Luminescence Quenching of a Phosphorescent Conjugated Polyelectrolyte

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Abstract: The photophysical and luminescence quenching properties of a platinum(II) acetylide-based conjugated polyelectrolyte, Pt-p, which features carboxylic acid solubilizing groups are reported. The Pt-acetylide polymer is water soluble, and it exhibits phosphorescence from a triplet π,π^* exciton based on the conjugated backbone. The phosphorescence from Pt-p is quenched by viologens with different charges (MV^+, MV^{2+}, and MV^{4+}), and in each case the quenching is dominated by a dynamic (diffusional) mechanism. Comparison of the Stern−Volmer quenching properties of Pt-p with those of a structurally analogous fluorescent organic polyelectrolyte leads to the conclusion that the amplified quenching effect, which is commonly observed for fluorescent conjugated polyelectrolytes, is not important for the platinum acetylide phosphorescent conjugated polyelectrolyte.

Introduction

Amplified quenching of fluorescent conjugated polymers has received considerable attention because of its potential for application in ultrasensitive chemo- and biosensors.[1−7] Amplified fluorescence quenching was first demonstrated in an organic-soluble poly(phenylene ethynylene) (PPE) functionalized with cyclophane receptors.[1] This work showed that the polymer's fluorescence is quenched approximately 60 times more efficiently as compared to an analogous monomer. Amplified quenching is attributed to the formation of an association complex between the quencher and the polymer chain, along with delocalization and/or rapid diffusion of the singlet exciton that is responsible for the polymer's fluorescence.

More recently, interest has focused on amplified quenching in fluorescent conjugated polyelectrolytes (CPEs).[4,8] This family of conjugated polymers features ionic solubilizing groups that make them soluble in water and other polar solvents. The fluorescence of CPEs is quenched by oppositely charged quencher ions very efficiently. Stern−Volmer quenching constants (K_{SV}) as high as 10^8 M^{-1} have been reported,[9] corresponding to efficient quenching at 1:1 polymer chain to quencher stoichiometry, with a million-fold signal amplification as

compared to quenching of the corresponding monomers.[4] Amplified quenching in CPEs is believed to arise due to ion-pairing between the polymer chain and the quencher ion, combined with highly efficient intra- and interchain exciton delocalization and diffusion.[4,9−11] The higher signal amplification that has been achieved in the CPE-ionic quencher systems, as compared to the organic soluble receptor-based system,[1] arises because the ion-pair association constants are enhanced in the polymer systems relative to the monomers, and because the CPEs have a tendency to self-assemble into nanoscale aggregates which promote interchain exciton diffusion.[11]

While association between the quencher and polymer chain is an important component of the amplified quenching effect, it is evident that delocalization and rapid intrachain diffusion of the singlet exciton also play an important role.[9,11,12] Theoretical and experimental studies indicate that in poly(phenylene vinylene) (PPV) and PPE-type conjugated polymers, the singlet exciton is delocalized over $10-20$ polymer repeat units (PRUs), and that the exciton hops between adjacent chromophores on a chain via a dipole−dipole-type (Förster) coupling mechanism with rates on the order of $1-0.1$ ps^{-1}.[13] These effects combined ensure that during its 1 ns lifetime, a typical singlet exciton will sample an entire conjugated polymer chain that consists of $100-1000$ PRUs.

In conjugated polymers, the singlet exciton decays primarily by radiative (fluorescence) and nonradiative decay channels; however, in some cases, intersystem crossing to produce the

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Scheme 1
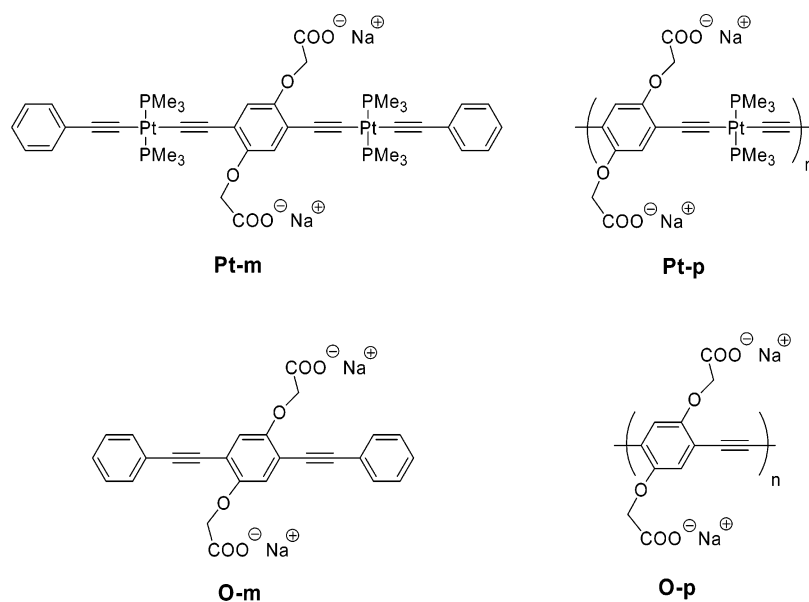
triplet exciton is competitive.[14−16] Although room-temperature luminescence from the triplet exciton (phosphorescence) in conjugated polymers is rare, due to the importance of triplet excitons to the performance of polymer light-emitting diodes,[17] there has been considerable recent interest in characterizing the properties of the triplet in conjugated materials.[15,16,18−22] Insight into the structure and spectroscopy of the triplet exciton in conjugated systems has been gained via the study of conjugated oligomers and polymers that contain heavy metals that are strongly coupled to the π-conjugated electronic system. Of particular importance has been work on polymers and oligomers that contain platinum(II) acetylides.[18−20,23] These materials have optical properties that are remarkably similar to those of all-organic PPE-type materials, yet due to strong spin−orbit coupling induced by the Pt center they exhibit high intersystem crossing efficiency and room-temperature phosphorescence. In addition, the triplet exciton has a considerably longer lifetime as compared to the singlet, with typical lifetimes on the order of $10-100$ μs. Spectroscopic studies of Pt-acetylide polymers and oligomers demonstrate that the triplet exciton is much less delocalized as compared to the singlet exciton in π-conjugated polymers.[20,23,24] In particular, the available evidence indicates that the triplet exciton is confined to two or at most three repeat

