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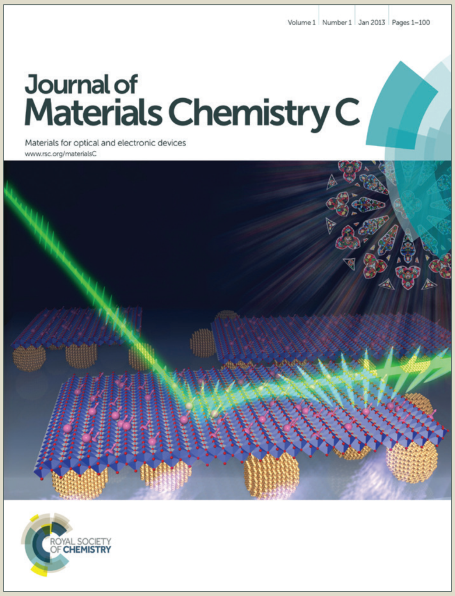

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Photo-induced fluorescence quenching in conjugated polymers dispersed in solid matrices at low concentration

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Abstract:

When isolated conjugated polymer (CPs) chains are studied by single molecule spectroscopy, excitation power density in the range of 10-1000 W/cm^2 is normally used. We show that at such excitation power densities the fluorescence ability of CPs is significantly reduced. A new methodological approach allowed us to measure the fluorescence quantum yield (QY) of thin matrix polymer films doped with fluorophores at very low concentration using fluorescence microscopy. Fluorescence QYs of different conjugated polymers (P3HT, MEH-PPV, PFBV and cyclodextrin-coated PFBV-Rtx) and a reference perylene diimide dye dispersed in PMMA matrix were measured as a function of the excitation power density that ranged from ~10^{-4} to 100 W/cm^2. Already at the excitation power of 0.1 W/cm^2 (the power density of the Sun light at the Earth) a detectable reduction of the fluorescence QY was observed for most of the polymers. The origin of the QY reduction is exciton annihilation by photo-generated triplet and/or change-transfer states. Insulation by cyclodextrin was found to decrease significantly the effect of the non-emissive quenching states.

1. Introduction:

Conjugated polymers (CPs) are attracting great interest due to their potential applications in organic light-emitting diodes, solar cells, lasers and displays.[1-4] CPs and their oligomers are more and more used in biology and medicine as luminescent sensors due to their great sensitivity to the environment.[5] The origin of such sensitivity is in complex molecular interactions strongly dependent on the chain internal organization on the molecular and supramolecular levels. This is the main reason why many important fundamental issues including the nature of light absorbing and fluorescing states, mechanisms of exciton quenching, energy and charge transfer and the role of the polymer conformation in optical and electronic properties remain controversial.[6]

The excited state dynamics in these materials is very complex as there are different types of accessible photoexcited states including singlet excitons, triplet excitons and charge separated states. Quantitative determination of the singlet excitons relaxation channels is complicated due to many competing processes involved. Signatures of nonemissive or low fluorescence yield states, such as polarons (photogenerated charge carriers), interchain aggregates, triplets and excimers have been reported.[6-13] These excited species directly or indirectly induce fluorescence quenching. The fluorescence quantum yield (QY) of a CP in films is generally several times lower than that in solution due to much larger contribution of the above mentioned non-radiative processes in densely packed polymer chains in solid films.[6,14]

Single molecule spectroscopy (SMS) is a powerful technique that allows excited state processes in conjugated polymers to be probed at the individual chain level beyond ensemble averaging.[15] In SMS, an excitation power density of the range of 10-1000W/cm^2 is usually used in the continuous wave regime. Similar or even higher excitation intensities are common in fluorescence microscopy where single molecules and conjugated polymers nanoparticles[16,17] are used as probes.[18] Such averaged powers are by orders of magnitude larger than those typically used in ensemble optical spectroscopy measurements. Can such high excitation power density influence the observed properties of individual CPs? To date, little systematic attention has been paid to this issue.

In this contribution we report the dependence of fluorescence QY on the excitation power density for several commonly studied conjugated polymers including rr-P3HT and MEH-PPV dispersed in poly(methyl methacrylate) (PMMA) matrix mimicking conditions of SMS experiments. Depending on the polymer, the fluorescence intensity decreased by a factor of 1.5 to 5 when the excitation power goes up to 100 W/cm^2. We will try to rationalize the observed difference by taking into account difference in polymer chain chemical structure, conformation and interaction with the environment. It will be shown that classical model of singlet-triplet annihilation in restricted domains cannot directly explain the experimental data.[19]

2. Experimental:

2.1 Sample preparation

Conjugated polymers regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT, M_n=39 kD), poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV, M_n≈100 kD, polydispersity index PI≈6) and the reference dye *N,N′*-bis(2,6-dimethylphenyl)perylene-3,4,9,10-tetracarboxylic diimide (DXP)[20] were purchased from Sigma Aldrich. The polyfluorene bis-vinylphenylene (PFBV) and the same polymer protected by a functionalised cyclodextrin shell (PFBV-Rtx, polyrotaxane) were synthesized according to the published procedure.[21] PFBV-Rtx possessed the following parameters: M_n= 29 kD, PI=1.76, threading ratio 0.8 cyclodextrins per distyrylbenzene unit, degree of functionalization of cyclodextrin 0.98 butanoate ester per cyclodextrin OH group. The same polymer without cyclodextrin insulation (PFBV) possessed M_n=5.4 kD and PI=2.21. Both polymers were on average approximately 20 nm or 10 monomer units, long.

