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## Solid State Solvation Effect

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### Personnel

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Emission and absorption spectra of many organic dyes in *liquid solutions* depend on the local electric fields generated by the surrounding polar solvent molecules. This “solvation effect” is a result of intermolecular solute-solvent interaction forces (such as dipole-dipole or dipole-induced dipole) that tend to stretch molecular bonds and shift charge distribution on molecules, altering the energy difference between the ground and excited states of the solute. Our experiments confirmed that the solvation effect is also present in *molecular solids* where closely packed polar molecules can generate large local electric fields. In the following two studies we develop a theoretical framework describing the effect.

#### Influence of Local Electric Fields on the Exciton Behavior in Amorphous Organic Thin Films

Performance of active organic opto-electronic devices is governed by the energy band structure of constituent thin films. In this project we examine the changes in the energy structure of amorphous molecular organic thin films due to local fields. Our goal is to develop a method for better predicting and ultimately fine-tuning the energy levels of such materials.

This work has grown out of two recent reports by our group [Bulovic *et al.*, Chem. Phys. Lett. **287**, 455 (1998) and **308**, 317 (1999)] describing red shifts in the emission spectrum of amorphous organic thin films doped with the red laser dye DCM2 (chemical structures of materials used in this project are shown in Fig. 42). In these reports it was shown that by changing the concentration of DCM present in a film of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) from 0.9% to 11%, the peak luminescence wavelength was shifted from  $\lambda=570$  nm to  $\lambda=645$  nm. Because DCM2 dye is highly polar (with a dipole moment  $\mu\sim 11$ D in the ground state) and TPD is a non-polar molecule, increasing the dye concentration should enhance the local electric fields present in the film. The

increase in the local fields is expected to shift the energy structure of polar DCM molecules resulting in the observed spectral shift.

A subsequent report by Baldo, *et al.* [Chem. Phys. Lett. **347**, 297 (2001)] argued that the spectral shift is actually due to a progressive increase in the presence of aggregated dye molecules with increasing dye concentration, rather than the enhancement in the local fields. These authors posit that the emission of aggregate dye molecules is red-shifted and of similar efficiency to the emission of monomer dye molecules resulting in an overall luminescence red-shift at higher dye concentrations. We set out to clarify this issue, by developing experiments to distinguish between these two models, with the express purpose of generating a full-description of this solid-state solvation effect.

Photoluminescence measurements were performed on films consisting of a polystyrene (PS) matrix doped with a trace concentration of DCM2 laser dye, and between 0% and 35% by weight of the polar Camphoric Anhydride (CA) molecules. Upon excitation by  $\lambda=480$  nm light only the fluorescence of DCM2 molecules was observed. This system allows us to keep the DCM2 concentration constant, and thereby fix DCM2 aggregation effects, while still modifying the local fields in the film by changing the concentration of CA. The polymer host material polystyrene was chosen because it provides a non-polar background for the system. The polar camphoric anhydride was chosen because it has a large dipole moment ( $\mu\sim 6$ D in ground state) with a low molecular weight, and it is essentially optically inactive over the range of wavelengths relevant for studying the properties of DCM2.

For a fixed DCM2 concentration of  $< 0.005\%$ , the DCM2 emission spectrum shifts continuously from 2.197 eV (565.0 nm) to 2.016 eV (615.5 nm) for CA concentrations ranging from 0% to 35% (see Fig. 42). These results

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ranging from 0% to 35% (see Figure 42). These results show that large shifts in emission spectra can be observed in films that have negligible DCM2 aggregation. Furthermore, the spectral shift is correlated with the increase in the concentration of polar molecules in the amorphous host thin film. Assuming minimal CA:DCM2 aggregation, these results are consistent with the local-field-induced shifts proposed by Bulovic *et al.*

The Bulovic *et al.* study, however, gives no detailed description of the physical mechanism for the spectral

Although further experiments must be performed, our present understanding is that the static fields in the doped films are the result of the arrangement of CA molecules around each DCM2 molecule during the formation of the film. Depending on the precise conditions under which the film forms, the extent to which this relaxation can proceed may change. For instance, if an arbitrary film is formed very rapidly and its constituent molecules afforded very little excess energy, it may be possible to entirely eliminate spatial correlation between molecules. On the other hand, annealing films

