# Energy Transfer from Fluorene-Based Conjugated Polyelectrolytes to On-chain and Self-Assembled Porphyrin Units

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ABSTRACT: A new water soluble fluorene-based polyelectrolyte containing on-chain porphyrin units has been synthesized via Suzuki coupling, for use in optoelectronic devices. The material consist of a random copolymer of poly{1,4-phenylene-[9,9bis(4-phenoxy butylsulfonate)]fluorene-2,7-diyl} (PBS-PFP) and a 5,15-diphenylporphyrin (DPP). The energy transfer process between the PBS-PFP units and the porphyrin has been investigated through steady state and time-resolved measurements. The copolymer PBS-PFP-DPP displays two different emissions one located in the blue region of the spectra, corresponding to the fluorene part and another in the red due to fluorescent DPP units either formed directly or by exciton transfer. However, relatively inefficient energy transfer from the PFP to the on-chain porphyrin units was observed. We compare this with a system involving an anionic blue lightemitting donor PBS-PFP and a anionic red light-emitting

**INTRODUCTION** The development of efficient conjugated polymer (CP) materials for organic electronics is a challenging area, with intensive ongoing research in topics such as organic light emitting diodes (OLEDs), organic field effect transistors, photovoltaics, sensors, and nanowires.<sup>1-6</sup> The addition of different chromophores as functional units to these CP systems allows the introduction of new properties, by tuning the emission through electronic energy transfer, and hence, the design of new intelligent materials.<sup>4-9</sup> In OLEDs, full-color displays can be achieved by combining blue light-emitting fluorescent materials (either as emitter or as hosts) with green and red fluorescent dopants as the emitters.<sup>10–14</sup> Initial studies on such energy transfer systems generally used blends of donor and acceptor. However, this has the limitation that it often leads to phase separation. Greater efficiency may be anticipated if the chromophore is attached to the CP, either by covalently bonding in the backbone or by linking to the side chains. When bonding is in the main chain, the electronic structure, HOMO/LUMO levels,

energy acceptor *meso*-tetrakisphenylporphyrinsulfonate (TPPS), self-assembled by electrostatic attraction induced by  $Ca^{2+}$ . Based on previous studies related to chain aggregation of the anionic copolymer PBS-PFP, two different solvent media were chosen to further explore the possibilities of the self-assembled system: dioxane-water and aqueous nonionic surfactant *n*-dodecylpentaoxyethylene glycol ether ( $C_{12}E_{5}$ ). In contrast, with the on-chain PBS-PFP-DPP system the strong overlap of the 0-0 emission peak of the PBS-PFP and the Soret absorption band of the TPPS results in an efficient Förster transfer. This is strongly dependent on the solvent medium used. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 1408–1417, 2012

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and bandgaps of CPs can be manipulated through arrangement of electron, or energy donor (D), and acceptor (A) units.<sup>15–17</sup> Such covalent attachment of a dye molecule to the polymer backbone will broaden the absorption window of the CP and extend it to longer wavelengths.<sup>18–20</sup> This is of particular importance in polymer bulk heterojunction solar cell devices, as extending the spectral range of the polymeric material to the red region will increase light absorption by the active layer, leading to higher short-circuit currents and efficiencies.<sup>18–22</sup> In contrast to these structural and spectral advantages, experimental studies indicate that intrachain energy transfer in isolated polymer chains is up to an order of magnitude less efficient than energy transfer between chains in polymer films.<sup>23</sup> Our goal is to develop methods of increasing electronic energy transfer within isolated CP chains.

Poly(*para*-phenylene) type polymers and the related polyfluorenes (PFs) are a particularly interesting class of CPs.

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**PBS-PFP-DPP** 

SCHEME 1 Chemical structures of the homopolymer PBS-PFP, the DPP monomer and the copolymer PBS-PFP-DPP.

