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# Photoluminescence Quenching of Conjugated Macromolecules by Bipyridinium Derivatives in Aqueous Media: Charge Dependence

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Quenching of the photoluminescence from a water-soluble conjugated macromolecule, poly[5-methoxy-2-(4-sulfobutoxy)-1,4-phenylenevinylene], by neutral 4,4'-dipyridyl and by six bipyridinium derivatives with different charges was studied. For the neutral quenchers, the linear Stern–Volmer constant ( $K_{sv}$ ) was  $(1-2) \times 10^5 \text{ M}^{-1}$ . For the charged quenchers,  $K_{sv}$  increases when the charge on the quencher is increased, from  $(1-3) \times 10^6 \text{ M}^{-1}$  for singly charged quenchers to  $2 \times 10^7 \text{ M}^{-1}$  for bipyridinium derivatives with charge +2 and +4, consistent with static quenching via the formation of a complex between the positively charged polymer and the positively charged quencher. A modified Stern–Volmer equation, including the sphere-of-action contribution, is used to discuss the upward curvature observed in the Stern–Volmer plots at higher concentrations.

## Introduction

Photoinduced electron transfer from conjugated polymers to electron acceptors, such as TCNQ or  $\text{C}_{60}$  and its soluble derivatives, has been extensively investigated.<sup>1</sup> The presence of the electron acceptor in conjugated polymers facilitates the separation of the photogenerated carriers, and the quantum efficiency for charge separation approaches unity because of the fact that the forward electron-transfer process occurs in the subpicosecond time domain, faster than any competing process.<sup>2</sup> Because of the very high charge-transfer efficiency, conjugated polymers have shown great potential as novel materials in photovoltaic cells and photodetector applications.<sup>3</sup> The fact that the efficient electron-transfer process quenches the photoluminescence of the conjugated polymer is also of great interest in that the conjugated polymers offer promise for use as chemical sensors<sup>4</sup> and as high-sensitivity biosensors.<sup>5,6</sup> The photoluminescence of a water-soluble derivative of poly(phenylene vinylene) is quenched by methyl viologen ( $\text{MV}^{2+}$ ) via photoinduced electron transfer. When the viologen is linked to a

biologically interesting ligand (e.g., biotin) and used as quencher, the quenched fluorescence can be fully recovered upon binding between the biotin and the specific protein, avidin. Formation of the biotin–avidin complex removes the quencher from the immediate vicinity of the polymer chain and thereby shuts down quenching.<sup>5</sup> If this phenomenon can be generalized, it could lead to a new class of high-sensitivity biosensors with implications for drug development, toxicology, and medical diagnostics.<sup>6</sup>

The lithium sulfonate terminal groups on poly[5-methoxy-2-(4-sulfobutoxy)-1,4-phenylenevinylene], MBL-PPV (Figure 1), are of fundamental importance to the biosensor concept. Salt dissociation ( $\text{R-SO}_3\text{Li} \rightleftharpoons \text{R-SO}_3^- + \text{Li}^+$ ) makes the negatively charged luminescent polymer water-soluble. As a result, the cationic electron acceptor ( $\text{MV}^{2+}$ ) and the anionic polymer form a weak complex. This complex formation leads to a remarkably large Stern–Volmer constant,  $K_{sv} > 10^7$ .<sup>5,6</sup> Subsequently, it was shown that static quenching by complex formation dominates at low quencher concentrations and quenching within a sphere-of-action becomes important at higher quencher concentrations.<sup>7</sup>

In this paper, we examine how the absolute charge and the charge distribution within structurally related quencher molecules affect quenching. Specifically, we report quenching studies of MBL-PPV by 4,4'-dipyridyl (DPy) and six bipyridinium derivatives, 1-(4''-sulfobutoxy)-4,4'-bipyridinium ( $\text{SB1V}^0$ ), 1,1'-di-(4''-sulfobutoxy)-4,4'-bipyridinium ( $\text{SB2V}^0$ ), 1-methyl-1'-(4''-sulfobutoxy)-4,4'-bipyridinium ( $\text{SB2V}^+$ ), 1-methyl-4,4'-bipyridinium iodide ( $\text{MV}^+$ ), di-1,1'-dimethyl-4,4'-bipyridinium diiodide ( $\text{MV}^{2+}$ ), and  $\alpha,\alpha'$ -di-(1-(1'-methyl)-4,4'-bipyridinium)-*p*-xylene tetraiodide ( $\text{MV}^{4+}$ ) (Figure 1).

