BNL-114328-2017-JA

Influence of Nanostructure on the Exciton Dynamics of Multichromophore Donor-Acceptor Block Copolymers

J. Xia, M, Y. Sfeir

Submitted to ACS Nano

May 2017

Center for Functional Nanomaterials

Brookhaven National Laboratory

**U.S. Department of Energy
USDOE Office of Science (SC),
Basic Energy Sciences (SC-22)**

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE- SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Influence of Nanostructure on the Exciton Dynamics of Multichromophore Donor-Acceptor Block Copolymers

Jianlong Xia[†], Erik Busby[§], Samuel N. Sanders[†], Clarion Tung[†], Angelo Cacciuto^{†,*}, Matthew Y. Sfeir^{§,*}, Luis M. Campos^{†,*}

[†]Department of Chemistry, Columbia University, New York, New York 10027, United States

[§]Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States

Supporting Information Placeholder

ABSTRACT: We explore the synthesis and photophysics of nanostructured block copolymers that mimic light harvesting complexes. We find that the combination of a polar and electron rich boron dipyrromethene (BODIPY) block with a non-polar electron poor perylene diimide (PDI) block yields a polymer which self-assembles into ordered “nanoworms”. Numerical simulations are used to determine optimal compositions to achieve robust self-assembly. Photoluminescence spectroscopy is used to probe the rich exciton dynamics in these systems. Using controls, such as homopolymers and random copolymers we analyze the mechanisms of the photoluminescence from these polymers. This understanding allows us to probe in detail the photophysics of the block copolymers, including the effects of their self-assembly into nanostructures on their excited-state properties. Similar to natural systems, ordered nanostructures result in properties that are starkly different than the properties of free polymers in solution, *e.g.* enhanced rates of electronic energy transfer and elimination of excitonic emission from disordered perylene diimide trap states.

Keywords: Nanotechnology, Photophysics, Organic Electronics, Polymer Chemistry, Self-Assembly, Excitonics

Mimicking light-harvesting complexes of biological systems using synthetic materials can lead to a fundamental understanding of photophysical mechanisms to control electronic energy transfer (EET) through molecular design.¹ This understanding can be translated into devices powered by the sun. But natural photosynthetic systems comprise dozens of hierarchically ordered chromophores, which collectively lead to function.²⁻³ It is the exquisite ensemble that drastically differentiates the mode of operation from its individual components, funneling, modulating, and directing the harvested energy to active centers. While many types of small molecules and their assembled superstructures have been studied, as well as macromolecular materials, there remains a need to understand and control the hierarchical self-assembly of multichromophoric materials, as well as their photophysical processes.⁴⁻⁹

Recently, Scholes and co-workers developed guidelines to design synthetic light-harvesting materials, focusing on energy requirements and connectivity. In this vein, nanostructured assemblies of small molecules have been shown to affect photophysical phenomena. Examples include superstructures of single-chromophore amphiphilic cyanine dyes that yield light-harvesting bilayered nanotubes, and supramolecular donor-acceptor-donor (DAD) ribbons, among other.¹⁰⁻¹²

Macromolecular synthetic chemistry has evolved to the point that complex architectures can be readily made.¹³⁻¹⁹ With appropriate molecular engineering, various physical, optical, and electronic properties can be modulated to mimic biological functions.

Among these properties, understanding photoinduced EET is important to elucidate the underpinning processes from light-harvesting complexes so that synthetic materials can be engineered with unprecedented control of function. For example, most studies of donor-acceptor architectures by self-assembly have been carried out using single-chromophore units containing the appropriate recognition elements.²⁰⁻²² In order to investigate how EET is channeled in multichromophore donor-acceptor systems (Figure 1A), we designed diblock copolymers that can self-assemble into hierarchical core-shell structures using polar and non-polar interactions (Figure 1B).²³ These systems can provide insights into the EET process in solutions of free polymers as a function of interchromophore ordering. This allows for probing of molecular/excimer emission and EET in a system analogous to biological systems that efficiently channel energy to active centers.²⁴

Figure 1. A) Chemical structure of homopolymers, as well as energetics of the monomers.²⁵ B) Diblock copolymers can be self-assembled by addition of water to yield nanoworm structures, with the polar PBOD block on the outside and the PPDI block in the core.