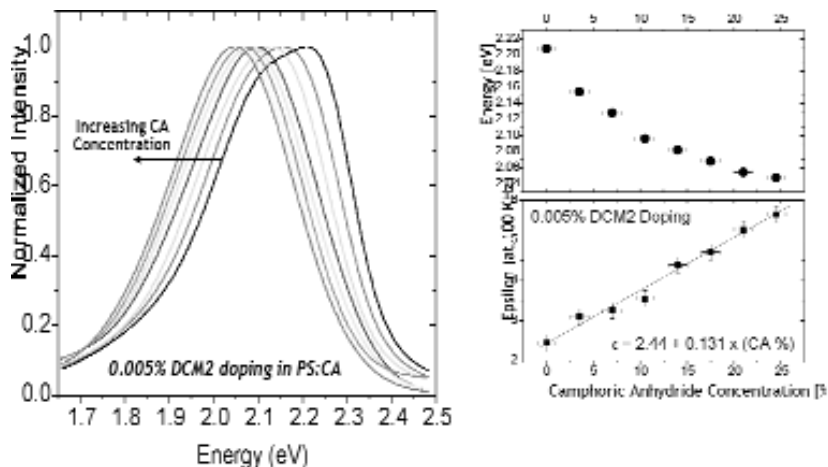


Fig. 42: (left) PL spectra of 0.005% DCM2 in PS:CA films. The spectrum red-shifts as the CA concentration is changed from 0 to 25%. (middle) Chemical structures of CA, DCM2, and PS. (right) Change of the peak luminescence energy and the dielectric constant as a function of CA doping.

shifts, leaving it unclear whether the shifts are due to static fields in the material, leading to a built-in Stark effect, or if they are due to dynamic relaxations in the material, leading to a solvatochromic shift as observed in liquids. By comparing emission and absorption spectra of PS:CA:DCM2 films, we are able to identify the extent to which static fields and dynamic relaxations are separately contributing. Surprisingly, initial measurements indicate that the spectral shifts follow the predictions of the solvation theory (although contributions from a static field could still be present).

after growth, or growing films very slowly, might enhance this spatial correlation. We expect that further study of this effect will provide considerable insight into the extent over which we can control molecular energy level structure by modifying the surrounding medium.

#### Exciton Diffusion and the Excitonic Density of States in Amorphous Organic Thin Films

In this project we investigate the process of exciton diffusion in amorphous organic thin films. As we will

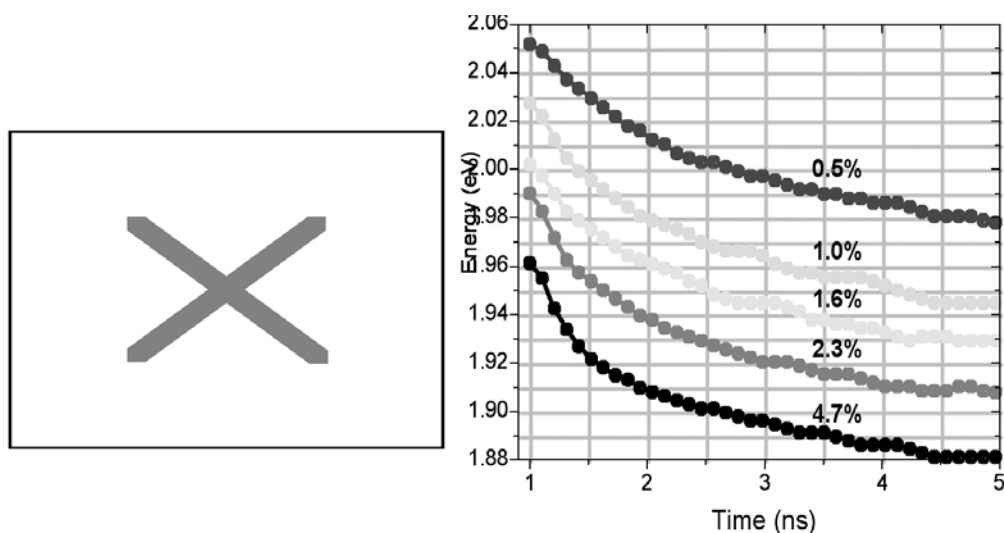


Fig. 43: (left) Spectral evolution of the PL spectrum of 4.7% DCM2 in Alq3 as a function of time after 100fs excitation with 400 nm light. (Inset) Schematic illustration of the experimental measurement. (right) Evolution of the peak of the photoluminescence spectra of Alq3:DCM2 films with different DCM2 concentrations (indicated in the plot).

show below, the experimental observation of this process is integrally related to the excitonic density of states (DOS) in such films, and part of this project includes also the direct measurement of the DOS.

