Oligothiophene Nanoparticles: Photophysical and Electrogenerated Chemiluminescence Studies

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S *Supporting Information*

ABSTRACT: Thiophene oligomer nanoparticles (NPs) were studied by fluorescence spectroscopy and electrogenerated chemiluminescence (ECL). Distinct spectroscopic differences between aggregates or NPs of thiophene hexamers having differing substitution patterns of solubilizing alkyl groups were observed. The α,ω-unsubstituted thiophene hexamer, **Hexamer-2**, exhibited fluorescence properties that were similar in solution and as colloidal NPs; there was only a small red shift compared with what was observed for the discrete system dissolved in tetrahydrofuran (THF). In contrast, the oligomer substituted in the α,ω-positions with branched alkyl substituents (**Hexamer-1**) displayed a gradual bathochromic shift of the fluorescence maximum in proportion to the amount of a poor solvent (water) added to the THF solution. Moreover, the fluorescence characteristics for the oligomer(s) dissolved in a mixture of THF and water were similar to those seen by annihilation ECL in a mixture of benzene/acetonitrile. On this basis, we conclude that annihilation ECL may be a useful technique for monitoring the formation of organic nanoparticles.

SECTION: Spectroscopy, Photochemistry, and Excited States
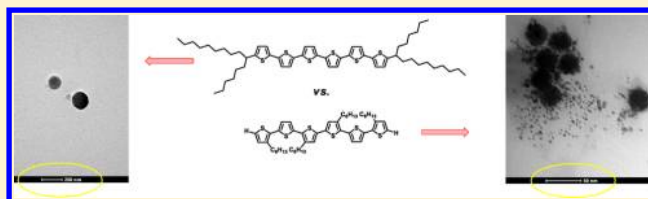
Aggregates of various sizes have been studied for decades, and understanding the factors in their formation and structure is of significance in self-organization and supramolecular chemistry.[1−14] On the basis of this prior work, it is now appreciated that the use of mixtures of "good" and "poor" solvents provides a useful technique for obtaining aggregates having different shapes as well as differing photophysical and structural properties.[5−9,14] Oligothiophenes are good model compounds for such studies because they are π-conjugated and able to form highly ordered assemblies. They have also been actively studied for many applications, ranging from transistors and light-emitting diodes to photovoltaic devices.[13,15,16] Ellinger et al. studied the aggregation behavior of α-mono and α,ω-disubstituted oligothiophenes with linear, branched, and mixed alkyl substituents[17,18] From UV/vis absorbance and fluorescence measurements, as well as AFM imaging, they showed that branched α,ω-substituted thiophene oligomers form aggregates in 1,1,2,2-tetrachloroethane with and without addition of a poor solvent, methanol. Here, we present photophysical and ECL studies of aggregates of two oligothiophene hexamers with different substitution patterns.

The structures of the compounds studied in this work, **Hexamer-1** and **Hexamer-2**, are presented in Scheme 1. Detailed synthetic, electrochemical, and photophysical procedures for these compounds are described elsewhere.[19] Both oligomers contain the same number of thiophenes (six) as well as multiple long alkyl chains to enhance their solubility in polar organic solvents. The two compounds are distinguished by their alkyl substitution patterns, and we hypothesized that these structural differences would affect their self-assembly behavior.

Hexamer-1 is characterized by long, branching alkyl chains in the α,ω-positions, while **Hexamer-2** is unsubstituted at the α,ω-positions and contains alkyl substituents along the oligomer backbone.

To test whether **Hexamer-1** and **Hexamer-2** were capable of forming NPs in solution, a poor solvent for the oligomers, water, was gradually added to independent THF solutions of the oligomers. The addition process was accompanied by a change in the color of the solutions from green to orange. Images of the UV-irradiated solutions of **Hexamer-1** and **Hexamer-2** in 1:9 v/v THF/water as well as in pure THF are shown in Figure 1.

