

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

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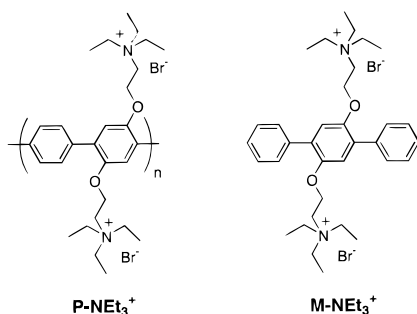
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Application of fluorescent conjugated polymers to “amplified” sensing of chemical and biological analytes has received considerable recent attention.^{1–8} Fluorescence sensing is amplified by conjugated polymers because of the “molecular wire effect”,^{1,2} 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;^{1,2,5–7} however, several recent reports feature fluorescent thin film sensors that operate by coming into contact with a liquid- or vapor-phase analyte.^{3,4} 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.⁸

In the present contribution we describe fluorescence quenching of the water soluble, poly(*p*-phenylene)-based polycation, P-NEt₃⁺ dibromide by several anionic quenchers, including Ru(phen')₃⁴⁻ and Fe(CN)₆⁴⁻ in aqueous solution (phen' = 4,7-bis(4-sulfophenyl)-1,10-phenanthroline). P-NEt₃⁺ fluorescence is quenched by these anions with considerably higher efficiency compared to a terphenyl model compound, M-NEt₃⁺ dibromide. Amplified quenching of P-NEt₃⁺ 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 ¹ππ* exciton rapidly brings it into contact with the ion-paired quencher.⁹ We also establish that quenching of P-NEt₃⁺ by Ru(phen')₃⁴⁻ occurs via energy transfer by observing the metal complexes' photoluminescence when the excitation light is absorbed mainly by the polymer.



Polycation P-NEt₃⁺, prepared by Suzuki coupling,¹⁰ 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 = 1.16.¹⁰ As illustrated in Figure 1a, in aqueous solution P-NEt₃⁺ features an absorption at $\lambda_{\max} =$

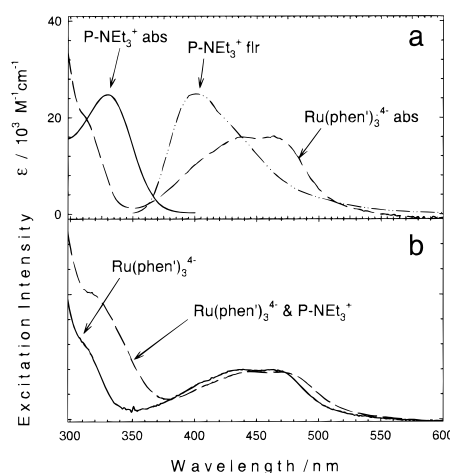


Figure 1. (a) UV-Visible absorption spectra of P-NEt₃⁺ (—) and Ru(phen')₃⁴⁻ (---) in H₂O. Fluorescence of P-NEt₃⁺ in H₂O (—••—••). (b) Emission excitation spectrum with detector set at emission wavelength corresponding to Ru(phen')₃⁴⁻ MLCT emission ($\lambda_{\text{em}} = 610$ nm). (solid line): Ru(phen')₃⁴⁻ only, $c = 1$ μM ; (dashed line): P-NEt₃⁺ and Ru(phen')₃⁴⁻ both at $c = 1$ μM .