RESULTS AND DISCUSSION

The materials design is shown in Figure 1. Both chromophores (BODIPY-donor and PDI-acceptor) have a similar optical energy gap, but offset energy levels as shown. In order to investigate how hierarchical structures affect EET as compared to fully solvated polychromophores, the BODIPY was synthesized containing a polymerizable norbornyl unit on one end, and a polar swallow-tail based on tetraethylene glycol. Similarly, the PDI acceptor also contained the same polymerizable unit, but using a non-polar swallow-tail based on alkyl chains. These monomers were then polymerized individually to obtain homopolymers of each, as well as a statistical block copolymer where both donor and acceptor were polymerized at the same time, as controls.

Self-Assembly Simulations

We guided the synthesis of the block copolymers (BCPs) by developing a simple numerical model (the details are included in the supporting material) for the block copolymer. Using the molecular dynamics simulations package LAMMPS we traced a phase diagram in terms of the bending rigidity of the polymer's back-bone, K_B , and the strength of the attractive interaction between the side-chains ϵ , to ensure that we obtain cylindrical structures that are reminiscent of other tubular light-harvesting systems.^{10, 26-27} For small values of ϵ , the copolymers are disordered and remain in the fluid state. For fairly flexible backbones with $K_B < 5 k_B T$, the copolymers self-assemble into micelles. For $\epsilon \geq 1.5 k_B T$ and $K_B > 5 k_B T$, nanoworms are observed. Nanoworms are cylindrical with the nonpolar tails buried in the interior. Kinks in the nanoworms are a result of geometric frustration that develops in the self-assembly dynamics especially for large values of ϵ .

Figure 2. A) A phase diagram for the block copolymers shows that for weak nonpolar tail interaction strengths $\epsilon < 1.0 k_B T$, self-assembly does not occur and the system remains fluid while block copolymers with flexible backbones $K_B < 10 k_B T$ form micelles. Nanoworms form in a large region of phase space for rigid backbones

$K_B > 10 k_B T$ and with nonpolar tail interactions $\epsilon > 1.0 k_B T$. B) TEM image of nanoworms made from the 45K block copolymer assembled from THF/Water mixture. Further details of the block copolymer characterization and assembly are provided in the SI.

We also simulated the effect of varying the molecular weight of one block with respect to the other, and find that at low molecular weight of the nonpolar block, nanoworms do not form, and assemble into small micellar-like aggregates instead. At high molecular weight, tails from individual copolymers can bind simultaneously to several different cylindrical segments, resulting in complex, disordered three-dimensional networks. These results can be understood, to some degree, with simple geometrical arguments by looking at the effective shape of the copolymer for the different parameters of the model and the relative balance between attractive and steric interactions.²⁸ Simulations point to 50-50 molecular weight being ideal for nanoworm formation. From this insight, we focused on BCPs with equivalent degrees of polymerization of each donor and acceptor units, and focused on self-assembly and photophysics of a M_n 45Kg mol⁻¹ block copolymer with $\Phi = 1.2$.

Experimental Self-Assembly

The BCP self-assembly was induced by solvent exchange, dissolving 1mg of PBOD-*b*-PPDI in 1 mL of THF, adding 1mL water drop wise, and finally letting the THF evaporate slowly. With this approach, the expected cylindrical core-shell structure shown in Figure 1B contains the polar tetraethylene oxide chains on the outside, placing the PBOD in the shell, and forcing the hydrophobic PPDI block on the inside.²⁹⁻³¹ The resulting structures were characterized by TEM, and the images shown in Figure 2B confirm the cylindrical nanoworm structures predicted by the calculations. Moreover, the nanoworms also exhibit kinks along the tubular structure, as observed in the simulations.

