

Solid State Solvation in Amorphous Organic Thin Films

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The photoluminescence (PL) of the red laser dye DCM2, doped into blended thin films of polystyrene (PS) and the polar small molecule camphoric anhydride (CA), redshifts as the CA concentration increases. The DCM2 PL peaks at 2.20 eV ($\lambda = 563$ nm) for pure PS films and shifts to 2.05 eV ($\lambda = 605$ nm) for films with 24.5% CA (by mass). The capacitively measured electronic permittivity also increases from $\epsilon = 2.4$ to $\epsilon = 5.6$ with CA concentration. These results are consistent with the theory of solvatochromism developed for organic molecules in liquid solvents. To our knowledge, this work is the first application of a quantitative theory of solvation to organic molecules in amorphous thin films with continuously controllable permittivity, and demonstrates that “solid state solvation” can be used to predictably tune exciton energies in organic thin film structures.

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Performance of active organic optoelectronic devices is governed by the structure and alignment of the electronic energy levels of the constituent molecules. Although detailed understanding of the properties of individual, isolated organic molecules exists, once incorporated into amorphous thin films within active devices the properties of these same molecules can be radically different. In this Letter we demonstrate that one general mechanism for altering the energy structure of organic molecules is solid state solvation, the solid state analog of liquid state solvation. By comparing a numerical model to experimental data we show that this phenomenon can be predictably controlled to provide a new method for engineering energy structure in amorphous organic thin films.

This work builds on recent reports by Bulović *et al.* describing spectral redshifts in the emission of amorphous organic thin films doped with the red laser dye [2-methyl-6-[2-(2,3,6,7-tetrahydro-1H, 5H-benzo [i,j] quinolizin-9-yl)-ethenyl]-4H-pyran-4-ylidene] propane-dinitrile (DCM2) [1,2]. The authors found that the peak electroluminescence wavelength of DCM2 doped organic light emitting diodes shifted from $\lambda = 570$ nm to $\lambda = 645$ nm as the DCM2 concentration in films of *N, N'*-diphenyl-*N, N'*-bis(3-methylphenyl)-[1, 1'-biphenyl]-4, 4'-diamine (TPD) was changed from 0.9% to 11% (by mass). Because DCM2 is a highly polar molecule (with electric dipole moment $\mu \approx 11$ D in the ground state [3]), and TPD is nearly nonpolar (with $\mu \approx 1$ D in the ground state [4]), it was proposed that increasing the DCM2 concentration increased the strength of the local electric fields present in the film, and that this increase in the local fields was the cause of the spectral shift. The mechanism was termed “solid state solvation,” as the authors viewed it as a solid state analogue to the solvation mechanism underlying solvatochromism of organic molecules in liquids.

DCM2 readily aggregates at the concentrations used in the above work, and a subsequent study suggested that

high electric fields associated with local ordering of the polar DCM2 molecules in aggregate domains contribute to the observed spectral shifts [5]. In the present work, we employ a new material system designed to demonstrate DCM2 spectral shifts like those found by Bulović *et al.* in the absence of DCM2 aggregation. This is achieved by using a low DCM2 dopant concentration in a two-component host consisting of polystyrene (PS) and the polar small molecule camphoric anhydride (CA).

The films are spun cast at 2000 rpm from solutions with a total concentration of PS:CA:DCM2 of 30 mg/ml. The solutions are made by first dissolving PS in a mixture of pure chloroform and 20 mg/ml CA chloroform solution to obtain the proper PS:CA ratio. Then a small amount of 0.033 mg/ml DCM2 chloroform solution is added to yield the desired DCM2 mass fraction.

The DCM2 concentration in the films is kept constant and low (0.005% by mass, unless otherwise indicated), thereby fixing and limiting DCM2 aggregation effects. At the same time, the dielectric properties of the film are modified by changing the concentration of CA, which has a large ground state dipole moment ($\mu \approx 6$ D [6]) relative to its molecular weight and is optically inactive at wavelengths relevant for studying DCM2 PL. The PS provides a transparent, nonpolar host matrix for the film.