Samples were prepared by spin-casting of the polymer solutions in toluene containing 9 mg/mL poly(methyl methacrylate) as matrix polymer (PMMA, Aldrich, Mw ≈ 996 000, PMMA was added in the last dilution stage) onto cleaned glass substrates to yield a uniform film with a thickness of ≈40 nm (measured by profilometer). The concentration of the active materials relative to the matrix was documented by measuring the optical density at 458 nm in a 1 cm cell of the toluene solutions (OD_{sol}) used for spin casting of the samples. OD_{sol} = 0.01 corresponds ca 2×10^{-5} w/w P3HT/PMMA and ca 10^{-5} w/w MEH-PPV/PMMA which is approximately 100 times larger than used in SMS experiments. PMMA was chosen because it is the most commonly used matrix polymer in SMS.

2.2 Instrumental

A home-built wide-field fluorescence microscope based on Olympus X71 with Ar-ion laser as an excitation source was used. The fluorescence was collected by an objective lens (Olympus LUCPLanFI, 40X NA=0.6) and imaged by EMG CCD Camera (ProEM-512, Princeton Instrument). All samples were excited by linearly polarized light from Ar-ion laser at 458 nm. The excitation spot at the sample plane was approximately 30 micrometers in diameter. Exposure time of the camera was varied depending on the excitation power density. All the experiments were done in the nitrogen environment at room temperature. The excitation power density was varied from 6×10^{-4} to 100 W/cm^2 using a calibrated set of filters placed in the excitation beam. The samples were not moved during the excitation power scan. So, the very same place was exposed to the full range of powers. To minimize the irreversible photobleaching, the lowest possible exposure time was used at each excitation power condition and each experiment started from the lowest power. Then after taking the measurement at the highest power, data points upon decreasing the excitation power density were also collected to check the photobleaching (see ESI).

2.3 Brightness per Optical Density

Fluorescence QY is one of the most important characteristic of fluorescence. QY can be measured by either absolute[22] or relative[23] techniques. It is defined as:

$$\Phi = \frac{number\ of\ emitted\ photons}{number\ of\ absorbed\ photon} \qquad (1)$$

For dilute samples, like isolated molecules or thin films, it is very difficult to measure absorption directly. Therefore, relative methods are used. Relative fluorescence QY is proportional to fluorescence intensity normalized to the excitation power and concentration of the sample.

We designed a convenient experimental parameter called Brightness per Optical Density (BOD) for measuring fluorescence QY of thin matrix films doped by low concentration of fluorophores using fluorescence microscopy. An optical microscope provides a very good control of the excitation power, excitation area and sample position which makes it a very stable and convenient platform for quantitative fluorescence measurements. BOD is an ensemble variant of the parameter *Fluorescence Brightness* that is used for measuring of fluorescence QY of individual molecules.[24-26]

The number of photons detected by the CCD camera (N_{det}) from the whole excitation spot is the product of the total number of emitted photons (N_{all}) multiplied by the detection efficiency (η_{det}) of the set up:

$$N_{det} = N_{all}.\eta_{det} \qquad (2)$$

The detection efficiency is the product of optical collection efficiency for the particular sample geometry, transmission coefficient of the optics and quantum efficiency of the CCD.

In practice the excitation power density $P(x,y)$ in W/cm^2 is not uniform over the sample. However, the sample (a thin film of low optical density) is assumed to be uniform at the scale of $P(x,y)$ variations. Because fluorescence QY Φ can be dependent on excitation power density, it is itself also dependent on the position in the sample. So, QY must be a function of x and y as well: $\Phi=\Phi(\mathrm{P}(x,y))$.

The absorption cross section density parameter of the film can be defined as:

$$\rho = \frac{\sigma c V}{A} = \sigma c h = OD_{film}\ ln10 \qquad (3)$$

Where σ- molecular absorption cross section [cm^2], V and A are excited volume [cm^3] and excited area [cm^2] of the film, respectively, c – concentration of molecules in the film [cm^{-3}] and h – thickness of the film [cm], $\mathrm{OD}_{\mathrm{film}}$ – optical density of the film.

Since the optical density of the film is proportional to the optical density of the solution, (OD_{sol}) the film was spin cast from, we can write

$$\rho = OD_{film}\, ln10 = OD_{sol}K \qquad (4)$$

Where K is a constant dependent on the concentration of the matrix polymer in solution and the matrix film thickness.

The number of emitted photons is then:

$$N_{all} = \left(\frac{\tau}{h\nu}\right).\rho \int P(x,y)\Phi(P(x,y))dxdy \qquad (5)$$

Where τ - exposure time and $h\nu$ - excitation photon energy.

Assuming that the dependence of Φ on excitation power density P(x,y) is weak, we can simplify the situation:

$$N_{all} \approx \left(\frac{\tau}{h\nu}\right)\rho\,\Phi(\langle P\rangle)\int P(x,y)dxdy = \left(\frac{\tau}{h\nu}\right)\rho\,\Phi(\langle P\rangle)I \qquad (6)$$

Where I – total excitation power [W], <P> - averaged excitation power density [W/cm^2].

