Photoluminescence Dynamics in Singlet Fission Chromophore Liquid Melts

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Abstract

The effect of high temperature melting on the photophysics of three prototypical singlet fission molecules is investigated. Time-resolved photoluminescence is used to look at the melt phase of the molecules tetracene, diphenylhexatriene and rubrene. Chemical decomposition of tetracene precluded any detailed measurements on this molecule. In the diphenylhexatriene melt, a rapid singlet state nonradiative relaxation process outcompetes singlet fission. In the rubrene melt, singlet fission occurs at a rate similar to that of the crystal, but the decay of the delayed fluorescence is much more rapid. The rapid decay of the delayed fluorescence suggests that either the triplet lifetime is shortened, or the fusion probability decreases, or that both factors are operative at higher temperatures.

Introduction

Interest in singlet fission (SF) as a route toward more efficient solar energy conversion has inspired considerable theoretical and experimental work in order to understand how its rate depends on molecular packing.¹⁻² Perhaps the simplest way to experimentally vary intermolecular interactions is to go from the ordered environment of a crystal to a disordered environment. Recent results on pentacene and tetracene derivatives in statically disordered amorphous films³⁻⁷ and dynamically disordered liquids⁸⁻¹¹ have demonstrated that crystalline order between separate chromophores is not a requirement for rapid SF.

One disadvantage of disordered solids is that triplet exciton diffusion tends to be much slower than in a single crystal. This is because of the existence of static, low-energy sites that trap the exciton, preventing it from hopping to neighboring sites. However, simulations by Bässler suggested that disorder is not necessarily fatal for triplet exciton diffusion in a fluid environment.¹² Experiments on molten anthracene and naphthalene showed that these liquids could support long triplet lifetimes and enhanced triplet diffusion lengths.¹³⁻¹⁵ Later theoretical¹⁶ and experimental¹⁷⁻¹⁸ work on energy migration in dye molecule solutions demonstrated that liquid environments could also enhance singlet exciton diffusion rates. Presumably, the ability of liquid-state molecules to sample multiple configurations during their excited state lifetimes prevents the formation of static low energy trap sites. Since SF is already known to occur in disordered environments, we became interested in whether melt-phase SF chromophores could exhibit both SF and the long triplet lifetimes seen in anthracene melts.

In this work, we used time-resolved photoluminescence (PL) to look at the melt phase of the prototypical SF molecules rubrene (RUB), tetracene (TET) and diphenylhexatriene (DPH). We were hoping to find evidence that rapid SF was retained, as well as long triplet lifetimes as

observed for anthracene. Such a result would provide evidence that SF in a fluid medium could be a viable approach to making largescale homogeneous layers. The bulk of this paper will concentrate on RUB, where SF occurs in the melt but the triplet dynamics change considerably. In DPH, a new singlet relaxation channel arises that appears to outcompete SF. We could not measure reproducible data for TET due to chemical decomposition in the melt. In addition to being the first characterization of PL lifetimes for the melt phase of several important organic semiconductors, this work also suggests that chemical decomposition and accelerated nonradiative decay rates in melts can make them less than ideal phases for SF.

Experimental

Rubrene samples were prepared by placing 99.9% rubrene from Acros Organics into a melting point capillary until the level reached halfway up the tube. The capillary was evacuated until the internal pressure reached 1 mTorr. While still pulling vacuum on the sample, the capillary was flame sealed, leaving an ample space at the top to insure the flame did not directly heat the sample.

For high-temperature spectroscopic measurements, the sealed samples were placed within a modified Laboratory Devices Mel-Temp melting point apparatus. The faceplate of the melting point apparatus was removed and a custom aluminum faceplate was constructed to allow for excitation and photoluminescence collection. Temperatures of the melting point apparatus were measured using a Digi-Sense Thermocouple Thermometer. Magnetic field effects were tested through the use of a pair of cylindrical magnets (K&J Magnetics, part number DY0Y0-N50) that were positioned on both sides of the melting point apparatus. A Gauss-meter was used to measure a 1.5 kG magnetic field strength at the sample position.

