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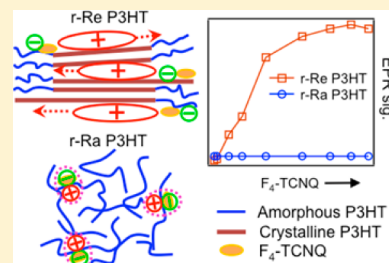
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S Supporting Information

ABSTRACT: The doping efficiencies of regioregular (r-Re) and regiorandom (r-Ra) poly(3-hexylthiophene) (P3HT) with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4 -TCNQ) were studied in solution using electron paramagnetic resonance (EPR), ^{19}F NMR, optical absorption, and Raman spectroscopy. EPR spectra of doped r-Re P3HT possess significantly larger amounts of paramagnetic species than r-Ra P3HT with similar F_4 -TCNQ loadings ($\sim 0.1\%$ up to 50%), which is confirmed by corresponding optical absorption spectra. ^{19}F NMR also show a rapid disappearance of the pristine F_4 -TCNQ signal when small amounts of r-Re P3HT are added due to minority paramagnetic species acting as efficient spin relaxation channels. Raman spectra of both P3HT variants indicate strong interactions with F_4 -TCNQ, however, the presence of free charges is only detected in r-Re samples owing to its ability to aggregate and adopt ordered conformations allowing for delocalization of hole charges after initial contact with the dopant.

SECTION: Energy Conversion and Storage; Energy and Charge Transport



Charge transfer doping of conjugated polymers by soluble small molecule acceptors has seen increased use for tuning their electronic properties (i.e., Fermi levels).^{1–3} An essential criterion for doping is sufficient energetic offset between the polymer highest occupied molecular orbital (HOMO) and the dopant acceptor lowest unoccupied molecular orbital (LUMO) levels.^{1,4,5} One of the best studied polymer/dopant systems meeting this criterion is poly(3-hexylthiophene) (P3HT) doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4 -TCNQ) where the P3HT HOMO lies at ~ 5 eV compared to the LUMO of F_4 -TCNQ at ~ 5.3 eV.^{3,5–9} Surprisingly, the maximum doping efficiency of P3HT/ F_4 -TCNQ is only about 5%, indicating that charges remain tightly bound or partial charge transfer occurs.¹⁰ Pingel and Neher recently showed compelling evidence for the integer charge transfer model where quantitative charge transfer occurs immediately upon P3HT and F_4 -TCNQ contact, but most charges remain in a tightly bound state, hence, lower than expected doping efficiencies.^{5,10} The interaction between P3HT and F_4 -TCNQ was also shown recently by Duong et al. to result in a new, ordered mixed phase with different packing characteristics than pristine aggregates.¹¹ Despite advances toward understanding the basic mechanisms of P3HT doping with F_4 -TCNQ, the role of polymer conformation and packing (aggregation) characteristics on doping efficiency remains relatively unexplored.^{1,2,4,10} This is especially important for doping solution-processed polymers since solvent–solute interactions regulate the folding and packing of chains that should impact P3HT/ F_4 -TCNQ charge transfer interactions.^{3,11}

We use a combination of electron paramagnetic resonance (EPR), NMR, optical absorption, and Raman spectroscopy on regioregular (r-Re) and regiorandom (r-Ra) P3HT variants doped with F_4 -TCNQ to understand how conformation and packing of polymer chains influence charge transfer interactions and doping efficiency. The primary difference between these two P3HT forms is their ability to form π -stacked aggregate structures and adopt ordered conformations, which is only possible in r-Re samples.^{12,13} It is proposed that aggregated P3HT chains act as precursors for doped species due to their relatively high intrachain order (planarity) allowing delocalization of hole carriers along the backbone.^{14–18} The fact that the amounts and sizes of P3HT aggregates in solution are small could place an upper limit on the maximum attainable doping efficiency.

