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Characterization of the Photoluminescence Quenching of Mixed Water-Soluble Conjugated Polymers for Potential Use as Biosensor Materials

E. López Cabarcos* and Sue A. Carter

Physics Department, University of California, Santa Cruz, California 95064

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ABSTRACT: The influence of oxygen and polymer concentration on the quenching of the photoluminescence (PL) from a water-soluble conjugated macromolecule, sodium poly[2-(3-thienyl)ethyloxy-4-butylsulfonate)] (PTE-BS), was investigated. The presence of oxygen in the polymer solution decreases the photoluminescence by 6.4%. The sharp changes observed in the PL when the concentration of the polymer is varied between 4×10^{-5} and 9×10^{-4} M result in small changes in the Stern−Volmer constant, K_{SV}, because the quenching is equally affected by the polymer concentration. Thus, K_{SV} only decreases from 2.4×10^{-4} down to 1.3×10^{-4} when the concentration of the polymer in the solution increases a factor of 10, from 1.8×10^{-4} up to 1.8×10^{-3} M. When the PL of the solution is 50% of its initial value (K_{SV} = 1/(quencher concentration)), a sharp change in the slope of the Stern−Volmer plots indicates the beginning of quenching saturation that occurs when most of the accessible polymer segments are quenched. Mixtures of the water-soluble polymers PTE−BS and MPS−PPV were also investigated to further understand the quenching process as well as to potentially increase sensitivity or selectivity to biological molecules. A modified version of the Stern−Volmer equation is required to describe the curvature observed in the PL plots of the polymers in the mixture. In the mixture, the increase of the K_{SV} of PTE−BS (the polymer with small molecular weight) is accompanied by a slight decrease of K_{SV} of the MPS−PPV polymer.

Introduction

In addition to the potential application of conjugated polymers in photovoltaic cells and optoelectronic devices,[1,2] new applications of these materials for biological and chemical sensors are emerging after the discovery that some of these polymers exhibit high sensitivity to fluorescence quenching (superquenching). Chen et al.[3] have demonstrated that the luminescence of the water-soluble polymer methoxypropyloxysulfonate−phenylenevinylene (MPS−PPV) can be quenched by using extremely low concentrations of methyl viologen (MV^{2+}). The same quenching effect was observed when MV^{2+} was linked to biotin, a small molecule that specifically binds the protein avidin. The unquenching observed when avidin is added to a quenched solution of MPS−PPV provides a quantitative assay for avidin that can be exploited to develop a new form of biosensors. Since then, intensive research has been carried out[1,2,4−9] to understand the origin of the enhanced quenching. More recently,[10] it has been found that gold nanoparticles increase even further the quenching effect by several orders of magnitude. The speculations about applications of these polymers in sensors began to become reality when first DNA detection using conjugated polymers was reported.[11,12]

While most of the initial studies have been on water-soluble PPVs, other water-soluble photoluminescent polymers also show promise as potential biosensor materials. In contrast to the PPV materials, polythiophenes belong to the family of water-soluble conjugated polymers that are currently commercially available; however, the quenching in these systems has not been largely studied. Previous results on MPS−PPV suggest that the quenching mechanism is based on ultrafast electron transfer from the polymer to the acceptor facilitated by the strong tendency of the quencher to associate with the polymer in aqueous solution in a process that some times has been compared to micellization.[7] If the acceptor is removed from the vicinity of the polymer chain, luminescence is recovered. Like MPS−PPV, sodium poly[2-(3-thienyl)ethyloxy-4-butylsulfonate)] (PTE−BS) is a conjugated water-soluble polythiophene material that is quenched by the cationic molecule MV^{2+}, suggesting it may be a viable candidate for biosensor applications.

In this paper we examine how some factors such as the presence of oxygen in the polymer solution and the polymer concentration influence the PL associated with the quenching mechanism in the commercially available polymer PTE−BS. We also study the quenching behavior of mixtures of PTE−BS ($M_w \sim 5000$) and MPS−PPV ($10^5 < M_w \sim 5000 < 10^6$) polymers using MV^{2+} as quencher in order to explore the use of polymer mixtures as a tool for gaining enhanced quenching. Furthermore, when two different polymer molecules interact with one another, the electrical properties as well as their luminescence of each polymer will be affected by interactions between the two polymer chains. The study of the PL of the polymers in the mixture could thus contribute to a better understanding of the underlaying mechanism of quenching.

Theory

In the photoluminescence of conjugated polymers, the wavelength of the emitted light is related to the energy gap between the highest occupied energy band (π-band) and the lowest unoccupied energy band (π^*-band). The π−π^* energy gap can be changed by modifying the polymer chemical composition or its configuration, and the wavelength of the emitted light can be selected by controlling the polymer structure.[13,14] In aqueous solutions, the luminescence of the polymers can be quenched by adding very low concentrations of a quencher that depend on whether the polymer is an electron acceptor

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* Corresponding author. E-mail: Cabarcos@ucsc.edu.