## Experimental Section

**Materials.** Water-soluble conjugated polymer, MBL-PPV,<sup>8,9</sup> and the quenchers<sup>9,10</sup> were synthesized in our lab. DPy and the other reagents were obtained from Aldrich Co. or Fisher Scientific Co. and used as received. The solutions were made in spectral

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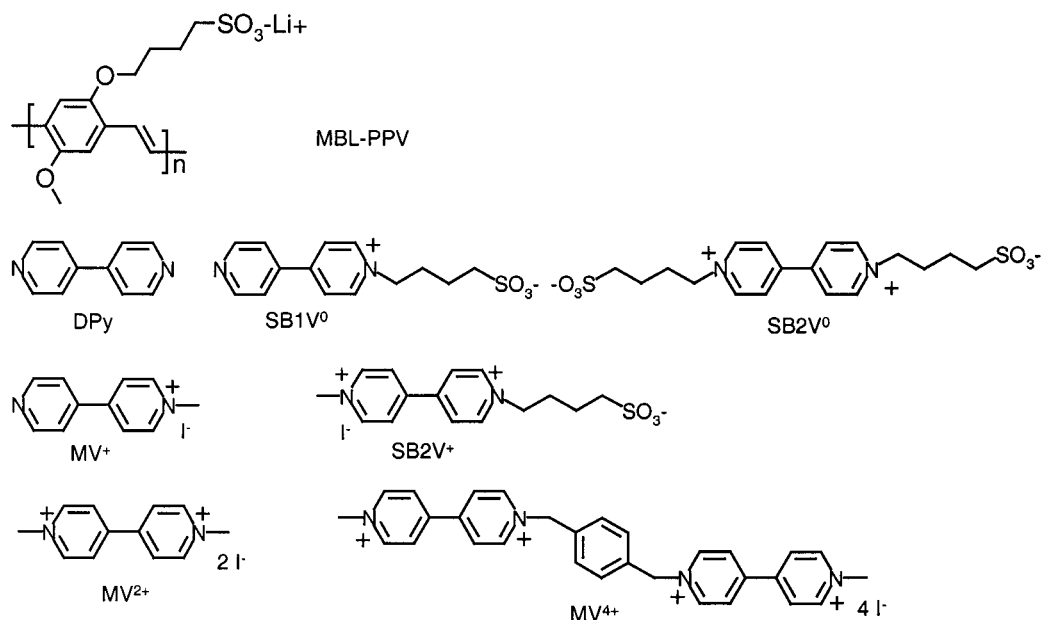
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**Figure 1.** Chemical structures of poly[5-methoxy-2-(4-sulfobutoxy)-1,4-phenylenevinylene](MBL-PPV), 4,4'-dipyridyl (DPY), and six bipyrindinium derivatives, SB1V<sup>0</sup>, SB2V<sup>0</sup>, MV<sup>+</sup>, SB2V<sup>+</sup>, MV<sup>2+</sup>, and MV<sup>4+</sup>.

grade water. The water used in making the stock solution of MBL-PPV and MV<sup>2+</sup> was purged with nitrogen for at least 4 h immediately prior to use.

#### UV-Visible Absorption Spectra and Emission Spectra.

The absorption spectra were taken on a Shimadzu UV-2401PC UV-vis recording spectrophotometer, and photoluminescence spectra were taken on a Spex Fluoromax-2 spectrometer. The solutions (MBL-PPV concentration of  $1 \times 10^{-4}$  M) for the absorption spectra measurements were made by diluting the stock solution to the desired concentrations using freshly N<sub>2</sub> purged water. The quenching studies were done in situ by taking the emission spectra of the solutions at a series of quencher concentrations and comparing the photoluminescence intensities (PL). The emission spectra (500–800 nm) were taken with excitation at 488 nm. The emission from MBL-PPV (with a concentration of  $1 \times 10^{-5}$  M in water) was first tested. Then, emission spectra of the quenched mixtures were taken after adding the calculated amount of the quencher stock solution and after the mixture solution was vortexed for about 1 min. The integration under the emission spectra was normalized to that of  $1 \times 10^{-5}$  M MBL-PPV solution and was taken as the PL intensity.

