University of Groningen

Detection of Ultralow Concentrations of Non-emissive Conjugated Polymer Aggregates via Fluorescence Correlation Spectroscopy

Wu, Eric C.; Stubbs, Regan E.; Peteanu, Linda K.; Jemison, Racquel; McCullough, Richard D.; Wildeman, Jurjen

Published in:
Journal of Physical Chemistry B

DOI:
[10.1021/acs.jpcc.7b01918](https://doi.org/10.1021/acs.jpcc.7b01918)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2017

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Wu, E. C., Stubbs, R. E., Peteanu, L. K., Jemison, R., McCullough, R. D., & Wildeman, J. (2017). Detection of Ultralow Concentrations of Non-emissive Conjugated Polymer Aggregates via Fluorescence Correlation Spectroscopy. *Journal of Physical Chemistry B*, 121(21), 5413-5421.
<https://doi.org/10.1021/acs.jpcc.7b01918>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Detection of Ultralow Concentrations of Non-emissive Conjugated Polymer Aggregates via Fluorescence Correlation Spectroscopy

Eric C. Wu,[†] Regan E. Stubbs,[†] Linda A. Peteanu,^{*,†} Racquel Jemison,^{†,§} Richard D. McCullough,^{†,||} and Jurjen Wildeman[‡][†]Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, United States[‡]Zernike Institute of Advanced Materials, Nijenborgh 4, 9747 AG Groningen, The Netherlands

S Supporting Information

ABSTRACT: The aggregation of conjugated polymers in common organic solvents is investigated using fluorescence correlation spectroscopy (FCS), burst analysis, and microscopy. Poly(3-hexylthiophene) and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] are both shown to form weakly bonded non-emissive aggregates in toluene that persist even at picomolar concentrations. These aggregates decrease the bulk emission intensity in solution but do not affect the fluorescence spectra or lifetimes, consistent with a static quenching mechanism. Passing the solutions through a syringe filter causes an increase in the number of emitters as measured by FCS, indicating that this process dissociates the aggregates. Films cast from solutions that have been filtered are more uniform and significantly more emissive than those made from unfiltered solutions. These results show that FCS is a highly sensitive probe of non-emissive aggregates in solution that have a deleterious effect on the emission properties and overall quality of spin-cast thin films, even at sub-nanomolar concentrations.

■ INTRODUCTION

Because they can serve both as charge conductors and fluorescence emitters, conjugated polymers are employed in organic electronics,¹ photovoltaics,² and organic electroluminescent devices (OLEDs).³ The performance of these devices is critically dependent on the packing of the polymers because their optical and electronic properties are altered significantly by interchain and intrachain interactions. For example, aggregation dramatically decreases the quantum yields of these polymers which severely limits luminescent device performance.^{4–11} Moreover, it is well-established that polymer preaggregation in the concentrated solutions used in the casting process directly impacts the resulting thin film properties.^{4,6,9,11–13} Past studies have also shown that solvent choice affects the properties of the cast film by controlling the propensity for aggregation.^{4,6,13–16} As one example, Schwartz et al. demonstrated that MEH-PPV adapts a more extended conformation in chlorobenzene than in tetrahydrofuran (THF) and that this favors aggregation.⁴ Another common solvent used in the processing of conjugated polymers, toluene,^{17,18} is expected to behave similarly to chlorobenzene in that interactions of the conjugated rings of the polymer with those of toluene should also favor planarization of the chains.¹⁰

Aggregation of conjugated polymers is typically detected via dynamic light scattering (DLS)^{4,6,7} or through perturbations to their emission spectra and/or lifetimes.^{12,14,19,20} Each technique has its limitations, however. DLS cannot detect aggregates

smaller than 5 nm. If the aggregates are non-emissive or have identical spectra and fluorescence lifetimes as the single chains, these properties cannot be used to detect aggregation. An alternative strategy is fluorescence correlation spectroscopy (FCS).^{21–28} When combined with fluorescence burst analysis, the effect of interchain interactions and the local solvent environment on the emission of the polymer chains can be inferred. This paper demonstrates that FCS is a viable technique for the detection of aggregation in conjugated molecules at picomolar concentrations by comparing their propensity to form aggregates in toluene versus THF. Aggregates present even at these low concentrations are shown to have a detrimental effect on the emission properties of films cast from solution. However, filtration of the starting picomolar solutions using a syringe filter disrupts these aggregates, resulting in a significant increase in emission intensity in solution and in the spin-cast thin films.

Two common conjugated polymers, poly(3-hexylthiophene) (P3HT) and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), were studied along with several oligomeric PPV-based compounds (Scheme 1). The oligomers serve as useful model systems for the longer polymer chains^{29–40} because, though they should have similar interchain

Received: February 27, 2017

Revised: May 3, 2017

Published: May 4, 2017

Scheme 1. Structures of (a) PPV oligomers ($n = 3$ for OPPV7 and $n = 6$ for OPPV13) and the polymers (b) MEH-PPV and (c) P3HT

interactions, they possess fewer defects⁴¹ and they have a single conjugation length. The absence of defects allows the effects of aggregation on emission quenching to be isolated from that due to energy transfer to a non-emissive defect site. The single conjugation length allows the propensity of aggregation as a function of chain length to be explored.