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or a donor.[5−7] After absorbing radiation by the polymer, an electron is excited to the π^*-band and can be transferred to the acceptor molecule within femtoseconds, a much faster process than the luminescence decay time. The electron and the hole (left in the polymer) are in different molecules, and luminescence is quenched. Conjugated polymers generally have large Stokes shifts, and the overlap of the absorption and emission spectra is not large enough for the ultrafast energy transfer that would be required to explain superquenching. Very recently,[15] it has been demonstrated using single-molecule spectroscopy in derivatives from poly(phenylenevinylene) that the chromophore units display spectral diffusion that can influence the polymer emission. Because of intramolecular interactions, the spectral diffusion follows Lorentzian-like statistics in the case of emission from multiple chromophores situated on the same macromolecule. Moreover, intermolecular interactions, such as interchromophoric coupling caused by aggregation, results in strong spectral broadening. However, different conjugated polymers exhibit universal fluorescence behavior on the single-chromophore level, and the structure−property correlations observed in these polymers may derive primordially from chain morphology rather than chromophoric properties.

The number of monomers per chain in photoluminescent (PL) conjugated polymers is not very large (between 10 and 1000), and the fluorescence quenching efficiency increases with increasing molecular weight. A quencher molecule can extinguish fluorescence from a large polymer segment. The quenching efficiency also increases with increasing tendency of the polymer to associate with the quencher in aqueous solution. This association can occur either through the formation of a nonluminescent complex betweeen the polymer and the quencher (static quenching) or due to collisions between the photoluminescent macromolecule and the quencher (dynamic quenching). Encounters, driven by diffusion, between the fluorophore polymer and quencher during the lifetime of the excited state can result in the formation of a nonfluorescent complex between the polymer and the quencher. This complex absorbs light and will frequently perturb the absorption spectrum of the fluorophore. Dynamic quenching only affects the excited state of the fluorophores, and thus no changes in the absorption spectra are predicted in this case. For both mechanisms,[16] the quantitative measure of the luminescence quenching efficiency is given by the Stern−Volmer constant K_{SV} defined by

$$\mathrm{PL}^0/\mathrm{PL} = 1 + K_{\mathrm{SV}}[\mathrm{Q}] \tag{1}$$

where PL^0 and PL are the intensity of fluorescence in absence and in the presence of the quencher respectively, [Q] is the concentration of quencher, and K_{SV} is the efficiency of quenching. In the case of static quenching K_{SV} is a measure of the association constant for complex formation ($K^{\mathrm{S}}{}_{\mathrm{SV}}$), whereas in the case of the dynamic quenching $K^{\mathrm{D}}{}_{\mathrm{SV}}$ is the product of the diffusion bimolecular rate constant K_{d} and the fluorescence lifetime τ_0. Since the fluorophore can be quenched both by collision and complex formation, the Stern−Volmer equation[16] is given by

$$\mathrm{PL}^0/\mathrm{PL} = 1 + (K^{\mathrm{S}}{}_{\mathrm{SV}} + K^{\mathrm{D}}{}_{\mathrm{SV}})[\mathrm{Q}] + K^{\mathrm{S}}{}_{\mathrm{SV}}K^{\mathrm{D}}{}_{\mathrm{SV}}[\mathrm{Q}]^2 \tag{2}$$

This equation describes the combination of both static and dynamic quenching. The positive curvature observed in the Stern−Volmer plots of polymers for high quencher concentrations is explained in some mathematical models with the concept of “sphere of action”.[5,7,17] Because of the large size of the polymer macromolecule in solution, at high quencher concentration there are always quencher molecules within a charge-transfer distance (sphere of action) from the polymer chain. Considering a sphere of volume v, the probability of finding a luminescence polymer without any quencher within the volume v is given by

$$f = \exp(-vN[\mathrm{Q}]) \tag{3}$$

where N is Avogadro's number. With this model, the quenching follows the relationship

$$\mathrm{PL}^0/\mathrm{PL} = (1 + K_{\mathrm{SV}}[\mathrm{Q}])\exp(vN[\mathrm{Q}]) \tag{4}$$

This modification of the Stern−Volmer equation is used to describe both the static and dynamic quenching in polymers.[5,7]

Experimental Section

1. Materials and Sample Preparation. Water-soluble conjugated polymer sodium poly[2-(3-thienyl)ethoxy-4-butylsulfonate] (commercially called ADS2000P) was purchased from American Dye Source and methyl viologen from Aldrich. Poly(2-methoxy-5-propyloxysulfonate−phenylenevinylene) was synthesized by Fred Wudl (UCLA). The molecular weight of PTE−BS was obtained from American Dye Source and is (4−6) × 10^3. For MPS−PPV the molecular weight estimated from light scattering measurements is (1−5) × 10^5. The polydispersity did not change during the PL measurements because we have prepared the solutions using always the same polymers. Solutions of PTE−BS with concentration 1.9 × 10^{-3} M and MPS−PPV with concentration 1.85 × 10^{-3} M were prepared and purged with nitrogen for several hours. All polymer concentrations given in the paper are expressed in monomer repeat units. The solutions for the absorption and fluorescence spectra measurements were made by diluting the stock solution to the desired concentration. For quenching measurements the emission from the PTE−BS or MPS−PPV with a concentration of 1.85 × 10^{-4} M in water were first tested. The emission spectra of quenched solutions were taken after the mixture solution of conjugated polymer and quencher was stirred for about 1 min.

