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Observation of the energy transfer sequence in an organic host–guest system of a luminescent polymer and a phosphorescent molecule



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ABSTRACT

We used steady state optical spectroscopies such as photoluminescence and photoinduced absorption (PA), and magnetic-field PA (MPA) for studying the energy transfer dynamics in films and organic light emitting diodes (OLED) based on host–guest blends with different guest concentrations of the fluorescent polymer poly-[2-methoxy, 5-(2'-ethyl-hexyloxy)phenylene vinylene] (MEHPPV-host), and phosphorescent molecule PtII-tetraphenyltetrazabenzoporphyrin [Pt(tpbp); guest]. We show that the energy transfer process between the excited states of the host polymer and guest molecule takes a 'ping-pong' type sequence, because the lowest guest triplet exciton energy, $E_T(\text{guest})$, lies higher than that of the host, $E_T(\text{host})$. Upon photon excitation the photogenerated singlet excitons in the host polymer chains first undergo a Förster resonant energy transfer process to the guest singlet manifold, which subsequently reaches $E_T(\text{guest})$ by intersystem crossing. Because $E_T(\text{guest}) > E_T(\text{host})$ there is a subsequent Dexter type energy transfer from $E_T(\text{guest})$ to $E_T(\text{host})$. This energy transfer sequence has profound influence on the photoluminescence and electroluminescence emission spectra in both films and OLED devices based on the MEHPPV-Pt(tpbp) system.

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1. Introduction

Organic light emitting diodes (OLED) have attracted considerable attention in recent years because of multiple commercial applications such as large area displays and white light illumination [1–15]. Understanding the physics of the organic active layers in such devices may help improve these applications. Light emission occurs in organic semiconductors such as π -conjugated polymers when excitons, which in the organics are relatively tightly bound electron–hole pairs, undergo radiative recombination to the ground state [7]. In most polymers singlet excitons may radiatively recombine in the form of fluorescence (FL); whereas the radiative recombination of triplet excitons to the singlet ground state is forbidden due to the spin selection rule; when this is broken due to spin–orbit coupling then a relatively weak phosphorescence (Ph) emission is also obtained.

According to spin statistics of the injected electron hole recombination in OLED, we expect that the density ratio of formed singlet to triplet excitons be 1:3 [8]; this, in turn sets a high efficiency limit to the electroluminescence (EL) emission from

singlet excitons. Therefore harvesting light emission of triplet excitons in the form of electro-phosphorescence (EPh) has been crucial for increasing OLED performance. One way for achieving EPh in OLED is by adding to the polymer heavy atom molecules [9], which have large spin orbit coupling that relaxes the spin selection rules for the triplet Ph emission. The Ph emission is beneficial to display applications not only because of enhanced luminance due to the favorable spin statistics for the electrically generated triplet excitons, but also for producing broad light emission that is necessary for white-OLED (WOLED) illuminators. To achieve such broad EL emission there exist several methods that involve triplet excitons: one is to use simultaneously both EPh and electro-FL such as in Pt-rich polymers [10]; another method is to use host–guest system, where the host has blue FL emission and the guest emits red Ph; yet another method is to use EPh and also enhance the singlet emission (EFL) via triplet–triplet annihilation (TTA) or thermally activated delayed fluorescence [11–15].

In this work we studied the photophysics and EL emission of solution processed films and OLEDs based on pristine and various blends of the polymer poly-[2-methoxy, 5-(2'-ethyl-hexyloxy)phenylene vinylene] (MEHPPV-host; Fig. 1(a) inset) and phosphorescent molecule PtII-tetraphenyltetrazabenzoporphyrin [Pt(tpbp)-guest; Fig. 1(b) inset], for investigating the energy transfer processes that occur between the singlet and triplet manifolds in this host–guest system. MEHPPV is a widely used luminescent polymer

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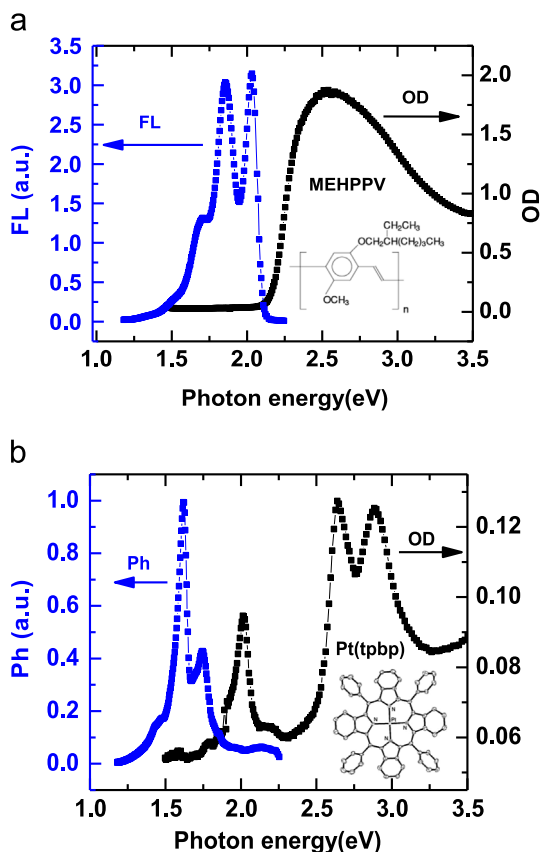


