Electronic Supplementary Material (ESI) for Chemical Communications

Surfactant controlled aggregation of conjugated polyelectrolytes

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Materials

Conjugated polyelectrolyte sodium poly[2-(3-thienyl)-ethoxy-4-butylsulfonate] (PTEBS) was purchased from the American Dye Source (Quebec, Canada) with a molecular weight of 840000-1000000 g mol^{-1} and used as received. Conjugated polyelectrolyte poly[9,9'-bis[6"-(N,N,N-trimethylammonium)hexyl]fluorene-co-alt-phenylene] dibromide (FPQ-BR) was synthesized as reported previously with a molecular weight of 26,000 g mol^{-1}.[1] The dye standard coumarin 6 and surfactants sodium dodecylsulfate (SDS) and dodecyltrimethylammonium bromide (DTAB), were purchased from Sigma-Aldrich (St. Louis, MO) and used as received. Surfactant decylamine (DEC) and salt tetrapropylammonium bromide (TPA) were ordered from Acros Organics (Geel, Belgium) and used as received. All solid state characterisation was completed on 12 mm diameter spec2000 fused silica substrates purchased from UQG Optics Limited (Cambridge, England) and cleaned via sonication in acetone and IPA before use.

Sample preparation

All sample solutions analysed had a total volume of 5 mL. Aqueous samples were prepared by mixing solutions of PTEBS (0.01 mg mL^{-1}) or FPQ-BR (0.02 mg mL^{-1}) in distilled water with the desired surfactant concentration and left to stand for at least an hour. The same samples were used for each of the spectroscopic and particle size measurements. Note that FPQ-BR is not directly soluble in distilled water and was dissolved at 1 mg mL^{-1} in methanol and then diluted (~50-fold) in distilled water to the desired concentration.

Thin solid films of PTEBS with varying concentrations of DTAB were prepared on 12 mm diameter fused silica spec2000 substrates pre-cleaned via sonication in acetone and IPA. Films were cast via spin coating (8000 rpm) pre-prepared mixtures of concentrated PTEBS (6 mg mL^{-1}, 1:3 methanol : distilled water) with the desired concentration of DTAB surfactant in distilled water (1:1 PTEBS:DTAB solution ratio).

Methods

Absorption spectroscopy

Absorption spectroscopy (UV-Vis) was performed with an Agilent 8453 UV-Visible spectrophotometer over the range 220-1100 nm using a quartz cuvette with 1 cm path length. All spectra were baseline corrected ($Abs_{800\ nm} = 0$) before further analysis was completed.

Fluorescence spectroscopy

Fluorescence spectroscopy was performed with a Shimadzu RF-5301PC spectrofluorophotometer using a quartz cuvette with 1 cm path length and four polished sides, the slit widths on the spectrofluorophotometer were set to 3 nm resolution (for both excitation and emission) for PTEBS samples, and 1.5 nm for FPQ samples. All excitation wavelengths were at absorption maximum. All emission spectra were corrected for absorption by dividing by the optical density at the fluorescence excitation wavelength. The inherent quantum efficiency of PTEBS was calculated by using coumarin 6 dissolved in ethanol as a standard ($QE_{coumarin\ 6} = 0.78$).[2]

Dynamic Light Scattering (DLS)

DLS measurements were carried out using a Malvern Zetasizer Nano-ZS. Experiments were performed in a quartz cell with a 1 cm path length at 25°C. The size for each sample was averaged over nine measurements (3 sets of tests each with 3 samples) with the refractive index of the conjugated polyelectrolytes set to 1.5. Samples were prepared as described above.

Surface Tension

Surface tension measurements were recorded using a NIMA technology surface pressure sensor type PS4. 20 mL solutions of the CPE at the same concentration used above and the desired surfactant concentration were analysed with the results averaged over three measurements. To ensure that the samples are clean and contained no contaminants, all glassware was initially soaked in 5 M KOH solution and then thoroughly washed with double distilled deionised water.