We begin by evaluating EPR spectra in the X-band range of r-Re and r-Ra P3HT samples in chlorobenzene solutions with varying amounts of F_4 -TCNQ (Figure 1). Spectra are measured in the dark at 298 K and both types of P3HT had similar molecular weights (~ 50 – 60 kDa) and were prepared at the same concentration (1 mg/mL) in a dry nitrogen environment. Additional details of sample preparation and instrumentation are provided in the Supporting Information. Both pristine P3HT and F_4 -TCNQ solutions are EPR silent, although a weak signal was observed in aged F_4 -TCNQ samples exposed to air for several days (see Supporting Information). A distinct resonance appears at 3346.35 G once both components are

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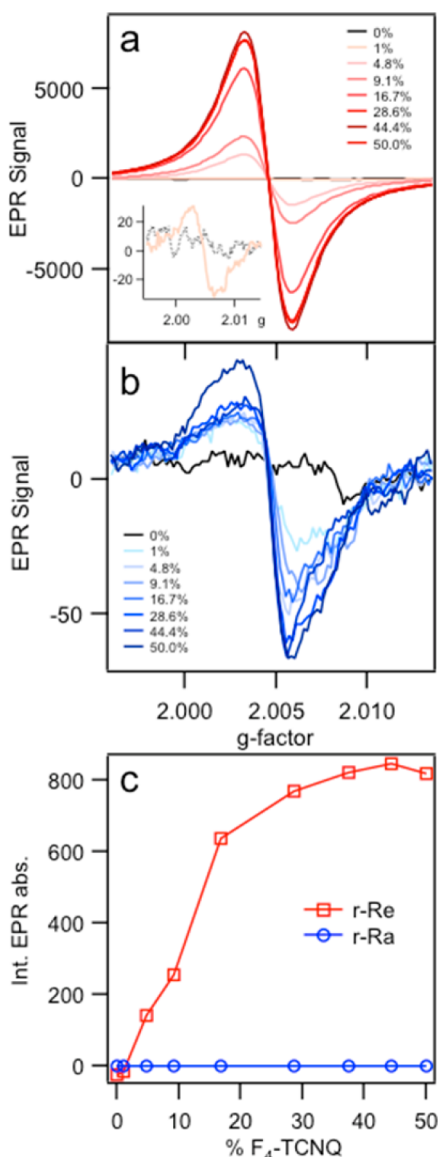


Figure 1. X-band EPR spectra of F₄-TCNQ doped P3HT chlorobenzene solutions. (a) regioregular (r-Re), (b) regiorandom (r-Ra), and (c) comparison of integrated EPR signals from both forms as a function of dopant concentration.

combined and EPR spectra of doped P3HT thin film samples show similar features as solution spectra in Figure 1 (see Supporting Information).

EPR spectra of r-Re samples (Figure 1a) confirm the presence of paramagnetic species at dopant levels as small as ~1%. The signals show little evidence of anisotropy probably from the lack of extended order and correspond to a *g*-value of ~2.0046 which is slightly larger than that of a free electron (*g* = 2.0023) but within the range commonly observed for organic radicals.¹⁹ A rapid increase of the EPR signal was observed for up to ~20% F₄-TCNQ loading followed by gradual increases at larger loadings up to the maximum 50% loading used. In contrast, EPR spectra of r-Ra P3HT show much smaller signals for the same F₄-TCNQ loadings indicating very few paramagnetic species formed, albeit the *g*-value is similar. Integrated EPR absorption for both P3HT types are shown in Figure 1c that better highlight these trends.

Putatively, the rapid increase of the doped r-Re EPR signal for F₄-TCNQ loadings up to 20% corresponds to the dopant filling accessible P3HT sites. The apparent saturation of the EPR signal at F₄-TCNQ loadings higher than ~25% suggests the lack of available dopant binding sites and complete complexation of P3HT chains. Based on these EPR results, it is proposed that efficient doping is facilitated by P3HT aggregates, which only occur in r-Re P3HT.^{12,20,21}

A different perspective of polymer/dopant interactions is obtained from ¹⁹F NMR spectroscopy to track the signatures of fluorine atoms on F₄-TCNQ using P3HT as the dopant. Starting with neat F₄-TCNQ in deuterated chloroform solutions, a characteristic resonance at −131 ppm is observed that originates from the equivalent fluorine atoms on F₄-TCNQ (see Supporting Information).²² Small quantities of r-Ra or r-Re P3HT solutions (1 mg/mL) are added causing a loss of ¹⁹F signal due to P3HT/F₄-TCNQ interactions. Integrated spin densities of ¹⁹F NMR spectra from F₄-TCNQ solutions with varying amounts of r-Re and r-Ra P3HT are shown in Figure 2.

