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An efficient guest/host fluorescent energy transfer pair based on the naphthalimide skeleton, and its application in heavily-doped red organic light-emitting diodes



PIGMENTS

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ABSTRACT

A red aggregation-emission-enhancement guest fluorophor and a green host compound both based upon the naphthalimide skeleton namely, 11-*tert*-butyl-((E)-4-(2-(7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)vinyl)-7H-benzimidazo[2,1-a]benzo[de]isoquinolin-7-one and 2-(4-*tert*-butylphenyl)-6-(9-(4-*tert*-butylphenyl)-9H-carbazol-3-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione, have been synthesized. They form an efficient energy transfer pair due to their structural similarity. As a consequence of the aggregation characteristics of the red guest, and the high energy-transfer efficiency between the host and guest as well, the 6 wt% heavily-doped organic light-emitting diode based on these naphthalimides shows high performance, with maximum brightness of 6250 cd m⁻² and current efficiency of 3.13 cd A⁻¹. In contrast, the reference device using tris(8-hydroxyquinolinato)aluminium (III) as host just exhibits peak luminance of 1160 cd m⁻² and current efficiency of 0.75 cd A⁻¹. The drastically enhanced device performance was attributed to the much better energy transfer efficiency between the host and guest, which stems from their good structural similarity.

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1. Introduction

Organic light-emitting diodes (OLEDs) have been regarded as the "third-generation of flat panel displays", and have attracted enormous attention in recent years [1–4]. Compared to electrophosphorescent devices, highly efficient fluorescent OLEDs are more promising with respect to display applications due to their faster response time, relatively low efficiency roll-off at high current densities, and longer operational lifetime [5,6]. To realize full color display, efficient red, green, and blue OLEDs are required, yet compared to green OLEDs whose maximum current efficiencies (η_{Lmax}) have reached 30 cd A⁻¹ [7–9], blue ($\eta_{\text{Lmax}} = 9.1$ cd A⁻¹) [10] and red ($\eta_{\text{Lmax}} = 12$ cd A⁻¹) [11] OLEDs are much inferior in terms of efficiency. It should be pointed out that the η_{Lmax} of 12 cd A⁻¹ for a

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red OLED was achieved at a rather low doping level of 0.5 wt%, and would drop drastically with increasing dopant concentration, while such a low doping level would result in the need of strict manufacturing control [12,13], which is unattractive for the mass production of OLEDs. In fact, the optimum doping concentrations of red OLEDs are usually limited to low levels, since most of the red fluorophors comprise donor- π -acceptor (D- π -A) molecular structure, consequently, they generally suffer from severe dipole-dipole and $\pi - \pi$ intermolecular interactions, which make them highly susceptible to aggregation-induced quenching (AIQ). Therefore, the alleviation of intermolecular interactions is a key factor to solve the AIQ problem for the luminogens [14,15]. To realize the isolation of a fluorophore, the ideal strategy is to construct dendritic lightemitting materials, in which the luminescent core is surrounded by light-harvesting antennal dendrons [15–17]. Nonetheless, the disadvantage of this approach lies in the need of elaborate and tedious synthesis and purification.

Recently, an unusual aggregation-induced-emission (AIE) or aggregation-emission-enhancement (AEE) property has been demonstrated to be effective on solving the adverse AIQ problem of

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fluorophors, and such AIE/AEE active compounds are promising candidates for fabricating heavily-doped and non-doped OLEDs [18]. For example, by incorporating propeller-like tetraphenylethene (TPE) units into dithiophenylbenzothiadiazole moiety, Tang et al. developed some red AIE-active luminogens [19,20], and the derived non-doped OLEDs show η_{Lmax} of 2.4 cd A⁻¹; while by integration of triphenylamine (TPA) bridges and TPE peripheries into benzothiadiazole core. Xu et al. developed a star-shaped orange AIE compound, and non-doped OLEDs based on it show η_{Lmax} of 6.81 cd A^{-1} [21]. Nevertheless, most of the discovered AIE/AEE luminogens are greenish-blue [22–24] and yellow [25,26] dyes, and red AIE/AEE active fluorophors are relatively few. Actually, the D- π -A red AIE-active luminogens reported so far generally bear cyano-substituted vinyl [27,28], benzothiadiazole [19-21] or benzobisthiadiazole [29] acceptor (A) subunits, thus the development of novel AIE/AEE active red fluorophors are deserving of effort and attention.

