Aggregation of Poly(*p*-phenylene ethynylene)s Containing Nonpolar and Amine Side Chains

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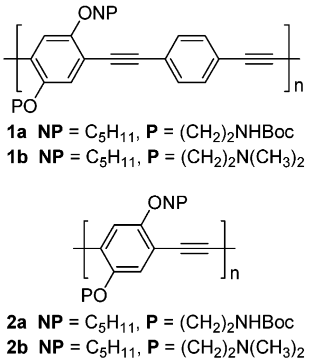
Herein, we report on conjugated, facially amphiphilic poly(*p*-phenylene ethynylene)s (*p*-PPE) with *N*-(*tert*-butyl)carbamate (Boc) groups that aggregate in chloroform/methanol solutions but do not exhibit the expected bathochromic shifts in ultraviolet−visible (UV−vis) absorbance and fluorescence emission spectra. In contrast, tertiary amines of the same architecture do shift upon aggregation and are shown to be interfacially active by visualization of stabilized toluene droplets in water using confocal laser scanning microscopy (CLSM). These oil droplets are selectively visualized due to the red-shifted absorbance upon aggregation of the polymer chains at the interface.

The study of conjugated polymer systems, such as *p*-PPEs,[1,2] has been a source of intrigue for the past two decades with increased interest following the report by Friend et al. in 1990 of the first polymer light-emitting device (LED) based on poly(phenylene vinylene) (PPV).[3] These polymers remain an important area of research to industrial and academic communities with the emergence of the first commercial polymer LEDs in 2000.[4] Other conjugated polymers have been studied including poly(thiophenes)[5,6] and poly(phenylenes)[7,8] for applications in various electronic devices as well as sensors. In the case of biological sensors, examples include water-soluble, cationic, conjugated polymers based on PPV or poly(fluorene) backbones for use as DNA detection devices.[9−11] Using *p*-PPEs, Swager and co-workers pioneered studies on the amplification properties of conjugated polymers to build sensors for low-level detection of analytes including 2,4,6-trinitrotoluene (TNT).[12]

Most conjugated polymers are based on an aromatic backbone and often aggregate due to aromatic π interactions.[13−15] Since the photoluminescence of these polymers is strongly influenced by intermolecular packing, several studies have been performed to understand the effect such aggregation has on the optical spectra of *p*-PPEs.[16,17] Previous work has demonstrated that most PPE derivatives aggregate in poor solvent and in the solid state, typically resulting in the quenching and bathochromic shift of fluorescence emission.[18−21] Because many potential applications of PPEs rely on their enhanced emissive properties, fluorescence quenching is problematic, and therefore, preventing aggregation is an important research topic. In prior studies, bulky, alkyl side chains were placed on every other ring of a *p*-PPE and studied at the air−water interface.[22,23] These large diisopentyl groups showed only minor spectral changes upon two-dimensional ordering due to an interchain distance of approximately 4.9 Å, in contrast to the smaller dimethyl groups, which had substantial bathochromic shifts with an interchain packing distance of 4.0 Å.[22,23] In addition, a relatively simple bis(2-(*S*)-methylbutoxy)-substituted PPE studied for chirooptical properties did not show UV−vis spectral changes associated with aggregate formation upon addition of methanol, suggesting this branched side chain can affect intermolecular packing.[24−27] Another report showed longer side chains delayed aggregation and spectral changes upon the introduction of nonsolvent. In the case of solid films, Yang and Swager incorporated very large, three-dimensional pentiptycene groups into a PPE backbone and found the reduction of interpolymer π-associations gave enhanced quantum yields, solubility, and film stability.[28]



1a NP = C_5H_{11}, **P** = $(CH_2)_2NHBoc$
1b NP = C_5H_{11}, **P** = $(CH_2)_2N(CH_3)_2$

2a NP = C_5H_{11}, **P** = $(CH_2)_2NHBoc$
2b NP = C_5H_{11}, **P** = $(CH_2)_2N(CH_3)_2$

Figure 1. Polymers with NP and P groups prepared for aggregation studies.

Previously, we synthesized *m*-PPEs with nonpolar (NP) alkyl and polar (P) cationic side chains, which organized at the air−water interface, exhibited activity against phospholipid membranes, and aggregated in solution.[29] These molecules are described as facially amphiphilic polymers (FAp) since the NP and P side chains extend from opposite sides of the structure, and the organization of these polymers at the air−water interface resembles the self-assembly of amphiphilic, β-sheet-forming peptides.[30] Because of our interest in these systems, we explored the aggregation behavior and interfacial activity of *p*-PPE derivatives which have increased backbone rigidity and enhanced optical properties compared to their *meta* derivatives. Due to the amphiphilic nature of these structures, they should segregate to interfaces, raising questions about the connection between interfacial activity and aggregation in these PPE systems. Herein, we discuss these new *p*-PPE derivatives and their aggregation in organic solvents as well as the selective visualization of their self-assembly at oil−water interfaces due to the red-shifted absorption generated upon aggregation.

