Chemical Physics 358 (2009) 147–155

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Triplet dynamics and charge carrier trapping in triplet-emitter doped conjugated polymers

A. Kadashchuk [a,d,*], S. Schols [a,b,c], A. Vakhnin [d], J. Genoe [a], P. Heremans [a,b]

[a] IMEC v.z.w., SOLO-PME, Kapeldreef 75, B-3001 Leuven, Belgium
[b] Katholieke Universiteit Leuven, Electrical Engineering Department, B-3001 Leuven, Belgium
[c] Aspirant at the FWO-Vlaanderen, Egmontstraat 5, 1000 Brussels Belgium
[d] Institute of Physics, Natl. Acad. Sci. of Ukraine, Prospekt Nauki 46, 03028 Kiev, Ukraine

ARTICLE INFO

Article history:
Received 20 October 2008
Accepted 19 January 2009
Available online 23 January 2009

Keywords:
Conjugated polymer
Phosphorescence
Metal–organic complex
Energy transfer
Charge carrier trapping
Time-resolved photoluminescence
Thermally-stimulated luminescence

ABSTRACT

Phosphorescent (Ph) properties and charge carrier trapping have been studied in conjugated polymer CNPPP with incorporated red-emitting $Btp_2Ir(acac)$ metal–organic complex by time-resolved photoluminescence and thermally-stimulated luminescence (TSL) techniques. We characterized intrinsic Ph of CNPPP matrix and dynamics of triplet excitations of $Btp_2Ir(acac)$ confined by the polymer host. Combined studies of time and intensity dependence of guest Ph have demonstrated that the observed decrease in the Ph efficiency in CNPPP:$Btp_2Ir(acac)$ system at increasing excitation intensity is dominated by mutual host–guest triplet–triplet annihilation. We observed Ph spectral diffusion effects at 10 wt.% of $Btp_2Ir(acac)$ dispersed in a polymer matrix, which is a proof for the triplet excitons migration though the manifold of triplet-emitter sites, and which governs the Ph concentration quenching effect. TSL measurements have provided direct evidence that the triplet-emitter molecules create a deep charge trap in the conjugated polymer and allowed trap characterization.

1. Introduction

Organic light-emitting diodes (OLEDs) have been extensively investigated for full-color plat-panel display applications and illumination light sources because of their merits of high luminance, low drive voltage, and variety of emission colors. Internal quantum efficiency of electro-fluorescence OLEDs is limited to be around 25% according to simple spin statistics [1]. In order to overcome this efficiency limit of fluorescent OLEDs, phosphorescent emitters doped into host material have been used. Phosphorescent emitters are low-molecular weight phosphorescent dye molecules incorporating a heavy metal atom with strong spin–orbit coupling that mixed singlet and triplet states. The radiative decay of triplet states becomes allowed and the efficiency of intersystem crossing is also enhanced. As result, the lowest triplet state is efficiently populated and produces light emission with large quantum yield. Phosphorescent emitters in both small organic molecule hosts and polymer hosts allow for harvesting singlet and triplet excitons and, therefore, internal quantum efficiency of the OLED devices can be greatly enhanced approaching 100% [2].

For the preparation of polymer electro-phosphorescent polymer light-emitting diodes, the commonly used concept is to blend a low-molecular weight phosphorescent emitter into a proper polymer matrix. Transfer of excited state energy thus plays an important role in the operation of these devices. Singlet and triplet excitons can be first generated by electron–hole recombination in the polymer host and then transfer their energy to the dopant. Alternatively, the triplet state of the phosphorescent emitter may be formed by charge transfer from the host followed by charge recombination at the guest molecule. In both cases, the singlet and triplet energy levels of the host have to be well above the triplet state of the guest emitter to be efficient and prevent back transfer. The actual transfer of excitation to the guest molecule can occur via different mechanisms: Förster transfer of singlet excitons generated on the polymer matrix to the guest, Dexter transfer of both singlet and triplet excitons generated on the host to the dopant, as well as the direct generation of singlet and triplet excitons on the guest [3,4]. A specific feature of devices based on phosphorescence is that long phosphorescent (Ph) lifetimes leads to saturation of emissive sites, and annihilation of triplet excitations may also cause significant efficiency losses. As a result, efficiency of such OLED devices tends to decrease at high current densities [5].