EXPERIMENTAL SECTION

Bulk and single-molecule fluorescent techniques were used to examine MEH-PPV, two shorter chain oligomers (OPPV7 and OPPV13), and three P3HT polymers of three different chain lengths (25-mer, 50-mer, and 70-mer). Solutions (10 μM) of each compound were made by dissolving the solid material in toluene or THF. The solutions for FCS measurements were diluted with solvent to a concentration of ~ 10 pM. The solutions were passed through syringe filters having a hydrophobic PTFE membrane and pore size of 0.20 μm (EMD Millipore) unless otherwise noted. The sample films are made from 10 μL of 10 μM solutions spin-cast at 3000 rpm and dried for 30 s (Laurell WS-650MZ-23NPP). Absorption and emission spectra were collected using an Agilent Cary 50 Bio UV-vis spectrometer and Jobin-Yvon FluoroMax 2, respectively.

For confocal microscopy, the excitation source was either a 440 or 485 nm pulsed diode laser (Picoquant). A 1.4 NA 100 $\times$ oil objective (Olympus UPlanSAPO 100 $\times$ 1.4 oil) was mounted on an inverted microscope (Olympus IX-71). The emission was directed through a 100 μm pinhole to a 50–50 beam splitter (Semrock), which split the emission onto two single photon avalanche diodes (Micro Photon Devices PDM50). A long-pass filter (475 nm for OPPV7 or 515 nm for all other compounds) was placed in front of the beam splitter to remove scattered light. Time-tagging of the photons

Figure 1. (a) TIRF images of P3HT 25 in toluene (1) unfiltered and (4) filtered, MEHPPV in toluene (2) unfiltered and (5) filtered, and MEHPPV in THF (3) unfiltered and (6) filtered, and the distributions of pixel intensities for (b) P3HT 25 in toluene, (c) MEHPPV in toluene, and (d) MEHPPV in THF. In the images, the dark level is set at 600 cps which is higher than the background noise level of the camera. The black dashed line represents the background noise level of the camera.

was performed using the PicoHarp 300 and PHR 800 electronics (Picoquant). All of the data were collected and analyzed using the SymPhoTime software package (Picoquant).

Total internal reflection (TIRF) microscopy was performed using through-objective excitation via a 60× oil 1.4 NA oil immersion objective on an inverted microscope (Olympus IX-71). The excitation source was the 488 nm output of an Ar–Kr laser (Coherent). The images were collected using a CCD camera (Photometrics Evolve 512 EMCCD). A 515 nm long-pass filter was placed after the microscope to remove scatter.

FCS measures the diffusion of the fluorescent probes by monitoring the fluctuations of the photon intensities $I(t)$ in the focal volume. The FCS curve, $G(\tau)$, is calculated by cross-correlating the photon intensities of the two detectors²⁷

$$G(\tau) = \frac{\langle \delta I(t) \delta I(t + \tau) \rangle}{\langle I(t) \rangle^2} \quad (1)$$

where $\langle \rangle$ denotes average over the entire trajectory and $\delta I(t)$ is the deviation from the mean photon intensity at time t .

$$\delta I(t) = I(t) - \langle I(t) \rangle \quad (2)$$

Here, the focal volume is assumed to have a three-dimensional Gaussian shape, and the FCS curve is fitted to⁸

$$G(\tau) = \frac{1}{N} \sum_{i=1}^n a_i \left(1 + \frac{\tau}{\tau_{D_i}} \right)^{-1} \left(1 + \frac{1}{\omega^2} \left(\frac{\tau}{\tau_{D_i}} \right) \right)^{-1/2} \quad (3)$$

where N is the average number of molecules in the focal volume, n is the number of species, a_i is the contribution of the i th species, τ_{D_i} is the characteristic residence time for the i th species, and ω ($= z_0/r_0$) characterizes the dimension of the focal volume with z_0 and r_0 being the axial and radial dimensions of the focal volume, respectively. For all FCS fits, $\omega^2 = 5$. ω^2 is calculated by fitting the FCS curves of a dye, Nile Red, in acetonitrile to a simple diffusion model (single diffusion constant).

RESULTS AND DISCUSSION

The TIRF images of films cast from unfiltered and filtered 10 μ M solutions of P3HT 25 and MEH-PPV in toluene and the distribution of pixel intensities are presented in Figure 1.

Though absorbance measurements (not shown) showed that between 1 and 10% of the conjugated polymer sample is lost through filtration, the films cast from filtered solutions were up to five times brighter than those cast from the unfiltered solutions. For comparison, films made from THF did not show an increase in brightness after filtering (Figure 1d). The poor quality of the unfiltered toluene films is consistent with the formation of aggregates in toluene prior to casting as aggregates typically have lower quantum yields than isolated chains.^{4–11} Past studies have shown that the average energy transfer length in bulk conjugated materials ranges from 5 to 10 nm.^{42–47} Low-quantum-yield aggregates can therefore serve as energy traps that quench large area of the films. This would lower the overall brightness of the films and make them appear less uniform. To determine whether these conjugated polymers have a strong propensity to aggregate in toluene, the diffusion rates, the absorption/emission spectra, and the fluorescence lifetimes of the filtered and unfiltered solutions were examined.

The absorption spectra of all six compounds are essentially unchanged upon filtering though the intensities decrease slightly due to loss of material in the process (not shown).

