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Communications to the Editor

“Surfactochromic” Conjugated Polymers: Surfactant Effects on Sugar-Substituted PPEs

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In this Communication the influence of surfactants on the emissive properties of a water-soluble sugar-substituted poly(*p*-phenyleneethynylene) (PPE, **3**) is reported.

Whitten demonstrated that the interaction of a negatively charged, water-soluble conjugated polymer of the poly(*p*-phenylenevinylene) (PPV) type with cationic surfactants (in water) leads to a dramatic increase of the fluorescent quantum yield of the PPV, however, without a large change of the emission wavelength.[1,2] Water quenches the fluorescence of conjugated polymers. The large relative increase of the quantum yield of the PPV upon addition of the surfactant “restores” the fluorescence intensity to that observed for similar PPVs in organic solvents. It is proposed to call the change of optical properties of conjugated materials upon addition of surfactants “surfactochromicity”. This effect must be of great importance in the application of conjugated polymers for biosensory processes where issues of signal enhancement and suppression play a crucial role.[3−6]

While the interaction of conjugated polyelectrolytes with oppositely charged surfactants or amphiphilic counterions is strong and well-established,[1−4] the interaction of nonionic water-soluble conjugated polymers with nonionic surfactants has not been studied. Such systems should likewise be surfactochromic and will have great potential in biosensory and biodevice applications.[6,7]

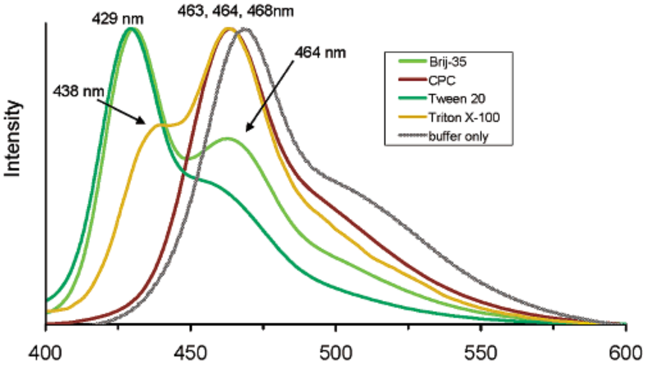

Figure 1. Emission spectra of **3** in different surfactant solutions (0.5 mg L^{-1} polymer in phosphate buffered saline (PBS), 10% w/v surfactant, λ_{ex} 385 nm, 25 °C): (gray —) PBS, no surfactant; (red —) cetylpyridinium chloride (CPC); (yellow —) Triton X-100 (160 mM); (green —) Tween 20 (81 mM); (light green —) Brij 35 (82 mM). The emission spectra were normalized so that the emission maxima intensities of all the samples are identical.

The water-soluble sugar-substituted PPE **3** undergoes surfactochromic changes in emission[8−10] in the presence of the nonionic amphiphiles Brij 35, Triton X-100, and Tween 20.[11] The absorbance of **3** shows little to no change upon varying surfactant type (Tween 20, Triton X-100, Brij 35, cetyltrimethylammonium bromide (CTAB), cetylpyridinium chloride (CPC), and sodium dodecyl sulfate (SDS)) or concentration (1−10% surfactant). The UV−vis spectrum of **3** in water/buffer/detergent mixtures is identical to the absorbance of dialkoxy-PPEs in chloroform,[12] suggesting that the backbone of **3** is nonplanarized under these conditions.

The polymer **3** was obtained by a Pd-catalyzed coupling[10] of the bis-glucosylated diiodide (**1**) with 1,4-diethynyl-2,5-bisdodecoxybenzene (**2**) under standard

