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## Amplified Fluorescence Quenching in a Poly(*p*-phenylene)-Based Cationic Polyelectrolyte

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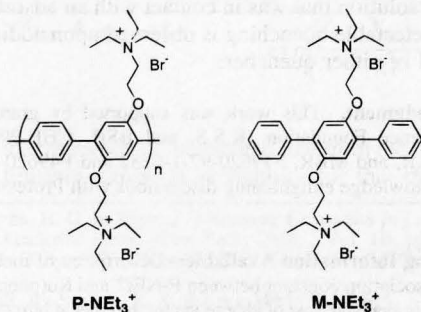
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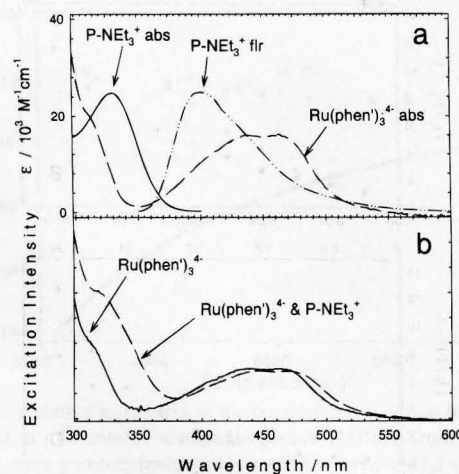
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Application of fluorescent conjugated polymers to “amplified” sensing of chemical and biological analytes has received considerable recent attention.<sup>1–8</sup> Fluorescence sensing is amplified by conjugated polymers because of the “molecular wire effect”,<sup>1,2</sup> which causes a polymer to be quenched by a considerably lower analyte concentration than its monomer analogue. Most sensor work has been carried out to date using polymers dissolved in an organic solvent,<sup>1,2,5–7</sup> however, several recent reports feature fluorescent thin film sensors that operate by coming into contact with a liquid- or vapor-phase analyte.<sup>3,4</sup> Although these studies demonstrate amplified quenching to allow trace detection of analytes, the systems are limited because the polymers only dissolve in organic solvents. A sensor would be more useful if it operates in an aqueous environment. This issue was addressed by a recent report that demonstrated fluorescence quenching of a water soluble sulfonatoalkoxy poly-(phenylene vinylene) polyanion by methyl viologen at nM concentrations.<sup>8</sup>

In the present contribution we describe fluorescence quenching of the water soluble, poly(*p*-phenylene)-based polycation, P-NEt<sub>3</sub><sup>+</sup> dibromide by several anionic quenchers, including Ru(phen)<sub>3</sub><sup>4-</sup> and Fe(CN)<sub>6</sub><sup>4-</sup> in aqueous solution (phen' = 4,7-bis(4-sulfophenyl)-1,10-phenanthroline). P-NEt<sub>3</sub><sup>+</sup> fluorescence is quenched by these anions with considerably higher efficiency compared to a terphenyl model compound, M-NEt<sub>3</sub><sup>+</sup> dibromide. Amplified quenching of P-NEt<sub>3</sub><sup>+</sup> arises because (1) ion-pairing enhances the concentration of the anionic quencher in the vicinity of the polyelectrolyte, and (2) the high mobility of the <sup>1</sup>π,π\* exciton rapidly brings it into contact with the ion-paired quencher.<sup>9</sup> We also establish that quenching of P-NEt<sub>3</sub><sup>+</sup> by Ru(phen)<sub>3</sub><sup>4-</sup> occurs via energy transfer by observing the metal complexes' photoluminescence when the excitation light is absorbed mainly by the polymer.



