Organic light-emitting diodes using 3,6-difluoro-2,5,7,7,8,8-hexacyanoquinodimethane as p -type dopant

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Organic light-emitting diodes using 3,6-difluoro-2,5,7,7,8,8-hexacyanoquinodimethane as *p*-type dopant

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We demonstrate that 3,6-difluoro-2,5,7,7,8,8-hexacyanoquinodimethane (F2-HCNQ) can serve as an excellent electrical doping material for hole transport materials with the highest occupied molecular orbital level as high as 5.4 eV, such as N,N'-di(naphthalene-1-yl)-N,N'-diphenyl-benzidine (NPB). With its relatively strong electron-accepting ability and high thermal stability, F2-HCNQ doped NPB organic light-emitting diode (OLED) showed improved power efficiency with low driving voltage. The tris(8-hydroxyquinoline)aluminum based OLED with F2-HCNQ doped NPB layer and Cs_2O doped bathophenanthroline electron transport layer exhibits power efficiency of 3.6 lm/W with driving voltage of 3.2 V at 100 cd/m^2. © 2009 American Institute of Physics. [DOI: 10.1063/1.3073719]

In the past two decades, organic light-emitting diodes (OLEDs) have received much attention due to their potential commercial application for flat panel displays and large area solid state illumination light source.[1–4] Recently, the development of the OLED technology is focused mainly on the direction of lowering operation voltage to reduce power consumption,[5,6] improving color purity[7,8] and lifetime,[9–11] as well as increasing device efficiency via triplet emitters.[12,13] In order to lower the operation voltage and power consumption, the concept of electrical doping, which is adopted from inorganic semiconductors, is widely employed. It has been shown that OLEDs with *p*-doped hole transport layer and/or *n*-doped electron transport layer can result in a better Ohmic contact, smaller carrier injection barriers, and a larger built-in potential of Schottky or *p-n* junction that allow efficient carrier injections.[5,14] Meanwhile the resulted better electrical conductivity of the doped transport layer can provide efficient carrier transport, hence lowering the operation voltage and concomitantly improving the power efficiency. Regarding molecules served as the *p*-dopant in organic semiconductors, several strong electron acceptors or oxidants had been used, such as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ),[6] $SbCl_5$,[15] I_2,[16] WO_3,[17] ReO_3,[18] and MoO_x.[19–21] Despite the intensively explored *p*-type electrical doping system, problematic issues still remain. The problems related to inorganic materials include noncompatible high deposition temperature, pixel crosstalk, low optical transparency, or material toxicity. Conversely, with respect to the organic dopant, i.e., F4-TCNQ, it generally has very high vapor pressure, hence tends to be evaporated at very low temperature under vacuum and likely leads to contamination of the deposition chamber rendering the doped layer thermally unstable, thus device performance

deterioration. It has been found that due to the instability of the F4-TCNQ doped N,N'-di(naphthalene-1-yl)-N,N'-diphenyl-benzidine (NPB) layer, which was served as the intermediate connector in tandem OLED, severe increase in driving voltage had been observed during operation.[22] Although a more stable *p*-doping system with a new dopant having deposition temperature over 150 °C had been reported, its structure had not been disclosed.[23] Thus, good *p*-type dopants for organic electrical doping are still lacking and in great demand.

We reported recently that molecule 3,6-difluoro-2,5,7,7,8,8-hexacyanoquinodimethane (F2-HCNQ) is a stronger electron acceptor than F4-TCNQ.[24] It was also demonstrated that F2-HCNQ could act as an excellent *p*-dopant in the 4,4',4''-tris(*N*-(2-naphthyl)-*N*-phenylamino)triphenylamine (2-TNATA) film. In this work, we report the utilization of F2-HCNQ as *p*-type dopant with matrix of 2-TNATA and NPB in OLED devices. We will demonstrate that while F4-TCNQ can be used as *p*-dopant for 2-TNATA, it does not work with NPB matrix, whereas F2-HCNQ is a good *p*-type dopant both for 2-TNATA and NPB.