PFs display high photoluminescence (PL) efficiencies and quantum yield, both in solution and in solid state, with emission wavelengths in the blue spectral region, in addition to good thermal and photostablility.<sup>24,25</sup> Fluorene-based copolymers are also attractive as energy donors in Förster resonance energy transfer<sup>26,27</sup> (FRET). By doping, or covalent attachment of a lower bandgap material in the PF main chain, the polymer emission can be tuned to longer wavelengths by FRET.<sup>28</sup> For red emission, either polar moieties, such as electron donor substituted pyran derivatives, or nonpolar ones involving extensive  $\pi$  conjugation, such as perylene derivatives or porphyrin-type macrocyclic compounds have been studied.<sup>29,30</sup> Systems involving PFs and red emitting porphyrins are particularly good candidates for FRET, because of the excellent spectral overlap of donor emission and acceptor absorption.<sup>30-35</sup> Porphyrins are compounds of interest due to their valuable photophysical properties<sup>36</sup> that allow their use in a large number of practical applications, such as molecular photonic devices, artificial photosynthetic systems and dye-sensitized solar cells.4,18,37-39 Porphyrins bearing hydrophilic pendant groups are able to interact with relevant biomolecules, as nucleic acids, polypeptides, and proteins.<sup>40</sup> In addition, these are excellent systems for testing models of electronic energy transfer in CPs.41-44 In particular, the Förster model for electronic energy transfer using point dipoles appears to break down at small PF-porphyrin distances, and the efficiency of energy transfer is suggested to show considerable differences if the two moieties are colinear or cofacial.43 In this article, we compare singlet-singlet electronic energy transfer in two Fluorene-based anionic conjugated polyelectrolytes, which have different PF-porphyrin orientations. For the collinear system, we synthesized an anionic poly(fluorene-alt-phenylene) with porphyrin units incorporated randomly on the backbone (Scheme 1). In the second system, we have self-assembled the polymer and porphyrin fluorophore. We have previously shown electronic



energy transfer within a self-assembled system involving anionic porphyrins and cationic fluorene-based conjugated polyelectrolytes.<sup>32</sup> Metal ions, such as calcium(II), can also induce self-assembly of anionic conjugated polyelectrolytes.<sup>45,46</sup> We extend this to calcium(II) induced self-assembly of an anionic poly(fluorene-*alt*-phenylene) conjugated polyelectrolyte and an anionic tetraphenylporphyrin and have studied the electronic energy transfer, both in large aggregates and surfactant modulated systems, as models for cofacial energy transfer.

#### **EXPERIMENTAL**

#### Synthesis

2,7-Dibromo-9,9-bis(4-sulfonylbutoxyphenyl)fluorene and poly {1,4-phenylene-[9,9-bis(4-phenoxy-butylsulfonate)]fluorene-2,7diyl} (PBS-PFP) were prepared according to published procedures and have been described elsewhere.<sup>41</sup> The synthesis of dipyrromethane and 5,15-diphenylporphyrin (DPP) was carried out with slight modifications of previously described methods.<sup>47,48</sup> See Supporting Information for the compounds characterization.

#### 5,15-Dibromo-10,20-diphenylporphyrin

DPP (300 mg, 0.58 mmol) were dissolved in 300 mL of CHCl<sub>3</sub> and 2.4 mL of pyridine. The mixture was cooled to 0 °C and 240 mg of *N*-bromosuccinimide (1.22 mmol, 2.1 eq) were added and the solution was stirred for 60 min. The reaction was quenched with acetone (50 mL) and the solvent was evaporated yielding a product that was washed with methanol.<sup>48</sup> Recrystallization from toluene/MeOH gave 347 mg of the title compound as purple crystals (0.56 mmol, 96%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 9.62 (d, J = 4.7 Hz, 4H, H<sub> $\beta$ </sub>), 8.84 (d, J = 4.7 Hz, 4H, H<sub> $\beta$ </sub>), 8.17–8.15 (m, 4H, Ph-Ho), 7.83–7.75 (m, 6H, Ph-H*m*,*p*), –2.72 (br s, 2H, NH).

The HOMO values of the DPP were measured using atmospheric pressure photoelectron spectrometry (Riken *Keiki AC-2*) and the LUMO calculated from the HOMO and optical band-gap (determined via the intersection of the absorption and emission thin film spectra).<sup>49–51</sup> HOMO = 5.04 eV and LUMO = 3.17 eV.