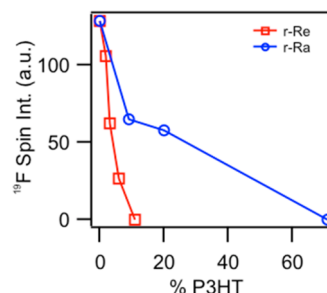


Figure 2. Integrated ¹⁹F NMR intensities of F₄-TCNQ with varying amounts of r-Re and r-Ra P3HT in deuterated chloroform solutions.

Interestingly, both P3HT types show a similar decrease in signal at P3HT loadings ~1%. However, r-Re samples show rapid decay to background levels at ~10% P3HT loading, whereas r-Ra samples exhibit a more gradual decay to background levels only at much larger P3HT content (~70%).

There are two possible origins for the disappearance of the ¹⁹F signal that may be operative: (i) reduction in the amount of neutral, diamagnetic F₄-TCNQ and (ii) minority paramagnetic species acting as a relaxation agent.²³ At low P3HT levels (~1%), both types are expected to behave similarly due to the large excess of F₄-TCNQ, hence, the similar decrease in ¹⁹F signals. The rapid loss of ¹⁹F signal in r-Re samples is expected to originate from creation of paramagnetic relaxation centers that are much more efficient in quenching the ¹⁹F signal of pristine, uncomplexed F₄-TCNQ. The slower decay of the ¹⁹F signal for larger r-Ra P3HT loadings suggests that signal loss arises from loss of pristine F₄-TCNQ with little to no contribution from paramagnetic species. EPR and NMR trends indicate that F₄-TCNQ interacts differently with each P3HT form, or integer charge transfer occurs for both forms but efficient doping is only realized when the polymer can adopt ordered structures.

We next turn to optical absorption spectroscopy, which should produce distinctly different lineshapes depending on whether charges remain bound or completely separate following encounter between each P3HT variant and F₄-TCNQ dopants.¹⁰ For example, absorption transitions from F₄-TCNQ anions appear in the NIR region in r-Re P3HT samples that have been successfully explained by the integer charge

transfer model.¹⁰ If integer charge transfer is not operative in r-Ra P3HT, a hybrid transition corresponding to a charge transfer complex between P3HT and F₄-TCNQ should be expected.¹⁰ Absorption spectra of r-Re and r-Ra P3HT in chlorobenzene solutions were recorded at several F₄-TCNQ amounts and displayed in Figure 3. The characteristic F₄-

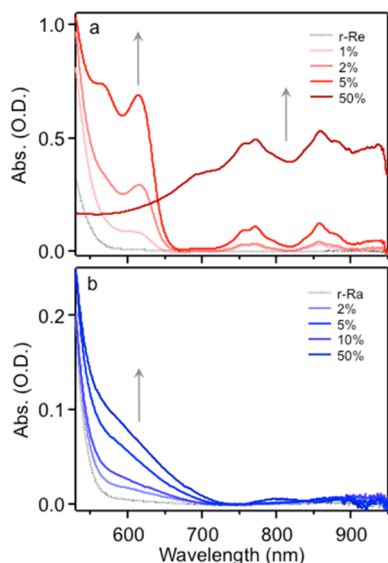


Figure 3. Optical absorption spectra of F₄-TCNQ doped (a) r-Re and (b) r-Ra P3HT chlorobenzene solutions normalized to the P3HT maximum.

