

Self-Assembly of Poly{1,4-phenylene-[9,9-bis(4-phenoxy-butylsulfonate)]fluorene-2,7-diyl} with Oppositely Charged Phenylenevinylene Oligoelectrolytes

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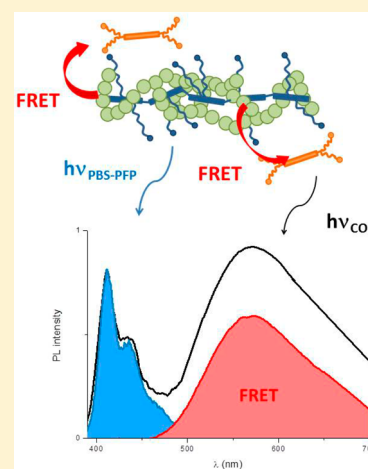
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S Supporting Information

ABSTRACT: The interaction of the water-soluble conjugated polyelectrolyte (CPE) poly{1,4-phenylene-[9,9-bis(4-phenoxy-butylsulfonate)]fluorene-2,7-diyl} (PBS-PFP) (degree of polymerization, DP, ~3–6) with various concentrations of a homologous series of oppositely charged amphiphilic phenylenevinylene oligomers was investigated in water:dioxane mixtures and in aqueous micellar solutions of the non-ionic surfactant *n*-dodecylpentaerythritol ether. The excellent spectral overlap between the CPE fluorescence and the conjugated oligoelectrolyte (COE) absorption indicates that energy transfer between these is a highly favored process, and can be tuned by changing the COE chain length. This is supported by time-resolved fluorescence data. The overall results provide support for different types of self-assembly, which are sensitive to the solvent environment and to the size of the phenylenevinylene oligoelectrolyte chain. It is suggested that large aggregates are formed in water:dioxane mixtures, while decorated core-shell structures are present in the surfactant solutions.



INTRODUCTION

Conjugated polyelectrolytes (CPEs) are rigid-rod macromolecules with π -conjugated backbones bearing pendant ionic groups that induce solubility in polar solvents. CPEs are of interest, in part, because they combine the optoelectronic properties of neutral conjugated polymers with the electrostatic behavior of polyelectrolytes.^{1–3} To date, CPEs have been used as fluorescent quenching probes to detect specific analytes via electron and energy transfer mechanisms, or via analyte-induced polymer aggregation.^{4–6} They have also been employed as energy donors to amplify the signal output of dye-labeled biomolecules via Förster resonance energy transfer (FRET).^{7–10} Moreover, CPEs have attracted significant attention as active materials in polymer optoelectronics such as electron injection and/or transport layers, as light emitting diodes (PLEDs) or field-effect transistors (FETs), and as electron donors in organic photovoltaic cells (OPVs).^{11–16} CPEs have also been suggested for use in hybrid nanodots and other organic–inorganic materials for two-photon fluorescence imaging and solid-state sensing.^{17,18}

CPEs undergo spontaneous self-assembly with amphiphilic molecules, such as surfactants, forming polymer–surfactant complexes with different structures and conformations from that of the free polymer.^{19–21} Non-ionic surfactants tend to

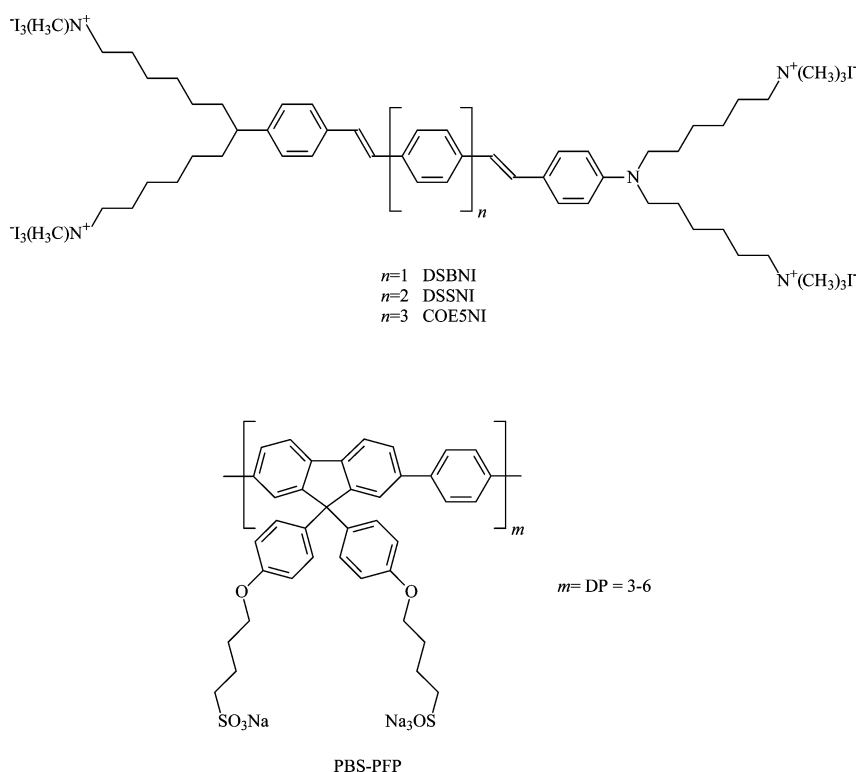
break up interchain polymer aggregates and form mixed CPE–surfactant cylindrical micelles, in which the polymer is incorporated in the core of the micelle as isolated chains.^{22,23} Thus, the optical and electrostatic properties of CPE assemblies can be tuned by combining them with the appropriate surfactants in a process designated as “surfactochromicity”.^{23,24} Interaction with oppositely charged surfactants leads to the formation of complex multilayered structures. The formation of CPE/surfactant complexes has been shown to have important practical consequences, for instance, in the performance of bulk-heterojunction (BHJ) solar cells. The use of poly[3-(6-trimethylammoniumhexyl)thiophene] (PTMAHT)/sodium dodecyl benzene sulfate was shown to increase the power conversion efficiency relative to the device fabricated without surfactant. The presence of surfactant improves the miscibility of the PTMAHT at the interface, leading to increased charge transport efficiency.²⁵ Another example of technological relevance is the stabilization of the mesomorphic β -phase in devices containing poly(9,9-dioctylfluorene) (F8) or F8 derivatives. It is known that devices in which the F8 derivatives

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Scheme 1. Molecular Structures of the Cationic Distyrylbenzene Oligoelectrolytes (COEs) DSBNI, DSSNI, and COESNI and Anionic CPE PBS-PFP (Where DP Is the Degree of Polymerization)



are in a β -phase (aligned in a more planar configuration) exhibit efficient blue electroluminescence and good charge transport properties. The control and formation of long-range ordered multilayers was possible through the complexation of an F8 water-soluble derivative with a zwitterionic surfactant. In these self-assembled structures, the exciton quenching is highly reduced due to the more ordered packing of CPE backbones.²⁶

