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Exciton–Exciton Annihilation as a Probe of Interchain Interactions in PPV–Oligomer Aggregates

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S Supporting Information

ABSTRACT: One measure of exciton mobility in an aggregate is the efficiency of exciton–exciton annihilation (EEA). Both exciton mobilities and EEA are enhanced for aggregate morphologies in which the distances between chromophores and their relative orientations are favorable for Förster energy transfer. Here this principle is applied to gauge the strength of interchain interactions in aggregates of two substituted PPV oligomers of 7 (OPP7) and 13 (OPP13) phenylene rings. These are models of the semiconducting conjugated polymer MEH–PPV. The aggregates were formed by adding a poor solvent (methanol or water) to the oligomers dissolved in a good solvent.

Aggregates formed from the longer-chain oligomer and/or by addition of the more polar solvent showed the largest contribution of EEA in their emission decay dynamics. This was found to correlate with the degree to which the steady-state emission spectrum of the monomer is altered by aggregation. The wavelength dependence of the EEA signal was also shown to be useful in differentiating emission features due to monomeric and aggregated chains when their spectra overlap significantly.

■ INTRODUCTION

Understanding how aggregation affects the emission and charge transport properties of conjugated materials is critical for optimizing their design and processing conditions for device applications. Methods to reliably identify the degree of aggregation in a solution prior to spin-casting and in the resulting film are therefore important for improving device performance. Whereas it is commonplace to use steady-state emission spectroscopy to identify the spectral features characteristic of the aggregate form, spectral interpretation can be complicated by overlap with bands due to isolated chains or, in the case of polymers, chain segments. One strategy to disentangle such spectra is via measurements of exciton–exciton annihilation (EEA) which is a process that is highly sensitive to inter-chromophore interactions. Many multi-chromophoric systems including conjugated polymers,^{1–12} dendrimers,¹³ J-aggregates,¹⁴ and plant light-harvesting complexes exhibit EEA, even at relatively low light fluences.¹⁵ EEA is characterized by an increase in the excited-state decay rate and a sublinear scaling of the signal amplitude with photon flux. EEA can occur when more than one chromophore within the aggregate is excited within a single laser pulse. In EEA, energy transfer between two excited subunits drives one to a higher-lying excited state (S_n), while the other directly repopulates the ground state.¹⁶ The highly excited chromophore can exhibit a faster excited-state decay rate and a decreased emission yield compared to the isolated chromophore in its S_1 state because

additional nonradiative channels can be accessed at high energy. The probability of EEA increases with excitation fluence due to the greater likelihood of simultaneously exciting two chromophores separated by a distance within their Förster radii ($< \sim 4$ nm) or larger distances if energy migration is highly efficient.¹⁷ Under these conditions, inter-chromophore energy transfer becomes competitive with the decay of an excitation localized on a single molecule. The sublinear dependence of the emission yield on laser power reflects the fact that at least one of the two chromophores involved in the annihilation event decays nonradiatively to the ground state.

Once a highly excited species is formed via EEA, it has several possible deactivation pathways. It can experience a rapid nonradiative decay directly from the state populated via EEA or undergo vibrational relaxation to S_1 from which it is likely to emit. In both cases, the neutral ground state is reformed. The excess energy may also facilitate charge separation and polaron formation.^{3,18–20} Singlet fission to form two neutral triplets can also be observed.²¹ Enhancing the efficiencies of polaron formation and of singlet fission at low excitation powers is of particular interest in optimizing materials for device applications.²² Transient absorption measurements to identify the final

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state in the annihilation process in the aggregates studied here are in progress.

EEA observed in isolated polymer chains such as MEH–PPV in solution^{3,10,11} has been attributed to rapid migration of the excitations along the chain in these multichromophoric systems. It has also been correlated with more ordered chain packing in chiral stacks of oligomeric PPVs⁴ and with increased β -phase content in polyfluorene films.¹² Here we show that EEA is a useful tool for disentangling overlapping emission spectra arising predominantly from monomeric versus aggregated chains by measuring the contribution of EEA to the fluorescence dynamics at each vibronic band in a series of oligomeric PPV (OPP_V, Chart 1) nanoaggregates.

Chart 1. OPPV Oligomer Structures^a

^aFor OPPV7, $n = 3$, and for OPPV13, $n = 6$.

