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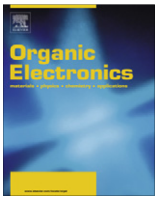

An alternative way to use the triplet energy of fluorescent dyes in organic light-emitting devices via an external iodide

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ABSTRACT

An unusual heavy atom effect has been identified in an organic light emitting device (OLED) containing polyvinylcarbazole (PVK) as the host, the red fluorescent dye 2-{2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-yl)-vinyl]-pyran-4-ylidene}-malononitrile (DCM2) as the emitter, and non-emitting 1,8-diiodooctane (RI) as a heavy atom source instead of a rare metal. The intensity of electroluminescence (EL) of DCM2 changes with the concentration of RI, with a maximum EL intensity obtained for DCM2 at a concentration of 0.25% of RI. Photoluminescence (PL) spectra of PVK–DCM2 films show increased singlet emission from DCM2 in the presence of iodide at 12 K. The enhanced fluorescence induced by iodide is caused by energy transfer from both the singlet and triplet states of PVK to the singlet states of DCM2. These results suggest an alternative way to use the triplet energy of fluorescent materials with external heavy atoms rather than conventional phosphorescent dyes containing rare heavy metal atoms.

1. Introduction

The internal quantum efficiency of electroluminescence (EL) from fluorescent materials in organic light-emitting devices (OLEDs) is limited to 25% by the spin statistics for excitons that are formed by electrons and holes injected from the cathode and anode, respectively [1]. The 75% of energy in the triplet state of fluorescent molecules is lost in non-radiative energy transfer processes. However, in phosphorescent molecules, the triplet state mixes with the singlet state because of spin–orbit coupling, leading to radiative transitions from the original triplet state to the ground state. Therefore, both singlet and triplet energies are harvested, so the maximum internal quantum efficiency of electrophosphorescence from a phosphorescent material is expected to be 100% [2–4]. The heavy atom effect (HAE) is commonly used to induce intersystem crossing and make full use of triplet excited state energy. Up to now, there are two ways to achieve it in OLEDs. One method is to use heavy atoms such as Pt [2], Ir [3], Os [4], and Re [5] centers coordinated to phosphorescent dyes to induce significant spin–orbit coupling. Using this approach, nearly 100% internal quantum efficiencies have been obtained [6–8]. Another method is to use a phosphor-sensitizer containing heavy atoms in the device [3,9], allowing use the triplet energy of the host fluorescent molecules. However, expensive rare metals are required in both of the above approaches. It is known that some inexpensive heavy atoms, e.g., iodine and bromine, can also induce a HAE [10–12], but this has not been exploited in OLEDs to date.

Here we introduce a HAE induced by inclusion of non-radiative iodide into a host–guest fluorescent OLED to harvest both the singlet and triplet energy of fluorescent molecules as an alternative to expensive phosphorescent rare metal complex. To date, such a HAE induced by

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external iodide in an OLED has not been reported. Direct energy transfer from the triplet state of the host fluorescent dye to the singlet state of the guest fluorescent dye was observed. This indicates an alternative way of using the triplet energy of fluorescent materials in OLEDs without using expensive rare metals.

2. Experimental section

OLEDs were fabricated by the method described in our previous report [13]. Before fabrication, the ITO/glass substrate was cleaned by successive ultrasonication in deionized water, acetone, and ethanol for 20 min. PEDOT:PSS was spin-coated onto the pre-cleaned ITO at 3000 rpm. The film was annealed at 200 °C in air for 5 min and then under vacuum for 15 min. PVK:1% DCM2:x% RI ($x = 0$, 0.25, 0.58, 1.00, and 5.00) films were prepared by spin-coating a solution with a total concentration of 12 mg/mL in chloroform on the PEDOT:PSS layer at 3000 rpm. An electron transporting layer of BCP (30 nm) was thermally evaporated onto the emitting layer at a pressure of 8×10^{-4} Pa. An electron injecting LiF layer (0.5 nm) and Al cathode (100 nm) were subsequently thermally deposited. The EL emitting area was defined using a shadow mask with openings 2 mm in diameter. The thickness of the depositing layer was monitored with a quartz crystal microbalance. The EL properties of the devices were measured with a spectrophotometer (PR 650, Photo Research, USA) and a source meter (2611, Keithley, UK) at room temperature without encapsulation. Photoluminescence (PL) spectra of PVK:0.3% DCM2 (Film I) and PVK:0.2% DCM2:0.3% RI (Film II) films prepared by spin-coating a solution with a total concentration of 12 mg/mL in chloroform on quartz substrates at 12 K were measured with a spectrophotometer (Spex Fluorolog-3, Instruments SA ,USA).