units in a typical π-conjugated system.[20,23] This effect was predicted many years ago by theory,[25] and it can be qualitatively understood by recognizing that the primary mechanism for singlet delocalization is dipole−dipole coupling which depends weakly on distance, whereas triplet state delocalization involves exchange interactions that are strongly distance dependent.[26]

In view of the significant difference in spatial delocalization and lifetime between the triplet and singlet excitons, we became curious as to whether amplified quenching would also be observed in a conjugated polyelectrolyte in which the triplet exciton dominates the photophysics. On one hand, it seemed possible that amplified quenching would be attenuated because the triplet exciton is spatially confined, and because it may also diffuse along a polymer chain more slowly than the singlet due to weak interchromophore coupling afforded by exchange interactions. On the other hand, it also seemed plausible that because of its longer lifetime, dynamic quenching of the triplet exciton via intrachain diffusion of the exciton to the quencher "trap" site would be highly efficient.

To explore these effects, we prepared and carried out a photophysical investigation of a novel platinum(II) acetylide-based conjugated polyelectrolyte (Pt-p, Scheme 1). This polymer is a weak polyelectrolyte that is water soluble. By analogy to other π-conjugated Pt-acetylide polymers and oligomers, Pt-p exhibits moderately intense phosphorescence at room temperature, and its photophysical properties are dominated by the triplet exciton. The corresponding model oligomer, Pt-m, was also prepared to provide a benchmark for the luminescence quenching experiments. In addition, a PPE-type organic conjugated polyelectrolyte, O-p, and its corresponding model oligomer, O-m, were prepared and investigated. Due to the structural similarity between O-p and Pt-p, these two polyelectrolytes are expected to exhibit similar solution properties. In addition, because O-p features strong fluorescence, quenching studies of this material provide insight into the amplified quenching effect in a system which is structurally analogous to Pt-p, yet its photophysical properties are dominated by the singlet exciton.

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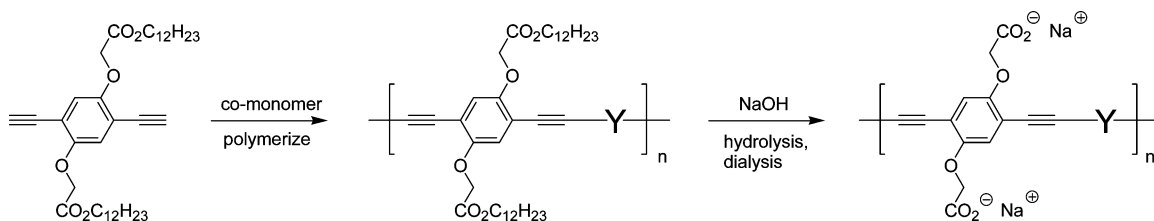(23) Liu, Y.; Jiang, S.; Glusac, K.; Powell, D. H.; Anderson, D. F.; Schanze, K. S. *J. Am. Chem. Soc.* **2002**, *124*, 12412−12413.
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Scheme 2

Table 1. Photophysical Data and Stern−Volmer Luminescence Quenching Constants[a]

| material | λ_{abs}/nm | λ_{em}/nm | ϕ_{em}/% | τ_{em} | MV$^+$ K_{SV}/10^5 M^{-1} | | MV^{2+} K_{SV}/10^5 M^{-1} | | MV^{4+} K_{SV}/10^5 M^{-1} | |
					I^0/I[b]	τ^0/τ[c]	I^0/I[b]	τ^0/τ[c]	I^0/I[b]	τ^0/τ[c]
O-m	304	395	92	1.6 ns	0.091		0.16		0.66	
	357									
O-p	317	470	6.3	0.3 ns (0.88)[d]	8.5		6[e]		36[e]	
	428			3.3 ns (0.12)						
Pt-m	374	548	6.2	31 μs	3.3	3.0	7.1	5.9	5.3	4.6
Pt-p	398	548	0.75	19 μs	9.0	5.8	9.6	7.1	11[e]	1.5

[a] All measurements on argon-outgassed solutions in water, pH = 6.5. [b] Stern−Volmer constants obtained from steady-state emission quenching. Where plots are curved, the K_{SV} values represent the slope of the linear region at low quencher concentration. The estimated error in K_{SV} values is ±10%. [c] Stern−Volmer constants obtained from lifetime quenching. [d] Biexponential decay; numbers in parentheses indicate the relative amplitude of the lifetime component. [e] Stern−Volmer plot is curved upward.

