

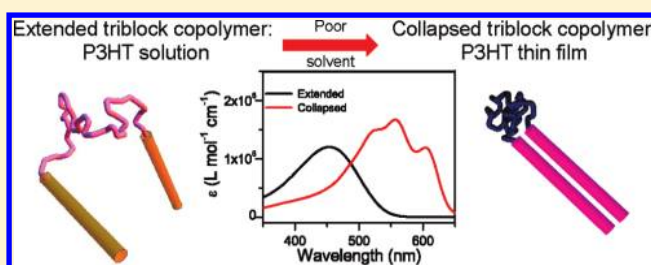
Mimicking Conjugated Polymer Thin-Film Photophysics with a Well-Defined Triblock Copolymer in Solution

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Supporting Information

ABSTRACT: Conjugated polymers (CPs) are promising materials for use in electronic applications, such as low-cost, easily processed organic photovoltaic (OPV) devices. Improving OPV efficiencies is hindered by a lack of a fundamental understanding of the photophysics in CP-based thin films that is complicated by their heterogeneous nanoscale morphologies. Here, we report on a poly(3-hexylthiophene)-*block*-poly(*tert*-butyl acrylate)-*block*-poly(3-hexylthiophene) rod-coil-rod triblock copolymer. In good solvents, this polymer resembles solutions of P3HT; however, upon the addition of a poor solvent, the two P3HT chains within the triblock copolymer collapse, affording a material with electronic spectra identical to those of a thin film of P3HT. Using this new system as a model for thin films of P3HT, we can attribute the low fluorescence quantum yield of films to the presence of a charge-transfer state, providing fundamental insights into the condensed phase photophysics that will help to guide the development of the next generation of materials for OPVs.



INTRODUCTION

Poly(3-hexylthiophene) (P3HT) and its derivatives are among the most studied π -conjugated polymers and widely utilized in OPVs¹ because of their high hole mobilities.² While the power conversion efficiencies for some OPVs derived from P3HT and related polymers are approaching the levels of interest for industrial exploitation, that is, 8.3%,³ a fundamental understanding of the photophysics and morphologies of thin films of P3HT is crucial to optimize OPV performance.⁴ However, the inherent heterogeneity of these polymer thin films makes them exceedingly difficult to probe on any submacroscopic level. To avoid the complexity of such systems, many groups have tried to mimic the thin-film photophysics in solution by adding a poor solvent to solutions of P3HT and P3HT derivatives.^{5–11} Unfortunately, none of them were able to fully reproduce in a controllable way the spectroscopic properties of thin films of P3HT. Specifically, the kinetic stability and the number of chains involved in the resulting aggregates were uncontrolled and unknown.

Here, we report on the photophysics of a newly synthesized conjugated rod-coil-rod triblock copolymer composed of two regioregular P3HT chains covalently linked to both ends of a poly(*tert*-butyl acrylate) (PtBA) chain: P3HT-*b*-PtBA-*b*-P3HT (Figure 1). This new model system has rendered it possible to reproduce the electronic spectra—in solution—of P3HT in both the solvated and the condensed phases; the triblock copolymer in a good solvent behaves as P3HT in solution, whereas in a poor solvent, the two chains of P3HT interface as they would in a thin film. The collapsed triblock copolymer in solution is fully reversible, stable for long periods (> 1 year),

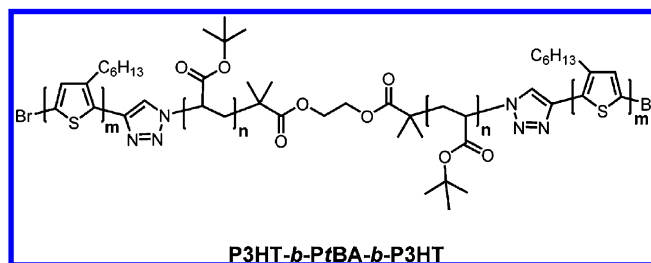


Figure 1. The rod-coil-rod triblock copolymer shown consists of two poly(3-hexylthiophene) (P3HT) chains covalently linked to both ends of a poly(*tert*-butyl acrylate) (PtBA) chain.

and its formation is concentration-independent. As such, the triblock copolymer in a poor solvent is a good model system to address open questions regarding film photophysics and if these phenomena are related to the interaction of two chains or the result of the larger three dimensional structure in the thin film. For example, thin films of P3HT exhibit a dramatic drop in the fluorescence quantum yield compared with solution. This fluorescence quenching in CP chains has been attributed to a number of causes: a high yield of nonemitting species, such as polarons, or charge-transfer excitons directly generated from the photoexcitation,^{12,13} and/or by the lower oscillator strength for emission in H-aggregates in the interchain interactions.^{14,15}

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The delocalization of polarons over a number of neighboring chains as a result of interchain interactions appears to be a key parameter in the generation of charge-transfer states as well as in the quenching of fluorescence.^{16,17} With our model system, where only two chains of P3HT are interacting, a long-range energy transfer within a three-dimensional network is not possible given the small size of the system. However, the interchain electronic interactions are nearly identical to those of the film and are sufficient to explain the large fluorescence quenching present in thin films of P3HT. We also report on the presence of charge-transfer excitons involved in the fluorescence quenching mechanism.

