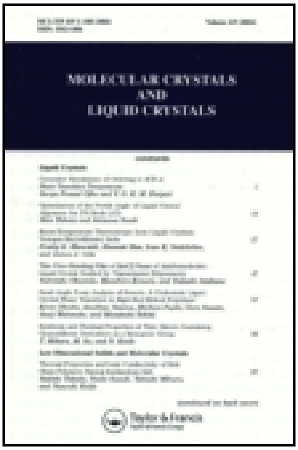

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Measurements of Photoluminescence Quantum Efficiencies in Conjugated Polymers: Implications for Polymer Photophysics and for Light-Emitting Diodes

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MEASUREMENTS OF PHOTOLUMINESCENCE QUANTUM EFFICIENCIES IN CONJUGATED POLYMERS: IMPLICATIONS FOR POLYMER PHOTOPHYSICS AND FOR LIGHT-EMITTING DIODES.

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Abstract The photoluminescence properties of conjugated polymers are currently of great interest, since the radiative decay of singlet excitons is the process by which light emission occurs in polymer light-emitting diodes. We describe here accurate measurements of photoluminescence efficiencies in solid films of conjugated polymers, using an integrating sphere to collect the emitted light. Values in excess of 40% are measured for cyano-substituted derivatives of poly(*p*-phenylenevinylene) (PPV). In PPV itself, measured photoluminescence efficiencies of 27%, combined with time-resolved measurements of the luminescence decay, suggest that the species produced by photoexcitation is predominantly the singlet exciton responsible for luminescence.

The photoluminescence spectrum and the rate of radiative decay can be strongly affected by the presence of dielectric or metal interfaces. We model here the effects of optical interference in a number of multi-layer structures. We compare these results with measured photoluminescence efficiencies in LED-like structures, and discuss the implications for the efficiency and emission characteristics of polymer light-emitting diodes.

1. INTRODUCTION

The luminescence properties of conjugated polymers are of considerable interest, both because of the fundamental information that can be obtained about exciton formation and decay, and because of the potential applications for conjugated polymers as the emissive material in light-emitting diodes (LEDs).[1, 2] Luminescence in conjugated polymers is believed to be the result of radiative decay of singlet excitons. Competing non-radiative processes provide additional means of decay, and therefore reduce the efficiency of luminescence. If radiative and non-radiative decay are both monomolecular processes with rates τ_r^{-1} and τ_{nr}^{-1} respectively, the overall luminescence decay will be exponential, with a lifetime, τ, given by

$$\tau^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}. \tag{1}$$

The efficiency for radiative decay of singlet excitons is then given by

$$q = \tau/\tau_r. \tag{2}$$

The efficiency of radiative decay of singlet excitons, q, sets an upper limit on the quantum efficiency which can be obtained in a polymer LED.

In a photoexcitation experiment, a useful figure which can be measured is the photoluminescence (PL) efficiency, defined as the number of photons emitted in photoluminescence per absorbed photon. This figure depends both on q, and on the fraction, η, of absorbed photons which lead to the formation of singlet excitons. The PL efficiency, Q, is given by $Q = \eta\, q$.

On the basis of sub-picosecond stimulated-emission experiments, Rothberg and coworkers have recently suggested that in poly(*p*-phenylenevinylene) [PPV], only about 10% of the photoexcited species are singlet excitons, and that the rest are spatially-indirect polaron pairs which do not result in radiative decay.[3] In this case, the measured PL efficiency would be only 10% of the efficiency for radiative decay of singlet excitons, corresponding to a value of $\eta = 0.1$. Accurate measurements of the PL efficiencies of conjugated polymers are therefore important, both to understand the photophysics of exciton formation and decay, and to determine the maximum efficiencies that may be achieved in polymer LEDs. In contrast to measurements of PL efficiencies in solution, measurements on thin solid films are not straightforward, since the angular distribution of the emitted light is highly sensitive to the refractive index of the material, and to the orientation of emitting dipoles within the film.[4, 5] Estimates of absolute PL efficiencies from a single measurement of light output in the forward direction[6] must therefore be treated with considerable caution.