FRET offers the possibility of developing self-assembled structures composed of CPE energy donors coupled with appropriate energy acceptors for applications in new synthetic light harvesting strategies, as illustrated by the energy transfer between anionic fluorene-*alt*-phenylene based CPEs and oppositely charged Ru(II) complexes.²⁷ The emission spectrum of the fluorene based anionic poly{1,4-phenylene-[9,9-bis(4-phenoxy-butylsulfonate)]fluorene-2,7-diyl} (PBS-PFP) has a good overlap with the lowest singlet-singlet transition in the absorption spectrum of (2,2-bipyridyl)ruthenium(II) (Ru-(bpy)₃²⁺). As a result, electronic energy from excited singlet or triplet states of the donor or acceptor can be channelled to the triplet state of the metal complex due to fast (sub-picosecond range) intersystem crossing in this metal complex to the emitting metal-to-ligand charge transfer (³MLCT).²⁷ Reynolds²⁸ achieved efficient FRET in multilayer film architectures built via the inexpensive layer-by-layer technique using two emissive conjugated polyelectrolytes. However, it has also been shown with a polyfluorene derivative to which a polypyridylruthenium(II) complex is covalently linked that electron transfer competes with energy transfer.²⁹

In this study, with the aim of developing new self-assembled structures in which singlet-singlet excited-state energy transfer is favored, the anionic conjugated polyelectrolyte poly{1,4-phenylene-[9,9-bis(4-phenoxy-butylsulfonate)]fluorene-2,7-diyl} PBS-PFP has been used as an energy donor and cationic

phenylenevinylene COEs as acceptors (Scheme 1). The excellent spectral overlap between the CPE fluorescence and the oligoelectrolyte absorption indicates that the energy transfer process is highly favored and can be tuned by changing the COE chain length.³⁰ Studies of energy transfer in this system are likely to be relevant to optimizing energy migration in conjugated polymer/oligomer blends.

EXPERIMENTAL SECTION

Materials. The oligoelectrolytes DSBNI³¹ (trimer, $n = 1$), DSSNI³² (tetramer, $n = 2$), and COESNI³³ (pentamer, $n = 3$) were synthesized as previously described. The copolymer PBS-PFP was synthesized as previously reported³⁴ via Suzuki coupling of the corresponding dibrominated and diboronic acid monomers. The relatively low apparent molecular weight (M_w of 2100 g/mol, PD = 1.6) as calculated from GPC (NMP, LiBr, UV detection) may result from interactions of the anionic polyelectrolyte with the column material. The material structures are depicted in Scheme 1.

Solution Preparation. The measurements were performed in water and dioxane:water (1:1). All the solvents were of spectroscopic grade, and Milli-Q water was used. To ensure almost complete dissolution of the copolymer, solutions were stirred overnight. The non-ionic surfactant *n*-dodecylpentaethylene glycol ether (C₁₂E₅) was purchased from Aldrich and used without further purification.

Steady-State Spectroscopic Measurements. Absorption spectra were recorded using a Shimadzu UV-2100 spectrophotometer with a minimum resolution of 0.2 nm. For the steady-state measurements, fluorescence spectra were recorded with a Horiba-Jobin-Ivon SPEX Fluorog 3-22 spectrometer and were corrected for the instrumental response of the system. The fluorescence quantum yields of PBS-PFP

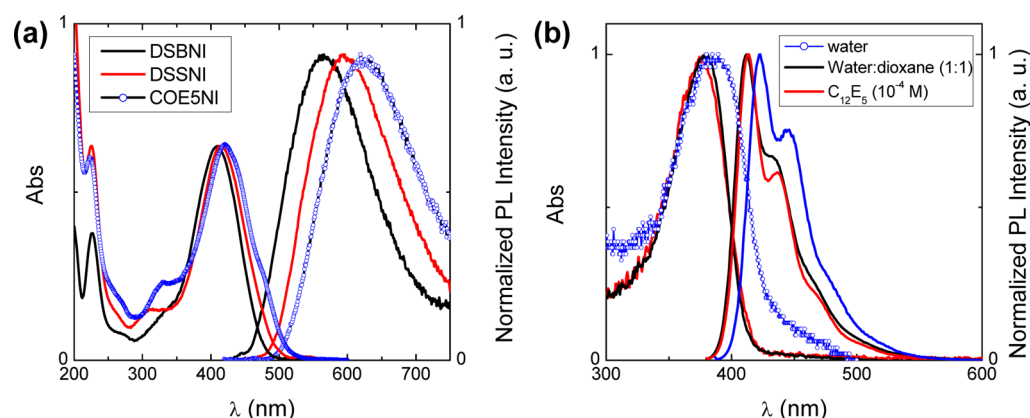


Figure 1. (a) Normalized absorption and fluorescence spectra of aqueous distyrylbenzene oligoelectrolyte (ca. 4×10^{-6} M) solutions. (b) Normalized absorption and fluorescence spectra of PBS-PFP (ca. 5×10^{-6} M) in three different solvents: water:dioxane (1:1, v/v), aqueous C₁₂E₅ solution (10^{-4} M), and water.

and of the conjugated oligoelectrolytes were determined using quinine sulfate in 0.5 M H₂SO₄ and fluorescein at pH 12, respectively.

TCSPC Experiments. Picosecond time-resolved fluorescence measurements were performed using a home-built picosecond TCSPC apparatus, in which the excitation source consists of a picosecond Spectra Physics mode-lock Tsunami laser (Ti: sapphire) model 3950 (repetition rate of about 82 MHz, tuning range 700–1000 nm), pumped by a Millennia Pro-10s, frequency-doubled continuous wave (CW), diode-pumped, solid-state laser ($\lambda_{\text{em}} = 532$ nm). A harmonic generator model GWU-23PS (Spectra-Physics) is used to produce the second and third harmonic from the Ti:sapphire laser exciting beam frequency output. The samples were measured with excitation at 372 nm, and the horizontally polarized output beam from the GWU (second harmonic) was first passed through a Thorlabs depolarizer (WDPOL-A) and after by a Glan-Thompson polarizer (Newport 10GT04) with vertical polarization. Emission at 90° geometry collected at magic angle polarization was detected through a double subtractive Oriel Cornerstone 260 monochromator by a Hamamatsu microchannel plate photomultiplier (R3809U-50). Signal acquisition and data processing was performed employing a Becker & Hickl SPC-630 TCSPC module. Fluorescence decays and the instrumental response function (IRF) were collected using 4096 channels in a 0.814 ps/channel scale, until 5×10^3 counts at maximum were reached. The full width at half-maximum (fwhm) of the IRF was about 22 ps and was highly reproducible with identical system parameters. A more detailed description of this equipment can be found in ref 35.

RESULTS AND DISCUSSION

Absorption and Fluorescence. Oligoelectrolytes. The absorption maxima of the three cationic phenylvinylene oligoelectrolytes (COEs), shown in Scheme 1, in aqueous solutions are observed in the 408–420 nm range (Figure 1A). The modest red-shift in the absorption wavelength maxima across the oligoelectrolyte series (12 nm) is consistent with the effect of increasing conjugation length on the electronic structure (Figure 1A and Table 1). However, a much more pronounced red-shift is seen in the photoluminescence (PL) spectra, varying from 562 to 624 nm, Figure 1A.