## Results and Discussion

**Data Analysis.** Because DPY and the bipyrindinium derivatives do not absorb at the excitation wavelength (488 nm) or in the MBL-PPV emission region (500–800 nm) (for instance, MV<sup>2+</sup> absorption has peaks at 226.6 and 256.2 nm and cutoff at 312.2 nm), there is no “inner-filter” effect. Thus, the PL data from the quenched polymer solution mixtures were normalized to a constant polymer concentration ( $1 \times 10^{-5}$  M) by absorption normalization (eq 1) or by linear concentration normalization (eq 2).<sup>11</sup>

$$PL = PL_{\text{exp}} \times \frac{I_0(\lambda) [1 - \exp(-A_1)] Q_1}{I_0(\lambda) [1 - \exp(-A_0)] Q_0} \approx PL_{\text{exp}} \times \frac{1 - \exp(-A_1)}{1 - \exp(-A_0)} \approx PL_{\text{exp}} \times \frac{A_1}{A_0} \quad (1)$$

where  $PL_{\text{exp}}$  and PL are the photoluminescence intensity before and after the normalization.  $I_0(\lambda)$  is the intensity of the incident beam.  $A_0$  and  $A_1$  are the absorbance values at 488 nm of the MBL-PPV solution ( $1 \times 10^{-5}$  M) and quenched polymer solution mixtures, respectively.  $Q_0$  and  $Q_1$  are the quantum efficiency values of MBL-PPV without and with the presence of the quencher, respectively, which do not change for dilute polymer solutions ( $10^{-5}$  M) with a small percentage change (less than 20%).

$$PL = PL_{\text{exp}} \times \frac{1 - \exp(-A_1)}{1 - \exp(-A_0)} = PL_{\text{exp}} \times \frac{1 - \exp[-\epsilon(\lambda)_1 C_1 l]}{1 - \exp[-\epsilon(\lambda)_0 C_0 l]} \approx PL_{\text{exp}} \times \frac{C_1}{C_0} \quad (2)$$

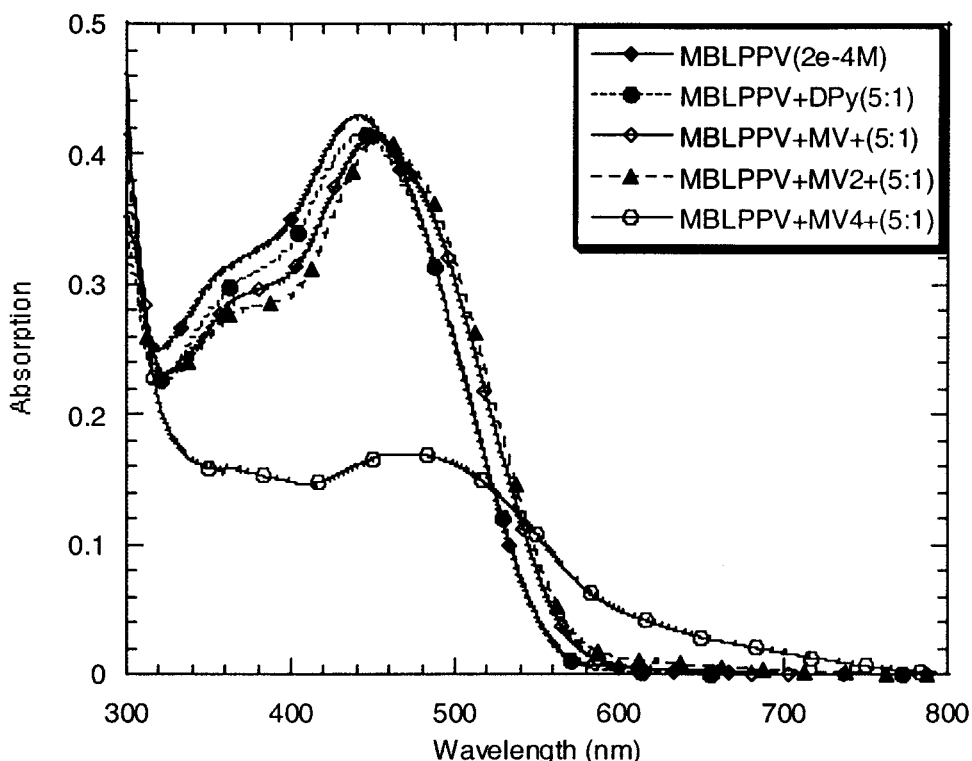
where  $\epsilon(\lambda)_0$ ,  $C_0$ , and  $\epsilon(\lambda)_1$ ,  $C_1$  are the absorption coefficients and the concentrations of MBL-PPV in pure MBL-PPV solution ( $1 \times 10^{-5}$  M) and the quenched mixtures, respectively.  $l$  is the absorption pathway length of the cuvette. At a very low polymer concentration ( $10^{-5}$  M via repeat unit) and for small volume changes (less than 20%), there is no change of the absorption coefficient and the PL quantum efficiency of the polymer because of no conformation changes of polymer chains. The same Stern–Volmer plots were obtained when the linear concentration normalization and absorption normalization were performed.

