{1}{\pi}\int_0^\pi I(\varphi_{ex}, \varphi_{fl})\,d\varphi_{fl}$. This function is equivalent to that obtained in experiments where linear excitation polarization is rotated and there is no analyzer in the fluorescence path.[29] Analogous averaging over φ_{ex} can be performed to obtain the fluorescence intensity $I_F(\varphi_{fl})$ modulated due to fluorescence anisotropy under circularly polarized excitation (see below). It is worth noting that for any kind of photoluminescent multichromophoric system both $I_F(\varphi_{fl})$ and $I_E(\varphi_{ex})$ have the functional form $\propto 1 + M\cos(2(\varphi - \varphi_0))$, where $0 \le M \le 1$ and $0 \le \varphi_0 \le \pi$ are the polarization modulation depth and phase, respectively. Modulation depth of fluorescence (M_F) and excitation (M_E) can thus be obtained from $I_F(\varphi_{fl})$ and $I_E(\varphi_{ex})$, respectively. We also did direct measurements of $I_F(\varphi_{fl})$ by using circular polarized excitation light (section 3.4).

3. Results and Discussion

3.1. Fluorescence-Intensity Transients and Fluorescence Decays. Up to 105 individual MEH-PPV molecules were studied by TTTR technique. The fluorescence-intensity transients of three representative molecules (molecule **1**, **2**, and **3**) are shown in Figures 2A, 3A, and 4A, respectively. The intensity transients

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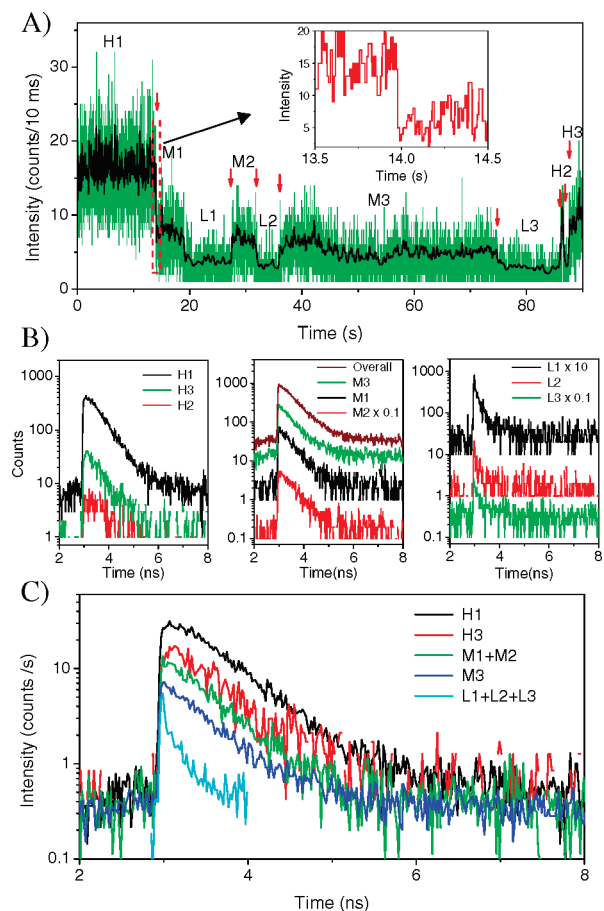
Figure 2. Single molecule **1**: (A) Green line, fluorescence time transient with 10 ms bin size; black line, 100 points FFT smoothing of the time transient. The transient was divided into a series of periods according to the average intensity level (H, high intensity; M, medium intensity; L, low intensity). (Inset) Enlargement of the transient upon intensity change. (B) Fluorescence decay curves for different periods. (C) Decays of fluorescence intensity (count/s) for different periods (see the text).

(green lines) were obtained by counting the number of photons arriving within 10-ms bins. The background level was about 2 counts per 10 ms and mostly originated from the APD dark counts. The transients were manually divided into a series of periods according to their intensity levels (high level, H1, H2, ...; medium level, M1, M2, ...; and low level, L1, L2, ...). Two different types of intensity changes were observed: one occurred abruptly within 10 ms (Figures 2 and 3), while the other happened much more slowly on a time scale of ~1 s (Figure 4).

Single photon counting fluorescence decay histograms (for example, see Figure 2B) were generated separately for every period and then fitted by single- and/or double-exponential functions. Furthermore, by dividing the total number of photon counts by the collection time (the length of the period), decays of fluorescence intensity (counts/s) were obtained (see Figures 2C, 3B, and 4B). Note that the intensity fluctuations within each period were mainly due to shot noise, and the fluorescence lifetime was confirmed to be constant during each chosen period.