Time-resolved PL data were obtained using front-face detection with a Hamamatsu C4334 Streakscope picosecond streak camera with 2.5 nm wavelength resolution and 15 ps time resolution. Unless otherwise specified, the fluorescence decays were integrated over 550-700 nm. The 800 nm output of a Coherent Libra regenerative amplifier (1 KHz repetition rate) was frequency doubled in a beta-barium borate crystal to generate the 400 nm pulses, which were then focused with a 20 cm focal length lens onto the samples in the capillary.

Results and Discussion

The PL spectra of crystalline RUB can vary considerably. In general, there is a high energy emission with a well-defined vibronic peak progression, starting at 560 nm, often accompanied by a red-shifted emission that is centered from 620 nm to 650 nm and is more or less featureless.¹⁹ The 560 nm emission is intrinsic to the crystal, while the redshifted emission was originally assigned to oxidized rubrene molecules²⁰ but is now thought to originate from disordered regions of the crystal (these may be generated by oxidation of surrounding molecules).²¹⁻²² The steady-state PL of crystalline samples is usually a mixture of both types. Our samples were powdered in order to pack the melting point capillary, and this process leads to an unstructured emission peaked at around 600 nm, shown in Figure 1, the same wavelength observed for most single crystals.^{21, 23} This redshifted emission probably reflects strong self-absorption in the sample¹⁹, but may also include contributions from defect states created by powdering. After the crystal melts, this emission shifts slightly to higher energy and broadens, but does not undergo dramatic changes in shape or intensity. After the sample is cooled down again, we find that the emission of the solid has redshifted to 650 nm. This is consistent with the findings of Podzorov and coworkers that melting and reforming the crystal leads to enhanced

low-energy emission.²¹ This melt-induced change in the PL is not due to chemical decomposition. When the melted crystal was redissolved in methylene chloride, the original RUB absorption and fluorescence spectra were recovered.

In crystalline form, the RUB PL signal reflects both SF and triplet fusion, which occur on different timescales.²⁴⁻²⁶ These two processes lead to a prompt PL decay that reflects the lifetime of the initially excited singlet state, followed by a longer-lived component due to delayed fluorescence generated by triplet-triplet recombination. In the first 100 ps, where the signal decays by about one natural log, the decay is dominated by the $S_1 \rightarrow T_1 + T_1$ fission process. The prompt decay in the 1 ns time window, shown in Figure 2a, corresponds to a singlet lifetime of ~60 ps that remains remarkably constant over the temperature range 20-340°C. Femtosecond transient absorption experiments on crystalline RUB suggested that the majority of SF occurs within 1 ps²⁷, but later experiments indicated that this rate may depend on excitation density and thermal load.²³ Our excitation densities are below those typically used in transient absorption experiments, and our SF time of 60 ps approaches the 35 ps time seen at the lowest fluences in such experiments.²³ But the distorted PL spectrum makes it impossible to unequivocally identify the emitting species as the high energy species, so it is also possible that we are measuring the dynamics of a subset of sites within the crystal rather than the majority species seen in the transient absorption experiments.

After 100 ps., the $T_1 + T_1 \rightarrow S_1$ fusion processes start to equilibrate the singlet and triplet populations. Up to 310°C, the post-100 ps region of the PL decay is unchanged to within the experimental noise. After melting at 340°C, there is a noticeable slowing of the later decay in the 0.1-0.8 ns region. This slight increase in the PL signal may reflect an increased fusion rate, rather than slower fission. When we shift to observing the PL decay on longer timescales, the

delayed fluorescence decreases dramatically, as shown in Figure 2b. The PL spectra in both the early and late time regimes are identical (Figure 2b, inset), confirming that the long decay component reflects delayed fluorescence. Note that the slight enhancement of the melt PL in the 1 ns window is canceled out by a more rapid PL decay over the next 20 ns. The crossing of the melt and 20°C decays can be discerned in Figure 2a at about 0.8 ns.

