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Oxadiazole-carbazole polymer (POC)-Ir(ppy)$_3$ tunable emitting composites

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ABSTRACT

POC polymer is an oxadiazole-carbazole copolymer we have previously synthetized and established as light emitting material in Organic Light Emitting Devices (OLEDs), although POC quantum yield emission efficiency and color purity still need to be enhanced. On the other hand, tris[2-phenylpyridinato-C2,N] iridium(III) (Ir(ppy)$_3$) complexes, namely Ir(ppy)$_3$ are among the brightest luminophores employed in green light emitting devices. Our aim, in this work, is to take advantage of Ir(ppy)$_3$ bright emission by combining the Ir complex with blue emitting POC to obtain tunable light emitting composites over a wide range of the visible spectrum.

Here we have investigated the optical proprieties POC based nanocomposites with different concentrations of Ir(ppy)$_3$, ranging from 1 to 10 wt%. Both spectral and time resolved fluorescence measurements show an efficient energy transfer from the polymer to the dopants, resulting in white-emitting composites. The most intense and stable emission has been found when POC was doped with about 5 wt % concentration of Ir(ppy)$_3$.

1. Introduction

Organic light-emitting diodes (OLEDs) are at the base of new flat-panel display and solid-state lighting technologies fabricated by low-cost solution processing. The employment of thin layers of conjugated polymers as active layers in OLEDs devices allows to easily reach these objectives [1]. Derivatives of poly(*p*-phenylenevinylene) [2] and polyfluorene [3–5] are the most commonly used conjugated polymers in OLEDs. The fluorine-based polymers are efficient blue emitters, although their electroluminescence often presents a green component due to the formation of fluorenone units [6,7] that compromise color purity. In order to have a balanced carriers recombination, the polymer should have good carrier transport properties, as well as energy-level matching with electrodes for effective charge injection [1,2,6,7]. In many cases, the use of ambipolar host materials permits the fabrication of efficient OLEDs with relatively simple device architectures [8]. The blending or the doping in the same polymer of molecules possessing both the hole-transporting donor and electron-transporting acceptor functionalities, provide an ambipolar host for the emissive layer. Oxadiazole/carbazole derivatives meet all these requests. Indeed carbazole is the hole-transporting functional moiety and oxadiazole is the electron-transporting component. Among all polymeric hosts under investigation, carbazole-based materials are studied for their wide band gap and their remarkable thermal, photochemical and chemical stability [8,9].

Several polymers serving as hosts for red, green, and, in some cases, blue-green phosphors have been developed, based on carbazole donors and oxadiazole acceptors [10,11–14,15,16]. Some carbazole-oxadiazole materials have been used as fluorophores or hosts for longer wavelength emitting fluorophores in fluorescent OLEDs [8,14,17].

A great variety of composite emission properties can be tuned within the visible spectra range, combining emitting polymers and highly emissive dopants [18,19]. In particular, phosphorescent dopants can be dispersed in a polymer host and work as emissive layer via energy transfer from the matrix, so that the OLEDs can harvest triplet [20] excitons and achieve an internal electron-to-

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photon quantum efficiency close to 100%. Indeed, during the device operation, electrons and holes are injected from electrodes to the polymer host and generate singlet and triplet excitons. The excitons are transferred to the triplet states of the phosphorescent dopants and generate light. An ideal polymer host, on one hand, should own proper low unoccupied molecular orbital (LUMO)/high occupied molecular orbital (HOMO) energy levels matching with the cathode/anode to facilitate charge carrier injection. On the other hand, it should have a high triplet energy level (ET) to prevent triplet energy back transfer from the dopant to the host leading to the consequent quenching of triplet excitons. Unfortunately, polymer host materials with both high ET and proper LUMO/HOMO energy levels are rare. This motivates our work. We have studied an oxadiazole/carbazole polymer (POC) previously synthesized in our laboratories [14,16]. In the POC polymer, the active oxadiazole/carbazole units are intercalated by aliphatic segments, in order to improve the solubility in several organic solvents, ensuring good film morphology. POC has already been employed as active layer in OLED devices showing broad emission [21] or as blue light source in nanocomposites with red emitting InP QDs [22] and CdSe quantum dots [23]. Composites obtained by blending a conducting polymers with the phosphorescent dopant benefit on one side and from the easy and low cost processability of polymers and on the other side from phosphorescent dopants high photoluminescence quantum efficiency.

In this work, we present new broadband emitting composites obtained by doping POC polymer with the iridium complex tris[2-phenylpyridinato-C2,N]iridium(III) Ir(ppy)$_3$, a well-known green emitter widely used in phosphorescent polymer OLEDs [21,24–26,27]. We discuss the spectroscopic properties of the pure POC polymer and the POC-Ir(ppy)$_3$ composites and their possible interaction phenomena. We aim at exploring the possibility to use of POC-Ir(ppy)$_3$ composites for broad emission applications.