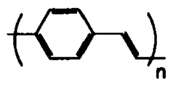
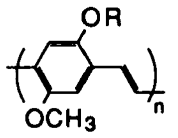
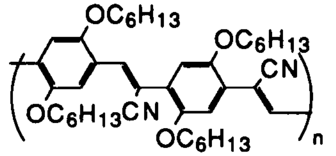
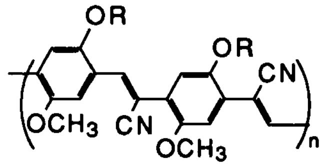
In this paper, we present the results of direct measurements of the absolute PL efficiency in solid films of conjugated polymers performed using an integrating sphere to collect the emitted light.[7] Until now, this technique has only been applied to a small number of conjugated polymers.[8, 9] We also investigate the effect of the sample geometry and structure on the PL efficiency, and model these results by considering the influence of the local environment on the radiative decay rate.

2. INTEGRATING SPHERE MEASUREMENTS

Polymer samples were mounted at the centre of an integrating sphere, and excited by an argon-ion laser. The signal detected by a silicon photodiode mounted at an aperture in the sphere is proportional to the total amount of light produced within the sphere, irrespective of its angular distribution.[10] A filter is used to prevent laser light reaching the detector, and a baffle prevents light from reaching the detector directly from the sample. The incident laser power is subsequently measured using the integrating sphere with the sample and filter removed.

It is important to allow for the effects of laser light that is not absorbed when first incident on the sample, but which may be absorbed after subsequent reflections from the sphere walls. Also, the spectral response of the sphere throughput and of the detector must be taken into account. These corrections, and other details of the measurement technique, are described elsewhere.[7]

TABLE I. Measured photoluminescence efficiencies. R = $CH_2CH(C_2H_5)C_4H_9$.

Polymer	Structure	Reference	PL efficiency	Error
PPV		11	0.27	±0.02
MEH-PPV		12	0.10 - 0.15	±0.01
CN-PPV		13	0.35 - 0.46	±0.02
MEH-CN-PPV		14	0.48	±0.02

The polymers studied here were PPV, poly(2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylenevinylene) [MEH-PPV], and two cyano-substituted dialkoxy-PPVs [CN-PPV and MEH-CN-PPV], as shown in Table I. PPV was formed by the THT precursor route; the precursor was heated at 280°C for 12 hr under dynamic vacuum at a pressure of less than 5 x 10^{-6} mbar. The results obtained for these polymers are shown in Table I. Excitation was at 488 nm, except for the PPV, which was excited at 458 nm. It is difficult to assess the scale of any systematic errors present in this experiment; the errors shown represent a rough estimate of the likely error due to the measurement technique. The values obtained on different films made from the same batch of polymer were consistent, provided that the films were kept in the dark and under nitrogen until measurement. For MEH-PPV and CN-PPV where several batches were available, a range of efficiencies was measured, as shown in Table I. The PL efficiency of all the polymers studied was found to be reduced by photo-oxidation. Further discussion of sample ageing is given elsewhere.[7]

3. DISCUSSION

The PL efficiencies for the polymers measured here are encouragingly high for polymers in the solid state. The value of 0.27 for PPV, in particular, is higher than the value measured in MEH-PPV, and is significantly larger than the value estimated by Lemmer *et al.* for PPV.[15] The PL efficiency of MEH-PPV in solution has been estimated to be between 0.20 and 0.35.[16, 17] The values of up to 0.15 measured here for solid films suggest that extra non-radiative channels are present in the solid state. The values measured here are similar to the PL efficiencies of 11-13% reported for solid films of poly(2-methoxy-5-decyloxy-*p*-phenylenevinylene).[8] The PL efficiencies in excess of 0.40 for the cyano-substituted materials are consistent with the high electroluminescence (EL) efficiencies obtained in these materials.[13, 14] As discussed earlier, the PL efficiency is given by the product of the branching ratio, η, with the efficiency of radiative decay of the singlet exciton, q. Since q cannot be more than unity, the value of 0.27 obtained for the PL efficiency in PPV sets a lower limit on the branching ratio, η. In order to obtain a better estimate of η, it is useful to estimate q by studying the decay of the PL on a picosecond timescale. The PL lifetime was therefore measured in the same sample used for the PL efficiency measurement, and a lifetime of 320 ps was obtained.[7]

PL lifetimes of 1.2 ns have been measured by Yan *et al.* for PPV samples with a low density of oxygen defects, implying a radiative lifetime of at least 1.2 ns.[18] Taking $\tau_r = 1.2$ ns gives a value of $q = 0.28$. The measured PL efficiency of 0.27 therefore suggests a value of η close to unity, implying that the species produced by photoexcitation is predominantly the singlet exciton. We note, however, that the radiative lifetime is sensitive to the size of the emitting chromophore, and may therefore depend on the degree of conjugation of the material studied. If the radiative lifetime in the material studied here is significantly less than in the material studied by Yan *et al.*, then a smaller value of η would be required. An additional source of possible error here is the difference in excitation wavelength between the PL efficiency measurement (458 nm) and the time-resolved measurement (405 nm). Changing the excitation wavelength from 458 nm to 405 nm has, however, been found to have only a very small effect on the PL efficiency in high-quality PPV.[19] We note that value of η estimated here is significantly larger than the value of $\eta = 0.1$ estimated by Yan *et al.* on the basis of sub-picosecond stimulated-emission measurements.[3]