Table 1. Molar Extinction Coefficients (ϵ), Absorption ($\lambda_{\text{abs}}^{\text{max}}$) and Fluorescence ($\lambda_{\text{em}}^{\text{max}}$) Wavelength Maxima, Stokes Shifts (Δ_{SS}), and Fluorescence Quantum Yields (ϕ_{PL}) for the Investigated Oligoelectrolytes in Aqueous Solutions

oligoelectrolytes	ϵ (L mol ⁻¹ cm ⁻¹)	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\lambda_{\text{em}}^{\text{max}}$ (nm)	Δ_{SS} (cm ⁻¹)	ϕ_{PL}
DSBNI	6.0×10^4	408	565	6811	0.41
DSSNI	6.6×10^4	412	595	7465	0.06
COE5NI	9.3×10^4	420	620	7681	0.05

The absorption and emission spectra of the oligomers were also found to be dependent on the polarity of the solvent, and a large hypsochromic shift in the emission maxima was observed upon going from a polar to a non-polar environment (see Figure S1 in the Supporting Information and refs 32 and 36). In aqueous media, the absorption and emission spectra are devoid of vibronic structure and the photoluminescence quantum yields (ϕ_{PL}) are low with the exception of DSBNI (Table 1). Indeed, this effect is more pronounced for the DSSNI and COE5NI oligoelectrolytes compared to the shorter DSBNI, probably because of its larger hydrophobic component which may lead to self-quenching of the PL.^{32,36}

From Table 1, it can also be noted that the Stokes shift increases with the oligomer size, consistent with the different nature of the ground and first excited singlet states and with conformational disordering in the ground state which is more pronounced in the oligomer with $n = 5$ due to the increase in the number of possible conformers. Large Stokes shift (Δ_{SS}) values indicate substantial differences between the equilibrium structures of the two electronic states.³⁷

PBS-PFP. The PBS-PFP absorption and PL spectra in three different solvent media are presented in Figure 1B. In aqueous solutions, the PBS-PFP copolymer is characterized by a broader absorption and weaker, red-shifted PL spectra when compared to the spectra in the other two solvents. Earlier work with rigid rod phenylene and related fluorene based conjugated polyelectrolytes such as the “hairy-rod” PBS-PFP has shown that these polyelectrolytes have a strong tendency to cluster in aqueous solutions, resulting in low solubility and low fluorescence quantum yields.^{23,38–41} It has been shown that it is possible to break up these clusters/aggregates, either by adding a cosolvent, such as dioxane, or an appropriate surfactant above its critical micelle concentration (cmc).^{22,42,43} Upon addition of C₁₂E₅ (10^{-4} M) or dioxane

(50%), blue-shifts in the absorption and PL maxima are observed, and are accompanied by marked increases in the PL intensity^{22,44} (note that in Figure 1B the spectra are normalized) and ϕ_{PL} (Table 2).

Table 2. Summary of the PBS-PFP UV–Vis and PL Wavelength Maxim and Photoluminescence Quantum Yield (ϕ_{PL}) in Dioxane:Water (1:1, v/v) and Aqueous Surfactant Solution

solvent	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\lambda_{\text{em}}^{\text{max}}$ (nm)	ϕ_{PL}
50% dioxane	376	412	0.52
C ₁₂ E ₅	380	413	0.55
water	387	423	0.14

The PL spectrum of PBS-PFP in the presence of the surfactant C₁₂E₅ shows a more pronounced vibronic fine structure compared to the emission in the water:dioxane solvent system. These observations are, in large part, attributed to surfactant induced “break-up” of polymer clusters, due to the incorporation of the copolymer into C₁₂E₅ aggregates.^{43,44} The increased vibronic structure suggests decreased conformational flexibility compared with water:dioxane mixtures. The blue-shift in the emission maxima, as well as the relatively high ϕ_{PL} when compared with the situation in pure water (Table 2 and Figure 1B), suggests the existence of isolated copolymer chains in both solvent systems.

Self-Assembled PBS-PFP and *p*-Phenylenevinylene Oligoelectrolyte Systems. The interaction between PBS-PFP (with a degree of polymerization, DP, 3–6) and the three conjugated oligoelectrolytes was studied at a constant PBS-PFP

concentration (4.4×10^{-6} M, based on the polymer repeat unit) in both the water:dioxane and aqueous C₁₂E₅ solution (10^{-4} M) solvent systems. We will focus our discussion on the PBS-PFP/DSSNI system, since this COE was shown to induce the most dramatic changes in the photophysical behavior of PBS-PFP. Figure 2 shows the absorption spectral changes of PBS-PFP during gradual addition of the DSSNI in the two solvent media. In both solvent systems, the gradual addition of COE results in an increase of the absorbance at the wavelength maximum ($\lambda_{\text{abs}}^{\text{max}}$), a red-shift of $\lambda_{\text{abs}}^{\text{max}}$, and the appearance of a new COE-related absorption band at the red edge of the absorption spectra (Figure 2). Comparing the absorption spectrum of the PBS-PFP/DSSNI (6.48×10^{-7} M) self-assembled system and the sum of the absorption spectra of isolated PBS-PFP and DSSNI (6.48×10^{-7} M) systems, it is possible to assign the new absorption band to the COE (Figure S2, Supporting Information). The absorption bands of the mixtures are slightly broader and red-shifted relative to the sum of the two components, suggesting the formation of PBS-PFP/DSSNI self-assembled structures.

The effect of the conjugated oligoelectrolytes on the spectral properties of PBS-PFP is more evident in the PL spectra (Figure 2, middle hand panels). Upon addition of the COE, the PBS-PFP PL intensity is strongly quenched at very low COE concentrations (50 nM), and this is accompanied by the appearance of a new emission band in the range 560–620 nm, assigned to the COE (Figure 2 and Table 3). Although the PL spectra are obtained with excitation at 360 nm, i.e., at the maximum absorption wavelength of PBS-PFP, the conjugated oligoelectrolytes also absorb at this wavelength. Hence, the appearance of the PL band might result from the direct