2. Experimental

2.1. Materials

The POC polymer, shown in Fig. 1a, has been synthesized and characterized according to the synthesis process previously reported in Refs. [12,16,21].

Briefly, POC is a copolyester, obtained by polycondensation reaction between a di-hydroxyl OC monomer and two different acyloylchlorides (dodecanedioyl dichloride and decanedioyl dichloride 1:1) in a mixture of pyridine/N-methylpyrrolidinone. The high glass transition temperature of POC (~100 °C) guarantees good film morphology stability at room temperature. Good quality films, characterized by a uniform coverage of the substrate and small surface roughness, have been achieved by a one-step spin coating procedure.

Ir(ppy)$_3$ is a bright green emitter largely employed in phosphorescent polymer OLEDs [28,29,30]. In our system we use POC as a polymer host due to its large band gap and a triplet state energy sufficiently above that of the Ir(ppy)$_3$ (guest) to guarantee the confinement of the triplet excited state on the guest.

POC and Ir(ppy)$_3$ molecular structures are shown in Fig. 1a). HOMO and LUMO energy levels of POC have been previously determined by cyclic voltammetry [22] and are reported together with the Ir(ppy)$_3$ energy levels in Fig. 1b).

2.1.1. POC-Ir(ppy)$_3$ composites preparation

POC has been dissolved in 1,1,2,2-tetrachloroetane (TCE) at the concentration of 20 mg/mL and the solution has been stirred for 15 min at 60 °C for 1 h. Various amounts of Ir(ppy)$_3$, previously dissolved in TCE (20 mg/mL), have been added to the polymer solution to obtain mixtures with 1, 3, 5, 10 wt% of Ir(ppy)$_3$. The resulting solutions have been stirred for 2 h at room temperature.

Homogeneous films (thickness of 80–100 nm) have been prepared by spin coating the solutions on quartz substrates (600 rpm for 30 s) at room temperature. The substrates have been precleaned by sonication in acetone and subsequently in isopropanol.

2.2. Experimental techniques and methods

The neat POC polymer and POC-Ir(ppy)$_3$ films have been characterized by UV–Vis absorption spectroscopy by a Perkin Elmer Lambda 900 Spectrophotometer.

Photoluminescence emission (PL) of the pure polymer and the composites was measured using a Fluorolog 3 Horiba Jobin Instruments SA. The film surface roughness was measured by means of a contact TENCOR profilometer.

Time-resolved fluorescence measurements were carried out using a diode laser based Time Correlated Single Photon Counting (TCSPC) spectrometer from IBH (UK). A sub-nanosecond LED (1 MHz repetition rate) with time width of 500 ps was used as excitation source. A MCP-PMT detector was used for collecting the fluorescence decay signals. Fluorescence decays were recorded at the magic angle (54.7°) with respect to the vertically polarized excitation light [22,31,32]. All characterizations were carried out in air at room temperature.

3. Results and discussion

The POC photoluminescence emission and Ir(ppy)$_3$ complex absorption spectra present a good spectral overlap, as shown in Fig. 2. This is a first favorable condition for an efficient energy transfer between the polymer and the dopant to take place. According to Forster energy transfer theory, it is possible to calculate the energy transfer critical radius R_0, i.e. the distance between a host and a guest at which the efficiency of energy transfer is 50%,

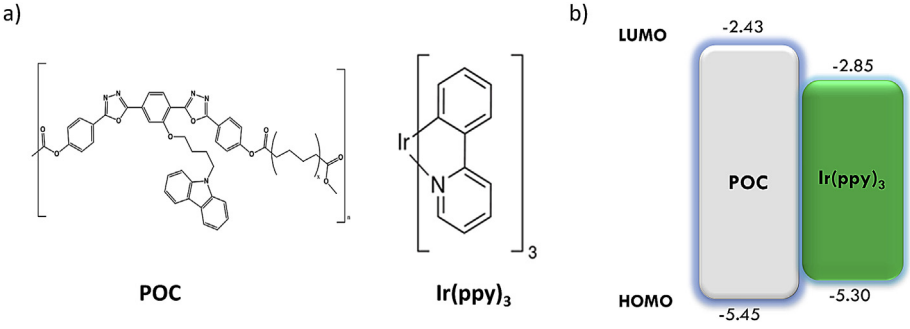

Fig. 1. POC and Ir(ppy)$_3$ molecular structures b) HOMO and LUMO levels for POC polymer and Ir(ppy)$_3$.