References:

1. O. K. Nag, M. Kang, S. Hwang, H. Suh, and H. Y. Woo, *J. Phys. Chem. B,* 2009, **113**, 5788-5793

2. G. A. Reynolds, and K. H. Drexhage, *Optics Commun.* 1975, **13**, 222-225

Additional Figures

Fig S1. Absorption Spectra of PTEBS with varying DTAB concentrations in distilled water.

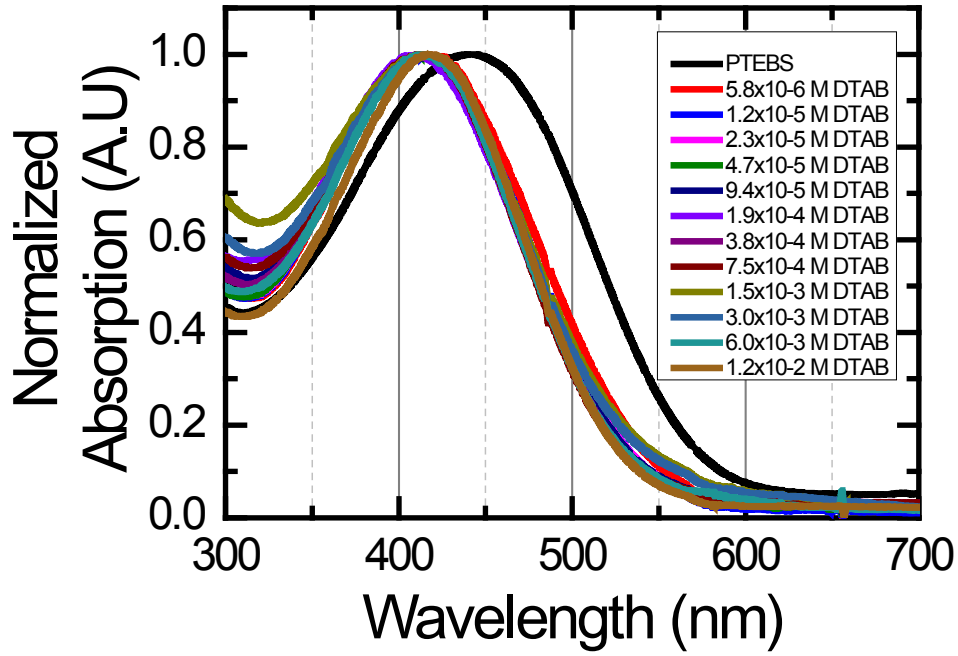

Fig S2. PL intensity of FPQ-BR as a function of surfactant concentration for SDS and DTAB surfactants, and particle sizes for the same solutions.

