

A Comparison of Crystalline- and Graft Polymer-Based Chemosensors

Steven J. Broadwater, Mary Kay Hickey, and D. Tyler McQuade*

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853

Received March 18, 2003; E-mail: dtm25@cornell.edu

Transduction schemes whose sensitivity is related to an exciton randomly walking through a thin film have become an important component in chemosensor development.¹ The random walk allows an exciton to survey a large area, thus maximizing the probability that the exciton will encounter an analyte/trap. The concentration of analytes needed to elicit a measurable response is dictated by the diffusion length of the exciton, the energy-transfer rate between donor and trap, and the excited-state lifetime of the trap.² The energy migration process is typically modeled by using either an exciton-hopping (Dexter) or a dipole–dipole-coupling model (Forster).^{3–6}

The majority of chemosensors employing energy migration have been constructed using conjugated polymers.⁷ This bias toward conjugated polymers may be due to early suggestions that energy migration along rigid conjugated polymer backbones is crucial to realize exceptional signal amplification.⁸ However, reports by a number of groups using flexible conjugated polymers also show high sensitivity in solution, implying that intrachain hopping may be more important.^{9–12} If exciton-hopping is the major mechanism, a rigid conjugated polymer is unnecessary. For example, it has been known for at least 70 years that excitons within crystalline and graft polymer films diffuse between 450 and 1350 Å, hopping between molecules 1500–40 000 times.^{13–16} The efficient hopping within crystalline and graft copolymer films makes these materials attractive alternatives to conjugated polymers.

Here, we report that an acid-responsive dye embedded in a small-molecule donor matrix can be exploited to create an acid-sensitive indicator. In addition, the system is extended and made potentially practical by grafting the donor dye to a methacrylate polymer. These two preparations vary interchromophore orientation, distance, organization, and film properties. Despite the differences, the same amplification phenomenon is observed in each film. The improved mechanical properties of the graft polymer allowed a mechanistic investigation of the energy-transfer mechanism.

The crystalline films were prepared by drop casting two commercially available dyes, **1** and **2**. These dyes were selected because (1) both are robust laser dyes, (2) dye **2**'s photophysics are strongly altered by protonation of the pyridyl moiety, and (3) the spectral overlap integral between the emission spectrum of **1** and the absorption spectrum of **3** is large. Figure 1 features the thin-film absorption and emission spectra of **1** and **2** before and after exposure to trifluoroacetic acid (TFA) vapor. Dye **1** undergoes very little

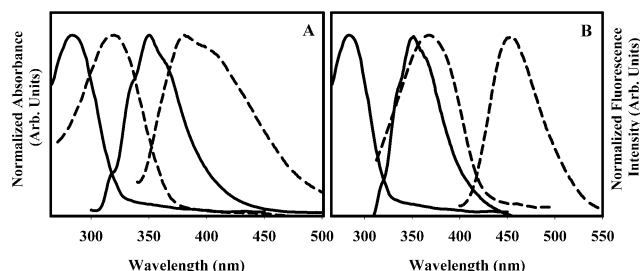


Figure 1. Photophysics of solid solutions of dyes in PMMA before (A) and after (B) exposure to TFA vapor. (A) Absorbance and emission spectra of **1** (ex. 320 nm; solid lines) compared to the spectra of **2** (ex. 340 nm; dashed lines). (B) Absorbance and emission spectra of **1** (ex. 320 nm; solid lines) compared to the spectra of **3** (ex. 380 nm; dashed lines).

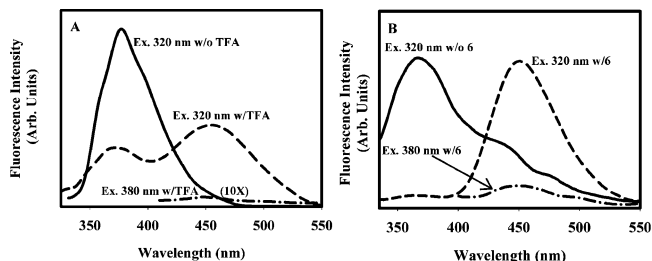
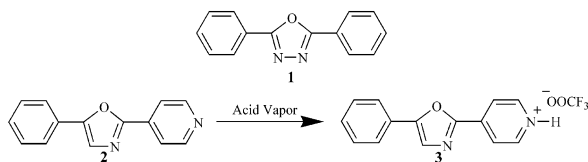


Figure 2. (A) Emission spectra from a crystalline film of **1** and **2** (100:1) before and after TFA and (B) a solid solution of **5** (300:1) with and without **6**, the solid lines and the dashed lines result from excitation at 320 nm and the dashed–dotted–dashed lines result from excitation of the exposed films at 380 nm.

exposure was accomplished by placing the films into a large vessel containing a few drops of TFA or other volatile acids. The exposure times varied, but the film's photophysics changed rapidly, remaining constant after 30 s. X-ray powder diffraction data obtained before and after film exposure indicate that the crystalline packing does not change within experimental error.

Upon exposure to TFA, a film's luminescence becomes dominated by emission from **3**. Six different ratios of **1**:**2** were investigated (10:1, 100:1, 200:1, 500:1, 1000:1, 1500:1), with 100:1 providing the optimum amplification. The emission spectra from a 100:1 (**1**:**2**) film before and after exposure to TFA vapor are shown in Figure 2. The emission from **3** is 79 times larger when **1** is excited and energy transfers to **3** than when **3** is excited directly,¹⁷ illustrating the utility of using a donor phase to increase the signal from a few acceptor molecules.¹⁸ Since the band resulting from **3** is only present upon exposure to analyte, the system is considered a turn-on chemosensor, meaning that negligible background exists before exposure to analyte. In addition, these thin films respond to acids of varying strengths. AcOH and HCl vapor also provide a similar response. The response is fully reversed by exposing the films to triethylamine vapor. The films can be subjected to multiple rounds of acid/base vapor exposure before salt buildup begins to diminish the transparency.