The observed color change upon the addition of water was consistent with aggregate formation. Moreover, the behavior was dependent on solute concentration, as well as the volume fraction of water (Figure S1 in the Supporting Information). To probe these correlations further, fluorescence spectra of **Hexamer-1** and **Hexamer-2** with different compositions of THF/water were acquired at several different concentrations. In general, there was a large variation in the fluorescence spectra of **Hexamer-1** depending on both the concentration and solvent composition (Figure 2a−c and Supporting Information Figure S2a). This was not true for **Hexamer-2**, which did not show a pronounced change in its fluorescence behavior even in the presence of large quantities of water (Figure 2d). In contrast, the fluorescence spectra of **Hexamer-1**

Scheme 1. Structures of Hexamer-1 and Hexamer-2
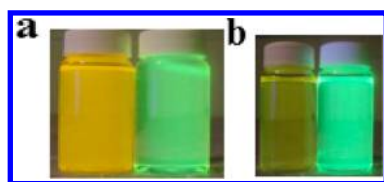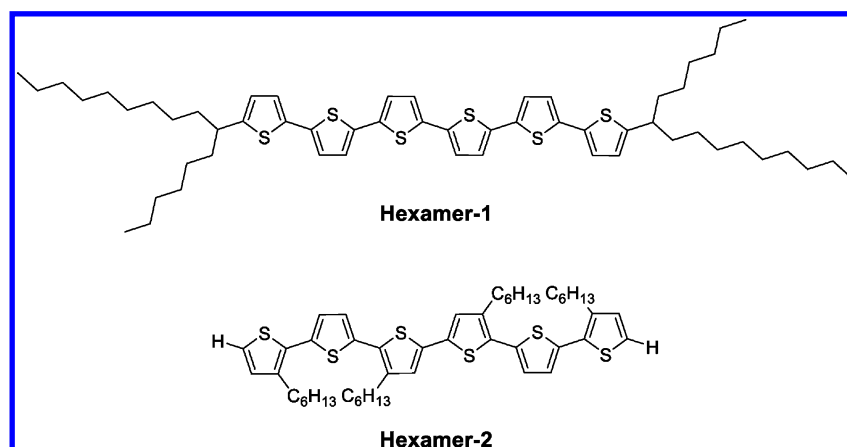

Hexamer-1

Hexamer-2

Figure 1. Images of 0.1 mM solutions of (a) **Hexamer-1** and (b) **Hexamer-2** in both 1:9 v/v THF/water (left vial) and pure THF (right vial). The solutions were irradiated with a hand-held UV lamp.
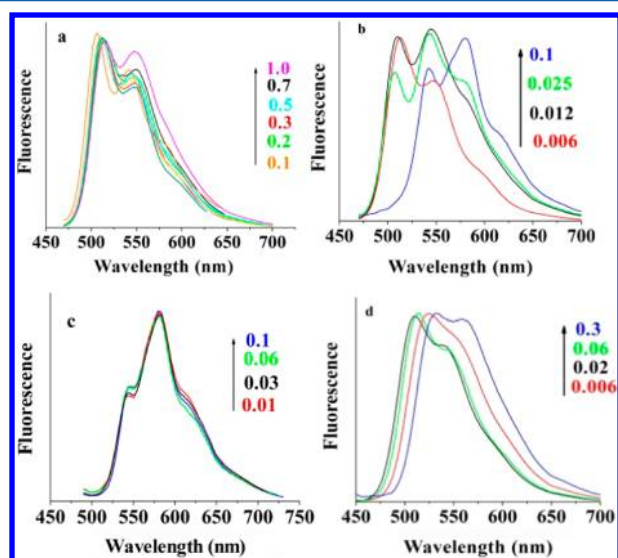

Figure 2. Normalized fluorescence spectra for (a−c) **Hexamer-1** and (d) **Hexamer-2** for different concentrations and ratios of THF/water: (a) 85% THF/15% water; (b) 50% THF/50% water, (c) 15% THF/ 85% water; (d) 10% THF/90% water (v/v). The numbers in the legend correspond to the initial concentrations of hexamer in mM. The emission spectra were taken with excitation at the wavelength of the absorption maxima.

were characterized by a progression with peaks at 520, 542, and 582 nm, whose relative intensities depended on the volume fraction of water in the solvent. Each of these features corresponded to the formation of differently sized particles, with the optical changes reflecting the equilibria between discrete solvated species and the NPs. At lower volume fractions of water, the 0−0 transition at 520 nm dominated, and the spectral shape resembled the fluorescence spectrum of fully dissolved **Hexamer-1**, with little concentration dependence

(Figure 2a). When the major component of the solvent mixture was water, as is the case for the compositions shown in Figure 2c, the peak at 582 nm became more prominent. These spectral changes were consistent with the formation of aggregates and a decrease in the concentration of dissolved **Hexamer-1**. An intermediate case was observed in the case of **Hexamer-1** in 1:1 v/v THF/water (Figure 2b). In this mixture, the oligomer exhibited spectral features (absorption and emission) character-istic of both dissolved species and aggregate-like species depending on the concentration of the oligomer, with aggregate-like spectral features becoming dominant as the concentration increased.