■ EXPERIMENTAL SECTION

Synthesis and Purification. All chemicals were purchased from Aldrich, Alfa Aesar, or Fisher and were used as received. THF was dried over 3 Å molecular sieves and deoxygenated using a Vacuum Atmospheres Company solvent purification system.

Triblock copolymer P3HT-*b*-PtBA-*b*-P3HT was synthesized by the Cu-catalyzed coupling of ethynyl-terminated P3HT and α,ω -diazido-PtBA using a modified, previously reported procedure¹⁸ (Figure S7, Supporting Information). Briefly, a 25 mL Schlenk flask charged with a stir bar, THF (5 mL), ethynyl-terminated P3HT (25 mg, 0.0025 mmol),¹⁹ α,ω -diazido-PtBA (25 mg, 0.0010 mmol), copper(I) bromide (10 mg, 0.070 mmol), and pentamethyldiethylenetriamine (24 mg, 0.140 mmol) was degassed using three consecutive freeze–pump–thaw cycles, refilled with N₂, and stirred at 60 °C for 36 h. After cooling to room temperature, the reaction mixture was filtered through neutral alumina and concentrated in vacuo to afford the crude product. Pure triblock copolymer was obtained from this mixture by preparative gel permeation chromatography (GPC). GPC was performed at 40 °C on a GPCmax VE-2001 (Viscotek) equipped with three fluorinated polystyrene columns (IMBHMW-3078, IMBMMW-3078, and IMBLMW-3078) arranged in series. The detector was a UV–vis photodiode array detector tuned at 450 nm. The eluent was tetrahydrofuran (THF) stabilized with butylated hydroxytoluene (BHT). The number-average molecular weight (M_n) and polydispersity indices (PDI) are reported relative to polystyrene standards. The ¹H NMR spectrum and the IR spectrum of the purified triblock copolymer are reported in Figures S10 and S12 (Supporting Information), respectively.

Steady-State Spectroscopy. UV–vis absorption spectra were recorded from 350 to 650 nm with a monobeam UV spectrophotometer (8453 UV–visible spectroscopy system, Agilent Technologies Inc.). Fluorescence spectra were measured with a fully corrected Fluorolog-3 (Jobin-Yvon) spectrofluorometer. Samples in solution were contained in a 1 cm fused-silica cuvette. Thin films of P3HT were spin-coated on a microscope cover glass and out of a highly concentrated solution of 10 kDa P3HT in toluene. The quantum yields of fluorescence were determined by using P3HT in toluene as a standard ($\Phi_F(\text{P3HT}) = 42\%$).⁹ Fits were done under Origin with the sum of three Gaussian functions sharing the same spectral width with a constant energy spacing, chosen to be 0.18 eV.

Molar Extinction Coefficient Spectrum. The molar extinction coefficient spectrum of the extended triblock was extracted from the absorption spectrum of the triblock copolymer in 100% toluene after normalization by the concentration of the triblock copolymer. This concentration

was determined from Beer–Lambert law using the absorbance at 455 nm and the extinction molar coefficient of the triblock copolymer at 455 nm, that is, $\epsilon = 964\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ (considering an extinction molar coefficient of $8000 \text{ L mol}^{-1} \text{ cm}^{-1}$ per monomer unit).¹² The molar extinction coefficient spectrum of the collapsed triblock was obtained by subtraction of the extended triblock spectrum to the concentration-normalized triblock copolymer absorption spectrum in 50/50% toluene/methanol. The subtraction was afforded until the two extinction molar coefficient spectra were overlaid at 487 nm, by definition of an isosbestic point.

Fluorescence Correlation Spectroscopy. Fluorescence correlation spectroscopy (FCS) measurements were done on a confocal microscope described in ref 20 with an extended beam of the collimated 488 nm line of an Ar⁺ gas laser to a diameter of about 1 cm and coupled into the objective. The fluorescence signal was collected through the same objective, focused on two avalanche photodiodes (SPCM-AQR-16, PerkinElmer) for detection, and the signal was correlated by an ALV-5000 fast hardware correlation card.

■ DISCUSSION

Synthesis and Purification. The rod–coil–rod triblock copolymer, P3HT-*b*-PtBA-*b*-P3HT, was synthesized by “clicking” two low polydispersity index (PDI) P3HT chains with alkynyl termini to a PtBA core that featured complementary azide end groups (for more details on the synthesis, see the Experimental Section). After purification via gel permeation chromatography (GPC), a triblock copolymer composed of two rodlike 10 kDa regioregular P3HT chains covalently linked to a 26 kDa PtBA coil polymer with an overall number-average molecular weight (M_n) of 46 kDa and PDI = 1.2 was obtained (Figure S1, Supporting Information).

