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Decay of phosphorescence and delayed fluorescence of organic materials

A.K. Luka[1], R.N.Baghel[2] and V.K.Chandra[3]

[1]Department of Physics, Government Nagarjuna Science College, Raipur-492010 (C.G.), India.
[2] School of Studies in Physics and Astrophysics , Pt. Ravishankar Shukla University, Raipur – 492010 (C.G.), India.
[3]Department of Electrical and Electronics Engineering, Chhatrapati Shivaji Institute of Technology, Shivaji Nagar, Kolihapuri, Durg – 491001, India.

Abstract

The Present paper reports the decay of phosphorescence and delayed fluorescence of organic material poly (2,7-(9,9-bis(2-ethyl-hexyle-flourene) (PF2/6). On the basis of the rate equation for the generation , recombination and diffusion of triplet excitons expressions are derived for the decay time of phosphorescence and delayed fluorescence of organic materials. The lifetime of phosphorescence is comes out to be twice the decay time of delayed fluorescence. The intensity of phosphorescence depends linearly on the intensity of the laser light used for exciton , however the intensity of light depends quadritically on the intensity of the laser light used for excitation. A compression is made between the theoretical and experimental results, in which a good agreement is found.

Keywords: Decay, phosphorescence, fluorescence

INTRODUCTION

Electron-hole bound pair is known as exciton and there are two kinds of excitons: the Wannier (or Wannier-Mott) exciton and the Frenkel exciton. The Wannier exciton model expresses an exciton as composed of an electron in the conduction band and a hole in the valence band bound together by the Coulomb interaction. In other words, a Wannier exciton is analogous to a hydrogen atom. This model works well for inorganic semiconductors such as IIIb-Vb and IIb-VIb compounds. The Wannier exciton moves in a crystal but does not contribute to electrical conduction as its total charge is zero. It emits luminescence by the recombination of the electron and hole composing it. The expanse of the wavefunctions of electron and hole in a Wannier exciton is usually much larger than the lattice constant. Wannier excitons are stable only at relatively low temperatures, where the binding energies of excitons are higher than the thermal energy. Luminescence of Wannier excitons is observed only at low temperatures. At higher temperature of the materials, where the thermal energy is higher, the excitons are no longer stable and in such condition band-to-band luminescence appears. The Frenkel exciton model is used in cases where the expanse of the electron and hole wavefunctions is smaller than the lattice constant. Typical examples of the materials producing Frenkel excitons are : organic molecular crystals such as anthracene and inorganic complex salts including transition-metal ions such as vanadets (e.g. YVO_4), tungstates ($CaWO_4$), cyanoplatinates [$BaPt(CN)_4.4H_2O$] and uranyl salts ($Cs_2UO_2Cl_4$). In fact, in these materials, luminescence characteristics are similar to those of isolated molecules or complex ions.

If the spins of electron and hole in an exciton are antiparallel, then the total spin is zero and such exciton is known as singlet exciton because it gives only energy state. On the other hand, if the spins of electron and hole in an exciton are parallel, then the total spin is one and such exciton is known as triplet exciton because it gives rise to three energy states. When certain organic solids are expose to ultraviolet light, then in addition to flouroscence and phosphorescence, a delayed flouroscence is produced [1-6]. The present paper reports the decay of phosphorescence and delayed fluorescence in organic materials.

Theory

As phosphorescence and delayed fluorescence are both decays from the triplet state T_1 . They are related to the time dependence of tiplet exciton density n. We can write the following equation:

$$\frac{dn}{dt} = \alpha I_e - \beta n - \gamma n^2 + D\,\overline{\nabla^2 n} \qquad \text{-----(1)}$$

where α is the proportionality constant and β and γ are rate constants for the monomolecular and bimolecular exciton recombination, respectively. The terms on the right side describe from left to right dependence from excitation intensity I_e, decay of phosphorescence and decay of decayed fluorescence and diffusion.