Experimental Section

Complete details concerning the synthesis, characterization, and purification of Pt-m, Pt-p, O-m, and O-p are provided as Supporting Information. The quenchers, MV$^+$ and MV^{4+}, were prepared according to literature procedures.[27] The water used in all experiments was prepared in a Millipore Milli-Q plus purification system and displayed a resistivity of ≥18.2 MΩ cm^{-1}. Variable pH absorption and emission measurements were obtained using 1 mM acetate buffer. The samples used for emission spectroscopy were optically dilute (i.e., the absorbance at all wavelengths was <0.2). Photoluminescence quantum yields were determined using Ru(bpy)$_3$$^{2+}$ in water as standard (Φ = 0.055).[28] Luminescence quenching experiments were conducted using 10 μM solutions of O-p, O-m, Pt-p, and Pt-m. Solutions of Pt-p and Pt-m were deoxygenated by bubbling with argon for 15 min prior to all measurements.

UV−visible absorption spectra were obtained on a Cary 100 instrument. Steady-state photoluminescence spectroscopy was carried out on a SPEX Fluorog 2 instrument. Emission spectra were corrected by using correction factors generated in-house with a standard calibration lamp. Photoluminescence decay lifetimes for O-m and O-p were determined by time-correlated single photon counting on an instrument that was constructed in-house. Excitation was provided by a near-UV light-emitting diode (λ_{em} = 370 nm, nanoLED-03, IBH, Glasgow, U.K.) operating at a 100 kHz repetition rate. Photoluminescence decay lifetimes for Pt-m and Pt-p were determined using the third harmonic output of a Nd:YAG laser (355 nm, Spectra Physics, GCR-14) as the excitation source. The light emitted from the sample was focused onto the slit of a monochromator (Oriel Corp., 72250) and was detected with a photomultiplier tube.

Results and Discussion

Synthesis and Characterization. The two conjugated polyelectrolytes that are the focus of the present investigation were prepared via the sequence illustrated in Scheme 2. In each case, step-growth polymerizations were carried out to afford precursor polymers in which the carboxyl groups are protected as dodecyl
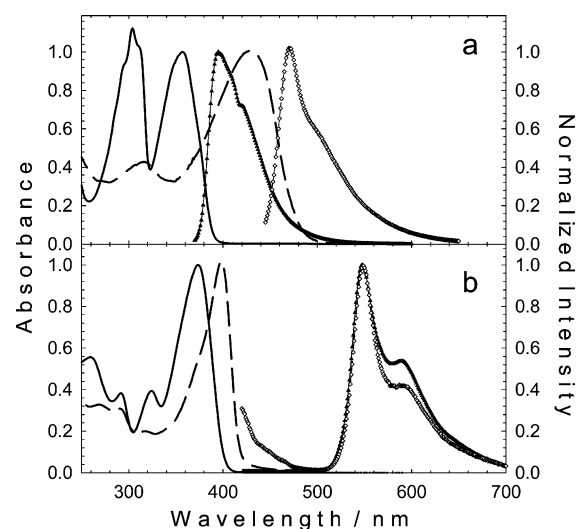
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Figure 1. Absorption and emission spectra in aqueous acetate buffer solution, pH = 7. (a) (—) O-m, absorption; (−▲−▲) O-m, fluorescence; (− −) O-p, absorption; (−◇−◇) O-p, fluorescence. (b) (—) Pt-m, absorption; (−▲−▲) Pt-m, phosphorescence; (− −) Pt-p, absorption; (−◇−◇) Pt-p, phosphorescence.

esters. The diester precursor polymers are soluble in organic solvents (e.g., THF, CHCl$_3$), and consequently their molecular weights could be characterized by GPC. GPC analysis (using polystyrene standards) of the diester precursor polymer of O-p afforded M_n = 15 800 g mol^{-1} and M_w = 31 500 g mol^{-1} (PDI = 1.99), and for the diester precursor of Pt-p, M_n = 23 100 g mol^{-1} and M_w = 36 600 g mol^{-1} (PDI = 1.58). The polyelectrolytes were obtained by base-promoted hydrolysis of the esters, and the final materials were purified by dialysis against Milli-Q water using an 8 kD molecular weight cutoff dialysis membrane. The final polyelectrolytes were characterized via ^{1}H NMR (and in the case of Pt-p, ^{31}P NMR) spectroscopy.