Addition of a Poor Solvent. Previous studies have shown that, upon addition of a poor solvent to solutions of P3HT or P3HT derivatives, the absorption spectrum is red shifted^{5–10} similarly to the shift observed upon concentration (i.e., from solution to the formation of a thin film).¹² As a poor solvent (methanol) is added to a solution of the aforementioned triblock copolymer in a good solvent (toluene),¹⁰ the absorption peak is red shifted from 455 to 560 nm, as shown in Figure 2a. The red shift of the absorption spectrum in P3HT thin film^{21–23} and in P3HT aggregates in solution^{5–10} was interpreted to arise from the increased coplanarity forced by interchain interactions. Similarly, the red shift observed for the triblock copolymer in a poor solvent can be attributed to the interchain interactions of P3HT chains generating more planar conformations. Despite the lowering of the solvent quality by the addition of a poor solvent, the solution of collapsed triblock copolymer is stable over time (at least a year, Figure S2, Supporting Information), in contrast to previous reports which have described the precipitation of P3HT homopolymer aggregates formed in poor solvents.⁷ The stability of the triblock copolymer is likely the result of it being a unimolecular aggregate composed of two intramolecularly interacting chains of P3HT, which does not generate larger aggregates, and the presence of the PtBA polymer, which has a higher solubility in methanol.²⁴

The spectral changes that occur upon lowering the solvent quality exhibit a clear isosbestic point at 487 nm, indicating an interconversion between only two absorbing species. Moreover, the kinetics of the system can be described by only two single values after single value decomposition (SVD) analysis (Figure

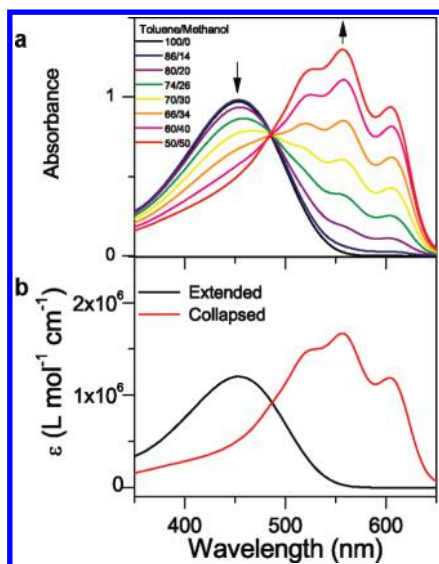


Figure 2. UV-vis absorption spectra of the P3HT-*b*-PtBA-*b*-P3HT triblock copolymer for various ratios of toluene and methanol solvents with respect to toluene (a). The arrows show the decay and increase of the bands centered at 455 and 560 nm, respectively. Molar extinction coefficient spectra of the extended triblock (b, black) and the collapsed triblock (b, red) extracted from the UV-vis absorption spectra represented in (a).

S3, Supporting Information), which is also in good agreement with the complete description of every absorption spectra by a linear combination of the spectrum of only two absorbing species. The molar extinction coefficient spectra of these two species, which will be referred to as the extended triblock and the collapsed triblock, respectively, are represented in Figure 2b. These two spectra were extracted from the absorption spectra of the triblock copolymer in 100% toluene (good solvent) and 50/50% toluene/methanol (poor solvent) with respect to the overlying of the two molar extinction coefficient spectra at 487 nm, per the definition of an isosbestic point. The extended triblock spectrum shows a broad π - π^* electronic transition band centered at 455 nm, which closely resembles the photophysical characteristics of highly regioregular P3HT chains in a good solvent.²⁵ The collapsed triblock spectrum was red shifted, with a peak centered at 560 nm and two additional vibronic structures at 525 and 605 nm and were attributed to the C=C double bond stretching vibrational mode (energy of 0.18 eV)²⁶ coupled to the π - π^* electronic transition. This result suggested to us that the ground state of the collapsed triblock contains a smaller distribution of torsional conformers and conjugation lengths compared with that of the extended triblock. The ratio of the 0-0 transition to the 0-1 transition increases with increasing methanol content, which indicates an increase of the collapsed triblock concentration in comparison to the extended triblock concentration. Moreover, the collapsed triblock appears to have similar features as those of a thin film of P3HT.