We perform three measurements on our films. First, we measure PL spectra with a SPEX fluorimeter employing a monochromator and a cooled photomultiplier tube. The films are excited using $\lambda = 480$ nm light, which is absorbed only by the DCM2 molecules in the films. To limit photobleaching of DCM2, the films are epoxy sealed in a nitrogen glove box between two glass slides, immediately after spinning. Second, we measure the thin film electronic permittivity in a capacitor structure using an HP 4192A impedance analyzer at zero bias with a 5 mV rms ac test signal. The capacitor structure consists of a 30 nm thick thermally evaporated aluminum bottom electrode, a 250 nm thick PS:CA:DCM2 film, and a 50 nm thick

thermally evaporated aluminum top electrode. The total device area was 2.5 mm^2 . The aluminum layers are grown at rates of 0.2 nm/s at pressures of $1 \times 10^{-6} \text{ Torr}$. The thicknesses of all the film layers are directly measured using profilometry. Finally, we measure the index of refraction of each film by ellipsometry.

For a fixed DCM2 concentration of 0.005%, we find that the peak of the DCM2 emission spectrum shifts from 2.20 eV ($\lambda = 563 \text{ nm}$) to 2.05 eV ($\lambda = 605 \text{ nm}$) as the CA concentration changes from 0% to 24.5% (see Fig. 1). Identical results are obtained on films in which the DCM2 concentration is increased to 0.05%, indicating that the spectral shift is not related to aggregation. The electronic permittivities of the films, measured at 1 MHz, are plotted in Fig. 2 (identical results were obtained at 10 and 100 kHz), calculated with the assumption that the device structure forms a parallel plate capacitor with a leaky dielectric. The permittivity increases with increasing CA concentration, following a linear relationship: $\epsilon = 2.44 + 0.13 (\text{CA}\%)$. In contrast, the index of refraction

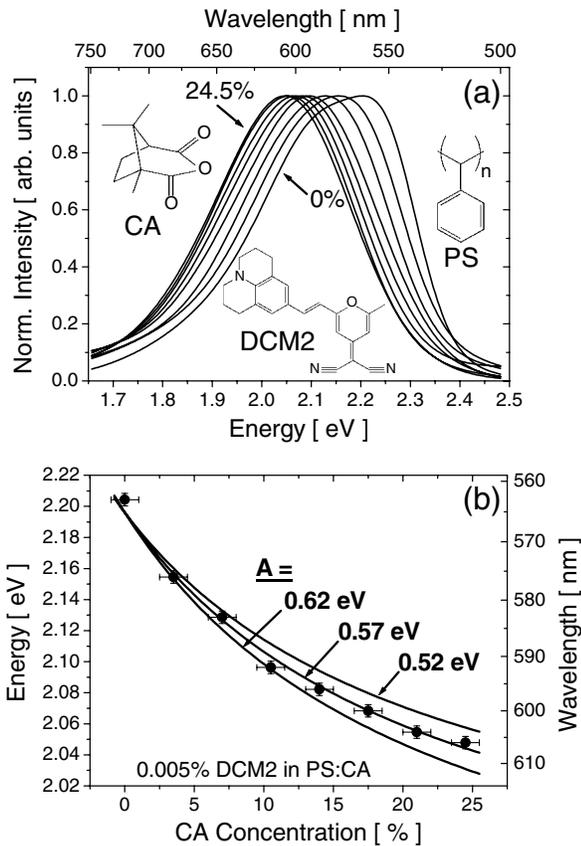


FIG. 1. Spectral shift in PL of 0.005% DCM2 doped into PS:CA thin films as the CA concentration is varied from 0% to 24.5%. The evolution of the normalized PL spectra (a) and the peak of the PL spectra (b) are shown. Three fits (solid lines) using the OLM theory [Eq. (3)] are also shown in (b), with $A = 0.57$ yielding the optimal fit. The chemical structures of PS, CA, and DCM2 are inset in (a).

of the films is nearly constant with values of between 1.55 ± 0.05 and 1.65 ± 0.05 for all samples.

The theory of solvatochromism relates the experimentally observed changes in emission and absorption spectra of a solute to the electronic permittivity of a solvent. The theory primarily considers the following: (1) the response of the solvent molecules to changes in the solute charge distribution $\rho(\vec{r})$ following photon absorption and emission (i.e., the dynamic solvation of the solute), and (2) the interaction of the solute with the local electric field \vec{E}^{loc} produced by the surrounding solvent molecules.