## Poly{1,4-phenylene}-*co*-{[9,9-bis(4-phenoxy-butylsulfonate)] fluorene-2,7-diyl}-*alt*-{1,4-phenylene(5,15-diphenylporphyrin) PBS-PFP-DPP

For the preparation of the copolymer PBS-PFP-DPP, a mixture of 2,7-dibromo-9,9-bis(4-sulfonylbutoxyphenyl)fluorene (0.742 g, 0.90 mmol), 5,15-dibromo-10,20-diphenylporphyrin, DPP (0.062 g, 0.10 mmol), 1,4-benzenediboronic acid (0.166 g, 1 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (50 mg), and Na<sub>2</sub>CO<sub>3</sub> (1.0 g, 9.4 mmol)<sup>41</sup> in 40 mL of THF and 20 mL of water were reacted for 4 days at 110 °C. The aqueous layer was washed with chloroform and concentrated to dryness. The residue was extracted with dichloromethane via Soxhlet, redissolved in a mixture of water and THF 50% (v/v) and purified by dialysis using a membrane with a cutoff of 3500 g mol<sup>-1</sup>. Based on the monomer/DPP ratio in the starting reaction mixture, the copolymer is expected to contain on average 10% (mol %) DPP units. Total yield of the copolymer PBS- PFP-DPP was 655 mg (91%). <sup>1</sup>NMR (600 MHz, *d*-THF 50% D<sub>2</sub>O, ppm) 8.95–8.87 (ar-H DPP), 8.2–6.6 (ar-H DPP and ar-H fluorene), 4.1–3.9 ( $\gamma$  –CH<sub>2</sub>), 2.98–2.86 ( $\alpha$  –CH<sub>2</sub>), 2.0–1.9 ( $\beta$ ,  $\delta$  –CH<sub>2</sub>).

GPC (NMP, LiBr, UV-detection)  $M_{\rm w} = 1400$  g mol<sup>-1</sup>,  $M_{\rm w}/M_{\rm n} = 1.4$ . The  $M_{\rm w}$  of the copolymer is likely to be considerably underestimated due to the interactions between the polyelectrolyte and the column material.

#### **Steady State Spectroscopic Measurements**

The measurements were recorded in water, and dioxanewater (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. Nonionic surfactant n-dodecylpentaoxyethylene glycol ether  $(C_{12}E_5)$  was purchased from Aldrich and used without further purification. 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. Fluorescence quantum yields were measured using quinine sulfate in 0.5 M sulfuric acid (for the poly(fluorene-alt-phenylene) region) and meso-tetrakis-phenylporphyrin (TPP) in toluene (for the DPP region) as references. Corrections were made for changes in refractive index.<sup>52</sup>

#### **Picosecond TCSPC Experiments**

Picosecond time-resolved fluorescence measurements were performed using a home-built picosecond time correlated single photon counting (TCSPC) apparatus, in which the excitation source consists of a picosecond Spectra Physics modelock Tsunami laser (Ti:sapphire) model 3950 (repetition rate of about 82 MHz, tuning range 700-1,000 nm), pumped by a Millennia Pro-10s, frequency-doubled continuous wave, diode-pumped, solid-state laser ( $\lambda_{em} = 532$  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 afterwards 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 using a Becker & Hickl SPC-630 TCSPC module. Fluorescence decays and the instrumental response function (IRF) were collected using 4096 channels in a 0.814, 6.1, and 9.8 ps/channel scale, until 1.5  $\times$  10<sup>3</sup> and 3  $\times$ 10<sup>3</sup> counts at maximum were reached. The full width at halfmaximum (fwhw) 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. 53.

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TABLE 1 Spectral and Photophysical Parameters of PBS-PFP-DPP in Dioxane–Water (1:1) and 1  $\times$  10<sup>-4</sup> M C<sub>12</sub>E<sub>5</sub>

Solvent	Absorption max (nm)	Emission max (nm)	$\Phi_{\rm F}~{\rm PF}~\lambda_{\rm exc}$ 362 (nm)	$\Phi_{\rm F}$ DPP $\lambda_{\rm exc}$ 362 (nm)
Dioxane-water (1:1)	365, 420 (PF, DPP)	410, 650 (PF, DPP)	0.41	0.013
$1\times10^{-4}$ M aqueous $C_{12}E_5$	367, 425 (PF, DPP)	411, 655 (PF, DPP)	0.34	0.017