To rule out the possibility of solvatochromism, we also recorded the fluorescence spectra of **Hexamer-1** in a variety of different solvents (Figure S2b in the Supporting Information). No substantial correlation was observed between the solvent dielectric constant (i.e., polarity) and the spectral shape. This result leads us to suggest that the changes in optical properties were due to the formation of nanostructures of different sizes and shapes upon the addition of water to THF solutions of **Hexamer-1**, rather than to a solvatochromic effect.

As mentioned previously, the fluorescence of **Hexamer-2** did not vary as significantly in response to changes in solvent composition or solute concentration as compared to that of **Hexamer-1**, although a slight red shift and growth of the peak at 560 nm was observed (Figure 2d). The color of the solution changed from a greenish blue to a light yellow−green upon adding water to the mixture (Figure 1b). The solvent dependence for **Hexamer-2** is shown in Figure S2c (Supporting Information). As was the case with **Hexamer-1**, similar behavior was observed for a range of different solvents.

As can be seen from an inspection of Figure 3, **Hexamer-1** in 9:1 v/v water/THF exhibited a fluorescence spectrum that was nearly identical to that recorded in the condensed phase (i.e., as a thin film). This result was consistent with the formation of large particles whose spectral properties resembled that of the bulk material. In contrast, **Hexamer-2** displayed a fluorescence maximum in the same water/THF mixture that was blue-shifted by about 100 nm compared to what was seen with the film. The difference in spectral features was ascribed to a lower level of aggregation for **Hexamer-2** than **Hexamer-1** in 9:1 v/v water/THF.

Both **Hexamer-1** and **Hexamer-2** exhibited similar spectral features when tested as films (Figure 3a,b, black lines). Such a finding correlated with the absorbance observations, where the
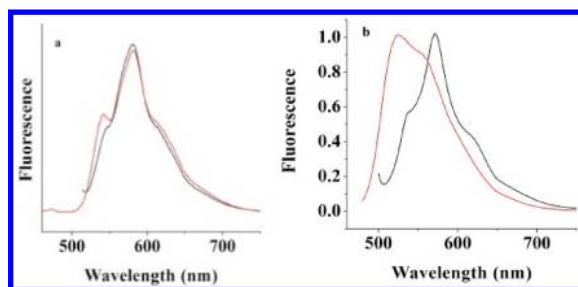
Figure 3. Fluorescent spectra of 0.01 mM solutions in 10% THF/90% water of (a) **Hexamer-1** and (b) **Hexamer-2** (red lines). Also shown for comparison is the emission spectrum of vacuum-evaporated films (black lines).

absorption spectra of **Hexamer-1** in 9:1 v/v water/THF showed the presence of multiple vibronic states presumably due to the geometric restrictions associated with the formation of aggregates (Figure 4a). In contrast, no vibronic features were
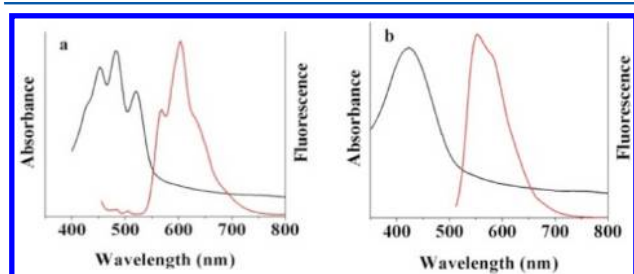

Figure 4. Absorbance and fluorescence data for 0.01 mM solutions of (a) **Hexamer-1** and (b) **Hexamer-2**.

visible for **Hexamer-2** (Figure 4b). The absorption spectrum of **Hexamer-2** NPs was also similar to that of both **Hexamer-1** and **Hexamer-2** in pure THF.[19] Gradual precipitation over time was also noticed for organic NPs of **Hexamer-1** at high concentrations and high ratios of water to THF, while colloidal particles of **Hexamer-2** were stable for weeks. The differences between the photophysical properties of the systems were attributed primarily to a higher degree of $\pi-\pi$ stacking for **Hexamer-1** compared with **Hexamer-2**.[20]