2. Methods. The fluorescent spectra were taken on a LS45 Perkin-Elmer luminescence spectrometer. The fluorescent spectra were obtained by exciting PTE−BS at 400 nm and MPS−PPV at 500 nm, near their respective absorption peaks. The study was carried out in aqueous solutions of PTE−BS and MPS−PPV with concentration varying between 10^{-4} and 10^{-6} M. For each sample, we recorded the PL spectra at varying concentrations of MV^{2+}, thus allowing a good determination of K_{SV}. The absorption spectra were taken on a UV−vis spectrometer (N&K Technology Inc.).

Results and Discussion

1. PTE−BS. a. Oxygen Quenching of PTE−BS. Figure 1 shows the UV−vis absorbance spectrum of pure PTE−BS (8 × 10^{-5} M) in aqueous basic solution with oxygen and how the spectrum changes after 2 h of oxygen removal by means of bubbling nitrogen through the solution. For PTE−BS, the maximum of absorbance appears around 400 nm, and the removal of oxygen by nitrogen results in a near uniform increase of the absorbance across the whole UV−vis wavelength range. Oxygen is expected to quench the polymer to some

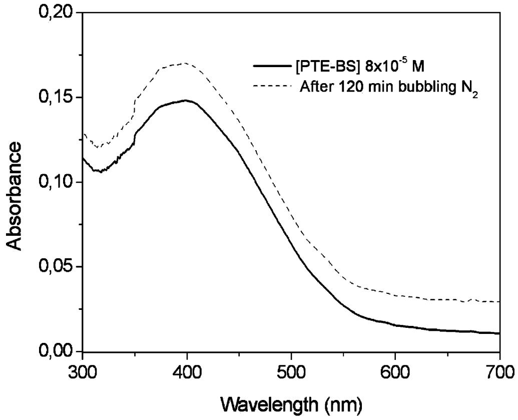

Figure 1. Absorption spectra of PTE−BS (8 × 10^{-5} M) in water with oxygen (solid line) and after 2 h of nitrogen bubbling through the solution.

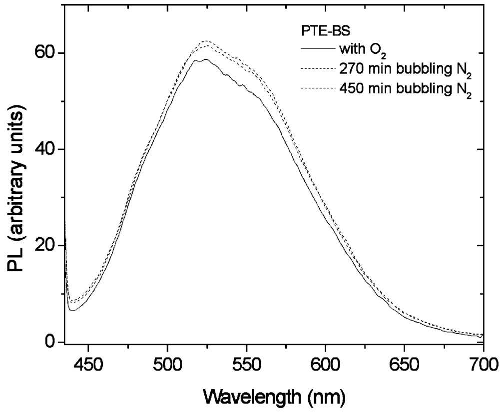

Figure 2. Fluorescence spectra (excited at 400 nm) of PTE−BS (8 × 10^{-5} M) aqueous solutions taken during the getting rid off oxygen process.

extent, and if the oxygen quenching is very high, this would limit the biosensor applications of PTE−BS. Nonetheless, as is illustrated in Figure 2, the amount of fluorescence quenching observed after bubbling nitrogen for 7.5 h is 6.4% and tends to stabilize around this value.

b. Self-Absorption Quenching: Influence of PTE−BS Concentration in the PL Emission. We have investigated the influence of the PTE−BS concentration in the PL intensity. For this experiment the solutions were prepared by diluting with water 3 mL of 9 × 10^{-4} M solution of PTE−BS to the desired polymer concentration. Then, emission spectra were taken after stirring for 1 or 2 min. Figure 3a shows that in the range of polymer concentration between 9 × 10^{-4} and 3.4 × 10^{-4} M the PL intensity increases when the polymer concentration decreases and is accompanied by a blue shift of the peak from 562 down to 529 nm. For more dilute solutions, the PL intensity decreases with decreasing polymer concentration, as is illustrated in Figure 3b. Between 10^{-4} and 10^{-5} M, the PL intensity is strongly affected by the polymer concentration. Figure 4 shows the concentration dependence of fluorescence intensity of pure PTE−BS in water with $\lambda_{\mathrm{ex}} = 400$ nm and $\lambda_{\mathrm{em}} = 562$ nm. This behavior can be explained[18] taking into account that the fluorescence emission intensity as a function of solute concentration is given by

$$\mathrm{PL} = CI_0 \times 10^{-\epsilon_{\mathrm{x}}bc}(1 - 10^{-\epsilon_{\mathrm{x}}bc}) \times 10^{-\epsilon_{\mathrm{m}}bc} \qquad (5)$$

where C is a constant of proportionality depending on the emitting molecule, I_0 is the radiant power striking the cell, b is beam path length, c is the concentration of polymer, and ϵ_{x} and ϵ_{m} are the molar absorptivities for the excitation and emission wavelengths, respectively. For PTE−BS concentrations smaller than 3.4 × 10^{-4} M (approximately around this value because solutions are filtered and some polymer is always left within the filter), the emission intensity increases with increasing polymer concentration because the absorption is small, and the emission is then proportional to the concentration of polymer. For PTE−BS concentrations higher than ~4.5 × 10^{-4} M, the emission is quenched by self-absorption as well as increased interactions between chains. The change observed in the shape of the emission spectrum for high polymer concentrations would thus result from the wavelength dependence of the emission intensity.