EXPERIMENTAL METHODS

Nanoaggregates of oligomeric and polymeric conjugated materials^{23–33} were formed by addition of a nonsolvent (e.g., methanol (MeOH) or water) to a 1–10 μ M stock solution of the oligomers in a good solvent such as methyl tetrahydrofuran (MeTHF) or tetrahydrofuran (THF) and vortexed. The aggregate spectra and dynamics were studied in fluid suspension. The size distributions of the resulting aggregates were determined by dynamic light scattering (DLS) using a Malvern Zetasizer Nanoseries ZS instrument. The fluorescence upconversion experiments were performed at the Center for Functional Nanomaterials at Brookhaven National Laboratories.³⁴ The excitation wavelength was 420 nm, the spot size was 1×10^{-3} cm², and the laser repetition rate was 1 kHz. Under these conditions, 10 μ W corresponds to 10 μ J/cm² or $\sim 2 \times 10^{13}$ photons/cm². The excitation wavelength lies at the peak of the OPPV7 absorption band but on the blue edge of the OPPV13 absorption band near the half-maximum point.³⁵ The collection wavelengths were all ± 5 nm. All decays are fit to a multiexponential model, which is found to be adequate to reproduce the experimental curves, rather than to a nonexponential (stretched exponential) model. The multiexponential model was chosen because we feel that reporting distinct decay components better captures the physical effects arising from more than one distinct emitter type than would reporting a single stretching exponent.

RESULTS AND DISCUSSION

The vibronic structure of the emission spectra of PPV-type oligomers and MEH–PPV itself is a sensitive probe of their degree of aggregation.^{29,35–44} In the series of substituted oligomeric PPVs studied here, the aggregation-induced spectral perturbations increase with increasing solvent polarity and oligomer chain length.^{35,36} For example, the emission spectrum of the shorter-chain oligomer aggregates (i.e., OPPV7, Figure 1) is either unchanged (MeTHF:MeOH) or shows a small red shift and a slight change in the relative peak heights (THF:water) compared to the monomer.^{35,36} The differences observed between the two solvent systems can be rationalized

Figure 1. OPPV7 monomer and aggregate emission spectra. Monomer spectra were obtained in the absence of MeOH or water. Intensities are arbitrary.

by considering the increased interaction strength (or, equivalently, the reduced solubility) of OPPV7 in THF:water versus MeTHF:MeOH. In previous work, we used the effects of filtration on the aggregate suspensions as a qualitative measure of their interchain interactions. Specifically, syringe filtration of the suspension of OPPV7 in THF:water (60% water) was shown to produce a nonemissive eluant which means that the aggregates are entirely trapped within the filter.³⁶ In contrast, after filtering OPPV7 aggregates formed in MeTHF:MeOH, the emission of the original solution is recovered in the elutant quantitatively. This suggests that the aggregates are disrupted on filtration. In principle, this would also be seen if a significant number of monomeric chains are present in the suspension. However, dynamic light scattering and fluorescence imaging results did not support this interpretation.³⁵

In contrast to what is seen in OPPV7, aggregation significantly alters the overall vibronic envelope of OPPV13 (Figure 2).^{35,36} Specifically, with increased proportions of poor solvent, intensity is lost in the spectral origin and gained in the vibronic replicates. These changes have alternatively been interpreted within a modified H/J aggregate model^{45,46} or as arising from a mixture of emitter types.^{40,47,48} Evidence for the latter model is that the spectra at low percentages of poor solvent (i.e., <50% water, Figure 2) can be decomposed into contributions from the monomer and from the aggregate (>50% water, Figure 2), meaning that they arise from a combination of both emitter types. This is demonstrated in the Supporting Information (Figure S2).

The solvent-induced spectral changes in OPPV13 are more obvious in THF:water than in MeTHF:MeOH and occur at a lower percentage of poor solvent.³⁶ As discussed above, this can be attributed to tighter packing of the chains in the THF:water aggregates combined with the presence of fewer unaggregated chains in the suspension.^{35,36}

Comparing Figures 1 and 2 highlights an interesting difference between the shorter- and longer-chain species which is that the emission spectra of the latter are more highly

Figure 2. OPPV13 monomer and aggregate emission spectra as a function of varying ratios of MeTHF:MeOH (top) and THF:water (bottom). Monomer spectra were obtained in MeTHF and THF, respectively.

perturbed in the aggregate form. The excited state dynamics follows the same trend, as discussed below and in refs 35 and 36. In analogy to the previous discussion comparing the effects of THF:water and MeTHF:MeOH as the aggregating solvents, we attribute the effect of oligomer chain length to stronger interchain interactions in aggregates of OPPV13 versus OPPV7 that is due to greater dispersion forces between the longer chains. This was assessed in prior work^{35,36} in which aggregates of OPPV13 in MeTHF:MeOH were shown to be trapped upon syringe filtration of the fluid suspensions, whereas those formed from OPPV7 were not.