As shown in Fig. 1, the lowest unoccupied molecular orbital (LUMO) of F2-HCNQ (−5.59 eV) is deeper than that of F4-TCNQ (−5.33 eV). Regarding the *p*-type doping mechanism, it is widely accepted that doping occurs via transferring of an electron from the highest occupied molecular orbital (HOMO) of host to the LUMO of dopant, resulting in the formation of free holes. In order to serve as *p*-dopant, the LUMO of dopant is required to locate close to or below the HOMO of the host. Thus F2-HCNQ, with deeper LUMO, is expected to have a broader choice for host.

For OLED devices study, we fabricated Alq_3 based devices using 2-TNATA doped with F4-TCNQ and F2-HCNQ, respectively. The device configuration is ITO/undoped or doped 2-TNATA (60 nm)/NPB(10 nm)/Alq_3(60 nm)/LiF(0.8 nm)/Al(100 nm), where the undoped, 2% F4-

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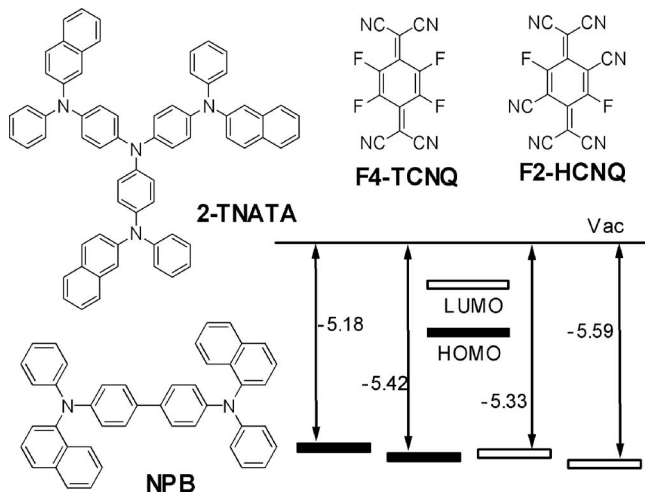c)Electronic mail: fredchen@mail.nctu.edu.tw.

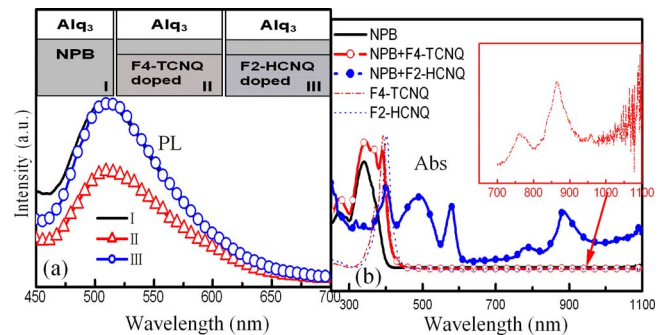FIG. 1. The chemical structures of organic materials along with the relevant energy levels for *p*-doping.

FIG. 3. (Color online) (a) PLs of Alq_3 from films I, II, and III. The insets are the layer structures; (b) Absorbance of NPB, F4-TCNQ mixed NPB, F2-HCNQ mixed NPB, F4-TCNQ, and F2-HCNQ in dilute dichloromethane solution; the inset is the enlarged part from F4-TCNQ mixed NPB solution spectrum.

TCNQ doped, and 2% F2-HCNQ doped devices are represented as A, B, and C, respectively, whose EL performances are shown in Fig. 2. It is noted in Figs. 2(a)–2(c) that B and C exhibit almost the same degree of current and brightness improvement compared to the undoped device A. At current density of 10 and 50 mA/cm^2, the driving voltages of doping devices decrease, with values of 5.0 and 6.7 V for B, 4.9 and 6.5 V for C, and 5.2 and 7.1 V for A, revealing the advantages of doping. It also can be noticed that the efficiencies of the doped 2-TNATA devices are only slightly higher at high current density than the undoped one. This might be attributed to the unbalanced carriers in the devices. The results clearly show that both F4-TCNQ and F2-HCNQ are good dopant materials for 2-TNATA. However, the benefit of using F2-HCNQ lies in its higher thermal stability, which can lead to higher reliability of the doping system. As studied in our previous work,[24] the F2-HCNQ doped 2-TNATA can keep its hole conducting character up to 85 °C; however, the hole conductivity of F4-TCNQ doped 2-TNATA system dropped dramatically after 65 °C annealing.