Dynamic light scattering (DLS) and transmission electron microscopy (TEM) measurements in 10% THF were carried out to confirm the formation of NPs (Figure 5 and Figure S3 in
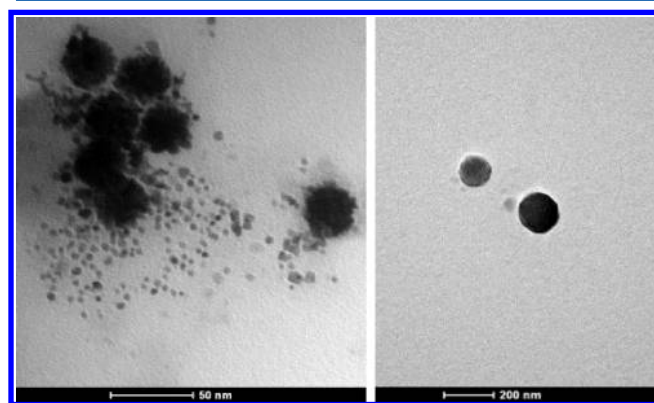

Figure 5. TEM images of the **Hexamer-1** (right) and **Hexamer-2** (left) prepared from 0.006 mM 10% THF/90% water. Size marker: (left) 50 nm; (right) 200 nm.

the Supporting Information). The TEM results were consistent with the formation of NPs with an average size of 15−100 nm in the case of **Hexamer-2** and larger agglomerates in the case of **Hexamer-1**. DLS analyses also provided support for the notion that large particles are formed. In this case, the inferred particle size distribution (Figure S3, Supporting Information) may be skewed by the effect of larger particles on the total signal. Nevertheless, the same trend was revealed by DLS and by TEM in that larger particle sizes were recorded for **Hexamer-1**; this proved particularly true when the analyses were made prior to filtration of the sample with a 500 nm filter (Figure S3, Supporting Information). In fact, in the absence of filtration, average particle sizes of 300 nm were observed for **Hexamer-1** instead of the ~150 nm sized particles seen for **Hexamer-2**. The samples used for these measurements were obtained by evaporation of the solvent. Therefore, aggregation of the monomers as a result of removing solvent cannot be ruled out. However, even taking into account such possible effects, notable differences in particle size were seen for the two hexamers.

ECL is a useful technique that can be used to monitor formation of aggregated species.[12,21] Previous studies showed that it is possible to form aggregates by annihilation ECL in a mixture of organic solvents.[12] The electrochemical results obtained for **Hexamer-1** showed the presence of reversible cathodic and anodic waves within the potential range studied (Figure 6a).[19] The annihilation ECL spectrum of **Hexamer-1** obtained in a mixture of 1:1 v/v benzene/acetonitrile is shown in Figure 6b.
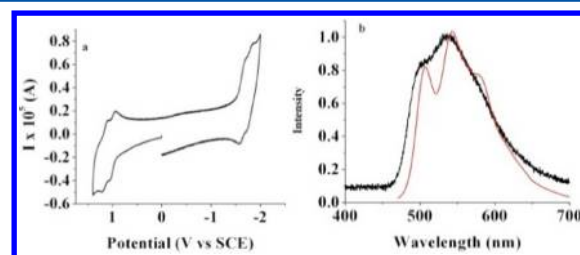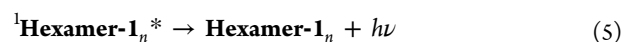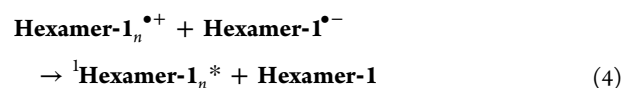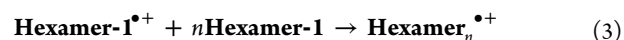

Figure 6. Cyclic voltammetry of (a) 0.14 mM solution of **Hexamer-1** in a 1:1 v/v mixture of benzene/acetonitrile. Scan rate = 1 V/s. (b) ECL annihilation results for the 0.02 mM **Hexamer-1** (black line) fitted to the fluorescence results for 0.025 mM in 1:1 v/v mixture of THF/water (red line).