c. PTE−BS Quenching by MV^{2+}. The PL quenching of PTE−BS by MV^{2+} was investigated in two solutions with polymer concentrations 1.8 × 10^{-4} and 9.0 × 10^{-4} M, at both sides of the maximum of the curve of Figure 4. In the case of concentration 1.8 × 10^{-4} M, we repeated the experiment with samples in which oxygen was not withdrawn to estimate its influence in K_{SV}. In Figure 5a we present the fluorescence spectra from aqueous solution of PTE−BS (1.8 × 10^{-4} M) in the presence of a series of concentrations of MV^{2+} which range from 1.1 × 10^{-6} M at the top of the plot down to 7.6 × 10^{-4} M at the bottom of the plot when the quenching of PTE−BS is around 73%. In Figure 5b we show the quenching of a more concentrated 9.0 × 10^{-4} M solution. Figure 5c shows the fluorescence spectra of a solution with the same polymer concentration than that of Figure 5a but in which oxygen was not removed. The corresponding Stern−Volmer plots are shown in Figure 6a−c, and all of them present similar features. Independently of the

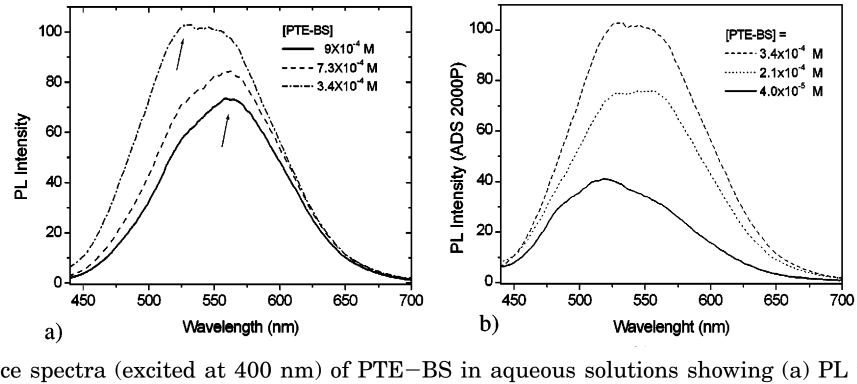

Figure 3. Fluorescence spectra (excited at 400 nm) of PTE−BS in aqueous solutions showing (a) PL increases upon dilution from 9 × 10^{-4} down to 3.4 × 10^{-4} M and (b) PL decreases upon dilution from 3.4 × 10^{-4} down to 4.0 × 10^{-5} M.

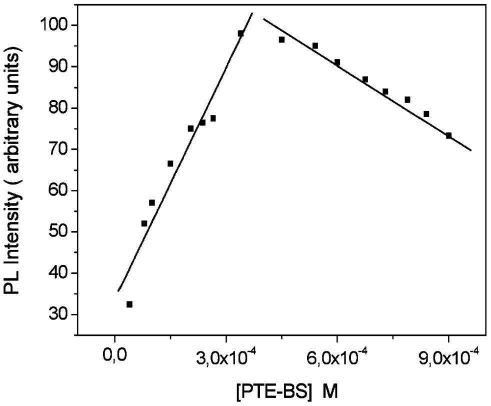

Figure 4. Fluorescence intensity (excited at 400 nm) as a function of the concentration of PTE−BS in aqueous solutions.

PTE−BS concentration, or if oxygen is present or not, two regions can be distinguish corresponding to low and high MV^{2+}concentration. At low quencher concentrations, the dependence of fluorescence intensity on the quencher concentration is given by eq 1. However, as can be seen in Figure 6a−c, as the MV^{2+} concentration increases, there is a conspicuous change in the slope of the SV plot around the value $[MV^{2+}] = 1/K_{SV}$. The values of K_{SV} and crossover quencher concentration are given in Table 1. The presence of oxygen does not affect the value of K_{SV} (within the experimental error); however, it is influenced by the polymer concentration. Even though a dependence of K_{SV} with the number of polymer repeating units has been reported[19] for polylysine polyelectrolytes, we believe that the decrease observed in the K_{SV} when the polymer concentration increases is mainly due to the change of the molar absorptivities with the polymer concentration and also the formation of aggregates. The quencher crossover concentration seems to be affected by both the presence of oxygen and the polymer concentration. Furthermore, according to eq 2, at high quencher concentrations an exponential increase of the PL intensity is expected because quenching by acceptors within the sphere-of-action becomes very important; however, this is the opposite behavior to what we observe. The change of the slope appears around the value $K_{SV} = 1/[\text{quencher}]$ (when $PL = PL^0/2$), indicating that quenching saturation, due to the lack of unquenched polymers, is responsible for this effect. While oxidation reactions involving molecular oxygen tend to be slow, the larger slope observed in the sample with oxygen indicates that at this stage some oxidation occurs.