Polycation P-NEt<sub>3</sub><sup>+</sup>, prepared by Suzuki coupling,<sup>10</sup> was fully characterized by NMR, elemental analysis and GPC which indicated  $M_n = 12.4$  kD ( $X_n = 28$ , corresponding to over 50 phenylene rings) and PDI = 1.16.<sup>10</sup> As illustrated in Figure 1a, in aqueous solution P-NEt<sub>3</sub><sup>+</sup> features an absorption at  $\lambda_{max} =$



**Figure 1.** (a) UV-Visible absorption spectra of P-NEt<sub>3</sub><sup>+</sup> (—) and Ru(phen)<sub>3</sub><sup>4-</sup> (---) in H<sub>2</sub>O. Fluorescence of P-NEt<sub>3</sub><sup>+</sup> in H<sub>2</sub>O (—••—••). (b) Emission excitation spectrum with detector set at emission wavelength corresponding to Ru(phen)<sub>3</sub><sup>4-</sup> MLCT emission ( $\lambda_{em} = 610$  nm). (solid line): Ru(phen)<sub>3</sub><sup>4-</sup> only,  $c = 1 \mu\text{M}$ ; (dashed line): P-NEt<sub>3</sub><sup>+</sup> and Ru(phen)<sub>3</sub><sup>4-</sup> both at  $c = 1 \mu\text{M}$ .

330 nm and a strong blue fluorescence with  $\lambda_{max} = 408$  nm ( $\tau \approx 600$  ps). These features are very similar to those of other PPP-type polymers indicating that the nominal photophysics of P-NEt<sub>3</sub><sup>+</sup> is not strongly influenced by the presence of the quaternary ammonium side-groups.<sup>11–14</sup> The fluorescence of P-NEt<sub>3</sub><sup>+</sup> in aqueous solution is quenched by a variety of anions at a very low concentration. Examples of this effect are illustrated in the Stern–Volmer (SV) plots shown in Figure 2a and 2b, which illustrate quenching of P-NEt<sub>3</sub><sup>+</sup> by Ru(phen)<sub>3</sub><sup>4-</sup> and Fe(CN)<sub>6</sub><sup>4-</sup>. The SV plots exhibit upward curvature and the quenching efficiencies depend strongly on the polymer concentration.<sup>15</sup> Both of these features indicate that the quencher anions preassociate with P-NEt<sub>3</sub><sup>+</sup> (i.e., quenching is static).<sup>16–18</sup> Ru(phen)<sub>3</sub><sup>4-</sup> and Fe(CN)<sub>6</sub><sup>4-</sup> quench the fluorescence of the monomer dication terphenyl model (M-NEt<sub>3</sub><sup>+</sup>), also by a static quenching mechanism. However, the quenching of the model is much less efficient—a large stoichiometric excess of the quencher is needed to significantly quench the fluorescence of M-NEt<sub>3</sub><sup>+</sup>.<sup>19</sup> The fact that the anions quench M-NEt<sub>3</sub><sup>+</sup> less efficiently than P-NEt<sub>3</sub><sup>+</sup> indicates that the polymer chain amplifies the quenching.

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(15) SV quenching efficiencies obtained by “best fit” linear least-squares are as follows: [P-NEt<sub>3</sub><sup>+</sup>] = 1.0  $\mu\text{M}$ ,  $K_{SV}(\text{Ru}(\text{phen})_3^{4-}) = 1.4 \times 10^8 \text{ M}^{-1}$  and  $K_{SV}(\text{Fe}(\text{CN})_6^{4-}) = 9.3 \times 10^7 \text{ M}^{-1}$ ; [P-NEt<sub>3</sub><sup>+</sup>] = 10  $\mu\text{M}$ ,  $K_{SV}(\text{Ru}(\text{phen})_3^{4-}) = 8.0 \times 10^5 \text{ M}^{-1}$  and  $K_{SV}(\text{Fe}(\text{CN})_6^{4-}) = 5.4 \times 10^5 \text{ M}^{-1}$ .