3.1.1. Abrupt Intensity Fluctuations (Blinking) Accompanied by Changes in Fluorescence Decay Kinetics. Figures 2 and 3 represent abrupt changes in the fluorescence intensities of single molecules. For example, from H1 to M1 (Figure 2A, inset), the fluorescence intensity of molecule **1** dropped from ~15 to ~5 counts in a single step (i.e., within 10 ms). Such sudden
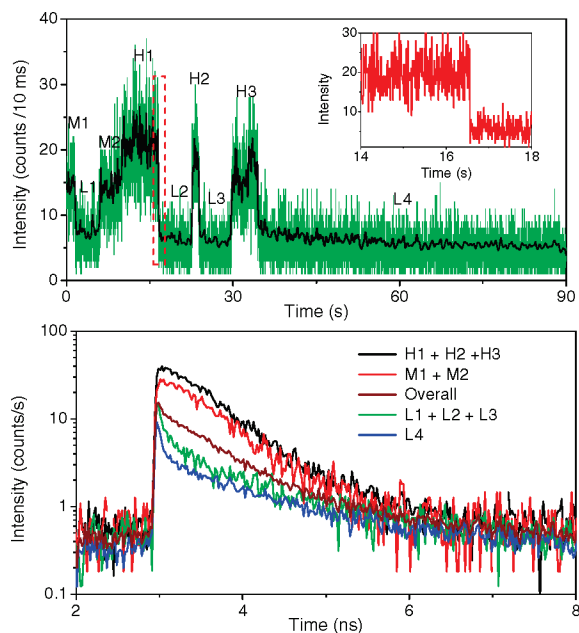

Figure 3. Single molecule **2**: (A) Fluorescence time transient with 10 ms bins (green line) and the same transient after smoothing (black line). Inset: enlargement of the transient upon abrupt intensity change. (B) Decays of fluorescence intensity (count/s) for different periods.
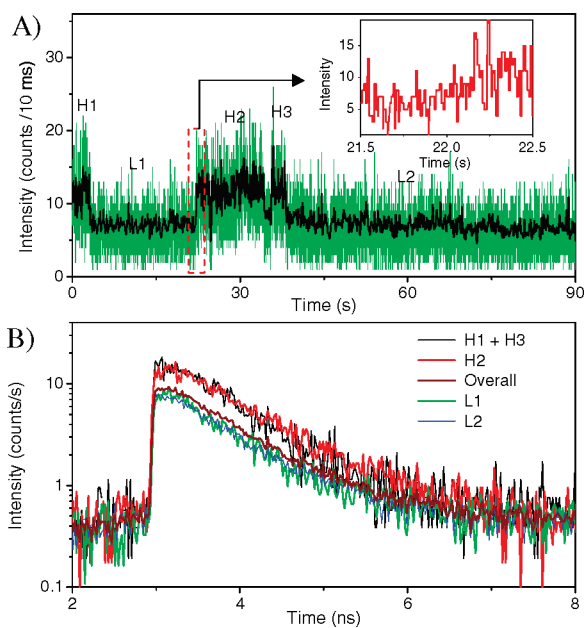

Figure 4. Single molecule **3**: (A) Fluorescence time transient with 10 ms bins (green line) and the same transient after smoothing (black line). (Inset) Enlargement of the transient upon intensity change. (B) Decays of fluorescence intensity (count/s) for different periods.

changes (indicated by red arrows) were found between every two neighboring periods in Figure 2A.

The decays for the nine periods in Figure 2A were classified into three groups according to their relative intensity levels (Figure 2B). Interestingly, the decay curves within each group possess nearly the same profile, suggesting a strong correlation between fluorescence dynamics and the intensity levels in molecule **1**. Fluctuation of fluorescence dynamics was also observed in molecule **2** (Figure 3) and other single MEH-PPV molecules upon abrupt intensity changes (blinking).

Table 1. Fitting Parameters[a] for the Fluorescence Kinetics of Molecule **1** (Figure 2)

period	A_1	τ_1 (ps)	A_2	τ_2 (ps)	χ^2
H1 (1exp)	1	600	—	—	1.01
H3 (1exp)	1	580	—	—	1.03
M1 (1exp)	1	352	—	—	1.07
M1 (2exp)	0.494	583	0.506	60	1.02
M2 (1exp)	1	376	—	—	1.06
M2 (2exp)	0.537	604	0.463	52	1.01
M3 (1exp)	1	314	—	—	1.12
M3 (2exp)	0.538	590	0.462	70	1.01
L1 (2exp)	0.056	537	0.944	40	1.002
L3 (2exp)	0.088	808	0.912	75	1.03

[a] Parameters of single (1exp) or double (2exp) exponential fits to the fluorescence decays: τ_1 and τ_2 are the lifetimes, and A_1 and A_2 are the pre-exponential factors ($A_1 + A_2 = 1$), respectively. For periods H1 and H3, good single-exponential fits were achieved. The fitting parameters for H2 and L2 are not listed because of insufficient photon counts.

The fluorescence dynamics at different blinking states (intensity levels) will be described in detail below.