Their emission intensities increased after filtration though generally by a factor lower than that observed in the TIRF images. After the spectra were corrected for concentration by dividing by the absorbance at $\lambda = 465$ nm, the observed enhancement was 1–5%, 6–10%, and 1–3% for P3HT 25, P3HT 50, and P3HT 70, respectively. The corresponding quantities were 13–17%, 170–800%, and 2–27% for OPPV7, OPPV13, and MEHPPV, respectively. The emission spectra, however, are essentially unchanged on filtration (Figure 2a,b)

Figure 2. Normalized emission spectra of (a) P3HTs and (b) PPVs in toluene excited at 465 nm. The (—) unfiltered sample and (---) filtered samples are compared.

as are the absorption spectra (not shown). This contrasts with past studies of aggregated P3HTs and PPVs that were deliberately aggregated by addition of a poor solvent such as methanol or water. In these instances, significant spectral changes were observed in absorption and emission such as a shift in λ_{max} and a change in the relative intensities of the 0–0 band relative to the vibronic replicates.^{7,9} The similarity between the unfiltered and filtered spectra in toluene therefore suggests that the aggregates formed are not emissive.

Further evidence that this is the case comes from the fact that the emission lifetime is also essentially unchanged on filtration (Table S1). Changes in the fluorescence lifetime are often indicative of aggregation. For example, if the aggregates form excimers, the fluorescence lifetime typically increases due to the diminished transition moment to the ground state.⁴⁸ The lifetime could also decrease if the aggregates form low-energy dark states that cause an increase in the nonradiative decay

constant.^{7,49,50} For two of the P3HT samples, there was an increase in the amplitude of a 4 ns component after filtering, which could indicate the presence of excimers. However, this component represents at most 20% of the overall amplitude of the decay (Table S1) and therefore does not provide a very reliable tool for probing aggregation.

In summary, the emission intensities of the samples dissolved in toluene are strongly enhanced on filtering, though neither the absorption/emission spectra nor the fluorescence lifetimes are appreciably affected. This is consistent with the formation of non-emissive aggregates (i.e., static quenching) that are present in low enough concentration that they cannot reliably be detected via absorption. Single-molecule fluorescence methods were then used to confirm this interpretation. The fluorescence intensities of the polymers and oligomers were first measured in toluene solution using the confocal microscope at 10 pM. The average intensities for each sample were calculated by summing the number of photons collected by both detectors over a 5 min period. These were background corrected by subtracting the average intensity of the solvent. For all six samples, the increase in the average intensity upon filtering was similar to that seen in the corresponding film samples via TIRF (Table 1). In addition, as the length of the

Table 1. Fluorescence Intensities of P3HT Polymers, MEH-PPV, and PPV Oligomers Measured Using the Confocal Microscope

	$\langle I_{\text{filtered}} \rangle / \langle I_{\text{unfiltered}} \rangle$
P3HT 25	1.51 ± 0.03
P3HT 50	1.4 ± 0.1
P3HT 70	2.5 ± 0.4
OPPV 7	1.31 ± 0.08
OPPV 13	1.46 ± 0.07
MEH-PPV	3.6 ± 0.5

chain increased, the ratio of the average intensity after to before filtering, $\langle I_{\text{filtered}} \rangle / \langle I_{\text{unfiltered}} \rangle$, also increased in all but the case of P3HT 25 and P3HT 50, which showed a small decrease.

In general, two different aspects of FCS are useful in detecting aggregation: the shape of the normalized FCS curve and the value of $G(0)$ for the un-normalized curve. The $G(0)$ value may be used to infer the presence of *non-emissive* species, whereas the shape of the FCS decay is sensitive to the presence of *emissive* aggregates. Here, we focus on the former, while the latter will be discussed in a future contribution.

At $\tau = 0$, eq 1 becomes $G(0) = 1/N$, which means $G(0)$ is inversely proportional to the number of emitters, $\langle N \rangle$, in the focal volume. A larger $G(0)$ therefore means there are fewer emitters in the focal volume. The brightness per molecule can be calculated by multiplying the average intensity by $G(0)$.

$$B \text{ (brightness per molecule)} = \langle I \rangle G(0) = \frac{\langle I \rangle}{\langle N \rangle} \quad (5)$$

The FCS curves for all six compounds are shown in Figure 3, while $G(0)$ and the brightness per molecule are tabulated in Tables 2 and 3.

For all six compounds, the value of $G(0)$ decreases after filtering, indicating that the average number of emitters in the focal volume increases. However, the overall shape of the normalized FCS curves is unchanged, which suggests that the average size of the emitting species is unchanged by filtration (Figure 4 and Figures S7–S11). The effect of filtering is

therefore to break up weakly bound aggregates into smaller aggregates or single chains. This was confirmed by decreasing the pore size of the filter. As one example, OPPV13 in toluene, the decrease in $G(0)$ is larger when the 0.1 μm versus the 0.2 μm pore filter is used (Figure 5) because more aggregates are disrupted.

Because $\langle I \rangle$ increases and $G(0)$ decreases with increased chain length, the ratio of B_{filtered} to $B_{\text{unfiltered}}$ remains close to 1. This demonstrates that the quantum yields of the emitters are not affected by filtering, confirming again that the aggregates in toluene are *non-emissive*. We previously showed that the diffusion rates, emission spectra, and fluorescence lifetimes were not affected by filtering. Again, if the aggregates were emissive, significant changes in these properties would be expected. The data further show that, as the length of the polymers increases, the ratio $\langle N \rangle_{\text{filtered}} / \langle N \rangle_{\text{unfiltered}}$ increases. This trend suggests that longer chains are more likely to form aggregates than are the shorter chain species. This is not surprising as longer chains will have stronger interchain dispersion interactions. Moreover, if the solvent-chain interactions are unfavorable, longer chains will experience more of these, which will also drive aggregation.