4. OPTICAL INTERFERENCE EFFECTS

It is well established that the presence of dielectric or metal interfaces in the vicinity of an excited molecule can have a significant effect on its radiative lifetime.[4] In the simple case of an emitting dipole oscillating parallel to and very close to a perfectly reflecting surface, the field due to the dipole will interfere destructively with the reflection from the surface. This leads to a greatly reduced radiative rate, and a correspondingly increased radiative lifetime. In the presence of competing non-radiative processes, this will lead to a decrease in the PL efficiency, according to Equation 2. Light-emitting diodes are complicated optical structures with several interfaces which may affect the radiative lifetime. In order to study these effects, we have measured the PL efficiency of CN-PPV in a number of multi-layer planar structures comprising layers of glass, CN-PPV, indium-tin oxide (ITO) and aluminium with laser excitation from various directions, as described in Table II. It can be seen from the results shown in Table II that there is a significant change in PL efficiency between the different structures.

The radiative lifetime in a multi-layer structure in general depends on the thicknesses

TABLE II. Measured PL efficiencies and calculated average radiative rates for various multi-layer structures. Values are shown as a percentage of the value for case (a). Excitation was at 488 nm onto the first layer shown in the second column. ITO and CN-PPV thicknesses were 150 nm and 200 nm respectively.

	Structure	PL efficiency	Average radiative rate
a	CN-PPV/glass	100%	100%
b	glass/CN-PPV	100%	100%
c	CN-PPV/ITO/glass	78%	89%
d	glass/ITO/CN-PPV	57%	63%
e	glass/ITO/CN-PPV/Al	47%	73%

and refractive indices of the various layers, and on the positions and orientations of the emitting dipoles within the structure. Many of these parameters are not accurately known at present for the structures described in Table II. A simple model, based on the theory of Crawford,[20] was therefore used to calculate the radiation field generated by a dipole embedded in one of the layers of an arbitrary n-layer system. The refractive indices of polymer, ITO and glass were taken to be 1.6, 1.9 and 1.5 respectively. The radiative rate was determined by integrating the radiated power over all angles. The distribution of excited dipoles was determined from the measured absorption coefficient. Detailed discussion of the model and the assumptions made is given elsewhere.[21]

The average predicted radiative rate for an excited molecule in each of the measured structures is shown in the final column of Table II. It can be seen that there is a good qualitative correlation between the measured efficiencies and the calculated radiative lifetimes, indicating that changes in radiative lifetime are important in determining the PL efficiency in simple polymer structures. A quantitative prediction of PL efficiencies will require the PL efficiency to be calculated as a function of position within the structure according to Equation 2 using experimentally determined radiative and non-radiative rates. Changes in the non-radiative rate due to the proximity of interfaces will also need to be taken into account. In the presence of metal interfaces, as in structure (e), absorption of emitted light by the metal, and non-radiative decay due to coupling to surface plasmon modes in the metal are important.[22] We calculate that in structure (e), 5% of the radiated light will be absorbed by the aluminium, and coupling into plasmon modes will provide an extra non-radiative channel with a non-radiative rate equal to 13% of the calculated radiative rate. These effects are likely to explain the low PL efficiency for this structure. These results indicate that the efficiency of radiative decay of singlet excitons in LED structures may be significantly lower than the PL efficiency measured in a polymer film on a glass substrate.

4. CONCLUSIONS

Measurements of the absolute photoluminescence quantum efficiencies have been performed for a number of conjugated polymers commonly used for electroluminescence.

PL efficiencies in excess of 0.4 have been measured for cyano-substituted PPV derivatives. The measured PL efficiency of 0.27 in PPV suggests that photoexcitation in this polymer predominantly produces the singlet exciton responsible for luminescence. The presence of dielectric or metal interfaces has been found to have a significant effect on both the measured PL efficiency and the predicted radiative lifetime. These results indicate that careful control of the position of exciton formation in polymer LEDs will be important in optimising their efficiency.

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