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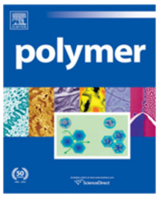

Cationic fluorene-thiophene diblock copolymers: Aggregation behaviour in methanol/water and its relation to thin film structures

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ABSTRACT

Optical spectroscopy and photophysical measurements on cationic fluorene-thiophene diblock copolymers in solution show distinct properties for the two blocks, with clear indications of singlet exciton migration from the polyfluorene to polythiophene blocks. Electrical conductivity measurements and small angle X-ray scattering studies show that different aggregates are formed in water and methanol. This may be associated both with different solubilities of the two blocks and with the effect of solvent on the degree of dissociation of the ionic part. Atomic force microscopy (AFM) shows that different nanostructures are deposited from the two solvents, with large, vesicular structures deposited on mica from methanolic solution. Aggregation behavior is also found to be modulated, and to lead to more rigid thiophene blocks, by addition of the oppositely charged surfactant sodium dodecylsulfate.

1. Introduction

The combination of solubility in polar and protic solvents and excellent spectral properties make conjugated polyelectrolytes good candidates for chemical and biological sensing and for the preparation of a variety of devices using solvent-based methodologies [1,2]. Simultaneous control of morphology and electronic properties of conjugated organic polymer thin films is important for their application in optoelectronic devices, and when prepared using solvent-based processing techniques, the nanostructure of deposited films will be influenced by the structures of species present in solution. Diblock copolymers have considerable potential in this area, and can form various structures, including conventional spherical and cylindrical micelles, vesicles, together with a variety of less conventional ones, such as toroids and gyroids [3,4]. These depend on the relation between polarity and rigidity of the two constituent blocks, and can be modulated by changes in solvent, temperature, etc.

Alternating fluorene-thiophene copolymers have outstanding electronic properties [5–7] and exhibit excellent photophysical and charge transport characteristics, with potential in bulk heterojunction photovoltaics and other systems. All-conjugated, diblock copolymers of polyfluorene (PF) and polythiophene (PT) are also potentially valuable advanced materials for many of these applications [8–10]. These can be considered to be rod–rod copolymers, and their amphiphilic properties at air–water interfaces and in Langmuir–Blodgett films lead to vesicular, and related lamellar, structures [11]. The chain conformation of the polythiophene block can be modulated by its environment, and the introduction of ionic side chains on this segment should lead to fluorene-thiophene copolymers in which their diblock incompatibilities, and hence their aggregation behaviour, can be tuned by changing solvent, ionic strength, temperature, or by addition of appropriate additives, e.g., surfactants. These cationic diblock copolymers may also be water soluble, which will be valuable for self-assembly [12], chemical and biological sensing [1,2], and for device preparation by solvent-based methodologies. We report the spectral and photophysical behaviour of cationic, all-conjugated fluorene-thiophene diblock copolymers in methanolic and aqueous solutions, together with structural studies in solution using electrical conductivity measurements and small angle X-ray scattering (SAXS), and show how this relates to structures of thin films obtained from these solvents as seen by atomic force microscopy (AFM).

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2. Experimental section

The cationic, conjugated diblock copolymers of the fluorene-thiophene type were synthesised in three steps. In the first, monobromo-terminated regioregular poly(3-bromohexylthiophene) (Br-P3BrHT) (molecular weight $\overline{M}_n$ of 10,000) was prepared in a protocol described by McCullough et al. [13]. The second step involved a "grafting from" synthesis of the PF2/6 block by Suzuki cross coupling of 2-bromo-9,9-bis(2-ethylhexyl)fluoreneboronic ester using $Pd(PPh_3)_4$ as catalyst and Br-P3BrHT as macromolecular endcapper followed by careful purification of the diblock copolymer. The resulting non-ionic diblock copolymer has $\overline{M}_n$ 18,000, giving a molecular weight for the PF block of $\approx$8000. This corresponds to roughly 20 fluorene and 40 thiophene repeat units per diblock copolymer. The final step towards the polyelectrolytes involved quarternization of this precursor with trimethylamine or pyridine.