To confirm the conclusions derived from FCS regarding the effects of sample filtration, the distributions of photon per burst were analyzed (Figure 6). If the number of emitter increases upon filtering, the number of bursts should also increase. On the other hand, if the quantum yield of the emitters increases, the distribution would shift to the right. More bursts were collected from the filtered than from the unfiltered solutions, though both were at the same concentration, and the measurements were performed over the same amount of time. This result suggests that the increase in intensity postfiltering is due to an increase in the number of emitters and not to a change in the quantum yield, which again confirms the FCS results. Moreover, the number of bursts increased by 26%, which is close to the increase in the number of emitter measured in FCS (Table 2).

Overall, the methods described are a remarkably sensitive probe of aggregation in solution given that they are performed at picomolar concentrations. Here, we will generalize our results to show how $G(0)$ and B can be used to probe other possible types of aggregation behavior. First, if the individual chains are well solvated and isolated in solution, or if they form stable aggregates that are smaller than the pore size of the filters, they should not be affected by the filtration process. In this situation, both $G(0)$ and B would be unchanged after filtering. This is the case for OPPV13 and P3HT25 in good solvents such as 2-methyltetrahydrofuran (MeTHF) (Figure 7). Second, if the solvent forces the chain to be in a thermodynamically metastable state that has lower quantum yield, such as a self-collapsed conformation with large torsional strains,^{8,56,51} filtering could cause the chains to relax to a more stable conformation that has a higher quantum yield. In this situation, since the number of emitters stays constant, $G(0)$ would not change. However, B would increase due to the increased quantum yield. Lastly, if the chains form large emissive aggregates that are removed by the filters, $G(0)$ would increase after filtration because the number of emitters would decrease.

Finally, we briefly speculate on the origin of the quenching behavior observed in toluene. Many models of quenching have been proposed for conjugated molecules. Singlet–triplet and singlet–singlet exciton annihilation⁵² or the formation of

Figure 3. FCS of filtered and unfiltered polymers in toluene: (a) P3HT 25; (b) P3HT 50; (c) P3HT 70; (d) OPPV7; (e) OPPV13; (f) MEH-PPV.

Table 2. Effect of Filtration on the Values of $G(0)$ in Toluene

	$G_{\text{unfiltered}}(0)$	$G_{\text{filtered}}(0)$	$G_{\text{filtered}}(0)/G_{\text{unfiltered}}(0)$	$\langle N \rangle_{\text{filtered}}/\langle N \rangle_{\text{unfiltered}}$
P3HT 25	0.73 ± 0.02	0.62 ± 0.02	0.86 ± 0.04	1.18 ± 0.05
P3HT 50	0.94 ± 0.07	0.59 ± 0.02	0.62 ± 0.05	1.6 ± 0.1
P3HT 70	0.97 ± 0.10	0.40 ± 0.03	0.42 ± 0.05	2.4 ± 0.3
OPPV7	0.49 ± 0.03	0.40 ± 0.02	0.82 ± 0.06	1.2 ± 0.1
OPPV13	0.25 ± 0.01	0.17 ± 0.01	0.68 ± 0.05	1.5 ± 0.1
MEH-PPV	0.34 ± 0.04	0.11 ± 0.01	0.34 ± 0.05	3.0 ± 0.5

polareons^{53–55} are frequently invoked explanations for a decreased quantum yield. Very recently, Scheblykin et al. proposed that MEHPPV chains could form “dark regions” when the chains are self-collapsed,⁵⁶ and Vanden Bout and co-workers reported that the quantum yield of aggregate decreases in relatively polar solvent due to the stabilization of a non-radiative charge-transfer (CT) state.⁵⁷ We speculate that the

non-emissive aggregates in toluene are H-aggregates as originally described by Kasha and Davydov^{58,59} and elaborated upon by Spano.^{60–65} Using two coupled chains as a model, two different types of aggregates are categorized based on whether, in the lower excitonic level, the two molecular transition moments are aligned in-phase (J-aggregate) or out-of-phase (H-aggregate).^{58–66} Relative to the isolated monomers,

Table 3. Effects of Filtration on Brightness Per Molecule in Toluene

	$B_{\text{unfiltered}}^a$	B_{filtered}^a	$B_{\text{filtered}}/B_{\text{unfiltered}}$
P3HT 25	1310 ± 30	1680 ± 70	1.28 ± 0.06
P3HT 50	1120 ± 60	960 ± 50	0.86 ± 0.06
P3HT 70	1040 ± 60	1070 ± 60	1.03 ± 0.08
OPPV7	850 ± 20	890 ± 50	1.04 ± 0.06
OPPV13	1620 ± 70	1600 ± 80	0.98 ± 0.06
MEH-PPV	1240 ± 80	1000 ± 50	0.81 ± 0.07

^aIn cps (counts per second) per emitter. **Figure 4.** Normalized FCS curves for unfiltered and filtered OPPV13 in toluene. **Figure 5.** FCS of OPPV13 in toluene with different filters.

strongly coupled J-aggregates exhibit a red-shifted absorption band and strong emission, while H-aggregates have a blue-shifted absorption band and weak emission.^{9,59,67} The π - π interactions between toluene and the conjugated polymers likely favor a more planar conformation of the chains that is conducive to forming well-ordered strongly coupled and therefore non-emissive H-aggregates.^{60–65} As a result of this solvent interaction, H-aggregates observed in toluene are potentially more ordered and less emissive than those observed in other solvents. Another possibility is that conjugated polymers form weakly emissive excimers in the unfiltered solution as the planarized chains would also be conducive to

Figure 6. Distribution of photons per burst for unfiltered and filtered P3HT 25 in toluene collected over 1 h. **Figure 7.** FCS of filtered and unfiltered (a) OPPV13 and (b) P3HT 25 in MeTHF.

excimer formation. Due to the forbidden nature of the transition, excimers also have weak oscillator strengths to the ground state. This, combined with an increase in the probability of nonradiative decay due to the long radiative lifetime, could also result in complete emission quenching.^{31,39,40,48,68–71} While charge separation (polaron formation) would also be favored by chain stacking, the low dielectric environment of toluene makes that pathway appear less likely.