Spectroscopic Experiments

We now turn to photoluminescence (PL) spectroscopy to characterize the photophysics arising in these multichromophore systems. To investigate the effects of linking BODIPY and PDI together in pendant block copolymers, we first investigate the PL spectra, shown in Figure 3.

Figure 3. PL spectra of the various polymers studied here in chloroform. The labels PBOD and PPDI correspond to the homopolymers; PBOD-*r*-PPDI is the statistical copolymer; PBOD-*b*-PPDI is the diblock copolymer fully dissolved; and NW-PBOD-*b*-PDI is the nanoworm formed by self-assembly of the diblock copolymer.

We begin our discussion by focusing on the simplest systems – the homopolymers. In both the PDI homopolymer and the BODIPY homopolymer, the chromophores are pendant from the backbone of the norbornyl polymer; however, despite very similar chemical environments PBOD and PPDI solutions behave remarkably differently.

The PL spectrum of the PBOD in chloroform shows one emission feature, with a peak at 530 nm (Figure 3). BODIPY is particularly notable for its small Stokes shift and relative insensitivity to its environment.³² Consistent with this observation, we find that PBOD (9,000 g/mol, $\Phi=1.07$) behaves as an ensemble of chromophores with minimal evidence for significant chromophore-chromophore interaction, i.e. we see no evidence of excimer formation as a result of the close proximity of nearest-neighbor chromophores. We note that our measurement is only sensitive to changes in photoluminescence spectrum and lifetime, we cannot comment on the potential for exciton transport since it does not lead to PL quenching.

The PL of PPDI (4,400 g/mol, $\Phi=1.02$) shows two features, a narrow peak with a maximum at 550 nm, and a broad peak with a maximum at 650 nm (Figure 3). The highest energy feature (550 nm) originates from excitonic PDI emission, as observed in solutions of individual molecules of PDI monomer. This excitonic emission extends to lower energies (more clearly shown in the PBOD-*r*-PPDI spectrum), but in PPDI, this low energy tail is obscured by a more intense second PL feature. This second PL feature is emission from PDI excimer.³³⁻³⁴ In PPDI, the covalent attachment of chromophores to a common backbone effectively forms a solution-phase 1-dimensional molecular fiber. As a result of efficient inter-chromophore coupling, PPDI readily forms excimers. This is evidenced by the broad red-shifted photoluminescence seen in PPDI, the extended photoluminescence lifetime compared to molecular PDI, and the identical photoluminescence excitation spectra of the exciton and excimer emission features (SI). Though the PPDI PL spectrum is predominantly excimer emission, significant excitonic PL is also observed. Given that excimer formation occurs on an ultrafast timescale, any persistent excitonic PDI emission likely originates from PDI chromophores in regions of the polymer where structural disorder prevents efficient inter-chromophore coupling and resultant excimer formation.

Figure 4. Exciton dynamics, along with instrument respons function (IRF) probed at the wavelengths of maximum absorption for each feature (PBOD exciton near 530 nm, PDI excimer near 550 nm and PDI excimer near 680 nm). The arrival time of the excitation pulse (time zero) is offset by 1 ns to accomodate the log scaling of the time (x) axis.

