Signal Amplification of a “Turn-On” Sensor: Harvesting the Light Captured by a Conjugated Polymer

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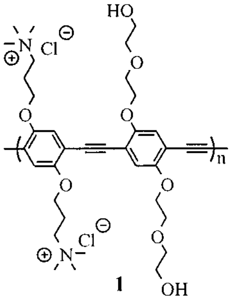
Excited states can travel large distances in multiple dimensions within conjugated polymer thin films.[1] The facile transport of exitons within these materials has made them attractive candidates for creating a variety of electrooptical devices,[2] and vectorial transport has been exploited in light-harvesting systems.[3] Recently, we have reported highly sensitive chemosensors which utilize the large random walk of exitons within conjugated polymer thin films to amplify signals resulting from a binding event.[4] In our studies involving fluorescent conjugated polymers, we have designed systems where association of an electron-poor analyte results in a dramatic decrease (a “turn-off”) in the polymer’s initial fluorescence intensity.[4b−e,6] Despite the signal amplification embodied in our earlier systems, a sensor in which the fluorescence intensity is turned-on from an initially low level would be much more sensitive.[5] Herein, we present a chemosensor design where we substantially amplify the output of a pH-sensitive fluorophore using energy harvested from a conjugated polymer.[6]



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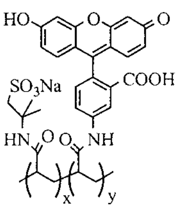

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The construction of thin films was accomplished via layer-by-layer deposition[7] of a new water-soluble, cationic poly(*p*-phenlyene ethynylene) (PPE) (**1**) and an anionic polyacrylate (**2**).[8,9] The system is designed so that pH alters the absorption cross-section, energy migration efficiency, and emission efficiency of the fluoresceinamine (FA) dye appended off of polymer **2**. In this case, the dye acts as a shunt, withdrawing energy from the conjugated polymer. At high pH, FA is highly absorptive and highly fluorescent, while at low pH, the dye’s extinction coefficient decreases and the fluorescence is lost. In our case, electrostatic binding of anionic polymer **2** onto the cationic surface formed by depositing **1** directly onto a glass substrate provides a facile method for placing the appended FA in close proximity to the conjugated polymer.[10] The sulfonate co-monomer comprising polymer **2** was selected to ensure that the polymer would remain ionic over a wide pH range. Polymer **1** was synthesized via an aqueous-DMF Sonagashira-Hagihara cross-coupling and polymer **2** via radical polymerization.[11]

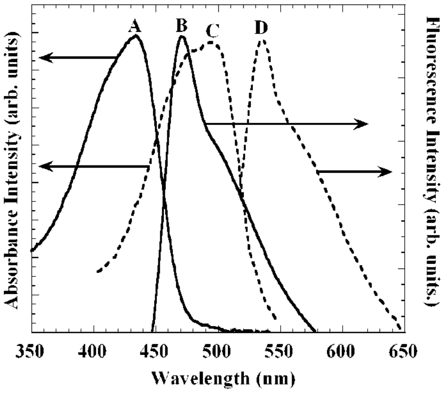

Figure 1. Normalized absorbance and emission spectra for polymers **1** and **2**: A is the absorbance of a thin film of polymer **1** on glass and B is the emission (excited at 420 nm). (C) Absorbance spectrum of a film of polymer **2** and (D) emission (excited at 500 nm).

Polymer **1** and the FA dye appended to the polyacrylate (**2**) were selected so that the polymer emission overlaps the absorbance band of the dye (Figure 1). This overlap encourages Fluorescence Resonance Energy Transfer (FRET) between the polymer and the dye.[12] The absorbance maximum of polymer **1** is centered at 439 nm and the emission maximum is centered at 471 nm. The absorbance maximum of the polymer-bound FA dye is 490 nm and the emission band is centered at 535 nm.

The films were deposited onto base-washed glass slides by alternate immersion into 1 mg/mL solutions of **1** and **2**. The deposition was monitored by UV/vis spectroscopy and the optical density increased linearly over twenty depositions (10 for each polymer).[13] In contrast to the UV/vis results, the fluorescence spectrum of **1** did not increase after each successive deposition. The self-quenching was investigated further by measuring the quantum yields (QY) of polymer **1** (420 nm) alone and polymer **1** separated via polymer **2**, as well as by sulfonated poly(styrene) (PSS). PSS was chosen because it has no absorption bands above

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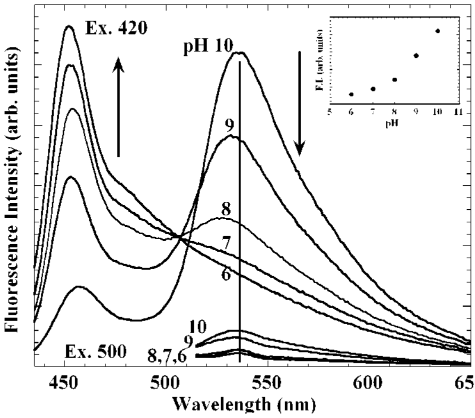

Figure 2. A film composed of **2** electrostatically bound to **1** on glass was used. The film was dipped into a 0.001 M $KHPO_4$ solution at the denoted pH. The PL spectra spanning from 435 to 650 nm and the spectra beginning at 515 nm were excited at 420 and 500 nm, respectively. Inset: The emission maximum of the FA band after excitation at 420 nm plotted against the pH.[18]

