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}-malono-nitrile (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.

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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

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,
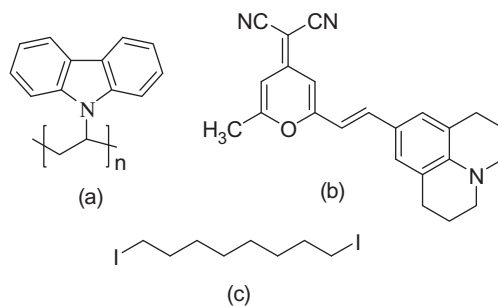

Fig. 1. Chemical structures of (a) PVK, (b) DCM2, and (c) RI.
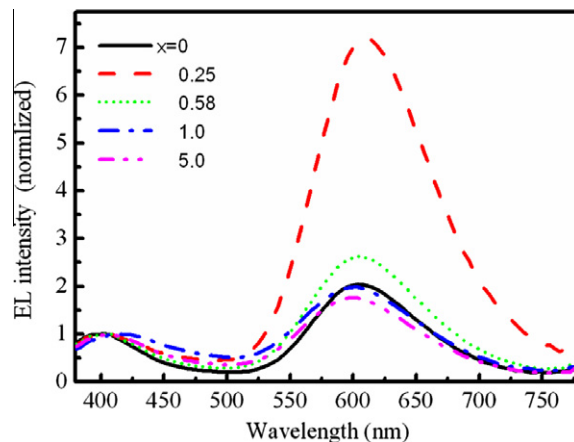

Fig. 2. EL spectra of devices I–V, normalized to the emission of PVK (around 400 nm).

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].

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
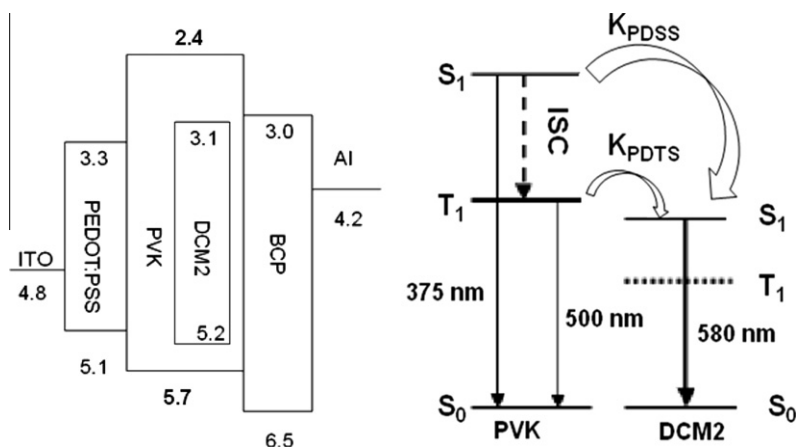
Fig. 3. The energy levels and proposed energy transfer processes in the OLEDs (ISC is intersystem crossing induced by the HAE, K_{PDSS} and K_{PDTS} are energy transfer processes from the singlet and triplet states of PVK to the singlet state of DCM2, respectively).

states), then the prohibited transition is allowed, and triplet emission can be observed [2]. As shown in Fig. 2, the EL spectra are normalized to the EL from PVK. The highest intensity of EL from DCM2 is obtained at a concentration of RI of 0.25%, and the intensity decreases as the concentration of RI increases from 0.25 to 5%. The significant dependence of the intensity of emission from DCM2 on the concentration of RI indicates that RI has a great influence on energy transfer from PVK to DCM2.