Photophysics of the Conjugated Polyelectrolytes. Figure 1a compares the absorption and emission spectra of the organic polymer and model compound in water at pH = 7, and the absorption and emission band maxima are listed in Table 1.
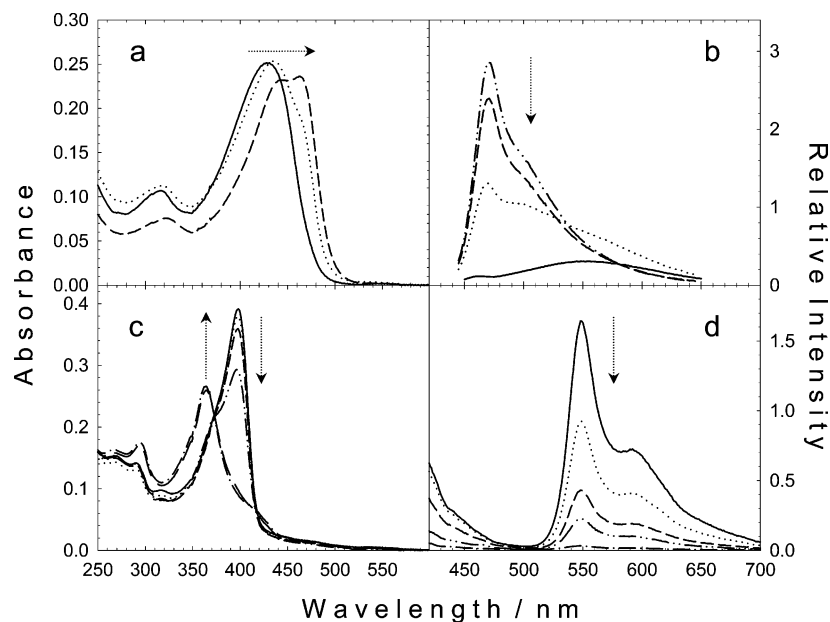
Figure 2. Absorption and emission spectra as a function of pH in aqueous acetate buffer solution. (a) O-p absorption; (—) pH = 5.5; (•••) pH = 5.0; (— — —) pH = 4.5. (b) O-p fluorescence; (—•—) pH = 6.5; (— — —) pH = 6.0; (•••) pH = 5.5; (—) pH = 5.0. (c) Pt-p absorption; (—) pH = 6.0; (•••) pH = 5.5; (— — —) pH = 5.0; (—••—) pH = 4.5; (— — —) pH = 4.0; (—•—) pH = 3.5. (d) Pt-p emission; (—) pH = 6.0; (•••) pH = 5.5; (— — —) pH = 5.0; (—••—) pH = 4.5; (—•—) pH = 4.0; (— — —) pH = 3.5.

The model, O-m, has two absorption bands in the UV; the long wavelength band (λ_{max} = 357 nm) is due to the long-axis polarized π,π^* transition. The model features a high quantum yield, short lifetime, blue-violet emission, which is Stokes-shifted only slightly from the absorption (Table 1). The fluorescence is believed to arise from the long-axis polarized π,π^* excited state. The organic polymer, O-p, features a single broad absorption band that is red-shifted significantly from the model's absorption. The polymer exhibits a moderately intense, short-lifetime fluorescence that is Stokes shifted only slightly from the absorption band. The band shape of the fluorescence from O-p is typical of that observed for PPE-type polymers in good solvents,[1,29] suggesting that at neutral pH the polymer is not strongly aggregated.

Figure 1b illustrates the absorption and emission of the Pt-acetylide model and polymer in water at pH = 7. The model and the polymer both exhibit a single broad absorption feature in the near-UV region. The absorption of Pt-p is red-shifted slightly from that of the model, giving evidence that in the Franck−Condon singlet excited state that is produced by light absorption there is a higher degree of delocalization in the polymer as compared to the monomer. The emission of Pt-m and Pt-p is dominated by a structured band that is significantly Stokes-shifted from the absorption. The emission is long-lived (τ = 31 μs and 19 μs for Pt-m and Pt-p, respectively), and on this basis it is assigned to phosphorescence from the $^3\pi,\pi^*$ excited state. Interestingly, the emission λ_{max} is virtually identical in the model and polymer. This finding highlights the fact that the triplet exciton is not significantly delocalized in the polymer. This observation is consistent with the results of a previous investigation of Pt-acetylide oligomers which suggested that the triplet is localized on a chromophore consisting of Ph−C≡C−Pt−C≡C−Ph−C≡C−Pt−C≡C−Ph (where Ph = 1,4-phenylene).[23] In addition, the optical properties of the water soluble

Pt-acetylides are very similar to those of structurally similar Pt-acetylide oligomers and polymers that have been investigated in organic solvents and in thin films.[23,30−33] This indicates that the polar aqueous environment has little effect on the electronic structure or energy of the $^3\pi,\pi^*$ exciton in the Pt-acetylide polymer.

Effect of pH on the Optical Properties of O-p and Pt-p. In previous investigations, we have shown that CPEs aggregate in poor solvents or when the charge on weak acid solubilizing groups is neutralized by protonation.[34,35] Similar behavior is observed for the weak polyelectrolytes that are the subject of the present investigation. Figure 2a and b illustrates the changes in the absorption and fluorescence spectra of O-p as a function of pH over the range pH = 6.0−4.5. With decreasing pH, the absorption and fluorescence of the polymer red-shift; note that, at low pH, the fluorescence is considerably weaker and appears as a broad, structureless band. Virtually identical changes in the absorption and fluorescence have been observed in structurally related PPE-type conjugated polyelectrolytes.[34,35] By analogy to the previously studied polymers,[36] the broad fluorescence observed for O-p is attributed to an excimer-like state that dominates the photophysics of the aggregated polymer. The aggregate is believed to consist of π-stacked chains produced at low pH because interchain charge repulsion is reduced by protonation of the weakly acidic carboxylic acid groups.[34,35] The red-shifted absorption in the aggregate arises due to increased