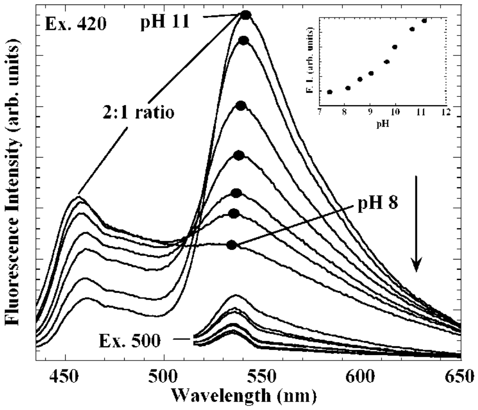

Figure 3. A film composed of **2** electrostatically sandwiched between two layers of **1** on glass was used. The film was dipped into a 0.001 M $KHPO_4$ solution at various pH values. The PL spectra spanning from 435 to 650 nm and the spectra beginning at 515 nm were excited at 420 and 500 nm, respectively. Inset: The emission maximum of the FA band after excitation at 420 nm plotted against the pH.[18]

300 nm.[14] One layer of polymer **1** has a modest QY of 8%. A film composed of two layers of **1** separated by a layer of PSS has a QY of 3.7%, corroborating that polymer **1** self-quenches. A two-layer film consisting of a layer of **2** (deposited at pH 8) on a layer of **1** has a QY of 1.6%. A three-layer film consisting of two layers of **1** separated by **2** has a similar QY of 1.5%. We attribute the self-quenching to interpolymer interactions mediated by the ionic shielding provided by the presence of the anionic polymer.[15] Despite self-quenching, which limits the amplification, multiple layer films respond to pH in a different manner than a bilayer of **1** and **2** (vide infra).

Initially, bilayer films composed of one layer of **2** deposited onto a layer of **1** were immersed in solutions of varying pH.[16] The dried film's response after removal from the solution was measured in air by selectively exciting **1** (420 nm)[17] and comparing the resulting emission at 535 nm to direct excitation of the FA dye (500 nm) (Figure 2). At pH 11, >90% of the conjugated polymer's emission is transferred to the dye. In contrast, the FA's fluorescence is completely absent at pH 6.

At each pH, the measured excitation at 420 nm resulted in an approximate 10-fold increase in the emission at 535 nm relative to that measured by direct excitation (500 nm) of the FA. Excitation spectra indicate that the emission at 535 nm is maximal when **1** is excited at its absorbance maxmium, further corroborating that the amplification observed results from energy transfer.[19] Recently, a self-assembled mixed monolayer containing laser dyes electronically coupled to chromogenic dendrons was reported to display similar amplification.[20]

This two-layer system responds between pH 11 and 6. At pH 6, the spectrum resulting from excitation at 420 nm is the same as that observed for films consisting solely of **1**. In contrast, at pH 11 the spectrum is almost completely dominated by the dye's emission, clearly establishing an on−off response to pH. Placing a layer of **1** on top of a bilayer of **1** and **2** provides a film that responds differently to pH (Figure 3). As stated above, the deposition of more than one layer of **1** does not result in an increase in the fluorescence intensity. However, a three-layer film has a ratio between the polymer **2** emission maximum (at low pH) and polymer **1** emission maximum (at high pH) of >2; whereas the two-layer film has a ratio of only 1. The number of polymer **1** layers surrounding polymer **2** clearly influences the film's response. We suggest that the addition of a second polymer layer increases the amount of energy harvested by the film, thus increasing the available energy accessible to the dye. However, the level of signal amplification remains the same due to the increase in the emission resulting from direct excitation of the dye. The increased emission from direct excitation of the dye indicates that the second layer of **1** may also influence the photophysical properties of the dye.

A plot of the dye's emission peak versus pH for the three-layer film (inset, Figure 3) displays a sigmoidal shape consistent with a titration. The pK_a has been shifted to approximately 9, which is higher than that observed previously (6.5).[8a] The shift is most likely due to the destabilization of the phenolic anion of FA by the highly anionic environment provided by polymer **2**.

The combination of layer-by-layer deposition, of pH-sensitive dye, and the transport properties of a conjugated polymer has produced a chemosensor displaying a dramatically brighter response. The easy synthesis of polyacrylates containing appended dyes makes this system very flexible and represents a simple approach for creating different chemosensors in which an analyte-sensitive dye is electrostatically bound to a cationic conjugated polymer.

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Supporting Information Available: Experimental details, characterization of polymers **1** and **2**, excitation spectra, and a plot of the OD versus layer (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) This self-quenching may be enhanced by layer interpenetration. See: Baur, J. W.; Rubner, M. F.; Reynolds, J. R.; Kim, S. *Langmuir* **1999**, *15*, 6460.

(16) Polymer **1**'s photophysical properties are invariant to changes in pH.

(17) Excitation of a thin film of **2** at 420 nm results in a negligible amount of emission at 535 nm.

(18) The films can be used multiple times with only slight loss in signal over time. The signal loss is most likely to desorption of polymer **2**.

(19) See excitation spectra in Supporting Information. The excitation spectra has a 10-fold amplification between the absorbance maximums of **1** and **2**, further indicating an energy transfer mechanism.

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