During the quenching experiments, the color of the samples slightly changes from pale orange before quenching to very pale pink after quenching. To investigate this, we have recorded the UV/vis spectra of polymer solutions with different quencher concentrations. As shown in Figure 7, the absorbance spectrum of PTE−BS exhibits a broad maximum at 405 nm (3.06 eV) and a small shoulder at around 257 nm (4.8 eV). When MV^{2+} is added to the solution, a strong increase in the absorption at 257 nm and a red shift of the maximum from 405 to 437 nm are observed. The PL quenching of conjugated polymers depends on the charge of the quencher, and this effect was investigated by Wang et al.[7] They found that when the charge of the quencher increases, there is an increase in K_{SV} accompanied by a spectral shift which also increases with the quencher charge. If the change of slope in the SV plot were attributed to some screening effect of the MV^{2+} charge (like polymer−quencher micelle formation), a blue shift and not a red shift had to be observed. On the other hand, an isosbestic point can be seen at 430 nm, and this point appears when one absorbing species is converted to another absorbing species during a chemical reaction, and the spectra of the pure compounds cross each other at some wavelength. However, the increase in absorption at 257 nm is not due to a chemical reaction but to the increase of MV^{2+} concentration in the solution, as is illustrated in Figure 8. In this figure we show the absorbance of pure MV^{2+} solution as a function of MV^{2+} concentration. The absorbance of pure PTE−BS and pure MV^{2+} was added and then subtracted from the absorbance of the solution with the

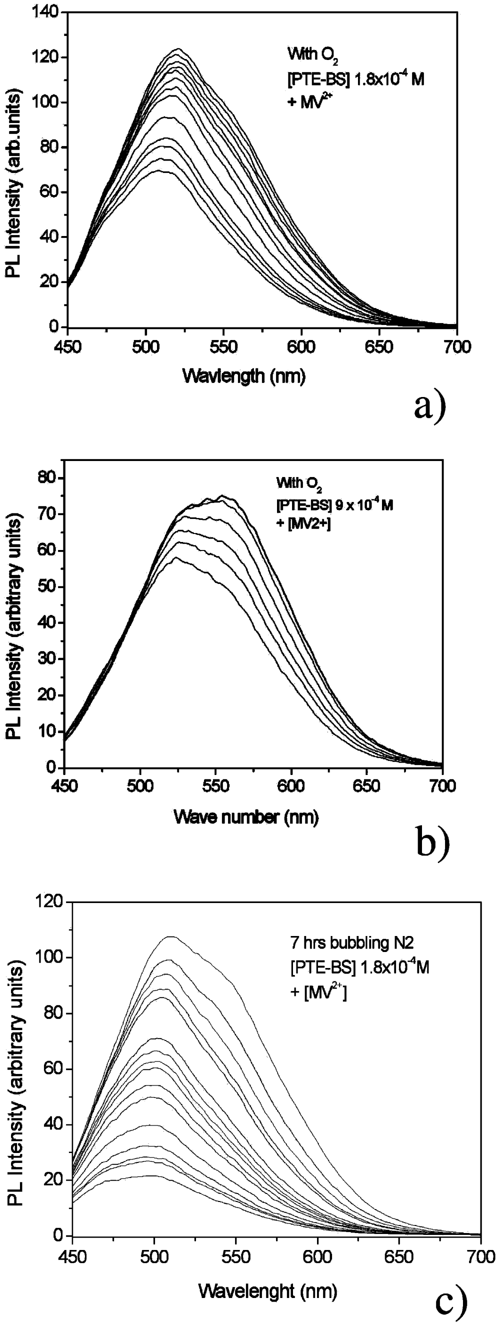

Figure 5. Fluorescence spectra of water solutions of PTE−BS (excited at 400 nm) in the presence of MV^{2+} for concentrations of PTE−BS: (a) 1.8×10^{-4} M with nitrogen bubbling for 7 h, (b) 9.0×10^{-4} M with oxygen, and (c) 1.8×10^{-4} M with oxygen.