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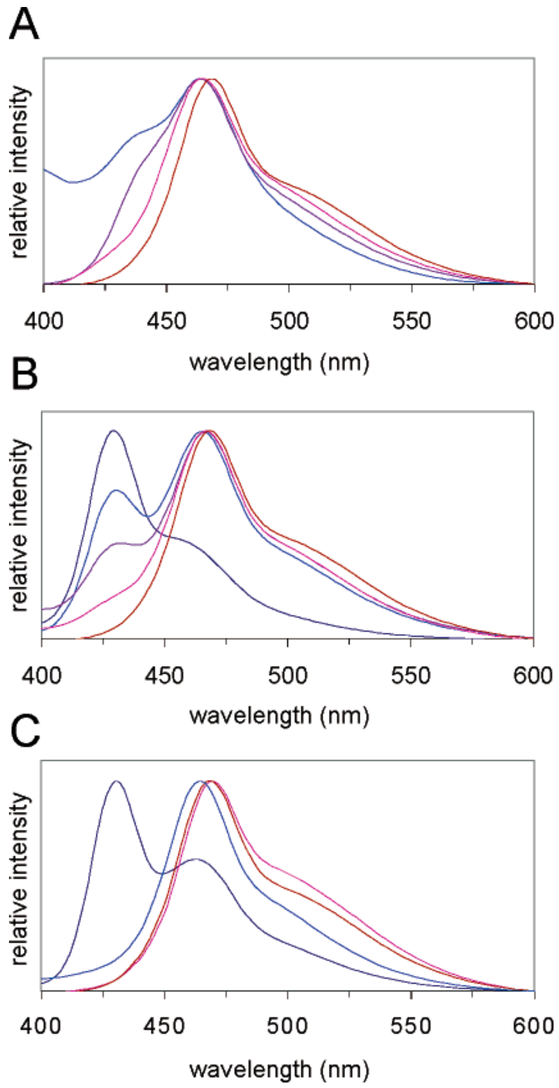


Figure 2. Normalized emission spectra of **3** in different surfactants varying their concentrations (0.5 mg L^{-1} **3** in phosphate buffered saline plus surfactant, λ_{ex} 385 nm, 25 °C). (A) Triton X-100: (orange —) PBS, 0% w/v surfactant, (red —) 0.1% w/v surfactant (1.6 mM), (purple —) 1% w/v surfactant (16 mM), (blue —) 10% w/v surfactant (160 mM). (B) Tween 20: (orange —) PBS, 0% surfactant, (red —) 0.1% w/v surfactant (0.81 mM), (purple —) 0.5% w/v surfactant (4.1 mM), (blue —) 1% w/v surfactant (8.1 mM), (purple —) 10% w/v surfactant (81 mM). (C) Brij 35: (orange —) PBS, 0% surfactant, (red —) 1% w/v surfactant (8.2 mM), (blue —) 5% w/v surfactant (41 mM), (purple —) 10% w/v (82 mM) surfactant. The emission spectra were normalized so that the emission maxima of all the samples are identical.

conditions.[13] Approximately half of the acetyl groups fall off during the coupling, with piperidine acting as a deacetylation reagent, so that R = H or Ac. The loss of acetyl groups was quantified by ^{1}H NMR and by IR spectroscopies.[14] The resulting polymer is soluble in water, DMSO, and THF.

In water, **3** shows a relatively weak emission at 468 nm with a shoulder at 512 nm (Figure 1).[8−10] Addition of the ionic surfactants CTAB, CPC, or SDS leads to a small blue shift in fluorescence and decreases the emission at 512 nm. The presence of nonionic surfactants provides a large response in the emission of **3**. The presence of Triton X-100 induces a subtle shift, and the emission of **3** begins to display a shoulder around 430 nm, providing evidence that the polymer aggregates are being broken up. The presence of Brij 35 causes an increase in the 430 nm peak while diminishing the 460 nm emission of **3**. After the addition of Tween 20 the solution of **3** shows a small shoulder in the emission of **3** at 460 nm with the emission at 429 nm being most intensive. The apparent trend for disassembling aggregates of **3** suggests that the deaggregating power of the surfactants is Tween 20 > Brij 35 > Triton X-100 and stems probably from the enhanced solubilization of the sugar side chains in **3** by Tween. Importantly, these effects are only evident in emission and not in absorption, suggesting that the planarization of the backbones of the PPEs does not play a large role under these conditions (Figure 1).

