Tuning the Properties of Conjugated Polyelectrolytes through Surfactant Complexation

Liaohai Chen,*[‡] Su Xu,[‡] Duncan McBranch,[†] and
David Whitten*[†]

Bioscience Division and
Chemical Science and Technology Division
Los Alamos National Laboratory
Los Alamos, New Mexico 87545
QTL Biosystems, LLC, Santa Fe, New Mexico 87501

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Conjugated polymers related to poly(phenylene vinylene) (PPV) have been widely recognized as versatile "electronic materials" for applications ranging from light-emitting diodes (LEDs) to separations.[1−5] Major effort has been focused on determining the relationship between polymer chemical structure and conformation and the corresponding physical and chemical properties. A popular research theme has focused on tuning polymer properties by rational design and synthesis at the level of the conjugated repeat unit. For example, the emission wavelength and fluorescence quantum efficiency may be tuned by changing the chemical structure of the unit cell (tuning of the π-electron density)[6] as well as constructing unit cells with varying degrees of rigidity.[7] The former has been utilized to vary the π-electron band over the entire visible range to obtain variable-color LEDs. The latter provides additional tuning over some 100 nm (e.g. regioregular vs regiorandom polythiophene), and also impacts bulk properties such as conductivity and fluorescence quantum efficiency (QE). These approaches often involve formidable synthetic efforts. Hence, a simple technique to tune polymer properties without synthesizing new chemical structures is extremely desirable.

Charged polymers (polyelectrolytes) can form stable complexes with oppositely charged amphiphilic molecules (surfactants), and the polymer−surfactant complex may have a very different geometric conformation than the free polymer.[8−12] Previous studies with conjugated polymers and surfactants have focused on the use of surfactant to aid in processing of polyaniline derivatives.[13−21] We demonstrate that by combining conjugated polyelectrolytes with appropriate surfactants, one may control the geometric conformation of the polymer, and thereby tune its optical and chemical properties. Specifically, we report complexes between the anionic polymer poly(2,5-methoxy-propyloxysulfonate phenylene vinylene) (MPS-PPV) and a series of cationic surfactants. Remarkably, the fluorescence quantum yield of MPS-PPV is enhanced by more than an order of magnitude simply by adding a small amount of the surfactant dodecyltrimethylammonium bromide (DTA**)**.

MPS-PPV is a water-soluble conjugated polymer, with molecular weight estimated to be (1−5) × 10^5 (∼1000 monomer repeat units per polymer chain). The synthesis of MPS-PPV was carried out using the Gilch polymerization procedure.[22] The absorption spectrum of MPS-PPV shows a broad band at 400−550 nm (typical for substituted PPV polymers). The emission spectra of MPS-PPV in waters are strongly dependent on the excitation wavelength. An emission maximum is observed at 500 nm, when exciting at 400 nm, while excitation at 500 nm results in an emission maximum shifted to ∼590 nm. A similar trend is observed in the excitation spectra, in which maxima are observed at 380 or 425 nm when monitored at 500 or 589 nm, respectively. This site-selective fluorescence is a signature of a heterogeneous distribution of independent emitters. It is well-known that the absorption and emission maxima may be red-shifted by increasing the conjugation length (the effective range of π-electron delocalization, which is approximately 10−15 unit cells).[23] The results indicate a broad distribution of conjugation lengths for MPS-PPV in solution. This is expected if the polymer chains have a distribution of chain conformations or molecular weight. The changes observed when surfactant is added show that chain conformational disorder is the dominant cause of the variation of spectra in Figure 1.1.