The rise and decay of phosphorescence and delayed fluorescence are linked to n by the following relationships:

Intensity of phosphorescence $I_p \propto n$ ------(2)
Intensity of delayed fluorescence $I_f \propto n^2$ -----(3)

For solving Eq. (1) the term αI_e can be neglected, as the crystal is not excited during the decay. The diffusion term can be neglected because it can be considered a small perturbation in first order. Thus, we get the following equation:

$$\frac{dn}{dt} = -\beta n - \gamma n^2$$

$$or\ \frac{dn}{\gamma n^2 + \beta n} = -dt$$

$$or\ \frac{dn}{n} - \frac{dn}{n+\frac{\beta}{\gamma}} = -\beta dt \qquad \text{--------(4)}$$

The integration of Eq. (4) gives
--------(5)

$$\log\frac{(n_0\gamma+\beta)n(t)}{(n(t)\gamma+\beta)n_0} = -\beta t \qquad \text{--------}(5)$$

$$or\ \frac{n(t)}{n_0}\cdot\frac{(n_0\gamma+\beta)}{(n(t)\gamma+\beta)} = exp^{-\beta t}\ \text{--------}(6)$$

From Eq. (6), we get

$$n(t) = n_0\, e^{-\beta t}\left[\frac{1}{1+\frac{\gamma n_0}{\beta}(1-exp^{-\beta t})}\right] \quad \text{------}(7)$$

It is to be noted that the term in square brackets is a deviation from the exponential behavior and represents the influence of triplet annihilation. For part of our result analysis Eq.(7) can be used in the following form:

$$y = In\left(\frac{n(t)}{n_0}\right) = -\beta t - In\left(1+\frac{\gamma n_0}{\beta}\left(1-exp^{-\beta t}\right)\right)]\ (8)$$

Now, we would like to linking Eq.(7) to I_p and I_f. For this purpose let us assume that a fraction A of the first order decay i.e. from the transition $T_0 \rightarrow S_0$ is radiative. This yields a phosphorescence intensity of

$$I_p = A\beta = n_0\left[\frac{A\beta}{1+\frac{\gamma n_0}{\beta}(1-exp^{-\beta t})}\right]exp^{-\beta t}$$

------------ (9)

Let us assume that a fraction β of the triplet-triplet annihilation results in the production of the fluorescing singlet excitation S^*. Thus, the intensity of delayed fluorescence intensity can be expressed as

$$I_f = \frac{1}{2}(\beta\gamma)n^2$$

$$or\ \frac{1}{2}(\beta\gamma)n_0\left[\frac{1}{1+\frac{\gamma n_0}{\beta}(1-exp^{-\beta t})}\right]^2 exp^{-2\beta t}$$

-----------(10)

Infect, the triplet lifetime τ_T is defined as

$$\tau_T = \frac{1}{\beta} \qquad \text{----------}(11)$$

The lifetime of phosphorescence and delayed fluorescence are therefore related in the following way

$$\tau_T = \tau_P = 2\tau_f \qquad \text{-----------}(12)$$

Equation (12) indicates that the lifetime of phosphorescence is twice of the delayed phosphorescence lifetime.

Experimental Support

The phosphorescence and delayed fluorescence of poly (2,7-(9,9-bis(2-ethy-lhexyl-fluorene)) (PF2/6) films have been studied by Hertel and Bassler [1].

In order to fabricate films of approximately 100 nm thickness and high optical quality PF 2/6 was spun cast from toluene solution containing 1% of the material by weight on fused silica substrates. A 300 nm PF2/6 film on a fused silica substrate was obtained by spin costing a toluene solution of 2% by weight.

The third harmonic of N_d –YAG laser at 3.49 eV was used for exciting the luminescence of the films. The duration of the light pulse was 5 ms. The luminescence from an illuminated spot size of 3 mm in diameter was passed through a monochromator onto an optical multichannel analyzer. A variable delay of 100 ns to 10 ms after optical excitation allowed the detection of weak delayed luminescence after the intence prompt luminescence. For time dependent measurement of the DF in PF2/6 films, a single photon counting (SPC) setup was employed in addition. The decay up to 5 ms was recorded with a channel width of 320 ns. A channel width of 2.56 μs was applied for times up to 50 ms. Except for intensity dependent measurements the laser intensity was kept below 100 μJ/(cm^2× pulse) to avoid damages of the samples.

In fig. 1 the inset shows the molecular structure of PF2/6 with R=2 ethyl-hexyl. The upper spectrum is the phosphorescence emission of a 100 nm PF2/6 film, whereas the lower spectrum picture the phosphorescenc of a 300 nm PF2/6 film. Both spectra were recorded at 80K with a time delay of 1 ms after excitation with 2.89 eV laser light [1-6]. Fig.2 shows dependence of fluorescence delayed fluorescence and phosphorescence intensity of a PF2/6 film on pump intensity at 80K. The time delay for measurement of DF and Ph was 1μs . The photon energy for optical excitation wa 3.49 eV [1-6]. Fig.3 illustrates delayed fluorescence intensity Vs time of a PF2/6 film at 83 K and 298K. Excitation was at 3.49 eV [1-6]. Fig.4 show dependence of phosphorescence and DF intensity upon time for t>100 ms of a PF2/6 film at 80K. The PF2/6 film was excited at 3.49 eV [1-6].