Recently, a comprehensive study has been performed to investigate triplet dynamics in ladder-type methyl-poly(*para*-phenylene) (MeLPPP) doped by platinum(II) octaethylporphine (PtOEP) complex [6–8]. Since both the S_1 and T_1 levels of the dopant are

---

* Corresponding author. Address: Institute of Physics, Natl. Acad. Sci. of Ukraine, Prospekt Nauki 46, 03028 Kiev, Ukraine.
E-mail addresses: kadash@iop.kiev.ua, kadashchuk@yahoo.com (A. Kadashchuk).

0301-0104/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemphys.2009.01.008

below those of the matrix [9–11] both Förster-type host–quest singlet–singlet and Dexter-type triplet–triplet energy transfer can be envisaged. Triplet–triplet annihilation is believed to be one of the major quenching mechanisms in phosphorescent OLEDs [12]. The longer lifetime for triplet excitons actually diminishes one of the advantages of dye doping of organic light-emitting devices, the ability to eliminate concentration quenching. One way to solve these problems is to use dopants with shorter triplet exciton lifetime. Therefore Ir complexes are more attractive candidates than platinum porphyrins owing to about one order of magnitude shorter lifetimes, which typically range from 1 μs to 14 μs.

In this work we explore the phosphorescent properties of the host–guest system based on red-light-emitting bis[2-(2′-benzothienyl)pyridinato-N,C$^{3'}$] (acetylacetonate) iridium ($\mathrm{Btp_2Ir(acac)}$) ($\mathrm{Btp_2Ir(acac)}$) doped in poly[1,4-bis(6′-cyano-6′-methylheptyloxy) phenylene] (CNPPP). Similarly to the above MeLPPP/PtOEP host–guest system, both the S_1 and T_1 levels of the $\mathrm{Btp_2Ir(acac)}$ dopant are below those of the CNPPP polymer matrix, however the phosphorescent lifetime of $\mathrm{Btp_2Ir(acac)}$ is tenfold shorter than that of PtOEP. We demonstrate that this results in different mechanisms dominated Ph properties. We also present direct evidence that the phosphorescent metal–organic complexes do act as charge traps and characterized these traps by means of charge trapping spectroscopy. In addition, it confirmed the notion that metal–organic complexes behave electronically not different from conventional all-organic small molecules.

2. Experimental

CNPPP was purchased from H.W. Sands Corp. and the triplet-emitter compound $\mathrm{Btp_2Ir(acac)}$ from American Dye Source Inc. The structural formulas of these compounds are shown in Fig. 1. All materials were used as received. Films of polymer doped with triplet-emitter molecules were prepared by dissolving the appropriate ratios of $\mathrm{Btp_2Ir(acac)}$ and CNPPP in toluene, and then spin-coating the resulting solutions on a precleaned quartz substrate. After deposition, the films were dried in a nitrogen glove-box at room temperature. Film thickness was typically 200 nm.

Spectroscopic measurements of prompt fluorescence (PF) and delayed emission as delayed fluorescence (DF) and phosphorescence (Ph) of both frozen diluted solutions and films were carried out within a temperature range from 77 K to 300 K, using the temperature regulating nitrogen cryostat. All measurements were done in nitrogen atmosphere. A nitrogen laser with pulse duration of 4 ns operated at 10 Hz was used for optical excitation at 337 nm. The emission spectra were recorded using a triple-grating monochromator coupled to an intensified CCD camera (PI-MAX from Princeton Instruments) with a time gated, intensified diode array detector, which was synchronized by the electrical trigger of the laser. The detection window was selected between 100 ns and 10 ms. A variable delay of 75 ns–10 ms after optical excitation allowed the detection of weak delayed luminescence after the intense prompt fluorescence. To increase the signal-to-noise ratio, spectra were accumulated by averaging over 100···300 pulses.