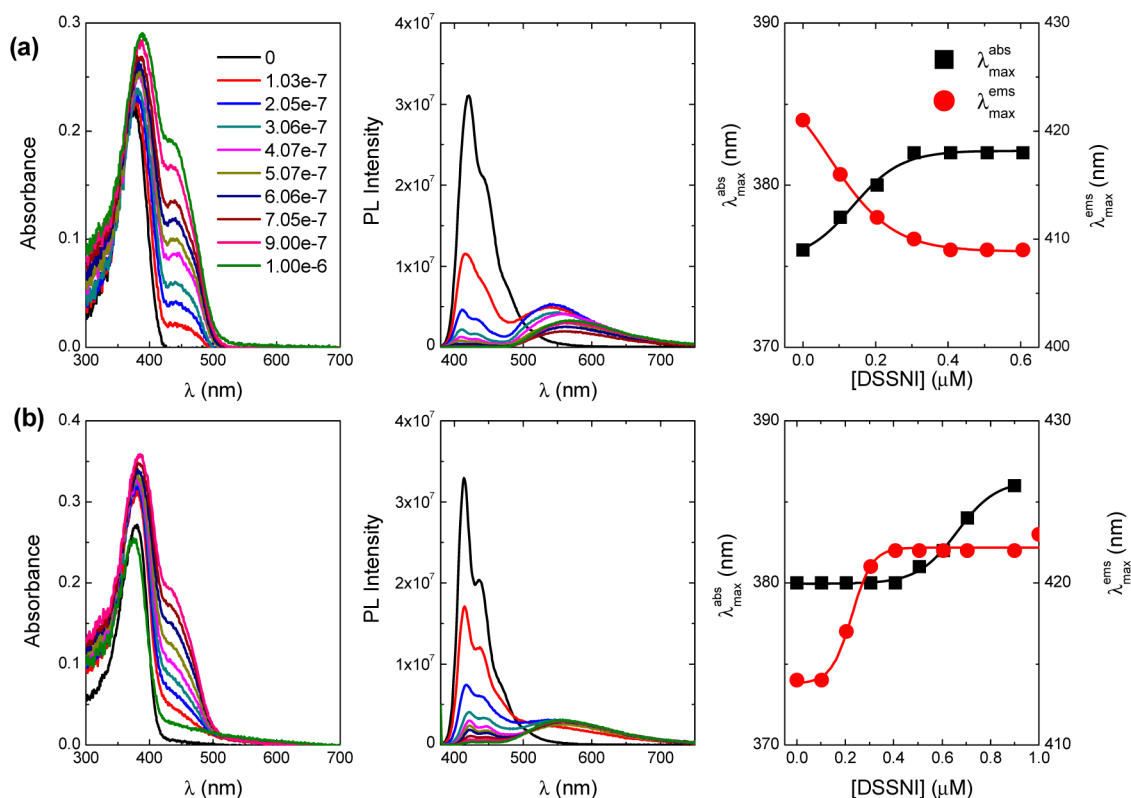


Figure 2. Absorption spectra (left panels), emission spectra (middle panels), and dependence of the maxima absorption and emission wavelength of PBS-PFP (right panels) of PBS-PFP in water:dioxane (1:1, v/v) mixtures (a) and in 10^{-4} M aqueous C₁₂E₅ solutions (b), with increasing concentrations of DSSNI. The emission spectra were collected at $\lambda_{\text{exc}} = 360$ nm and $T = 25$ °C.

Table 3. Maxima Absorption and Emission Wavelengths of the Pure COE and PBS-PFP/COE (1 μ M) Self-Assembled Systems in Dioxane:Water (1:1, v/v) and Aqueous $C_{12}E_5$ Surfactant Solution

system	solvent	absorption		emission	
		$\lambda_{\text{PBS-PFP}}$ (nm)	λ_{COE} (nm)	$\lambda_{\text{PBS-PFP}}$ (nm)	λ_{COE} (nm)
DSBNI	$C_{12}E_5$		416		500
DSSNI	$C_{12}E_5$		430		540
COESNI	$C_{12}E_5$		440		580
DSBNI	Dx:H ₂ O		411		509
DSSNI	Dx:H ₂ O		427		576
COESNI	Dx:H ₂ O		433		610
PBS-PFP/DSBNI	$C_{12}E_5$	380	433	417	557
PBS-PFP/DSSNI	$C_{12}E_5$	385	432	425	559
PBS-PFP/COESNI	$C_{12}E_5$	380	440	414	560
PBS-PFP/DSBNI	Dx:H ₂ O	380	430	410	550
PBS-PFP/DSSNI	Dx:H ₂ O	389	434	404	570
PBS-PFP/COESNI	Dx:H ₂ O	378	443	412	560

excitation of the COE rather than any excitation energy transfer (FRET) from the PBS-PFP to the COEs. In fact, both processes are occurring, as demonstrated by the emission spectra of the DSSNI in the presence and absence of PBS-PFP (Figure S5, Supporting Information) and the excitation spectra presented in Figure S6 (Supporting Information). Indeed, the excitation spectra collected at 600 nm (where only the COEs

emit) display both PBS-PFP and COE bands, confirming the occurrence of energy transfer from PBS-PFP to the COE.

Figure 3 shows the Stern–Volmer plot for the three PBS-PFP/COE systems in water:dioxane (1:1, v/v) and aqueous $C_{12}E_5$ (10^{-4} M) solutions. In these plots, the I_0/I ratio is given as a function of the COE concentration, where I_0 and I are the maximum emission intensities in the absence and presence of the COE. Comparing the PBS-PFP/COE system in the two solvents, it can be seen from the initial slope of the Stern–Volmer plots that the quenching efficiency is higher in water:dioxane than in aqueous $C_{12}E_5$ solution. Additionally, these plots reveal that the self-assembled systems do not follow the linear Stern–Volmer relation expected for collisional quenching.^{30,45} Instead, the plots for both solvent systems have an upward curvature, which suggests combined dynamic and static quenching, where the fluorophore can be quenched both by collision and by complex formation with the same quencher,³⁰ as already observed in a self-assembled system of the cationic poly{9,9-bis[6-(*N,N,N*-trimethylammonium)-hexyl]fluorene-*co*-1,4-phenylene} dibromide (HTMA) and an anionic porphyrin derivative.⁴⁵

Moreover, our data for the PBS-PFP/COE systems show that the COE quenching efficiency does not exclusively depend on the strong electrostatic interaction between the sulfonate groups of PBS-PFP and the four cationic trimethylammonium groups, $N(\text{CH}_3)^{3+}$, on each oligomer molecule. Figure 3 demonstrates that this effect is balanced by the size of the COE