## **RESULTS AND DISCUSSION**

## **Absorption and Fluorescence**

The anionic copolymer poly(fluorene-*alt*-phenylene)-porphyrin (PBS-PFP-DPP) (Scheme 1) was studied by UV-Vis absorption, PL spectroscopy and time-resolved fluorescence (TCSPC) measurements. Anionic fluorene-based conjugated polyelectrolytes tend to aggregate in aqueous solution to form ill-defined clusters.<sup>54</sup> To minimize this, measurements have been made in a 1:1 dioxane–water mixture and in water in the presence of  $1 \times 10^{-4}$  M nonionic surfactant  $C_{12}E_{5}$ .

In both solvent systems two characteristic absorption regions are observed in the UV–Vis absorption spectrum, which are attributed to the poly(fluorene-*alt*-phenylene) backbone (broad absorption at 365 nm) and to the on-chain porphyrin (DPP) units (various bands between 420 and 650 nm)—Table 1, Figures 1 and 2. The strong narrow absorption peak at 420 nm and the four smaller absorption peaks between





**FIGURE 1** (a) Absorption (solid line) and emission spectra (dashed line) of PBS-PFP-DPP in dioxane-water (1:1), with excitation at 365 nm (dashed line) and 420 nm (dotted line). The inset depicts the 600-750-nm region of the PBS-PFP-DPP emission shown in the main plot. (b) Fluorescence excitation spectra with emission at 410 nm (solid line) and emission at 655 nm (dashed line) of PBS-PFP-DPP in dioxane-water (1:1).

**FIGURE 2** (a) Absorption (solid line) and emission spectra (dashed line) of PBS-PFP-DPP in 1  $\times$  10<sup>-4</sup> M aqueous C<sub>12</sub>E<sub>5</sub> solution, with excitation at 365 nm (solid line) and 420 nm (dotted line). (b) Fluorescence excitation spectra with emission at 410 nm (solid line) and emission at 655 nm (dashed line) of PBS-PFP-DPP in 1  $\times$  10<sup>-4</sup> M aqueous C<sub>12</sub>E<sub>5</sub>.



FIGURE 3 Spectral overlap between the donor PBS-PFP (dotted line) and the acceptor DPP (full line).

520 and 650 nm correspond to the so-called "Soret" and "Q" bands, respectively, typical of porphyrins.<sup>55</sup> The presence of four absorptions in the Q band region, corresponding to the (0,0) and (0,1) vibronics of the  $Q_x$  and  $Q_y$  bands, confirms that the porphyrin is present as its free base. Excitation of PBS-PFP-DPP at 365 nm leads to emission from both PF and DPP, whereas excitation at 420 nm shows only emission from the DPP units (Figs. 1 and 2). Fluorescence excitation spectra for emission in the porphyrin region reveals two maxima in the PF and DPP region, demonstrating efficient electronic energy transfer from the fluorene to the porphyrin units. However, differences in the relative intensities are observed in dioxanewater and in  $1 \times 10^{-4} \; \text{M}$  aqueous  $C_{12} E_5$  solutions. In particular, the ratio of PF to DPP intensities is higher in  $C_{12}E_5$  solution than in dioxane-water. Small angle X-ray scattering (SAXS), cryotransmission electron microscopy, molecular dynamics simulations,<sup>56</sup> together with small angle neutron scattering (SANS) on PBS-PFP solutions in the presence of  $C_{12}E_{5}^{57}$ strongly suggest that in the presence of  $C_{12}E_5$ , the CP is present as a mixed cylindrical aggregate in which the polymer backbone is surrounded by a layer of surfactant molecules. Furthermore, a similar effect was observed with the closely related poly{9,9-bis[6-(*N*,*N*,*N*-trimethylammonium)alkyl]fluorene-co-1,4-phenylene} iodide cationic conjugated polyelectrolyte.<sup>58</sup> This is expected to have the two effects of increasing backbone rigidity and at the same time decreasing solvent access to the PF chain. We believe that with PBS-PFP-DPP, the increased rigidity will facilitate on-chain exciton migration and, hence, the efficiency of energy transfer to the porphyrin unit.