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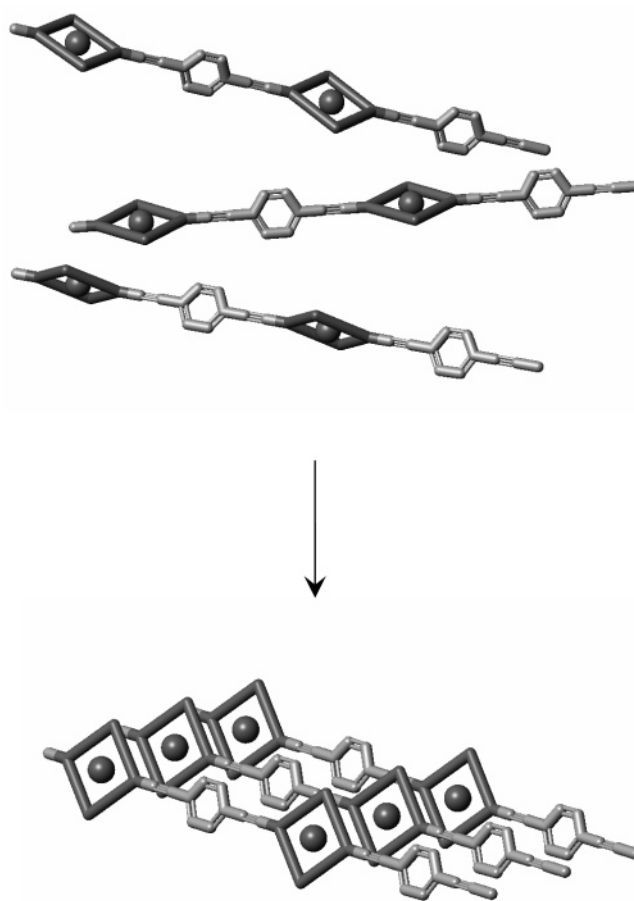
π-conjugation along the polymer backbone resulting from coplanar orientation of the phenylene rings that is imposed by π-stacking in the aggregate.[37]

Figure 2c and d illustrates the absorption and emission spectra of Pt-p as pH is varied over the range 6.0−3.5. The changes observed for Pt-p are also believed to arise because the polymer aggregates as pH is reduced; however, interestingly the effects of aggregation are different for Pt-p relative to those of O-p. In particular, the absorption of Pt-p blue-shifts with decreasing pH, while the phosphorescence decreases in intensity. Importantly, the decrease in phosphorescence intensity is not accompanied by a decrease in lifetime. This observation indicates that the aggregation-induced emission quenching has the characteristics of static quenching.[38,39] Apparently, excitons that are produced in close proximity to the aggregate are quenched rapidly, whereas those that are distal (or on an unaggregated chain) are unable to diffuse to the aggregate site.

The absorption of Pt-p features a clear isosbestic point as pH is varied, suggesting that the absorption shift is associated with a specific change in conformational state of the polymer. We believe that the change in the absorption of Pt-p that accompanies aggregation arises for similar reasons as the red-shift that is observed in absorption of the O-p aggregate. Thus, it is likely that the Pt-p aggregate also consists of stacked polymer chains in which the planes defined by the square-planar PtP_2C_2 units and the phenylene rings are in an all coplanar orientation. The absorption of the polymer blue-shifts because in this conformation the extent of π-conjugation through the Pt actylide units is decreased relative to that for the "twisted" conformation (see Scheme 3). In support of this premise, X-ray crystal structures of Pt-acetylide oligomers[33,40] and electronic structure calculations[41] indicate that, in the preferred conformation of the ground state, the phenylene rings are twisted more than 60° relative to the plane defined by the PtP_2C_2 unit (as shown schematically in the upper portion of Scheme 3). The preference for the twisted conformation may arise due to steric interactions between the phenylene units and the alkyl phosphines, and also because $d\pi$−$p\pi$ interactions are optimal when the Pt d_{xy} (in-plane) orbital is involved.

An important question concerns the basis for phosphorescence quenching in the Pt-p aggregate. This behavior differs from what is typically observed for fluorescent conjugated polymers, where aggregation is typically manifested by a red-shift and broadening of the emission.[34,42−46] The aggregate emission in conjugated

Scheme 3

polymers is analogous to fluorescence from an excimer, which is well-documented in many small-molecule fluorophores (e.g., the pyrene excimer).[47] Excimer fluorescence arises from a singlet excited-state complex in which the excitation is stabilized by delocalization over the two chromophores.[47,48] Importantly, although triplet excimers have been postulated to exist as intermediates in photochemical processes,[49,50] unambiguous evidence for phosphorescence from a triplet excimer has never been obtained.[51,52] The available evidence indicates that triplet excimers are not stabilized significantly relative to the locally excited state, and when formed they decay rapidly by intersystem crossing to the ground state (therefore, phosphorescence cannot compete).[52] Thus, it possible that the phosphorescence quenching that is observed in the Pt-p aggregate arises because nonradiative decay of the triplet aggregate state is too fast for phosphorescence to be competitive.