Among various kinds of electroluminescent (EL) materials, 1,8naphthalimide derivatives have attracted much attention due to their high photoluminescence (PL) quantum yields (QYs) and good optical, thermal and chemical stabilities [29,30]. By introducing substituents with different electron-donating capability, such as alkyl (aryl) amino [31,32], alkynyl/alkenyl [33,34], and aryloxy [35] groups into the 4-position of 1,8-naphthalimides, the PL emission colour of the dyes can be readily tuned from yellowish green to pure blue. Yet with respect to red electrofluorescent naphthalimides, to our knowledge, there have only been three reports so far. The pioneering work on red EL naphthalimide has been demonstrated by Tian and co-workers. Although the derived OLED showed a satisfactory emission colour ($\lambda_{ELmax} = 620$ nm), the maximum brighness was as low as 15 cd m^{-2} [36]. Using 4-(phenyl)(anthracen-9-yl)amino-1,8-naphthalic anhydride as the emitting material, Cheng et al. have fabricated an OLED with relatively high luminance of 4470 cd m⁻², but its λ_{ELmax} was only 607 nm, and the emission color was orange [31]. Recently, Deng et al. [37] reported a high performance orange naphthalimide-based OLED with maximum luminance of 6600 cd m^{-2} , however, the emission colour was quite unsatisfactory ($\lambda_{ELmax} = 540$ nm). Compared to 1,8-naphthalimide, 7H-benzimidazo[2,1-a]benzo[de]isoquinolin-7one, the condensation product of 1,8-naphthalic anhydride and benzene-1,2-diamine, possesses a more extended conjugate system. However, the benzimidazo[2,1-*a*]benzo[*de*]isoquinolin-7-one derivatives reported are generally green or yellow fluorescent dyes, and to our knowledge, there are no red examples based on this skeleton up to now. Herein, we design and synthesize an AEEactive red D- π -A compound, namely, 11-tert-butyl-((E)-4-(2-(7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)vinyl)-7H-benzimidazo[2,1-a]benzo[de]isoquinolin-7-one (FNIb), in which 7H-benzimidazo[2,1-a]benzo[de]isoquinolin-7-one acts as the acceptor (A) subunit, ethenylidene as the π -bridge, and (fluoren-2-yl)diphenylamine as the electron donor (D) subunit, respectively. An OLED using **FNIb** as emissive guest is found to show high EL performance even at a high doping level of 6 wt%.

Furthermore, as the EL behaviour of doped OLEDs is closely related to the doping matrix, the selection of appropriate host material is also one of the key factor in the optimizion of device performance [38]. To be a promising host candidate, good carrier transporting capability, proper energy level match-ups with the neighboring functional layers, and effective energy transfer (ET) from host to guest are required [39]. To achieve efficient ET, there are two prerequisites: (1) large spectral overlap of PL emission band of the host and absorption spectrum of the guest [38,39]; (2) good structural similarity between the host and guest [40–42]. However, despite the effective spectral overlap between **FNIb** and tris(8-hydroxyquinolinato)aluminium (Alq₃), the well-known electron-

transporting host material, quite low ET efficiency between Alq₃ and **FNIb** is oberved. Consequently, we constructed a new host material with a naphthalimide skeleton, namely, 2-(4-*tert*-butylphenyl)-6-(9-(4-*tert*-butylphenyl)-9*H*-carbazol-3-yl)-1*H*-benzo [*de*]isoquinoline-1,3(2*H*)-dione (**4CzTNA**). The results indicate that although **4CzTNA** possesses analogous energy levels to those of Alq₃, it shows drastically higher PL efficiency, and could form an much more efficient ET pair with **FNIb**. OLEDs using **4CzTNA** instead of Alq₃ as host exhibit much enhanced EL performance.