Four polymers were prepared by standard Sonogashira−Hagihara polymerization methods and are shown in Figure 1.[31] These polymers were characterized by ^1H and ^{13}C NMR, and molecular weight values were obtained by gel permeation chromatography based on polystyrene standards. Polymers were prepared with P and NP groups on every other (**1a**, **1b**) and every (**2a**, **2b**) aromatic ring. In addition, the NP groups were

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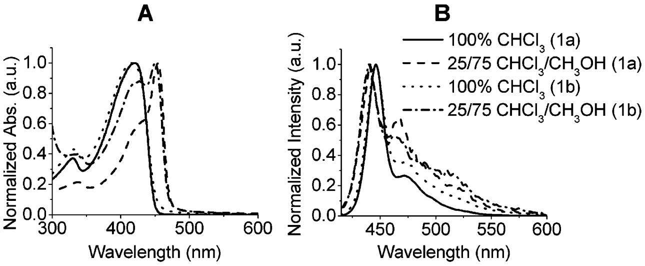

Figure 2. Normalized (A) absorbance and (B) emission spectra of polymers **1a** and **1b** in chloroform and 25/75 chloroform/methanol mixtures. For absorption spectra, λ_{max} (CHCl$_3$) equals 420 and 417 nm for **1a** and **1b**, respectively. Emission λ_{max} (CHCl$_3$) occurs at 446 nm for both polymers.

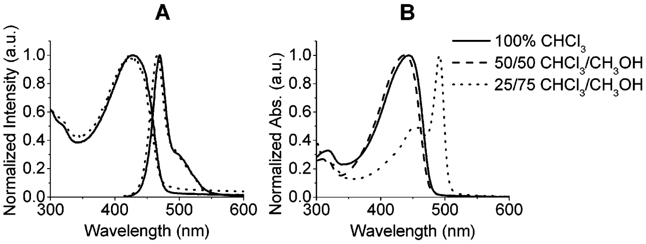

Figure 3. (A) Normalized absorbance and emission intensity spectra of polymer **2a** and (B) normalized absorbance spectra of polymer **2b** in chloroform and chloroform/methanol mixtures. For absorption spectra, λ_{max} (CHCl$_3$) equals 429 and 443 nm for **2a** and **2b**, respectively. Emission λ_{max} (CHCl$_3$) occurs at 470 nm for **2a**.

always pentoxy chains while the P substituents were either a tertiary or *N*-Boc ethoxy amine. During the course of characterizing these polymers with *N*-Boc amine P groups, we observed interesting UV−vis and fluorescence spectra upon aggregation. Therefore, the aggregation behavior of all four polymers was studied by UV−vis and fluorescence spectroscopy as the solvent was changed from chloroform, a good solvent for these polymers, to chloroform/methanol solutions, a poor solvent. The data are shown in Figures 2 and 3. The absorption and emission spectra of polymers **1a** and **1b** in chloroform were as expected with absorbance λ_{max} at 420 and 417 nm, respectively.[2] The maximum emission was observed at 446 nm for both polymers. When methanol, the nonsolvent, was added to these chloroform solutions, a new, red-shifted band was observed in the UV−vis spectra as expected for aggregated systems.[16−21] These changes were first observed in solutions of 50/50 chloroform/methanol, and the spectra in 25/75 chloroform/methanol are shown in Figure 2 as an example of the new bands. The emission spectra showed similar trends to previous reports upon aggregation with increased vibronic structure and red-shifted intensity. In addition, the emission intensity was substantially decreased, which is consistent with aggregation, although the spectra in Figures 2 and 3 are normalized to illustrate the growth of the higher wavelength bands. By contrast, when **2a** was treated under identical conditions, no changes were observed in the UV−vis or emission spectra (see Figure 3A) despite the presence of visible aggregates. This large difference between polymers **1a** and **2a** could result from differences in the substitution pattern of the repeat unit or the presence of the large Boc group on every ring. The substitution pattern was not expected to produce such changes on the basis of previous literature reports.[2,32] However, to distinguish between substitution pattern and large Boc groups, we prepared polymer **2b**. When this polymer was studied in chloroform and chloroform/methanol solutions, the UV−vis spectra (Figure 3B) showed red-shifted absorbance similar to that observed for **1a** and **1b** and in contrast to that found for **2a**. Addition of methanol during sample preparation induced visible aggregation of the four polymer systems discussed here. However, only for **2a** did the UV−vis and emission spectra *not* shift upon aggregation. Therefore, it appears that the presence of a single Boc group on every aromatic ring, **2a**, and not substitution pattern, prevents changes in the UV−vis and emission spectra despite visible molecular aggregation in this system. It is expected that **1a** can close-pack intermolecular chains (less than 4.5 Å)[16,17,33,34] by stacking Boc substituted aromatic rings onto unsubstituted rings, which is not possible for **2a**. Although prior work has used two large alkyl side chains to limit close intermolecular stacking,[12,16,17,24] the use of a single protecting group to decrease interchain packing and thus limit aggregate influence on the electronic spectra has not been reported.