Besides surfactant type, it was of interest how surfactant concentration would affect the optical properties of **3**. In Figures 1 and 2, the data are normalized to best display the changes in the *shape* of the emission spectra. In Figure 2a the shape of the curve changes, exhibiting a subtle blue shift, as surfactant concentration is increased, suggesting dissolution of polymer aggregates. Upon addition of Triton X-100 the emission intensity of **3** increases 20-fold. This behavior is similar to Whitten's observation of increased fluorescence of PPVs upon addition of ionic surfactants.[1]

Figure 2b shows a marked change in the spectral shape of **3** upon the addition of Tween 20. As suggested by the data in Figure 1, Tween 20 is an excellent solvating agent for **3**. A complete disappearance of the aggregate band at 520 nm is observed as surfactant is added. A nearly complete conversion to the low wavelength band at 430 nm suggests almost full deaggregation. Finally, it is interesting to note the dramatic change of emission wavelength upon addition of higher concentrations of Brij 35 to **3**. Low concentrations of Brij, up to 8 mM (1%), have virtually no effect on the aggregation of **3**; however, at higher concentrations, near complete breakup of the aggregates of **3** is recorded. This case is similar to the one where Tween 20 was added to **3**, suggesting a critical surfactant deaggregation concentration. These effects are only observed in a regimen that is significantly above the critical micelle forming concentration (cmc) of the surfactants under observation (see Scheme 1 for the cmc of Triton X-100, Brij 35, and Tween 20).[11]

The temperature dependence of the emission of **3** in the presence of surfactants was examined. It would be expected that an increase in temperature would enhance solubility of **3** either with or without surfactant present. Additionally, one would expect to see blue-shifted emissions resulting from this improved dissolution of aggregates (Figure 3). In the presence of Brij 35, an increase in the emission intensity of **3** was observed with no blue shift, and with Triton X-100 added an increase in emission intensity of **3** was accompanied by the expected blue shift of the emission. In the absence of surfactant a *decrease* in the intensity of the emission from **3** was observed with a relative increase in the aggregation band of **3** centered at 520 nm. Similarly, with Tween 20 as the surfactant, a rise in temperature resulted in a decrease in emission intensity of **3** as well as a red shift.

Several conclusions can be gleaned form these data: (1) Nonionic surfactants interact with **3** in an aqueous environment at surfactant concentrations that are well above the cmc, leading to a blue-shifted emission and a breakup of aggregates of **3** (Tween 20, Brij 35) or to 20-fold enhanced emission (Triton X-100). The blue shift is more pronounced the more concentrated the surfac-