Using eq. 2, 4 and 6, we can express the observed emission intensity N_{det} [photons] detected by the CCD camera as:

$$N_{det} \approx K\eta_{det}\left(\frac{\tau}{h\nu}\right) OD_{sol}\,\Phi(\langle P\rangle)I \qquad (7)$$

The number of detected photons normalized to the sample concentration (OD_{sol}) and the excitation power (I) and exposure time (τ) is that parameter BOD (Brightness per Optical Density):

$$BOD = \frac{N_{det}}{I\,\tau\,OD_{sol}} \approx \frac{1}{h\nu}K\eta_{det}\,\Phi(\langle P\rangle) \qquad (8)$$

So, BOD [$W^{-1}s^{-1}$] is directly proportional to the fluorescence QY of the sample. The proportional constants reflect the sample preparation (K) and the setup (η_{det}). Note that the coefficient η_{det} is dependent not only on the optics, but also on the orientation of the molecule transition dipole moment in space as will be discussed below.

Differences between the absorption cross sections of the molecules in solutions and in the solid matrix can reduce the accuracy of the absolute measurement of QY using BOD. However, we do not expect errors due to this effect more to be than 30% when the experiment is carried out at room temperature and the sample is excited close to its absorption maximum. This is because the absorption spectrum width is usually much larger than the spectral shift. Structure and spectra of different polymers are shown in ESI. The most important source of random errors is the PMMA film thickness and its variation over the sample area. In order to minimize this error we used several different samples of each polymer and measured BOD in several places in each sample. As for the excitation power dependence of normalized BOD or QY, the errors are quite small (+-10%) as can be seen by data point position fluctuations in Fig. 2.

3. Results and discussions

3.1 Fluorescence quantum yield at low excitation intensity limit

BOD of PMMA films doped with different polymers and with the reference dye DXP as a function of the excitation power density was measured (Figure 1). All samples showed the same qualitative behavior: BOD is constant until a certain excitation level (different for different samples), and then decreases (with sample-dependent rate) with further increasing of the excitation intensity.

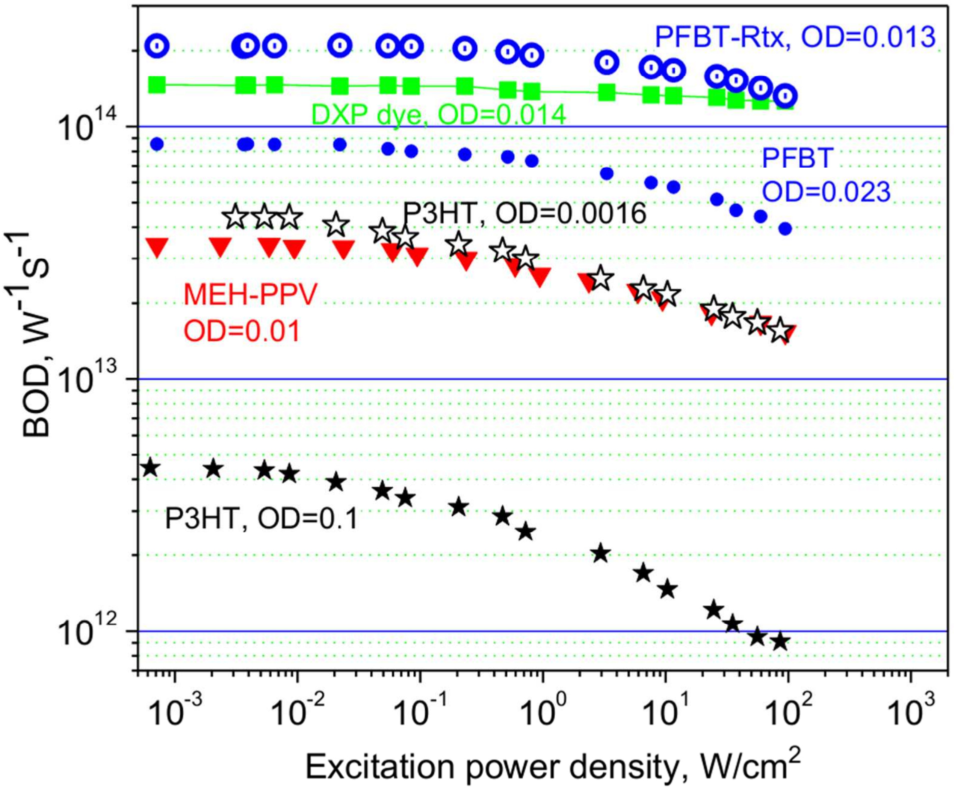

Figure 1. *Brightness per Optical Density (BOD) of different polymers and the reference dye DXP dispersed in PMMA film as function of excitation power density (λ_{ex}=458). Optical density (OD) at 458 nm of the solutions used for spin casting of the films is indicated. All experiment were carried out in N_2 environment.*

BOD can be related to the absolute QY of each polymer if we take BOD of DXP as a reference with QY=93%.[20] It is surprising, however, that BOD of PFBV-Rtx is 1.4 times larger than that for DXP, which would mean that this polymer has QY much larger than 100%. How can that be possible?