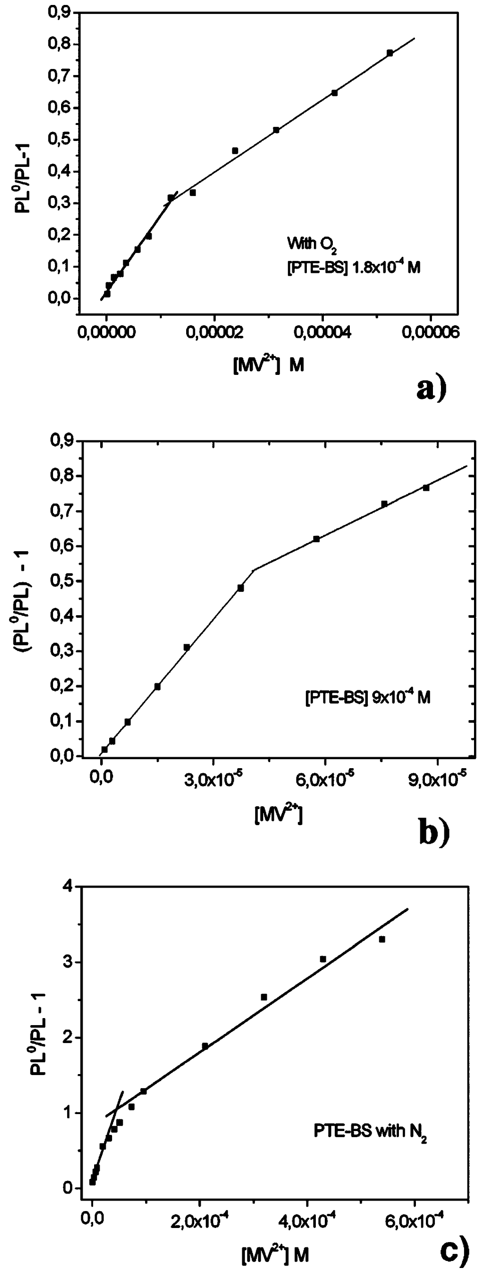

Figure 6. Stern–Volmer plot for quenching of the fluorescence by MV^{2+} for PTE–BS aqueous solution of concentrations: (a) 1.8×10^{-4} M with nitrogen, (b) 9.0×10^{-4} M with oxygen, and (c) 1.8×10^{-4} M with oxygen.

Table 1. Values of K_{SV}, the Slope of the Second Line in the SV Plots, and the Quencher Crossover Concentration for PTE–BS

[PTE–BS]	1.8×10^{-4} M with N_2	1.8×10^{-4} M with O_2	1.8×10^{-3} M with O_2
K_{SV} (M^{-1})	2.4×10^4	2.4×10^4	1.3×10^4
second slope (M^{-1})	0.47×10^4	1.1×10^4	0.54×10^4
[MV^{2+}] at crossover	4.6×10^{-5}	1.2×10^{-5}	4.1×10^{-5}

same concentration of both compounds, and the result is presented in Figure 9. The peak at 502 nm (2.57 eV) and the isosbestic point at 430 nm support the argument that some new species has formed that would be the responsible for this absorption peak.

2. MPS–PPV. The quenching of MPS–PPV by MV^{2+} has been studied by Chen et al.,[3] and they found $K_{SV} = 1.7 \times 10^7$ M^{-1} working with solutions of concentration 10^{-5} M MPS–PPV and 10^{-7} M MV^{2+}. Figure 10 shows the fluorescence spectra from aqueous solutions 1.9×10^{-4} M MPS–PPV excited at 500 nm (upper curve) and after addition of several amounts of MV^{2+}. In our case, the SV plot (Figure 11) indicates that $K_{SV} \cong 1.3 \times 10^6$ M^{-1}, around 1 order of magnitude smaller than the one reported previously. We attributte this difference in K_{SV}

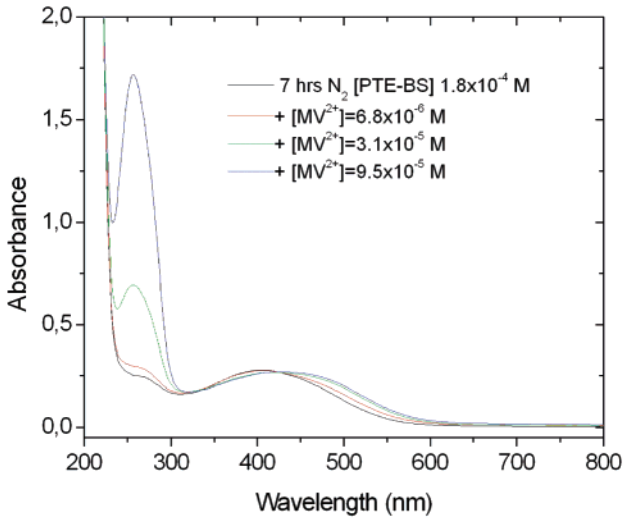

Figure 7. Evolution of the absorption spectra for PTE–BS as a function of the concentration of the quencher added.

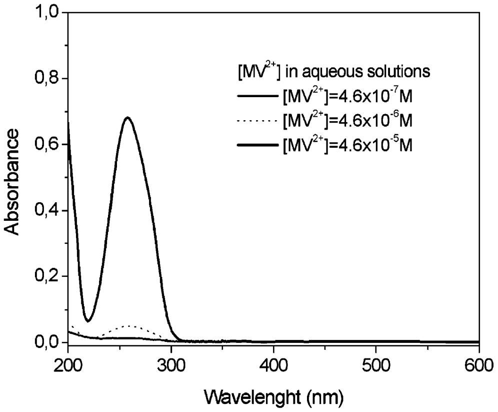

Figure 8. Evolution of the absorption spectra for pure MV^{2+} as a function of the concentration.