Fig. 1. Absorption and emission spectra of (a) MEHPPV polymer film; (b) film of isolated Pt(tpbb) molecules prepared as 2 wt% in polystyrene matrix. The insets in (a) and (b) show the molecular structure of MEHPPV and Pt(tpbb), respectively.

having red FL emission (~ 2.05 eV) [16], whereas Pt(tpbb) is a phosphorescent molecule with large spin–orbit coupling that leads to strong Ph emission in the near-IR spectral range (~ 1.76 eV) [17,18]. In host–guest type OLED electrons and holes are initially injected into the organic host material; some of them eventually recombine into polaron pairs having singlet and triplet spin configurations, which subsequently form respectively singlet and triplet excitons in the host. These excitations transfer to the phosphorescent guest emitter via Förster/Dexter energy transfer processes [19,20]. We expected to have high Eph efficiency in OLED based on this host–guest system because of spectral overlap of the host emission band and guest absorption band (see below) that leads to Förster resonant energy transfer (FRET) process. Alas, because the lowest triplet exciton energy in the guest, $E_T(\text{guest})$ (~ 1.76 eV) [21] is higher than that in the host, $E_T(\text{host})$ (~ 1.3 eV) [22,23], the EL efficiency in OLED based on this blend sharply decreases with the guest molecules concentration, indicative of the existence of a new non-radiative recombination channel that becomes active in this host–guest system. We identify this channel as Dexter energy transfer from $E_T(\text{guest})$ to $E_T(\text{host})$ that eventually leads to energy dissipation in the form of heat.

In our studies we used various cw optical spectroscopies such as steady state photoluminescence (PL), photoinduced absorption (PA), and EL, as well as the technique of magnetic-field PA (MPA). We found that the steady-state density of triplet excitons in the host polymer substantially increases with the concentration of the guest molecules in the blend. This is concluded from both PA spectra and MPA responses, and indicates that the energy transfer process in this blend occurs in the form of a ‘ping-pong’ type sequence, as follow. Upon photoexcitation of the host polymer the photogenerated singlet excitons undergo a FRET energy transfer to

the guest singlet excitons, which eventually decay into the guest triplet excitons via intersystem crossing. Finally the guest triplet excitons transfer to the host triplet excitons via a Dexter type reaction. This ‘ping-pong’ type energy transfer process is detrimental to the EL quantum efficiency in OLED based on this host–guest system, since it opens an efficient non-radiative decay process. Our results may serve to judiciously choose an efficient host–guest pair that would not quench the EL emission in OLED at relatively small guest molecules concentration.

2. Experimental

The organic polymer MEHPPV was purchased from American Dye source Inc., and the Pt(tpbb) molecules powder was purchased from Richest Group Ltd. The organic films for the optical studies were prepared in toluene at a concentration of 10 mg/ml. The solutions of MEHPPV and MEHPPV blended at the desired percentage weight of Pt(tpbb) were stirred overnight and then drop-casted onto sapphire substrates. For the Pt(tpbb) optical studies we needed to measure a mixture of Pt(tpbb) in polystyrene (2% by weight) in order to avoid the problem of Ph-quenching due to molecules aggregation in a pure Pt(tpbb) film.

For the PA and PL studies we placed the films in a closed cycle He refrigerator cryostat at 50 K. The steady state PA spectrum was measured using a standard set-up [24]. We used for excitation a cw Ar⁺ laser beam at $\hbar\omega = 2.5$ eV that was modulated at frequency f of 310 Hz, and the output beam of an incandescent tungsten/halogen lamp as probe. The changes, ΔT in the probe transmission, T induced by the laser pump excitation was measured using a lock-in amplifier referenced at f , a monochromator, and various combinations of gratings, filters, and solid-state photodetectors spanning the spectral range $0.3 < \hbar\omega(\text{probe}) < 2.3$ eV. This set-up was also used for measuring the PL spectrum. The PA was obtained from the relation $PA = -\Delta T/T$, the negative fractional change in transmission.

The same set-up was used for the MPA measurement, with an external magnetic field provided by an electromagnet that produced field, B up to 1800 G that was applied parallel to the film surface. Since the materials of most mirrors and posts contain some magnetic impurities that can react with the applied magnetic field, care was taken to use non-magnetic optical elements in our optical set up. In addition, we also performed several control experiments to minimize possible magnetic field artifacts. The MPA(B) response is defined by the relation $MPA(B) = [PA(B) - PA(0)]/PA(0)$, where $PA(B)$ is the PA at field strength B and $PA(0)$ is the PA at $B = 0$.

The same host–guest solutions were used for fabricating OLEDs. The OLED structure was in the form of ITO/HTL/active layer/Ca/Al. HTL was a hole transport layer of 40 nm thick film of PEDOT:PSS poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate); the luminescent layer was a 100 nm film of MEHPPV or its blend with Pt(tpbb); and the cathode was a calcium film (20 nm thick) and aluminum layer for protection; the OLED area was 2 mm \times 2 mm. The OLED fabrication comprised of several steps. First, the anode ITO substrate was cleaned by ultrasonic treatment with acetone, 2% micro-90 soap, de-ionized water, methanol and propanol; each for 10 min. Subsequently the PEDOT:PSS was spin coated onto the ITO substrate, and heat treated for 30 min at 100 °C. The resulting bilayers were transferred to a glove-box filled with nitrogen atmosphere, where the host–guest solutions were spin coated at 2000 rpm. The OLED fabrication process was finalized with the deposition of Ca and Al layers using a thermal evaporation bell-jar inside the glove-box.

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