# Temperature dependence of the triplet diffusion and quenching rates in films of an Ir(ppy)$_3$-cored dendrimer

J. C. Ribierre,[1] A. Ruseckas,[1] I. D. W. Samuel,[1] S. V. Staton,[2] and P. L. Burn[2,3]

[1]*Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St. Andrews, North Haugh, St. Andrews, Fife KY16 9SS, United Kingdom*

[2]*Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Mansfield Road, OX1 3TA Oxford, United Kingdom*

[3]*Centre for Organic Photonics and Electronics, University of Queensland, Chemistry Building, St. Lucia, Queensland 4072, Australia*

We study photoluminescence and triplet-triplet exciton annihilation in a neat film of a *fac*-tris(2-phenylpyridyl)iridium(III) [Ir(ppy)$_3$]-cored dendrimer and in its blend with a 4,4′-bis(*N*-carbazolyl)biphenyl host for the temperature range of 77−300 K. The nearest neighbor hopping rate of triplet excitons is found to increase by a factor of 2 with temperature between 150 and 300 K and is temperature independent at lower temperature. The intermolecular quenching rate follows the Arrhenius law with an activation energy of 7 meV, which can be explained by stronger dipole-dipole interactions with the donor molecule in the higher triplet substate. The results indicate that energy disorder has no significant effect on triplet transport and quenching in these materials.

PACS number(s): 78.55.−m, 78.66.Qn, 78.55.Kz, 78.20.−e

## I. INTRODUCTION

Organic light emitting diodes (OLEDs) are one of the most promising candidates for low-cost full-color flat panel displays. In particular, electroluminescent devices based on phosphorescent organic molecules have received considerable attention due to their ability of generating light from both singlet and triplet excitons which can lead to remarkably high efficiencies.[1–4] Maximum internal quantum efficiencies approaching 100% have been demonstrated in OLEDs using phosphorescent organometallic complexes based on iridium(III).[5,6] An external electroluminescence quantum efficiency (EQE) of 19% has already been reported in devices using a green emitting cyclometalated iridium(III) complex.[6–9] These phosphorescent materials are also very attractive for displays because of their excellent color tunability. Blue and red OLEDs based on iridium(III) complexes have shown EQE up to 14.4% and 13%, respectively.[10,7]

Triplet exciton diffusion is an important process in the operation of phosphorescent OLEDs and can lead to luminescence quenching by exciton-exciton annihilation[11] and traps.[12] Triplet exciton migration between phosphorescent molecules including iridium(III) complexes is controlled by a Dexter-type electron exchange mechanism.[13,14] The transport of triplet excitons has been reported as a function of temperature in several organic glasses[15] as well as in poly-(fluorene) derivatives[16] and this thermally activated process was described in the framework of the disorder model. In contrast, temperature-independent triplet diffusion was recently reported in a ladder-type conjugated polymer.[17] The decrease of phosphorescence lifetime with an increase of the concentration of phosphorescent chromophores (concentration quenching) has also been observed in iridium(III) complexes[12] and is governed by Förster-type dipole-dipole interactions.[18] The effect of temperature on both the exciton diffusion and intermolecular quenching in iridium(III) complexes has not been reported and could give further insight into these processes.

In this study, we have investigated the temperature dependence of the phosphorescence quenching and the triplet-triplet exciton annihilation rate in a neat film of a first generation Ir(ppy)$_3$-cored dendrimer (IrG1) with phenylene-based dendrons and 2-ethylhexyloxy surface groups and as a 20 wt % film blended with 4,4′-bis(*N*-carbazolyl)biphenyl (CBP). Such solution processable phosphorescent dendrimers have been successfully employed in OLEDs with external quantum efficiencies as high as 16%.[19,20] We have found a weak dependence of the triplet exciton diffusion on temperature, which suggests a narrow distribution of triplet energies. The intermolecular quenching rate appears to follow the Arrhenius law with an activation energy of $7 \pm 1$ meV. This value is similar to the energy gap of 9 meV between the lower and higher emissive triplet substates in *fac*-tris(2-phenylpyridyl)iridium(III) [Ir(ppy)$_3$] previously determined by time resolved photoluminescence (PL) studies[21] and suggests that dipole-dipole interactions, which control concentration quenching in these materials, are stronger when the molecule is in the higher triplet substate.