UV/vis absorption and photoluminescence (PL) spectra were measured on a Shimadzu UV-2100 and a Jobin–Ivon SPEX Fluorolog 3-22 spectrometer, respectively. Fluorescence spectra were corrected for the wavelength response of the system. Solutions of the diblock copolymers were prepared the day before the experiment, in water and methanol, and stirred overnight. Slow decreases in intensity with time of the spectra were observed in water, but not with methanol solutions. These may be associated with phase separation. Fluorescence decay times with picosecond time resolution were obtained using a previously described system [14]. The excitation at 370 or 423 nm used the frequency doubled output of a Ti: Sapphire laser (Tsunami X – Spectra Physics), pumped with a solid state laser (Millennia X – Spectra Physics). Measurements were carried out by exciting the samples with vertically polarized light and setting the emission polarizer at the magic angle. Alternate collection of 10^3 counts of pulse and sample were carried out until 5 or 10 kCounts at the maximum were reached. Decays collected with 10 and 20 kCounts at the maximum channel provided identical results. The experimental excitation pulse (FWHM $=$ 19 ps) was measured using a LUDOX scattering solution in water, whose transmittance at the excitation wavelength was matched to that of the sample. The time resolution of the apparatus is ca. 3 ps.

Flash photolysis experiments were performed with an Applied Photophysics laser flash photolysis equipment pumped by the third harmonic (355 nm) of a Nd:YAG laser (Spectra Physics). Signals were detected with Hamamatsu IP28 and R928 photomultipliers and transient spectra were obtained by monitoring the optical density change at 5–10 nm intervals over the 300–850 nm range, averaging at least 10 decays at each wavelength. Quantum yields for triplet state formation (Φ_T) were obtained by the singlet depletion method. Further details have been given elsewhere [15].

Singlet oxygen ($^1\Delta_g$) yields and lifetimes were obtained by direct measurement of the phosphorescence at 1270 nm following irradiation of an aerated solution of the polymers in benzene with a frequency tripled pulse (355 nm) from a Nd:YAG laser, as described in detail elsewhere [16]. The quantum yield of singlet oxygen formation was determined by comparison of the initial emission intensity for optically matched solutions at the excitation wavelength ($A_{355} = 0.5$) with 1H-phenalen-1-one taken as standard, using $\Phi_\Delta = 0.93$ in benzene solution [17].

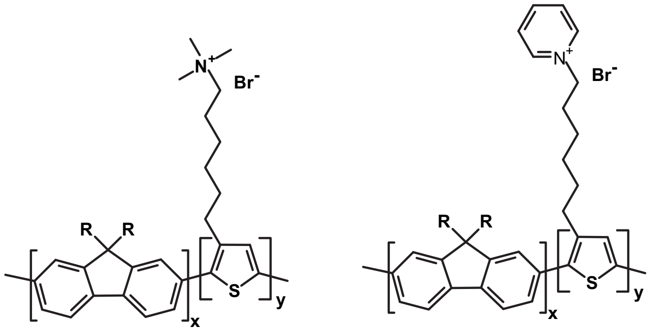
For electrical conductivity measurements, electrical resistances were measured on solutions with a Wayne-Kerr model 4265 Automatic LCR meter at 1 kHz and a Shedlovsky-type conductance cell [18]. The cell constant (approximately 0.1012 cm^{-1}) was determined to ±0.02% from measurements with KCl (reagent grade, recrystallized and dried using the procedure and data from Barthel et al. [19]). Measurements were made at 25.00 ± 0.01 °C in a Grant thermostat bath.

SAXS experiments of PFO-*b*-P3TMAHT in solution were performed at the I711 beamline at MAX-lab in Lund (Sweden) [20]. The X-ray energy was 11.3 keV and the sample-to-detector distance was 1.288 m, yielding a *q*-range of 0.1–1.2 nm^{-1}. The beam size was 0.30 mm × 0.30 mm (vert. × hor.). The scattering patterns were measured using a MarCCD165 detector. The intensity scale was calibrated using water.