Spano et al. have developed a weakly coupled H-aggregates model to reproduce the experimental data obtained for thin films of P3HT.^{14,26,27} This H-aggregates model assumes that the spectra have a Franck-Condon vibronic progression. Following previous H-aggregates models for P3HT, we utilize a Huang-Rhys factor of 1 and assume that the 0.18 eV C=C stretching vibration predominantly couples the electronic transition.²⁶ The weak coupling assumes that the interchain

interactions gives rise to an excitonic band with a bandwidth that is on par or smaller than the energy of this dominant vibronic mode coupled to the π - π^* electronic transition. As the collapsed triblock appears to be a good model for the P3HT thin film, we applied the weakly coupled H-aggregates model to it to extract the exciton bandwidth. The collapsed triblock molar extinction coefficient spectrum was fit to the sum of three Gaussian functions sharing the same spectral width with a constant energy spacing, chosen to be 0.18 eV. The good quality of this fit (Figure 3) is consistent with previous

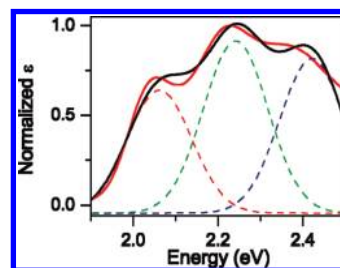


Figure 3. Normalized molar extinction coefficient spectrum of the collapsed triblock (black) and its fit to the sum of three Gaussian functions (red) and the three Gaussian functions (green, blue, and red dashed lines).

theoretical results for P3HT films.²⁶ The peak ratio of the 0-0 transition and the 0-1 transition of the absorption spectrum can be used to estimate the strength of the excitonic coupling. From this fit, we estimate an exciton bandwidth of the dimer triblock of 114 meV. This value is in good agreement with the values reported for P3HT films under different processing methods.^{14,28}

Number of Chains in the Collapsed Triblock. An important remaining question was to determine whether the collapsed triblock arises from the collapse of the two P3HT chains within a single triblock copolymer chain or if it results from aggregation of many different copolymers with one another. As we have already emphasized, the collapsed triblock is stable over time despite the low solvent quality, suggesting that only the two P3HT chains on either end of the PtBA linker are involved in the aggregation event. To characterize the number of chains involved in the formation of the collapsed triblock, fluorescence correlation spectroscopy (FCS) measurements were carried out on the same initial concentration of triblock copolymer in good and poor solvents, respectively (Figures 4 and S4 (Supporting Information)). FCS allows us to

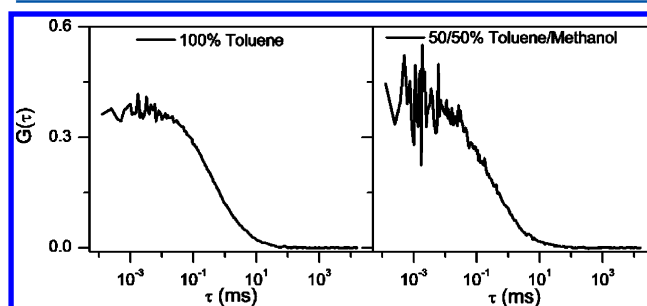


Figure 4. Fluorescence correlation spectroscopy (FCS) curves of the same initial concentration of P3HT-*b*-PtBA-*b*-P3HT triblock copolymer in 100% toluene (good solvent, left panel) and 50/50% toluene/methanol (poor solvent, right panel) under excitation at 488 nm.

evaluate the number of emitting molecules within the focused spot of a 488 nm laser in a confocal microscope by detecting correlations in the fluctuations of the fluorescence signal detected by two avalanche photodiodes.²⁹ From the fluorescence correlation traces, the inverse of the average emitting molecule numbers in the focal volume is determined directly from the amplitude of the initial plateau in the autocorrelated signal. For the same initial concentration of the triblock copolymer, the average number of emitting molecules is 2.4 ± 0.6 and 2.8 ± 0.8 in good and poor solvents, respectively. Therefore, the number of emitting sites remains constant in both solutions. The above results demonstrate that the collapsed triblock is an aggregate involving just the two chains of P3HT within a single triblock copolymer molecule. It is possible that the lower concentration used for FCS measurements (~ 1000 times more diluted than for absorption conditions) results in a sample free of large aggregates. However, we have shown that the triblock aggregation kinetics and spectra are independent of the initial concentration of the copolymer (Figure S5, Supporting Information). This is the first report of an aggregate of P3HT chains in which the number of chains is rigorously known.

Molecular Weight Effect on the Interchain Interactions in Two Different Triblock Copolymers. A second triblock copolymer ($M_n = 63$ kDa, PDI = 1.2) with larger P3HT chains ($M_n = 21$ kDa, PDI = 1.1) and a PtBA chain of similar length ($M_n = 21$ kDa) was synthesized to probe whether the interchain interactions in the collapsed triblock are dependent on P3HT chain length. As shown in Figure 5, for

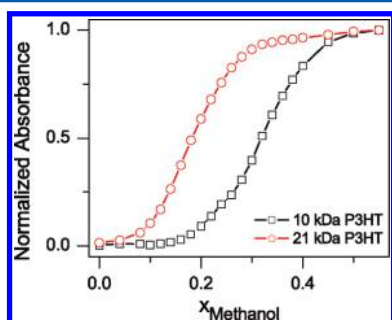


Figure 5. Normalized absorption evolution at 560 nm (absorption peak of the collapsed triblock) as a function of the volume fraction of methanol added to the triblock copolymers in 100% toluene for two different molecular weight triblock copolymers: $M_n(\text{P3HT}) = 10$ kDa (black squares) and $M_n(\text{P3HT}) = 21$ kDa (red circles); $M_n(\text{PtBA}) = 21$ kDa for both copolymers.