TCNQ anion absorption transition emerges in the NIR region for r-Re samples from both solution and thin film samples (see Figure 3a and Supporting Information, respectively).^{10,11} Similar to trends in EPR spectra, the F₄-TCNQ anion absorption oscillator strength reaches a maximum in the range of ~30–40% dopant concentration and shows only gradual increases past this level (data not shown). It is also noteworthy that P3HT centered transitions with resolved vibronic structure appear and increase with F₄-TCNQ content. Although this line shape bears similarity to P3HT aggregate absorption transitions, we do not expect doping by F₄-TCNQ to induce aggregation similar to pristine P3HT. Instead, hole injection should increase P3HT backbone planarity most likely from increased chain rigidity and planarity.^{14–17} Prior to dopants filling all available sites, the doping-induced extended chain planarity results in excitons with J-aggregate character, which is apparent from the prominent 0–0 transition at ca. 620 nm (Figure 3a). In a related study involving doping of P3HT/PCBM blends, we demonstrated that while pristine type P3HT aggregates decrease with increasing F₄-TCNQ loading, their optical spectra show increased J-type exciton coupling indicating increased chain planarity (intrachain order).^{24,25} The emergence of a new, ordered mixed phase reported by Duong et al. at the expense of pristine P3HT aggregates is consistent with this assignment.¹¹ At larger dopant loading, all pristine aggregates are converted to this mixed phase and doping efficiency plateaus, as observed in EPR data in Figure 1.

Conversely, the addition of F₄-TCNQ to r-Ra P3HT samples shows very weak F₄-TCNQ anion transitions barely discernible above backgrounds and noise at the largest dopant loading. A weak and broadened transition does appear on the red onset of the pristine-type r-Ra P3HT singlet exciton transition

suggesting a charge transfer complex type absorption band.²⁶ This feature might suggest that oxidation potentials are different for r-Re and r-Ra P3HT forms with the latter being larger. However, it is also possible that tightly bound, localized charges following integer charge transfer between r-Ra P3HT and F₄-TCNQ could give rise to similar features owing to enhanced overlap between hole and electron wave functions.

Additional insight into the nature of P3HT/F₄-TCNQ interactions and the roles of P3HT conformation and aggregation properties on doping efficiency are obtained from Raman spectroscopy. Figure 4 shows Raman spectra of r-Re

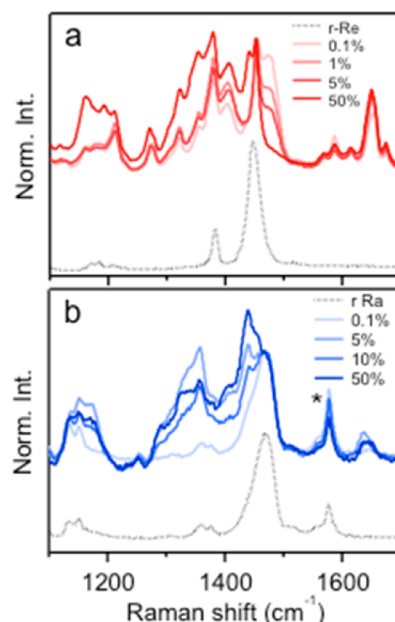


Figure 4. Raman spectra of F₄-TCNQ doped (a) r-Re and (b) r-Ra P3HT chlorobenzene solutions at selected dopant loadings ($\lambda_{\text{exc}} = 780$ nm). Asterisk denotes a chlorobenzene (solvent) Raman peak.

and r-Ra P3HT solutions with varying amounts of F₄-TCNQ are measured using NIR laser excitation ($\lambda_{\text{exc}} = 780$ nm). This excitation wavelength is off resonance with P3HT optical transitions ensuring that excited state contributions from P3HT are negligible. Both r-Re and r-Ra samples (Figures 4a and b, respectively) show significant changes in lineshapes with dopant loading, tentatively suggesting that integer charge transfer occurs in both forms. In particular, large changes in the characteristic P3HT backbone stretching region (~1370–1515 cm⁻¹) are apparent in both samples, namely, splitting of the dominant C=C and C–C symmetric stretches (~1450 cm⁻¹ and ~1370 cm⁻¹, respectively) in addition to the appearance of new transitions indicating substantial charge transfer interactions. Doping-induced changes in Raman spectra are similar to previous reports of polythiophene doped via electrochemically or small molecules (e.g., I₂).^{27–32}