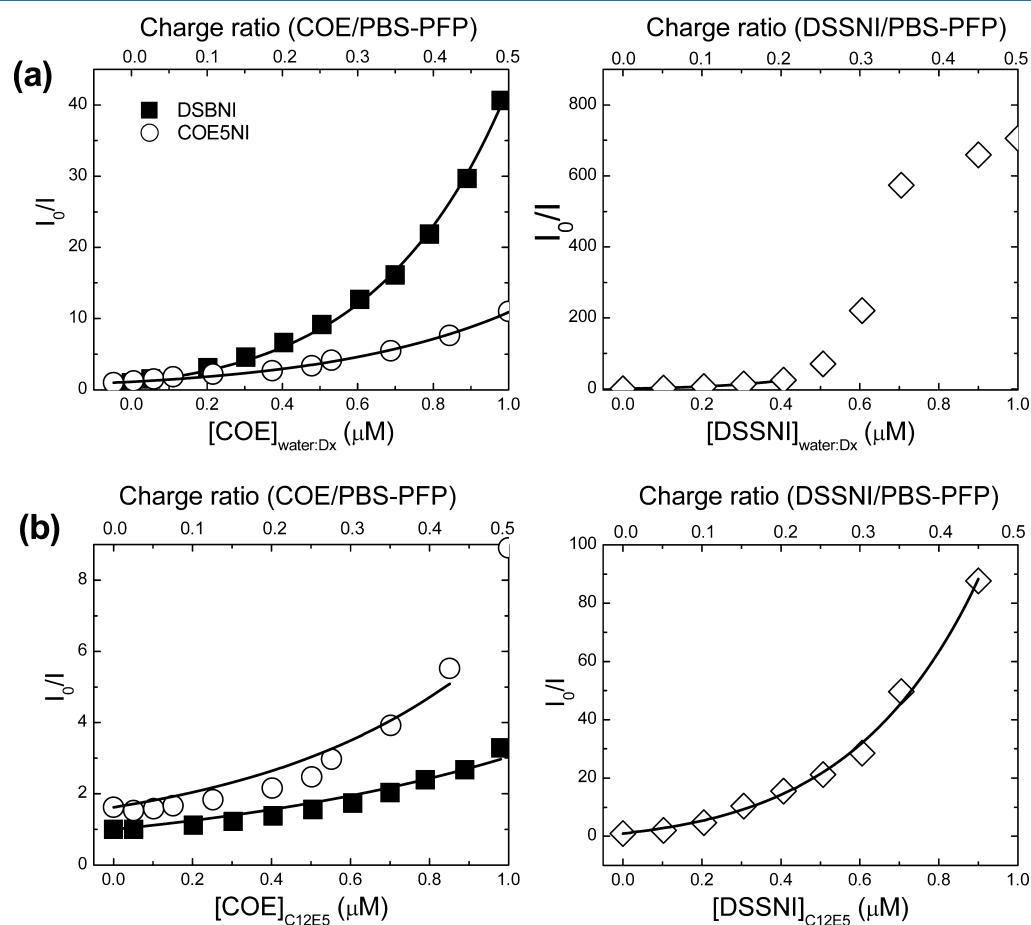


Figure 3. Stern–Volmer plots of PBS-PFP in the presence of DSBNI (■) and COESI (○) (left) and DSSNI (right) in water:dioxane (1:1, v/v) (a) and 10^{-4} M aqueous $C_{12}E_5$ solution (b).

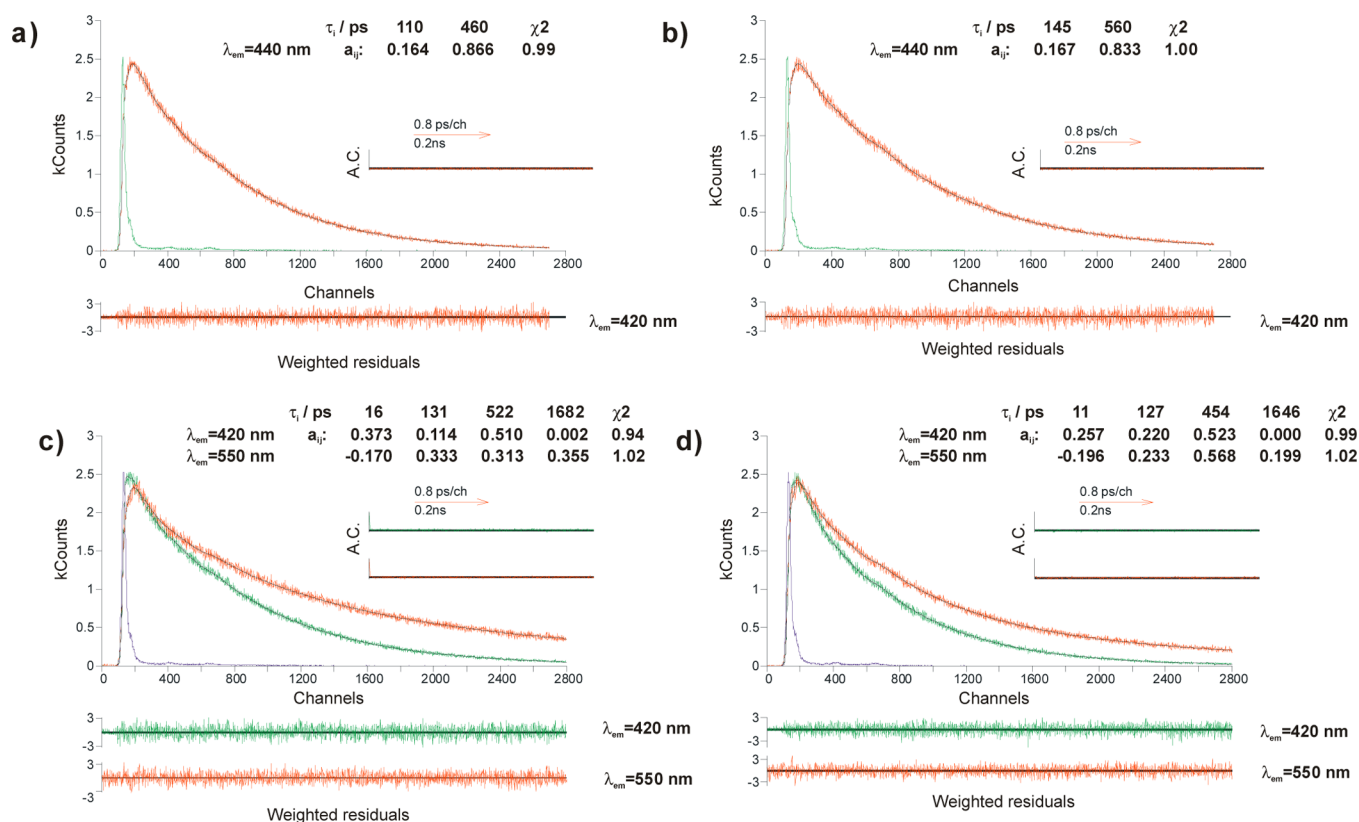


Figure 4. Fluorescence emission decays of PBS-PFP (4.4×10^{-6} M) in (a) 10^{-4} M $C_{12}E_5$ solution and (b) water:dioxane (1:1, v/v) mixture. Parts c and d are the fluorescence emission decays of PBS-PFP/DSSNI (2.5×10^{-7} M) in water:dioxane (1:1 v/v) and PBS-PFP/DSSNI (5×10^{-7} M) in $C_{12}E_5$ surfactant, respectively, collected at 420 and 550 nm. The fluorescence decays were obtained with $\lambda_{exc} = 378$ nm at 298.15 K. The instrumental response function (IRF) is also presented. For a better judgment of the quality of the fits, weighted residuals (W.R., scale $-3 \leq \sigma \leq +3$), autocorrelation functions (A.C.), and χ^2 are also presented.

and the resulting positioning of the positive charges. The highest efficiency was obtained for DSSNI ($n = 4$), whereas the longer chain COESNI ($n = 5$) shows the lowest quenching efficiency when compared to the other two oligomers. A similar effect has been observed in the binding of gemini surfactants to this PBS-PFP.⁴⁶ The interaction depends on the positional match between the corresponding charged functional groups of CPE and quencher.