AFM measurements were performed using a diInnova microscope from Veeco in the tapping mode at room temperature under ambient conditions. The silicon cantilevers used were between 215 and 235 μm in length and had a resonance frequency of approximate 84 kHz; the tip height was between 15 and 20 μm. The polymer films were prepared by drop-casting of PF2/6-*b*-P3TMAHT solutions (1.water: 0.1 mg/mL; 2. methanol: 0.03 mg/mL) onto mica and subsequent drying in a desiccator at room temperature. The solutions were filtered through 0.25 μm PTFE-filters prior to casting.

3. Results and discussion

We have studied the cationic, all-conjugated AB diblock copolymers poly[9,9-bis(2-ethylhexyl)fluorene]-*b*-poly[3-(6-trimethylammoniumhexyl)thiophene] bromide (PF2/6-*b*-P3TMAHT) and poly-[9,9-bis(2-ethylhexyl)fluorene]-*b*-poly[6-(N-(pyridiyl)hexyl) thio-phene] bromide (PF2/6-*b*-P3PyHT), as well as poly[9,9-dioctylfluorene]-*b*-poly[3-(6-trimethylammoniumhexyl)thiophene] bromide (PFO-*b*-P3TMAHT, with linear octyl side chains at the fluorene unit) in methanolic and aqueous solution by UV/vis absorption, photoluminescence (PL) spectroscopy, and electrical conductivity measurements. The structures are given in Scheme 1, and for simplicity, we will mainly concentrate on PF2/6-*b*-P3TMAHT. Two characteristic bands were seen in the UV/vis absorption spectrum (Fig. 1(a)), and are attributed to polyfluorene and polythiophene blocks. Excitation of PF2/6-*b*-P3TMAHT at 390 nm leads to emission from both blocks (Fig. 1(a)), while the fluorescence excitation spectra of PF2/6-*b*-P3TMAHT in water and methanol with observation in the P3TMAHT emission region (Fig. 1 (b)) shows excitation maxima in both PF and PT regions, demonstrating efficient electronic energy transfer from fluorene to thiophene blocks. Differences were observed in the ratio of the two absorption or excitation bands between water and methanol, which reflect differences in the conformation or nature of the species present in the two solvents. The overall PL in water is weak, and is dominated by that from the P3TMAHT block, showing efficient energy migration along the chain. The PL becomes stronger



PF2/6-b-P3TMAHT (R: 2-ethylhexyl) **PF2/6-b-P3PyHT** (R:2-ethylhexyl)
PFO-b-P3TMAHT (R: octyl)

Scheme 1. Structures of cationic, all-conjugated diblock copolymers from ref. [10].

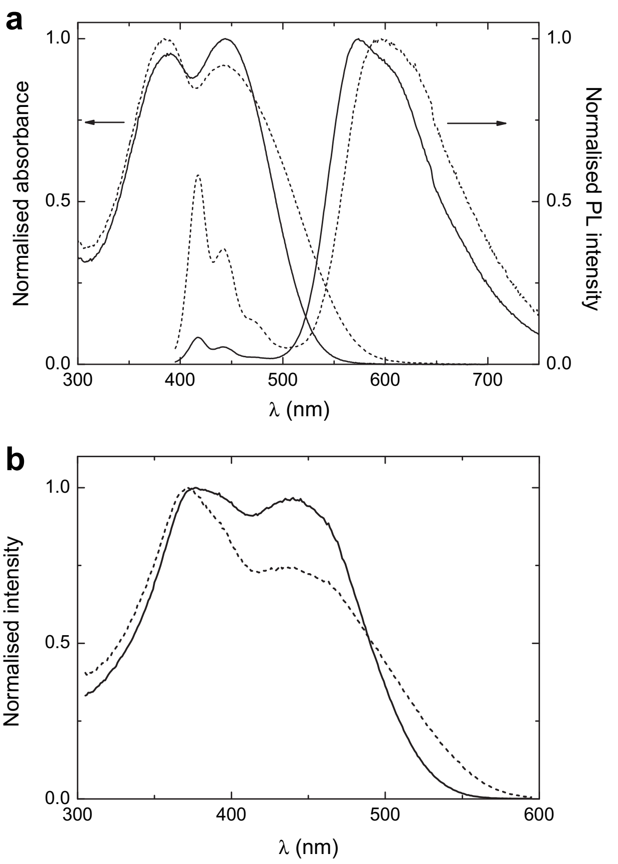


Fig. 1. a) Absorption (left) and emission spectra (λ_{ex} = 390 nm, right) of PF2/6-*b*-P3TMAHT in methanol (solid lines), and in water (dashed lines); b) Fluorescence excitation spectra (λ_{em} = 600 nm) of PF2/6-*b*-P3TMAHT in methanol (solid line) and in water (dashed line) at a concentration of ~0.01 mg/mL.

