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Exciton dynamics in ladder-type methyl-poly(para-phenylene) doped with phosphorescent dyes

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Abstract

The luminescence of a ladder-type methyl-poly(para-phenylene) (MeLPPP) doped with platinum–porphyrin dye PtOEP covering the concentration 10^{-3}–5% by weight has been measured employing cw and transient techniques. Upon excitation into the range of absorption of the host, strong phosphorescence of the dopant is observed. Possible ways of populating the dopant triplet state are considered.

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1. Introduction

Conjugated polymers are disordered systems with a variety of new spectroscopic and dynamic features having a large potential for application in optoelectronic devices. An important reason for this is their high luminescence efficiency that is due to the strong binding between the electron and hole produced by either optical or electrical excitation, causing formation of neutral excitons. The transfer of energy to phosphorescent dye molecules blended into the active layer of polymer LEDs is widely used to improve their luminescent properties [1,2].

In this work, we investigated the photoluminescent properties of the ladder-type methyl-poly (para-phenylene) polymer doped with Pt(II)Octaethylporphine (PtOEP). Since both the S_1 and T_1 levels of the dopant are below those of the matrix [3,4], both Förster-type host–quest singlet–singlet and Dexter-type triplet–triplet energy transfer can be envisaged. The results will demonstrate that the

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dominant transfer channel is Förster-type transfer from the S_1 state of the polymer to the dopant. The absence of triplet–triplet energy transfer in the system under investigation due to low efficiency of intersystem crossing in polymer that leads to very small population of its triplet state.

2. Experiment

PtOEP was purchased from Porphyrin Products Inc. and was used as received. Benzil was carefully purified by repeated recrystallization from ethanol followed by vacuum sublimation. MeLPPP is a well-characterized fluorescent polymer, which has intensively been studied as an emitter in polymer LEDs [5]. MeLPPP blended with a certain amount of PtOEP or/and benzil was spin coated from toluene solution (10 mg/ml) at 2000 rpm, resulting in a layer thickness of 50 nm.

Experimental setup used for cw and transient measurements is described in detail elsewhere [6,7].

3. Results and discussion

Introduction of PtOEP to the polymer leads to the appearance of a new emission that is attributed to the phosphorescence of the dopant. There are two possible pathways for populating the triplet state of dopant, i.e. (i) intersystem crossing of the S_1 state of MeLPPP into its triplet manifold followed by triplet migration towards the dopant, and (ii) singlet energy transfer from the host to the dopant followed by intersystem crossing within the latter. In order to distinguish this question we measured the steady state and the transient fluorescence of MeLPPP because in the latter case the PF intensity and decay time should progressively decrease upon increasing of the dopant concentration. The experiment is clearly in favour of the second option, i.e. singlet energy transfer being the rate–limiting step. The reduction of the cw-PF intensity and of the PF-lifetime ($1/e$ lifetime) are observed as the dopant concentration increases. It is gratifying to note that identical result is observed in the both cases. It remains to be clarified, though, which transfer mechanism is applicable. From the current experimental observation that the PF-quenching in MeLPPP–PtOEP system is temperature insensitive within the temperature 293–4.2 K it is obvious that no efficient equilibrium exciton diffusion can be involved. The other extreme is Förster type, i.e. dipole–dipole controlled single–step transfer from an excited donor to an acceptor. In order to assess the importance of this mechanism, one has to calculate the relevant critical distance R_0 at which excitation transfer and fluorescence decay of donor contribute equally according to Förster theory [8]:

$$R_0^6 = \frac{9000(\ln 10)\kappa^2\phi_D^0}{128\pi^5 n^4 N_A}\int_0^\infty \frac{F_D(v)\varepsilon_A(v)}{v^4}\,dv, \qquad (1)$$

where ϕ_D^0 is quantum yield of the donor fluorescence, n is the refractive index of medium, N_A is the Avogadro's number, κ is the molecular orientation factor (2/3 for random orientation), v is the wavenumber, $F_D(v)$ is the corrected fluorescence intensity of the donor with the total intensity normalized to a unity and $\varepsilon_A(v)$ is the extinction coefficient of the acceptor at v.

Using the calculation absorption spectrum of PtOEP solution in toluene and the estimated fluorescence yield of 0.5 for MeLPPP and a refractive index of 2, $R_0 = 3\,\mathrm{nm}$ is obtained. It corresponds to a critical concentration of $C_{0,\mathrm{th}} = 0.015\,\mathrm{M}$. However, the experimental value for the concentration at which the PF intensity drops by factor of 2 is almost one order of magnitude lower, i.e. $C_{0,\ \mathrm{exc}} = 2.5 \times 10^{-3}\,\mathrm{M}$, than $C_{0,\mathrm{th}}$. This is a consequence of the fact that a conjugated polymer differs from a typical Förster-type energy transfer system. While Förster's theory is based upon the assumption of a spatially fixed point dipole, the excited state of MeLPPP can be considered as that of oligomeric subunits which include 12 backbone phenylene rings of a polymer chain (5 nm) [9]. This translates into an R_0 value larger than evaluated from spectral overlap.

Oxygen is a notorious triplet quenching in organic solids, the notion being that the quenching is due to the motion of the triplet exciton. Obviously, a significant lifetime shortening of PtOEP phosphorescence and a decrease of its