**Absorption.** Figure 2 shows the UV-visible spectra of pure MBL-PPV ( $2 \times 10^{-4}$  M in water) and of mixtures of MBL-PPV with the quenchers (polymer repeat unit/quencher = 5:1). With neutral DPY there is no spectral shift. For MV<sup>+</sup>, MV<sup>2+</sup>, and MV<sup>4+</sup>, there is a bathochromic shift of 7, 12, and 20 nm, respectively (Table 1). The increase in spectral shift with increasing quencher charge indicates that the equilibrium constant for complex formation is favored by Coulomb attraction. In fact, with

(9) All reactions were conducted in dry glassware under a nitrogen atmosphere and with magnetic stirring. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Varian Inova 400 NMR spectrometer operating at 400.1 and 100.6 MHz, respectively. Detailed syntheses and characterization will be published elsewhere.

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**Figure 2.** UV-visible spectra of MBL-PPV and the quenched mixtures: MBL-PPV ( $2 \times 10^{-4}$  M) (◆), MBL-PPV + DPy (5:1) (●), MBL-PPV + MV<sup>+</sup> (5:1) (◇), MBL-PPV (5:1) (▲), and MBL-PPV + MV<sup>4+</sup> (5:1) (○).

**Table 1. Photoluminescence Quenching of MBL-PPV by Bipyridinium Derivatives**

quencher	charges	$\lambda_{\max}$ Shift (nm)	$K_{sv}$ ( $M^{-1}$ ) (linear)	$V$ or $V'$	$\alpha$
DPy	0	1	$1.9 \times 10^5$	$1.9 \times 10^5$	1
MV <sup>+</sup>	1	7	$3.3 \times 10^6$	$3.0 \times 10^5$	1.6
MV <sup>2+</sup>	2	12	$1.9 \times 10^7$	$4.8 \times 10^6$	25
MV <sup>4+</sup>	4	20	$2.2 \times 10^7$	$1.2 \times 10^7$	63
SB1V <sup>0</sup>	0	0.5	$1.3 \times 10^5$		
SB2V <sup>0</sup>	0	2	$1.4 \times 10^5$		
SB2V <sup>+</sup>	1	9.5	$1.0 \times 10^6$		

MV<sup>4+</sup> and MBL-PPV, precipitation (cloudy "solutions") occurs at a concentration of  $4 \times 10^{-5}$  M, indicating very strong complex formation. There is no spectral shift for SB1V<sup>0</sup> and SB2V<sup>0</sup>, but there is a 9.5 nm shift for SB2V<sup>+</sup> (Table 1). Moreover, quenching studies in buffer solutions indicate that ionic screening turns off the static quenching from charged quenchers, MV<sup>+</sup>, MV<sup>2+</sup>, and MV<sup>4+</sup>, but does not affect the quenching by neutral DPy.<sup>12</sup> These data are consistent with complex formation between the anionic polymer and charged quenchers.