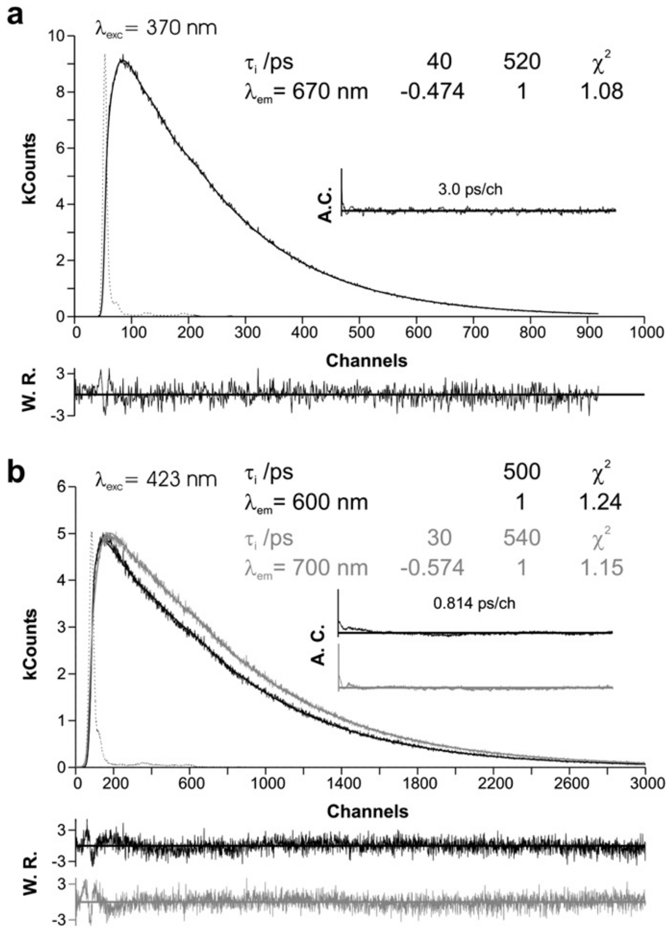


Fig. 2. Fluorescence emission decays for PF2/6-*b*-P3TMAHT in methanol obtained with a) λ_{exc} = 370 nm and b) λ_{exc} = 423 nm. The dashed lines in the decays are the instrumental response function (IRF). For a better judgment of the quality of the fits weighted residuals (W.R.), autocorrelation functions (A.C.) and chi-square values (χ^2) are also presented.

and more structured in methanol. Fluorescence quantum yields (Φ_f) of PF2/6-*b*-P3TMAHT and PF2/6-*b*-P3PyHT were determined in water and methanol (Table 1).

Fluorescence decays of PF2/6-*b*-P3TMAHT were also obtained in these two solvents upon excitation into both the fluorene (370 nm) and thiophene (423 nm) bands. In methanol, excitation at 370 nm and observation in the fluorene emission region gave a fast decay which was difficult to analyse because of the strongly overlapping absorption from the thiophene segment. However, when the emission was observed in the thiophene region (600 nm, Fig. 2(a)) following excitation at 370 nm, two components were observed, with a rise time of 40 ps and a slower decay component (520 ps). Excitation in the thiophene region and observation at 600 nm (Fig. 2(b)) showed just the long lived decay component, whose lifetime (500 ps) was identical, within experimental error, to that seen upon 370 nm excitation. We believe that the fast component observed upon excitation into the fluorene region may include contributions from both energy migration (either on-chain or interchain) in the excited singlet state between the fluorene and thiophene blocks, and conformational relaxation within the polyfluorene block (as previously observed with PF2/6 [21]), the polythiophene block or involving both block units. Indeed, the fast process has a lifetime (30–40 ps in Fig. 2) which is consistent with both conformational relaxation [21] and singlet exciton hopping along the chain, as seen with fluorene-fluorenone random copolymers [22]. Based on the current experiments it is not possible to differentiate between these two processes, and it is likely that they are simultaneously present and associated with this same lifetime component. The longer component, which is typical of the fluorescence decay times of polythiophenes [23], corresponds to the decay of the thiophene block. The fluorescence decay of PF2/6-*b*-P3TMAHT in water was considerably more complex, and could only be fitted by three exponentials, even upon excitation in the thiophene block. This additional third exponential in water, when compared with the behaviour in methanol, is likely to be associated with the poorer solubility in this solvent leading to some degree of aggregation (intermolecular association) with an individualized structure emitting isolated and uncoupled to the solubilised polymer (associated with the two remaining emission decay times).