2. Experimental

2.1. Materials and instrumentation

All the chemicals were purchased from Aldrich and Acros Chemical Co., and were used without further purification. The solvents were of analytical grade and freshly distilled before use. N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were dried with calcium hydride and diphosphorus pentoxide, respectively, and freshly distilled before use. ¹H NMR and ¹³C NMR spectra were recorded on a BRUKER (AVII-400) spectrometer in CDCl₃ using TMS as internal standard. High resolution TOF-MS spectra were recorded on a Waters Q-TOF-Premiter instrument. Infrared Spectroscopy (IR) measurement has been performed on Nicolet 6700 FT-IR Spectrometer Thermo Scientific. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on TGA Q500 and DSC Q100 instruments under nitrogen atmosphere at a heating rate of 10 °C/min. PL emission spectra of both solution and thin-film samples were recorded on a Perkin-Elmer LS55 fluorescence spectrophotometer at 298 K, while the absolute PLQYs of the film samples were determined on a Horiba Jobin Yvon-Edison Fluoromax-4 spectrometer equipped with an integrating sphere and digital photometer. The UV-vis absorption spectra were measured on a Perkin-Elmer Lambda 950 scanning spectrophotometer. All the thin film samples were spincoated from corresponding chloroform solution with concentration of 25 mg mL⁻¹ at a speed of 2000 rpm on quartz substrates. Cyclic voltammetry (CV) measurement was carried out on a PAR-STAT 2273 electrochemical workstation at room temperature in anhydrous dichloromethane solution using tetrabutylammonium perchlorate (0.1 mol L^{-1}) as supporting electrolyte at a scanning rate of 50 mV s⁻¹. The CV system was constructed using a threeelectrode electrochemical cell consisted of a Pt-wire working electrode, a Pt-wire counter electrode, and a Ag/AgNO₃ reference electrode (0.1 mol L⁻¹ in MeCN) under protection of nitrogen, and each measurement was calibrated with ferrocene/ferrocenium redox system as an internal standard.

2.2. OLED fabrication and measurements

Indium-tin oxide (ITO) coated glass substrates were pre-cleaned and oxygen plasma treated for 15 min. Organic functional layers were thermoevaporated in vacuum (3×10^{-4} Pa) with deposition rate of 0.2–0.5 Å s⁻¹. After that, metallic cathode was deposited with rate of 3–5 Å s⁻¹ at 3×10^{-3} Pa. The current density-voltageluminance (*J-V-L*) characteristics were measured with a Keithley 4200 and an ST-86LA luminance meter, and EL spectra and Commission Internationale de l'Eclairage (CIE) coordinates were determined with an OPT-2000 instrument. All the measurements were carried out in ambient atmosphere without encapsulation.

2.3. Synthesis

The detailed synthetic routes to the target compounds **4CzTNA**, 11-*tert*-butyl-((*E*)-3-(2-(7-(diphenylamino)-9,9-diethyl-9*H*-

fluoren-2-yl)vinyl)-7*H*-benzimidazo[2,1-*a*]benzo[*de*]isoquinolin-7one **FNIa** and **FNIb** are outlined in Scheme 1. Intermediates 9-(4*tert*-butylphenyl)-9*H*-carbazole (1) [43], 3-bromo-9-(4-*tert*-butylphenyl)-9*H*-carbazole (2) [44] 9-(4-*tert*-butylphenyl)-3-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (3) [45], 2-(4*tert*-butylphenyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (4) [46], 4-*tert*-butylbenzene-1,2-diamine (5) [47,48] and 7-bromo-9,9-diethyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine (7) [49] were prepared according to reported procedures.

2.3.1. Synthesis of bromo- and tert-butyl-modified benzimidazo [2,1-a]benz[de]isoquinolin-7-ones (**6a-6d**)

A flask was charged with 4-bromo-1,8-naphthalic anhydride (2.18 g, 7.87 mmol), 4-*tert*-butylbenzene-1,2-diamine (1.3 g, 7.88 mmol) and acetic acid (50 mL). The mixture was heated under reflux for 5 h. After cooling to room temperature, the mixture was poured into ice water. The precipitate was filtered, washed with water and dried in *vacuo*. The crude product was composed of an inseparable mixture of isomers (**6a**–**d**) as a yellow solid in 76.5% yield.