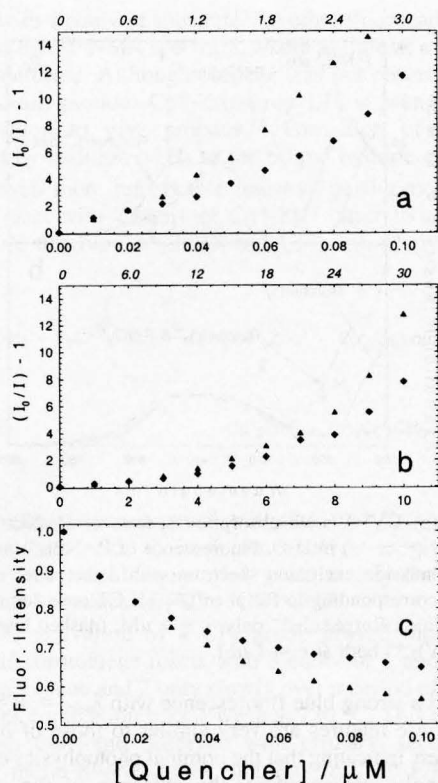
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**Figure 2.** Stern–Volmer quenching plots for  $P-NEt_3^+$  in  $H_2O$ , ( $\blacktriangle$ )  $Ru(phen)_3^{4-}$  and ( $\blacklozenge$ )  $Fe(CN)_6^{4-}$ . (a)  $[P-NEt_3^+] = 1 \mu M$ ; (b)  $[P-NEt_3^+] = 10 \mu M$ . Italic numbers at the top of (a) and (b) indicate the ratio  $[quencher]/[polymer]$ , where  $[polymer] = [repeat\ unit]/X_n$ . (c) Relative fluorescence intensity of adsorbed film of  $P-NEt_3^+$  as a function of added quencher to an aqueous solution that is in contact with film, ( $\blacktriangle$ )  $Ru(phen)_3^{4-}$  and ( $\blacklozenge$ )  $Fe(CN)_6^{4-}$ .

There are several noteworthy features with respect to the  $P-NEt_3^+$  quenching data. First, given the short fluorescence lifetime of the polymer, the extraordinary quenching efficiencies clearly indicate that quenching involves an ion-pair between the small molecule tetra-anions and  $P-NEt_3^+$ .<sup>20</sup>  $Ru(phen)_3^{4-}$  quenches more efficiently than  $Fe(CN)_6^{4-}$ , suggesting that the larger “amphiphilic” Ru-complex anion associates more strongly with  $P-NEt_3^+$ . Second, in the quenching studies carried out with  $[P-NEt_3^+] = 1 \mu M$  (repeat unit concentration), greater than 90% quenching is observed at  $[quencher] \approx 0.08 \mu M$ , which corresponds to approximately 12 repeat units per quencher. As such, the quenchers are present at 2:1  $[quencher]:[polymer]$  ratio (Figure 2a), and on average binding of one or two quenchers per  $P-NEt_3^+$  chain effectively “turns off” the fluorescence of the entire polymer.<sup>21</sup> This implies that in  $P-NEt_3^+$ , the  $^1\pi,\pi^*$  exciton diffuses along the polymer chain to the quencher on a time scale that is rapid compared with its lifetime (600 ps).<sup>9</sup> Time-resolved fluorescence experiments were carried out to determine if the fluorescence decay of  $P-NEt_3^+$  in the presence of  $Ru(phen)_3^{4-}$  exhibits a “fast” decay component ( $\tau \ll 600$  ps) arising from the polymer-quencher ion pair. However, a fast decay component is

(19) SV quenching efficiencies obtained by “best fit” linear least-squares are as follows:  $[M-NEt_3^+] = 10 \mu M$ ,  $K_{SV}(Ru(phen)_3^{4-}) = 24000 M^{-1}$  and  $K_{SV}(Fe(CN)_6^{4-}) = 8900 M^{-1}$ .

(20) The  $K_{SV}$  values obtained at  $[P-NEt_3^+] = 1 \mu M$  imply second-order quenching rate constants that are in excess of the diffusion-controlled rate by a factor of  $10^9$ .