3. Results and discussion

3.1. EL properties

Because the singlet energy and triplet levels of polyvinylcarbazole (PVK) [14] are both higher than the singlet energy level of 2-{2-methyl-6-[2-(2,3,6,7-tetrahydro-1H, 5H-pyrido[3,2,1-ij]quinolin-9-yl)-vinyl]-pyran-4-ylidene}-malononitrile (DCM2) [15], PVK was used as the host in the emitting layer of OLED, the red fluorescent dye DCM2 was used as the guest (emitter), and 1,8-diiodooctane (RI) was used as the source of external heavy atoms (Fig. 1). Unlike heavy metal atom complexes such as tris(2-phenylpyridine)iridium (Ir(ppy)$_3$), RI is non-emissive so back energy transfer from the fluorophores to RI can be neglected when analyzing the optical properties of the OLEDs. To measure the HAE of RI, OLEDs with structures of ITO/PEDOT:PSS/PVK: 1% DCM2: x% RI/BCP/LiF/Al were fabricated, where PEDOT:PSS is poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) and used as a hole transporting buffer layer, BCP is 2,9-dimethyl-4,7-dipenyl-1,10-phenanthroline and acts as an electron transporting material, x is the concentration of RI with $x = 0$, 0.25, 0.58, 1.00, and 5.00, and the devices are numbered I, II, III, IV, and V, respectively. The concentration of DCM2 was fixed at 1%; such a low level of doping was chosen to avoid concentration quenching [5].

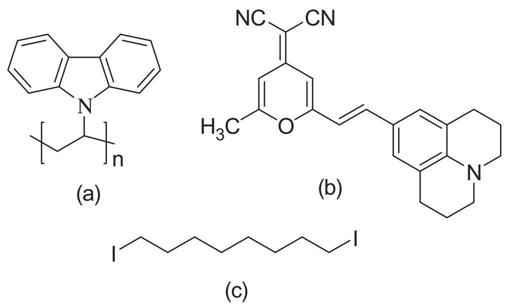

Fig. 1. Chemical structures of (a) PVK, (b) DCM2, and (c) RI.

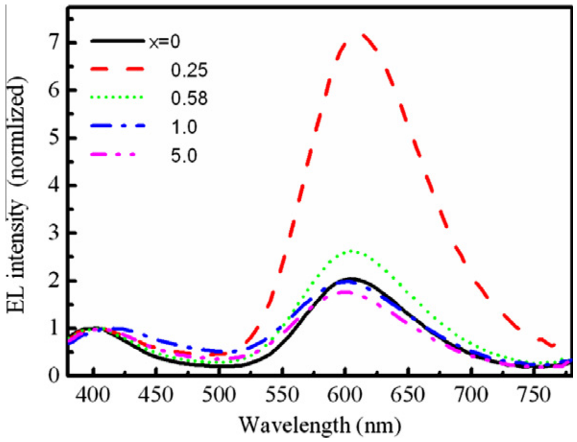

Fig. 2. EL spectra of devices I–V, normalized to the emission of PVK (around 400 nm).

The EL spectra of OLEDs containing various concentrations of RI are shown in Fig. 2. Singlet emissions from DCM2 and PVK are observed at around 600 and 400 nm, respectively. The appearance of emission from PVK is attributed to incomplete energy transfer from PVK to DCM2. Triplet-based emission from PVK and DCM2 is not observed. This indicates that the spin–orbital interaction is still not strong enough to change the state properties even in the presence of an external heavy atom (i.e., outside the emitting molecule), thus the intersystem crossing (ISC) from the singlet to the triplet state in either PVK or DCM2 is still prohibited. As a result the phosphorescence of PVK and DCM2 is not observed. This is also the same as the result of phosphorescent sensitizer, even no triplet emission from any fluorescent dyes could be observed although phosphorescent sensitizer (external heavy atom) is present [3]. This is different with the case of phosphorescent dyes containing an internal heavy atom (i.e., inside the emitting molecule, such as Ir(ppy)3), in which the spin–orbital interaction is strong enough to change the properties of state (i.e., a mixture of singlet and triplet