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Communications to the Editor

Water-Soluble Conjugated Oligomers: Effect of Chain Length and Aggregation on Photoluminescence-Quenching Efficiencies

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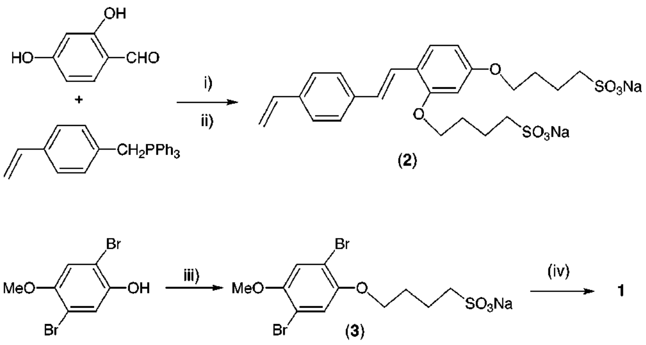
Conjugated polymers serve as highly responsive optical platforms for chemical and biological sensors.[1] Their structure may be envisioned as a series of "oligomeric sequences" or conjugation lengths with delocalized molecular structures which are held in close proximity by virtue of the polymer backbone. Energy migration along this backbone is facile,[2] allowing photoexcitations to ultimately reside in low-energy sites; for example, near an ionically bound acceptor molecule. Under these circumstances, very high quenching efficiencies can result from the efficient electron transfer from the excited state of the conjugated polymer to the lowest unoccupied molecular orbital of the acceptor.[3]

These optoelectronic properties make water-soluble conjugated polymers of particular interest for substrate detection in biological media.[4] Under dilute conditions the Stern−Volmer constant (K_{SV}) for poly(2,5-methoxy-propyloxysulfonatephenylene vinylene) (MPS-PPV) quenched with methyl viologen (MV^{2+}) is in the order of $\sim 1.7 \times 10^7$ M^{-1}. At higher MV^{2+} concentrations, quenching becomes superlinear and is best described by a sphere of action mechanism.[5]

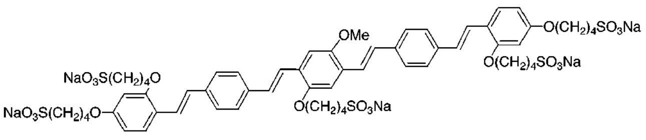
Several questions remain on how the polymer structure affects the photophysical processes of interest. In particular, addition of surfactant results in increased fluorescence quantum yields, but a reduced fluorescence quenching efficiency.[6] It is not clear at this stage to what extent the enhancement is due to changes in polymer coil dimensions or to polymer aggregate breakup. The contributions of intrachain energy transfer, interchain aggregation and quencher/polymer association constants to K_{SV} have yet to be fully deconvoluted.[1] Furthermore, the statistical distribution of polymer chains, coupled to batch-to-batch variability, make a detailed correlation between polymer structure and optical performance difficult to obtain.

Scheme 1[a]

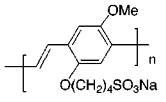


[a] (i) NaH/DMF; (ii) 1,4-butane sultone/DMF; (iii) NaH/DMF, 1,4 butane sultone; (iv) 2 **2**, Pd(OAc)$_2$, NaOAc/H$_2$O.

In analogy to the elucidation of structure/property relationships in other conjugated polymers, the study of the fluorescence and quenching efficiencies of a well-defined water soluble phenylene-vinylene oligomer should give insight into some of the uncertainties raised above.[7] For this purpose we targeted compound **1** and prepared it according to the sequence of reactions in Scheme 1. The Heck-coupling reaction[8] of **3** with 2 equiv of **2** (step iv) proceeds in 68% yield. The ^1H NMR spectrum of **1** in D_2O is broad at room temperature, but the signals become narrow at elevated temperatures (90 °C), allowing for compound characterization and for routine purity check. Molecular weight was confirmed using electrospray mass spectrometry.



(1)



(MPS-PPV)

At a concentration of 1.9×10^{-6} M, the absorption and emission maxima of **1** appear at 415 and 500 nm, respectively. In the presence of MV^{2+}, the absorption maximum shifts to 425 nm. We propose that this red-shift reflects the polarity change in the vicinity of the chromophore by the close proximity of MV^{2+}, consistent with the formation of a static complex. Stern−Volmer analysis of fluorescence quenching with MV^{2+}, under the dilute quencher regime, gave a linear plot from which $K_{SV} = 4.5 \times 10^5$ M^{-1} was obtained. Figure 1a shows the effect of adding 0.9 equiv of MV^{2+} to a solution of **1**.

The fluorescence lifetime of **1**,[9] was determined to be 1.4 ns.[10] Using this value and assuming a dynamic quenching mechanism, one can estimate the dynamic quenching rate constant to be $k_q = K_{SV}/\tau_f \approx 3.2 \times 10^{14}$ M^{-1} s^{-1}, well above values for diffusion controlled quenching.[11] Static quenching therefore dominates and is favored by ion pairing between **1** and MV^{2+}. Note that the K_{SV} value of **1** is large, but considerably lower than the K_{SV} value of MPS−PPV/MV^{2+} (1.7×10^7 M^{-1}) under similar conditions