Photoluminescence quantum yield (PLQY) measurements made for the PBS-PFP-DPP copolymer in the solvent mixture dioxane-water (1:1) and in an aqueous solution of nonionic surfactant  $C_{12}E_5$  are presented in Table 1. The energy transfer quantum yields for PFP to DP units is greater in  $C_{12}E_5$  solution than in 1/1 dioxane water. This may be associated with the decrease in conformational disorder when encapsulated by the surfactant and is consistent with the results from the fluorene excitation spectra. There is a slight decrease in the PLQY values for the copolymer PBS-PFP-DPP compared with that of the polymer without the porphyrin chromophore, PBS-PFP, for As shown in Figure 3, there is a strong overlap between the 0-0 emission band of the homopolymer PBS-PFP and the Soret absorption of the DPP; as the emission from the Soret band is weak, it acts as a dark state and the emission arises preferentially from the lowest energy  $Q_x$  band.<sup>35</sup>

#### **Time-Resolved Fluorescence**

Fluorescence decays were obtained in the dioxane-water (1:1) mixture on excitation in the poly(fluorene-*alt*-phenylene) unit (372 nm) and collected at the PF and DPP emission maximum (Figure 4 and Table 2). A value of 550 ps ( $\tau_3$ ) that dominates the decay, together with a shorter lifetime value of 60 ps ( $\tau_1$ ), is found when the data is collected



**FIGURE 4** Fluorescence emission decay for PBS-PFP-DPP in dioxane water (1:1) collected at (a) 410 nm and (b) 650 nm obtained with  $\lambda_{\rm exc}$  372 nm at 298.15 K. 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  $\chi^2$  are also presented.

	$\lambda_{em}$ (nm)	τ <sub>1</sub> (ns)	τ <sub>2</sub> (ns)	τ <sub>3</sub> (ns)	τ <sub>4</sub> (ns)	a <sub>i1</sub>	a <sub>i2</sub>	a <sub>i3</sub>	a <sub>i4</sub>	$\chi^2$
Dioxane-Water (1:1)	410	0.06	-	0.55	-	0.140	-	0.860	-	1.05
	650	-	0.13	0.61	8.60	_	0.227	0.401	0.372	0.98
C <sub>12</sub> E <sub>5</sub>	410	0.05	-	0.59	-	0.388	-	0.612	-	1.04
	650	-	0.37	-	9.00	_	0.366	-	0.634	0.96

**TABLE 2** Fluorescence Decay Times ( $\tau_i$ ) and Pre-Exponential Factors ( $a_{ij}$ ) for the Copolymer PBS-PFP-DPP Obtained with Excitation at 372 nm, Emission ( $\lambda_{em}$ ) at the Wavelength Maxima and T = 298 K

at 410 nm (see Figure 4a) in agreement with previous observations.<sup>60</sup> The longer decay lifetime  $(\tau_3)$  has a value very close to the previously described for PBS-PFP dispersed in the  $C_{12}E_5$  micellar system<sup>41,61</sup> and is attributed to the natural decay of the PF backbone.<sup>41</sup> The fast component  $(\tau_1)$  is suggested to be related either to the formation of an initially formed nonrelaxed conformer, that decays giving rise to a more stable one,<sup>60</sup> or to on-chain energy transfer process.<sup>60</sup> Nevertheless, sums of three discrete exponentials functions were needed to fit the excited state data collected at 650 nm. In dioxane-water, an intermediate decay component of 130 ps is observed. A similar decay time of  $\sim$  130 ps has been reported previously for the cluster morphology adopted by polyelectrolytes in solution.<sup>62</sup> However, this seems unlikely in this case and in agreement with suggestions of a closely related self-assembled porphyrin/conjugated polyelectrolyte system, we feel that the component is more likely due to exciton migration along the polymer chain.<sup>32</sup> This component becomes longer lived and more important in C<sub>12</sub>E<sub>5</sub> solutions, the system showing more efficient energy migration from PF to DPP units. The 8.60 ns component is assigned to emission from the DPP units, in agreement with the values published for PPV and PF doped with porphyrins.<sup>34,63</sup>



SCHEME 2 Structure of the electronic energy acceptor TPPS.