Time-Resolved Fluorescence Measurements on the Self-Assembled Systems. Further information on the interactions in these self-assembled systems was obtained from time-resolved fluorescence. Excellent fits of the emission decays collected at the PBS-PFP maxima could be achieved by using sums of two discrete exponentials (see Figure 4). Fluorene-based polymer fluorescence decays frequently need more than one exponential for a good fit, and this fluorene-based polyelectrolyte is no exception.^{47,48} The longest lifetime component (τ_3), which dominates the decay, is associated with the decay of the poly(fluorene-phenylene) relaxed structure. The data indicates a reduction in the longest lifetime from 560 ps in water:dioxane to 490 ps in $C_{12}E_5$ aqueous solutions (Figure 4A and B), which is probably a consequence of (small) environmental polarity changes.⁴⁹ The assignment of the shortest component (τ_1) is not completely free of uncertainties but is generally believed that it includes contributions from conformational relaxation,⁴⁸ and, possible, energy migration along the polymer chain.⁵⁰ The τ_1 values of a series of four poly[2,7-(9,9-bis(2-ethylhexyl)fluorene)] fractions (PF2/6) have been shown to be very dependent on the polyfluorene

backbone chain length and on the solvent viscosity.⁴⁸ In particular, the shorter component associated with the conformational relaxation process of the polyfluorene backbone was found to vary from 100 ps (DP = 5) to 60 ps (DP = 205) in decalin. It was shown that the activation energy barrier associated with the conformational relaxation process decreases with increasing chain length (molecular weight), which results in a decrease of the shorter decay time. This result fully supports the assignment of this short-lived component to the conformational relaxation of the PBS-PFP backbone. In dioxane:water (1:1) solutions, with a higher molecular weight PBS-PFP polymer ($M_n = 6500$ g·mol⁻¹, chain length DP ~ 8),⁴⁷ the shorter lifetime was found to be 60 ps; with the PBS-PFP under investigation, which has DP = 3–6, τ_1 increases to 145 ps. Additionally, in the present study, the shorter component, τ_1 , increases from 110 to 150 ps when going from water:dioxane to micellar solutions, and is most probably associated with a slower conformational relaxation of the CPE backbone in the later medium, which is in agreement with encapsulation of the CPE by surfactant, as suggested by the enhancement of PBS-PFP ϕ_{PL} in $C_{12}E_5$ (Table 2).

Parts c and d of Figure 4 show the time-resolved fluorescence decays of the anionic PBS-PFP polyelectrolyte in the presence of DSSNI, collected at the PBS-PFP emission wavelength (420 nm) and at the DSSNI emission wavelength (550 nm). The longest decay time (1.6–1.7 ns) is associated with a species that only emits at 550 nm, i.e., to the DSSNI decay time. The shortest decay time, of tens of picoseconds, appears as a decay component at 420 nm and a rise time at 550 nm. As mentioned

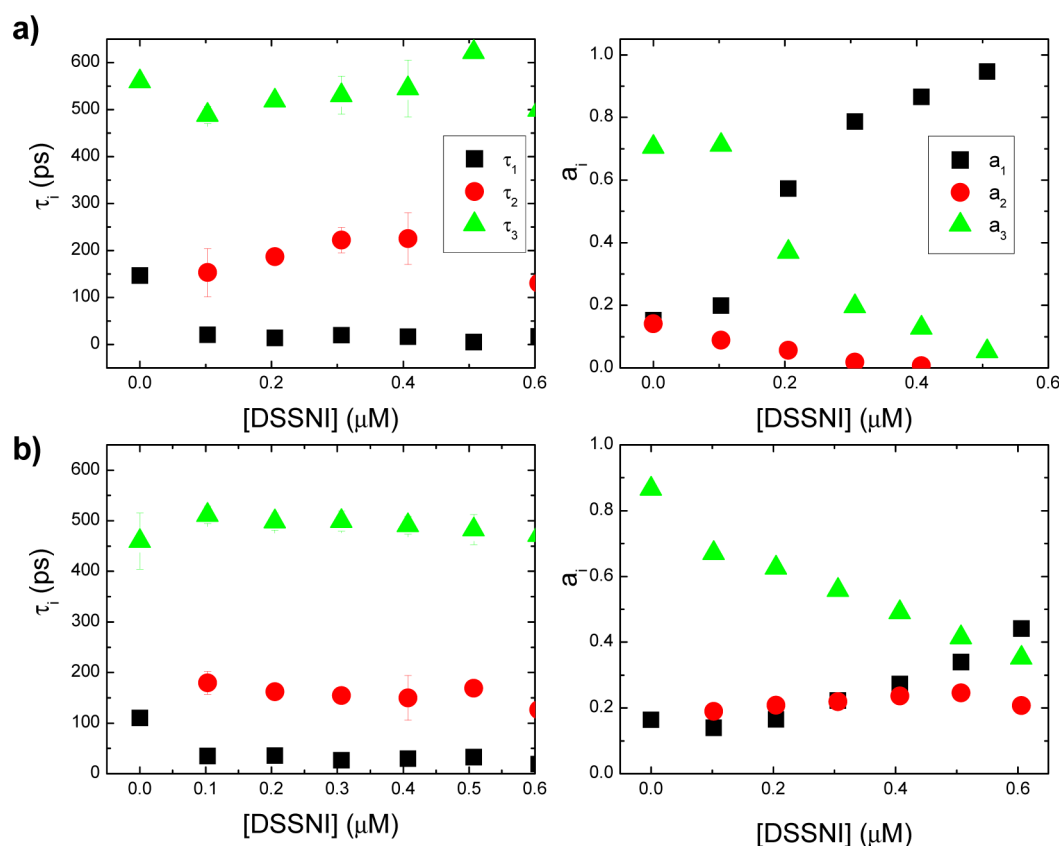


Figure 5. Fluorescence decay times (τ_i) and amplitudes (a_i), collected at 420 nm, of PBS-PFP/DSSNI in (a) water:dioxane (1:1, v/v) mixture and (b) 10^{-4} M $C_{12}E_5$, with increasing phenylenevinylene oligoelectrolyte concentration.

above, these fast decay times may be associated with excitation energy migration along the polymer chain between segments of different conjugation lengths, conformational and/or solvent relaxation, and energy transfer from polymer to acceptor.⁵¹ Although all these processes are possible, in the present self-assembled system, we believe that the correspondence between the increase in emission in the COE region and the decay in the CPE indicates a significant contribution from intermolecular energy transfer from PBS-PFP to adjacent DSSNI molecules.

The fluorescence decay times of 131 (τ_2) and 522 ps (τ_3) in water:dioxane and 127 and 454 ps in aqueous $C_{12}E_5$ are present at both emission wavelengths. At 420 nm, these stem from the complex emission of PBS-PFP. Dias et al. have attributed the decay time of a few hundred picoseconds lifetime (τ_2) to the decay of a singlet exciton located in the backbone, whose contribution to the overall decay depends on the degree of polymer aggregation;⁵² the long-lived emission from the isolated copolymer chains (when $[DSSNI] = 0$ M) is replaced by species with shorter fluorescence lifetimes (induced copolymer aggregates) formed on copolymer-COE self-assembly. If τ_2 and τ_3 are associated with the multiexponential behavior commonly found in polyfluorene derivatives, it is expected that the pre-exponential factors associated with τ_2 and τ_3 will only have a small contribution at 550 nm. However, this is not the case when DSSNI is present in solution (Figure 4c and d). In part, this stems from the multiexponential fluorescence profile of DSSNI (46, 360, and 1640 ps in water:dioxane and 130, 560, and 1830 ps in $C_{12}E_5$), which has been observed with several other oligo and poly-(phenylenevinylene) derivatives. However, it is also possible that the 300–600 ps lifetime has some contribution from the

equivalent component in PBS-PFP, resulting from energy migration and funneling from isolated sites on the CPE chain to the conjugated segment in closest contact to the COE, where energy transfer occurs.