## II. EXPERIMENT

The chemical structures of the molecules considered in this study are given in the inset of Fig. 1. Thin films of IrG1 and blends of IrG1:CBP (20 wt %) were deposited onto quartz substrates by spin coating from chloroform solution (20 mg/ml) at a spin speed of 1000 rpm for 60 s. The solutions of the dendrimer samples were prepared immediately before processing. The films were then placed into a cryostat (Oxford Instruments, Optistat DN) in order to control the temperature from 77 to 300 K. Their absorption spectra were recorded on a Cary Varian 300 absorption spectrophotometer and their steady state PL spectra were measured with a Jobin Yvon Fluoromax 2 fluorimeter. Photoluminescence transient decays were measured by time-correlated single-photon counting. Excitation was obtained from the third harmonic of a Nd doped yttrium aluminum garnet laser at 355 nm at a
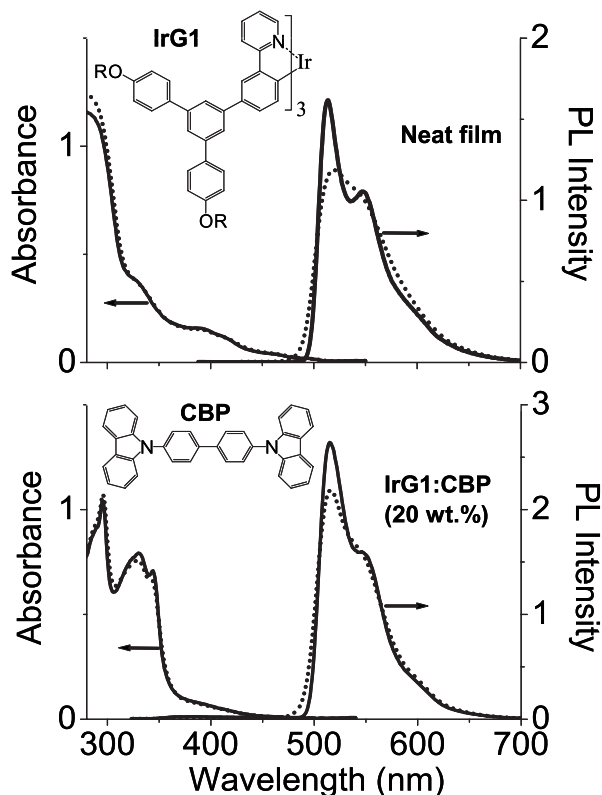
FIG. 1. Absorption and PL spectra of a neat film of IrG1 and IrG1:CBP (20 wt %) blended film at 77 K (solid line) and room temperature (dotted line). The excitation wavelength was 355 nm. The chemical structures of IrG1 and CBP are given in the insets. $R$=2-ethylhexyl.

repetition rate of 10 kHz. The excitation spot size corresponding to the full width at half maximum was measured with a beam profiler to be 0.45 mm. The detection wavelength was set at the maximum of the PL spectra. Excitation intensity was varied with neutral density filters.

### III. RESULTS AND DISCUSSION

Figure 1 shows the absorption and phosphorescence spectra in IrG1 and IrG1:CBP (20 wt %) films measured at 77 K and at room temperature. The stated blend ratio (20 wt % in this case) refers to the proportion of IrG1 in the blend, and we use this notation throughout the paper. Absorption in the neat film between 330 and 500 nm is associated with the "metal-to-ligand charge transfer" (MLCT) transitions[22] although it should be noted that these are not pure MLCT transitions.[23] The intense absorption band below 320 nm is due to the $\pi$-$\pi^*$ transitions of the ligand and the biphenyl units in the dendrons. The small overlap between the absorption and PL spectra in IrG1 neat films leads to a Förster radius of around 2 nm.[14] In the framework of the Förster energy transfer model, it has been demonstrated earlier that, despite this small but finite value of the Förster radius, dipole-dipole interactions govern the intermolecular concentration quenching in iridium complexes.[12,24] In the blend, the two peaks observed at 330 and 344 nm are characteristic of the carbazole units of the CBP. The absorption spectra are found to not change significantly with temperature but the PL spectra broaden with increasing temperature, which indicates a wider distribution of triplet energies sampled by the triplet excitons.