High-Intensity Levels—Monoexponential Decay. All the fluorescence kinetics for the high-intensity periods (H1, H2, and H3) in molecule **1** can be fitted by single-exponential decay function, giving the same lifetime (~600 ps) within the limit of experimental errors (Table 1). Remarkably, monoexponential fluorescence decay dynamics were also observed in molecule **2** and in all the other single MEH-PPV molecules at quencher-free state (high intensity level) including in some stable nonblinking molecules. One can explain this monoexponential decay behavior by assuming that all the emitted photons came from one emitting species or several emitting species with similar lifetimes.[23]

It is well-known that the fluorescence lifetime of a chromophore depends strongly on its length (N). According to the exciton model,[12,49,50] the radiative lifetime decreases almost linearly with increasing N for $N > 5$ monomer units. PPV oligomers in solution show monoexponential fluorescence decay dynamics.[51] Radiative lifetime changes from 2.7 ns for trimer to 1.25 ns for hexamer.[51] Fluorescence lifetime also decreases with length (1.7 ns for trimer and 0.52 ns for hexamer). If a quencher interacting with excited molecules by long-range Förster mechanism is added to the solution, the fluorescence kinetics becomes nonexponential.[39] Therefore, the nonradiative component most likely originates from internal conversion and intersystem crossing.

Typical lifetimes measured for MEH-PPV in good solvents are in the range of 0.2–0.5 ns,[52–54] while in films and poor solvents decays become nonexponential with the main component around 0.3 ns.[44,54] In our experiments, MEH-PPV single molecules being at a high intensity level showed monoexponential behavior with lifetimes in the range of 0.4–1.2 ns. These lifetimes are shorter than those reported recently for very short individual MEH-PPV chains (1.2–1.4 ns).[55] This difference might be due to short chains mainly consisting of short chromophores with relatively long lifetimes.

Medium- and Low-Intensity Levels—Fast Component Appears. We first fitted the decay curves for the M periods of molecule **1** by single-exponential function, resulting in shorter lifetimes than those for the H periods (Table 1). However, the fits (not shown) were not satisfying for the initial part of the decays, as reflected by the goodness-of-fit parameter (χ^2) shown in Table 1. While the decay curve for each H period had a maximum at ca. 100 ps after the start pulse ($\Delta t = 0$) due to the shape of the IRF (see Experimental Section), the decay curves of the M periods reach their maxima just after the start pulse (Figure 2B,C), implying the existence of a fast decay component as a result of exciton quenching. The lifetime for this fast component ($\tau_2 = 50-70$ ps) was obtained by fitting the decay curves for M periods by double-exponential functions. At low-intensity periods (L1, L2, ...), the fast component became more prominent, providing the possibility for a more accurate fit (Table 1). Control measurements confirmed that this fast component was not from any possible artifacts such as light from impurities in the matrix, background fluorescence, and direct light from the excitation laser pulse.

The long decay components for the M periods were very similar in lifetime to the monoexponential decays during the H periods. Thus, the decays for the M periods can be regarded as intermediate between those for H and L periods. Note that the decay curves generated from all photons (regardless of the intensity level) have very similar profiles to those from the M periods, as shown in Figure 2B.

Molecule **2** showed a similar distinctive fast decay component (70 ps) upon abrupt intensity drops (Figure 3). However, contrary to molecule **1**, the slow component at off states (L periods) showed a substantially longer lifetime (1150 ps) than that for H periods (730 ps). This long lifetime component might result from unquenched chromophores with shorter conjugation lengths or from disordered H-aggregates (see ref 56 and references therein). On the other hand, the long tail may also be related to delayed fluorescence due to exciton formation via recombination of initially created charge-separated species.[41,43,44] Among the examined molecules, only eight showed such long lifetime component in blinking-off state.

A fast fluorescence decay component could always be observed in single MEH-PPV molecules upon abrupt emission intensity drop. With the limit of our time resolution, its lifetime varied in the range of 20–120 ps for different molecules, with a distribution centered around 50 ps.

More than a half of the investigated molecules (~54%) possessed medium intensity levels similar to those of molecule **1**. The coexistence of a fast fluorescence decay component and unaffected component at medium intensity levels gives a picture as follows: the quenching efficiency is close to unity for a fraction of chromophores, while almost zero for the others. It is interesting to understand why a part of a polymer chain could remain unaffected while the other parts are being quenched entirely. A simple explanation is that the unaffected chromophores are far away (spatially separated) from the quencher. On the other hand, some chromophores may avoid being

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quenched even if they are close to the quencher due to unfavorable orientation, mismatched energy levels, or the presence of a competing energy-transfer pathway leading to another energy trap rather than to the quencher.

3.1.2. Smooth Intensity Fluctuations Not Accompanied by Fluorescence Decay Change. For molecule **3**, much slower fluorescence intensity changes (happened during ~1 s) were observed (Figure 4A, inset). Note that such slow intensity changes were still fast enough to appear like "blinking" when looked at on the time scale of seconds. To distinguish from abrupt blinking considered above, from now on we term this kind of slow changes as "smooth fluctuations". Investigation of the fluorescence decays for molecule **3** gave much different results to those of molecules **1** and **2**. Single-exponential decay kinetics were found for all the periods (Figure 4B). The lifetime was constant during the whole measurement, despite of the large fluctuations in the emission intensity. This result suggests that abrupt changes and smooth fluctuations were induced by very different mechanisms.