Upon adding the cationic detergent DTA (2×10^{-6} M) to an aqueous MPS-PPV solution (2.2×10^{-5} M in repeat units), the photophysical properties of MPS-PPV change dramatically. The emission spectrum of the polymer/surfactant complex (Figure 2) shows well-defined vibrational structure with a maximum at 563 nm, while the absorption spectrum is narrowed and red-shifted (inset, Figure 2). More strikingly, the fluorescence of the polymer−surfactant mixture is much stronger than that for the polymer alone: the QE of the polymer is increased approximately 20-fold upon addition of the surfactant (sample excited at 500 nm). Furthermore, the emission spectra are now wavelength-independent (Figure 1-II). Time-resolved photoluminescence (PL) reveals that the fluorescence decay kinetics are described by single exponential decay with a lifetime of 1.2 ps. This contrasts to the fluorescence for the polymer solution alone where the early fluorescence decay is dominated by double exponential components with lifetimes of 0.2 and 2.4 ps, respectively. This suggests that nonradiative decay pathways in the polymer are eliminated.

The complexation between the polymer and oppositely charged detergent is believed to be driven by a combination of Coulombic attraction between the ionic units of the polyion and the cationic surfactant headgroups, and by favorable entropy changes resulting from release of interfacial water molecules.[8] This serves to extend the MPS-PPV chains, inhibiting the folding of the polymer chains, reducing the conformational disorder, and increasing the QE. The

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* Address correspondence to this author.

[‡] Los Alamos National Laboratory.

[†] QTL Biosystems.

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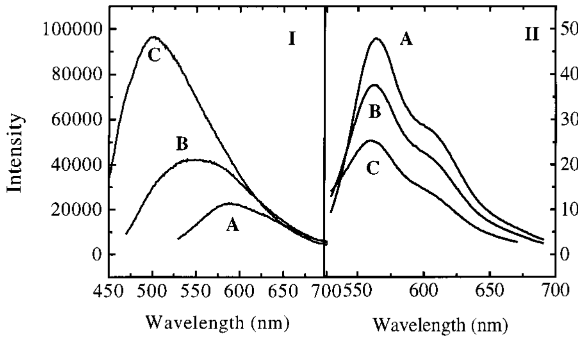

Figure 1. The emission spectra of MPS-PPV in water ([MPS-PPV] = 2.2×10^{-5} M): (I) MPS-PPV alone and (II) in the presence of 6×10^{-6} M DTA; (A) excited at 400 nm, (B) excited at 450 nm, (C) excited at 500 nm.

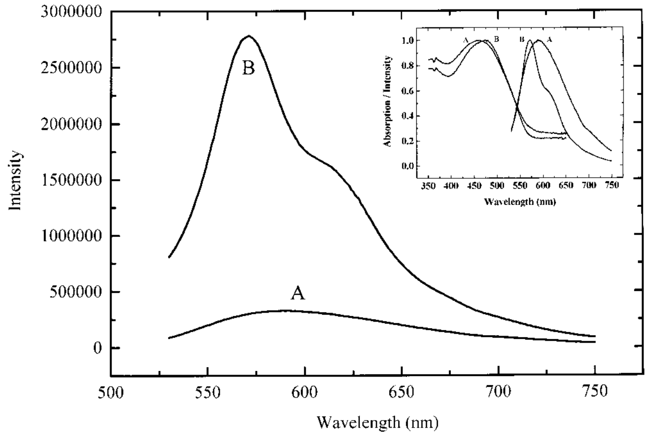

Figure 2. The emission spectra of MPS-PPV in water ([MPS-PPV] = 2×10^{-5} M): (A) MPS-PPV alone and (B) in the presence of 2×10^{-6} M DTA. Inset: Normalized absorption and emission spectra of MPS-PPV in water.