Table 1
Photophysical parameters for diblock copolymers PF2/6-*b*-P3TMAHT and PF2/6-*b*-P3PyHT in water and methanol.

Compound	Solvent	Φ_f	τ_f/ps (600 nm emission)	Φ_T	Φ_Δ	τ_T/μs
PF2/6-*b*-P3TMAHT	MeOH	0.16	40, 520[a] 500[b]	0.17	0.13	14.7
	H_2O	0.035	[c]	[d]	[d]	15.9
PF2/6-*b*-P3PyHT	MeOH	0.17	[d]	0.12	0.11	13.9
	H_2O	0.070	[d]	[d]	[d]	19.8

[a] Excitation at 370 nm.
[b] Excitation at 423 nm.
[c] Complex decays observed.
[d] Not measured.

Marked solvatochromic effects on PL are seen in water and methanol, and are similar to those observed in binary tetrahydrofuran–water mixtures [24]. Since similar behaviour is observed with the *n*-octyl derivative PFO-*b*-P3TMAHT, we feel these must result from conformational changes within the polythiophene block. As with fluorene-thiophene alternating copolymers [25], fluorescence quantum yields were considerably less than normally found with polyfluorenes [26], suggesting significant triplet formation. To test this, transient absorption spectra were obtained by flash photolysis in water and methanol. The spectra in methanol are given in Fig. 3, and show bleaching of the ground state absorption around 450 nm and the appearance of new bands around 600 nm, assigned to triplet states. Both transient absorption maxima and ground state bleaching in the singlet–triplet difference spectra are essentially those of the polythiophene block [14–16]. Polyfluorene triplet–triplet absorption maxima appear at wavelengths >700 nm [26]. However, although triplet-hopping is possible along poly(*p*-phenylene) chains [27], the fact that polyfluorenes only show low intersystem crossing yields [16,26] suggest this is an unlikely mechanism. Instead, it is more probable that the triplet state formed on the thiophene block upon excitation in the fluorene block arises from energy migration in the singlet state followed by $S_1 \rightarrow T_1$ intersystem crossing in the oligothiophene unit, which is known to have high quantum efficiency [23]. Triplet lifetimes (τ_T) are comparable to those found with polythiophenes [23] and alternating fluorene-thiophene copolymers [25]. Sensitised singlet oxygen yields (Φ_Δ) were determined, and are close to Φ_T. Since the sum of Φ_f and Φ_T is considerably less than unity, internal conversion must be an important excited-state deactivation pathway.

To obtain further insight into the behaviour of these diblock copolymers in solution, the electrical conductances were studied in water and methanol solution. The specific conductances of PF2/6-*b*-P3TMAHT, κ (calculated from experimental specific conductance and corrected for the initial specific conductance of solvent), as function of diblock copolymer concentration are shown in Fig. 4.