To explore the excited state dynamics of the pendent donor/acceptor chromophores, we begin with the statistical distribution of PDI and BODIPY chromophores in PBOD-*r*-PPDI. In this system, the average chromophore is adjacent to a chromophore of the other species. As a result, PBOD-*r*-PPDI serves as an example of BODIPY-PDI dynamics in the nearest-neighbor limit. The PL spectrum of PBOD-*r*-PPDI shows excitonic emission from PDI with no significant contribution from PDI excimer or from BODIPY. This demonstrates that BODIPY excitations are quenched efficiently by neighboring PDI chromophores through either energy or electron transfer. Distinguishing these two types of transfer using techniques such as transient absorption spectroscopy is challenging due to similar locations of the absorption (spectra in SI), and therefore ground-state bleaches for PDI and BODIPY. However, quantitative quenching demonstrates effective coupling of BODIPY excitations to PDI. Irrespective of the specific mechanism, the efficiency of quenching results from the close proximity of adjacent chromophores in the randomly polymerized material and the significant energetic overlap between the BODIPY and PDI excitons.

In addition to quenching the BODIPY PL, PBOD-*r*-PPDI also shows a significantly different photoluminescence spectrum (Figure 3), yet similar PDI exciton decay dynamics (figure 4B), as compared to PPDI. The PL spectrum of PBOD-*r*-PPDI does not show significant excimer emission. Formation of an excimer requires an extended system of interacting chromophores, as are present in PPDI. However, the statistical distribution of BODIPY interrupts efficient inter-molecular interactions between PDI chromophores. As a result, most PDI chromophores do not meet the

structural requirement for excimer formation. While the presence of PDI efficiently quenches BODIPY excitons, the equivalent decays of PDI excitons in PPDI and PBOD-*r*-PPDI show that the presence of BODIPY has a minimal effect on the PDI exciton decay. There are also some minor differences in the initial PL dynamics of PDI excitons in PBOD-*r*-PPDI, relative to PPDI and PBOD-*b*-PPDI. The sub-ns decay observed in PBOD-*r*-PPDI is assigned to the quenching of PDI excitons by BODIPY units. This feature is absent in PBOD-*b*-PPDI, suggesting that charge transfer from the PDI exciton outcompetes radiative decay and excimer formation only in regions where a small number of consecutive PDI units are found. In regions with a larger number of consecutive PDI units, the exciton decay of PBOD-*r*-PPDI are identical to PBOD-*b*-PPDI.

Moving onto the diblock copolymer, PBOD-*b*-PPDI provides the ability to investigate the effects of excimer formation on EET in these systems. Structurally, PBOD-*b*-PPDI is a strand of PPDI and a strand of PBOD joined at the ends. As a result, the PDI will readily form excimers due to efficient inter-chromophore coupling along the backbone of one block. However, the presence of the BODIPY block enables quenching of excimers on faster time-scales than in PPDI homopolymer. Indeed, the PDI excimer PL is quenched fully within ~ 30 ns timescale (Figure 4C), which we attribute to hole transfer to BODIPY. The transfer kinetics are likely limited by transport along the polymer chain and BODIPY-PDI coupling at the interface. Interestingly, we do not see any quenching of excitonic PDI emission by BODIPY (Figure 4B). Given that PDI excitons will remain excitonic only if excimer formation is not possible, we interpret this lack of PDI exciton quenching as a result of diminished inter-chromophore coupling in disordered regions. In these areas of significant disorder, excitons are trapped in areas of negligible mobility and will, therefore, behave similarly to isolated PDI.

We also investigate photophysics in the self-assembled nanoworm structures (Figure 2), which we name NW-PBOD-*b*-PPDI (Figure 3, 4C). The micelle-like nanoworms orient the polar BODIPY in the shell, and the non-polar PDI is sequestered in the center. The result is increased intermolecular PDI coupling caused by the combined effects of multiple strands aggregating and the transition from a 1D molecular fiber system in solution to a 3D nanoparticle system in the nanoworm aggregates. The primary photophysical manifestation of this structural assembly is the funneling of the energy from the outer BODIPY to the inner PDI chromophores, as summarized in Figure 5.