2.3.2. Synthesis of 9,9-diethyl-N,N-diphenyl-7-vinyl-9H-fluoren-2amine (**8**)

A flask was charged with a mixture of **7** (1.2 g, 2.53 mmol), Pd(PPh₃)₄ (0.058 g, 0.05 mmol), tributylethenylstannane (0.88 g, 2.78 mmol), 2,6-di-*tert*-butylphenol (0.06 g, 0.28 mmol) and

toluene (20 mL). The reaction mixture was heated to reflux for 10 h under N₂. After cooled down to room temperature, saturated aqueous KF solution (50 mL) was added and the resulting mixture was stirred over night at room temperature. The mixture was diluted with CH₂Cl₂ (100 mL) and washed with brine, dried under anhydrous magnesium sulfate, then the solvent was removed in vacuum. The crude product was purified by column chromatography over silica using petroleum ether as elute to vield pure product as white solid. Yield: 68.2%. m.p.: 122–124 °C. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.58–7.53 (m, 2H), 7.36 (d, I = 8.0 Hz, 1H), 7.33 (s, 1H), 7.28-7.22 (m, 2H), 7.12-7.09 (m, 5H), 7.03-6.98 (m, 3H), 6.82-6.75 (m, 1H), 5.77 (d, I = 17.6 Hz, 1H), 5.23 (d, J = 10.8 Hz, 1H), 1.98–1.85 (m, 4H), 0.35 (t, J = 7.2 Hz, 6H).¹³C NMR (100 MHz, CDCl₃), δ (ppm): 150.6, 149.2, 147.0, 146.2, 140.3, 136.4, 1358.4, 134.8, 128.1, 124.4, 122.8, 122.6, 121.4, 119.3, 111.6, 55.0, 31.6, 30.9, 28.7, 28.4, 21.7, 13.1, 7.5. FT-IR (KBr, cm⁻¹): 3098 (=CH₂), 2959 (-CH₃), 2926 (-CH₂), 1319 (ArN). TOF-MS: m/z Found 438.2193 $(M + Na^{+})$, and Calc. for $C_{31}H_{29}N$ for $(M_w + Na^{+})$: 438.2198.

2.3.3. Synthesis of 2-(4-tert-butylphenyl)-6-(9-(4-tert-

butylphenyl)-9H-carbazol-3-yl)-1H-benzo[de]isoquinoline-1,3(2H)dione (**4CzTNA**)

A flask was charged with a mixture of **3** (1.14 g, 2.60 mmol), **4** (1.0 g, 2.40 mmol), Pd(PPh₃)₄ (0.08 mg, 0.07 mmol), aqueous Na₂CO₃ solution (2 M, 70 mL), ethanol (50 mL) and toluene (80 mL). The reaction mixture was heated at 100 °C for 24 h under N₂. After



Scheme 1. The synthetic routes to compounds 4CzTNA, FNIa and FNIb. Reagents and reaction conditions: (i) Pd(OAc)₂, P(*t*-Bu)₃·BF₄, K₂CO₃, toluene, 120 °C; (ii) NBS, DMF, 0 °C in the dark; (iii) bis(pinacolato)diboron, Pd(ppf)Cl₂, KOAc, 1,4-dioxane, 90 °C; (iv) HOAc, reflux; (v) EtOH reflux; (vi) CH₂ = CHSnBu₃, Pd(PPh₃)₄; (vii) Pd(PPh₃)₄, Na₂CO₃(aq)/EtOH/Toluene = 7/5/8, 110 °C; (viii) Pd(OAc)₂/P(*o*-tol)₃, Et₃N/DMF.

cooling to room temperature, the mixture was poured into water (150 mL), then extracted with CH₂Cl₂, washed with brine, dried under anhydrous magnesium sulfate. After the removal of solvent in vacuo, the crude product was purified by column chromatography over silica using petroleum ether/dichloromethane as eluent to afford yellow solid. Yield: 70.3%, m.p.: 294 °C. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.73 (d, J = 7.2 Hz, 1H), 8.69 (d, J = 6.8 Hz, 1H), 8.48 (d, I = 9.6 Hz, 1H), 8.30 (s, 1H), 8.19 (d, I = 7.6 Hz, 1H), 7.87 (d, I = 7.6 Hz, 100 Hz)I = 7.6 Hz, 1H), 7. 75–7.71 (t, I = 8.4 Hz, I = 7.6 Hz, 1H), 7.67 (d, *I* = 8.4 Hz, 2H), 7.61–7.45 (m, 8H), 7.35–7.27 (m, 3H), 1.45 (s, 9H), 1.39 (s, 9H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 164.9, 164.7, 151.5, 151.0, 148.4, 141.8, 141.1, 134.7, 133.6, 132.8, 131.7, 131.4, 130.8, 130.4, 129.4, 128.5, 128.1, 128.00, 127.1, 126.9, 126.7, 126.7, 126.6, 123.7, 123.2, 123.1, 121.9, 121.5, 120.6, 120.4, 110.4, 110.3, 35.0, 34.9, 31.6, 31.5. FT-IR (KBr, cm⁻¹): 3052 (Ar, C=H), 2961 (-CH₃), 1701 (C=O), 1262 (ArN). TOF-MS: *m/z* Found 649.2832 (*M* + Na⁺), and Calc. for $C_{44}H_{38}N_2O_2$ for $(M_w + Na^+)$: 649.2831.