Below we show that the wavelength dependence of the EEA probability can differentiate the emission features due primarily to monomer-like emitters versus tightly packed emitters. In addition, the contribution of EEA to the overall decay kinetics is shown to correlate to the proportion of aggregated chains in the sample and to the interchain interaction strength.

For comparison to the aggregated forms, the dynamics of monomeric OPPV7 and OPPV13 were measured as a function of wavelength and excitation power. Both exhibit wavelength-independent decays which, at low powers (20–50 μW , Figure 3), are in good agreement with previous TCSPC results (650 ps for OPPV7 and 565 ps for OPPV13).³⁵ A small (<10%) rise component is seen in OPPV7 that is attributable to excited-state structural relaxation (Table 1). At higher powers (300–600 μW), the lifetimes decrease slightly (Figure 3), particularly for OPPV7. This reduction in lifetime could be indicative of EEA on a single chain, as was previously reported in a five-ring oligomer.¹⁸ However, as the signal from both oligomers remains linear at the higher powers (not shown), the EEA contribution to the overall dynamics appears minimal.

Aggregating OPPV7 in MeTHF:MeOH does not significantly change its emission spectrum or yield (Figure 1).³⁵ Likewise, the dominant decay component in the aggregate

Figure 3. OPPV7 (top) and OPPV13 (bottom) monomer emission decays and fits as a function of excitation laser power.

Table 1. Emission Decay Kinetics for OPPV7 Aggregates

sample	power ^a	500 ^b	530	570
MeTHF	50	24 ^c (–8) ^d	11 (–9)	9 (–16)
		674 (92)	683 (91)	734 (84)
		10 (–13)	8 (–16)	7 (–21)
75% MeOH	25	522 (87)	532 (84)	651 (79)
		3 (1)	11 (–1)	9 (–13)
		666 (99)	637 (99)	658 (87)
65% water	600	12 (–1)	8 (–1)	8 (19)
		629 (99)	649 (99)	700 (81)
		388	350	485
80% Water	150	28 (28)	47 (38)	37 (–9)
		292 (72)	378 (62)	395 (91)
		61 (33)	82 (42)	
10–20	600	437 (67)	585 (58)	358
		4 (26)	5 (21)	6 (17)
		65 (45)	59 (44)	69 (44)
		393 (29)	388 (35)	457 (39)

^aIn μW . ^bIn nm. ^cIn ps. ^dAmplitudes normalized to 100; negative sign denotes a rise.

(Table 1) is essentially that of the monomer. The emission decay is essentially independent of collection wavelength and laser power (Figure 4 and Table 1). The latter indicates that EEA is inefficient in these species.

Though the lifetimes of OPPV7 and its aggregate in MeTHF:MeOH are unaffected by increasing excitation power, their power saturation behavior is quite different. Specifically, the monomer emission yield is linear up to 1200 μW (not shown), while that of the aggregate is sublinear at all but the lowest powers used ($\leq 50 \mu\text{W}$, Figure 5). An enhanced saturation rate for the aggregate could be rationalized if its oscillator strength is significantly larger than that of the monomer. Though this could possibly be expected from a large number of closely coupled chromophores, it is not apparent from comparing the linear absorption spectra of the monomeric and aggregated oligomers.³⁵ Moreover, though a larger extinction coefficient implies a faster radiative rate, the decay rate of OPPV7 is essentially unchanged on aggregation.

Figure 4. OPPV7 MeTHF:MeOH aggregate emission decays at low and high excitation powers.

Figure 5. Power dependence of emission intensity of OPPV7 aggregates formed in 75% MeOH (top) and 80% water (bottom) measured at a delay of 6 ps (dark circles) collecting at 500 nm. The light squares provide a guide to the eye that indicates the expected signal assuming a zero intercept and a linear increase in emission with power starting from the lowest power used (25 μ W).

An alternative mechanism for the enhanced saturation rate in the aggregates is that their emission is quenched essentially instantaneously (i.e., by a “static” mechanism) above a threshold laser power. In transient spectroscopic studies of PPV in thin films, Bardeen and co-workers observed similar behavior and attributed it to photoinduced generation of free charges or nonemissive charge-transfer states with large effective quenching radii (estimated as $> \sim 4$ nm) that persist for several nanoseconds.⁴⁹ For the emission lifetime to be unaffected by energy transfer, this process must be faster than the experimental time resolution.^{3,7,18,19,27,50–54} The observed emission quenching would be the only evidence for enhanced charge separation in these aggregates but is consistent with several other reports of photoinduced quenchers in PPV-type materials. In these studies, the spectral features associated with the quencher are found to overlap significantly with excitonic bands and have a relatively low formation efficiency (5–10%).^{51,55–57} However, as a single charge can quench

thousands of emitters due to efficient energy transfer,^{32,58} present evidence does not completely rule out polaron formation as the origin of enhanced power saturation in the aggregates.