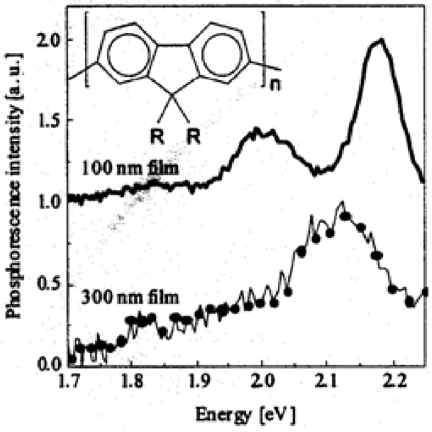

Fig 1. The inset shows the molecular structure of PF2/6 with R=2 ethyl-hexyl. The upper spectrum is the phosphorescence emission of a 100 nm PF2/6 film, whereas the lower spectrum picture the phosphorescenc of a 300 nm PF2/6 film. Both spectra were recorded at 80K with a time delay of 1 ms after excitation with 2.89 eV laser light. (after ref. 1)

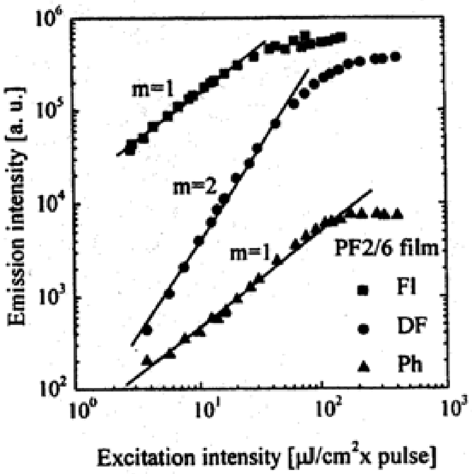

Fig 2. Dependence of fluorescence delayed fluorescence and phosphorescence intensity of a PF2/6 film on pump intensity at 80K. The time delay for measurement of DF and Ph was 1μs . The photon energy for optical excitation wa 3.49 eV. (after ref. 1)

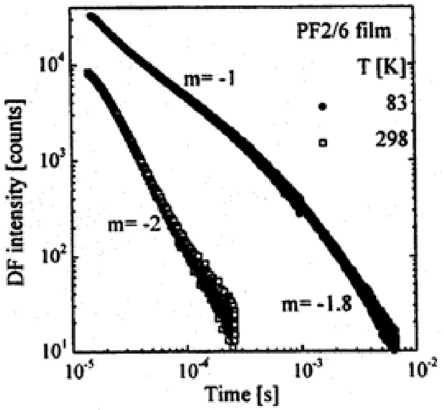

Fig 3. Delayed fluorescence intensity Vs time of a PF2/6 film at 83 K and 298K. Excitation was at 3.49 eV. (after ref. 1)

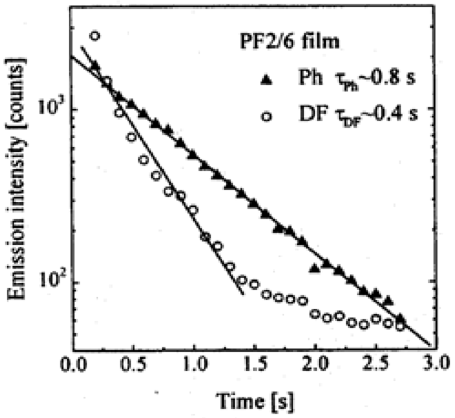

Fig 4. Dependence of phosphorescence and DF intensity upon time for t>100 ms of a PF2/6 film at 80K. The PF2/6 film was excited at 3.49 eV. (after ref. 1)

CONCLUSION

On the basis of the rate equation for the generation, recombination and diffussions of triplet excitons expressions are derived for the decay time of phosphorescence and delayed fluorescecne of organic materials. It is shown that the lifetime of phosphorescence is twice the decay time of delayed fluorescence . The intensity of phosphorescence depends linearly on the intensity of the light used for exciton, however, the intensity of light depends quadritifally in the intensity of light used for excitaion. A comparision is made between the theoretical and experimental results, in which a good agreement is found.

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