CONCLUSIONS

FCS and burst analysis are shown to be viable techniques to probe aggregate formation in conjugated polymers at picomolar concentrations not detectable using absorption/emission spectra, fluorescence lifetime, or DLS. By measuring the values

of $G(0)$ and the brightness per emitter, the effects of filtering, changing the solvent environment, or other perturbations on conjugated polymers can be better understood. In the examples presented here, FCS is used to show that conjugated molecules form non-emissive aggregates in toluene that persist upon dilution to picomolar concentrations. Reducing aggregation by filtering the solutions prior to casting is shown to significantly enhance the uniformity and emission yield of the resulting films. These findings help to rationalize previous reports that have emphasized the importance of using freshly prepared solutions of conjugated polymers in toluene for film processing.^{8,10}

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.7b01918.

Fluorescence lifetime and FCS data along with fits for the data; a brief discussion on the sensitivity of FCS measurements (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: peteanu@cmu.edu.

ORCID

Eric C. Wu: 0000-0003-4614-4635

Linda A. Peteanu: 0000-0003-0075-6521

Present Addresses

[§](R.J.) American Chemical Society, 1155 Sixteen Street, NW, Washington, DC 20036.

^{||}(R.D.M.) Harvard University, 1350 Massachusetts Avenue, Cambridge, MA 02138.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

L.A.P. acknowledges NSF CHE-1363050 for support of this work and Dr. Mircea Cotlet for helpful discussions.

■ REFERENCES

- (1) Sirringhaus, H.; Tessler, N.; Friend, R. H. Integrated Optoelectronic Devices Based on Conjugated Polymers. *Science* **1998**, *280*, 1741–1744.
- (2) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. Hybrid Nanorod-Polymer Solar Cells. *Science* **2002**, *295*, 2425–2427.
- (3) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdahl, M.; Salaneck, W. R. Electroluminescence in Conjugated Polymers. *Nature* **1999**, *397*, 121–128.
- (4) Nguyen, T.-Q.; Doan, V.; Schwartz, B. J. Conjugated Polymer Aggregates in Solution: Control of Interchain Interactions. *J. Chem. Phys.* **1999**, *110*, 4068–4078.
- (5) Nguyen, T.-Q.; Kwong, R. C.; Thompson, M. E.; Schwartz, B. J. Improving the Performance of Conjugated Polymer-Based Devices by Control of Interchain Interactions and Polymer Film Morphology. *Appl. Phys. Lett.* **2000**, *76*, 2454–2456.
- (6) Schwartz, B. J. Conjugated Polymers as Molecular Materials: How Chain Conformation and Film Morphology Influence Energy Transfer and Interchain Interactions. *Annu. Rev. Phys. Chem.* **2003**, *54*, 141–172.
- (7) Sherwood, G. A.; Cheng, R.; Smith, T. M.; Werner, J. H.; Shreve, A. P.; Peteanu, L. A.; Wildeman, J. Aggregation Effects on the

Emission Spectra and Dynamics of Model Oligomers of MEH-PPV. *J. Phys. Chem. C* **2009**, *113*, 18851–18862.

(8) Lin, H.; Hania, R. P.; Bloem, R.; Mirzov, O.; Thomsson, D.; Scheblykin, I. G. Single Chain versus Single Aggregate Spectroscopy of Conjugated Polymers. Where is the Border? *Phys. Chem. Chem. Phys.* **2010**, *12*, 11770–11777.

(9) Brazard, J.; Ono, R. J.; Bielawski, C. W.; Barbara, P. F.; Vanden Bout, D. A. Mimicking Conjugated Polymer Thin-Film Photophysics with a Well-Defined Triblock Copolymer in Solution. *J. Phys. Chem. B* **2013**, *117*, 4170–4176.

(10) Wang, D.; Yuan, Y.; Mardiyati, Y.; Bubeck, C.; Koynov, K. From Single Chains to Aggregates, How Conjugated Polymers Behave in Dilute Solutions. *Macromolecules* **2013**, *46*, 6217–6224.

(11) Hong, J.; Jeon, S. K.; Kim, J. J.; Devi, D.; Chacon-Madrid, K.; Lee, W.; Koo, S. M.; Wildeman, J.; Sfeir, M. Y.; Peteanu, L. A. The Effects of Side-Chain-Induced Disorder on the Emission Spectra and Quantum Yields of Oligothiophene Nanoaggregates: A Combined Experimental and MD-TDDFT Study. *J. Phys. Chem. A* **2014**, *118*, 10464–10473.

(12) Hao, X.-T.; McKimmie, L. J.; Smith, T. A. Spatial Fluorescence Inhomogeneities in Light-Emitting Conjugated Polymer Films. *J. Phys. Chem. Lett.* **2011**, *2*, 1520–1525.

(13) Nguyen, T.-Q.; Yee, R. Y.; Schwartz, B. J. Solution Processing of Conjugated Polymers: the Effects of Polymer Solubility on the Morphology and Electronic Properties of Semiconducting Polymer Films. *J. Photochem. Photobiol., A* **2001**, *144*, 21–30.