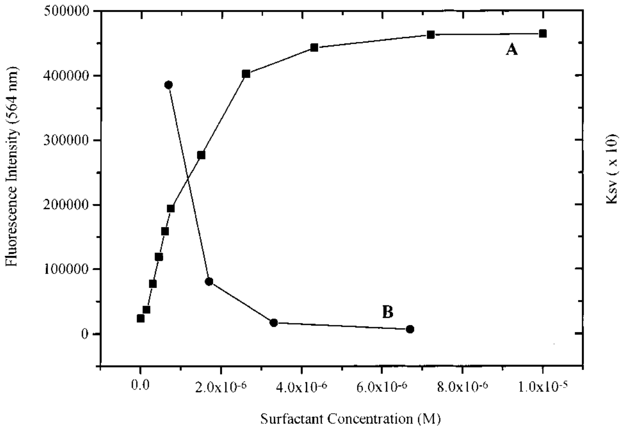

Figure 3. (A) Fluorescence intensity (excited at 500 nm and monitored at 564 nm) of MPS-PPV as a function of DTA concentration; (B) quenching constant (K_{sv}) of methyl viologen (MV^{2+}) to MPS-PPV as a function of DTA concentration.

effect of increased QE by reduced chain folding is expected on two grounds. First, it reduces the number of kink defects, which can serve as trapping and nonradiative recombination sites. Second, it frustrates the tendency of polymer chains to self-associate (aggregate). Interchain interactions create sites for interchain charge transfer reactions and excimer formation, which strongly compete with radiative emission processes.[24] The more ordered and homogeneous conformation of the polymers in the MPS-PPV/DTA complex is confirmed by the spectral features, a narrowed and red-shifted absorption spectrum, together with a well-defined vibronic structure in emission, a reduction of the apparent offset between absorption and emission maxima (Stokes shift), and a reduction of the dependence of emission spectrum on excitation wavelength (site-selective fluorescence).

Even a small amount of the surfactant can dramatically enhance the fluorescence properties of MPS-PPV. Curve A in Figure 3 illustrates the fluorescence intensity (excited at 500 nm and monitored at 564 nm) as a function of added surfactant. Even at a surfactant:polymer ratio as low as 1:100 (surfactant molecules per repeat unit of the polymer), noticeable emission enhancement is detected. The marked change at such low concentrations, presumably due to a conformational change of the polymer, suggests that the surfactant chains are oriented along the polymer backbone to maximize their interaction. This is reasonable, since such an arrangement can minimize the contact of the hydrophobic aliphatic chains with water molecules.

The amplification effect saturates when the ratio reaches 1:3.[25] This matches the result from a resonance light scattering (RLS) experiment which shows that the size of the polymer−surfactant complex increases with the surfactant:polymer ratio, until the ratio reaches 1:3.[26] Shorter chain surfactants (containing four and eight carbons) were also studied, but they have smaller effects on the polymer fluorescence compared to DTA (containing 12 carbons). A longer chain surfactant (containing 18 carbons) was also investigated; it also exhibits a smaller effect on the polymer fluorescence than DTA, likely due to its poor solubility in water, and its tendency to self-micellize.

The surfactant also markedly changes the quenching behavior for methyl viologen (MV^{2+}). The MPS-PPV/MV^{2+} system has an extremely large quenching constant ($K_{sv} \sim 2 \times 10^7\ M^{-1}$) due to a combination of ultrafast energy migration along the polymer chain and the efficient complexation and charge-transfer quenching between the polymer and MV^{2+}.[27] This has been used to construct highly sensitive chemical and biological sensors. When DTA is present in the polymer solution, as shown in curve B of Figure 3, the K_{sv} value for MV^{2+} decreased. K_{sv} for MPS-PPV/MV^{2+} is depressed by more than 2 orders of magnitude at a surfactant:polymer ratio of 1:10. This suggests that the surfactantchains along the polymer backbone may be acting to both extend the polymer and hinder association of MV^{2+} with the polymer.

In conclusion, the interaction between conjugated polymers and appropriate functionalized surfactants provides a simple yet powerful way to tune the optical and electronic properties of these materials. Given the employment of fluorescent conjugated polymers in devices ranging from sensors to LED displays, which depend on high stability and highest possible photoluminescence efficiencies, these techniques may prove of broad application and utility.

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