Having explored the solution aggregation of these polymers, we sought to utilize their amphiphilic character to study their aggregation at and stabilization of oil−water interfaces. Because FAps are known to be interfacially active,[30] the ability of polymer **2b** to assemble at oil−water interfaces was studied by CLSM with toluene/water systems. This polymer was dissolved in toluene (0.01 wt % solution) and added to an acidic water solution (0.5 N HCl). Upon shaking, the toluene visually dispersed and was stabilized compared to solutions without **2b**. In the absence of **2b**, toluene spheres immediately coalesced to reform an oil layer whereas toluene droplets stabilized with **2b** remained intact for extended periods of time (over 6 months). Because of the red-shifted absorption of **2b** upon aggregation, the aggregated chains could be selectively visualized when excited with 488 nm light, which was utilized to obtain a CLSM image. Figure 4 shows a representative CLSM image of a stabilized toluene droplet with **2b** demonstrating preferential segregation and aggregation at the oil−water interface. Along with the CLSM image, the normalized absorbance and emission spectra of **2b** in the oil−water experiment as well as dissolved in toluene are shown. The UV−vis and emission spectra of **2b** in toluene were essentially identical to those collected in CHCl$_3$ (Figure 3B). However, the stabilized spheres exhibited red-shifted absorbance and emission bands which confirm aggregation of **2b** at the interface. In addition to the interfacial properties of the FAps, the inherent fluorescence and spectral changes upon aggregation of **2b** allow this system to be directly visualized here without the need to add other reagents, like dyes, to the system, which could influence interfacial activity. Therefore, the emission observed in Figure 4 *must* be due to preferential segregation and aggregation of polymer **2b** at the interface and not individual polymer chains.

In this work, FAps based on *p*-PPE were synthesized with NP and P groups and found to aggregate in solution, as expected, with the introduction of a nonsolvent. However, for **2a**, which contains bulky, Boc groups on every aromatic ring, spectral shifts were not observed despite aggregation. Because biological sensing from conjugated polymers requires these strongly hydrophobic polymers to be used in aqueous environments

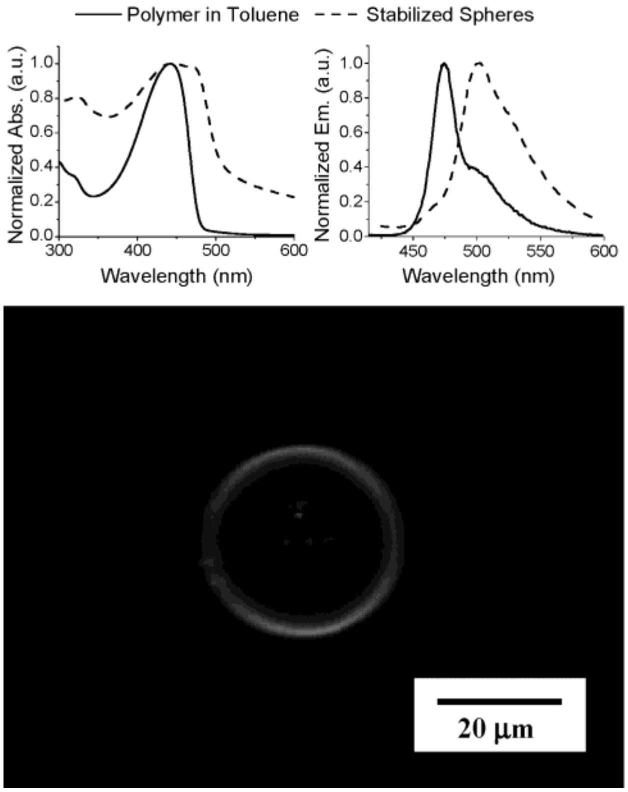

Figure 4. Stabilization of toluene in water by polymer **2b** aggregates (excited at 488 nm with Ar laser, scanned emission from 500 to 580 nm, 20× magnification) as visualized with CLSM. Normalized UV−vis and normalized fluorescence emission spectra of polymer **2b** in toluene and in the oil−water experiments, confirming aggregation by red-shifted absorption and emission. UV−vis spectrum of stabilized spheres does not return to 0 au at long wavelength due to particle scattering.

that promote aggregation, new routes to limit aggregation, like simple, bulky side chains, may prove useful. The electronic spectra of polymers, like **2b**, without bulky groups change upon aggregation which facilitates selective visualization upon aggregation at oil−water interfaces. Current research is focused on obtaining structural information on aggregates from these systems to determine whether molecular ordering is present as well as further characterization of these systems to stabilize oil−water interfaces.