Two aspects of these plots can be noted. Firstly the specific conductances for aqueous solutions are significantly greater than those in methanol. This can be related to differences in both dielectric constant and viscosity between water (78.48 and 0.8949 mPa s) and methanol (32.64 and 0.541 mPa s) [28], and after correcting for viscosity, differences in the electrical conductance of PF2/6-*b*-P3TMAHT can be assigned to the effect of dielectric constants, where a lower degree of polymer dissociation is expected with the less polar methanol. The second observation is that whereas a linear dependence of specific conductivity on concentration is seen in methanol, this is not true in water. From the difference between the electrical conductivity in water and methanol, $\Delta\kappa$, ($=\kappa_W - \kappa_{MeOH}$), we see an alteration in the solution behaviour at 0.163 ($\pm$0.001) μM PF2/6-*b*-P3TMAHT – see arrow in Fig. 4b). This behaviour can be explained either by an increase in the dissociation degree or an alteration of the size and shape of the polymer; the former is unlikely, since the degree of dissociation would be expected to decrease with an increase of concentration. Consequently, we favour the latter explanation: an alteration in the structure involving a re-organization of the charge distribution, with a consequent increase of the available “free” charge. The above observations all point to differences in the behaviour of these all-conjugated diblock copolymers in water and methanol, which are likely to influence the aggregation state in these solvents. In particular, the degree of counter-ion dissociation in the polythiophene block is anticipated to affect its conformation due to different electrostatic interactions.

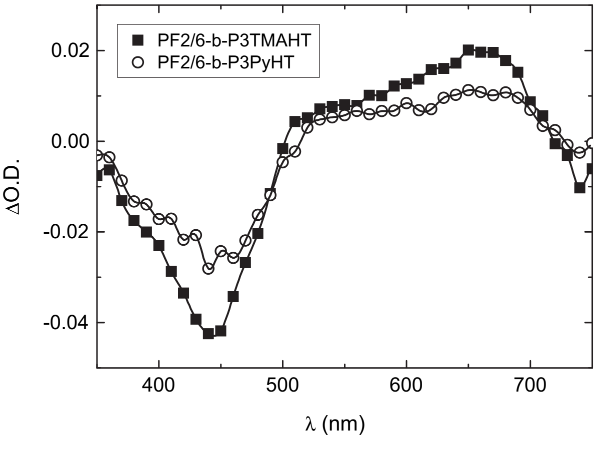


Fig. 3. Transient absorption spectra observed following excitation at 355 nm of solutions of PF2/6-*b*-P3TMAHT and PF2/6-*b*-P3PyHT in methanol.

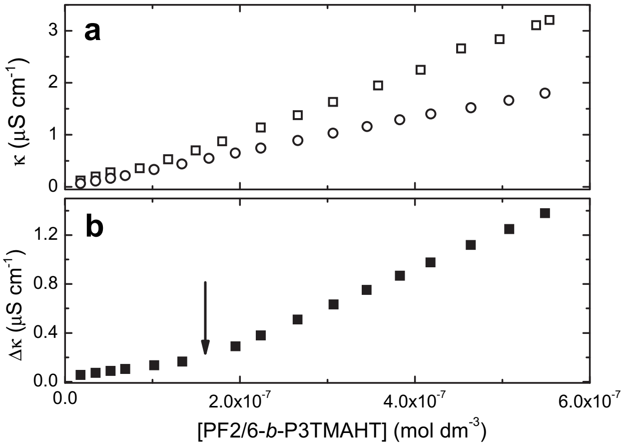


Fig. 4. a) Electrical specific conductance of PF2/6-*b*-P3TMAHT in water (□) and methanol (○) and b) difference between their specific conductances in water and in methanol, $\Delta\kappa = \kappa_W - \kappa_{MeOH}$, as a function of PF2/6-*b*-P3TMAHT concentration. The arrow shows the inflexion point at [PF2/6-*b*-P3TMAHT] = 0.163 ($\pm$0.001) μM.