(21) The association constant for  $Ru(phen)_3^{4-}$  binding to  $P-NEt_3^+$  has been determined independently ( $K_b = 4.6 \times 10^5 M^{-1}$ , see Supporting Information). Based on this  $K_b$ , we estimate that for a solution containing  $[P-NEt_3^+] = 1 \mu M$  and  $[Ru(phen)_3^{4-}] = 80$  nM (> 90% fluorescence

not observed, indicating that quenching is instantaneous on the time scale accessible with our instrumentation (200 ps). We conclude that exciton diffusion and quenching occurs with a rate in excess of  $10^{10} s^{-1}$ .

Emission excitation spectroscopy indicates that quenching involves energy transfer from the  $P-NEt_3^+$   $^1\pi,\pi^*$  exciton to the triplet metal-to-ligand charge transfer ( $^3MLCT$ ) state of  $Ru(phen)_3^{4-}$ . Thus, Figure 1b compares excitation spectra for MLCT emission at 610 nm from a solution containing  $1 \mu M Ru(phen)_3^{4-}$  only, and for a solution of  $Ru(phen)_3^{4-}$  and  $P-NEt_3^+$  where both the quencher and repeat unit concentration =  $1 \mu M$ . The significant aspect is that the excitation spectrum of the mixture displays considerably enhanced excitation efficiency in the UV region where  $P-NEt_3^+$  absorbs ( $\lambda = 300\text{--}375$  nm). This feature establishes that light absorbed by  $P-NEt_3^+$  leads to emission from the MLCT state of  $Ru(phen)_3^{4-}$ . In essence the  $Ru(phen)_3^{4-}$  that is ion-paired with the  $P-NEt_3^+$  chain acts as a low-energy photoluminescent trap for the highly mobile  $^1\pi,\pi^*$  exciton. While the exciton is expected to be very mobile,<sup>1,9,22,23</sup> long-range energy transfer may be facilitated by dipole–dipole (Förster) coupling between the  $P-NEt_3^+$  donor and the  $Ru(phen)_3^{4-}$  acceptor. Indeed, a computation based on the spectra and photophysical properties of the two chromophores indicates that the Förster transfer distance ( $R_0$ ) is  $\approx 40 \text{ \AA}$ .<sup>24</sup> Quenching by  $Fe(CN)_6^{4-}$  may also occur by energy transfer, however, since this complex does not photoluminesce it is not possible to confirm that the excited-state complex is produced by quenching.

Although we expected that increasing the  $P-NEt_3^+$  concentration would attenuate the efficiency by which the anions quench the polymer, the effect is larger than anticipated. Specifically,  $Ru(phen)_3^{4-}$  and  $Fe(CN)_6^{4-}$  quench the polymer approximately 100-fold less efficiently when  $[P-NEt_3^+] = 10 \mu M$  compared to that for  $[P-NEt_3^+] = 1 \mu M$  (compare Figure 2a and 2b). The decreased quenching efficiency may arise from aggregation of the polycation at higher concentration.

To demonstrate amplified quenching in a solid-state sensor, quenching studies were carried out with  $P-NEt_3^+$  thin films.<sup>25,26</sup> Hydrophilic glass slides that had been immersed into an aqueous solution containing  $P-NEt_3^+$  (3 mM in repeat units) for 15 min followed by a rinse in distilled water were examined by absorption and photoluminescence spectroscopy. This analysis indicated the presence of a thin adsorbed  $P-NEt_3^+$  film (absorption,  $\lambda_{max} = 339$  nm,  $A_{max} = 0.011$ ; fluorescence,  $\lambda_{max} = 410$  nm).<sup>27</sup> Photoluminescence from the film is quenched strongly when exposed to dilute solutions of  $Ru(phen)_3^{4-}$  or  $Fe(CN)_6^{4-}$ . Figure 2c illustrates a plot of fluorescence intensity vs amount of quencher added to an aqueous solution that was in contact with an adsorbed film of  $P-NEt_3^+$ . Detectable quenching is observed upon addition of less than 20 nM of either quencher.

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**Supporting Information Available:** Description of method used to determine association constant between  $P-NEt_3^+$  and  $Ru(phen)_3^{4-}$  (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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