Comparison of P3HT/F₄-TCNQ spectra with that of pristine F₄-TCNQ (see Supporting Information) demonstrates that these spectral changes do not originate from the simple superposition of polymer and dopant lineshapes.^{33,34} Closer inspection reveals more drastic changes in doped r-Re spectra at even small dopant loading that we attribute to facile polaron generation. It is also interesting to note that the Raman excitation wavelength is resonant with the F₄-TCNQ anion absorption spectrum observed only in doped r-Re samples

(Figure 3a). This feature suggests that resonance enhancement contributions from these species may be important and can possibly explain the greater apparent sensitivity to dopant loading observed in r-Re Raman spectra.

The data in Figures 1–4 demonstrate that efficient doping occurs only in r-Re samples although both P3HT variants show evidence for charge transfer interactions with F_4 -TCNQ dopants. As mentioned above, only r-Re P3HT chains are capable of assuming ordered conformations and forming well-packed aggregated structures that promote hole delocalization along the backbone necessary for efficient doping. The fact that aggregated P3HT chains are immobilized in relatively ordered (planarized) conformations minimizes torsional reorganizational barriers associated with intrachain charge delocalization.³⁵ Charge injection into these aggregate precursors results in doped chains that are more rigid and planar leading to increased apparent J-aggregate exciton character in optical spectra. On the other hand, disordered P3HT chains possess large torsional disorder (i.e., r-Ra P3HT) that impede intrachain hole delocalization resulting in tightly bound electrons (F_4 -TCNQ) and holes (P3HT). Similar dependences of doping efficiency with P3HT conformation and packing have also been reported in previous EPR studies of heavily doped r-Re and r-Ra P3HT.³²

The proposed delocalization of holes along aggregated P3HT chains following integer charge transfer can now explain EPR trends from Figure 1. For example, this process implies fast relaxation time scales of these carriers causing their signatures to be masked in room temperature EPR spectra. This is supported by previous light-induced EPR studies of hole polarons of conjugated polymer/fullerene blends reporting weak hole polaron signals above ca. 200 K³⁶ that were attributed to fast spin relaxation processes. Additionally, optical lineshapes of P3HT polarons are broad and featureless extending into the NIR region which is consistent with delocalization over many segments.^{37,38} We therefore assign the characteristic EPR signal in Figure 1 as originating from F_4 -TCNQ anions owing to their localized nature. This assignment was confirmed from EPR studies of F_4 -TCNQ reduced by ferrocene that possess a g-value of 2.0047 (see Supporting Information), virtually identical to that found in P3HT/ F_4 -TCNQ samples in Figure 1.