(14) So, W. Y.; Hong, J.; Kim, J. J.; Sherwood, G. A.; Chacon-Madrid, K.; Werner, J. H.; Shreve, A. P.; Peteanu, L. A.; Wildeman, J. Effects of Solvent Properties on Spectroscopy and Dynamics of Alkoxy-Substituted PPV Oligomer Aggregates. *J. Phys. Chem. B* **2012**, *116*, 10504–10513.

(15) Huser, T.; Yan, M. Solvent-Related Conformational Changes and Aggregation of Conjugated Polymers Studied by Single Molecule Fluorescence Spectroscopy. *J. Photochem. Photobiol., A* **2001**, *144*, 43–51.

(16) Bolinger, J. C.; Traub, M. C.; Brazard, J.; Adachi, T.; Barbara, P. F.; Vanden Bout, D. A. Conformation and Energy Transfer in Single Conjugated Polymers. *Acc. Chem. Res.* **2012**, *45*, 1992–2001.

(17) Günes, S.; Neugebauer, H.; Sariciftci, N. S. Conjugated Polymer-Based Organic Solar Cells. *Chem. Rev.* **2007**, *107*, 1324–1338.

(18) Shen, W.; Xiao, M.; Tang, J.; Wang, X.; Chen, W.; Yang, R.; Bao, X.; Wang, Y.; Jiao, J.; Huang, L.; et al. Effective Regulation of the Micro-Structure of Thick P3HT:PC71BM Film by the Incorporation of Ethyl Benzenecarboxylate in Toluene Solution. *RSC Adv.* **2015**, *5*, 47451–47457.

(19) Fauvett, T. J.; Zheng, T.; Jackson, N. E.; Ratner, M. A.; Yu, L.; Chen, L. X. Photophysical and Morphological Implications of Single-Strand Conjugated Polymer Folding in Solution. *Chem. Mater.* **2016**, *28*, 2814–2822.

(20) Thomas, A. K.; Brown, H. A.; Datko, B. D.; Garcia-Galvez, J. A.; Grey, J. K. Interchain Charge-Transfer States Mediate Triplet Formation in Purified Conjugated Polymer Aggregates. *J. Phys. Chem. C* **2016**, *120*, 23230–23238.

(21) Aragón, S. R.; Pecora, R. Fluorescence Correlation Spectroscopy as a Probe of Molecular Dynamics. *J. Chem. Phys.* **1976**, *64*, 1791–1803.

(22) Rigler, R.; Mets, Ü.; Widengren, J.; Kask, P. Fluorescence Correlation Spectroscopy with High Count Rate and Low Background: Analysis of Translational Diffusion. *Eur. Biophys. J.* **1993**, *22*, 169–175.

(23) Gell, C.; Brockwell, D. J.; Beddard, G. S.; Radford, S. E.; Kalverda, A. P.; Smith, D. A. Accurate Use of Single Molecule Fluorescence Correlation Spectroscopy to Determine Molecular Diffusion Times. *Single Mol.* **2001**, *2*, 177–181.

(24) Moerner, W. E.; Fromm, D. P. Methods of Single-Molecule Fluorescence Spectroscopy and Microscopy. *Rev. Sci. Instrum.* **2003**, *74*, 3597–3619.