Numerous previous reports have established the importance of exciton diffusion by Forster energy transfer in amorphous organic thin films. For example, many groups studying organic light emitting diodes

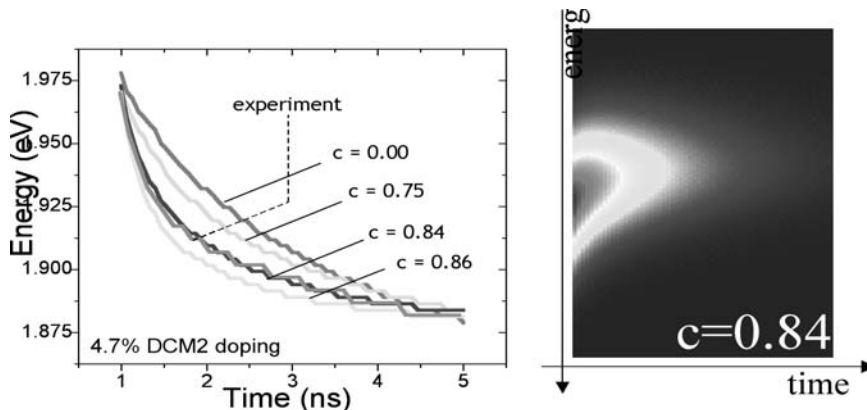


Fig. 44: (left) Comparison of the measured peak PL energy as a function of time, and the theoretical predictions based on the exciton diffusion model, for an Alq3 film doped with 4.7% DCM2. The different values for  $c$  correspond to different density of states functions. Higher values of  $c$  indicate a narrower density of states, limiting at a delta function for  $c=1.0$ . For  $c=0$ , the density of states is simply the ensemble PL spectrum obtained immediately after the arrival of the laser pulse (i.e. before any diffusion occurs). (right) A PL intensity image of the emission spectrum as a function of time, produced by the simulator for the value of  $c$  best reproducing the experimental data. A spectral shift towards lower energies is observed.

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have demonstrated that excitons formed at a specific film interface can migrate significant distances from that interface. While such diffusion can involve energy transfers between dissimilar molecules, the bulk of exciton diffusion occurs through Forster energy transfer between like molecules. The probability of exciton energy transfer is proportional to the overlap between the absorption spectrum of the final state and the emission spectrum of the initial state. An exciton is, therefore, far more likely to transfer from a higher energy site to a lower energy site than vice versa because the overlap between the respective emission and absorption spectra is larger in the former case. Consequently, diffusion by Forster energy transfer should progressively drive excitons towards the lowest energy sites in the system. The disorder in the amorphous neat films introduces a distribution of excitonic energies among different molecular sites, the lowest ones of which are preferentially occupied in the diffusion process.

The exciton diffusion process can explain our recent observation of spectral shifts in the time resolved photoluminescence (PL) spectra of thin films of Alq<sub>3</sub> doped with the red laser dye DCM2 (Figure 43). The films were excited by  $\lambda = 400$  nm 100 fs pulses, and the signal was detected with a Hamamatsu Streak Camera with a maximum time resolution of 2 ps. In these measurements, we found that the PL spectra progressively red-shifted with time for the entire lifetime of the emission signal. For DCM2 doping levels of between 0.5% and 5%, we observed spectral shifts of more than 0.7 eV, with a small but continuous increase in the shift from lower to higher dopings (Figure 43).

The spectral shifts are consistent with the exciton diffusion model. The smaller shifts observed for the samples with lower DCM2 concentration (larger DCM2 spacing) are consistent with the Forster energy transfer mechanism that is a very strong reciprocal function of distance (falling off as  $R^{-6}$ ). We simulated numerically the

diffusion process, starting with a large collection of spatially distributed DCM2 sites, with energies appropriate for the provided Density Of States (DOS). We then populate these sites with excitons, and allow them to either emit, or Forster energy transfer to another site during each time slice. The probabilities for these events are determined by supplied parameters. By tracking million excitons, we obtained smooth, repeatable ensemble PL spectra. In the course of these simulations, it became clear that given the “right” DOS function, we could very closely reproduce the observed experimental results (Figure 44). However, so long as the DOS function remains a completely free parameter of the model, this remains a less than rigorous test of the theory.

The DOS of DCM2 molecules in our films can be separately determined by employing single-molecule spectroscopy (SMS). We measure PL spectra of films with a low concentration of lumophores so that we can spatially resolve the individual molecules using a confocal microscope. The DOS of states so obtained is in a good agreement with the DOS predicted by our model.