Figure 2 shows the excitation density dependence of the PL kinetics in the neat IrG1 film and the blend of IrG1 with
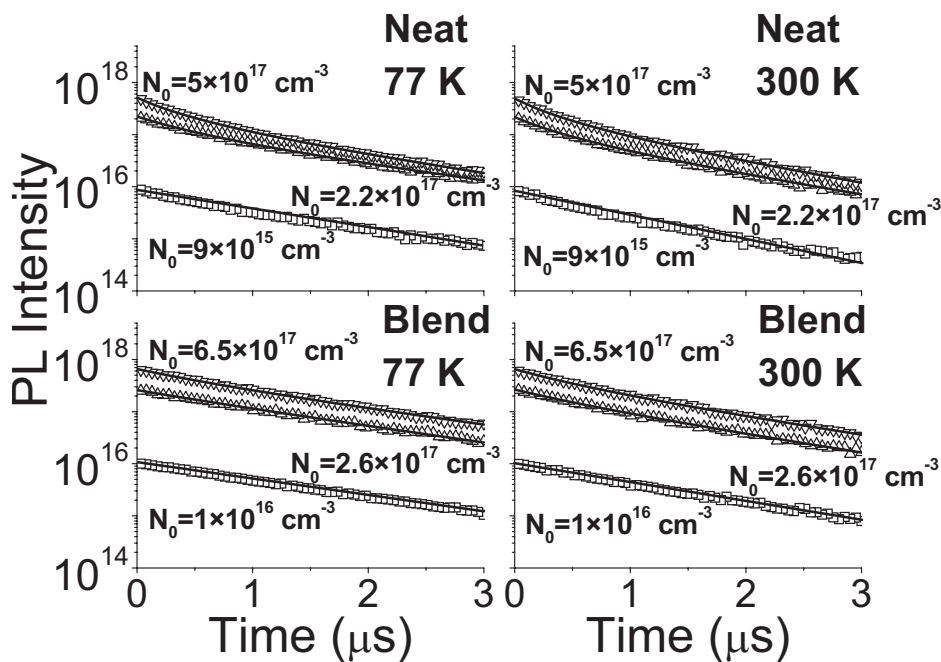


FIG. 2. Intensity dependence of the PL kinetics of a neat film of IrG1 and IrG1:CBP (20 wt %) blended film at 77 and 300 K. Solid lines are the best fits calculated from Eq. (2).
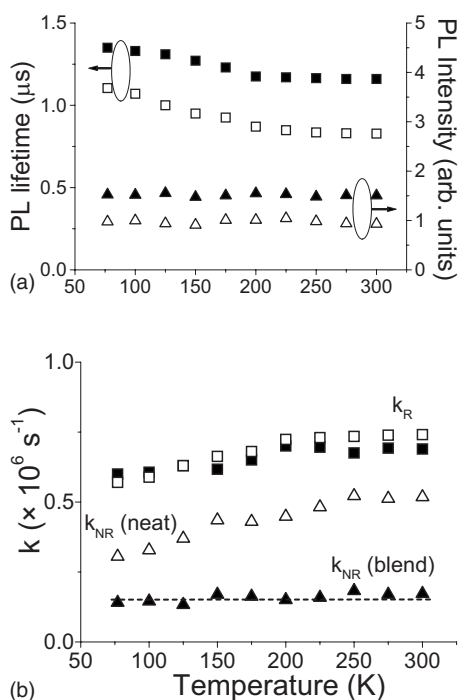
FIG. 3. (a) Temperature dependence of the PL lifetime (squares) and the integrated phosphorescence intensity (triangles) in a neat film of IrG1 (open symbols) and IrG1:CBP (20 wt %) blended film (solid symbols). The phosphorescence intensities were obtained from the PL spectra integrated over all wavelengths. (b) Temperature dependence of the radiative (squares) and nonradiative (triangles) decay rates in the neat film of IrG1 (open symbols) and IrG1:CBP (20 wt %) blended film (solid symbols).