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Supporting Information Available: Experimental procedures for polymer syntheses, absorbance and emission spectra from aggregation experiments, and CLSM images. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537−2574.
(2) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605−1644.
(3) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539−541.
(4) Stewart, M. *Chem. Eng. News* **2001**, *79*, 104.
(5) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904−912.
(6) Bjornholm, T.; Greve, D. R.; Reitzel, N.; Hassenkam, T.; Kjaer, K.; Howes, P. B.; Larsen, N. B.; Bogelund, J.; Jayaraman, M.; Ewbank, P. C.; McCullough, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 7643−7644.
(7) Scherf, U.; Mullen, K. *Polymer* **1992**, *33*, 2443−2446.
(8) Harrison, B. S.; Ramey, M. B.; Reynolds, J. R.; Schanze, K. S. *J. Am. Chem. Soc.* **2000**, *122*, 8561−8562.
(9) Gaylord, B. S.; Heeger, A. J.; Bazan, G. C. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 10954−10957.
(10) Stork, M.; Gaylord, B. S.; Heeger, A. J.; Bazan, G. C. *Adv. Mater.* **2002**, *14*, 361−366.
(11) Wilson, J. N.; Wang, Y. Q.; Lavigne, J. J.; Bunz, U. H. F. *Chem. Commun.* **2003**, 1626−1627.
(12) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593−12602.
(13) Waters, M. L. *Curr. Opin. Chem. Biol.* **2002**, *6*, 736−741.
(14) Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. *J. Chem. Soc., Perkin Trans. 2* **2001**, 651−669.
(15) Sandman, D. J. *Trends Polym. Sci.* **1997**, *5*, 71−74.
(16) Kim, J. S.; McHugh, S. K.; Swager, T. M. *Macromolecules* **1999**, *32*, 1500−1507.
(17) Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Bunz, U. H. F. *Macromolecules* **1998**, *31*, 8655−8659.
(18) Kim, J.; Swager, T. M. *Nature (London)* **2001**, *411*, 1030−1034.
(19) Levitus, M.; Schmieder, K.; Ricks, H.; Shimizu, K. D.; Bunz, U. H. F.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 4259−4265.
(20) Li, H.; Powell, D. R.; Hayashi, R. K.; West, R. *Macromolecules* **1998**, *31*, 52−58.
(21) Weder, C.; Wrighton, M. S. *Macromolecules* **1996**, *29*, 5157−5165.
(22) McQuade, D. T.; Kim, J.; Swager, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 5885−5886.
(23) Kim, J.; Levitsky, I. A.; McQuade, D. T.; Swager, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 7710−7718.
(24) Fiesel, R.; Scherf, U. *Macromol. Rapid Commun.* **1998**, *19*, 427−431.
(25) Fiesel, R.; Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Scherf, U.; Bunz, U. H. F. *Macromol. Rapid Commun.* **1999**, *20*, 107−111.
(26) Wilson, J. N.; Steffen, W.; McKenzie, T. G.; Lieser, G.; Oda, M.; Neher, D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2002**, *124*, 6830−6831.
(27) Zahn, S.; Swager, T. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4225−4230.
(28) Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321−5322.
(29) Arnt, L.; Tew, G. N. *J. Am. Chem. Soc.* **2002**, *124*, 7664−7665.
(30) Arnt, L.; Tew, G. N. *Langmuir* **2003**, *19*, 2404−2408.
(31) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467−4470.
(32) Wilson, J. N.; Windscheif, P. M.; Evans, U.; Myrick, M. L.; Bunz, U. H. F. *Macromolecules* **2002**, *35*, 8681−8683.
(33) Bredas, J. L.; Cornil, J.; Beljonne, D.; dos Santos, D.; Shuai, Z. G. *Acc. Chem. Res.* **1999**, *32*, 267−276.
(34) Cornil, J.; dos Santos, D. A.; Crispin, X.; Silbey, R.; Bredas, J. L. *J. Am. Chem. Soc.* **1998**, *120,* 1289−1299.

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