There is an important parameter in the eq. 8 which can be dependent on the particular molecule. It is the fluorescence light detection efficiency of the setup that is dependent on the orientation distribution of the light-absorbing and light-emitting transition dipole moments. As a first approximation, the dependence is twofold: i) the excitation probability depends on the square of the projection of the transition dipole moment to the sample plane and ii) the collection efficiency of a given objective lens also depends on the angle between the optical axis and the dipole moment. See e.g.[27] and references therein.

We do not know the distributions of orientations for our polymers and the standard (DXP dye). Uncertainty in the molecular orientation in matrix films limits the accuracy of the absolute fluorescence QY measurements using BOD. It has been shown that neither small dye molecules nor conjugated polymers possess perfectly random orientation in thin PMMA films.[28,29] There are no, however, published studies comparing orientation distributions of dye molecules and long CP chains. Taking into account the fact that the lengths of PFBV-Rtx (20 nm) and all other polymers are much larger than that of DXP (~2.5 nm) and comparable with the PMMA film thickness (ca. 40 nm) it is natural to assume that conjugated polymers must be preferentially aligned along the substrate plane while DXP can adopt much more random 3D orientation.

In order to estimate the effect of orientation, as a first approximation, we assume that DXP adopts random orientation in film while the polymers are oriented in the sample plane. The probability of excitation is proportional to the cosine square of the angle between the vectors of the dipole moment and electric field. This function averaged over 2D and 3D random orientations is equal to 1/2 and 1/3 respectively. Thus the brightness of dipoles oriented in the sample plane should be $\xi=3/2=1.5$ times larger than that of the same dipoles oriented in 3D. Note, that we did not consider the effect of orientation on the light collection efficiency which can increase the factor even more.[27]

Therefore, we need to take factor ξ this into account while calculating QY of the CPs (Table 1):

$$\Phi_{\mathrm{sample}} = \frac{1}{\xi}\Phi_{\mathrm{ref}}\frac{\mathrm{BOD}_{\mathrm{sample}}}{\mathrm{BOD}_{\mathrm{ref}}} \qquad (9)$$

Let us discuss QYs at the low excitation power density limit. The highest QY was obtained for the cyclodexrin-protected polymer PFBV-Rtx. Its QY is 85%, in agreement with the previous publications[25] where it was measured using brightness of individual molecules. The next is “naked” PFBV with QY around 36%, then goes MEH-PPV with QY of 14% and the lowest yield (2 and 20% for the high and low concentration, respectively) was obtained for P3HT (Table1).

A clear concentration dependence of QY was observed for P3HT (Fig. 1). BOD increased nearly 10 times when we decreased the concentration by a factor of 100 (from ~2×10^{-4} to ~3×10^{-6} w/w P3HT/PMMA). We did not observe any concentration dependence of BOD for the other polymers in the given concentration range. Note that the concentrations used in this study (OD in absorption maximum <0.1 in solution, 1 cm cell) are usually considered in literature as very low.

Table 1. Absolute Brightness per Optical Density (BOD) and fluorescence quantum yield (Φ) for the studied conjugated polymers and the reference dye DXP measured by 40^X dry objective lens. Excitation power density was 2×10^{-3} W/cm^2 @ 458 nm. OD at 458 nm was used in the calculations.

Molecules dispersed in PMMA film of 40 nm thickness	Absolute BOD [$W^{-1}s^{-1}$], accuracy ± 20%	$\Phi^{a)}$ Errors are estimated without considering the orientation factor $^{b)}$
DXP	1.45×10^{14}	0.93 [ref [28]]
P3HT(OD_{sol}=0.1, aggregated)	4.4×10^{12}	0.018±0.01
P3HT(OD_{sol}=0.0016, isolated chains)	4.3×10^{13}	0.18±0.1
MEH-PPV	3.4×10^{13}	0.14±0.07
PFBV	8.54×10^{13}	0.36±0.15
PFBV-Rtx	2.0×10^{14}	0.85±0.3

a) Calculated using eq. 9.

b) The data may contain a systematic error due to uncertainty in the orientation factor ξ, however, such error should appear as a constant factor similar to all polymers, thus having no influence on the ratio of QYs of different polymers, see the text for details.

It is well-known that P3HT tends to form aggregates possessing low fluorescence QY.[30-32] Therefore, we conclude that chain aggregation is the reason of the observed concentration dependency. The fluorescence QY of 2% obtained for concentration of 2×10^{-4} w/w P3HT/PMMA (we refer to such concentrations as high in this study) is the same as measured for pristine P3HT films.[30] The aggregation tendency is extremely strong since a low QY was still observed at such low concentration. When the concentration was further reduced to 3×10^{-6} w/w P3HT/PMMA the QY went up to 20% accompanied by blue shift of the emission spectrum. This situation most probably corresponds to emission of isolated chains.