We also observe quantitative quenching of excitonic PDI PL by excimer formation in the nanoworms, as evidenced by the PL spectrum of PBOD-*b*-PPDI compared to NW-PBOD-*b*-PPDI (Figure 3). In the latter, only the PDI excimer PL persists. Quenching of exciton emission by excimer formation is commonly observed concomitant with strong association of PDI subunits in nanostructures.³⁵ Additionally, in NW-PBOD-*b*-PPDI the excimer PL decays by a factor of six times faster than in PPDI (5.4 ns compared to 34 ns average decay time, details of fitting in SI), which we assign to excimer quenching *via* hole transfer to BODIPY on a 6 ns time scale (Figure 4C). This is significantly accelerated relative to hole transfer in PBOD-*b*-PPDI, which results from increase inter-chromophore PDI coupling and a resultant increase in excimer mobility in the self-assembled system.

Figure 5. Schematic representation of light absorption and emission processes in PBOD-*b*-PDI and NW-PBOD-*b*-PDI.

CONCLUSIONS

In summary, The PL spectra and dynamics allow for the determination of the local environments for excitons and insights into their mobility. The PL dynamics provide a means of probing the inter-chromophore coupling and resultant exciton mobility within the extended PDI domains found in PPDI and PBOD-*b*-PPDI. We can also use the photoluminescence to ascertain structural changes resulting from self-assembly into nanoworms.

The PDI segments within these systems can be viewed as a molecular fiber, likely forming pi-stacked domains with relatively long range order. However, within PPDI and PBOD-*b*-PPDI, not all PDI chromophores are incorporated into the ordered molecular fiber. Likely owing to structural disorder in the polymer backbone or tethering groups, some PDI chromophores behave as individual units, despite having other chromophores in relatively close proximity. Thus, relative contribution of molecular (excitonic) and 1D aggregate (excimeric) PL gives an indication of the degree of structural ordering within the system.

Structural ordering is most apparent in the nanostructure NW-PBOD-*b*-PPDI, which shows quantitative quenching of excitonic PDI emission *via* excimer formation. In addition to favoring of excimer emission, the rate of PDI excimer quenching (by hole transfer to BODIPY) gives a relative measure of the excimer inter-chromophore coupling and carrier mobility within the PDI domain. This is clearly demonstrated by the 5-fold increase in quenching rate when PBOD-*b*-PPDI is self-assembled to form NW-PBOD-*b*-PPDI. In this more ordered system, the increase in inter-chromophore coupling yields more mobile excimers that are more quickly quenched at the BODIPY-PDI interface. Based on the rates of excimer decay (Figure 4C), self-assembly causes an increase in charge transfer quantum yield from 50% to 83%. The self-assembly based enhancement of charge transfer from excimers is an important proof of concept for the use of synthetic tubular nanostructures to mimic natural light harvesting systems.

EXPERIMENTAL METHODS

For photoluminescence and time-resolved photoluminescence measurements samples were recorded using excitation pulses from a picosecond supercontinuum laser (Fianium SC450-PP). The broadband laser output was spectrally filtered using a narrow bandpass filter (488 nm with 2 nm bandwidth) to achieve a fluence of $\sim 50 \text{ nJ/cm}^2$. Steady-state emission spectra were recorded using a spectrometer and liquid nitrogen cooled CCD camera (JY Horiba). Time-resolved photoluminescence data (SI) were measured using a spectrometer equipped with an avalanche photodiode and time correlated single photon counting electronics (Picoquant). The instrument response of this system is $\sim 100 \text{ ps}$. Photoluminescence excitation spectra were taken using an ISS PC1 spectrofluorimeter. Transient absorption spectra were collected using a previously described setup, where a commercial Ti:sapphire laser system (Spectraphysics), operating at 1 KHz, pumped an optical parametric amplifier (LightConversion) to generate $\sim 100 \text{ fs}$ pulses, and supercontinuum light was generated by passing a small portion of the 800 nm fundamental into a sapphire disk, and pump and probe delay were controlled by means of a mechanical delay stage.³⁶

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Contains UV-Visible linear absorption spectra, synthetic details, ^1H and ^{13}C NMR spectra, details of computational experiments, transient absorption spectra and excitation dependent photoluminescence spectra.