To investigate the potential advantage of F2-HCNQ, NPB was used as hole transport matrix in place of 2-TNATA. Previously, it was found in our study that when F4-TCNQ doped NPB served as hole injection/transport layer in Alq_3 based device with the configuration similar to device B, the device performance was poor. Although there was improved current density but there was decreased brightness and efficiency as well. To study the feasibility of using F2-HCNQ as *p*-dopant for NPB, we studied the photoluminescence (PL) of Alq_3 films on quartz substrate with structure of NPB (80 nm)/Alq_3(60 nm) (Film I), and 2% F4-TCNQ or F2-

HCNQ doped NPB (60 nm)/NPB(10 nm)/Alq_3(60 nm) (films II and III, respectively). These three films contain the same thickness of Alq_3 and also have the same total thickness. Film I, as a control, only contains pure NPB layer, while films II and III contain F4-TCNCQ or F2-HCNQ doped NPB layer plus a pure NPB buffer layer, respectively. The buffer layer is inserted to prevent the diffusion of dopant F4-TCNQ or F2-HCNQ to Alq_3,[25] thus avoiding Alq_3 emission quenching by dopant diffusion mechanism. The three films are excited with 430 nm excitation light at the Alq_3 side, and the PL spectra are shown in Fig. 3(a). It can be seen that the shape and the intensity of the luminescence from films I and III are almost the same, indicating that the codeposition of F2-HCNQ with NPB has no impact on the PL of Alq_3. However, compared to the undoped film I, PL intensity from film II decreases significantly, indicating there is luminescence quenching in film II. We attributed this quenching to the cross contamination of free F4-TCNQ species after F4-TCNQ and NPB codeposition because the electron-transfer from NPB to F4-TCNQ is not efficient to consume all the dispersed F4-TCNQ. The degree of reaction between the host and the *p*-dopant can be inferred from their mixture absorption spectra. As shown in Fig. 3(b), pure NPB solution shows no absorption peak above 340 nm. Upon adding F2-HCNQ, besides the absorption peak of 403 nm from F2-HCNQ, pronounced peaks located at 500–1000 nm appear, indicating the effective formation of charge transfer (CT) complexes between NPB and F2-HCNQ, which is conducive to high electrical conductivity and formation of an Ohmic contact at the electrode/doped-NPB interface. However, when F4-TCNQ is added to pure NPB solution, besides the additional peak of 391 nm from F4-TCNQ, there is no obvious absorption peak beyond 400 nm. The absorption
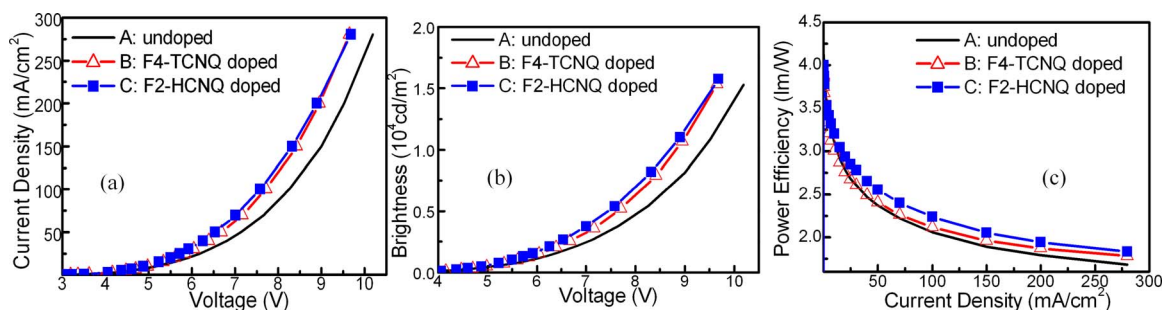