To obtain further information on the structures, PFO-*b*-P3TMAHT solutions were studied using SAXS. Fig. 5 plots the SAXS data of PFO-*b*-P3TMAHT in water and methanol (at a concentration of 6 mg/mL ≈ 10 mM repeat unit (r.u.)). Fully dissolved rod–rod polymers are expected to exhibit a monotonic −1 decay, Guinier plateau corresponding to the overall length of the polymer (~30 nm). However, no plateau is seen, and for $q < 0.3$ nm^{-1} the data are dominated by a decay of ≈−2.8. This implies that both samples contain polymer associations and that their structure on the length scale of ~10–70 nm can be understood in terms of mass fractals with the fractal dimension (D_m) ≈ 2.8. Similar data and interpretation have been reported for conjugated polymers by Chen et al. [29]. For $q > 0.3$ nm^{-1}, the data of PFO-*b*-P3TMAHT in methanol decays as $\sim q^{-1.56}$, which points to solvated worm-like polythiophene blocks on the length scale <10 nm. The polyfluorene blocks are most likely to be found in the aggregate interior, since fully dissolved PFO would decay distinctively as $\sim q^{-1}$. In contrast, the data of PFO-*b*-P3TMAHT in water show a broad feature around $q \sim 1$ nm^{-1}, which is interpreted as an interference maximum corresponding to a period of ~6 nm. This maximum is proposed to arise from the electrostatic interactions between PFO-*b*-P3TMAHT aggregates, with a PFO rich core and a charged P3TMAHT rich outer layer. Further small angle X-ray and neutron scattering experiments are in progress, both on the block conjugated polyelectrolytes and on the corresponding cationic thiophene oligomer, to obtain more information on these structures.

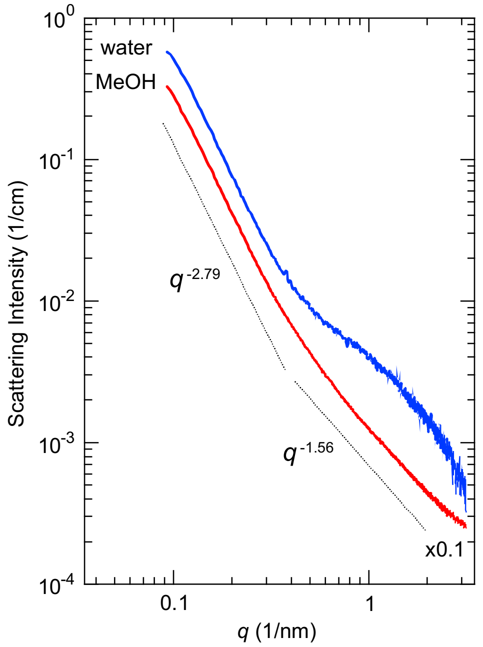


Fig. 5. SAXS data of PFO-*b*-P3TMAHT as dissolved in methanol (red) and water (blue) at a concentration of 10 mM (r.u.). The methanol data are shifted and multiplied by 0.1 for clarity. Dotted lines show decays of −2.79 and −1.56 for comparison (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

These observations all point to distinct differences of the intra- and inter-molecular structure of these diblock copolymers in water and methanol. In particular, differences in counter-ion dissociation in the polythiophene block will affect its conformation due to changes in electrostatic interactions. Further information was obtained by casting films of PF2/6-*b*-P3TMAHT onto mica surfaces and imaging their morphologies by atomic force microscopy (AFM).

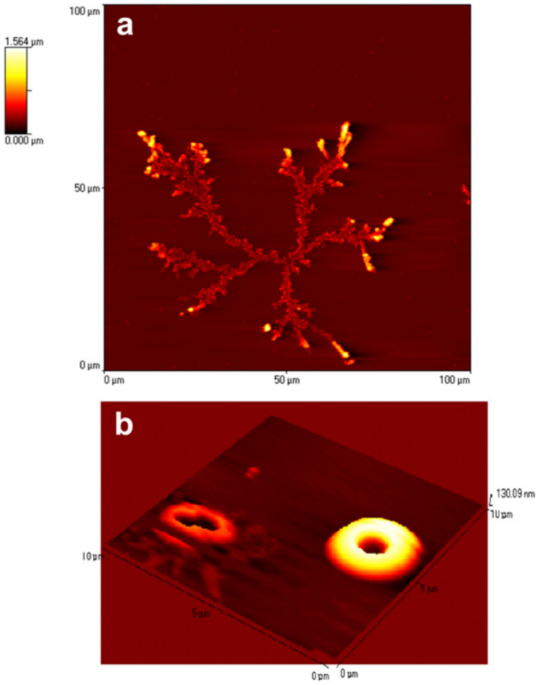


Fig. 6. Tapping-mode AFM image of PF2/6-*b*-P3TMAHT deposited on a mica support from: a) water (0.1 mg/mL); b) methanol (0.03 mg/mL, adapted from ref. [10]).