AUTHOR INFORMATION

Corresponding Author

*E-mail: lcampos@columbia.edu, msfeir@bnl.gov, ac2822@columbia.edu

Present Addresses

(J.X.) Department of Chemistry, Wuhan Institute of Technology
(E.B) Intel Corporation

Author Contributions

‡These authors contributed equally.

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

L.M.C. acknowledges support from the National Science Foundation (NSF CAREER DMR-1351293) and Cottrell Scholar Award. S.N.S. thanks the NSF for GRFP (DGE 11-44155). This research used resources of the Center for Functional Nanomaterials, which is a U.S. DOE Office of Science Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704. This project was funded through the Center for Redefining Photovoltaic Efficiency Through Molecular-Scale Control, an Energy Frontier Research Center funded by the US Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences under Award DE-SC0001085. A.C. acknowledges financial support from the National

Science Foundation under Grant No. DMR-1408259. We thank Dr. Wenyan Liu for assistance with TEM imaging.

REFERENCES

1. Scholes, G. D.; Fleming, G. R.; Olaya-Castro, A.; van Grondelle, R., Lessons from Nature about Solar Light Harvesting. *Nat. Chem.* **2011**, *3*, 763-774.
2. Collini, E.; Wong, C. Y.; Wilk, K. E.; Curmi, P. M. G.; Brumer, P.; Scholes, G. D., Coherently Wired Light-Harvesting in Photosynthetic Marine Algae at Ambient Temperature. *Nature* **2010**, *463*, 644-647.
3. Scholes, G. D.; Fleming, G. R., On the Mechanism of Light Harvesting in Photosynthetic Purple Bacteria: B800 to B850 Energy Transfer. *J. Phys. Chem. B* **2000**, *104*, 1854-1868.
4. Guo, C.; Lin, Y.-H.; Witman, M. D.; Smith, K. A.; Wang, C.; Hexemer, A.; Strzalka, J.; Gomez, E. D.; Verduzco, R., Conjugated Block Copolymer Photovoltaics with near 3% Efficiency through Microphase Separation. *Nano Lett.* **2013**, *13*, 2957-2963.
5. Lin, Y.-H.; Smith, K. A.; Kempf, C. N.; Verduzco, R., Synthesis and Crystallinity of All-Conjugated Poly(3-hexylthiophene) Block Copolymers. *Polym. Chem.* **2013**, *4*, 229-232.
6. Verduzco, R.; Botiz, I.; Pickel, D. L.; Kilbey, S. M.; Hong, K.; Dimasi, E.; Darling, S. B., Polythiophene-block-polyfluorene and Polythiophene-block-poly(fluorene-co-benzothiadiazole): Insights into the Self-Assembly of All-Conjugated Block Copolymers. *Macromolecules* **2011**, *44*, 530-539.
7. Guzman, C. X.; Calderon, R. M. K.; Li, Z.; Yamazaki, S.; Peurifoy, S. R.; Guo, C.; Davidowski, S. K.; Mazza, M. M. A.; Han, X.; Holland, G.; Scott, A. M.; Braunschweig, A. B., Extended Charge Carrier Lifetimes in Hierarchical Donor-Acceptor Supramolecular Polymer Films. *J. Phys. Chem. C* **2015**, *119*, 19584-19589.
8. Ley, D.; Guzman, C. X.; Adolffson, K. H.; Scott, A. M.; Braunschweig, A. B., Cooperatively Assembling Donor-Acceptor Superstructures Direct Energy Into an Emergent Charge Separated State. *J. Am. Chem. Soc.* **2014**, *136*, 7809-7812.
9. Fukuzumi, S.; Ohkubo, K.; Ortiz, J.; Gutierrez, A. M.; Fernandez-Lazaro, F.; Sastre-Santos, A., Formation of a Long-Lived Charge-Separated State of a Zinc Phthalocyanine-Perylenediimide Dyad by Complexation with Magnesium Ion. *Chem. Commun.* **2005**, 3814-3816.
10. Eisele, D. M.; Cone, C. W.; Bloemsmas, E. A.; Vlaming, S. M.; van der Kwaak, C. G. F.; Silbey, R. J.; Bawendi, M. G.; Knoester, J.; Rabe, J. P.; Vanden Bout, D. A., Utilizing Redox-Chemistry to Elucidate the Nature of Exciton Transitions in Supramolecular Dye Nanotubes. *Nat. Chem.* **2012**, *4*, 655-662.
11. Milota, F.; Prokhorenko, V. I.; Mancal, T.; von Berlepsch, H.; Bixner, O.; Kauffmann, H. F.; Hauer, J., Vibronic and Vibrational Coherences in Two-Dimensional Electronic Spectra of Supramolecular J-Aggregates. *J. Phys. Chem. A* **2013**, *117*, 6007-6014.
12. Siram, R. B. K.; Tandy, K.; Horecha, M.; Formanek, P.; Stamm, M.; Gevorgyan, S.; Krebs, F. C.; Kiriya, A.; Meredith, P.; Burn, P. L.; Nanddas, E. B.; Patil, S., Synthesis and Self-Assembly of Donor-Acceptor-Donor Based Oligothiophenes