CBP at 77 and 300 K. At low excitation densities ($N_0 < 2 \times 10^{17}$ cm$^{-3}$), the PL decays do not depend on the excitation density and can be fitted by a single exponential decay function with a characteristic lifetime $\tau$. Figure 3(a) shows the temperature dependence of $\tau$ and the integrated phosphorescence intensity measured in both the neat film of IrG1 and in the blend with CBP. While the phosphorescence intensity does not vary with temperature, the PL lifetime increases with decreasing temperature, this effect being more pronounced in neat film. This behavior is consistent with temperature-resolved phosphorescence measurements previously reported in Ir(ppy)$_3$ blends. These unusual phosphorescence characteristics are related to the presence of three triplet substates of the metal-to-ligand charge transfer ($^3$MLCT) transition in Ir(ppy)$_3$.[25–28] Such a zero-field splitting of the lowest triplet state is a direct consequence of the strong spin-orbit coupling in iridium(III) complexes. Finkenzeller and Yersin have performed PL measurements in dilute frozen Ir(ppy)$_3$ solution between 4 and 145 K where the changes in the measured phosphorescence lifetime are due to variations in the radiative rate constant and they have determined using a thermal equilibrium model the energy separations between these three substate levels and their radiative lifetimes.[21] The decay rates of each substate are independent of temperature but their relative populations do depend on temperature resulting in a temperature dependence of the measured radiative and phosphorescence lifetimes. Since the addition of

dendrons in IrG1 does not modify significantly the luminescence properties of the individual Ir(ppy)$_3$ chromophore[22] instead reduces the concentration quenching in the solid state, the dendritic structure is not expected to modify the splitting and the radiative lifetimes of the three substate levels measured in Ir(ppy)$_3$.

In previous work, we found using an integrating sphere[29] that the photoluminescence quantum yields (PLQYs) of an IrG1 neat film and the blend IrG1:CBP (20 wt %) at room temperature were 65% and 80%, respectively.[30] From these PLQY values, the temperature dependence of the integrated phosphorescence intensities, and the PL lifetimes, we could determine the temperature dependence of the radiative and nonradiative decay rates, noted $k_R$ and $k_{NR}$, respectively, in both the neat film and the blend using PLQY=$k_R/(k_R+k_{NR})$ and $1/\tau=k_R+k_{NR}$. We verified that the radiative decay rates in the neat film and in the blend were the same (within the 5% error in the measurements). As depicted in Fig. 3(b), $k_R$ increases with temperature from 77 to 200 K and is constant from 200 to 300 K. This result is consistent with the temperature dependence of the phosphorescence lifetime previously reported in Ir(ppy)$_3$ blends.[25–28] Triplets are split into substates where the highest energy substate has the highest $k_R$. The higher triplet substates are thermally populated when increasing the temperature and increase the radiative and phosphorescence decay rates. From our results, we can see that, above 200 K, the emission is strongly dominated by the higher triplet substate with the higher radiative decay rate. In addition, we note that the radiative lifetime of this higher substate agrees well with the value of 0.75 $\mu$s calculated by Finkenzeller and Yersin in Ir(ppy)$_3$ solution.[21] Below 200 K, the increase of $k_R$ with temperature is due to a contribution of the lower triplet substates.