3.1.3. Direct Correlation between the Intensity Fluctuation Type and the Presence of Excited-State Lifetime Change. Among the studied single MEH-PPV molecules, 87 molecules (~83%) showed abrupt intensity fluctuation (blinking), and 17 molecules (16%) showed "smooth fluctuations" (13 molecules showed both behaviors). We found that an abrupt change of fluorescence intensity was always accompanied by appearance (when intensity dropped down) or disappearance (when intensity jumped up) of a fast decay component, while for a smooth intensity fluctuation, no change in fluorescence decay (no resolvable fast component) could be observed.

Note that several single molecules (~8%) showed gradual and irreversible decrease (bleaching) of fluorescence intensity during the measurements. We did not see any fluorescence lifetime change in such cases either. If the bleaching resulted from generation of permanent quenchers, some changes in the lifetime (i.e., appearance of fast decay component) should have been observed. Therefore, the gradual bleaching processes can be seen as "destroying" the light-absorbing chromophores without creating any quenchers.

The large polydispersity in molecular weights of MEH-PPV could in principle result in a very broad distribution of fluorescence behaviors. However, our ongoing work confirms that the reported trends of fluorescence kinetics can be observed for MEH-PPV molecules of very different molecular weights.

3.1.4. The Origin of Smooth Intensity Fluctuations. Although the blinking effects in single conjugated polymer molecules have been addressed in many reports, only a few of them have discriminated between abrupt changes (distinct drops and jumps) and slow changes (smooth fluctuations). Huser et al. noticed that fluorescence intensity decreased gradually for single MEH-PPV molecules spin-cast from chloroform, while those spin-cast from toluene showed discrete intensity changes (blinking).[26] In a series of work by Fann et al. on single molecules of DOO-PPV, a polymer with a structure very similar to MEH-PPV, both single-step (intensity changed greatly within 10 ms) and multistep (small changes in each step) fluorescence intensity drops were observed. In all the above-mentioned work, the gradual intensity drops were attributed to one-by-one (or few-by-few) bleaching of chromophores in single polymer molecules, leading to relatively smooth fluorescence intensity decrease. In contrast, molecule **3** and its analogues showed both gradual decrease and gradual increase in emission intensity. As far as we know, such smooth intensity fluctuation in single conjugated

polymers has not been reported earlier. Attention has already been paid to smooth intensity fluctuations in PPV single nanoaggregates;[33] however, no lifetime data were given at that time.

It is difficult to find an explanation for smooth intensity fluctuations. As soon as we see the same monoexponential behavior upon fluctuations, the idea of variable efficiency of quenching[33] can be ruled out. Unchanged kinetics of the emitting states unambiguously indicates that the reason for smooth intensity fluctuations must originate from processes happening at light absorption and exciton generation stages. In this case, we can distinguish two possible reasons for reduced emission intensities: (1) changing of singlet excitons generation efficiency by light excitation and (2) changing of the absorption at the excitation wavelength. Rothberg and co-workers have proposed that direct photogeneration of charge-separated species instead of singlet excitons (branching effect) can occur in tightly packed regions of MEH-PPV films.[41,44] The branching effect can be more distinctly observed when the packed regions are directly excited by low-energy photons. One would then expect non-exponential decays because of delayed exciton formation via charge recombination. In the present case, the branching effect seems unlikely, since rather high photon energy excitation was used and single-exponential decays were obtained (we excited at 458 nm while the MEH-PPV film absorption has a maximum around 510 nm). Therefore, the smooth fluctuations were much likely caused by slow changes in the absorption of the molecule.

Fluorescence intensity fluctuations without lifetime change have been observed for single dye molecules.[57] A possible reason for such fluctuations is changing of the orientation of the dye in a matrix during the measurements.[45,58] This can change the light absorption efficiency (especially if the excitation light is linearly polarized) and emission detection efficiency when the emission transition dipole moment rotates out from the sample plane[59] and the numerical aperture of the objective lens is not very high. In order to apply this idea, one has to assume that a polymer chain as a whole can rotate substantially. This is unlikely because it is "fixed" in the surrounding inert polymer matrix under temperatures much lower than the matrix glass transition temperature. However, we cannot exclude changing of the angular light emission diagram of a polymer molecule as a reason for slow intensity fluctuations (see section 3.3).

Absorption spectral diffusion can be considered as another possible explanation of smooth fluctuations. A fluorescence spectral diffusion with typical amplitude 500 cm^{-1} has been reported for MEH-PPV at low temperature.[20,60] Unfortunately, there is no data available about absorption spectra of single polymer molecules. However, there is no reason to think that the density of light absorbing states is time-independent.[21] Due to interaction between neighboring chromophores in tightly packed regions, the density of states must include both excited states of individual chromophores and excited states delocalized over several chromophores like what happens in J and H aggregates (Frenkel type of exciton states, see e.g. ref 56 and references there in). These delocalized states are extremely

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sensitive to the slightest rearrangement of the polymer chain, which can be caused by thermal fluctuations or photochemical disturbance of the chain. Therefore, absorption spectral diffusion can account for observed slow intensity fluctuations with constant fluorescence lifetime. However, we have to admit that more research is needed to understand the origin of this phenomenon.