FIG. 2. (Color online) The device (a) *I*-*V*, (b) *B*-*V*, and (c) Eff.-*J* characteristics for undoped and doped 2-TNATA devices.
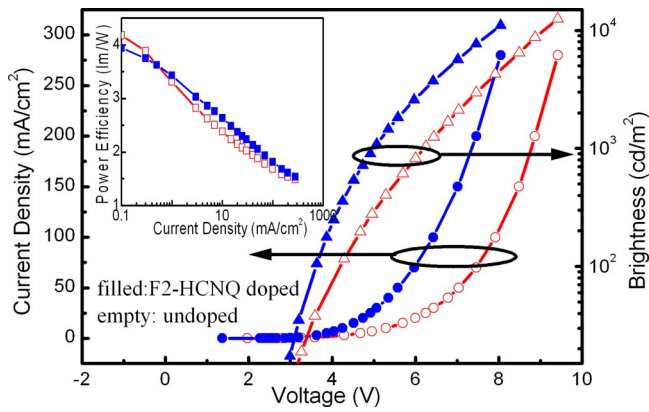
FIG. 4. (Color online) *I-V-B* features for undoped and F2-HCNQ doped NPB devices. The inset is their efficiency data.

from CT complexes between NPB and F4-TCNQ is only visible under enlarged scale as shown in the inset in Fig. 3(b), indicating that the reaction between NPB and F4-TCNQ to form CT complexes that is responsible for the doping effect is not favorable. In addition, the vapor pressure of F4-TCNQ is very high. Thus, after the coevaporation of NPB and F4-TCNQ, there may have been F4-TCNQ residues in the chamber, which could be evaporated simultaneously in the subsequent evaporation process. As a result, although doping F4-TCNQ in NPB leads to the current increasing in a device by the weak CT complex formation, the device brightness suffers from luminescence quenching from F4-TCNQ species by contamination. Based on these studies, it is clear that F2-HCNQ is a superior dopant for NPB.

F2-HCNQ doped NPB device (E) as well as its undoped control device (D) was fabricated, and their performance are shown in Fig. 4. Compared to D, the current density and the brightness of E are higher at same driving voltage. At current densities of 10 and 50 mA/cm^2, driving voltages for E are 4.3 and 5.6 V respectively, which are significantly lower than the corresponding values of 5.3 and 7.0 V for D. This outstanding *p*-type doping feature in F2-HCNQ doped NPB device is attributed to the compatible energy levels between the HOMO of NPB and the LUMO of F2-HCNQ, which allows the efficient electron transfer from NPB to F2-HCNQ. In addition, the high thermal stability of F2-HCNQ also prevents cross contamination; this will make the fabrication process more reproducible and assure the device quality.

To further explore the ability of F2-HCNQ as *p*-dopant, the device with both *p*-doped hole transport layer and *n*-doped electron transport layer (called *p-i-n* OLEDs) was fabricated with the structure of ITO/NPB: 2% F2-HCNQ (60 nm)/NPB (10 nm)/Alq (40 nm)/BPhen: 4%Cs_2O(20 nm)/LiF(0.8 nm)/Al(100 nm) (device F), where the Cs_2O was decomposed by *in situ* Cs_2CO_3 evaporation.[26] In F, while F2-HCNQ doped NPB layer enhances the hole injection and transport, Cs_2O doped BPhen layer served as an efficient electron injection and transport media, which leads to more balanced electron and hole available for recombination. As a result, F shows the highest performance, with power efficiencies of 3.22 and 2.52 lm/W, at current density of 10 and 50 mA/cm^2 under driving voltage of 3.8 and 5.0 V, compared to D and E, whose corresponding power efficiencies are 2.39 and 1.88, 2.63 and 2.05 lm/W, respectively.

In summary, we studied the doped OLED devices with *p*-type dopant F2-HCNQ. By doping into host material 2-TNANA as well as NPB, the current density and power efficiency can be improved. Due to the stronger electron-accepting ability, F2-HCNQ has a wider choice of host materials as compared to the state-of-the-art *p*-type dopant F4-TCNQ. Furthermore, F2-HCNQ is thermally stable, which will lead to more stable doped layer and allow better control of codeposition by thermal evaporation.

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