#### TPPS Self-Assembled with PBS-PFP via Calcium (II) Binding

With PBS-PFP-DPP, the porphyrin is expected to be collinear with the PF units. We will now discuss the second PFporphyrin energy transfer system, in which the anionic porphyrin meso-tetrakisphenylporphyrinsulfonate (TPPS) is selfassembled by calcium(II) ions to the homopolymer PBS-PFP (Scheme 2) and the PF and porphyrin units are expected to be cofacial. The potential application of this system in sensing and in molecular logic will be described elsewhere.<sup>64</sup> We have previously reported the photophysics of a cationic PFP system self-assembled by electrostatic interactions to TPPS.<sup>32</sup> These self-assembled systems have the advantage that by tuning the solvent and stoichiometry, it is possible to control the amount of porphyrin and, possibly, structural morphology and disorder of the materials. The characterization of the hydrophilic porphyrin has been described elsewhere.<sup>65</sup> The absorption and emission spectra of PBS-PFP were recorded in the same solvents used with PBS-PFP-DPP, dioxane-water (1:1) and 1  $\times$   $10^{-4}$  M aqueous  $C_{12}E_5$  solutions (above the surfactant critical micelle concentration).

Calcium (II) modulates the self-assembly between the two negatively charged components. Energy transfer from the PBS-PFP to the anionic porphyrin is evident from the PL spectra (Fig. 5). By adding different concentrations of porphyrin to the polyelectrolyte at fixed  $Ca^{2+}$  concentration 2  $\times$  $10^{-3}$  M, there was a decrease in the fluorescence band in the PF region and a corresponding increase seen in the emission band of the porphyrin ( $\lambda_{max} = 650$  nm). The quenching effect is most pronounced when the polyelectrolyte is dissolved in the dioxane-water cosolvent solution mixture, see Figure 6. As will be seen, significant differences are observed in energy transfer from PF to porphyrin units in the onchain and self-assembled systems, in agreement with the predictions of Wong et al.42 In addition to effects of orientation of the donor-acceptor units, other nonradiative deactivation processes may be possible in the PBS-PFP-DPP copolvmer, including charge transfer, triplet formation, excitonexciton annihilation, and molecular excimer formation.<sup>35,66,67</sup> With the low light intensity and dilute solutions used, the latter two processes are unlikely.

For the self-assembled system, control experiments of the effect of  $2 \times 10^{-3}$  M Ca<sup>2+</sup> on the PL of the PBS-PFP copolymer solutions were also performed and no significant differences were observed in the spectral shape or maximum (see Supporting Information). Nevertheless, the PLQY decreases



**FIGURE 5** PL spectra of PBS-PFP/Ca<sup>2+</sup> with increasing TPPS concentrations in water–dioxane (1:1) (left) and in 1  $\times$  10<sup>-4</sup>M C<sub>12</sub>E<sub>5</sub> (right). Ca<sup>2+</sup> concentration 2  $\times$  10<sup>-3</sup> M.

in the presence of  $Ca^{2+}$  as a consequence of the metal interaction with the polar copolymer side chains inducing aggregation.<sup>46</sup> The PL deactivation by Ca<sup>2+</sup> of the copolymer in the 1:1 dioxane-water mixture is 30% more effective than in the surfactant solution (see Supporting Information). The spectral changes observed in the PL spectra (Figure 7) are mainly due to the strong attenuation by the overlap of the absorption of the porphyrin Soret band and the PBS-PFP copolymer fluorescence (Fig. 3).<sup>32</sup> The PL quenching is more pronounced in dioxane-water (1:1) mixture, Figure 5 and Table 3, as calcium ion induces strong copolymer-aggregation,<sup>46</sup> and the large aggregates are likely to favor energy transfer from multiple PBS-PFP units toward TPPS. In contrast, for the self-assembled system in the presence of the nonionic surfactant, a lower PLQY was found for the TPPS on excitation of PBS-PFP (Table 3). It is known that  $C_{12}E_5$ wraps around the copolymer forming supramolecular structures that shield the PBS-PFP from the aqueous solvent.55,68 This means that calcium ions are likely to only bind to the



**FIGURE 6** PL maximum intensity as a function of TPPS concentration in water-dioxane (1:1) (left) and in  $1 \times 10^{-4}$  M  $C_{12}E_5$  (right); squares: PBS-PFP emission and triangles: TPPS emission.