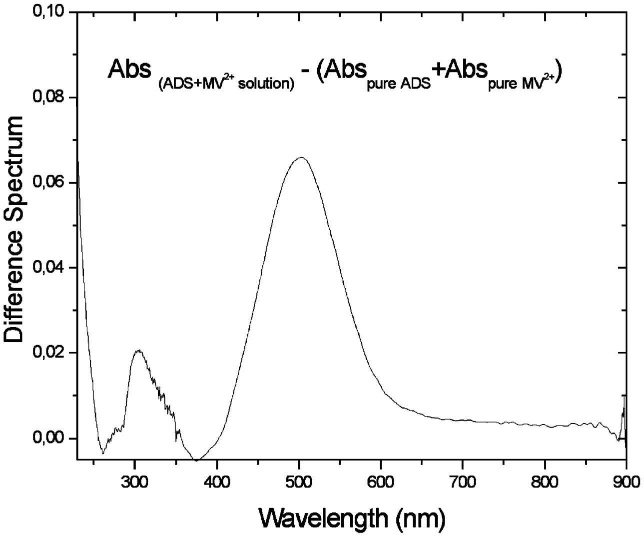

Figure 9. Difference spectrum obtained by subtracting from the absorption spectrum of a solution of PTE–BS and MV^{2+} the addition of the absorption spectra of the pure substances.

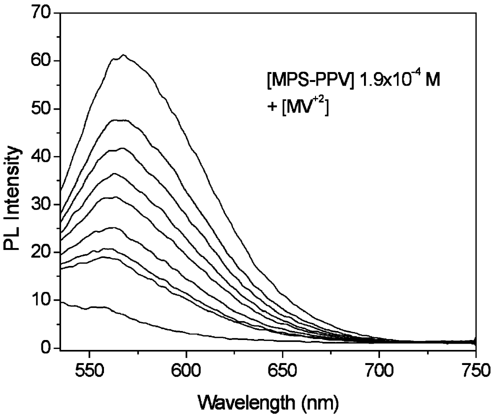

Figure 10. Fluorescence spectra of a water solution of MPS–PPV (excited at 500 nm) in the presence of MV^{2+}.

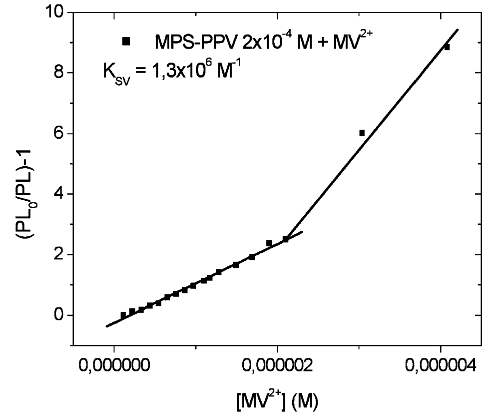

Figure 11. Stern–Volmer plot for quenching of the fluorescence by MV^{2+} for MPS–PPV aqueous solution of concentrations 1.9×10^{-4} M.

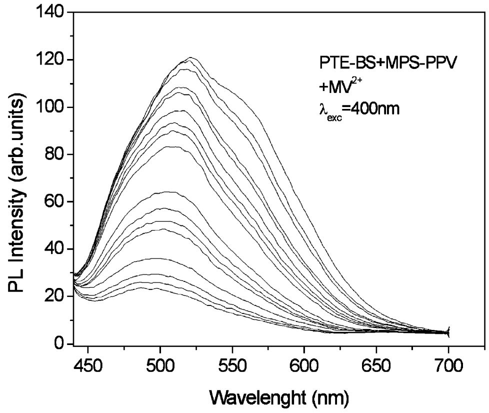

Figure 12. Fluorescence spectra of an aqueous mixture (50/50 v/v) of PTE–BS (1.8×10^{-4} M) and MPS–PPV (1.8×10^{-4} M) excited at 400 nm, in the presence of MV^{2+}.

to the fact that we worked with more concentrated polymer solutions and also to differences in the molecular weights of both polymers.

3. PTE–BS and MPS–PPV Mixture. A 50/50 v/v mixture of both polymers (approximately equimolar in monomer repeat units) was prepared using the concentration 1.8×10^{-4} M for PTE-BS and 1.9×10^{-4} M for MPS–PPV. Figure 12 shows the quenching of the PL of the mixture by MV^{2+} for 400 nm and Figure 13 for 500 nm excitation wavelength. As is illustrated in Figure 14, the SV plots of the mixture at both excitation wavelengths are characterized by downward curvature. At the higher quencher concentrations, most of the molecules are quenched, and the remaining fluorescence is from the inaccessible segments of the polymer chains. To analyze the quenching of two populations of fluorophores, a modified SV equation have to be used.[16] The hypothesis is the existence of two populations of fluorophores one of which is accessible to quenching whereas the other one is buried and therefore more difficult to reach by the quencher. The total fluorescence in absence of quencher will be

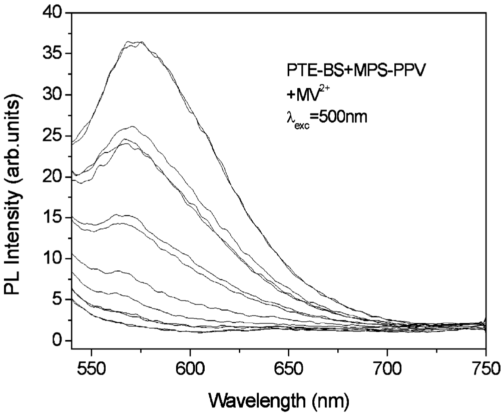

Figure 13. Fluorescence spectra of an aqueous mixture (50/50 v/v) of PTE–BS (1.8×10^{-4} M) and MPS–PPV (1.8×10^{-4} M) excited at 500 nm, in the presence of MV^{2+}.