Aggregating OPPV7 in the more polar solvent mixture of THF and water produces a small red shift of the emission spectrum (Figure 1) and a decreased lifetime as measured by TCSPC.³⁶ As expected, these effects are enhanced with increasing percentage of water.³⁶ The emission intensities in THF:water are more markedly sublinear in power (Figure 5) than are those in MeTHF:MeOH. Moreover, in THF:water, the emission decay rate is faster than that in the monomer and increases with laser power (Figure 6 and Table 1). This is

Figure 6. Emission decays of OPPV7 monomer and THF:water aggregates measured as a function of excitation power collecting at 500 nm.

consistent with an EEA mechanism. As the aggregates in both solvent pairs are comparable in size (mean diameter ~ 200 – 300 nm measured by DLS, Supporting Information Figure 1) and absorptivity (not shown), the initial spatial distributions of the excitons created within a single laser pulse should be similar. The fact that EEA occurs when aggregates are formed in THF:water but not in MeTHF:MeOH indicates that exciton migration is faster in THF:water. This suggests that the aggregated chains are more tightly packed and/or more ordered in the more polar solvent system.^{35,36}

Additional evidence for enhanced energy transfer in the THF:water aggregates is that they exhibit wavelength-dependent fluorescence dynamics. Specifically, a small contribution due to energy transfer from higher- to lower-energy chains appears as a fast decay component at 500 and 530 nm and a rise at 570 nm that can be seen at low powers (Figure 7, top, and Table 1). This was previously observed using TCSPC.³⁶ At high powers, the initial dynamics at all three wavelengths are dominated by fast decay due to EEA (Figure 7, bottom, and Table 1).

In the longer chain species, OPPV13, more significant changes in the spectra and photophysics occur on aggregation (compare Figures 1 and 2).³⁵ The intensity of the highest-energy band (510 nm, the electronic origin of the monomer) decreases relative to the lower-energy vibronic bands (540 nm and 580 nm) with increasing poor solvent in both solvent pairs. Moreover, the aggregates formed in both solvent pairs show wavelength-dependent fluorescence lifetimes as measured using TCSPC.³⁵ This arises because each aggregate contains two types of emitters that have spectral features and dynamics characteristic of the monomer and aggregate, respectively.^{35,48} As shown below, the relative contribution of EEA to the

Figure 7. Expanded view of OPPV7 THF:water emission decay kinetics at low and high powers.

ultrafast dynamics in the monomer and aggregate wavelength regions supports this picture.

Considering first OPPV13 in the MeTHF:MeOH solvent pair, three representative samples were formed from solutions containing varying percentages of poor solvent (Figure 8) and the decays were collected at wavelengths corresponding to the vibronic peaks of the emission spectra (510, 540, and 580 nm, see Figure 2). The overall trend (Figure 8) is faster decays with increased aggregation (higher percentage of MeOH, Figure 8) with the dynamics at 510 nm (monomer origin) being noticeably slower than those in the aggregate region (540–620 nm, Figure 2) at all but the highest MeOH percentage (70%).

Trends in the decay dynamics of OPPV13 as a function of percent MeOH, wavelength, and laser power (Table 2) can be used to propose assignments for the species associated with each decay component. We focus first on the low power results (20–40 μ W) as being representative of the quasi-linear regime. While the monomer is well fit at all wavelengths to a single exponential decay, a fast decay component appears (2–20 ps) at relatively small percentages of MeOH (Table 2, 40% MeOH). Its relative amplitude increases with increased aggregation (higher percent MeOH, Table 2). At 40% MeOH, this fast component is more prominent in the aggregate spectral region than at the monomer origin. It is therefore assigned to a combination of EEA and energy transfer in tightly packed chains, by analogy to the results for OPPV7 aggregates. The longer component (300–500 ps) is assigned to monomeric or weakly packed chains. Its relative amplitude is highest at the monomer origin and decreases at all wavelengths with increased poor solvent or increased aggregation (Table 2).