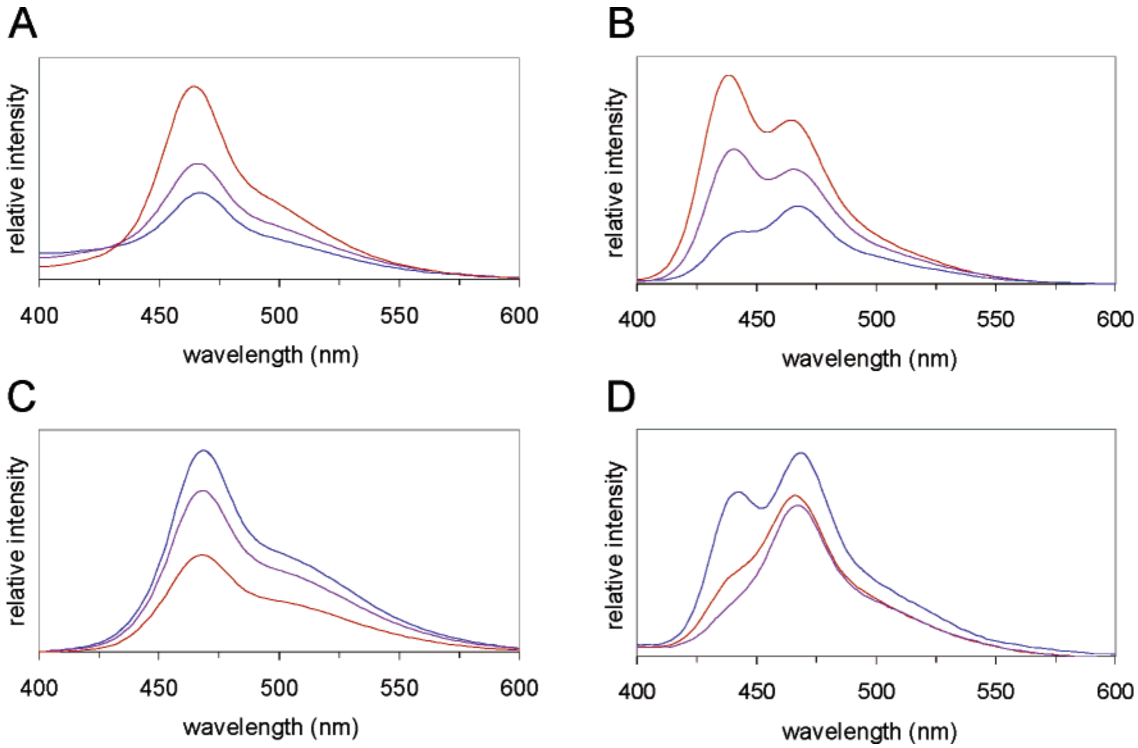
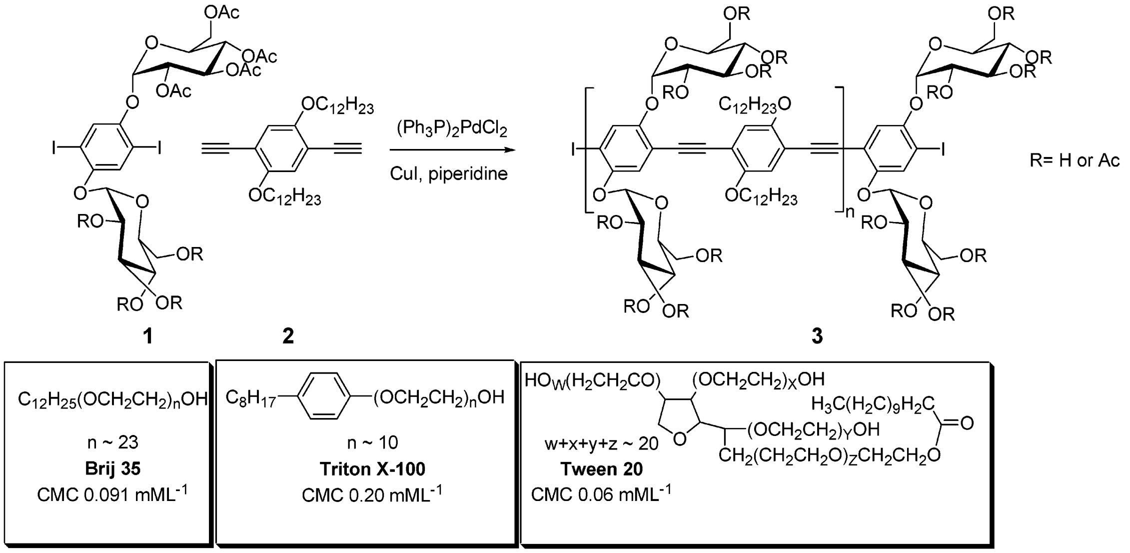


Figure 3. Emission spectra of **3** in different surfactants varying the temperature (0.5 mg L^{-1} **3** in phosphate buffered saline plus 5% surfactant, λ_{ex} 385 nm). (A) Brij 35: (blue —) 25 °C, (purple —) 50 °C, (red —) 75 °C (41 mM). (B) Triton X-100: (blue —) 25 °C, (purple —) 37 °C, (red —) 50 °C (80 mM). (C) PBS, no surfactant: (blue —) 25 °C, (purple —) 50 °C, (red —) 75 °C. (D) Tween 20: (blue —) 25 °C, (purple —) 37 °C, (red —) 50 °C (41 mM).

Scheme 1. Utilized PPE-Type Polymer 3 and Surfactants Including Critical Micelle Forming Concentrations (cmc)



tant solution is. (2) Increase in temperature leads to enhanced emission of **3** for Brij 35 and for Triton X-100, while the emission intensity decreases for **3** in buffer (PBS) and interestingly as well in the presence of Tween 20.[15]

The emissive properties of a water-soluble polymer such as **3** therefore can be easily manipulated by addition of nonionic surfactants. The fluorescence enhancement in particular will be critically important when exploring the lower threshold for the sensing of biological targets utilizing water-soluble PPEs.

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References and Notes

(1) (a) Chen, L. H.; Xu, S.; McBranch, D.; Whitten, D. *J. Am. Chem. Soc.* **2000**, *122*, 9302–9303. (b) Chen, L. H.; McBranch, D. W.; Wang, H. L.; Helgeson, R.; Wudl, F.; Whitten, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 12287–12292.