3.2 Excitation power dependence

The excitation power density at which QY starts to decrease, and the QY decreasing rate, are clearly different for different molecules. It is remarkable to observe that already at a power as low as the Sun power at the Earth (0.1 W/cm^2) a clear decrease of QY was observed for all polymers except of PFBV-Rtx and the reference dye DXP. P3HT appeared to be the most sensitive to excitation power density. Its fluorescence QY at low concentration conditions is suppressed by a factor of 3 at a power of 100 W/cm^2. Even larger suppression is observed for P3HT dispersed in PMMA at higher concentration (factor of 4 at 100 W/cm^2). QYs of unprotected PFBV and MEH-

PPV showed ca. 2 times decrease at 100 W/cm^2 in agreement with the literature data.[13] Note that such excitation power level is very typical for single molecule spectroscopy.

It is interesting to see that the cyclodextrin protection shifts the QY dependence of PFBV-Rtx relative to PFBV without change of its shape, to approximately 5 times higher excitation power density. So, clearly the protection reduces photo-induced quenching processes substantially most probably by reducing the generation yield of triplets and/or charged species, see below. In comparison to all studied polymers, the reference dye DXP showed the least sensitivity to the excitation power density. The QY decreased by only 10% at an excitation power density of 100 W/cm^2.

Note here that in order to control possible irreversible photobleaching, two excitation dependences from the same spot at the sample obtained upon going up and down with the power were compared. For all samples the fluorescence intensity was reduced by irreversible bleaching by not more than 10 %.(See supporting information S4)

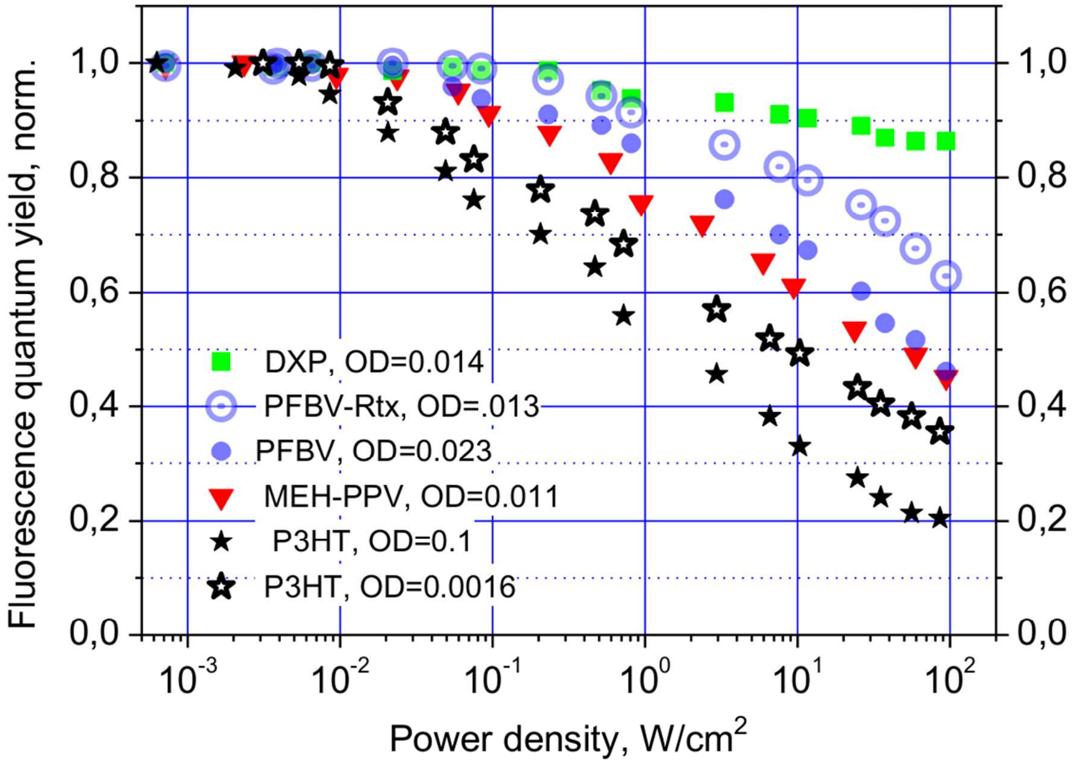

Figure 2. *Normalized fluorescence quantum yield (= normalized BOD) of different polymers and the reference dye DXP dispersed in PMMA film as function of excitation power density (the same experiments as in Figure 1).*

3.3 Mechanisms of photo-induced quenching

We can divide the quenching mechanisms into direct and indirect.[6,19,33,34] By direct mechanisms, we understand such processes as intersystem crossing (ISC), internal conversion (IC), direct charge generation (electron transfer) and energy transfer to a persistent quencher. The quencher can be an impurity and another non-emissive state due to e.g. chain aggregation. The probability of an exciton being deactivated by the listed processes is excitation power density independent. These processes depend on the polymer chemical structure as well on the polymer chain conformation, aggregation and environment in general. They determine BOD and QY at the zero excitation intensity limit.