the same amount of methanol added, the percentage of the collapsed triblock that is present in solution is larger for the longer triblock copolymer (63 kDa). A plateau, describing a mixture composed of 90% collapsed triblock and 10% extended triblock, is reached after the addition of 50% and 30% of methanol to the 46 and 63 kDa triblock copolymers, respectively. The absorption spectra of both copolymers in a 40/60% toluene/methanol mixture are similar after normalization (data not shown). Thus, the two P3HT chains within a triblock copolymer more readily interact with one another when their molecular weight is higher. However, the nature of the interchain interactions is nearly identical in both triblock copolymers, and it was not possible to obtain a solution containing more than 90% of the collapsed triblock.

Comparison to a Thin Film of P3HT. The triblock copolymer in a poor solvent generates a new species that is stable over time (> 1 year) at different initial concentrations, is fully reversible (Figure S6, Supporting Information), and involves only the two chains of P3HT in one triblock copolymer molecule. We have shown that the collapsed triblock is well described by the weakly coupled H-aggregates model (Figure 3), initially developed for thin films of P3HT. To directly compare the triblock copolymer in a poor solvent with a thin film of P3HT, the absorption spectra of the triblock copolymer in 50/50% toluene/methanol solution and that of a spin-coated thin film of 10 kDa P3HT are overlaid in Figure 6a.

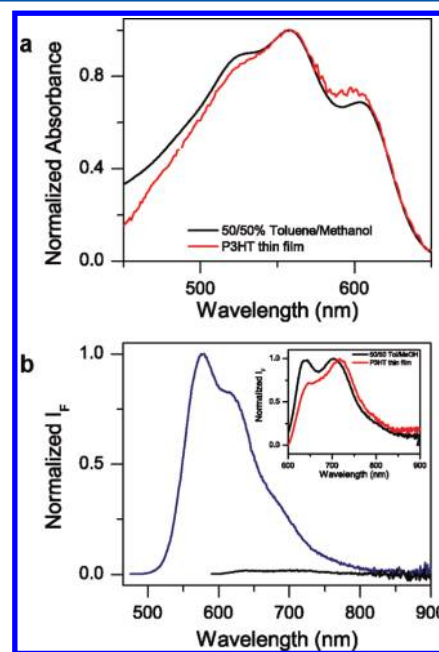


Figure 6. UV-vis absorption spectra of the triblock copolymer in 50/50% toluene/methanol (poor solvent, a, black) and a thin film of P3HT (10 kDa) spin-coated from toluene (a, red) after normalization at 560 nm, that is, the 0–1 transition. Emission spectra of the triblock copolymer in 100% toluene (b, blue, $\lambda_{\text{exc}} = 455$ nm) and 50/50% toluene/methanol (b, black, $\lambda_{\text{exc}} = 560$ nm) after normalization by the maximum of emission of the triblock copolymer in 100% toluene. Inset is the comparison of the emission spectra of the triblock copolymer in 50/50% toluene/methanol (black) and a thin film of P3HT (10 kDa) (red).

The peak positions are identical, although the 0–0 transition is slightly reduced in intensity for the triblock copolymer in a poor solvent after normalization at the 0–1 transition. The intensity of the 0–0 transition in comparison to that of the 0–1 transition is known to be correlated with the degree of crystallinity³⁰ as well as to the molecular weight of P3HT chains.³¹ As the molecular weights of P3HT are identical for both systems, only the first hypothesis can be considered. Moreover, a direct comparison between the fluorescence spectra of the triblock copolymer in a poor solvent and of thin film of P3HT reveals similar features (inset in Figure 6b). The two spectra are similar, although the 0–0 transition is more intense in the emission spectrum of the triblock copolymer in a poor solvent compared to a thin film of P3HT. The 0–0 transition is forbidden in H-aggregates, and the ratio of the 0–0 and 0–1 peak absorbance reflects the disorder in the H-aggregates.^{26,27} Thus, the triblock copolymer

is a good model for thin films of P3HT, but involves significantly fewer chromophores than are typically used in the weakly coupled H-aggregates model. Therefore, it is not surprising that the H-aggregates are more disordered in the triblock copolymer in a poor solvent than for a thin film of P3HT cast from toluene.

