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Photophysics, aggregation and amplified quenching of a water-soluble poly(phenylene ethynylene)†

Chunyan Tan, Mauricio R. Pinto and Kirk S. Schanze*
Department of Chemistry, University of Florida, Gainesville FL 32611-7200, USA.
E-mail: kschanze@chem.ufl.edu

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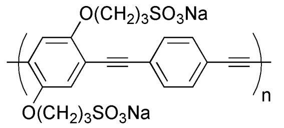
The fluorescence, absorption and fluorescence quenching properties of an anionic poly(phenylene ethynylene) are investigated in H_2O and MeOH solutions.

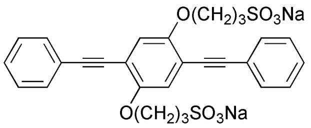
Water soluble, conjugated polyelectrolytes display optical and electronic properties that have proven useful for fabrication of sensors for ions, peptides, proteins and nucleic acids.[1,2] Considerable interest has surrounded the recent reports of amplified quenching[2] of the fluorescence from conjugated polyelectrolytes by ionic quenchers.[1,3-6] In particular, it was recently demonstrated that the fluorescence of a water soluble sulfonated poly(phenylene vinylene) (MPS-PPV) is quenched by cationic electron acceptors such as *N*,*N*′-dimethyl-4,4′-bipyridinium (MV^{2+}) at very low concentrations.[1,4–6] Stern–Volmer constants (K_{SV}) for MV^{2+} quenching of MPS-PPV range from 10^7 to 10^9 M^{-1}, and they vary with ionic strength, the presence of added surfactant, and polymer concentration.[1,4] These effects have been attributed in part to aggregation of MPS-PPV in water.[1,3–6]

Although the properties of MPS-PPV are remarkable and have led to development of a new class of fluorescence-based sensors for biological targets,[1] this polymer suffers from shortcomings such as a relatively low photoluminescence (PL) quantum yield. In addition, the fundamental processes responsible for the variation in quenching efficiency with solvent and polymer concentration are not fully understood.[6] Thus, the need exists to develop other conjugated polyelectrolyte systems that exhibit amplified quenching with improved properties such as a higher PL quantum yield. In addition, the study of related systems may improve our understanding of the fundamental processes involved in the amplified quenching process, and may lead to improved sensors.

Here we report the photophysical characterization and fluorescence quenching properties of the anionic conjugated polyelectrolyte PPE-SO_3^-, which has a backbone structure that is based on the poly(phenylene ethynylene) (PPE) architecture.†‡ The spectroscopic properties of the polymer vary strongly with solvent composition, and the spectral data suggest that in H_2O the polymer is strongly aggregated, but in MeOH solution it exists in a monomeric state.



PPE-SO_3^-



PE-SO_3^-

Fig. 1 illustrates absorption spectra of PPE-SO_3^- in H_2O, H_2O–MeOH (1 : 1) and MeOH. The absorption band progressively red-shifts and narrows with increasing volume fraction of H_2O in the solvent. In MeOH solution, the absorption maximum of the polymer (425 nm) is very similar to that of structurally-similar, organic-soluble PPEs in 'good' solvents (*i.e.*, where aggregation is expected to be minimal), while the spectrum of PPE-SO_3^- in H_2O is relatively red-shifted.[7]

Additional information concerning the effect of solvent on the solution state of the polymer comes from the fluorescence spectra, which are also presented in Fig. 1. In MeOH the fluorescence from the polymer is strong (ϕ_{fl} = 0.78) and it features a well-defined 0–0 band with λ_{max} = 447 nm, along with a clearly resolved vibrational progression at lower energy. The fluorescence decay time of PPE-SO_3^- in MeOH is nearly wavelength independent, and it is dominated by a short-lifetime component with τ = 420 ps (amplitude = 97%). Interestingly, as H_2O is added to the solvent, ϕ_{fl} decreases substantially, and a new broad and red-shifted fluorescence band appears. In pure H_2O the fluorescence is dominated by the broad band with λ_{max} = 548 nm and ϕ_{fl} = 0.10. In water the fluorescence decay is biexponential and wavelength dependent. Near the fluorescence maximum (λ = 550 nm) the decay can be fitted to two components with τ = 1.5 and 6.0 ns (amplitudes = 44 and 56%, respectively). On the blue side of the band, the lifetime of the short-lived component is shorter (τ_{short} = 550 ps).