An electronic transition on the solute produces a corresponding change in $\rho(\vec{r})$, which causes the surrounding solvent molecules to experience a new solute-induced electric field. The solvent molecules respond to this new field in two ways: (1) through electron cloud reorganization (i.e., polarizability), and (2) through gross spatial movement (i.e., physical translation and rotation). These two processes (referred to below as “fast” solvation [S_{fast}] and “slow” solvation [S_{slow}], respectively) can alter \vec{E}^{loc} , and hence also modify the energy levels of the solute. Figure 3 illustrates the impact of solvation on the ground and first excited excitonic energy levels for absorption and emission. Three different processes are shown: S_{fast} , S_{slow} , and the Franck-Condon (FC) shift (due to solute nuclear reorganization). The time scales are such that S_{fast} operates concurrent with the electronic transitions, while the FC shift and S_{slow} follow the electronic transitions, with the FC shift operating faster than S_{slow} in all known cases.

Neglecting effects on the electronic wave functions of the solute, the solvation induced change in the emission energy is due to the electrostatic interaction between $\rho(\vec{r})$ and \vec{E}^{loc} just before and after emission (i.e., states 3 and 4 in Fig. 3). This energy change $\Delta E_{\text{solv}}^{\text{el}}$ is given by

$$\Delta E_{\text{solv}}^{\text{el}} = \int [\phi_3^{\text{loc}}(\vec{r})\rho_3(\vec{r}) - \phi_4^{\text{loc}}(\vec{r})\rho_4(\vec{r})]d^3r,$$

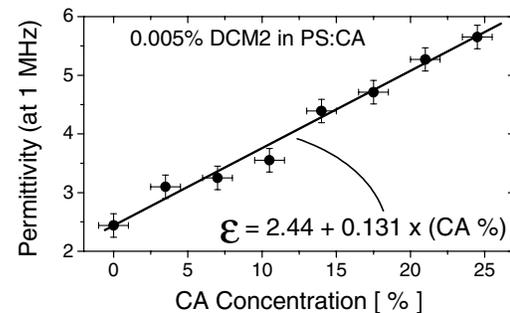


FIG. 2. Evolution of the electronic permittivity ϵ of PS:CA:DCM2 films as the CA concentration is varied from 0% to 24.5%. The measurements were performed using a thin film capacitor structure. A linear fit (solid line) is shown.

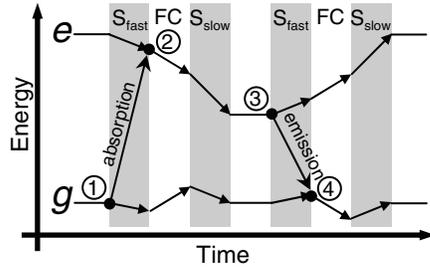


FIG. 3. Diagram of the evolution of the ground, g , and first excited, e , energy levels for a single cycle of absorption and emission. The energy changes due to the Frank-Condon shift, and the “fast” and “slow” solvation responses are denoted by “FC,” “ S_{fast} ,” and “ S_{slow} ,” respectively. States 1 and 3 describe the solute in equilibrium with its environment in the ground and excited states, respectively, while states 2 and 4 describe the solute immediately following excitation and relaxation, respectively. Note that the time axis is only schematic, as, for example, S_{fast} takes place over an infinitesimally short time as compared to FC and S_{slow} .

where ϕ_3^{loc} and ϕ_4^{loc} are the local potentials (corresponding to \vec{E}_3^{loc} and \vec{E}_4^{loc}) for states 3 and 4, respectively, while $\rho_3(\vec{r})$ and $\rho_4(\vec{r})$ are the associated solute charge distributions. While quantum mechanical calculations of $\rho_3(\vec{r})$, $\rho_4(\vec{r})$, ϕ_3^{loc} , and ϕ_4^{loc} are theoretically straightforward, the number of molecules involved makes this computationally impractical. Instead, most calculations are performed under the “continuum” approximation, in which the surrounding molecules are replaced by a continuous dielectric with the electronic permittivity ϵ and index of refraction n of the bulk solvent.