An alternate explanation for phosphorescence quenching in the Pt-p aggregate is the introduction of an energetically low-lying excited state based on interchain metal−metal interactions. In particular, the face-to-face interaction of two square-planar d^8 PtP_2C_2 units affords a manifold of energetically low lying

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excited states having $d\sigma^* \rightarrow p\sigma$ character.[53−55] It is possible that the interchain interactions in the Pt-p aggregate give rise to a $d\sigma^* \rightarrow p\sigma$ manifold which provides a pathway for rapid nonradiative decay of the triplet exciton.

Emission Quenching Studies. Prior to discussing the experimental results, it is necessary to briefly describe the model used to interpret the Stern−Volmer (SV) emission quenching data. This discussion is brief, and the reader is directed to the literature for more details concerning the analysis of quenching data.[38] When quenching of a chromophore occurs via mixed-mode static and dynamic pathways, in the limit of low quencher concentration, the emission intensity (I) obeys the following relationship,

$$\frac{I^{o}}{I} = 1 + (K_{a} + K_{sv}^{\tau})[Q] = 1 + K_{sv}^{I}[Q] \quad (1)$$

where K_{sv}^{I} is the slope of the emission intensity quenching SV plot, K_{a} is the association constant for the chromophore−quencher ground state (ion pair) complex, and K_{sv}^{τ} is the slope of the emission lifetime quenching SV plot (i.e., the SV constant for dynamic quenching). When the quenching process is moderately or strongly exothermic, $K_{sv}^{\tau} = k_{d}\tau^{o}$, where k_{d} is the diffusion rate constant ($\sim 10^{10}$ M^{-1} s^{-1}) and τ^{o} is the emission lifetime of the chromophore. For quenching of a chromophore with a relatively short emission lifetime ($\tau^{o} \approx 1$ ns), $K_{sv}^{\tau} \approx 10$ M^{-1}. In this case, if the chromophore and quencher form a relatively stable ground state (or ion-pair) complex ($K_{a} \geq 100$ M^{-1}), the emission intensity quenching SV plot affords a direct measure of the association constant, that is, $K_{sv}^{I} \approx K_{a}$. In contrast, if the emission lifetime of the chromophore is long (e.g., for a phosphorescent emitter), the value of K_{sv}^{τ} may be comparable to, or greater than, the ground-state association constant for the chromophore−quencher pair. In this case, the observed emission intensity quenching efficiency (K_{sv}^{I}) will be equal to the sum ($K_{a} + K_{sv}^{\tau}$). Note that when $K_{sv}^{\tau} \gg K_{a}$, $K_{sv}^{I} \approx K_{sv}^{\tau}$.

Stern−Volmer (SV) emission quenching experiments were carried out on the two anionic conjugated polyelectrolytes, O-p and Pt-p, as well as on the corresponding model compounds. Three cationic pyridinium ions (viologens) with different net charges were used as quenchers (Q): MV^{+} (*N*-methyl-4,4′-bipyridinium chloride), MV^{2+} (*N,N′*-dimethyl-4,4′-bipyridinium dichloride, paraquat), and MV^{4+} ($\alpha,\alpha′$-bis[1′-methyl-4,4′-bipyridinium]-*p*-xylene tetrachloride). These species quench excited states via photoinduced electron transfer.[56] Using these three pyridinium ions as quenchers, emission intensity quenching (I^{o}/I) studies were carried out for O-p and O-m, whereas intensity and lifetime quenching (τ^{o}/τ) was examined for Pt-p and Pt-m. The SV plots for O-p and Pt-p are shown in Figure 3, while SV quenching constants derived from all of the quenching studies are collected in Table 1.

First, we focus on the results for the organic materials O-p and O-m. For O-m, the SV plots (data not shown) are linear over the entire concentration range investigated ([Q] = 0−100
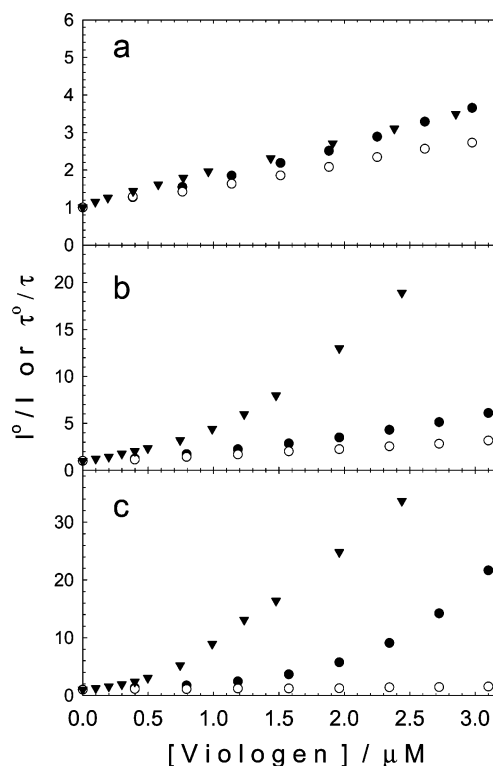
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Figure 3. Stern−Volmer quenching plots. (a) MV^{+} quencher. (b) MV^{2+} quencher. (c) MV^{4+} quencher. Legend: (▲) O-p; (●) Pt-p (I^{o}/I); (○) Pt-p (τ^{o}/τ).