The fluorescence properties of PPE-SO_3^- in MeOH are very similar to those exhibited by organic-soluble PPEs in good solvents,[7] suggesting that the polymer exists in a non-aggregated state in this medium. By contrast, the broad, less efficient, and longer-lived fluorescence observed from PPE-SO_3^- in H_2O is characteristic of conjugated polymer (and oligomer) aggregates.[6,8–10] The fluorescence properties of the polymer in H_2O strongly suggest that the photoluminescence emanates from an excimer-like state, which is presumably formed *via* inter-chain interactions. Furthermore, the very broad and strongly red-shifted band suggests strong inter-chain interactions, possibly due to π-stacking between adjacent polymer chains. This notion is also supported by the red-shift and narrowing of the absorption that occurs with increased volume fraction of H_2O. Specifically, these absorption features are consistent with increased structural order and conjugation length in the polymer.[8–10] We believe that the increased structural order and conjugation length arise due to face-to-face

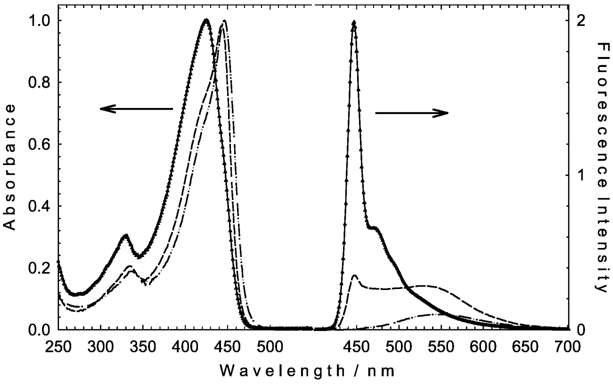


Fig. 1 Absorption (left) and fluorescence (right) spectra of PPE-SO_3^- in MeOH (▲), H_2O, (1 : 1) H_2O/MeOH (---), and H_2O (). Fluorescence spectra are area normalized to reflect relative quantum yields.

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† Electronic supplementary information (ESI) available: details regarding the synthesis and structural characterization of PPE-SO_3^- and PE-SO_3^-. See http://www.rsc.org/suppdata/cc/b1/b109630c/

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Table 1 K_{SV} Values for MV^{2+} quenching of PPE-SO_3^-

$[PPE\text{-}SO_3^-]/\mu M$	$K_{SV}(MeOH)/M^{-1}$	$K_{SV}(H_2O)/M^{-1}$
1	1.4×10^7	2.7×10^7
10	1.6×10^6	5.8×10^6

π-stacking between phenylene rings in adjacent chains. In order to optimize the π-stacking, the chains align with their long axes parallel, and on average the phenylene rings in each chain must be nearly co-planar. This aggregate conformation will optimize hydrophobic interactions between adjacent polymer chains, and at the same time will allow the polar sulfonate groups to extend into the aqueous solvent.

Stern–Volmer (SV) quenching of PE-SO_3^- and PPE-SO_3^- by MV^{2+} in H_2O and MeOH was also investigated. In all cases MV^{2+} quenches the fluorescence efficiently, and the mechanism for the quenching is believed to be electron transfer from the singlet excited state of the polymer (or model) to MV^{2+}.[1] The SV plot for MV^{2+} quenching of model PE-SO_3^- (c = 1 μM) is linear at low quencher concentrations, and K_{SV} values of 2.2×10^4 and 7.0×10^3 M^{-1} were obtained, in MeOH and H_2O, respectively. These K_{SV} values are large, given the relatively short fluorescence lifetime of PE-SO_3^- (1.53 and 1.83 ns in MeOH and H_2O, respectively). We conclude that the efficient quenching results from the presence of a ground-state association complex between PE-SO_3^- and MV^{2+}. The larger K_{SV} observed in MeOH likely reflects the fact that the association constant is larger in this medium.

MV^{2+} quenches PPE-SO_3^- several orders of magnitude more efficiently than the monomer PE-SO_3^-. The SV plots for PPE-SO_3^- are linear at very low $[MV^{2+}]$ (*i.e.*, < 0.05 equivalents of MV^{2+} per PPE-SO_3^- repeat unit), but they curve upward with increasing $[MV^{2+}]$. SV quenching constants extrapolated from fits to the linear region are listed in Table 1, and two general trends are evident from this data. First, in each solvent, K_{SV} decreases with increasing polymer concentration, and second quenching is slightly more efficient in H_2O than in MeOH.