3.2. Correlations between Excitation Anisotropy and Emission Anisotropy. ET between chromophores can be monitored to a certain extent by comparing arrangements of absorbing and emitting chromophores in individual polymer chains. Independent excitation polarization[29,61–63] and emission polarization[19,27,28,64] measurements have been performed for single conjugated polymers since several years ago. However, in order to see the correlations between organization of absorbing and emitting chromophores, single-molecule excitation and emission polarizations have to be measured simultaneously for the same molecules. Only a few such works have been reported in the literature.[14,65–67] Lupton et. al monitored the energy transfer processes between a conjugated polymer and an energy accepting dye by probing both the excitation and emission anisotropies of individual molecules.[14] The polymer in their studies (a polyindenofluorene derivative) had a relatively short and rigid backbone so that the polarization data could be well-assigned to different backbone conformations and quite clear energy redistribution schemes. When a polymer (such as MEH-PPV) possesses a flexible long chain, the situation becomes much more complicated and sufficient data must be collected in order to obtain statistically significant results that can demonstrate correlations between organizations of absorbing and emitting sites.

In this paper, both excitation and emission anisotropy were derived for the same single MEH-PPV molecules. The scatter graph in the bottom right of Figure 5 shows the correlation between the polarization modulation depths of fluorescence (M_F) and excitation (M_E). Each point in the figure represents the M_E and M_F values for one molecule. Note that the data were obtained before the molecules experienced any quenching or bleaching. Assuming that the emission quantum yield does not depend on the excitation light polarization, M_E tends to reflect the distribution of orientations of the absorbing chromophores (i.e., the conformation of the molecule), while M_F reflects the distribution of emitting site orientations.

To interpret this experimental result, we performed a simple simulation aimed at studying the dependence of the appearance of the scatter graph on the number of emitting chromophores in polymer chains. Specifically, we were interested in studying the dependence of the spread of the scatter graph points around the diagonal on the average number of emitting chromophores. For simplicity, the simulation assumed that the intensity of the emitters is the same and that geometrically the problem is 2D
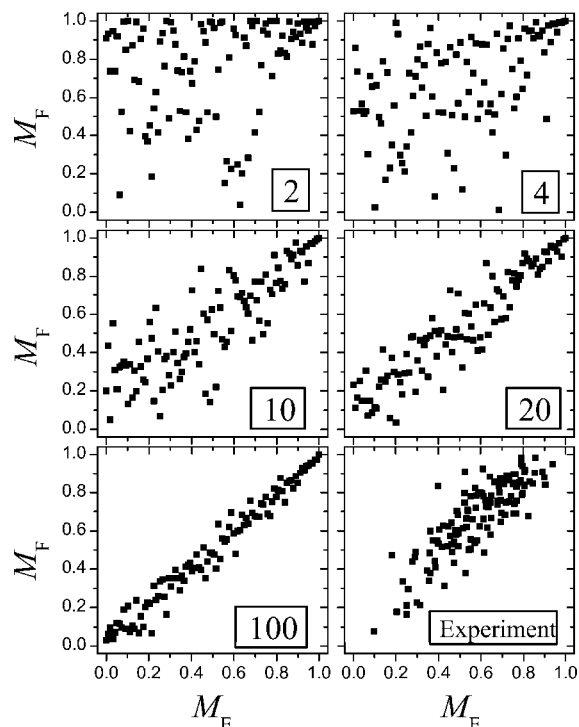
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Figure 5. Simulated and experimental M_F vs M_E scatter graphs. The numbers of emitting chromophores chosen for the simulations are indicated in the plots.

rather than 3D. Clearly, for the trivial case of a single emitter per chain (perfect irreversible downhill ET to a single chromophore) all the graph points would be located on the horizontal line corresponding to $M_F = 1$, regardless of M_E. In a general case, some distribution of orientations for every value of M_E had to be considered. The distribution function for orientations was chosen so that an ensemble of chromophores with such orientation distribution would exhibit the given M_E. We chose the angular distribution ($\rho_E(\phi)$, where $0 \leq \phi \leq \pi$) among the functions of the form

$$\rho_E(\phi) \propto \exp(-A \sin^2 \phi)$$

By varying the value of A from 0 to ∞, the excitation modulation depth M_E of the chromophore ensemble with orientation distribution $\rho_E(\phi)$ is changed from 0 to 1, so for every needed value of M_E a corresponding distribution $\rho_E(\phi)$ could be chosen.