μM), and the K_{sv} values span from 9.1×10^{3} to 6.6×10^{4} M^{-1}. In view of its short fluorescence lifetime (~ 1.6 ns), it is evident that quenching of O-m by the pyridinium ions occurs by a static quenching mechanism[38] arising due to ion-pair complex formation between the anionic fluorophore and the cationic pyridinium quencher. Thus, in this case, the association constant for ion-pair formation is reflected by K_{sv} (eq 1, $K_{a} \gg K_{sv}^{\tau}$), and, in accord with this notion, the K_{sv} values increase with increasing charge on the pyridinium ion quencher.

The SV plots for O-p shown in Figure 3 reveal several significant differences between the quenching of the polymer and model compound O-m. First, O-p is quenched at significantly lower concentration as compared to the model. For the MV^{2+} and MV^{4+} quenchers, more than 80% of the polymer's fluorescence is quenched at 1 μM quencher concentration. To attain a similar level of quenching with O-m, a quencher concentration in the range of 0.1−1 mM is required. This is a manifestation of the amplified quenching effect that has been reported previously in other conjugated polyelectrolytes.[4,34,57] Stern−Volmer constants for quenching of O-p extrapolated from the linear regions at low quencher concentration range from 2.9×10^{5} to 3.6×10^{6} M^{-1}. On the basis of these values, the polymer is quenched 20−60 times more efficiently relative to O-m. The degree of amplification of the quenching response is even more significant at higher quencher concentration due to the upward curvature in the O-p SV plots. Amplification of quenching in O-p is believed to arise due to ion-pair complex formation between O-p and the pyridinium ion quenchers, and because the exciton is strongly delocalized and is able to diffuse rapidly along a polymer chain to the site where the quencher is

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complexed. In effect, the quenching sphere of action of the viologens is spread out over a large number (>20) of polymer repeat units due to the exciton's high degree of delocalization and its high intrachain hopping rate.[11,58]

A second notable feature is that, although the SV plots for quenching of O-p by MV^{2+} and MV^{4+} are nearly linear at very low quencher concentration (<500 nM), they are curved upward at higher quencher concentration. The onset of the curvature occurs at lower concentration for MV^{4+} than for MV^{2+}, and as a result the tetravalent quencher is a considerably more effective quencher. This effect has been observed in the quenching of other conjugated polymers by polyvalent quencher ions.[9,11] We believe that it arises due to the ability of the polyvalent quencher ions to induce aggregation of the polymer chains.[11,59,60] Aggregation of the polymer chains allows interchain diffusion of the exciton, which effectively increases the sphere of action within which the viologen is able to efficiently quench a fluorescent exciton (i.e., because of polymer aggregation, a quencher is able to quench excitons produced on more than one polymer chain).[13]

Now, we turn to consider the quenching properties of the Pt-acetylide-based materials. There are several significant differences with respect to quenching of Pt-m and Pt-p as compared to quenching of the organic materials. First, all of the viologens quench Pt-m and Pt-p with close to the same efficiency. This result clearly indicates that there is little amplification of the quenching response for the polymer relative to that of the monomer model. The second noteworthy feature is that the K_{sv} values obtained for the Pt-p/MV^+ and Pt-p/MV^{2+} systems by intensity quenching (I^o/I vs [Q]) are only slightly larger as compared to those obtained by lifetime quenching (τ^o/τ vs [Q], see Table 1). A similar trend is seen for Pt-m quenching by all of the viologen quenchers. The close correspondence of the K_{sv} values derived from intensity and lifetime quenching indicates that dynamic quenching is the dominant mechanism for quenching in the Pt-acetylide materials; that is, the mechanism involves diffusion of the quencher to the excited-state complex (or exciton in the case of Pt-p). Interestingly, by using the K_{sv} values obtained by dynamic quenching and the emission lifetimes of Pt-m and Pt-p, we compute that the quenching rate constants (k_q) are close to those expected for diffusion-controlled collisional quenching between oppositely charged ions.[61,62] (For Pt-m, $k_q \approx (1-2) \times 10^{10}$ M^{-1} s^{-1}; Pt-p, $k_q \approx (3-4) \times 10^{10}$ M^{-1} s^{-1}. Diffusional quenching of Pt-p is expected to be more rapid because of the higher charge on the polymer chain.)

Importantly, the fact that diffusional quenching of Pt-m and Pt-p is dominant does not mean that there is not ion-pair complex formation between the cationic viologen quenchers and the anionic Pt-acetylides. The reason that static quenching is unimportant (even though ion-pairing occurs) is that, because of the long lifetime of the Pt-acetylides, dynamic quenching is so efficient that it masks the static quenching component (i.e., eq 1, $K_{sv}^\tau > K_a$). In support of this notion is the fact that the association constants calculated from the difference in the emission intensity and lifetime SV quenching constants for Pt-m are in the same range as the association constants obtained for quenching of O-m by the viologens ($K_a \approx K_{sv}^I - K_{sv}^\tau \approx 10^4 - 10^5$ M^{-1}, see eq 1).