Raising the laser power to above the signal saturation level produces two interesting effects. First, fitting the decays in the aggregate region requires incorporating a third decay component (30–50 ps) at higher powers, while the dynamics at 510 nm remain biexponential (40–65% MeOH, Table 2). This intermediate decay is therefore associated with aggregated chains and may reflect less efficient EEA in aggregate regions that are more disordered. Second, for the most highly aggregated sample (75% MeOH), the relative amplitude of

Figure 8. Wavelength dependence of the OPPV13 aggregate emission decays as a function of increasing MeOH percentages.

the longest decay component (i.e., that due to the monomer-like chains) actually *increases* with laser power, particularly in the predominantly monomer emission region. This initially counterintuitive result can be rationalized if the emission from the aggregated chains saturates at lower powers than that from the monomer-like emitters. This was found to be the case for OPPV7 (Figure 5).

In summary, the relative contribution of EEA and energy transfer to the fluorescence decay reflects the proportion of monomeric to aggregated chains in each wavelength region of the spectrum and therefore provides a framework within which to interpret complex overlapping spectral signals. In the case of OPPV aggregates, the ultrafast dynamics are fully consistent with the picture of variation in intensity at the spectral origin (510 nm) with percentage of poor solvent being due to the relative proportion of monomer-like chains in the suspension.

In a solvent pair with a larger polarity difference, THF:water, the contribution of the monomer-like decay is lower. As a result, the overall emission decay rate is faster than that in MeTHF:MeOH for a comparable percentage of poor solvent (Figure 9 and Table 3). The faster decays in THF:water versus MeTHF:MeOH connect the probability of EEA to increased aggregation in the more polar environment. This is consistent with our previous measures of chain–chain interaction strength.^{35,36,48} It is notable that the sub-5 ps component is larger at 510 nm than at 540 nm at low power (20 μ W) which is opposite the trend in MeTHF:MeOH (Figure 9 and Tables 2

Table 2. Emission Decay Kinetics for OPPV13 MeTHF:MeOH Aggregates

solvent	power ^a	510 ^b	540	580	620
MeTHF		559 ^c	575	576	573
40% MeOH	20–40	7 (23) ^d	9 (36)	19 (46)	19 (47)
		473 (74)	366 (64)	302 (54)	331 (55)
	240	5 (29)	3 (32)	3 (47)	1 (38)
			36 (20)	45 (23)	42 (24)
50–65% MeOH	20–240	486 (71)	510 (48)	538 (30)	475 (38)
		4 (44)	3 (35)	3 (46)	3 (49)
			32 (34)	41 (33)	44 (32)
			420 (31)	373 (21)	427 (19)
75% MeOH	10	442 (56)	3 (41)	9 (49)	13 (55)
		2 (62)			
	100	62 (38)	75 (59)	89 (51)	121 (45)
		2 (67)	2 (37)	6 (62)	4 (50)
		53 (15)	26 (46)	26 (29)	64 (50)
		570 (18)	397 (17)	272 (9)	

^aIn μW . ^bIn nm. ^cIn ps. ^dAmplitudes, normalized to 100.

Figure 9. Expanded view of OPPV13 in THF:water and MeTHF:MeOH (both 40:60) as a function of emission wavelength. The excitation power was 20 μW . Fits to the data are shown in dotted lines (see Tables 2 and 3 for fit parameters).

Table 3. Power Dependence of Emission Kinetics for OPPV13 THF:Water Aggregates

sample	power ^a	510 ^b	540	580	620
60% water	20	2 ^c (67) ^d	3 (39)	4 (33)	4 (43)
		123 (33)	42 (28)	51 (45)	64 (42)
	100		342 (33)	406 (22)	662 (15)
		1 (61)	1 (49)		
200		17 (52)	23 (31)		
		336 (20)	293 (20)		
	200	1 (55)	2 (51)		
		19 (25)	37 (29)		
600		323 (20)	390 (20)		
		2 (52)	2 (49)		
	600	27 (29)	41 (29)		
		369 (19)	411 (22)		

^aIn μW . ^bIn nm. ^cIn ps. ^dAmplitudes, normalized to 100.

and 3). This is consistent with the THF:water aggregates exhibiting both a higher probability of EEA at higher energies and fast energy transfer.

CONCLUSIONS

The relative contribution of EEA to the fluorescence dynamics is shown to reflect interchain interaction strength in conjugated organic aggregates. The wavelength dependence of the EEA signal is also an effective means of differentiating the emission features due to monomeric and aggregated chains when their spectra are highly overlapping. Application of this method to aggregates of oligomeric PPVs formed using two different solvent systems yields dynamical information that is complementary to morphological data previously obtained using fluorescence lifetime imaging methods.⁴⁸

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.6b11250.

Dynamic light scattering data showing the size distribution of aggregates formed from OPPV7 in MeTHF:MeOH and THF:water and an example of the decomposition of the OPP13 THF:water spectrum into contributions from the monomer and aggregated species (PDF)

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Notes

The authors declare no competing financial interest.

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