After choosing the distribution we generated a number of random values from it. These values represented the orientations of the linear emitting chromophores, their number being a simulation parameter. After obtaining the geometry of the set of emitters in this way, it was straightforward to calculate the polarization modulation depth of fluorescence from these chromophores under the assumption that they exhibit the same fluorescence intensity. The simulation was repeated for a range of M_E values (resulting in a simulated scatter graph M_F vs M_E) for five different numbers of emitting chromophores (resulting in the five simulated scatter graphs shown in Figure 5).

The plots show a very clear and intuitive trend: with the increase of the number of emitters, the plot points compress along the diagonal more and more. By comparison with the experimental plot, the presented examples enable us to suggest that a rough estimate of the number of emitters in our molecules is ∼20.

Admittedly, there is no reason for the number of emitters to be fixed in reality. For example, larger molecules may have more emitters and the number of emitter may very well be different even for molecules of the same mass. Moreover, we have made a few rather rough assumptions above. Therefore, the conclusion about the number of emitters ($\sim$20) should be considered as true as far as the order of magnitude ($\sim$20 rather than $\sim$1 or $\sim$100). It is also worth noting that the typical number of emitters can depend on M_E. One can see from the comparison that for high values of M_E the number of emitters can be smaller. Note that the experimental data points in Figure 5 are biased from around the $M_F = M_E$ diagonal toward higher values of M_F (more spots in the area $M_F > M_E$). This can be explained easily within the concept of downhill energy migration from shorter chromophores (having higher transition energy) to longer ones (having lower energy). In reality, if there is some preferential orientation of chromophores within a polymer chain, the longer chromophores will have that (or close) orientation more likely than an average random chromophore. Since the longer chromophores are the dominant emitters due to downhill ET, the emission is more polarized than expected.

3.3. The Model of Energy Migration Domains. In this section we mainly focus on the case of abrupt rather than smooth intensity fluctuations. We have seen from the lifetime experiments (section 3.1) that abrupt blinking resulted in the appearance of a fast component in fluorescence decay kinetics. The time constant of this component is several times smaller than the original lifetime. The decay time of the remaining component stayed unchanged or changed only slightly. The latter evidence indicates the existence of some kind of zones or domains in the polymer chains, each of the domains being quenched independently (if at all) of the other domains. These domains should be just a few, because otherwise the blinking would be weaker (smaller steps, though still abrupt). Energy transfer between the domains must be weak, because there would be no unaffected component left in the kinetics otherwise. Additionally, we have seen that before the quencher appears the molecules exhibit single-exponential fluorescence decay. This can happen in the case of a single emitter in every chain and in the case of multiple emitters with close fluorescence lifetime. Now, we have seen in section 3.2 the evidence that the typical total number of emitting chromophores is $\sim$20. This means that every domain contains a few emitting chromophores.

Considering the above statements, there are two sets of questions to be answered: (1) Why does an unquenched molecule have single-exponential decay kinetics? Can we expect the lifetime of the $\sim$20 emitters to be distributed narrowly enough for that? (2) Why can a whole domain containing a few exciton traps get quenched to almost 100%, whereas the rest of the domains stay unaffected? Why do not we observe intermediate quenching that would manifest itself with intermediate decay times?

On the basis of the presented experimental results, no single physical picture can be unambiguously derived. However, we can present one as a hypothesis. The above observations and questions can be explained and answered if we assume the following additional propositions to be true.

Intradomain ET is fast in comparison to the radiative lifetime, whereas interdomain ET is comparable with it. Due to the fast intradomain ET, an excitation performs a large number of hops over the chromophores of the domain. Uphill hops are less likely than downhill ones but nevertheless still much faster than the radiative lifetime. As a result of these assumptions, we conclude
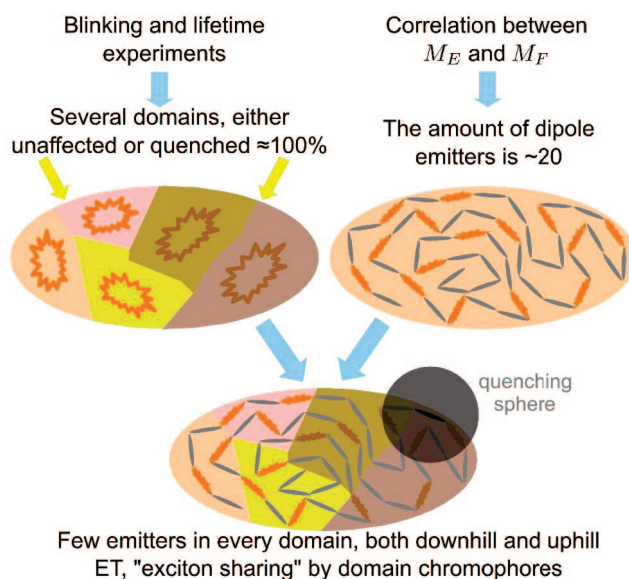

Figure 6. Experimental results, conclusions from them and unifying hypothesis.

that the excitation is "shared" among the chromophores of a domain. It spends more time on the lowest-energy chromophores (traps) but nevertheless visits most of the chromophores (except the highest-energy ones) during its lifetime. Thus, the domain emits "collectively" with single-exponential kinetics, and the decay rate is a weighed average of the decay rates of the domain chromophores. Unlike fluorescence lifetimes of the exciton traps themselves, these averages are not likely to differ significantly for different domains, which explains the single-exponential lifetime for the whole chain. At the same time, this picture explains the possibility of $\approx$100% quenching of one or several domains without affecting the rest: it is enough for the quencher to have only a part of a domain in its range to quench it strongly.