Remarkably, MV^{2+} quenching of PPE-SO_3^- (c = 1 μM) is more than 10^3 times more efficient compared to the monomer PE-SO_3^-. This increased efficiency is likely due in part to stronger association of MV^{2+} with the polymer; however, there clearly are other factors which contribute to the large amplification in queching response (*vide infra*). In MeOH, K_{SV} is decreased by a factor of ≈ 9 when $[PPE\text{-}SO_3^-]$ is increased 10-fold. This change in quenching efficiency is close to the expected value (10×) due to the change in PPE-SO_3^-/MV^{2+} stoichiometry. In H_2O, K_{SV} is also attenuated at the higher $[PPE\text{-}SO_3^-]$, however, the effect of concentration is less pronounced than in MeOH.

Amplified quenching has been observed in a variety of other conjugated polyelectrolytes, and it has been attributed to (1) the formation of a strong association complex between the polymer and the quencher ion, and (2) the ability of the singlet exciton to rapidly diffuse to the quencher 'trap' site.[1,3–6] We believe that a similar mechanism is operating in PPE-SO_3^-.

Due to the very clear spectral changes that occur in PPE-SO_3^- concomitant with aggregate formation (*i.e.*, Fig. 1), this system provides insight concerning the relationship between the presence of the cationic quencher and polymer aggregation. Specifically, Fig. 2 illustrates the absorption and fluorescence spectra of PPE-SO_3^- (c = 10 μM) in MeOH at various concentrations of MV^{2+}. Interestingly, addition of very small amounts of the dication clearly induces spectroscopic changes associated with the PPE-SO_3^- aggregates. In particular, addition of MV^{2+} causes the absorption band to red-shift, and at 0.2 equivalent (relative to repeat unit concentration) of added MV^{2+} the absorption is dominated by the new band which has a maximum at 448 nm. Although a charge transfer absorption band is expected to accompany formation of the PPE-SO_3^-/MV^{2+} ion-pair complex, the red-shifted band is too intense to be soley due to charge transfer. Thus, we believe that the new absorption band is due to PPE-SO_3^- aggregates. Changes in the fluorescence spectral bandshape that occur comcomitant to MV^{2+} addition confirm the presence of the aggregates. Although addition of MV^{2+} quenches the PPE-SO_3^- fluorescence, the fluorescence spectrum clearly broadens upon the addition of MV^{2+}. Interestingly, in solutions that contain MV^{2+} = 0.1–0.3 μM (0.01–0.03 equivalents), the fluorescence intensity *increases* in the 500–600 nm region, which is a clear sign that aggregation is induced by the addition of the quencher.

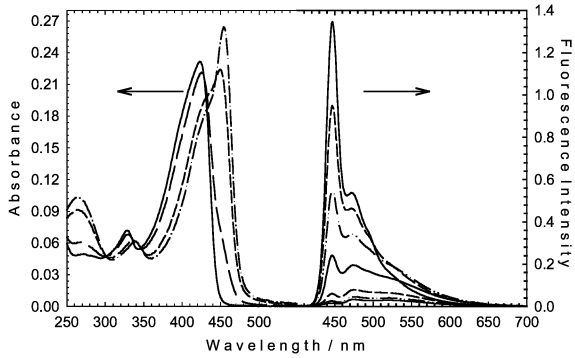

Fig. 2 Absorption (left) and fluorescence (right) spectra of PPE-SO_3^- in MeOH with added MV^{2+}. $[PPE\text{-}SO_3^-]$ = 10 μM. Absorption $[MV^{2+}]$ = 0, 0.65, 1.3, 1.9 μM, spectrum red-shifts with increasing $[MV^{2+}]$. Fluorescence: $[MV^{2+}]$ ranges from 0–0.8 μM, intensity decreases with increasing $[MV^{2+}]$.

These observations clearly indicate that that MV^{2+} acts as a template to induce aggregation of PPE-SO_3^-. Remarkably, this effect operates when the quencher is present at levels equivalent to only several quenchers per polymer chain. An interesting possibility is that if intrachain exciton migration occurs in these aggregates, then they may lead to further amplification of the quenching response. This factor may be responsible for the larger SV constants that are observed in H_2O compared to MeOH, since the polymer is fully aggregated in the former solvent. The possibility of enhanced amplified quenching in conjugated polymer aggregates is the subject of ongoing investigations.

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Notes and references

‡ The molecular weight of PPE-SO_3^- is estimated to be 100 kD (M_n) based on its ultrafiltration properties and iodine end-group analysis.

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