Model System to Probe the Effects of Interchain Interaction in Thin Film. Because the collapsed triblock copolymer mimicks P3HT thin-film photophysics, it can serve as a model for understanding the effects of interchain interactions found in thin films. Many properties of conjugated polymers change upon going from well-solvated chains in solution to densely packed chains in a film. This is due to primarily two effects, the first of which is interchain interactions or electronic states that arise from the close proximity of multiple polymer chains. Second, as a consequence of the chains being closer together, there is now a large three-dimensional network of interacting chains. This greatly amplifies the effects of any defects, as long-range energy transfer within this network allows excitation to migrate to these sites. Even if they are few in number, they can dominate the excited-state lifetime and emission spectroscopy. The collapsed triblock allows us to isolate only the effect of interchain interactions—in the absence of long-range, three dimensional energy transfer—as it is composed of only two interacting polymer chains. As such, it is easier to investigate the origin of issues that can be difficult to determine in thin films. For instance, upon going from solution to thin film, the fluorescence of P3HT is quenched ~ 20 times with the quantum yield falling from 33–42% to 1.6–2%.^{9,12,32,33} The origins of this phenomenon remain unclear, although it has been hypothesized that it could result from the interchain excitation having a lower emission yield, or from a small number of interchain traps that quench the emission from a large number of chains. To examine this, the quantum yield of the triblock copolymer in good and poor solvents were quantified. After adjusting for differences in the solvent refractive indices and the absorbances at the excitation wavelengths, the quantum yield of the triblock in a good solvent (100% toluene) was found to be 41%, while it fell to a mere 2% in a poor solvent (50/50% toluene/methanol). The corresponding fluorescence spectra are represented in Figure 6b after normalization by its maximum of fluorescence intensity in 100% toluene. The triblock copolymer fluorescence is quenched by a factor of 20 in going from a good to a poor solvent just as P3HT fluorescence is quenched by 20 times in going from solution to thin film. This reduction in fluorescence intensity was also observed in the FCS experiment, evidenced by the reduced signal-to-noise for the triblock fluorescence in going from good to poor solvent (Figures 4 and S4 (Supporting Information)).

It was previously demonstrated that the fluorescence quenching of P3HT in going from solution to film cannot be explained by a reduction of the exciton lifetime.^{34,35} Three main explanations have been proposed for the fluorescence quenching in thin films of P3HT: (i) photogeneration of nonemitting species, such as delocalized polarons, that can be associated with a three-dimensional energy transfer;^{16,17} (ii) the presence of H-aggregates with a lower oscillator strength for the emission of the Frenkel excitons;^{14,15} and (iii) production of interchain charge-transfer excitons (noted CT excitons).^{12,13} The hypothesis that involves polaron quenching is unlikely as the source of the reduced quantum yield for the triblock as it

uniformly shows a reduced quantum yield. It is unlikely in the absence of energy transfer among a large number of chains that each triblock would produce a quenching site in equal yield. However, even with only two interacting chains, it is possible to generate delocalized excited states, such as CT excitons, that will have a lower emission yield. Moreover, the two chains in the triblock system could fold back on themselves to generate states that may involve more than just two chromophores. This could lead to either a case of lower oscillator strength from H-aggregate-like states and/or delocalized charge-transfer states (or states that are a mixture of both).

To probe the hypothetical presence of excitons with CT character as the origin of the fluorescence quenching in the triblock copolymer in a poor solvent, we measured the absorption spectra of the triblock copolymer in two poor solvents, 50/50% toluene/methanol (polar solvent) and 15/85% toluene/hexanes (nonpolar solvent), as shown in Figure 7a. In both solvents, a mixture of the extended triblock and the

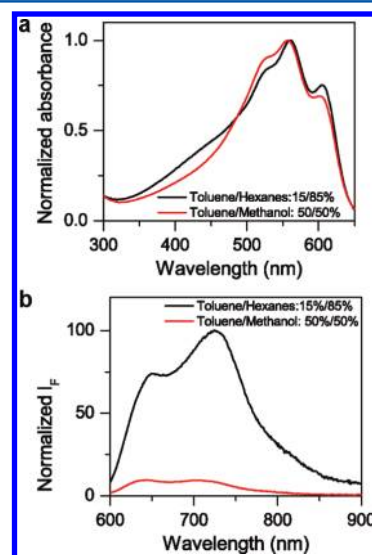


Figure 7. UV-vis absorption spectra of the triblock copolymer in 50/50% toluene/methanol (polar solvent, a, red) and in 15/85% toluene/hexanes (nonpolar solvent, a, black) after normalization at 560 nm, that is, the 0–1 transition. Emission spectra of the triblock copolymer in 50/50% toluene/methanol (b, red, $\lambda_{\text{exc}} = 560$ nm) and 15/85% toluene/hexanes (b, black, $\lambda_{\text{exc}} = 560$ nm) after normalization by the maximum of emission of the triblock copolymer in 15/85% toluene/methanol.

collapsed triblock is observed. In both polar and nonpolar solvent systems, 90% of the collapsed triblock was formed. Thus, the polarity of solvent is not the driving force to generate the collapsed triblock.