The dependence of the fluorescence decay times and amplitudes of the PBS-PFP/DSSNI self-assembled system on DSSNI concentration collected at 420 nm are depicted in Figure 5. The decay component associated with the isolated polymer chain decay time (τ_3) decreases slightly; however, its amplitude (a_3) is strongly reduced with increasing DSSNI concentration. An idea of what may be happening comes from studies of on-chain and interchain energy transfer in polyindenofluorenes,⁵³ where intrachain energy migration is found to be far less efficient than the interchain (or intermolecular) process. The decrease of the a_3 amplitude with the DSSNI concentration confirms that τ_3 (=450–600 ps) at 420 nm, where only PBS-PFP emits, cannot be connected with the presence of the oligoelectrolytes.²⁷ Equally important is the fact that the pre-exponential amplitude associated with the fast component (a_1), which is a decay when monitored in the region where only the polymer emits, increases with the addition of DSSNI. Thus, its increase in the presence of DSSNI can only be connected with energy transfer from neighboring conjugation segments of the fluorene-based polyelectrolyte to the cationic oligomers. Similar behavior has previously been reported for the PBS-PFP/tris(bipyridyl)ruthenium(II) self-assembled system in solution.²⁷

Aggregation Behavior. From the above, it can be clearly seen that the solvent medium plays an important role in the interaction between the anionic PBS-PFP and oppositely charged conjugated oligoelectrolytes. This is strongly related

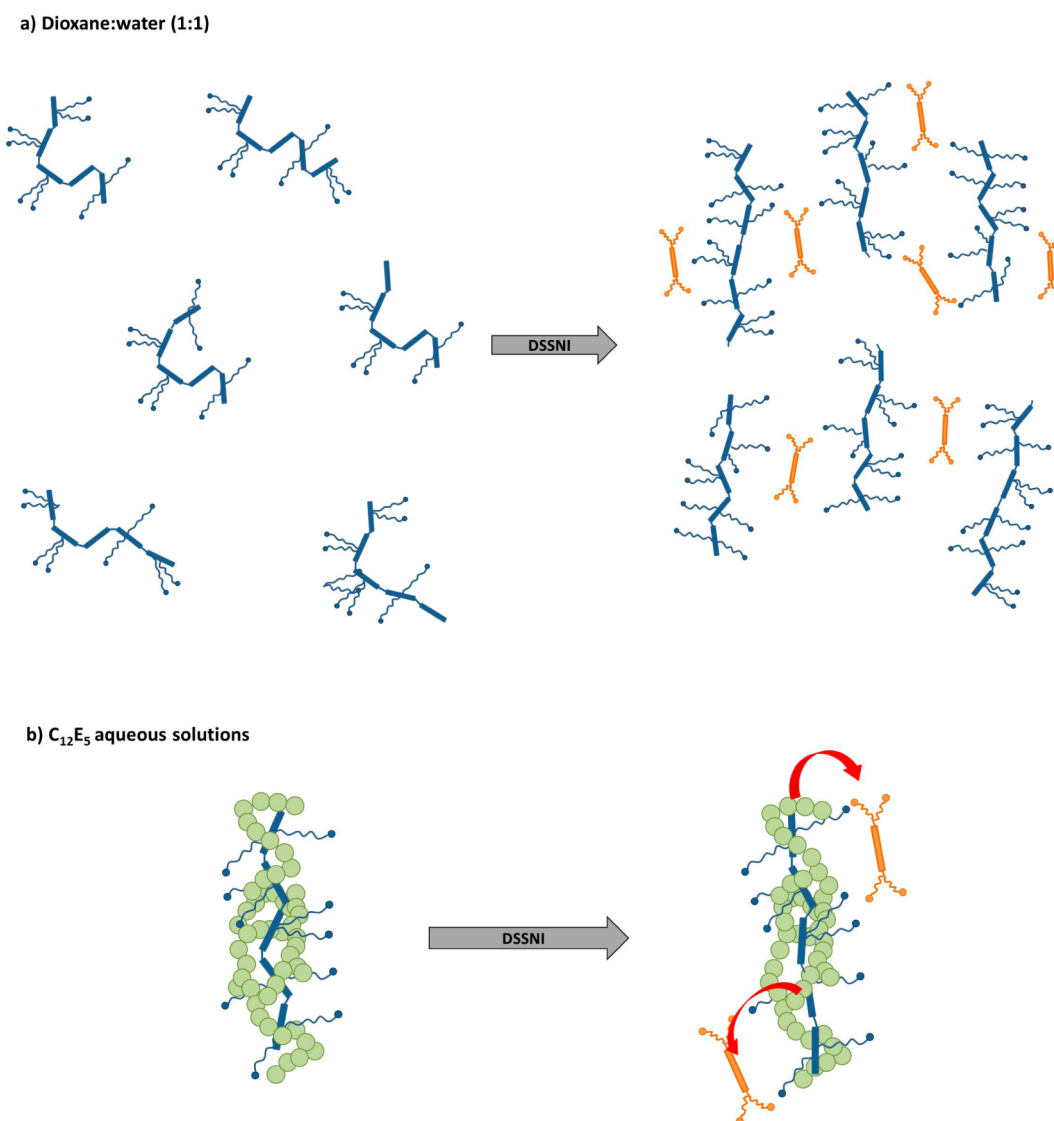


Figure 6. Schematic representation of the interaction between PBS-PFP and COE in (a) dioxane:water (1:1) and (b) $C_{12}E_5$ surfactant solutions.

to the conformations adopted by the conjugated polyelectrolyte and the local environment surrounding the PBS-PFP chains in solution. The conformation of PBS-PFP in solution is driven by hydrophobic and hydrophilic interactions between PBS-PFP polymer chains and the solvent. In the surfactant solutions, at concentrations above the $C_{12}E_5$ cmc, the interaction between the alkyl chain of the surfactant and the backbone of the CPE leads to the formation of cylindrical aggregates.²² Thus, the PBS-PFP hydrophobic chain is partially protected from the solvent (and from potential quenchers) and simultaneously adopts an extended conformation. In contrast, in water:dioxane (1:1, v:v), the polyelectrolyte conformation in solution results from the balance between the intrapolymeric interaction (hydrophobic and electrostatic interactions) and CPE–solvent interactions, which involve the hydrophilic interactions of the charged groups and the solvent, and the hydrophobic–hydrophilic interactions between the CPE backbone and the solvent.