Overall, we have shown that charge transfer doping efficiency by F_4 -TCNQ in solution depends on the ability of P3HT to form aggregates. Although F_4 -TCNQ interacts with both P3HT forms, intrachain hole delocalization is necessary to separate charge and therefore dope the polymer chain. This is a facile process in aggregated P3HT chains owing to their relatively high intrachain order that minimizes torsional reorganization energies. The price for such distortions is too high in r-Ra, or, unaggregated r-Re P3HT chains leading to poor doping efficiency. The dependence of doping efficiency on aggregates can limit maximum attainable doping efficiencies due to the limited amounts of these species in solutions. This limitation may potentially be overcome using solution-based self-assembly methods to fabricate semicrystalline nanofibers²⁵ that enable reliable control of P3HT aggregation characteristics, such as intrachain order, and possibly doping efficiency.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details and additional figures as described in the text. 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) Walzer, K.; Maennig, B.; Pfeiffer, M.; Leo, K. Highly Efficient Organic Devices Based on Electrically Doped Transport Layers. *Chem. Rev.* **2007**, *107*, 1233–1271.
- (2) Lüssem, B.; Riede, M.; Leo, K. Doping of Organic Semiconductors. *Phys. Stat. Sol. A* **2013**, *210*, 9–43.
- (3) Loiudice, A.; Rizzo, A.; Biasiucci, M.; Gigli, G. Bulk Heterojunction versus Diffused Bilayer: The Role of Device Geometry in Solution p-Doped Polymer-Based Solar Cells. *J. Phys. Chem. Lett.* **2012**, *3*, 1908–1915.
- (4) Mityashin, A.; Olivier, Y.; Van Regemorter, T.; Rolin, C.; Verlaak, S.; Martinelli, N. G.; Beljonne, D.; Cornil, J.; Genoe, J.; Heremans, P. Unraveling the Mechanism of Molecular Doping in Organic Semiconductors. *Adv. Mater.* **2012**, *24*, 1535–1539.
- (5) Pingel, P.; Schwarzl, R.; Neher, D. Effect of Molecular p-Doping on Hole Density and Mobility in Poly(3-hexylthiophene). *Appl. Phys. Lett.* **2012**, *100*, 143303–3.
- (6) Zhang, Y.; Blom, P. W. M. Enhancement of the Hole Injection into Regioregular Poly(3-hexylthiophene) by Molecular Doping. *Appl. Phys. Lett.* **2010**, *97*, 083303–3.
- (7) Han, X.; Wu, Z.; Sun, B. Enhanced Performance of Inverted Organic Solar Cell by a Solution-Based Fluorinated Acceptor Doped P3HT:PCBM Layer. *Org. Electr.* **2013**, *14*, 1116–1121.
- (8) Fujita, H.; Yuan, Y.; Michinobu, T. F_4 TCNQ Doping of P3HT:PCBM Photovoltaic Devices. *J. Photopolym. Sci. Technol.* **2011**, *24*, 311–315.
- (9) Hu, J.; Clark, K. W.; Hayakawa, R.; Li, A.-P.; Wakayama, Y. Enhanced Electrical Conductivity in Poly(3-hexylthiophene)/Fluorinated Tetracyanoquinodimethane Nanowires Grown with a Porous Alumina Template. *Langmuir* **2013**, *29*, 7266–7270.
- (10) Pingel, P.; Neher, D. Comprehensive Picture of p-Type Doping of P3HT with the Molecular Acceptor F_4 TCNQ. *Phys. Rev. B* **2013**, *87*, 115209–115217.
- (11) Duong, D. T.; Wang, C.; Antono, E.; Toney, M. F.; Salleo, A. The Chemical and Structural Origin of Efficient p-Type Doping in P3HT. *Org. Electron.* **2013**, *14*, 1330–1336.
- (12) Jiang, X. M.; Österbacka, R.; Korovyanko, O.; An, C. P.; Horovitz, B.; Janssen, R. A. J.; Vardeny, Z. V. Spectroscopic Studies of Photoexcitations in Regioregular and Regiorandom Polythiophene Films. *Adv. Funct. Mater.* **2002**, *12*, 587–597.
- (13) Tsoi, W. C.; Spencer, S. J.; Yang, L.; Ballantyne, A. M.; Nicholson, P. G.; Turnbull, A.; Shard, A. G.; Murphy, C. E.; Bradley, D. D. C.; Nelson, J.; Kim, J.-S. Effect of Crystallization on the Electronic Energy Levels and Thin Film Morphology of P3HT:PCBM Blends. *Macromolecules* **2011**, *44*, 2944–2952.
- (14) Brédas, J. L.; Thémans, B.; Fripiat, J. G.; André, J. M.; Chance, R. R. Highly Conducting Polyparaphenylene, Polypyrrole, and Polythiophene Chains: An Ab Initio Study of the Geometry and

Electronic-Structure Modifications upon Doping. *Phys. Rev. B* **1984**, *29*, 6761–6773.

(15) Navarrete, J. T. L.; Zerbi, G. Lattice Dynamics and Vibrational Spectra of Polythiophene. II. Effective Coordinate Theory, Doping Induced, and Photoexcited Spectra. *J. Chem. Phys.* **1991**, *94*, 965–970.