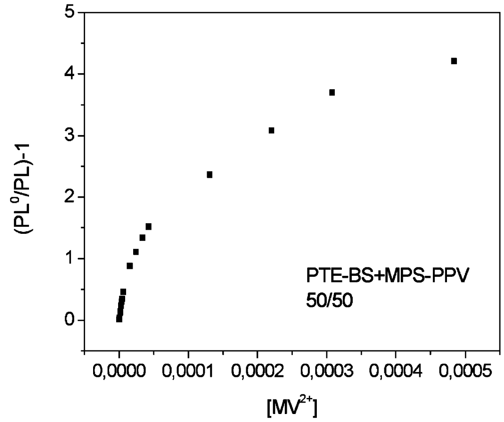

Figure 14. Stern–Volmer plot for quenching of the fluorescence by MV^{2+} of the 50/50 v/v mixture (excited at 400 nm) of PTE–BS and MPS–PPV.

$$PL^0 = PL^0_{acce} + PL^0_{buried} \tag{6}$$

where PL^0_{acce} and PL^0_{buried} refer to the PL intensity in the absence of quencher. When the quencher is added, the PL intensity arising from the accessible fraction decreases according to the SV equation, whereas the buried fraction remains unquenched. Therefore

$$PL = \frac{PL^a_{acce}}{1 + K_{SV}[Q]} + PL^0_{buried} \tag{7}$$

Subtraction of eq 5 from eq 4 yields

$$\frac{PL^0}{\Delta PL} = \frac{1}{f_a K_{SV}[Q]} + \frac{1}{f_a} \tag{8}$$

where K_{SV} is the SV constant of the accessible fraction of fluorophores, $\Delta PL = PL^0 - PL$, and f_a is the initial accessible fraction of fluorescence, $f_a = PL^0_{acce}/(PL^0_{acce} +$

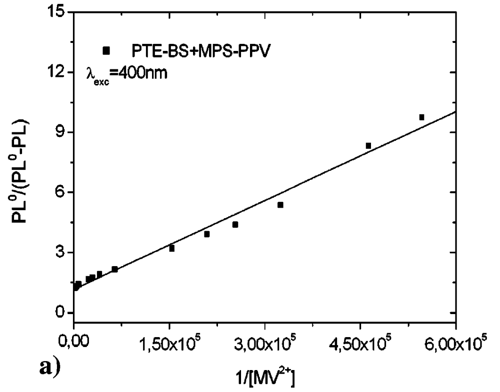

Figure 15. Modified Stern−Volmer plot for quenching of the fluorescence by MV^{2+} of the 50/50 v/v mixture of PTE−BS and MPS−PPV: (a) excited at 400 nm and (b) excited at 500 nm.

Table 2. Values of K_{SV} for the Pure Polymers and the Polymers in the Mixture in Aqueous Solutions

K_{SV} (M^{-1})	pure polymer	polymer in the 50% v/v mixture
PTE−BS	2.4×10^4	7.8×10^4
MPS−PPV	1.3×10^6	$0. 77 \times 10^6$

PL^0_{buried}). As can be seen in Figure 15a,b, the plot of $PL^0/\Delta PL$ vs 1/[Q] is linear for both the PTE−BS and the MPS−PPV in the mixture. The intercept of the straight line with the *y*-axis yields $f_a = 0.87$ and $f_a = 0.94$ for the PTE−BS and the MPS−PPV, respectively. The values of K_{SV} obtained from the slopes are given in Table 2, The mixture appears to enhances the fluorescence of the polymer with smaller molecular weight and on the contrary decreases the PL of the polymer with higher M_w.

Although the initial accessible fraction is smaller in PTE−BS, this polymer smaller molecular weight will tend to be distributed on the surface of the MPS−PPV aggregates. Thus, it seems that although in the mixture the fluorescence of both polymers can be quenched separately, there exists some coupling of the fluorescence of the individual polymers when they are mixed together in solution 1 to 1 M (in monomer repeat units).

Conclusions

Even though oxygen plays a role in the PL quenching of PTB−BS, the phenomena is equally observed in samples with and without oxygen and some other factors, such as polymer concentration, seem more important when dealing with quantitative results. Below the quencher crossover concentration, the PL quenching behavior is well described by the SV equation, whereas above this concentration some other factors like oxidation or quenching saturation have to be taken into account. A modified version of the SV equation is required to describe the curvature observed in the PL plots of the polymers in the mixture. Our study suggests that in the mixture the polymer with small molecular weight increases its K_{SV}, whereas the opposite behavior is observed for the polymer with the highest molecular weight. However, this conclusion is provisional to the 1/1 mixture studied here, and more research has to be performed before it could be extended.

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