**Stern–Volmer Studies.** As shown in Figure 3, PL<sub>0</sub>/PL increases linearly with DPy concentration giving  $K_{sv} = 1.9 \times 10^5 M^{-1}$ . On the basis of theoretical estimates from diffusion-controlled collisional quenching of fluorophores by O<sub>2</sub> in water<sup>13</sup> and experimental evidence of MEH-PPV quenching by C<sub>60</sub> in organic solvent (where  $K_{sv} = 1.8 \times 10^3 M^{-1}$ ),<sup>14</sup> we conclude that the large  $K_{sv}$  obtained

with DPy results from sphere-of-action quenching instead of purely dynamic quenching.

$$\frac{PL_0}{PL} = (1 + K_{sv}^D[Q]) \exp(V[Q]) \approx (1 + K_{sv}^D[Q])(1 + V[Q]) \approx 1 + V[Q] \quad (3)$$

Equation 3 describes dynamic quenching in terms of the Stern–Volmer constant,  $K_{sv}^D$ , and the sphere-of-action volume,  $V$ .<sup>15,16</sup> As shown in eq 3, at low quencher concentration and when  $K_{sv}^D \ll V$ , sphere-of-action quenching dominates. Because of the large radius of gyration of the MBL-PPV in aqueous solution, at high quencher concentrations there are always quencher molecules within charge-transfer range of one MBL-PPV polymer chain; that is, there are always quenchers within the sphere-of-action. On the basis of eq 3, data for DPy yield  $V = 2 \times 10^5 M^{-1}$ , corresponding to a radius of  $\sim 400$  Å. This length scale is consistent with the radius of gyration of the MBL-PPV.<sup>7</sup> Note, however, that  $K_{sv}$  for DPy/MBL-PPV in aqueous solution is 100 times larger than for MEH-PPV/C<sub>60</sub> in organic solvent (in both cases the quencher is neutral). Although the origin of the larger  $K_{sv}$  for DPy/MBL-PPV is not clear, the charged MBL-PPV chains (polyelectrolyte) are likely to be more extended in aqueous solution and consequently have a larger sphere-of-action volume.

For bipyridium derivatives, the Stern–Volmer plots are linear at low quencher concentrations (Figure 3, inset); the linear (static quenching) Stern–Volmer constants,  $K_{sv}^S$ , obtained from the slopes of the lines in the inset are listed in Table 1. The static quenching constant for MV<sup>+</sup> is about 15 times larger than  $K_{sv}$  for DPy. For MV<sup>2+</sup> and MV<sup>4+</sup>,  $K_{sv}^S$  increased by another order of magnitude. The