The temperature dependence of $k_{NR}$ strongly differs in the neat film and in the blend. In the blend, $k_{NR}$ does not change with temperature and presents a value of about 1.5 $\times 10^5$ s$^{-1}$. We assign this value as the nonradiative deactivation rate of isolated IrG1 in the solid state. This is supported by the PLQY value of 80% measured in a degassed IrG1 solution[22] and in a blend IrG1:CBP (10 wt %). In the IrG1 neat film, $k_{NR}$ is factors of 2 and 3 higher at 77 and 300 K, respectively, than in the blend, which can be explained by concentration quenching. The rate of concentration quenching $k_q$ in the neat IrG1 film due to intermolecular interactions can be defined as $k_q=k_{NR}$ (neat film) $-k_{NR}$ (blend), where $k_{NR}$ (neat film) and $k_{NR}$ (blend) are the $k_{NR}$ values measured in the IrG1 neat film and the blend of IrG1 with CBP, respectively. As shown in Fig. 4, $k_q$ decreases from $3.5 \times 10^5$ s$^{-1}$ at 300 K to $1.6 \times 10^5$ s$^{-1}$ at 77 K. These low values are due to the recent improvement in the film preparation procedure which enables the optimization of the PL efficiency by decreasing the quencher concentration.[30] The temperature dependence of $k_q$ can be described by the Arrhenius law: $k \propto \exp(-E_a/kT)$, where $E_a$ is the activation energy, $k$ is the Boltzmann constant, and $T$ is the temperature. The best fits were obtained with $E_a=7\pm 1$ meV. Such an Arrhenius-like temperature dependence shows that the Förster-type dipole-dipole interactions, which control phosphorescence quenching in iridium(III)-cored dendrimers, are thermally activated.
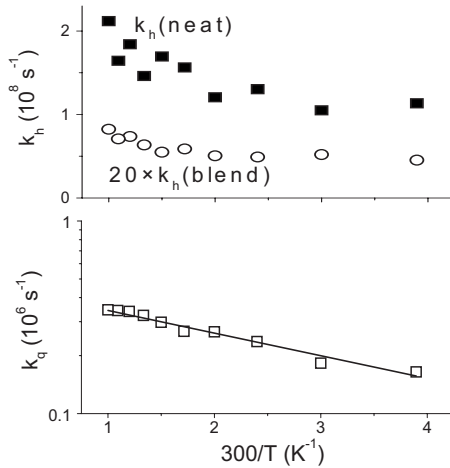
FIG. 4. Temperature dependence of the nearest neighbor hopping rate of triplet excitons for a neat film of IrG1 and IrG1:CBP (20 wt %) blended film. The quenching rate is also shown for the neat film (lower panel). The solid line is the fit determined from an Arrhenius equation with $E_a = 7$ meV.

The measured $E_a$ value is very close to the energy gap of 9 meV (80 cm$^{-1}$) between the lower and higher triplet substates determined in Ir(ppy)$_3$ by temperature dependent PL studies.[21] The Förster-type interactions of a molecule in a higher triplet substate with a neighboring molecule is expected to be higher because of the higher radiative decay rate of the higher triplet substate. In that case, thermal population of the higher triplet substate would increase intermolecular quenching by Förster-type interactions.

At high excitation densities ($N_0 > 2 \times 10^{17}$ cm$^{-3}$), the PL kinetics become faster due to triplet-triplet exciton annihilation (see Fig. 2).[11,14,31] Annihilation of two triplet excitons leads in these phosphorescent materials to the formation of one singlet excited state which converts rapidly to the triplet state and one triplet is lost into heat. The density of triplet excitons $N$, which is directly proportional to the phosphorescence intensity, can be described by a rate equation,

$$dN/dt = -N/\tau - \gamma N^2, \tag{1}$$

where $\tau$ is the PL lifetime in absence of annihilation and $\gamma$ is the annihilation rate. In the case of a time independent $\gamma$, the density of triplet excitons is given by

$$N(t) = \frac{N_0 \exp(-t/\tau)}{1 + \gamma \tau N_0 [1 - \exp(-t/\tau)]}, \tag{2}$$

where $N_0$ is the initial triplet population, which can be calculated from the excitation energy density. The solid lines in Fig. 2 correspond to the best fits obtained with this equation and the annihilation rates were found to halve when lowering temperature from 300 to 70 K (data not shown). We then calculated the nearest neighbor hopping rates of triplet excitons $k_h$ from the values of the annihilation rate. For diffusion limited annihilation in a three-dimensional case, which assumes that excitons can migrate in all directions and exciton diffusion is isotropic in the volume sampled by the excitons, $\gamma = 4\pi D R_a$, where $R_a$ is the reaction radius at which annihi-