By indirect mechanism, we imply different annihilation processes. Already at power densities as low as 0.01 W/cm^2, QY starts to decrease for P3HT. Now we are at the region where excitons (S_1) are also quenched by S-PA – singlet exciton annihilation with long-living photo-products (P):

$$P + S_1 = P^* + S_0 = P + S_0 + \text{heat} \qquad (10)$$

The longer the photoproduct´s lifetime the smaller the excitation power density is needed for BOD or QY to start to decrease. Photogenerated species when arranged according to increasing of their lifetimes form the following list: singlet excitons (< 1 ns, short-living product, it will be not discussed here), triplet excitons (microseconds – milliseconds), charged species (microsecond – milliseconds – seconds and longer). The bi-exciton quenching processes due to singlet and triplet states are called singlet-singlet and singlet-triplet annihilation respectively (S-SA and S-TA).[6,19,34]

Note here that at the single-molecule level, exciton annihilation processes involving triplets and long-living charged states appear as fluorescence blinking with the "off" times equal to the lifetime of the photoproduct[13,35-37], while S-SA appears as photon antibunching.[38] We also do not consider here such effect as saturation of the S_0-S_1 transitions which reduce the absorption cross section of the polymer chain. This is because such effects require order of magnitude larger excitation power densities.

The photogenerated species lifetimes often depend on the environment as much as on the conjugated polymers chemistry. For example triplet lifetime can decrease by orders of magnitude if oxygen is present in the sample. The second crucial parameter is the photo-generation yield of the species. It again varies within a great, often unknown range. For example the ISC triplet yield can be as large 75% for polythiophenes and just 1-2 % for MEH-PPV and other polymers studied here. [9,39] That is why the onset of the QY decrease is at 1-2 orders of magnitude lower excitation power for P3HT than for the other polymers. However, to a large extent the parameters of triplet states are unknown for the particular sample configuration. Even less is known about the photogenerated long-living charge-transfer states. Their generation yield in conjugated polymers is low and at least partially dependent on the presence of uncontrolled impurities in the sample. However, as mentioned before, low yield does not necessarily mean small quenching, because it is proportional to the lifetime of the quenchers, which can be very long.

Even if the particular quenching reaction is a short-range electron transfer, the effective exciton quenching distance can be up to several nanometers (there are reports of even tens of nanometers quenching radii[40,41]) due to migration of excitons in the conjugated polymer. Also direct quenching by one step FRET to a polaron (charge transfer state) can happen at distances of several nanometers.[42] In general quenching is more efficient for densely packed polymer conformations than for extended ones.

The sensitivity of chromophores to photo-induced quenching can be evaluated using Figure 2, where QY is normalized to its value at low excitation power density. The starting point of the decrement of QY and the decrement slope are different for different polymers. As becomes evident above, calculation of the efficiency of the S-PA is complicated and cannot be done since the parameters of the long-living photo-products are mostly unknown. The authors were not able to find in the literature a theoretical model of S-TA in restricted domains (polymer chain or an aggregate) under CW excitation. However, qualitatively, a model developed long ago for S-TA in aggregates of densely packed chlorophylls in photosynthetic aggregates can be applied.[19] In this model a domain consisted of N chlorophyll molecules contains m carotenoid molecules. Carotenoid molecules can bare long-living triplet states (up to m triplets per domain) that can quench singlet states of chlorophylls. In our case the domain is a CP molecule or an aggregate, each chromophore of the CP potentially can be converted to a triplet state (in this case m=N>>1). However, it is also possible that some special chromophores have much higher chance to bare triplet excitations due to preferential energy transfer to them[37] resulting in m<<N.

The second parameter of the model is the effectiveness of the quenching $R=\Phi_m/\Phi_0$, where Φ_m – fluorescence QY when maximum number of quenchers (m) is created in the domain and Φ_0 – fluorescence QY in the absence of the quenchers. We show here the equations for two limiting cases obtained for microsecond pulsed excitation regime:[19]

Limit of large domains ($m \to \infty$, many quenchers per domain)

$$\Phi/\Phi_0 = R + (1-R)\,\frac{\sqrt{1+2\frac{X}{R}}-1}{\frac{X}{R}} \qquad (11)$$

Limit of small domains (m=1, just one quencher per domain)

$$\Phi/\Phi_0 = R + (1-R)\,\frac{1}{X}(1-e^{-X}) \qquad (12)$$

Where X is proportional to the number of triplet (photoproduct) states generated per domain that is proportional to the excitation power density, the photoproduct generation yield and absorption cross section of the domain. The curves are shown in Figure 3.