- and Their Optoelectronic Properties. *J. Phys. Chem. C* **2011**, *115*, 14369-14376.
13. Coessens, V.; Pintauer, T.; Matyjaszewski, K., Functional Polymers by Atom Transfer Radical Polymerization. *Prog. Polym. Sci.* **2001**, *26*, 337-377.
 14. Matyjaszewski, K.; Xia, J., Atom Transfer Radical Polymerization. *Chem. Rev.* **2001**, *101*, 2921-2990.
 15. Wang, J.-S.; Matyjaszewski, K., Controlled/"Living" Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complexes. *J. Am. Chem. Soc.* **1995**, *117*, 5614-5615.
 16. Hawker, C. J.; Wooley, K. L., The Convergence of Synthetic Organic and Polymer Chemistries. *Science* **2005**, *309*, 1200-1205.
 17. Husseman, M.; Malmström, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J., Controlled Synthesis of Polymer Brushes by "Living" Free Radical Polymerization Techniques. *Macromolecules* **1999**, *32*, 1424-1431.
 18. Qiu, H.; Hudson, Z. M.; Winnik, M. A.; Manners, I., Multidimensional Hierarchical Self-Assembly of Amphiphilic Cylindrical Block Comicelles. *Science* **2015**, *347*, 1329-1332.
 19. Gadt, T.; Jeong, N. S.; Cambridge, G.; Winnik, M. A.; Manners, I., Complex and Hierarchical Micelle Architectures from Diblock Copolymers Using Living, Crystallization-Driven Polymerizations. *Nat. Mater.* **2009**, *8*, 144-150.
 20. Schenning, A. P. H. J.; v. Herrikhuyzen, J.; Jonkhøj, P.; Chen, Z.; Würthner, F.; Meijer, E. W., Photoinduced Electron Transfer in Hydrogen-Bonded Oligo(p-phenylene vinylene)-Perylene Bisimide Chiral Assemblies. *J. Am. Chem. Soc.* **2002**, *124*, 10252-10253.
 21. Hoeben, F. J. M.; Jonkhøj, P.; Meijer, E. W.; Schenning, A. P. H. J., About Supramolecular Assemblies of π -Conjugated Systems. *Chem. Rev.* **2005**, *105*, 1491-1546.
 22. Bu, L.; Pentzer, E.; Bokel, F. A.; Emrick, T.; Hayward, R. C., Growth of Polythiophene/Perylene Tetracarboxydiimide Donor/Acceptor Shish-Kebab Nanostructures by Coupled Crystal Modification. *ACS Nano* **2012**, *6*, 10924-10929.
 23. Topham, P. D.; Parnell, A. J.; Hiorns, R. C., Block Copolymer Strategies for Solar Cell Technology. *J. Polym. Sci., Part B: Polym. Phys.* **2011**, *49*, 1131-1156.
 24. Tran, H.; Gopinadhan, M.; Majewski, P. W.; Shade, R.; Steffes, V.; Osuji, C. O.; Campos, L. M., Monoliths of Semiconducting Block Copolymers by Magnetic Alignment. *ACS Nano* **2013**, *7*, 5514-5521.