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-NEt₃⁺ is not strongly influenced by the presence of the quaternary ammonium side-groups.^{11–14} The fluorescence of P-NEt₃⁺ 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-NEt₃⁺ by Ru(phen')₃⁴⁻ and Fe(CN)₆⁴⁻. The SV plots exhibit upward curvature and the quenching efficiencies depend strongly on the polymer concentration.¹⁵ Both of these features indicate that the quencher anions preassociate with P-NEt₃⁺ (i.e., quenching is static).^{16–18} Ru(phen')₃⁴⁻ and Fe(CN)₆⁴⁻ quench the fluorescence of the monomer dication terphenyl model (M-NEt₃⁺), 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 N-NEt₃⁺.¹⁹ The fact that the anions quench M-NEt₃⁺ less efficiently than P-NEt₃⁺ 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-NEt₃⁺] = 1.0 μM , $K_{\text{SV}}(\text{Ru}(\text{phen}')_3^{4-}) = 1.4 \times 10^6 \text{ M}^{-1}$ and $K_{\text{SV}}(\text{Fe}(\text{CN})_6^{4-}) = 9.3 \times 10^7 \text{ M}^{-1}$; [P-NEt₃⁺] = 10 μM , $K_{\text{SV}}(\text{Ru}(\text{phen}')_3^{4-}) = 8.0 \times 10^5 \text{ M}^{-1}$ and $K_{\text{SV}}(\text{Fe}(\text{CN})_6^{4-}) = 5.4 \times 10^5 \text{ M}^{-1}$.
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- (18) Static quenching is confirmed by the fact that the fluorescence lifetime of P-NEt₃⁺ does not vary with the quencher concentration.

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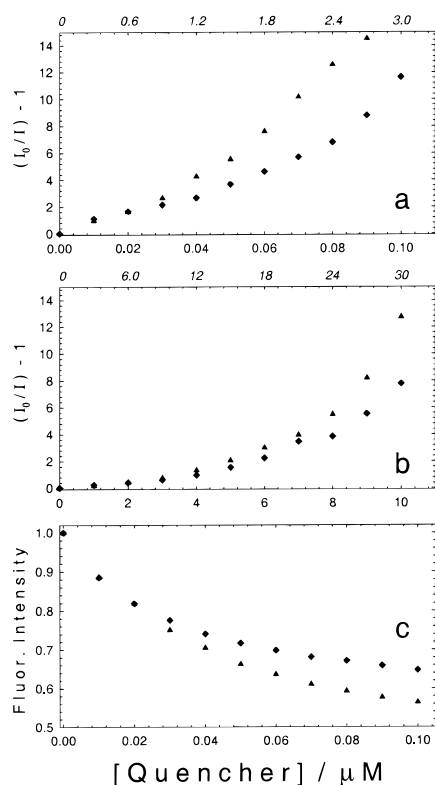


Figure 2. Stern–Volmer quenching plots for $P-NEt_3^+$ in H_2O , ($\blacktriangle$) $Ru(phen)_3^{4-}$ and ($\blacklozenge$) $Fe(CN)_6^{4-}$. (a) $[P-NEt_3^+] = 1 \mu M$; (b) $[P-NEt_3^+] = 10 \mu M$. Italic numbers at the top of (a) and (b) indicate the ratio $[quencher]/[polymer chain]$, where $[polymer] = [repeat unit]/X_n$. (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 $P-NEt_3^+$.²⁰ $Ru(phen)_3^{4-}$ 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 $[quencher]:[polymer chain]$ 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.²¹ 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).⁹ 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 10^8 .

(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 quenching, see Figure 1a) the concentration of polymer-bound $Ru(phen)_3^{4-}$ is ≈ 25 nM. Remarkably, the concentration of polymer-bound $Ru(phen)_3^{4-}$ corresponds closely to the polymer chain concentration, i.e., $([repeat unit]/X_n) = (1 \mu M/28) = 36$ nM, which indicates that $> 90\%$ quenching occurs when approximately one quencher is bound per chain.

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 ($\lambda = 300–375$ 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,^{1,9,22,23} 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 ≈ 40 Å.²⁴ 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.^{25,26} 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).²⁷ 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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(27) On the basis of the absorption, we estimate that the film coverage is approximately 2.4×10^{-10} mol·cm⁻² (repeat unit), which is approximately equal to the coverage expected for a single monolayer of the polymer.