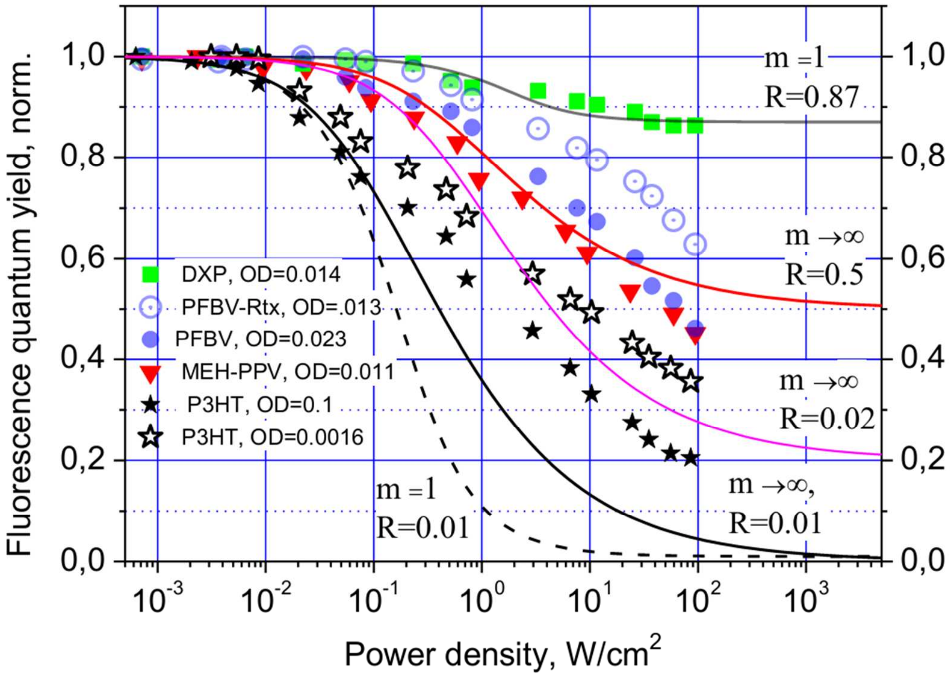

Figure 3. *Normalized fluorescence quantum yield (= normalized BOD) of different polymers and the reference dye DXP dispersed in PMMA film as function of excitation power density (the same experiments as in Figure 1). The thin lines are theoretical prediction of the domain model for different domain size limits (m→∞ and m=1) with different R values indicated on the graph.*

QY power dependence is determined by the combination of many physical parameters leading to model parameters R, m and the intensity scale X. The contributions of the individual parameters cannot be disentangled. However, some qualitative observations can be made.

Regardless to the domain size m and quenching efficiency R, the model cannot reproduce the experimental results (Figure 3). The problem is that experimental QY drops much too slowly with the increase of the excitation power density. A simple kinetic model without geometrical restriction[43,44] (see ESI) also cannot fit the data for the same reason (Fig. S4). Note that QY drop in photosynthetic aggregates was satisfactory described by the mentioned models.[19,45]

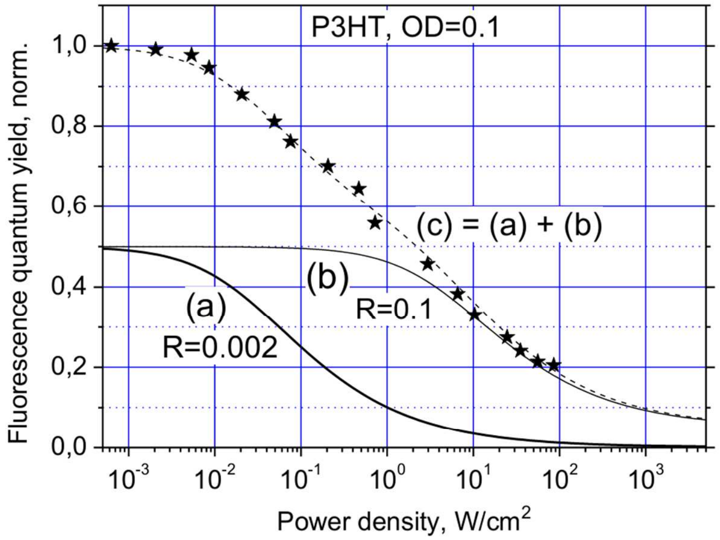

Figure 4. *Normalized fluorescence quantum yield for aggregated P3HT in PMMA. The data can be fitted by assuming that the polymer consist of two types of species (50/50) which possess 200 times different probability for the photogenerated quenching formation. The fitting function (c) is the sum of (a) and (b). The curves were obtained in the large domain limit. Parameter R is indicated on the plot.*

The only explanation is that the rates of the photoproduct formation as well as domain sizes and quenching volumes are broadly distributed. This may indicate that the generation yield (or lifetime) of triplet states and its quenching efficiency strongly depends on polymer chain conformation. It can be related to the same fundamental physics that stays behind power law distributions of blinking “on” and “off” times in single molecules and nanoparticles.[46]

To illustrate this, we can fit the P3HT data (Figure 4) assuming that the sample consist of two types molecules. Each type gives equal contribution to the total absorption, however, the first type of molecules has quencher generation yield 200 times larger than the second one.

The influence of the system size is illustrated by DXP which has the latest onset of the power-dependence. Because DXP is a small molecule, the quenching radius is equal to the size of the molecule (ca. 2.5 nm) while it can be more than 10 nm (for exciton diffusion-assistant quenching) in long conjugated polymers. Therefore, it is expected to have the onset of the QY drop at much higher excitation power for DXP in comparison with CPs as observed experimentally.

What is surprising however, that the QY of DXP drops extremely slowly with increasing excitation power. In the studied excitation power range, it appears that photo-products can only be generated (or live long enough) in a small fraction (13%, R=0.87) of DXP molecules. The fit using this assumption and small domain limit is presented in Figure 3. Note here that ISC yield is very small in perylene diimide dyes like DXP.[47] Therefore, we believe that it is photogenerated charged states that are responsible for the quenching.