- (25) Enderlein, J.; Gregor, I.; Patra, D.; Fitter, J. Art and Artefacts of Fluorescence Correlation Spectroscopy. *Curr. Pharm. Biotechnol.* **2004**, *5*, 155–161.
- (26) Enderlein, J.; Gregor, I.; Patra, D.; Dertinger, T.; Kaupp, U. B. Performance of Fluorescence Correlation Spectroscopy for Measuring Diffusion and Concentration. *ChemPhysChem* **2005**, *6*, 2324–2336.
- (27) Tcherniak, A.; Reznik, C.; Link, S.; Landes, C. F. Fluorescence Correlation Spectroscopy: Criteria for Analysis in Complex Systems. *Anal. Chem.* **2009**, *81*, 746–754.
- (28) Elson, E. L. Fluorescence Correlation Spectroscopy: Past, Present. *Biophys. J.* **2011**, *101*, 2855–2870.
- (29) Oelkrug, D.; Egelhaaf, H.-J.; Gierschner, J.; Tompert, A. Electronic Deactivation in Single Chains, Nano-Aggregates and Ultrathin Films of Conjugated Oligomers. *Synth. Met.* **1996**, *76*, 249–253.
- (30) Oelkrug, D.; Tompert, A.; Gierschner, J.; Egelhaaf, H.-J.; Hanack, M.; Hohloch, M.; Steinhuber, E. Tuning of Fluorescence in Films and Nanoparticles of Oligophenylenevinyls. *J. Phys. Chem. B* **1998**, *102*, 1902–1907.
- (31) van Hutten, P. F.; Krasnikov, V. V.; Hadzioannou, G. A Model Oligomer Approach to Light-Emitting Semiconducting Polymers. *Acc. Chem. Res.* **1999**, *32*, 257–265.
- (32) Bredas, J.-L.; Cornil, J.; Beljonne, D.; dos Santos, D. A.; Shuai, Z. Excited-State Electronic Structure of Oligomers and Polymers: A Quantum-Chemical Approach to Optical Phenomena. *Acc. Chem. Res.* **1999**, *32*, 267–276.
- (33) Bredas, J. L.; Beljonne, D.; Cornil, J.; Calbert, J. P.; Shuai, Z.; Silbey, R. Electronic Structure of π -Conjugated Oligomers and Polymers: A Quantum-Chemical Approach to Transport Properties. *Synth. Met.* **2001**, *125*, 107–116.
- (34) Collison, C. J.; Treemanekarn, V.; Oldham, W. J., Jr.; Hsu, J. H.; Rothberg, L. J. Aggregation Effects on the Structure and Optical Properties of a Model PPV Oligomer. *Synth. Met.* **2001**, *119*, 515–518.
- (35) Peeters, E.; Ramos, A. M.; Meskers, S. C. J.; Janssen, R. A. J. Singlet and Triplet Excitations of Chiral Dialkoxy-p-Phenylene Vinylene Oligomers. *J. Chem. Phys.* **2000**, *112*, 9445–9454.
- (36) Schenning, A. P. H. J.; Jonkhøj, P.; Peeters, E.; Meijer, E. W. Hierarchical Order in Supramolecular Assemblies of Hydrogen-Bonded Oligo(p-phenylene vinylene)s. *J. Am. Chem. Soc.* **2001**, *123*, 409–416.
- (37) Lim, S.-H.; Bjorklund, T. G.; Bardeen, C. J. Characterization of Individual Submicron Distyrylbenzene Aggregates Using Temperature-Dependent Picosecond Fluorescence and Atomic Force Microscopy. *J. Phys. Chem. B* **2004**, *108*, 4289–4295.
- (38) Bussian, D. A.; Summers, M. A.; Liu, B.; Bazan, G. C.; Buratto, S. K. Photon Pair Correlation Spectroscopy of Single Tetrahedral Oligophenylenevinylene Molecules at Room Temperature. *Chem. Phys. Lett.* **2004**, *388*, 181–185.
- (39) Gierschner, J.; Oelkrug, D. *Optical Properties of Oligophenylene-Vinyls*; American Scientific Publishers: Stevenson Ranch, CA, 2004.
- (40) Gierschner, J.; Ehni, M.; Egelhaaf, H. J.; Medina, B. M.; Beljonne, D.; Benmansour, H.; Bazan, G. C. Solid-State Optical Properties of Linear Polyconjugated Molecules: π -Stack Contra Herringbone. *J. Chem. Phys.* **2005**, *123*, 144914.
- (41) Summers, M. A.; Kemper, P. R.; Bushnell, J. E.; Robinson, M. R.; Bazan, G. C.; Bowers, M. T.; Buratto, S. K. Conformation and Luminescence of Isolated Molecular Semiconductor Molecules. *J. Am. Chem. Soc.* **2003**, *125*, 5199–5203.
- (42) Kroeze, J. E.; Savenije, T. J.; Vermeulen, M. J. W.; Warman, J. M. Contactless Determination of the Photoconductivity Action Spectrum, Exciton Diffusion Length, and Charge Separation Efficiency in Polythiophene-Sensitized TiO₂ Bilayers. *J. Phys. Chem. B* **2003**, *107*, 7696–7705.
- (43) Lüer, L.; Egelhaaf, H.-J.; Oelkrug, D.; Cerullo, G.; Lanzani, G.; Huisman, B.-H.; de Leeuw, D. Oxygen-Induced Quenching of Photoexcited States in Polythiophene Films. *Org. Electron.* **2004**, *5*, 83–89.
- (44) Lewis, A. J.; Ruseckas, A.; Gaudin, O. P. M.; Webster, G. R.; Burn, P. L.; Samuel, I. D. W. Singlet Exciton Diffusion in MEH-PPV Films Studied by Exciton-Exciton Annihilation. *Org. Electron.* **2006**, *7*, 452–456.
- (45) Goh, C.; Scully, S. R.; McGehee, M. D. Effects of Molecular Interface Modification in Hybrid Organic-Inorganic Photovoltaic Cells. *J. Appl. Phys.* **2007**, *101*, 114503.
- (46) Shaw, P. E.; Ruseckas, A.; Samuel, I. D. W. Exciton Diffusion Measurements in Poly(3-hexylthiophene). *Adv. Mater.* **2008**, *20*, 3516–3520.
- (47) Vogelsang, J.; Adachi, T.; Brazard, J.; Vanden Bout, D. A.; Barbara, P. F. Self-Assembly of Highly Ordered Conjugated Polymer Aggregates with Long-Range Energy Transfer. *Nat. Mater.* **2011**, *10*, 942–946.
- (48) Samuel, I. D. W.; Rumbles, G.; Collison, C. J. Efficient Interchain Photoluminescence in a High-Electron Affinity Conjugated Polymer. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1995**, *52*, R11573–R11576.
- (49) Cornil, J.; dos Santos, D. A.; Crispin, X.; Brédas, J. L. Influence of Interchain Interactions on the Absorption and Luminescence of Conjugated Oligomers and Polymers: A Quantum-Chemical Characterization. *J. Am. Chem. Soc.* **1998**, *120*, 1289–1299.
- (50) Tretiak, S.; Saxena, A.; Martin, R. L.; Bishop, A. R. Interchain Electronic Excitations in Poly(phenylenevinylene) (PPV) Aggregates. *J. Phys. Chem. B* **2000**, *104*, 7029–7037.
- (51) Barbara, P. F.; Hu, D.; Yu, J.; Wong, K.; Bagchi, B.; Rossky, P. J. Collapse of Stiff Conjugated Polymers with Chemical Defects into Ordered, Cylindrical Conformations. *Nature* **2000**, *405*, 1030–1033.
- (52) Steiner, F.; Vogelsang, J.; Lupton, J. M. Singlet-Triplet Annihilation Limits Exciton Yield in Poly(3-Hexylthiophene). *Phys. Rev. Lett.* **2014**, *112*, 137402.
- (53) Cook, S.; Furube, A.; Katoh, R. Analysis of the Excited States of Regioregular Polythiophene P3HT. *Energy Environ. Sci.* **2008**, *1*, 294–299.
- (54) Piris, J.; Dykstra, T. E.; Bakulin, A. A.; van Loosdrecht, P. H. M.; Knulst, W.; Trinh, M. T.; Schins, J. M.; Siebbeles, L. D. A. Photogeneration and Ultrafast Dynamics of Excitons and Charges in P3HT/PCBM Blends. *J. Phys. Chem. C* **2009**, *113*, 14500–14506.
- (55) Sheng, C. X.; Tong, M.; Singh, S.; Vardeny, Z. V. Experimental Determination of the Charge/Neutral Branching Ratio η in the Photoexcitation of π -Conjugated Polymers by Broadband Ultrafast Spectroscopy. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *75*, 085206.
- (56) Lin, H.; Tian, Y.; Zapadka, K.; Persson, G.; Thomsson, D.; Mirzov, O.; Larsson, P.-O.; Widengren, J.; Scheblykin, I. G. Fate of Excitations in Conjugated Polymers: Single-Molecule Spectroscopy Reveals Nonemissive “Dark” Regions in MEH-PPV Individual Chains. *Nano Lett.* **2009**, *9*, 4456–4461.
- (57) Hu, Z.; Willard, A. P.; Ono, R. J.; Bielawski, C. W.; Rossky, P. J.; Vanden Bout, D. A. An Insight into Non-Emissive Excited-States in Conjugated Polymers. *Nat. Commun.* **2015**, *6*, 8246.
- (58) Davydov, A. S. *Theory of Molecular Excitons*; McGraw-Hill: New York, 1962.
- (59) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. The Exciton Model in Molecular Spectroscopy. *Pure Appl. Chem.* **1965**, *11*, 371–392.
- (60) Spano, F. C. The Spectral Signatures of Frenkel Polarons in H- and J-Aggregates. *Acc. Chem. Res.* **2010**, *43*, 429–439.
- (61) Siddiqui, S.; Spano, F. C. H- and J-Aggregates of Conjugated Polymers and Oligomers: A Theoretical Investigation. *Chem. Phys. Lett.* **1999**, *308*, 99–105.
- (62) Spano, F. C. Excitons in Conjugated Oligomer Aggregates, Films, and Crystals. *Annu. Rev. Phys. Chem.* **2006**, *57*, 217–243.
- (63) Spano, F. C. Absorption and Emission in Oligo-Phenylene Vinylene Nanoaggregates: The Role of Disorder and Structural Defects. *J. Chem. Phys.* **2002**, *116*, 5877–5891.
- (64) Spano, F. C. Modeling Disorder in Polymer Aggregates: The Optical Spectroscopy of Regioregular Poly(3-hexylthiophene) Thin Films. *J. Chem. Phys.* **2005**, *122*, 234701.
- (65) Clark, J.; Silva, C.; Friend, R. H.; Spano, F. C. Role of Intermolecular Coupling in the Photophysics of Disordered Organic