 25. Shin, W. S.; Jeong, H.-H.; Kim, M.-K.; Jin, S.-H.; Kim, M.-R.; Lee, J.-K.; Lee, J. W.; Gal, Y.-S., Effects of Functional Groups at Perylene Diimide Derivatives on Organic Photovoltaic Device Application. *J. Mater. Chem.* **2006**, *16*, 384-390.
 26. Wasielewski, M. R., Self-Assembly Strategies for Integrating Light Harvesting and Charge Separation in Artificial Photosynthetic Systems. *Acc. Chem. Res.* **2009**, *42*, 1910-1921.
 27. Plimpton, S., Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput. Phys.* **1995**, *117*, 1-19.
 28. Intermolecular and Surface Forces A2 - Israelachvili, Jacob N. In *Intermolecular and Surface Forces (Third Edition)*, Academic Press: Boston, 2011; p iii.
 29. Kempe, K.; Wylie, R. A.; Dimitriou, M. D.; Tran, H.; Hoogenboom, R.; Schubert, U. S.; Hawker, C. J.; Campos, L. M.; Connal, L. A., Preparation of Non-Spherical Particles from Amphiphilic Block Copolymers. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 750-757.
 30. Lin, B. F.; Marullo, R. S.; Robb, M. J.; Krogstad, D. V.; Antoni, P.; Hawker, C. J.; Campos, L. M.; Tirrell, M. V., De Novo Design of Bioactive Protein-Resembling Nanospheres via Dendrimer-Templated Peptide Amphiphile Assembly. *Nano Lett.* **2011**, *11*, 3946-3950.
 31. Zhu, J.; Ferrer, N.; Hayward, R. C., Tuning the Assembly of Amphiphilic Block Copolymers through Instabilities of Solvent/Water Interfaces in the Presence of Aqueous Surfactants. *Soft Matter* **2009**, *5*, 2471-2478.
 32. Loudet, A.; Burgess, K., BODIPY Dyes and Their Derivatives: Syntheses and Spectroscopic Properties. *Chem. Rev.* **2007**, *107*, 4891-4932.
 33. 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.
 34. Margulies, E. A.; Shoer, L. E.; Eaton, S. W.; Wasielewski, M. R., Excimer Formation in Cofacial and Slip-Stacked Perylene-3,4:9,10-bis(dicarboximide) Dimers on a Redox-inactive Triptycene Scaffold. *Phys. Chem. Chem. Phys.* **2014**, *16*, 23735-23742.
 35. Supur, M.; Fukuzumi, S., Energy and Electron Transfer of One-Dimensional Nanomaterials of Perylenediimides. *ECS J. Solid State Sci. Technol.* **2013**, *2*, M3051-M3062.
 36. Sanders, S. N.; Kumarasamy, E.; Pun, A. B.; Trinh, M. T.; Choi, B.; Xia, J.; Taffet, E. J.; Low, J. Z.; Miller, J. R.; Roy, X.; Zhu, X. Y.; Steigerwald, M. L.; Sfeir, M. Y.; Campos, L. M., Quantitative Intramolecular Singlet Fission in Bipentacenes. *J. Am. Chem. Soc.* **2015**, *137*, 8965-8972.