We have to note that there is one issue which is not taken explicitly into account in the discussed annihilation models. It is triplet-triplet annihilation (T-TA)[33] that was proposed as an important process in MEH-PPV and F8BT conjugated polymers at excitation power densities larger than 100 W/cm^2.[13] The authors of the cited paper explained almost linear dependence of fluorescence intensity on the excitation power by saturation of the triplet exciton concentration at high excitation powers. In terms of our observables, it would mean that QY does not tend to zero with increasing of the power. QY should saturate than at a certain level corresponding to the maximum level of quenching at the saturated concentration of triplets. The excitation powers used by us are less than 100 W/cm^2. That is why, if the saturation effect exists, we did not quite reach it, however, our data indicate that the relative QY for P3HT aggregates possibly saturates at the level of approximately 0.1 (Fig. 3 and 4). Although, the full theoretical treatment of the problem is not available, we believe that at first approximation the effect of T-TA is taken into account by the parameter R of the domain model which explicitly sets the saturation level.

The ISC depends mainly on the chemical structure of the polymer. Due to the presence of sulfur atom in polythiophenes the spin-orbit coupling is quite strong leading to ISC yield as large as 75%. So S-T annihilation is probably the process responsible for much stronger excitation power dependence of BOD for P3HT than for other studied polymers where ISC yield is much smaller. [9,39]

The difference between P3HT at high concentration (aggregated form) and low concentration (isolated chains) can be explain by increasing of the quenching radius for aggregated P3HT (quenching in quasi 3D vs quasi 1D system) and thus higher quenching efficiency.[37] Also formation of polaron or CT states in aggregated P3HT could promote generation of long-living charged products that can also induce power dependent quenching.

It was shown before that the chain isolation with cyclodextrin removes ultrafast (or static) quenching at single-chain level.[25] Here we show that it also decreases quenching by photogenerated species (compare PFBV and PFVB-Rtx in Fig. 3). Our experimental data do not allow us to identify the origin of this effect. It is possible, however, that due to the static quenching in the “naked” PFBV[27] there is more chance of formation (or having longer lifetime) of long-lived charged products or triplet states than in the protected PFBV.

Conclusions

A simple optical microscopy method for estimation of fluorescence quantum yield of thin films of very low optical density is proposed. For the first time a detailed account of the fluorescence quantum yield excitation power density dependence is presented for several model conjugated polymers dispersed at low concentration in a PMMA matrix. The excitation power density was varied over more than 5 orders of magnitude from 6×10^{-4} to 100 W/cm^2. The excitation power dependence of fluorescence QY was assigned to exciton annihilation with photo-generated products like triplets and/or charged states. However, contrary to light-harvesting natural aggregates, the steepness of the QY decrease for all polymers was much too small to be explained by the annihilation with defined rates. The polymers must possess very broad distributions of the parameters of photogenerated quenchers like generation rates, quenching efficiency etc. Basically it means that in some polymer chains the annihilation efficiency is orders of magnitude larger than in some others. Remarkably that for P3HT the fluorescence QY starts to drop due to singlet-triplet annihilation already at excitation powers as low as 0.01 W/cm^2 that is one order of magnitude smaller than the Sun power at the Earth. These data are of immediate use for single molecule spectroscopy of conjugated polymers and their applications for biological imaging. At the typical excitation intensities in single molecule experiments (100 W/cm^2) one should expect 2 times reduction of QY due to reversible quenching by photogenerated products in polymers like MEH-PPV and 4 times reduction in polythiophenes. Isolation of conjugated backbone in conjugated polyrotaxanes not only increases QY at low excitation power limit, but also reduces the dependence of QY on the excitation power density.

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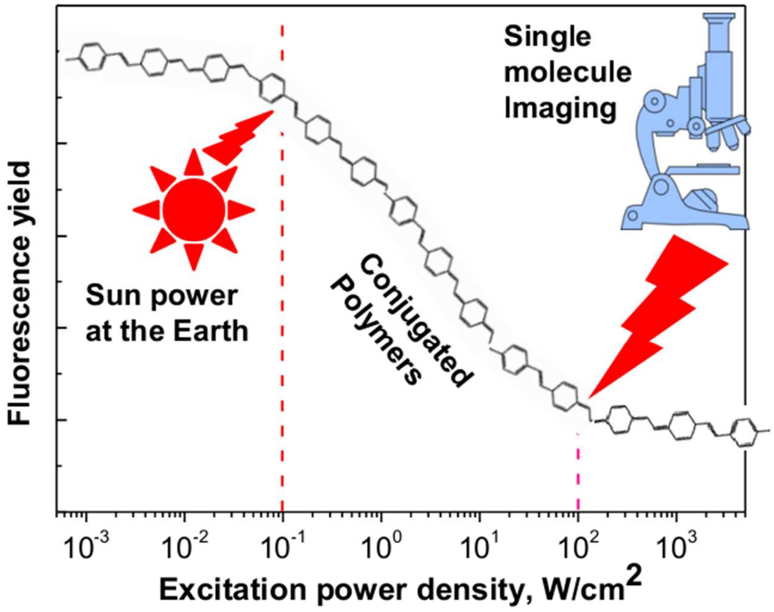
Electronic Supplementary Information (ESI) available:

Absorption spectra, chemical structures of the polymers, photobleaching control experiment, and a simple rate model of S-T annihilation.

TOC

Quenching by long-living photoproducs limits fluorescence yield of conjugated polymers



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