At very low quencher concentration (<1 μM), the SV plot for the Pt-p/MV^{4+} system is linear, and the emission intensity and lifetime are quenched equally. However, at higher [MV^{4+}], the intensity quenching plot is curved upward, while the lifetime quenching remains linear. This behavior signals that static quenching becomes significant in the Pt-p/MV^{4+} system when the quencher is present at relatively higher concentrations. Nevertheless, despite the fact that static quenching of Pt-p occurs with MV^{4+}, the metal-organic polymer is still quenched considerably less efficiently than O-p. For example, at [MV^{4+}] = 1 μM, approximately 90% of the fluorescence from O-p is quenched, whereas only 50% of Pt-p phosphorescence is quenched. The significant static quenching observed in the Pt-p/MV^{4+} system is believed to arise due to MV^{4+}-induced aggregation of the polymer. Thus, from this standpoint, the Pt-p/MV^{4+} system is different from the Pt-p/MV^+ and Pt-p/MV^{2+} systems. The fact that quenching is more efficient with the tetravalent quencher results from the fact that the triplet excitons are quenched due to interchain aggregation induced by the tetravalent quencher ion. Importantly, the strong quenching of Pt-p by MV^{4+} is not due to amplified quenching by the quencher ion.

Model To Explain Triplet Quenching in Pt-p. The Triplet Exciton Is Localized and Diffuses Slowly. For MV^+ and MV^{2+} quenching of Pt-p and Pt-m, there is some evidence for static quenching, as indicated by the fact that intensity quenching is slightly more efficient than lifetime quenching. Nevertheless, static quenching does not play a very large role in the overall quenching in the Pt-p/MV^+ and /MV^{2+} systems, because, due to the long lifetime of the triplet excited state, dynamic quenching is quite efficient. More important is the fact that static quenching of Pt-p by MV^+ and MV^{2+} is not much more efficient than static quenching of Pt-m. The lack of a significant increase in the static quenching component for Pt-p clearly indicates that the quencher interacts with the polymer in much the same was as it does with the monomer. Specifically, the data suggest that only excitons that are produced within the immediate vicinity (i.e., a few repeat units) of the quencher binding site are efficiently quenched. In addition, diffusion of excitons along the polymer chain to a quencher binding site is not competitive with normal diffusional quenching pathways (e.g., diffusion of the quencher to the exciton). This conclusion is based on the fact that the rate of diffusional quenching in the Pt-p/MV^+ and /MV^{2+} systems is close to the diffusion-controlled rate constant. If intrachain diffusion were rapid as compared to the triplet exciton decay rate, one would expect dynamic quenching to be considerably more efficient in Pt-p as compared to Pt-m.

Taken together, the Pt-p quenching data are consistent with a model in which (1) the triplet exciton is spatially confined; (2) intrachain triplet exciton diffusion is relatively slow (vide infra); and (3) interchain exciton diffusion is precluded by the fact that the triplet is quenched by interchain aggregates. These hypotheses are consistent with a growing body of evidence indicating that the structure and properties of the triplet exciton differ significantly from those of the singlet in conjugated polymers.[20,23,24] Thus, because the triplet is confined to a few

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repeat units on the polymer chain, the quencher's sphere of action is relatively small. In addition, the data suggest that the triplet diffuses along the chain several orders of magnitude more slowly than the singlet. This difference in diffusivity likely arises for two reasons. First, because the triplet is spatially localized (i.e., the average chromophore length for the triplet is 2 or 3 repeat units vs 10 or more for the singlet), the triplet exciton will require many more hops than the singlet to diffuse an equal distance along a chain. Second, because triplet–triplet hopping is mediated by exchange interactions, while the singlet hopping is mediated by dipole–dipole (and higher multipole) coupling,[13] the intrinsic rate of interchromophore hopping will also be significantly slower for the triplet exciton.

Taken together, these features conspire to lead to the result that, despite its 1000-fold longer lifetime as compared to that of the singlet, the triplet exciton is unable to efficiently sample a distance equivalent to an entire polymer chain during its 20 μs lifetime. This leads to the significant result of the present investigation: amplified quenching is not an important effect in phosphorescent π-conjugated Pt-acetylide polymers. The question as to whether this effect applies more broadly to the quenching of triplets in other π-conjugated polymer systems remains to be explored in future investigations.

Summary and Conclusions

In the present investigation, we have synthesized and characterized the photophysical properties of the novel Pt- acetylide-based conjugated polyelectrolyte, Pt-p. The polymer is soluble in water and polar organic solvents, and it exhibits moderately efficient phosphorescence at ambient temperature. At low pH where the weakly acidic carboxyl groups are protonated, Pt-p aggregates. The aggregate structure is believed to comprise face-to-face stacked chains, and the stacked aggregate structure results in a significant blue-shift of the polymer's absorption and quenching of its phosphorescence. The quenching of Pt-p phosphorescence by three cationic viologens is examined and compared to the quenching properties of a monomer model compound, Pt-m, and a structurally analogous fluorescent organic conjugated polyelectrolyte. The quenching experiments indicate the phosphorescent polymer is quenched with comparable efficiency as compared to the momoner model complex. On the basis of this result, we conclude that amplified quenching is not an important effect for Pt-acteylide polymers in which the luminescence originates from a triplet excited state.

Supporting Information Available: Complete details of the synthesis and characterization of O-m, O-p, Pt-m, and Pt-p. This material is available free of charge via the Internet at http://pubs.acs.org.

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