lation is faster than hopping and can be taken as the center-to-center spacing $R$ between phosphorescent emitters and $D = R^2 k_h / 3$ is the exciton diffusion constant. The intermolecular spacing $R$ was determined here assuming a film density of 1.1 g/cm$^3$ and by considering the molecules as hard spheres. The data shown in Fig. 4 were obtained in taking $R = 1.83$ nm for the IrG1 neat film and $R = 3.13$ nm for the IrG1:CBP (20 wt %) blend assuming a uniform distribution of the dendrimers in the CBP. The hopping rate in the IrG1 neat film is 3 orders of magnitude higher than the quenching rate, which suggests extensive migration of the triplets before their radiative relaxation or capture by quenchers. The triplet diffusion is found to increase with temperature by a factor of 2 from 150 to 300 K and to be nearly temperature independent at lower temperatures. The higher radiative decay rate of the higher triplet substate leads to stronger dipole-dipole interactions, which was suggested to control intermolecular quenching. It is plausible that the small changes observed in triplet diffusion are caused by stronger electron exchange interactions in the higher triplet substate. Another possible explanation is that the weak temperature dependence of the hopping rate is due to the energetic disorder of the hopping sites.

The narrow distribution of triplet energies suggests that triplet exciton diffusion in dendronized iridium(III) complexes is nearly nondispersive in both the neat film and when blended with CBP. Markham *et al.* used the time of flight technique to measure the temperature and voltage dependence of the charge carrier mobility in a neat IrG1 film and found a dispersive hole transport below 293 K.[32] In addition, Matsusue *et al.* measured an activation energy of approximately 300 meV from the temperature dependence of the hole and electron drift mobilities in Ir(ppy)$_3$:CBP blends.[33] Although the Dexter-type exchange mechanism can be viewed as a simultaneous double electron transfer with a rate proportional to the electron and hole transfer rates, our results suggest that the dispersivity of the triplet diffusion in these phosphorescent materials strongly differs from that of charge transport.

## IV. CONCLUSION

We have examined the influence of the temperature on the photophysical properties of an Ir(ppy)$_3$-cored dendrimer as a neat film and as a blended film. The temperature dependence of their phosphorescence decay rate supports the presence of emissive triplet substates previously identified in Ir(ppy)$_3$. The intermolecular quenching rate follows the Arrhenius law with an activation energy of $7 \pm 1$ meV, which is comparable with the energy gap between the lower and higher triplet substates in the Ir(ppy)$_3$ core. The triplet diffusion is found to be temperature independent between 77 and 150 K and slightly increases with temperature at higher temperatures. These results demonstrate that the thermal population of the higher substate level plays a critical role in these two independent processes and also suggest a narrow distribution of triplet energies in these materials. Finally, the comparison with data obtained in previous studies indicates that the dispersivities of charge transport and triplet exciton diffusion by the electron exchange mechanism are completely different.

[1] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, Nature (London) **395**, 151 (1998).

[2] C. Adachi, M. A. Baldo, S. R. Forrest, and M. E. Thompson, Appl. Phys. Lett. **77**, 904 (2000).

[3] M. A. Baldo, M. E. Thompson, and S. R. Forrest, Nature (London) **403**, 750 (2000).

[4] V. Cleave, G. Yahioglu, P. Le Barny, R. H. Friend, and N. Tessler, Adv. Mater. (Weinheim, Ger.) **11**, 285 (1999).

[5] B. W. D'Andrade, M. A. Baldo, C. Adachi, J. Brooks, M. E. Thompson, and S. R. Forrest, Appl. Phys. Lett. **79**, 1945 (2001).

[6] C. Adachi, M. A. Baldo, M. E. Thompson, and S. R. Forrest, J. Appl. Phys. **90**, 5048 (2001).

[7] X. Yang, D. C. Muller, D. Neher, and K. Meerholz, Adv. Mater. (Weinheim, Ger.) **18**, 948 (2006).