**FIGURE 7** PL spectra of PBS-PFP without TPPS (solid line) and with maxima TPPS concentration (dot line) obtained with excitation in the PF absorption maximum and TPPS emission (dash line) obtained with excitation at 420 nm, in water-dioxane (1:1) (right) and in  $1 \times 10^{-4}$  M C<sub>12</sub>E<sub>5</sub> (left).

exposed sulfonate groups on a single PBS-PFP chain, such that energy transfer is from one CPE molecule to the bound porphyrin. SAXS and SANS studies are in progress to obtain more structural information on these systems.

Fluorescence decays of the system PBS-PFP+ $Ca^{2+}$ +TPPS, with increasing anionic porphyrin concentration were collected at the PBS-PFP. The decays were fitted with sums of three discrete exponential functions and the corresponding decay times and amplitudes, as a function of the porphyrin concentration were plotted, Figure 8.

The dependence of the decay times and amplitudes, presented in Figure 8 is similar to the behavior observed for the system involving the cationic fluorene-based polyelectrolyte poly(9,9-bis(6'-N,N,N-trimethylammonium)hexyl)fluorene phenylene)bromide (HTMA-PFP) and different hydrophilic porphyrins.<sup>32</sup> The long component ( $\tau_3$ ) has a value very close to that previously reported for PBS-PFP with C<sub>12</sub>E<sub>5</sub> in water<sup>41</sup> and the presence of calcium does not seem to affect the lifetime of the polyelectrolyte, see Supporting Information. The PBS-PFP lifetime is, as previously observed in the PL data, quenched with increasing porphyrin concentration (Fig. 6). Attribution of the fastest component ( $\tau_1$  ca. 20 ps for a TPPS concentration of 8.03 × 10<sup>-7</sup> M) is still troublesome and it has been attributed to both energy transfer and

**TABLE 3** PL Quantum Yields of PBS-PFP/Ca<sup>2+</sup> Self-Assembled with TPPS in Dioxane–Water (1:1) and 1 × 10<sup>-4</sup> M  $C_{12}E_5$  (Ca<sup>2+</sup> Concentration 2 × 10<sup>-3</sup> M)

Solvent	TPPS (M)	$\Phi_{\sf F} \ {\sf PF}^{\sf a} \ \lambda_{\sf exc}$ 382 (nm)	$\Phi_{\rm F}  {\rm TPPS}^{\rm b}  \lambda_{\rm exc}$ 382 (nm)
Dioxane–Water (1:1)	$2.44\times10^{-6}$	0.06	0.07
C <sub>12</sub> E <sub>5</sub>	$2.44\times10^{-6}$	0.05	0.03

<sup>a</sup> Quinine sulfate was used as reference, phiF = 0.546.

<sup>b</sup> TPP was used as reference, phiF = 0.11.



**FIGURE 8** Fluorescence decay times ( $\tau_i$ ) and amplitudes ( $a_{ij}$ ) of PBS-PFP (10<sup>-6</sup> M) with Ca<sup>2+</sup> (1 × 10<sup>-3</sup> M) in 1 × 10<sup>-4</sup> M C<sub>12</sub>E<sub>5</sub> as a function of TPPS concentration.

conformational relaxation of the copolymer chain.<sup>32,60</sup> However, with the present system and based on the decay profile and data of Figure 9, a rise time (ca. 7 ps at the same TPPS concentration) is attributed to the fast component, providing evidence that energy transfer is taking place and dominating the deactivation pathways occurring in the excited states of the self-assembled donor/acceptor system. The origin of the intermediate lifetime component,  $\tau_2$ , has been discussed previously and attributed to exciton migration, either on-chain or intrachain (within aggregates).<sup>32,62</sup>



**FIGURE 9** Fluorescence emission decay of PBS-PFP (10<sup>-6</sup> M) with Ca<sup>2+</sup> (1 × 10<sup>-3</sup> M) in 1 × 10<sup>-4</sup> M C<sub>12</sub>E<sub>5</sub> and TPPS concentration maxima, obtained with  $\lambda_{exc}$  392 nm at 298.15 K. For a better judgment of the quality of the fits weighted residuals (W.R. scale,  $-3 \le \sigma \le +3$ ), autocorrelation functions (A.C.) and  $\chi^2$  are also presented.