To confirm that the PL decay reflects SF dynamics, we measure it in the absence and presence of a magnetic field. As observed in solid amorphous films⁴ and crystals²⁴, the RUB samples exhibit a strong magnetic field enhancement of the fluorescence on intermediate to long timescales in both the room temperature solid and in the melt (Figure 3). In an earlier paper, we calculated that enhanced fluorescence in the presence of a strong magnetic field was a symptom of aligned pairs.⁴ However, recent work by Tapping and Huang showed our analysis was flawed and that such an enhancement occurs for both aligned and randomly oriented pairs.²⁸ So the positive sign of the magnetic field effect is consistent with SF occurring between randomly oriented molecular pairs, as expected in a liquid. The magnetic field effect supports our hypothesis that the prompt and delayed PL decays reflect fission and fusion dynamics, respectively.

Because we are focusing into a 1 mm diameter capillary, a precise calculation of excitation density in the sample was not possible. Nevertheless, we did vary the incident excitation pulse intensity over an order of magnitude (1-15 microwatts, before focusing) and observed no change in the PL decay of the RUB melt, similar to our results on solid amorphous RUB.⁴ The lack of an intensity dependence for the delayed fluorescence is consistent with the dominant role of geminate recombination in our experimental regime. If nongeminate recombination played a significant role, this contribution would depend quadratically on

excitation density and the amplitude of the delayed fluorescence relative to the prompt fluorescence would increase with laser intensity.

The rapid decay of RUB's delayed fluorescence at elevated temperatures could arise from several different physical mechanisms. One concern we had was that rapid diffusion of small impurities like O₂ or metal atoms might lead to PL quenching in the high temperature melt. We tested for such effects in two ways. First, we compared results from two different RUB samples: one from crystals used as received from Acros Organics, and one from a ground-up single crystal grown by gradient vapor phase deposition, which presumably would have a lower level of chemical impurities. Both samples gave similar PL decays upon melting. Second, we tested for the effect of residual O₂ by evacuating a capillary to 10⁻³ Torr before flame sealing, and compared the results to those from a capillary that was not evacuated. Again, the PL signals from the different preparations were the same to within a few percent. Thus we think that the photophysical changes observed upon melting reflect changes in the intrinsic material structure, rather than changes in extrinsic impurity quenching.

To better understand the origin of the delayed fluorescence decay, we consider the simple kinetic model outlined in Equations (1) and (2).⁴ We assume that the triplet population consists of associated pairs (the *TT* state) produced by fission that can fusion back into the singlet state. This leads to a simple pair of rate equations:

$$\frac{dN_{S1}}{dt} = -k_{fiss}N_{S1} + k_{fus}N_{TT} \quad (1)$$

$$\frac{dN_{TT}}{dt} = -k_{trip}N_{TT} - k_{fus}N_{TT} + k_{fiss}N_{S1} \quad (2)$$

where k_{fiss} is the fission rate, k_{fus} is the fusion rate, and k_{trip} is the triplet decay rate. Two factors will affect whether the triplets produced by SF can give rise to delayed fluorescence: their

ability to fuse, as given by k_{fus} , and their lifetime, as determined by k_{trip} . In Figure 4, we show calculated PL decays obtained by allowing either k_{fus} to decrease or k_{trip} to increase with temperature. In both cases, the delayed fluorescence signal decreases. Comparing the calculated curves in Figure 4 to the experimental decays in Figure 2b, we see elements of both a decreased amplitude (predicted by a decreased k_{fus}) and a more rapid decay (as predicted by an increased k_{trip}). Both effects are expected. The fluid environment of the melt may facilitate triplet energy migration and separation of triplet pairs, lowering the probability of geminate fusion and thus k_{fus} , as shown in Figure 4a. More rapid triplet energy migration would also increase the probability of nongeminate fusion, but the lack of intensity dependence described in the preceding paragraph suggests that our excitation densities are low enough that this process is negligible. The existence of an intramolecular decay process for rubrene's triplet state has been inferred from solution measurements²⁹, and the activation energy from that work predicts a factor of 50 increase in k_{trip} from 298°C to 340°C. This is the same order of magnitude of the change seen in the simulations in Figure 4b. A more quantitative analysis of the relative roles of k_{fus} and k_{trip} would require more sophisticated modeling. Equations (1) and (2) do not include phenomena, like diffusion³⁰⁻³², that would be needed to accurately model the full dynamics of the triplet pairs.