2.3.4. Synthesis of 11-tert-butyl-((E)-3-(2-(7-(diphenylamino)-9,9diethyl-9H-fluoren-2-yl)vinyl)-7H-benzimidazo[2,1-a]benzo[de] isoquinolin-7-one (**FNIa**) and 11-tert-butyl-((E)-4-(2-(7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)vinyl)-7Hbenzimidazo[2,1-a]benzo[de]isoquinolin-7-one (**FNIb**)

A flask was charged with a mixture of **6** (0.94 g, 2.16 mmol), **8** (1.07 g, 2.59 mmol), $Pd(OAc)_2$ (1.0 mg, 0.043 mmol), $P(o-tolyl)_3$ (0.026 g, 0.086 mmol), triethylamine (1.53 g, 15.12 mmol) and DMF (30 mL). The reaction mixture was heated at 90 °C for 24 h under N₂. After cooled to room temperature, the mixture was poured into water (200 mL), and the red solid was collected, washed with water and dried in *vacuo*. The crude product was purified by column chromatograph over silica using toluene/ethyl acetate as eluent to afford pure product **FNIa** as dark-red solid, and **FNIb** as orange-red solid.

11-tert-butyl-((E)-3-(2-(7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)vinyl)-7H-benzimidazo[2,1-a]benzo[de]isoquinolin-7one (**FNIa**). Yield: 17.0%, m.p. 311 °C. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.71 (d, J = 7.6 Hz, 2H), 8.62 (d, J = 8.0 Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.89–7.88 (m, 3H), 7.76 (t, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.55 (s, 1H), 7.52–7.50 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 1H), 7.36 (d, *J* = 16 Hz, 1H), 7.29–7.25 (m, 5H), 7.14 (d, J = 8.0 Hz, 5H), 7.07–7.01(m, 3H), 2.08– 1.93 (m, 4H), 1.45 (s, 9H), 0.42 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 160.5, 151.7, 150.6, 149.4, 149.3, 147.9, 147.6, 144.0, 142.3, 139.5, 135.9, 135.3, 134.9, 131.5, 131.1, 130.1, 129.5, 129.2, 127.4, 126.9, 126.4, 124.2, 124.0, 123.5, 123.4, 123.1, 122.6, 122.2, 121.3, 120.6, 119.4, 119.2, 119.1, 116.3, 115.0, 56.1, 35.1, 32.7, 31.7, 8.6. FT-IR (KBr, cm⁻¹): 3034 (Ar, C=H), 2960 (-CH₃), 2853 (-CH₂), 1693 (C= 0), 1602 (C=N), 1314 (ArN). TOF-MS: *m*/*z* Found 740.3614 (*M* + H⁺), and Calc. for $C_{53}H_{45}N_{3}O$ for $(M_w + H^+)$: 740.3641.