Subsequently, we determined the fluorescence quantum yield of the triblock copolymer in two solvent systems: 50/50% toluene/methanol and 15/85% toluene/hexanes (Figure 7b), of which methanol and hexanes are the poor polar and poor nonpolar solvents, respectively. As polar solvents are known to stabilize charge-transfer states, we expected the quantum yield of fluorescence to increase as the polarity of the solvent decreased. Indeed, the quantum yield of fluorescence of the triblock copolymer in the nonpolar solvent system (15/85% toluene/hexanes) was found to be 10 times higher than that measured in the polar solvent system (50/50% toluene/methanol) (20% compared with 2%, Figure 7b). We therefore

concluded that the quenching of fluorescence observed in thin films of P3HT results primarily from interchain interactions that include contributions from excitons with CT character.

CONCLUSION

In conclusion, we have presented a new conjugated triblock copolymer composed of two chains of regioregular P3HT covalently attached to a flexible PtBA polymer. This triblock copolymer fully reproduces the spectroscopic characteristics of P3HT in solution and as thin films in good and poor solvents, respectively, evidenced by a red shifted ground-state absorption, the appearance of vibronic structures probing the ordering of the new species, and fluorescence quenching. The collapsed form of the triblock copolymer is stable over time, fully reversible, and concentration-independent. Interchain interactions of P3HT were found to be more efficient with larger P3HT chains. In the collapsed triblock obtained in a poor solvent, we have proven by FCS measurements that only two P3HT chains are interacting. Given their nearly identical spectral characteristics, this new, stable solution species makes an excellent model for thin films of P3HT. Collectively, this new model system has allowed us to clarify the origin of the large fluorescence quenching of P3HT from solution to thin film, which we observed for the triblock copolymer in going from a good solvent to a poor solvent. The nature of this fluorescence quenching cannot be explained by a three-dimensional energy transfer, but only by interchain interactions that generate charge-transfer states and/or H-aggregates. As such, the triblock copolymer is a promising compound because the thin film properties of P3HT can be probed directly in solution, as we did for the quantum yield of fluorescence. Fluorescence quenching in going from solution to thin film has also been observed for several other CP systems.^{32,33,36,37} That its origins arise solely from interchain interactions might be generalized to all CP chains and not only to P3HT.