The simplest such model (due to Onsager [7]) makes a number of further approximations. First, the molecule is spatially described by a spherical cavity of radius a embedded within the dielectric continuum. Second, $\rho(\vec{r})$ is reduced to the dominant component of its multipolar expansion, which for neutral molecules is the dipole moment. Recalling that the interaction energy between a dipole with moment $\vec{\mu}$ and an electric field \vec{F} is $-\vec{\mu} \cdot \vec{F}$, one can obtain

$$\Delta E_{\text{solv}}^{\text{l}} = -\frac{1}{a^3} \Delta \vec{\mu} \cdot (\Lambda \vec{\mu}_e + \Lambda_{op} \vec{\mu}_g), \quad (1)$$

where $\vec{\mu}_g$ and $\vec{\mu}_e$ are, respectively, the solute ground and excited state dipoles, $\Delta \vec{\mu} \equiv \vec{\mu}_g - \vec{\mu}_e$ and

$$\Lambda \equiv \frac{2(\epsilon - 1)}{2\epsilon + 1}, \quad \Lambda_{op} \equiv \frac{2(n^2 - 1)}{2n^2 + 1}. \quad (2)$$

Equation (1) is part of the Ooshika-Lippert-Mataga (OLM) treatment, first developed in the 1950s [8–10]. The separate terms dealing with ϵ and n^2 are associated with S_{slow} and S_{fast} , respectively. In using Eqs. (1) and (2) it is necessary to keep in mind that S_{slow} includes only responses that occur prior to the excited state relaxation, which on average takes a time τ to occur, where τ is the

excitonic radiative lifetime. As a result, the permittivity ϵ describing S_{slow} refers to ϵ at $\omega \approx 1/\tau$. One typically need not measure ϵ at this exact frequency, however, as it is constant for most organic solids from $\omega \approx 10$ kHz up until nuclear motion turns off (> 1 THz). Since for DCM2, $\tau = 3.3$ ns [11], it is sufficient to measure ϵ at 1 MHz. (When treating liquids, it is a common practice to use $\epsilon[\omega = 0]$, as it is often equal to $\epsilon[\omega \approx 1/\tau]$. In solids, however, this is not always the case, and it is preferable to use a high frequency value, as we have done.)

The OLM theory has been applied to many liquid systems and the predicted functional dependence of the spectral shifts on n^2 and ϵ consistently observed (see, for instance, [12]). We now apply this theory to the solid system of PS:CA:DCM2 thin films.

We first rewrite Eq. (1) as $\Delta E_{\text{solv}}^{\text{l}} = -A\Lambda - B\Lambda_{op}$, with the definitions $A \equiv \Delta \vec{\mu} \cdot \vec{\mu}_e/a^3$, $B \equiv \Delta \vec{\mu} \cdot \vec{\mu}_g/a^3$. We then write the total emission energy including solvation effects as $E^{\text{l}} = E_0^{\text{l}} + \Delta E_{\text{solv}}^{\text{l}}$, where E_0^{l} is the emission energy in vacuum (including the FC shift). Because the change in n of the PS:CA:DCM2 films as the CA concentration varies is minimal, we take the Λ_{op} term as approximately constant, leaving us with the functional form

$$\Delta E_{\text{solv}}^{\text{l}} = C - A\Lambda, \quad (3)$$

where C is constant. In Fig. 1(b) we plot three different fits to the spectral shift data, indicating the sensitivity of the fit to the choice of A . We find that the trend in the shift of the spectral peak is in excellent agreement with the solvation theory, with the optimal fit obtained for $A = 0.57 \pm 0.03$ eV.

It is difficult to evaluate the plausibility of this result based solely on the definition for A because of the arbitrariness of a and the necessity of knowing the exact ground and excited state dipole vectors for DCM2. However, we can look at solvation in solutions, where the solvation mechanism is known to operate. A plot of the peak emission energy for DCM2 in different solvents is shown in Fig. 4 against Λ for each solvent. Because n does not change significantly from one solvent to the other, ranging from 1.4 to 1.5, we again approximate the Λ_{op} term as constant. We find that the solvation theory is again in good agreement with the data, and obtain an optimal fit for $A = 0.55 \pm 0.03$ eV, nearly identical to the value obtained for DCM2 in PS:CA films.