As with the fluorescence spectrum acquired in the THF/water mixture, three signals were observed. A good correlation between the ECL results and the fluorescence spectrum supported the formation of aggregates by annihilation ECL. The mechanism of the ECL reaction can be represented by the following equations:

$$\textbf{Hexamer-1} + \text{e} \rightarrow \textbf{Hexamer-1}^{\bullet-} \tag{1}$$

$$\textbf{Hexamer-1} - \text{e} \rightarrow \textbf{Hexamer-1}^{\bullet+} \tag{2}$$

$$\textbf{Hexamer-1}^{\bullet+} + n\textbf{Hexamer-1} \rightarrow \textbf{Hexamer}_n^{\bullet+} \tag{3}$$

$$\textbf{Hexamer-1}_n^{\bullet+} + \textbf{Hexamer-1}^{\bullet-}$$
$$\rightarrow {}^1\textbf{Hexamer-1}_n^* + \textbf{Hexamer-1} \tag{4}$$

$${}^1\textbf{Hexamer-1}_n^* \rightarrow \textbf{Hexamer-1}_n + h\nu \tag{5}$$

Unfortunately, similar ECL experiments for **Hexamer-2** could not be carried out because of the instability of the oxidized products, an effect ascribed to the absence of α,ω-substituents.[19]

In sum, we showed that long alkyl chains can promote the formation of organic nanoparticles. The nature of the ensembles was found to depend on structure, with clear differences being seen between **Hexamer-1** and **Hexamer-2**. Therefore, on a number of levels, and in agreement with earlier studies,[17] the results detailed here serve to underscore the important role that substituents can play in regulating the formation of aggregates and NPs derived from similar organic cores.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental information, apparatus, and methods. 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.

■ REFERENCES

(1) Eisele, D. M.; Knoester, J.; Kirstein, S.; Rabe, J. P.; Vanden Bout, D. A. Uniform Exciton Fluorescence from Individual Molecular Nanotubes Immobilized on Solid Substrates. *Nat. Nanotechnol.* **2009**, *4*, 658−663.

(2) Zhao, Y. S.; Fu, H. B.; Peng, A.; Ma, Y.; Liao, Q.; Yao, J. N. Construction and Optoelectronic Properties of Organic One-Dimensional Nanostructures. *Acc. Chem. Res.* **2010**, *43*, 409−418.

(3) Gesquire, A. J.; Uwada, T.; Asahi, T.; Masahura, H.; Barbara, P. F. Single Molecule Spectroscopy of Organic Dye Nanoparticles. *Nano Lett.* **2005**, *5*, 1321−1325.

(4) Fu, H. B.; Yao, J. N. Size Effects on the Optical Properties of Organic Nanoparticles. *J. Am. Chem. Soc.* **2001**, *123*, 1434−1439.

(5) Leclere, P.; Surin, M.; Viville, P.; Lazzaroni, R.; Kilbinger, A. F. M.; Henze, O.; Feast, W. J.; Cavallini, M.; Biscarini, F.; Schenning, A. P. H. J.; Meijer, E. W. About Oligothiophene Self-Assembly: from Aggregation in Solution to Solid-State Nanostructures. *Chem. Mater.* **2004**, *16*, 4452−4466.

(6) Park, S.-J.; Kang, S.-G.; Fryd, M.; Saven, J. G.; Park, S.-J. Highly Tunable Photoluminescent Properties of Amphiphilic Conjugated Block Copolymers. *J. Am. Chem. Soc.* **2010**, *132*, 9931−9933.

(7) Kreyes, A.; Amirkhani, M.; Lieberwirth, I.; Mauer, R.; Laquai, F.; Landfester, K.; Ziener, U. The Longest β-Unsubstituted Oligothiophenes and Their Self-Assembly in Solution. *Chem. Mater.* **2010**, *22*, 6453−6458.

(8) Westenhoff, S.; Abrusci, A.; Feast, W. J.; Henze, O.; Kilbinger, A. F. M.; Schenning, A. P. H. J.; Silva, C. Supramolecular Electronic Coupling in Chiral Oligothiophene Nanostructures. *Adv. Mater.* **2006**, *18*, 1281−1285.