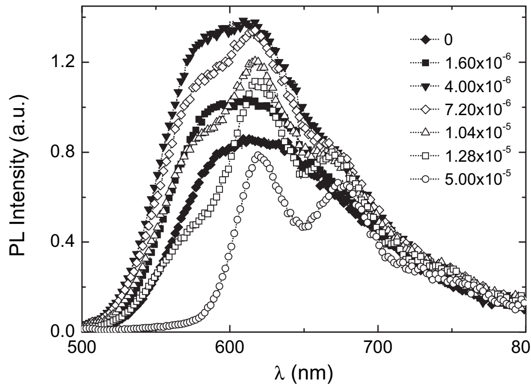


Fig. 7. Changes in fluorescence ($\lambda_{exc} = 430$ nm) of PF2/6-*b*-P3TMAHT in water upon addition of SDS (mol dm^{-3}).

Typical AFM images (Fig. 6) show striking differences. That from water, formed after slow solvent evaporation, shows fractal-like, poorly structured morphology. Similar fractal-like behaviour was seen with triblock polyaniline-polyfluorene-polyaniline copolymers [30]. In contrast, large, vesicular structures form from methanol, and fuse into lamellar structures at higher concentrations [24]. Similar, but smaller, vesicular structures have been found with the uncharged amphiphilic poly[9,9-bis(2-ethylhexyl)fluorene]-*b*-poly[3-(6-diethylphosphonatohexyl) thiophene] [4]. As with other amphiphilic block copolymers [31] these probably consist of double layers with the non-polar polyfluorene blocks inside and the polar polythiophene blocks as outer shell.

Finally, the behaviour of PF2/6-*b*-P3TMAHT in water has been studied in the presence of the oppositely charged surfactant sodium dodecylsulfate (SDS). Dramatic changes in the photoluminescence emission spectra were observed at surfactant concentrations below the critical micelle concentration (8.2 mM [32]), with a red shift in the emission of the polythiophene block (P3TMAHT) and the appearance of vibrational structure (Fig. 7). This suggests, as has been seen with oppositely charged surfactants and alternating conjugated polyelectrolytes [33,34], that charge neutralisation results in a self-assembly into ordered polyelectrolyte–surfactant complexes, and also with the diblock copolymers this leads to a more rigid conformation of the ionic polythiophene chains with an increased intra- and inter-chain order. This more rigid structure is associated with the quinoidal-like structure of oligothiophenes, which present similar vibrational resolution [35,36], indicating that with the gradual addition of surfactant to the diblock copolymer, the P3TMAHT polythiophene block is forming a more planar and rigid structure. Similar behaviour, but at higher surfactant concentrations, is observed upon addition of sodium octyl sulfate. Work is in progress to characterise the structures of aggregates produced.

4. Conclusions

We have shown that cationic fluorene-thiophene diblock copolymers can be dissolved in water and methanol to form different types of aggregate structures. The polyfluorene and polythiophene blocks show distinct absorption and fluorescence spectra, which are affected markedly by the solvent. Fast singlet state energy migration is observed from the polyfluorene to polythiophene blocks, which may proceed by either on-chain or inter-chain mechanisms. Significant triplet state formation within the polythiophene block is also observed upon photoexcitation. When excitation is in the polyfluorene unit this is likely to arise from singlet energy migration to the polythiophene unit followed by intersystem crossing. Information on aggregation in solution comes from both electrical conductivity and SAXS studies, and suggest that in methanol the polythiophene blocks have solvated worm-like polythiophene blocks, whereas in water a loosed array of aggregates is formed, whose structure arises from a polyfluorene rich core, driven through hydrophobic effects and a cationic polythiophene outer layer in which electrostatic effects are dominant. AFM measurements show that these aggregates lead to markedly different morphologies of films formed upon solvent evaporation, with poorly structured, fractal-like morphology from water, but large, vesicular structures from methanol. The aggregation in solution can be further modulated by addition of oppositely charged surfactants, leading to a more ordered polythiophene unit.

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