(16) Bredas, J. L.; Street, G. B. Polarons, Bipolarons, and Solitons in Conducting Polymers. *Acc. Chem. Res.* **1985**, *18*, 309–315.

(17) Brédas, J. L.; Wudl, F.; Heeger, A. J. Polarons and Bipolarons in Doped Polythiophene: A Theoretical Investigation. *Solid State Commun.* **1987**, *63*, 577–580.

(18) Zhang, R.; Li, B.; Iovu, M. C.; Jeffries-El, M.; Sauv  , G.; Cooper, J.; Jia, S.; Tristram-Nagle, S.; Smilgies, D. M.; Lambeth, D. N.; et al. Nanostructure Dependence of Field-Effect Mobility in Regioregular Poly(3-hexylthiophene) Thin Film Field Effect Transistors. *J. Am. Chem. Soc.* **2006**, *128*, 3480–3481.

(19) (a) Miller, J. S.; Krusic, P. J.; Dixon, D. A.; Reiff, W. M.; Zhang, J. H.; Anderson, E. C.; Epstein, A. J. Radical Ion Salts of 2,3-Dichloro-5,6-dicyanobenzoquinone and Metalloenes. A Reexamination of Their Magnetic and Spectroscopic Properties. *J. Am. Chem. Soc.* **1986**, *108*, 4459–4466. (b) Niklas, J.; Mardis, K. L.; Banks, B. P.; Grooms, G. M.; Sperlich, A.; Dyakonov, V.; Beaupre, S.; Leclerc, M.; Xu, T.; Yu, L.; Poluektov, O. G. Highly-Efficient Charge Separation and Polaron Delocalization in Polymer-Fullerene Bulk-Heterojunctions: A Comparative Multi-Frequency EPR and DFT Study. *Phys. Chem. Chem. Phys.* **2013**, *15*, 9562–9574.

(20) Park, Y. D.; Lee, S. G.; Lee, H. S.; Kwak, D.; Lee, D. H.; Cho, K. Solubility-Driven Polythiophene Nanowires and their Electrical Characteristics. *J. Mater. Chem. C* **2011**, *21*, 2338–2343.

(21) Moul  , A. J.; Meerholz, K. Controlling Morphology in Polymer–Fullerene Mixtures. *Adv. Mater.* **2008**, *20*, 240–245.

(22) Rainbolt, J. E.; Koech, P. K.; Polikarpov, E.; Swensen, J. S.; Cosimbescu, L.; Von Ruden, A.; Wang, L.; Sapochak, L. S.; Padmaperuma, A. B.; Gaspar, D. J. Synthesis and Characterization of p-Type Conductivity Dopant 2-(3-(Adamantan-1-yl)propyl)-3,5,6-trifluoro-7,7,8,8-tetracyanoquinodimethane. *J. Mater. Chem. C* **2013**, *1*, 1876–1884.

(23) Galya, L. G.; McCord, E. F.; Adamsons, K. Use of Paramagnetic Relaxation Agents in the Characterization of Acrylic Polymers: Application of Chromium (III) Acetylacetonate and Iron (III) Acetylacetonate. *Int. J. Polym. Anal. Charact.* **1996**, *2*, 293–303.

(24) Gao, J.; Roehling, J. D.; Li, Y.; Guo, H.; Moul  , A. J.; Grey, J. K. Effect of 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane Charge Transfer Dopants on the Conformation and Aggregation of Poly(3-hexylthiophene). *J. Mater. Chem. C* **2013**, DOI: 10.1039/C3TC31047G.

(25) Niles, E. T.; Roehling, J. D.; Yamagata, H.; Wise, A. J.; Spano, F. C.; Moul  , A. J.; Grey, J. K. J-Aggregate Behavior in Poly(3-hexylthiophene) Nanofibers. *J. Phys. Chem. Lett.* **2012**, *3*, 259–263.