(9) Henze, O.; Feast, W. J.; Gardebien, F.; Jonkheijm, P.; Lazzaroni, R.; Leclere, P.; Meijer, E. W.; Schenning, A. P. H. J. Chiral Amphiphilic Self-Assembled α,α'-Linked Quinque-, Sexi-, and Septithiophenes: Synthesis, Stability and Odd−Even Effects. *J. Am. Chem. Soc.* **2006**, *128*, 5923−5929.

(10) Ostrowski, D. P.; Lytwak, L. A.; Mejia, M. L.; Stevenson, K. J.; Holliday, B. J.; Vanden Bout, D. A. The Effects of Aggregation on Electronic and Optical Properties of Oligothiophene Particles. *ACS Nano* **2012**, *6*, 5507−5513.

(11) Brazard, J.; Ono, R. J.; Bielawski, C. W.; Barbara, P. F.; Vanden Bout, D. A. Mimicking Conjugated Polymer Thin Film Photophysics with a Well-Defined Triblock Copolymer in Solution. *J. Phys. Chem. B* **2012**, DOI: 10.1021/jp3001256.

(12) Suk, J.; Wu, Z.; Wang, L.; Bard, A. J. Electrochemistry, Electrogenerated Chemiluminescence, and Excimer Formation Dynamics of Intramolecular π-Stacked 9-Naphthylanthracene Derivatives and Organic Nanoparticles. *J. Am. Chem. Soc.* **2011**, *133*, 14675−14685.

(13) Loser, S.; Bruns, C. J.; Miyauchi, H.; Ortiz, P. P.; Fachetti, A.; Stupps, S. I.; Marks, T. J. A Naphthodithiophene-Diketopyrrolopyrrole Donor Molecule for Efficient Solution-Processed Solar Cells. *J. Am. Chem. Soc.* **2011**, *133*, 8142−8145.

(14) Steinberger, S.; Mishra, A.; Reinold, E.; Müller, C. M.; Ulrich, C.; Pfeiffer, M.; Bäuerle, P. A-D-A-D-A-Type Oligothiophenes for Vacuum-Deposited Organic Solar Cells. *Org. Lett.* **2011**, *13*, 90−93.

(15) Ucta, H.; Facchetti, A.; Marks, T. A. n-Channel Semiconductor Materials Design for Organic Complementary Circuits. *Acc. Chem. Res.* **2011**, *44*, 501−510.

(16) Mitschke, U.; Bäuerle, P. J. Synthesis, Characterization, and Electrogenerated Chemiluminescence of Phenyl-Substituted, Phenyl-Annulated, and Spirofluorenyl-Bridged Oligothiophenes. *J. Chem. Soc., Perkin Trans.* **2001**, *1*, 740−753.

(17) Ellinger, S.; Kreyes, A.; Ziener, U.; Hoffman-Richter, C.; Landfester, K.; Möller, M. Aggregation Phenomena of Long α- and α,ω-Substituted Oligothiophenes — The Effect of Branched vs Linear End-Groups. *Eur. J. Org. Chem.* **2007**, 5686−5702.

(18) Ellinger, S.; Ziener, U.; Thewalt, U.; Landfester, K.; Möller, M. Synthesis and Self-Organization of α,ω-Substituted Oligothiophenes with Long, Branched Alkyl Substituents. *Chem. Mater.* **2007**, *19*, 1070−1075.

(19) Nepomnyashchii, A. B.; Ono, R. J.; Lyons, D. M.; Sessler, J. L.; Bielawski, C. W.; Bard, A. J. Electrochemistry and Electrogenerated Chemiluminescence of Thiophene and Fluorene Oligomers. Benzoyl Peroxide as a Coreactant for Oligomerization of Thiophene Dimers. *Chem. Sci.* **2012**, *3*, 2628−2638.

(20) Balakrishnan, K.; Datar, A.; Naddo, T.; Huang, J.; Oitker, R.; Yen, M.; Zhao, J.; Zang, L. Effect of Side-Chain Substituents on Self-Assembly of Perylene Diimide Molecules: Morphology Control. *J. Am. Chem. Soc.* **2006**, *128*, 7390−7398.

(21) Nepomnyashchii, A. B.; Bröring, M.; Ahrens, J.; Krüger, R.; Bard, A. J. Electrochemistry and Electrogenerated Chemiluminescence of n-Pentyl and Phenyl BODIPY Species: Formation of Aggregates from the Radical Ion Annihilation Reaction. *J. Phys. Chem. C* **2010**, *114*, 14453−14460.