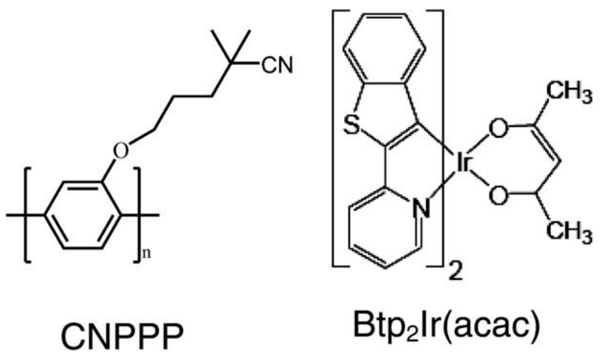

Fig. 1. The molecular structures of the CNPPP polymer and the red-light-emitting dye $\mathrm{Btp_2Ir(acac)}$.

Thermally-stimulated luminescence (TSL) is the phenomenon of luminescent emission after removal of excitation under conditions of increasing temperature. Generally, in the TSL method the trapping states are first populated by photogeneration of charge carriers, usually at low temperatures in order to prevent a fast escape. Then, the trapped charge carriers are released by heating up the sample with a linear temperature ramp, while the luminescence due to radiative recombination is recorded as a function of temperature. If an energy distribution of the trap states exists, TSL spectra are a complicated convolution of contributions from different traps at different energies and fractional heating techniques have to be applied, which are based on cycling the sample with a large number of small temperature oscillations superimposed on a constant heating run. Thus, the TSL is a useful tool for determining the trap depths even when traps are not well separated in energy, or are continuously distributed, and it also allows analysis of the trap spectra even when they are complex.

TSL measurements were carried out using a home-built setup operable from 4.2 K to 350 K using a temperature controlled helium cryostat. After cooling down to 4.2 K, the samples were photoexcited, usually for 30 s, by a high-pressure 500 W mercury lamp with an appropriate set of glass optical filters for light selection. After the photoexcitation, the TSL was detected in a photon-counting mode with a cooled photomultiplier, positioned next to the cryostat window. The TSL measurements were performed either at a constant heating rate of $\beta = 0.15$ K/s or in the fractional heating regime. The latter procedure allows the determination of trap depth when different groups of traps are not well separated in energy or are continuously distributed. The details of our TSL method were described previously [13,14].

3. Results

3.1. Photoluminescence studies

3.1.1. Pristine CNPPP films

Fig. 2 (curve 1) shows spectra of the prompt fluorescence from a pristine CNPPP film registered during the laser pulse at 77 K and

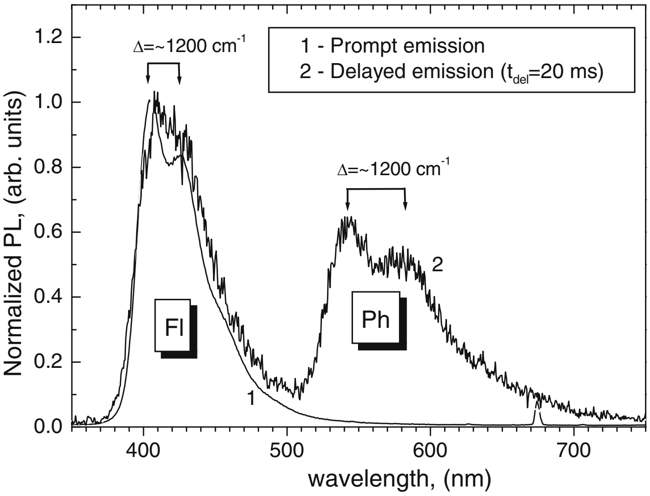

Fig. 2. Normalized spectra of prompt fluorescence (curve 1) and delayed emission (curve 2) from pristine CNPPP film at 77 K. Delayed emission was measured with 20 ms delay time after the laser pulse and with gate width of 6 ms.