Semiconductors: Aggregate Emission Regioregular Polythiophene. *Phys. Rev. Lett.* **2007**, *98*, 206406.

(66) Beljonne, D.; Cornil, J.; Silbey, R.; Millié, P.; Brédas, J. L. Interchain Interactions in Conjugated Materials: The Exciton Model versus the Supermolecular Approach. *J. Chem. Phys.* **2000**, *112*, 4749–4758.

(67) Clark, J.; Chang, J.-F.; Spano, F. C.; Friend, R. H.; Silva, C. Determining Exciton Bandwidth and Film Microstructure in Polythiophene Films Using Linear Absorption Spectroscopy. *Appl. Phys. Lett.* **2009**, *94*, 163306.

(68) Löwe, C.; Weder, C. Oligo(p-phenylene Vinylene) Excimers as Molecular Probes: Deformation-Induced Color Changes in Photoluminescent Polymer Blends. *Adv. Mater.* **2002**, *14*, 1625–1629.

(69) Jagtap, S. P.; Mukhopadhyay, S.; Coropceanu, V.; Brizius, G. L.; Brédas, J.-L.; Collard, D. M. Collard, D. M. Closely Stacked Oligo(phenylene ethynylene)s: Effect of π -Stacking on the Electronic Properties of Conjugated Chromophores. *J. Am. Chem. Soc.* **2012**, *134*, 7176–7185.

(70) Brown, K. E.; Salamant, W. A.; Shoer, L. E.; Young, R. M.; Wasielewski, M. R. Direct Observation of Ultrafast Excimer Formation in Covalent Perylenediimide Dimers Using Near-Infrared Transient Absorption Spectroscopy. *J. Phys. Chem. Lett.* **2014**, *5*, 2588–2593.

(71) Lindquist, R. J.; Lefler, K. M.; Brown, K. E.; Dyar, S. M.; Margulies, E. A.; Young, R. M.; Wasielewski, M. R. Energy Flow Dynamics within Cofacial and Slip-Stacked Perylene-3,4-dicarboximide Dimer Models of π -Aggregates. *J. Am. Chem. Soc.* **2014**, *136*, 14912–14923.