Finally, we wanted to see if the changes in the RUB melt could be observed in other SF molecules. Our attempts to measure the PL of the TET melt were not successful due to chemical decomposition at elevated temperatures in the melt. After cooling, the resultant solid had turned from orange to black and could not be fully dissolved in methylene chloride. The origin of this decomposition is not clear – it may involve residual impurities. O₂ is a possible candidate, but the dark color and insolubility of the solid make endoperoxide formation unlikely, as this product

would be soluble and absorb in the ultraviolet.³³ During these experiments, we did observe a single exponential decay for vapor phase tetracene with a lifetime of about 4 ns at 370 °C.

DPH did not decompose during the melting experiments, and its time-resolved PL data are shown in Figure 5. At room temperature, in a 1 ns window, the PL decay of the DPH sample is slightly slower than in our previous paper.³⁴ This may be due to having a mixture of crystal polymorphs in this powdered sample, since the SF rate is sensitive to molecular packing. Unlike RUB, both the prompt and delayed components are strongly affected by melting. The prompt decay time decreases from 130 ps to 20 ps in the melt, and the delayed fluorescence signal disappears completely. There was no measurable magnetic field effect on the PL decay in the melt, in contrast to crystalline DPH at room temperature.³⁴ We conclude that melting gives rise to a rapid nonradiative relaxation that competes effectively with SF. This lifetime shortening is not simply due to increased conformational freedom in the melt, because in room temperature liquid solutions DPH has an excited state lifetime on the order of nanoseconds.³⁵ Saltiel has suggested there exist intramolecular conversion pathways for DPH that do not involve torsional motion³⁶, and if one of these pathways is thermally activated, it could explain the rapid relaxation in the high-temperature melt. As with RUB, we did not observe any measurable change in the steady state absorption or fluorescence after the melted crystal was redissolved in methylene chloride, suggesting that chemical decomposition was negligible in this sample.

Conclusion

In this paper, we examined how high temperature melting affects the photophysics of three prototypical SF molecules. Chemical decomposition of TET prevented us from making any concrete observations on this molecule. In the DPH melt, a rapid singlet state nonradiative

relaxation short-circuits SF altogether. RUB is the most interesting case, because in the melt it undergoes SF at a similar rate to that observed for the room temperature crystalline powder. The ensuing triplet dynamics are quite different, however, with a rapid decay of the delayed fluorescence that suggests the triplet lifetime is shortened or possibly pair dissociation is enhanced. Transient absorption experiments would help clarify which factor determines the fate of the triplets at high temperatures. It is possible that a liquid composed of RUB chromophores (e.g. a derivative prepared as ionic liquid) might exhibit the desired combination of rapid SF and long triplet lifetimes and diffusion lengths.

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Figure 1. Time-integrated photoluminescence spectra of solid rubrene powder at room temperature (black), after melting at 340 °C (red) and after cooling back to room temperature (green).

Figure 2. **a)** The prompt fluorescence decays (0.0-0.9 ns) of solid rubrene at different temperatures and the melt at 340 °C. **b)** The delayed fluorescence decays (0-16 ns) of solid rubrene at different temperatures and the melt at 340 °C. **Inset:** The fluorescence spectra of the melt integrated over the time windows 0.0 to 0.5 ns (black) and 0.5 to 3.5 ns (red).

Figure 3. **a)** Time-resolved photoluminescence of the rubrene melt at 340 °C and **b)** solid rubrene powder at 20 °C. Both samples shown an enhancement of the fluorescence signal at longer times with the application of a 1.5 kG magnetic field. Note the different timescales of the two experiments due to the faster decay of the delayed fluorescence in the melt.

Figure 4. $N_{SI}(t)$ population decays (proportional to the observed photoluminescence signal) calculated using Equations (1) and (2). **a)** The triplet decay rate is set to $k_{trip}=0$ and the triplet fusion rate k_{fus} is varied. **b)** The triplet fusion rate is set to $k_{fus}=1 \text{ ns}^{-1}$ and the triplet decay rate k_{trip} is varied. For all calculations, $k_{rad}=0.06 \text{ ns}^{-1}$ and $k_{fiss}=15 \text{ ns}^{-1}$.

Figure 5. Photoluminescence decay of solid diphenylhexatriene at 20°C and the melt at 210°C.

The data have been integrated over the spectral window 425 to 550 nm.