The presented picture is outlined in Figure 6. Work is in progress at the moment, aimed at modeling ET in single MEH-PPV chains. Preliminary results confirm the suggested hypothesis and will be published elsewhere.

As one can see, the quenching efficiency depends both on the exciton migration domain size and the actual interaction distance between the exciton and quencher (gray circle in Figure 6). However, it is known that noncoherent exciton migration is a temperature-activated process.[39,68] It means that actual splitting of a polymer chain to exciton migration domains must be temperature dependent. Temperature dependence of exciton migration distance (meaning domain size in our language) has been studied in conjugated polymer films usually by observation of energy transfer to acceptor molecules (dyes) of known concentrations.[40,69] List et al. reported about 5 times decrease of the exciton migration efficiency upon cooling from room temperature to 77 K. The excitation energy transfer processes were successfully modeled as a combination of temperature-activated exciton diffusion and direct (Förster) energy transfer to acceptor molecules.[40] Observation of large amplitude fluorescence intensity jumps (blinking) at temperatures as low as 15 K for MEH-PPV single molecules is a clear indication of

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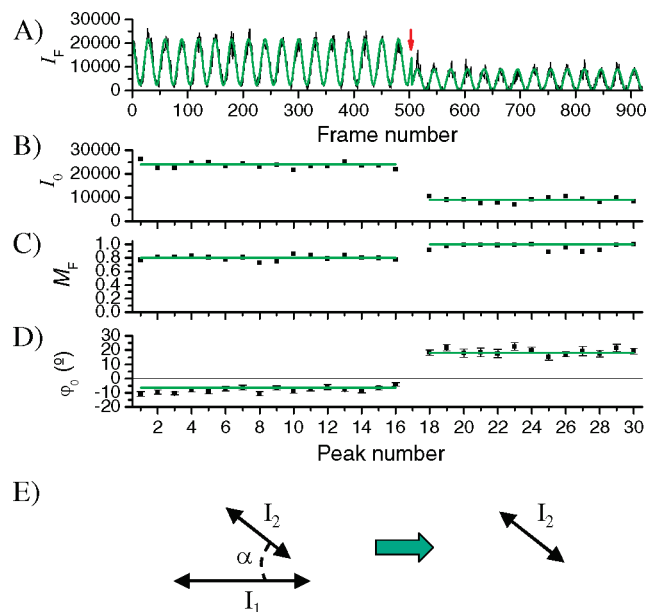
Figure 7. Polarization modulated fluorescence transient (A) of a single MEH-PPV chain (experimental results, black lines; model, green lines), for an exposure time of 100 ms. The molecule was modeled by two dipole emitters (E). Experimental and modeled transients for total intensity (B), modulation depths (C), and polarization phase angle (D) (see eq 1) are also shown.

the importance of direct long-range interaction between excitons and quenchers. On the other hand, the decrease of the average amplitude of intensity fluctuations (from 70% at 300 K to 40% at 77 and 15 K)[18,38] and the broadening of the fluctuation amplitude distributions upon lowering the temperature show that the exciton diffusion contributes significantly to the quenching process at room temperature.

3.4. Emission Polarization Changes upon Quenching. The measurements in section 3.2 probed the excitation and emission anisotropy of whole single molecules in quencher-free state. It is interesting to study the organization of different domains and individual properties of each domain in single conjugated polymer chains. Such information can be achieved by monitoring arrangement of emitting sites upon quenching event using polarization-sensitive SMS techniques.[19]

Circular polarized light was used for excitation. The fluorescence light was passing through a polarizer rotating at a constant frequency Ω. The detected fluorescence intensity (I_F) can be described by the following equation:

$$I_F = 1/2 I_0 [1 + M_F \cos 2(\Omega t - \varphi_0)] \tag{1}$$

$$I_0 = I_{max} + I_{min}$$

$$M_F = (I_{max} - I_{min})/(I_{max} + I_{min})$$

where I_{max} and I_{min} are the maxima and minima of the fluorescence intensity during each modulation cycle, respectively, I_0 is the total intensity without polarizer, M_F is the modulation depth, which has the same physical meaning as that mentioned in section 3.2, Ωt is the angle of the polarizer (i.e., φ_{fl}), and φ_0 is the phase angle where I_F reaches I_{max}. The values of I_0, M_F, and φ_0 can be obtained by fitting the intensity transient to the above equation.