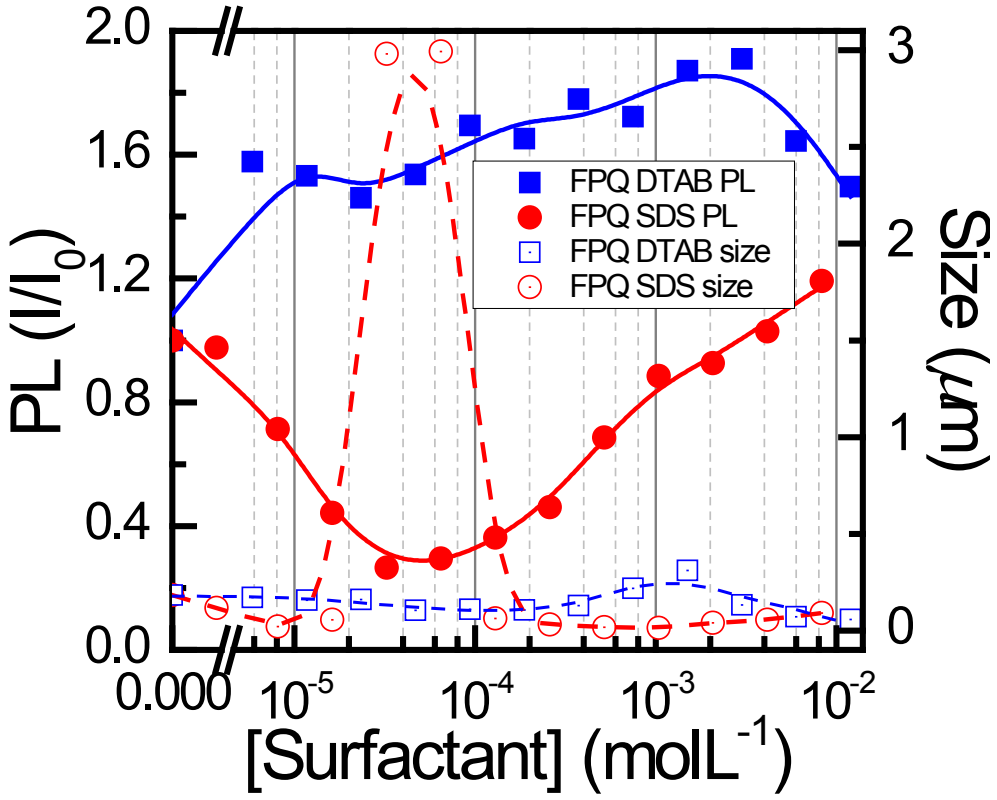

Fig S3. Surface tension as a function of SDS concentration for aqueous solutions of PTEBS compared with solutions lacking PTEBS.

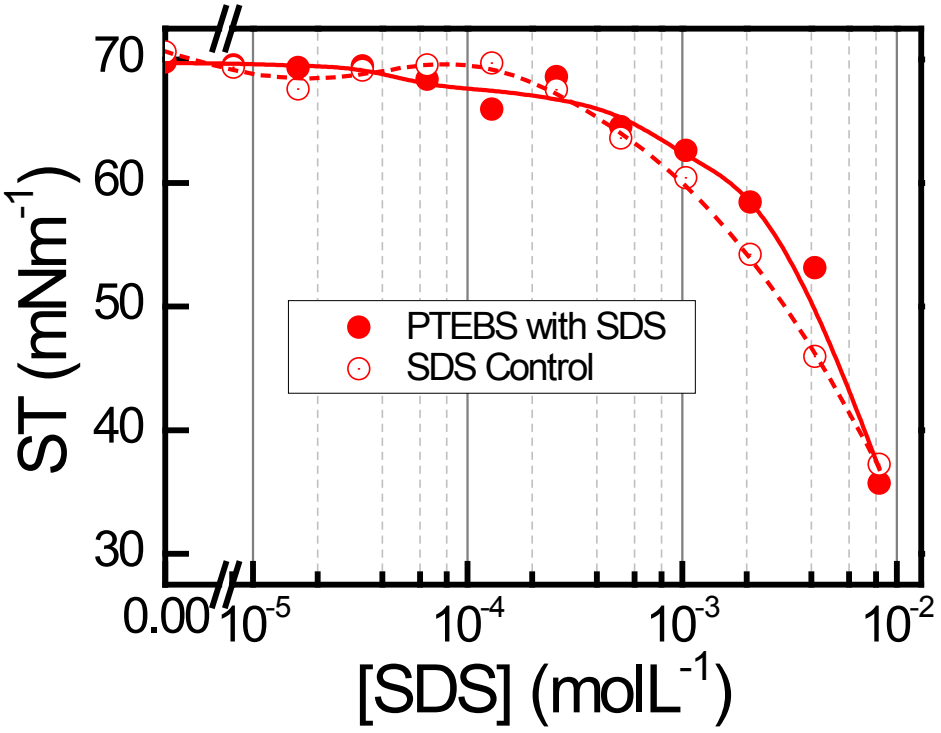

Fig S4. PL emission (λ_{exc} = 467 nm) and excitation (λ_{em} = 605 nm) spectra for a series of thin films of PTEBS with various DTAB concentrations. Inset: Variation of thin film PL intensity with added DTAB.