The FRET of the self-assembled system is always more efficient than in the PBS-PFP-DPP copolymer. This resembles the behavior described for poly[2-methoxy-5(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) porphyrin blends.69 As demonstrated by Morgado et al. the distribution of the porphyrin chromophore within the polymer does not match the one for the self-assembled system and the copolymer. Hence, the differences in the efficiency of the energy transfer and the concentration quenching effects might contribute for the different observations. The results are also in complete agreement with the ideas of Wong et al.<sup>42</sup> on cofacial energy transfer in PF-porphyrin systems being more efficient than the collinear case. Although the porphyrin ring and polymer backbone may not be perfectly parallel, a small deviation from cofacial geometry is not likely to significantly affect the efficiency of Förster energy transfer. Despite these authors have questioned the validity of the use of point dipoles in Förster theory<sup>70,71</sup> to treat electronic energy transfer between these donor and an acceptor units, it is instructive to compute the radius,  $R_0$  that identify the distance at which the transfer occurs with 50% efficiency. Table 4 comprises the  $R_0$  values for the PBS-PFP-DPP copolymer and for the self-assembled system PBS-PFP/TPPS.

**TABLE 4** Föster Radius,  $R_0$ , of PBS-PFP-DPP and of PBS-PFP with TPPS

Solvent	System	<i>R</i> <sub>0</sub> (Å)
Dioxane–Water (1:1)	PBS-PFP-DPP	62
	PBS-PFP/TPPS	47
C <sub>12</sub> E <sub>5</sub>	PBS-PFP-DPP	61
	PBS-PFP/TPPS	50

As expected the  $R_0$  value vary for the two systems according to PBS-PFP/TPPS  $\leq$  PBS-PFP-DPP. However, the efficiency of the porphyrin PL runs counter to expectation on the basis of Förster theory, as the copolymer PBS-PFP-DPP is the least efficient despite the larger  $R_0$  value.<sup>72</sup> As mentioned before, when we discussed the properties of the PBS-PFP-DPP, other factors than the Förster efficiency govern the copolymer PL efficiency.<sup>72</sup> Overall, the values calculated for the Förster distance are comparable to what had been determined for the singletsinglet Förster transfer, from fluorene-based polyelectrolytes and oppositely charged complexes and porphyrins.<sup>32,73</sup>

### CONCLUSIONS

We have explored the mechanisms for energy transfer in two fluorene-based conjugated polyelectrolytes (donor) systems, with on-chain porphyrin (acceptor) moieties and self-assembled with an anionic porphyrin bound electrostatically by  $Ca^{2+}$ .

Investigation of the photophysical properties of the conjugated polyelectrolytes (CPEs) leads to the conclusion that the polymers are relatively free from aggregation in the solvent mixtures,  $C_{12}E_5$  and water organic cosolvent.

Time-resolved experiments and steady state measurements have been conducted in solution to unravel the role of energy transfer on both systems. The energy transfer process in the PBS-PFP-DPP case should compete with other deactivation processes, such as radiative decay of the singlet excitons photogenerated on the donor-acceptor conjugated chains and copolymer solution conformational changes. The existing difference between the overall energy transfer efficiency among the PBS-PFP-DPP copolymer and the selfassembled system is attributed to the porphyrin chromophore content within the polymer, that is not necessarily equal to the TPPS in solution concentration. As observed by Morgado et al.<sup>69</sup> the energy transfer efficiency values in a MEH-PPV porphyrin blend and in a MEH-PPV-porphyrin copolymer are similar only when the copolymer possesses the highest porphyrin concentration. Furthermore, the spatial extent, intermolecular separation and relative orientations of transition dipole densities on the donor and acceptor PFporphyrin copolymers determinate the rate of electronic excitation transfer, as observed for the cofacial and collinear orientations between the donor and the acceptor.

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