(26) Panda, P.; Veldman, D.; Sweelssen, J.; Bastiaansen, J. J. A. M.; Langeveld-Voss, B. M. W.; Meskers, S. C. J. Charge Transfer Absorption for π -Conjugated Polymers and Oligomers Mixed with Electron Acceptors. *J. Phys. Chem. B* **2007**, *111*, 5076–5081.

(27) (a) Yong, C.; Renyuan, Q. IR and Raman Studies of Polythiophene Prepared by Electrochemical Polymerization. *Solid State Commun.* **1985**, *54*, 211–213. (b) Zhang, Y.; Gautam, B. R.; Basel, T. P.; Mascaro, D. J.; Vardeny, Z. V. Organic Bulk Heterojunction Solar Cells Enhanced by Spin Interaction. *Synth. Met.* **2013**, *173*, 2–9.

(28) Cao, Y.; Guo, D.; Pang, M.; Qian, R. Studies on Iodine Doped Thiophene Oligomers. *Synth. Met.* **1987**, *18*, 189–194.

(29) Tashiro, K.; Kobayashi, M.; Kawai, T.; Yoshino, K. Crystal Structural Change in Poly(3-alkylthiophene) Induced by Iodine Doping as Studied by an Organized Combination of X-ray Diffraction, Infrared/Raman Spectroscopy and Computer Simulation Techniques. *Polymer* **1997**, *38*, 2867–2879.

(30) Li, Y.; Qian, R. Stability of Conducting Polymers from the Electrochemical Point of View. *Synth. Met.* **1993**, *53*, 149–154.

(31) Elsenbaumer, R. L.; Jen, K. Y.; Miller, G. G.; Shacklette, L. W. Processible, Environmentally Stable, Highly Conductive Forms of Polythiophene. *Synth. Met.* **1987**, *18*, 277–282.

(32) Kanemoto, K.; Muramatsu, K.; Baba, M.; Yamauchi, J. Polaron Dynamics of Heavily Doped Regioregular and Regiorandom Poly(3-alkylthiophenes) Revealed by Electron Spin Resonance Spectroscopy. *J. Phys. Chem. B* **2008**, *112*, 10922–10926.

(33) (a) Kuzmany, H.; Stolz, H. J. Raman Scattering of TTF-TCNQ and Related Compounds. *J. Phys. C: Solid State Phys.* **1977**, *10*, 2241–2252. (b) Kim, J.-S.; Lee, S.-K.; Lee, H.-J.; Noh, D.-Y. A Charge-transfer Phenomenon between 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyano-p-quinodimethane (F₄TCNQ) and a Tetrathiafulvalene-Based Self-Assembled Monolayer Using an Indium-Tin Oxide Electrode. *Bull. Korean Chem. Soc.* **2010**, *31*, 4.

(34) Yim, K.-H.; Whiting, G. L.; Murphy, C. E.; Halls, J. J. M.; Burroughes, J. H.; Friend, R. H.; Kim, J.-S. Controlling Electrical Properties of Conjugated Polymers via a Solution-Based p-Type Doping. *Adv. Mater.* **2008**, *20*, 3319–3324.

(35) Roncali, J. Molecular Engineering of the Band Gap of π -Conjugated Systems: Facing Technological Applications. *Macromol. Rapid Commun.* **2007**, *28*, 1761–1775.

(36) Marumoto, K.; Takeuchi, N.; Ozaki, T.; Kuroda, S. ESR Studies of Photogenerated Polarons in Regioregular Poly(3-alkylthiophene)–Fullerene Composite. *Synth. Met.* **2002**, *129*, 239–247.

(37) Brown, P. J.; Sirringhaus, H.; Harrison, M.; Shkunov, M.; Friend, R. H. Optical Spectroscopy of Field-Induced Charge in Self-Organized High Mobility Poly(3-hexylthiophene). *Phys. Rev. B* **2001**, *63*, 125204–125214.

(38)   sterbacka, R.; An, C. P.; Jiang, X. M.; Vardeny, Z. V. Two-Dimensional Electronic Excitations in Self-Assembled Conjugated Polymer Nanocrystals. *Science* **2000**, *287*, 839–842.