[8] G. He, M. Pfeiffer, K. Leo, M. Hofmann, J. Birnstock, R. Pudzich, and J. Salbeck, Appl. Phys. Lett. **85**, 3911 (2004).

[9] M. Ikai, S. Tokito, S. Sakamoto, T. Suzuki, and Y. Taga, Appl. Phys. Lett. **79**, 156 (2001).

[10] S. J. Yeh, M. F. Wu, C. T. Chen, Y. H. Song, Y. Chi, M. H. Ho, S. F. Hsu, and C. H. Chen, Adv. Mater. (Weinheim, Ger.) **17**, 285 (2005).

[11] M. A. Baldo, C. Adachi, and S. R. Forrest, Phys. Rev. B **62**, 10967 (2000).

[12] Y. Kawamura, J. Brooks, J. J. Brown, H. Sasabe, and C. Adachi, Phys. Rev. Lett. **96**, 017404 (2006).

[13] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

[14] E. B. Namdas, A. Ruseckas, I. D. W. Samuel, S.-C. Lo, and P. L. Burn, Appl. Phys. Lett. **86**, 091104 (2005).

[15] R. Richert and H. Bässler, J. Chem. Phys. **84**, 3567 (1986).

[16] D. Hertel, H. Bässler, R. Guentner, and U. Scherf, J. Chem. Phys. **115**, 10007 (2001).

[17] M. Reufer, P. G. Lagoudakis, M. J. Walter, J. M. Lupton, J. Feldmann, and U. Scherf, Phys. Rev. B **74**, 241201(R) (2006).

[18] T. Förster, Discuss. Faraday Soc. **27**, 7 (1959).

[19] J. P. J. Markham, S.-C. Lo, S. W. Magennis, P. L. Burn, and I. D. W. Samuel, Appl. Phys. Lett. **80**, 2645 (2002).

[20] S.-C. Lo, N. A. H. Male, J. P. J. Markham, S. W. Magennis, P. L. Burn, O. V. Salata, and I. D. W. Samuel, Adv. Mater. (Weinheim, Ger.) **14**, 975 (2002).

[21] W. J. Finkenzeller and H. Yersin, Chem. Phys. Lett. **377**, 299 (2003).

[22] E. B. Namdas, A. Ruseckas, I. D. W. Samuel, S.-C. Lo, and P. L. Burn, J. Phys. Chem. B **108**, 1570 (2004).

[23] P. J. Hay, J. Phys. Chem. A **106**, 1634 (2002).

[24] J. C. Ribierre, A. Ruseckas, I. D. W. Samuel, K. Knights, S. V. Staton, and P. L. Burn, Phys. Rev. Lett. **100**, 017402 (2008).

[25] I. Tanaka, Y. Tabata, and S. Tokito, Jpn. J. Appl. Phys., Part 2 **43**, L1601 (2004).

[26] K. Goushi, Y. Kawamura, H. Sasabe, and C. Adachi, Jpn. J. Appl. Phys., Part 2 **43**, L937 (2004).

[27] I. Tanaka and S. Tokito, Appl. Phys. Lett. **87**, 173509 (2005).

[28] T. Tsuboi and N. Aljaroudi, Phys. Rev. B **72**, 125109 (2005).

[29] N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, R. R. Kessener, S. C. Moratti, A. B. Holmes, and R. H. Friend, Chem. Phys. Lett. **241**, 89 (1995).

[30] J. C. Ribierre, S. Stevenson, I. D. W. Samuel, S. V. Staton, and P. L. Burn, J. Disp. Technol. **3**, 233 (2007).

[31] A. Suna, Phys. Rev. B **1**, 1716 (1970).

[32] J. P. J. Markham, I. D. W. Samuel, S.-C. Lo, P. L. Burn, M. Weiter, and H. Bässler, J. Appl. Phys. **95**, 438 (2004).

[33] N. Matsusue, S. Ikame, Y. Suzuki, and H. Naito, Appl. Phys. Lett. **85**, 4046 (2004).