About 64 molecules were studied with this technique. In experiment, the cosine wave shape of the modulated intensity transient (Figure 7A, black solid line) was somewhat blurred

by irregular intensity fluctuations. Such irregular fluctuations were found much suppressed at low temperatures, indicating that they might come from thermoactivated fluctuations of orientations of the emitting chromophores or fluctuations of the energy redistribution over different chromophores.[19] The plots B, C, and D in Figure 7 display $I_0(t)$, $M_F(t)$, and $\varphi_0(t)$ with a temporal resolution of 3 s limited by the modulation cycle period.

Figure 7 shows the emission polarization results of a MEH-PPV molecule with a substantial quenching event during the measurement. Two different stages (stage 1 and 2) can be recognized from the modulated transient (Figure 7B). Stage 1 can be regarded as unquenched (quencher-free) state. The polarization modulation depth in stage 1 was relatively high ($M_F = 0.8$), suggesting that the molecule adopted a relatively ordered conformation ($M_E \approx M_F$ according to section 3.2). On the other hand, the emission was not completely polarized, i.e. $M_F < 1$, revealing that it was coming from two or more emitting chromophores of different orientations.

A dramatic decrease of emission intensity (indicated by red arrow) occurred upon transition from stage 1 to stage 2, accompanied by a jump in M_F and φ_0. It happened in less than 100 ms, indicating the occurrence of a fluorescence quenching event rather than slow changes of absorbing chromophores (section 3.1). According to the "energy migration domain" model described in section 3.3, this molecule consisted of at least two domains. In the simplest case, the substantially quenched chromophores can be assigned to one domain, while the remained emission with even higher modulation depth ($M_F \approx 1$) can be assigned to another domain.

Therefore, this particular molecule can be treated as two domains and at least one of them gives highly polarized fluorescence like a single dipole. It is reasonable to try to model each domain in this molecule as a dipole of certain emission intensity (I_1 and I_2, respectively; see Figure 7E). Another parameter of the model is the angle (α) between the two dipoles. This simple model gives a perfect fit to all the experimentally observed characteristics such as $I(t)$, $M_F(t)$, and $\varphi_0(t)$ (Figure 7) for $I_1/I_2 = 5/3$ and $\alpha = 38°$.

It turned out that the two-dipole model gives satisfactory fits to fluorescence polarization and intensity transients for about half of the investigated molecules. The angle between the dipoles varies from 0° to 90° for different molecules. Most of the time, the fluorescence anisotropy of a MEH-PPV molecule tended to increase when quenching happened.

Treating each domain as a single emitting dipole (i.e., $M_{F,domain} = 1$) means that all emitting chromophores have the same orientation in a domain. The success of this model shows that the emitting sites in a single molecule tend to locate in a few highly oriented regions rather than be distributed randomly, even when the observed excitation and fluorescence anisotropy were low. Previous studies on conjugated polymers indicated that the emitting sites are presumably situated in ordered regions containing parallel segments.[30,70] However, no direct evidence was given and the existence of such regions in single molecules was only a prediction from simulation results.[29,70] Our experimental results clearly state that the MEH-PPV single molecules embedded in the PMMA matrix did often possess such ordered regions.

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4. Conclusions

Fluorescence dynamics and conformations of single molecules of MEH-PPV dispersed in a PMMA matrix prepared from toluene solutions were studied. It is the first time experimental data on correlation between fluorescence intensity and picosecond fluorescence dynamics of a single conjugated polymer molecule were presented and combined with complementary studies of polarization in excitation and fluorescence.

MEH-PPV molecules in unquenched states possess monoexponential decay with lifetime from 0.4 to 1.2 ns. Two types of fluorescence intensity fluctuations were clearly distinguished: (1) abrupt sudden intensity changes (blinking) always accompanied by change of fluorescence decay kinetics and (2) smooth intensity variations without lifetime change.

Abrupt jumps of fluorescence intensity (blinking) were interpreted as a result of a fast exciton quenching with reciprocal rate between 20 and 120 ps. One possible explanation for smooth intensity changes can be slow variations of the amount of excitation energy absorbed by a molecule, e.g. due to spectral diffusion.

The clear correlation between the degree of anisotropy of absorbing and emitting states for individual MEH-PPV molecules shows that energy migration does not lead to trapping of excitons in a single or a very few emitting traps. There are many (10 or more) chromophores with different orientations contributing to the emission.

On the basis of fluorescence decay dynamics and the correlations between anisotropy of excitation and emission, we conclude that most of the molecules can be seen as being composed of several energy migration domains. We propose that those domains are parts of the polymer chain over which exciton can efficiently migrate during its lifetime. The blinking is a result of exciton quenching by Förster energy transfer to a photogenerated quencher. A domain (or several domains) can be strongly quenched if the quenching sphere (whose radius can be as large as several nanometers) covers a part of the domain(s).

Domain fluorescence is often highly polarized and it can be seen at first approximation as emission of a single dipole with certain oscillator strength. This can be regarded as direct evidence that the emitting sites in such domains are mainly located in ordered regions containing parallel segments.