(2) In a similar study Thünemann had demonstrated as early as 1999 that carboxylate-substituted PPEs can form complexes with cationic surfactants, but the utilized PPEs were not well-defined. The extracted optical properties were difficult to interpret: (a) Thünemann, A. F. *Adv. Mater.* **1999**, *11*, 127–130. (b) Thünemann, A. F.; Ruppelt, D. *Langmuir* **2001**, *17*, 5098–5102.

(3) Ho, H. A.; Boissinot, M.; Bergeron, M. G.; Corbeil, G.; Dore, K.; Boudreau, D.; Leclerc, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1548−1551.

(4) (a) Gaylord, B. S.; Heeger, A. J.; Bazan, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 896−900. (b) Gaylord, B. S.; Wang, S. J.; Heeger, A. J.; Bazan, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6417−6418. (c) Fan, C. H.; Plaxco, K. W.; Heeger, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 5642−5643.

(5) (a) Ewbank, P. C.; Nuding, G.; Suenaga, H.; McCullough, R. D.; Shinkai, S. *Tetrahedron Lett.* **2001**, *42*, 155−157. (b) McCullough, R. D.; Ewbank, P. C.; Loewe, R. S. *J. Am. Chem. Soc.* **1997**, *119*, 633−634.

(6) Wilson, J. N.; Wang, Y. Q.; Lavigne, J. J.; Bunz, U. H. F. *Chem. Commun.* **2003**, 1626−1627.

(7) Okada, S.; Peng, S.; Spevak, W.; Charych, D. *Acc. Chem. Res.* **1998**, *31*, 229−239.

(8) (a) Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Bunz, U. H. F. *Macromolecules* **1998**, *31*, 8655−8659. (b) Miteva, T.; Palmer, L.; Kloppenburg, L.; Neher, D.; Bunz, U. H. F. *Macromolecules* **2000**, *33*, 652−654.

(9) Kim, J.; Swager, T. M. *Nature (London)* **2001**, *411*, 1030−1034.

(10) (a) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605−1644. (b) Bunz, U. H. F. *Acc. Chem. Res.* **2001**, *34*, 998−1010. (c) Erdogan, B.; Wilson, J. N.; Bunz, U. H. F. *Macromolecules* **2002**, *35*, 7863−7864.

(11) The cmc of the utilized nonionic surfactants can be found on www.sigmaaldrich.com in the technical section.

(12) (a) Wilson, J. N.; Bangcuyo, C. G.; Bunz, U. H. F., unpublished results; $\lambda_{\mathrm{max(absorption)}}$ of both **3** and bisdodecoxy-PPE (in chloroform) are identical and appear at 450 ± 5 nm.[10a] Upon planarization of dodecyloxy-PPE a red shift of $\lambda_{\mathrm{max(absorption)}}$ to 478 nm is observed.

(13) Experimental: The interactions between **3** and both ionic (cetyltrimethylammonium bromide (CTAB), cetylpyridinium chloride (CPC), and sodium dodecyl sulfate (SDS)) and nonionic surfactants (Brij 35, Triton X 100, and Tween 20) were examined. All studies were carried out in phosphate buffered saline (PBS; 50 mM phosphate, pH 7.5, 150 mM NaCl, 2 mM KCl) with or without added surfactant. A PPE stock solution was made by dissolving **3** in DMSO (2 g L^{-1}). DMSO was utilized to ensure complete solubility of **3** at the high concentration. The solubility of **3** does not exceed approximately 1 mg L^{-1} in pure water. The stock solution of **3** was serially diluted with a surfactant stock solution prepared in water as necessary to provide solutions with varying surfactant concentrations and 0.5−5 mg L^{-1} PPE. Fluorescence emission spectra were recorded at 25, 37, 50, or 75 °C with excitation at 385 nm on a JASCO FP6200 fluorescence spectrometer equipped with a Peltier heating element. UV−vis spectra were taken on a JASCO V-500 spectrometer at ambient temperature.

(14) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593−12602.

(15) Kwak, J. C. T., Ed.; Polymer-Surfactant Systems; *Surfactant Sci. Ser.* **1998**, *77*, whole issue.

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