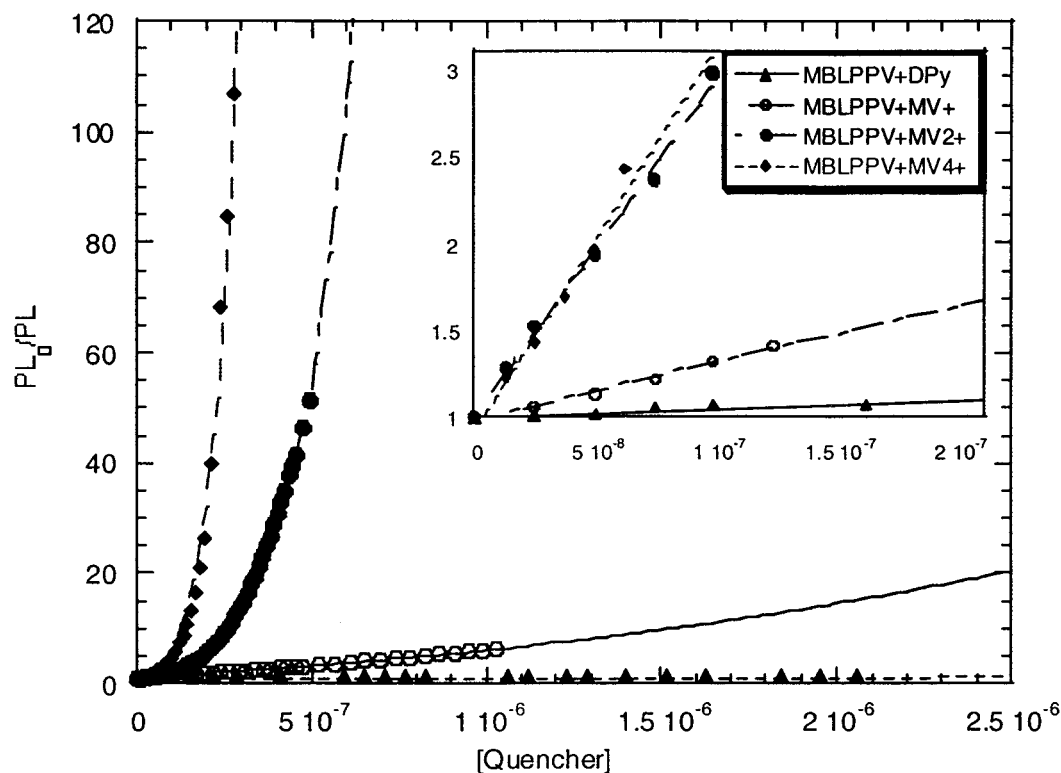
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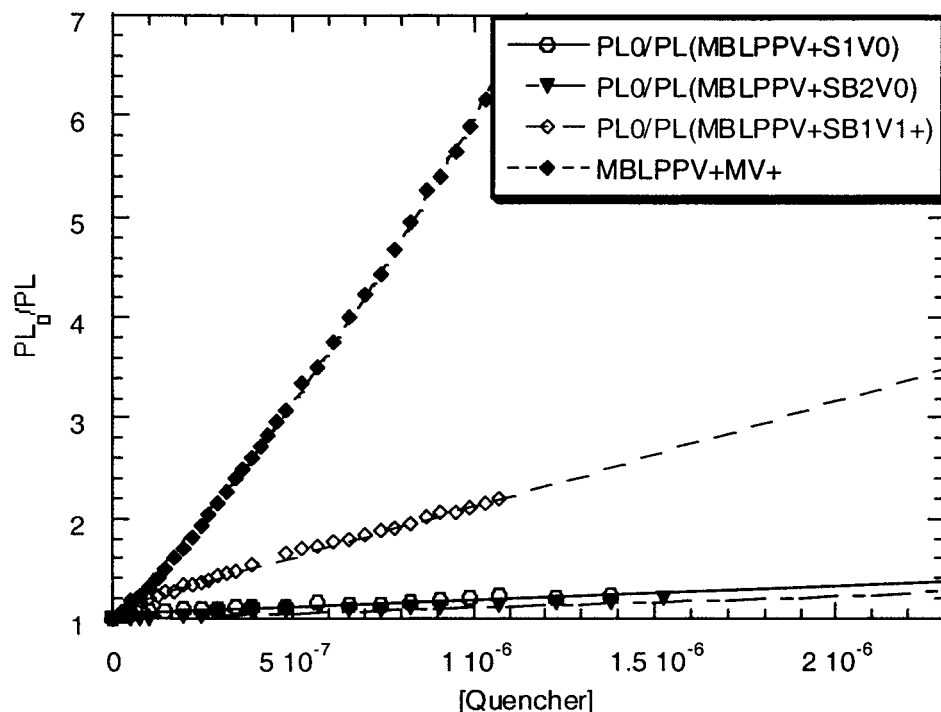
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**Figure 3.** Stern–Volmer plots of MBL-PPV ( $1 \times 10^{-5}$  M) quenching by bipyridinium derivatives (1): MBL-PPV + DPy ( $\blacktriangle$ ), MBL-PPV +  $MV^+$  ( $\circ$ ), MBL-PPV +  $MV^{2+}$  ( $\bullet$ ), and MBL-PPV +  $MV^{4+}$  ( $\blacklozenge$ ) (curves are fitted using the modified Stern–Volmer equation). Inset: low quencher concentration regime and linear static Stern–Volmer fittings.