The addition of the oppositely charged COE, and in particular of DSSNI, affects the photophysical properties of the PBS-PFP in both solvent systems. The marked differences seen in the two cases are consistent with differences in the type

of self-assembly, induced mainly by electrostatic interactions. In water:dioxane (1:1), the absorption maximum is shifted to longer wavelengths, while the PL maximum is blue-shifted with the increase in DSSNI concentration (see Table 3 and Figure 2a). Changes in absorption and emission maxima (Figure 2a), and in amplitudes in time-resolved fluorescence measurements (Figure 5a), show a sigmoidal dependence upon DSSNI concentration, indicating some critical aggregation process. In fact, the a_1 and a_3 values do not significantly change until a certain critical DSSNI concentration is reached, while above this a new plateau is reached (at $\sim 4 \times 10^{-7}$ M). These changes are in the concentration range at which the change in the maximum emission wavelength is observed (Figure 2a) and strongly suggest formation of mixed COE-CPE aggregates at a critical aggregation concentration around $0.200 \mu\text{M}$ COE. The formation of PBS-PFP/COE mixed aggregates corroborates well with the observed red-shift of the absorption spectra. When aggregates are present in solution, the excitation energy can migrate along the molecules in the aggregate until it is trapped at low energy sites. This leads to weak photoluminescence emission (low ϕ_{PL}) due to the high number of non-radiative relaxation pathways available.⁵⁴ The blue-shift of

the PL spectra observed in this solvent system may result from the emission of non-aggregated PBS-PFP chains and/or smaller PBS-PFP/DSSNI aggregates, whose emission becomes more important to the total emission at high DSSNI concentrations.

Preliminary small-angle X-ray scattering (SAXS) data confirms an increase of the scattering intensity at low q values (data not shown), indicating the presence of larger aggregates when COE is present in solution. This is similar to what is seen with surfactant–polyelectrolyte systems.⁵⁵ A schematic presentation of a possible structure is shown in Figure 6a.

With the surfactant solutions, both absorption and PL maxima are red-shifted upon addition of DSSNI (Figure 2b). It is also interesting to note that, in the aqueous $C_{12}E_5$ solutions, the new emission band has a maximum at ~ 560 nm, which does not depend on the COE length (Table 3). In this case, DSSNI is likely to be associated electrostatically with the cylindrical PBS-PFP/surfactant aggregates, as illustrated in Figure 6b. Red-shifts are seen in both the absorption and PL spectra in the surfactant solutions, suggesting an increase in the conjugation length of the polymer. However, these are observed at different DSSNI concentrations, suggesting that more than one effect is involved. One factor may be that binding of the COE reduces the conformational flexibility of the backbone, favoring emission from longer conjugation segments. Some support for this comes from time-resolved emission measurements.

In aqueous $C_{12}E_5$, the decay time of PBS-PFP (τ_1) increases upon addition of DSSNI, and the pre-exponential factor (a_1) vary linearly with increasing DSSNI concentration. This decay component is believed to have a contribution from CPE backbone conformational relaxation, and the increase in lifetime is consistent with decreased conformational mobility. As was mentioned above, in $C_{12}E_5$, the PBS-PFP is surrounded by a layer of surfactant molecules, forming rod-like core–shell aggregates.²² The linear dependence with DSSNI concentration of the pre-exponential factors indicates that the PBS-PFP/DSSNI/ $C_{12}E_5$ –water system forms a structure in which the COE molecules are increasingly bound to the PBS-PFP/ $C_{12}E_5$ aggregates (see Figure 6b). Although the total DSSNI concentration used is very low, due the presence of PBS-PFP/ $C_{12}E_5$ aggregates, the local concentration of DSSNI is much higher in the surrounds of these aggregates and DSSNI–DSSNI interactions might occur at high concentrations. Further support for this comes from the slight increase in the decay time assigned with the natural decay of DSSNI in the self-assembled system (collected at 550 nm); this increases from 1.64 to 2.01 ns with increasing DSSNI concentration from 2.5×10^{-7} to 8.65×10^{-7} M, which suggests interchromophore interactions.⁵⁶

CONCLUSIONS

The self-assembly between the anionic PBS-PFP polyelectrolyte and cationic phenylenevinylene oligoelectrolytes has been investigated via steady-state and time-resolved fluorescence in two different solvent systems, water:dioxane (1:1, v/v) mixtures, and aqueous $C_{12}E_5$ solutions. Förster resonance energy transfer is observed from the CPE to COE. The data imply that the quenching efficiency can be “tuned” by controlling the oligoelectrolyte size. The influence of the non-ionic surfactant $C_{12}E_5$ on the energy transfer of the PBS-PFP/phenylenevinylene oligoelectrolyte systems has been investigated and compared with the same systems in water:dioxane (1:1, v/v) mixtures. The PL decrease of PBS-PFP was

found to be less in aqueous 10^{-4} M $C_{12}E_5$ solutions than in the water:dioxane (1:1, v/v) mixture. In the presence of $C_{12}E_5$, the PBS-PFP copolymer exists as isolated chains that are surrounded by the non-ionic surfactant with the sulfonate groups of the side chains extended into the aqueous phase. Such a structure limits the accessibility of the conjugated PBS-PFP main chain to the COEs and is consistent with a core–shell structure (PBS-PFP/surfactant) that is decorated along the main chain with COE moieties. The modulation of the CPE–COE interaction is an important feature of this complex aggregation process. The differences in behavior promoted by DSSNI in the two solvent media also imply different effects on the PBS-PFP backbone conformation, which are consistent with differences in the self-assembly. While water:dioxane and $C_{12}E_5$ –water mixtures allow for a disruption of PBS-PFP clusters that are formed in aqueous solutions, the addition of DSSNI is shown to produce more complex aggregates with potentially interesting properties. PBS-PFP in dioxane:water promotes a relatively high degree of aggregation which might be important for applications where strong interchain interactions are expected to play an important role (e.g., for charge transport). The $C_{12}E_5$ –water system leads to the formation of structurally different aggregates without pronounced interchain interactions. In contrast, some DSSNI–DSSNI interactions are suggested for this system at higher COE concentration.

Thus, it has been demonstrated that conjugated oligoelectrolytes are efficient energy transfer acceptors. This opens the possibility of using these oligoelectrolytes as intermediators in several applications. Combining the optical and light-harvesting properties of CPEs with COEs, which can simultaneously work as acceptors and donors, it is possible to develop new platforms in which sequential energy transfer processes are possible.

ASSOCIATED CONTENT

Supporting Information

Absorption and emission spectra of DSBNI, DSSNI, and COENI in aqueous solutions, $C_{12}E_5$ solutions, and dioxane:water (1:1) mixtures; absorption spectra of PBS-PFP, DSSNI, and PBS-PFP/DSSNI mixed system; absorption and PL spectra of PBS-PFP with increasing concentrations of DSBNI and COESNI; PL spectra of DSSNI (6.48×10^{-7} M) and PBS-PFP/DSSNI (6.48×10^{-7} M) mixed system in 10^{-4} M aqueous $C_{12}E_5$ micelles; normalized excitation spectra of a PBS-PFP/COESNI (4.95×10^{-7} M) self-assembled system collected at 410 and 600 nm. 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.

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