ASSOCIATED CONTENT

Supporting Information

Purification of the triblock copolymer by GPC; temporal stability; single value decomposition analysis; additional FCS curves; initial concentration dependence; fully reversible kinetics; synthesis and characterization of the two precursors, Br–PtBA–Br and N₃–PtBA–N₃; and synthesis scheme and characterization of the triblock copolymer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Peet, J.; Heeger, A. J.; Bazan, G. C. *Acc. Chem. Res.* **2009**, *42*, 1700–1708.
- (2) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; Macdonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W. M.; et al. *Nat. Mater.* **2006**, *5*, 328–333.
- (3) Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W. *Prog. Photovoltaics* **2011**, *19*, 84–92.
- (4) Groves, C.; Reid, O. G.; Ginger, D. S. *Acc. Chem. Res.* **2010**, *43*, 612–620.
- (5) Inganas, O.; Salaneck, W. R.; Osterholm, J. E.; Laakso, J. *Synth. Met.* **1988**, *22*, 395–406.
- (6) Kiri, N.; Jahne, E.; Adler, H. J.; Schneider, M.; Kiri, A.; Gorodyska, G.; Minko, S.; Jehnichen, D.; Simon, P.; Fokin, A. A.; et al. *Nano Lett.* **2003**, *3*, 707–712.
- (7) Park, Y. D.; Lee, H. S.; Choi, Y. J.; Kwak, D.; Cho, J. H.; Lee, S.; Cho, K. *Adv. Funct. Mater.* **2009**, *19*, 1200–1206.
- (8) Rumbles, G.; Samuel, I. D. W.; Magnani, L.; Murray, K. A.; DeMello, A. J.; Crystall, B.; Moratti, S. C.; Stone, B. M.; Holmes, A. B.; Friend, R. H. *Synth. Met.* **1996**, *76*, 47–51.
- (9) Samuel, I. D. W.; Magnani, L.; Rumbles, G.; Murray, K.; Stone, B. M.; Moratti, S. C.; Holmes, A. B. Photoluminescence in poly(3-hexylthiophene). In *Optical Probes of Conjugated Polymers*; Vardeny, Z. V., Rothberg, L. J., Eds.; SPIE: Bellingham, WA, 1997; Vol. 3145, pp 163–170.
- (10) Yamamoto, T.; Komarudin, D.; Arai, M.; Lee, B. L.; Suganuma, H.; Asakawa, N.; Inoue, Y.; Kubota, K.; Sasaki, S.; Fukuda, T.; et al. *J. Am. Chem. Soc.* **1998**, *120*, 2047–2058.
- (11) Lee, E.; Hammer, B.; Kim, J.-K.; Page, Z.; Emrick, T.; Hayward, R. C. *J. Am. Chem. Soc.* **2011**, 10390–10393.
- (12) Cook, S.; Furube, A.; Katoh, R. *Energy Environ. Sci.* **2008**, *1*, 294–299.
- (13) Sheng, C. X.; Tong, M.; Singh, S.; Vardeny, Z. V. *Phys. Rev. B* **2007**, *75*, 085206.
- (14) Clark, J.; Silva, C.; Friend, R. H.; Spano, F. C. *Phys. Rev. Lett.* **2007**, *98*, 4.
- (15) Jiang, X. M.; Osterbacka, R.; Korovyanko, O.; An, C. P.; Horowitz, B.; Janssen, R. A. J.; Vardeny, Z. V. *Adv. Funct. Mater.* **2002**, *12*, 587–597.
- (16) Brown, P. J.; Sirringhaus, H.; Harrison, M.; Shkunov, M.; Friend, R. H. *Phys. Rev. B* **2001**, *63*, 125204.
- (17) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; et al. *Nature* **1999**, *401*, 685–688.
- (18) Li, Z. C.; Ono, R. J.; Wu, Z. Q.; Bielawski, C. W. *Chem. Commun.* **2011**, 47, 197–199.
- (19) Jeffries-El, M.; Sauve, G.; McCullough, R. D. *Macromolecules* **2005**, *38*, 10346–10352.
- (20) Adachi, T.; Brazard, J.; Chokshi, P.; Bolinger, J. C.; Ganesan, V.; Barbara, P. F. *J. Phys. Chem. C* **2010**, *114*, 20896–20902.
- (21) Park, Y. D.; Cho, J. H.; Kim, D. H.; Jang, Y.; Lee, H. S.; Ihm, K.; Kang, T. H.; Cho, K. *Electrochem. Solid-State Lett.* **2006**, *9*, G317–G319.
- (22) Reitzel, N.; Greve, D. R.; Kjaer, K.; Hows, P. B.; Jayaraman, M.; Savoy, S.; McCullough, R. D.; McDevitt, J. T.; Bjornholm, T. *J. Am. Chem. Soc.* **2000**, *122*, 5788–5800.
- (23) Xu, B.; Holdcroft, S. *Macromolecules* **1993**, *26*, 4457–4460.
- (24) Brandrup, J.; Immergut, E. H.; Grulke, E., Eds. *Polymer Handbook*, 4th ed.; Wiley: New York, 1999.
- (25) Mao, H. Y.; Xu, B.; Holdcroft, S. *Macromolecules* **1993**, *26*, 1163–1169.
- (26) Clark, J.; Chang, J. F.; Spano, F. C.; Friend, R. H.; Silva, C. *Appl. Phys. Lett.* **2009**, *94*, 3.

- (27) Spano, F. C. *Acc. Chem. Res.* **2010**, *43*, 429–439.
- (28) Paquin, F.; Latini, G.; Sakowicz, M.; Karsenti, P. L.; Wang, L. J.; Beljonne, D.; Stingelin, N.; Silva, C. *Phys. Rev. Lett.* **2011**, *106*, 4.
- (29) Haustein, E.; Schwille, P. *Annu. Rev. Biophys. Biomol. Struct.* **2007**, *36*, 151–169.
- (30) Brown, P. J.; Thomas, D. S.; Kohler, A.; Wilson, J. S.; Kim, J. S.; Ramsdale, C. M.; Sirringhaus, H.; Friend, R. H. *Phys. Rev. B* **2003**, *67*, 064203.
- (31) Chang, J. F.; Clark, J.; Zhao, N.; Sirringhaus, H.; Breiby, D. W.; Andreasen, J. W.; Nielsen, M. M.; Giles, M.; Heeney, M.; McCulloch, I. *Phys. Rev. B* **2006**, *74*, 115318.
- (32) Greenham, N. C.; Samuel, I. D. W.; Hayes, G. R.; Phillips, R. T.; Kessener, Y.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Chem. Phys. Lett.* **1995**, *241*, 89–96.
- (33) Li, Y. N.; Vamvounis, G.; Holdcroft, S. *Macromolecules* **2002**, *35*, 6900–6906.
- (34) Beljonne, D.; Cornil, J.; Silbey, R.; Millie, P.; Bredas, J. L. *J. Chem. Phys.* **2000**, *112*, 4749–4758.
- (35) Banerji, N.; Cowan, S.; Vauthey, E.; Heeger, A. J. *J. Phys. Chem. C* **2011**, *115*, 9726–9739.
- (36) Burrows, H. D.; de Melo, J. S.; Serpa, C.; Arnaut, L. G.; Monkman, A. P.; Hamblett, I.; Navaratnam, S. *J. Chem. Phys.* **2001**, *115*, 9601–9606.
- (37) Kim, J.; Swager, T. M. *Nature* **2001**, *411*, 1030–1034.