**Figure 4.** Stern–Volmer plots of MBL-PPV ( $1 \times 10^{-5}$  M) quenching by bipyridinium derivatives (2): MBL-PPV +  $MV^+$  ( $\blacklozenge$ ) (curve is fitted using the modified Stern–Volmer equation), MBL-PPV +  $SB2V^+$  ( $\diamond$ ), MBL-PPV +  $SB1V^0$  ( $\circ$ ), and MBL-PPV +  $SB2V^0$  ( $\blacktriangledown$ ) (curves are fitted using the linear static Stern–Volmer equation).

small difference between the  $K_{sv}$  values for  $MV^{2+}$  and  $MV^{4+}$  implies that both form relatively strong complexes with the anionic conjugated polymers.

As the concentration increases, the Stern–Volmer plots (Figure 3) for the charged quenchers become superlinear, consistent with sphere-of-action quenching.<sup>7,15</sup> Assuming the sphere-of-action volume constants for DPy,  $MV^+$ ,

$MV^{2+}$ , and  $MV^{4+}$  are approximately the same and are determined by the radius of gyration of MBL-PPV, the increase in the magnitude of the nonlinear contribution implies that the quenchers are not uniformly distributed. Thus, a modified Stern–Volmer equation was used to describe the combination of static quenching via complex formation plus dynamic quenching within the sphere-of-



action:

$$\frac{PL_0}{PL} = (1 + K_{sv}^S[Q]) \exp(\nu M[Q]) = (1 + K_{sv}^S[Q]) \exp(V[Q]) \quad (4)$$

where  $\alpha$  results from charge-induced enhancement of the local quencher concentration. As shown in Table 1,  $\alpha$  is smaller for  $MV^+$  than for  $MV^{2+}$  and  $MV^{4+}$  because the interaction between  $MV^+$  and the polymer chains is weaker than for  $MV^{2+}$  and  $MV^{4+}$ . Moreover, during the lifetime of the quencher excited states there is no electrostatic interaction between neutral  $(MV)^*$  and the polymer chains. As might be anticipated,  $\alpha$  is about twice as large for  $MV^{4+}$  as for  $MV^{2+}$ . Note, however, that quenchers with more than one charge might also initiate changes in the conformation of polymer chains and, in particular, might cause aggregation, as implied by the spectral changes shown in Figure 2.

Figure 4 shows the Stern–Volmer plots for  $SB1V^0$ ,  $SB2V^0$ , and  $SB2V^+$ . The behavior of  $MV^+$  is also shown to enable comparison between the data in Figures 3 and 4. Note that for  $SB1V^0$  and  $SB2V^0$ , the linear Stern–Volmer constant,  $K_{sv}$ , is similar to that for  $DPy$ ,  $1.3 \times 10^5 M^{-1}$  and  $1.4 \times 10^5 M^{-1}$ , respectively. Therefore, the total charge on the quencher determines quenching efficiency. In the case of  $SB2V^+$ , the Stern–Volmer plot is linear with  $K_{sv} = 1 \times 10^6 M^{-1}$ , similar to  $MV^+$ . The absence of superlinear behavior at higher quencher concentrations for  $SB2V^+$  might result from a reduction in the local concentration (smaller  $\alpha$ ) as a result of the repulsion between  $R-SO_3^-$  groups on polymer side chains and the  $R-SO_3^-$  group on  $SB2V^+$ .

In summary, we have studied the photoluminescence quenching of a water-soluble conjugated polymer, MBL-PPV, by  $DPy$  and six bipyridinium derivatives. There is no evidence of ground-state complex formation between MBL-PPV and the neutral quenchers. Sphere-of-action quenching dominates for the neutral quenchers, with a volume constant of  $2 \times 10^5 M^{-1}$ ; this is consistent with the estimated radius of gyration of the polymer in aqueous solution. UV–visible spectra show that the cationic quenchers form bound complexes with the anionic polymer. At low quencher concentrations, the linear Stern–Volmer plots indicate that  $K_{sv}^S$  increases with the charge on the quenchers. Superlinear quenching was observed for all the charged bipyridinium derivatives (except  $SB2V^+$ ) at higher concentrations. The greater the positive charge on the quencher, the sharper the upward curvature. From the point of view of quencher design, quenchers with higher charges form stronger complexes and yield higher local concentrations and thereby give rise to more efficient photoluminescence quenching.

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