The energy levels and proposed energy transfer processes in the OLEDs are shown in Fig. 3. For the five devices, the enhancement of singlet energy in DCM2 can only be obtained from two ways: by transfer from the singlet and triplet energy levels of PVK. The distance between the host (PVK) and the guest (DCM2), and the overlapping content of the host emission spectrum with the absorption spectrum of the guest are both unchanged because the concentration of DCM2 is fixed at 1%. Therefore, the energy transfer process from the singlet state of PVK to the singlet state of DCM2 (K_{PDSS}) remains the same. However, after 0.25% of RI is added to the emitting layer, the intensity of DCM2 emission at about 600 nm increases significantly, meaning that there is more energy transferred to the singlet state of DCM2. This additional energy can only be attributed to the transfer from the triplet excited state of PVK (K_{PDTS}), which occurs directly from the triplet state of PVK to the singlet state of DCM2. Without RI, the triplet energy of PVK is wasted in non-radiative energy transfer processes, so non-radiative iodide represents a new way to use the triplet energy of fluorescent molecules for emission. When the concentration of RI exceeds 0.25%, the HAE will also increase non-radiative energy transfer from the triplet state to the ground state of PVK. As a result, less energy can be transferred to the singlet state of DCM2, so the emission from DCM2 decreases. Triplet–triplet annihilation [2] as reported for electrophosphorescent devices might also make a contribution to the decrease in DCM2 emission as the concentration of iodide increases.

To get a quantitative interpretation for the energy transfer in the PVK–DCM2 system, we measured the maximum external quantum efficiency (EQE) for DCM2 to be
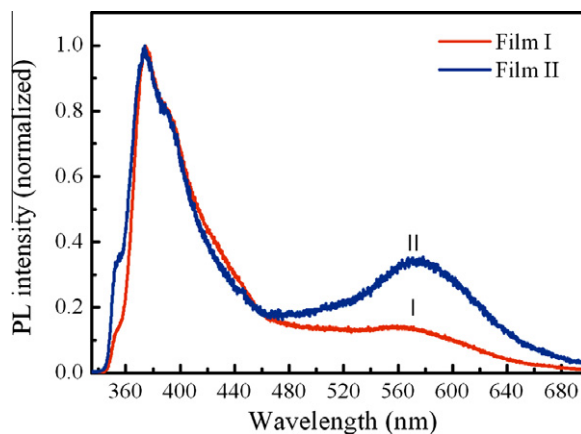
Fig. 4. PL spectra of PVK:0.3% DCM2 (Film I) and PVK:0.2% DCM2:0.3% RI (Film II) excited at 320 nm at 12 K.

0.046%, 0.031%, 0.064%, 0.028 %, and 0.030% for Device I, II, III, IV, and V, respectively (the low efficiency is due to the ineffective singlet–singlet energy transfer system of PVK–DCM2). In the presence of iodide, Device III containing 0.58% of iodide showed the highest EQE. This result indicates that an enhancement of quantum efficiency can be achieved by an external heavy atom without using phosphorescent dyes containing rare metals.

3.2. PL properties

To confirm the energy transfer processes in the OLEDs proposed in Fig. 3, the PL spectra of PVK–DCM2 films were investigated at 12 K, as shown in Fig. 4. Films containing PVK:0.3% DCM2 (Film I) and PVK:0.2% DCM2:0.3% RI (Film II) were fabricated by spin-coating. Singlet emission from PVK was observed at about 375 nm for both Films I and II, which has been normalized. At low temperature, phosphorescence from the triplet state of PVK should be observed at around 500 nm [16]. However, no obvious triplet emission from PVK was observed in the presence of

iodide. Because the concentration of DCM2 in Film II is lower than that in Film I, the intensity of emission from DCM2 in Film II should be lower than that in Film I [5]. However, the intensity of emission from DCM2 (at around 580 nm) is about 2.4 times greater for Film II containing RI than for Film I without RI. This also indicates increased energy transfer from PVK to the singlet state of DCM2 in the presence of RI, and provides further evidence for direct energy transfer from the triplet state of PVK to the singlet state of DCM2 (the process labeled K_{PDTS} in Fig. 3).

4. Conclusion

An unusual HAE was induced by the presence of external iodide in a system containing a fluorescent PVK host and fluorescent DCM2 guest. The intensities of the EL and PL peaks of DCM2 relative to those of PVK show a similar tendency as the content of iodide is varied, which indicates that direct energy transfer occurs from the triplet excited state of PVK to the singlet excited state of DCM2 induced by external heavy atoms of iodine. This result suggests an alternative way to use the triplet energy of fluorescent materials without using electrophosphorescent dyes containing rare metals.

Acknowledgments

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