The amplification observed with crystalline films is excellent, but the film-to-film and intrafilm reproducibility is difficult to



change upon exposure to acid, whereas **2**'s spectrum undergoes a 73-nm red-shift. The large spectral overlap integral for **1** and **3** facilitates energy transfer. Mixtures of **1** and **2** dissolved in chloroform were cast onto quartz plates, and emission spectra for each were recorded before and after exposure to acid vapor. The

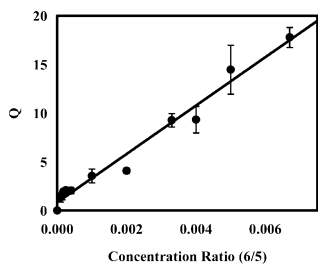
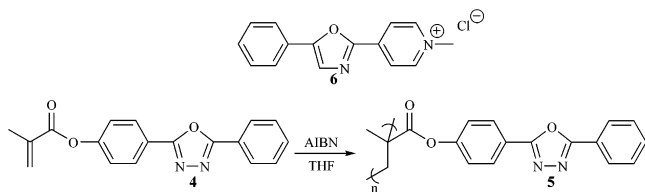


Figure 3. A plot of Q versus concentration ratio for a spin cast film in which **6** is suspended in **5**.

control due to inhomogeneous crystallization of the compounds onto the quartz plate. The error associated with each measurement prohibited a detailed investigation of the energy migration mechanism and prevents the films from being used as quantitative indicators. To solve these problems, donor dyes were grafted to a methacrylate polymer, **5**, synthesized via a radical polymerization of **4**. Films of the grafted donor provided excellent optical properties and were mechanically robust.

Mixtures of **5** and **2** were constructed and responded to TFA in the same manner as the crystalline films, except that the amplification observed was approximately 20-fold instead of 80-fold. Since the absolute concentration of **3** cannot easily be measured, a quantitative analysis of the energy-migration mechanism within these films was impossible. To reduce the system's complexity and obviate the risk of **3** being deprotonated or not fully protonated, **2** was methylated with methyl iodide and ion-exchanged to create **6** for use as a model of **3**. The spectral properties and films of **5** and **6** are identical to those of films of **5** and **3**, but by using **6** a more precise mixture can be created.

Twelve mixtures of **5**:**6** ranging from 10:1 to 10000:1 were spin cast onto quartz plates, creating a solid solution of **6** dispersed in **5**. The luminescence spectra indicated that energy migrated from **5** to **6**. Each spectrum was multimodal, having bands resulting from the emission of **5** and **6**. Again the amplification was determined by measuring the emission resulting from **6** when excited at 320 nm (excitation of the grafted dye) and 380 nm (direct excitation of **6**). In the worst case, 10 000:1, an enhancement of only 4 was observed, and in the best case, 300:1, the signal enhancement was 17. Nevertheless, as can be seen in Figure 2, amplification of 17 is still significant and is better than any previously reported system of this type.¹⁸



To better understand the mechanism of energy transfer within these films, each of the 12 spectra resulting from excitation of **5**:**6** mixtures were curve-fitted, and each band was integrated. These integrations were used to calculate the quenching factor (Q ; $I(\text{accep})/I(\text{donor}) \cdot (\Phi(\text{donor})/\Phi(\text{accep}))$).¹⁵ A plot of Q versus the concentration ratio of the acceptor provides evidence of the energy migration mechanism. Energy migration for Dexter and Förster processes has different dependences on donor/acceptor distances. For a Dexter process, quenching decays linearly as the acceptor concentration decreases. Alternatively, quenching decays nonlinearly for a Förster mechanism.¹⁵ For the system reported here, a plot of Q versus the acceptor concentration ratio is linear, indicating that

exciton migration via the Dexter mechanism is more prevalent than Förster migration, Figure 3. A Dexter mechanism implies that the main chain of the graft polymer does not prevent donor dyes from having overlapping wave functions.

From the slope of the plot, the average exciton was calculated to hop approximately 3800 times before being quenched.²⁰ Utilizing reported crystal structures for **1**, the average molecular distance (centroid-to-centroid of the oxadiazole ring) was found to be 9.7 Å.²¹ Assuming that the rate of energy transfer between donor and acceptor is infinite,⁵ the lower limit for the diffusion length was found to be 600 Å (diffusion length = (distance between hops) \times (number of hops)^{1/2}). This diffusion length is twice that found previously in graft polymer systems and a third of that reported for crystalline films.¹⁶

In conclusion, luminescent chemosensors can be constructed of small-molecule chromophores and still achieve amplification similar to that found in conjugated polymer films. Signal amplification can be achieved in both crystalline and donor-graft polymer films. Crystalline films provide much better amplification, but create films with very poor mechanical properties. Conversely, the donor-graft polymer films have excellent mechanical properties, but provide attenuated sensitivity. However, the sensitivity observed in the donor-graft polymer films is still better than similar approaches using conjugated polymers.¹⁸ Using the improved optical and mechanical properties of the donor-graft polymer films, the energy migration mechanism was investigated and, unexpectedly, appears to be exciton hopping between chromophores. Energy hopping can occur in the polymer films suggesting that grafted dyes could be used as alternatives to conjugated polymers in some applications.

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Supporting Information Available: Film preparation, synthesis, X-ray data, tabulated data, and quantum yields (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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