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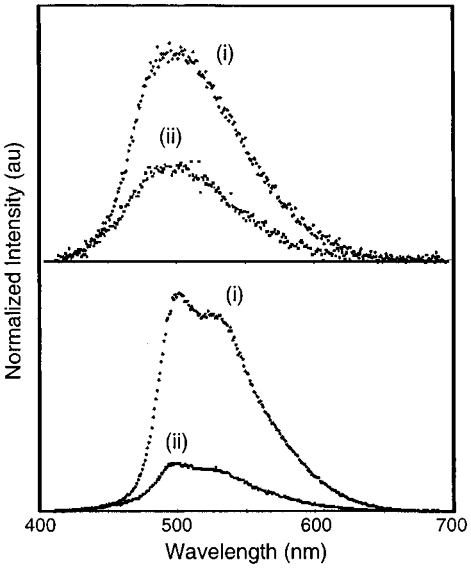

Figure 1. (a) Fluorescence data obtained for concentrations of (i) [**1**] = 4×10^{-6} M and (ii) [**1**] = 4×10^{-6} M and $MV^{2+} = 3.54 \times 10^{-6}$ M in H_2O, excited at $\lambda = 400$ nm. (b) Fluorescence data under identical conditions for (i) and (ii), with addition of [DTA] = 1.56×10^{-5} M.

(1.2×10^{-5} M in repeat units).[4] Thus, under these conditions the polymer is more effectively quenched by a factor of ~50.[12]

Light scattering experiments using the Wyatt EOS MALS software package ASTRA over a concentration range of 3.7×10^{-5} M to 7.1×10^{-5} M gave a molecular weight of ~1.7×10^6 g/mol and a radius of gyration of ~190 nm. Accordingly, even under dilute conditions, compound **1** self-assembles into large aggregates. The multiple range of environments encountered by **1** within these aggregates is likely responsible for the broad solution ^{1}H NMR spectra at room temperature.

Addition of the surfactant dodecyltrimethylammonium bromide (DTA) shifts the absorption maxima of **1** to 425 nm. A similar red-shift takes place in solutions of DTA and MPS-PPV.[6] In the case of **1**, however, changes in chain conformation (e.g., chain extension) cannot be responsible for the spectral shift. Figure 1b shows that with DTA the emission of **1** gains vibronic structure. Figure 2 shows that the total integrated emission of **1** increases in intensity with the addition of DTA, ultimately reaching a 6-fold increase and a quantum efficiency of ~50%. For comparison, under similar conditions, MPS-PPV shows a 20-fold increase in emission intensity.[6]

A dramatic departure in the properties of **1**, vis á vis MPS-PPV, is observed when the effect of surfactant on the quenching behavior for MV^{2+} is examined. In the case of MPS-PPV, the K_{SV} decreases with increasing surfactant concentration and at a DTA/polymer repeat unit ratio of 1:10, the K_{SV} decreases by 2 orders of magnitude.[6] A comparison of Figure 1b against Figure 1a shows that MV^{2+} quenches the emission of **1** more efficiently in the presence of DTA. Figure 2 tracks this effect as a function of [DTA] and shows that when [**1**] = 4×10^{-6} M and [DTA] = 1.56×10^{-6} M, $K_{SV} = 1.2 \times 10^6$ M^{-1}. *Therefore, there is greater optical amplification of the quenching process of **1** relative to MPS-PPV in the presence of surfactant.* Since surfactants are often required to stabilize biomolecular recognition events,[13] these results suggest the use of discrete molecules such as **1** in the design of fluorescence-based biosensors.

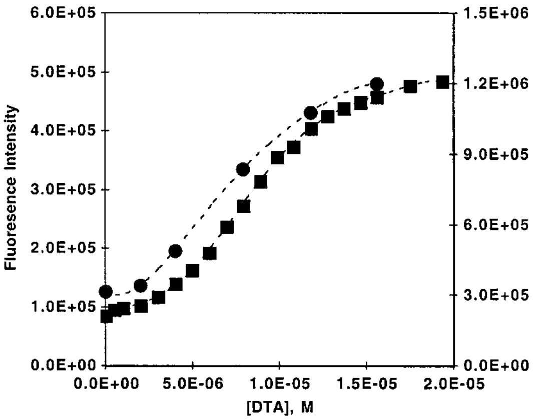

Figure 2. The effect of DTA concentration on: (a) the integrated fluorescence intensity of **1** as a function of DTA concentration ($\lambda_{exc} = 400$ nm) [squares]; (b) K_{SV} for **1**/MV^{2+} [circles].

Our current thinking is that DTA addition results in smaller aggregates containing mixtures of surfactant and oligomer.[14] The enhanced and vibronically defined emission of **1** indicates weaker interchromophore electronic coupling.[15] Therefore, the stronger fluorescence quenching by MV^{2+} with DTA cannot be accounted for by more efficient energy transfer. Instead, we propose that the larger surface-to-volume ratio in the smaller aggregates enables stronger (ground state) chromophore/quencher interactions.

In summary, we have reported the synthesis of oligomer **1**. Light-scattering experiments are consistent with extensive aggregation in water. Despite mechanistic uncertainties, it is highly relevant that the fluorescence of **1** can be more effectively quenched than that of the parent conjugated polymer, MPS-PPV. These observations open the opportunity for designing sensors that amplify analyte quenching within spontaneously formed supramolecular structures with potential advantages over polymer-based systems.

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Supporting Information Available: Complete details for the synthesis, spectroscopy and quenching studies of **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] Fluorescence-quenching of a poly(*p*-phenylene)-based cationic polyelectrolyte with anionic metal complexes has also been reported. A dicationic terphenyl model compound exhibits K_{SV} values more than 3 orders of magnitude smaller than those obtained with the polymer. See: Harrison, B. S.; Ramey, M. B.; Reynolds, J. R.; Schanze, K. S. *J. Am. Chem. Soc.* **2000**, *122*, 8561.

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