Indeed, based on very general arguments, for a particular molecule one would expect to find similar values for A in any condensed medium of comparable density. The molecular “volume” would tend to remain the same in all such media, and since the molecular charge distributions should not change radically, then the dipoles would also tend to remain the same. Therefore, obtaining nearly identical values of A for DCM2 in organic solvents and in PS:CA films provides strong evidence

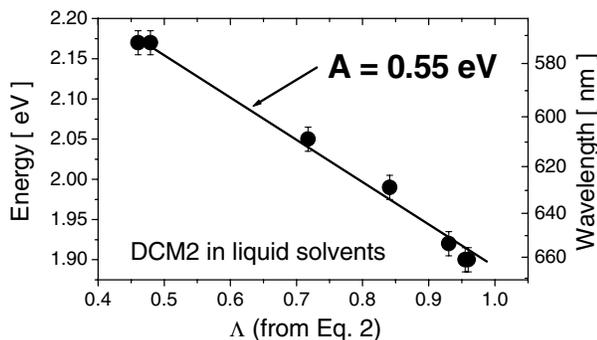


FIG. 4. Peak PL energy of DCM2 in seven different solvents plotted against the solvent Δ value [see Eq. (2)]: benzene ($\epsilon = 2.28$), toluene ($\epsilon = 2.38$), chloroform ($\epsilon = 4.81$), dichloromethane ($\epsilon = 8.93$), acetone ($\epsilon = 21.01$), methanol ($\epsilon = 33.0$), and acetonitrile ($\epsilon = 36.64$). Using Eq. (3) and $A = 0.55$, we obtain the solid line fit.

that solvation is the mechanism underlying the spectral shifts observed in the PS:CA:DCM2 system.

It should be noted that solid state solvation is not the only mechanism capable of producing spectral shifts which are dependent on the concentration of dipoles in a thin film. In a solid, the constituent molecules are sterically constrained, which can give rise to strong, permanent local electric fields. Such fixed local fields can lead to spectral shifts on individual molecules through the Stark effect. In the simplest case, the change in the energy of an electronic transition ΔE_{fixed} due to the presence of a fixed field \vec{F} is given by $-\vec{F} \cdot \Delta \vec{\mu}$. If the fields are random, as one would expect in a completely amorphous solid, then, after averaging over all the molecules in the film, there should be no net shift in either the absorption or emission spectra, though one might observe a broadening of the spectra, due to the increased dispersion in the absorption and emission energies that such fields would produce. However, if the molecular orientations are correlated, a net spectral shift could occur, as previously proposed for aggregated DCM2 molecules [5]. (Such correlation presumably occurs during film formation, when the constituent molecules have greater mobility than in the final film.)

Therefore, in general one should consider the contribution of both fixed local fields and solvation in evaluating the PL spectra of molecular organic thin films. In the PS:CA:DCM2 system, however, the solvation mechanism appears to dominate. This is demonstrated by the dramatic change in the electronic permittivity of PS:CA:DCM2 films with doping, which indicates that the CA molecules retain substantial orientational freedom in the solid state, consistent with weak fixed local

fields. And, as noted above, the application of dielectric continuum models to DCM2 in PS:CA yields parameters nearly identical to those obtained for DCM2 in liquids, where fixed fields are entirely absent.

In this Letter we presented experimental data demonstrating spectral redshifts in the PL of DCM2 doped into PS:CA films. We correlated these shifts with a dramatic increase in film permittivity due to CA doping. The OLM theory for solvatochromism fits the data and yields parameters consistent with those observed for DCM2 in solution. We concluded that in PS:CA films, the observed spectral shifts are due to solvation, without any appreciable contribution from fixed electric fields. Thus, we found the following: (1) solid state solvation occurs and can significantly alter molecular energy levels in an organic thin film, and (2) the associated dielectric continuum models applicable to liquids are also applicable to solids. Finally, given the controllable and continuous spectral shifts achieved in DCM2 emission with CA doping, we demonstrated the potential of solid state solvation as a mechanism for tuning exciton energies through host doping.

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