11-*tert*-butyl-((*E*)-4-(2-(7-(diphenylamino)-9,9-diethyl-9*H*-fluoren-2-yl)vinyl)-7*H*-benzimidazo[2,1-*a*]benzo[*de*]isoquinolin-7-one (**FNIb**). Yield: 15.2%, m.p.: 291 °C. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.62 (d, *J* = 7.2 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.54 (d, *J* = 1.6 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.74–7.70 (m, 2H), 7.67–7.63 (m, 2H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.29–7.25 (m, 5H), 7.16–7.13 (m, 5H), 7.07–7.01 (m, 3H), 2.09–1.94 (m, 4H), 1.45 (s, 9H), 0.44 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 160.4, 151.7, 150.6, 149.0, 147.9, 147.7, 142.7, 142.5, 141.6, 136.1, 135.8, 134.6, 131.9, 131.1, 129.8, 129.2, 127.4, 127.3, 126.7, 126.6, 124.0, 123.4, 122.7, 122.0, 121.3, 120.8, 120.7, 119.4, 119.0, 112.5, 56.1, 35.3, 32.7, 31.8, 8.6. FT-IR (KBr, cm⁻¹): 3035 (Ar, C=H), 2959 (-CH₃), 2869 (-CH₂), 1693 (C=O), 1618 (C=N), 1364 (ArN). TOF-MS: *m*/*z* Found 740.3616 (*M* + H⁺), and Calc. for C₅₃H₄₅N₃O for (*M*_w + H⁺): 740.3641.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic route to the target molecules are outlined in Scheme 1. It is noteworthy that through condensation of 4-bromo-1.8-naphthalic anhydride with 4-tert-butylbenzene-1.2-diamine. according to the ¹H NMR characterization result, an isomeric mixture of **6a–6d** could be prepared. Yet despite of our enormous efforts on separation, we fail to isolate them through either recrystallization or column chromatography due to their quite similar polarity, and the mixture exhibits only one spot on TLC in a large variety of eluents. This is consistent with the literature report [50]. Nevertheless, by Mizoroki–Heck cross-coupling of the mixture of **6a–6d** with **8**, the isomeric mixture of target molecules **FNIa**–**FNId** are found to show slightly different polarity. Through precise control on the proportion of toluene/ethyl acetate, FNIa and FNIb have been isolated via gradient column chromatography successfully, whereas the isolation of FNIc and FNId seems to be improbable by column chromatography, since they could not even be separated through high performance liquid chromatography (HPLC) technique (vide ESI). Consequently, only the photophysical properties of FNIa and FNIb have been investigated in detail.

To provide more solid evidence for the molecular structure of **FNIa** and **FNIb**, two-dimensional NMR (COSY, HMQC and HMBC) spectra of the two compounds have been recorded. As the ¹³C NMR signal of carbonyl-carbon atom should exhibit more downfield-shift effect than that of the imino-carbon atom [51,52], the signals at ~160 ppm and ~149 ppm should be assigned to the carbon atoms of carbonyl and imino groups, respectively. Therefore, through the HMBC correlations between corresponding carbon and hydrogen atoms, the molecular structures of **FNIa** and **FNIb** have been determined (illustrated in Scheme 1). All the NMR spectra of **FNIa** and **FNIb** have been shown in the Supporting Information.

3.2. Spectroscopic properties

3.2.1. UV-vis absorption and PL emission properties of **FNIa** and **FNIb**

In dilute dichloromethane solution (10^{-5} M^{-1}) , the λ_{ab} of **FNIa** and **FNIb** are located at 477 nm and 468 nm, respectively (shown in Fig. 1). The ~10 nm bathochromic-shifted λ_{ab} of **FNIa** relative to **FNIb** suggests that **FNIa** has more extended conjugation system. Under excitation at 400 nm, **FNIa** and **FNIb** emit red fluorescence with λ_{EMmax} of 652 nm and 664 nm, respectively (data summarized in Table 1). It is noteworthy that both **FNIa** and **FNIb** show obvious



Fig. 1. Normalized absorption and fluorescence spectra of FNIa and FNIb in dichloromethane solution.

 Table 1

 Photophysical properties of FNIa and FNIb in dichloromethane solution and polycrystalline powder state.

Compound	λ _{ab} (n	m)	λ _{EMma}	(nm)	PL QY		FWH	M (nm)
FNIa	477 ^a	477 ^b	652 ^a	647 ^b	0.004 ^a	0.016 ^b	91 ^a	56 ^b
FNIb	468 ^a	466 ^b	664 ^a	628 ^b	0.005 ^a	0.153 ^b	94 ^a	56 ^b

^a Photophysical properties mearsured in dichloromethane solution (10^{-5} M^{-1}) .

^b Photophysical properties mearsured in polycrystalline powder state.

solvatochromism effect. As shown in Fig. 2, they emit yellowish green light in cyclohexane, orange light in toluene, while red fluorescence in dichloromethane. Moreover, the spectral red-shift upon increasing solvent polarity is accompanied by decreasing PL intensity, and in highly polar media such as DMSO and MeCN, the PL emission of the two compounds becomes invisible. Such a sharp solvatochromism effect indicates a substantial contribution of intramolecular charge transfer (ICT) in the excited states of these two red fluorophors [53]. Although FNIa and FNIb exhibit analogous PL properties with respect to both emission color and PL QY in dilute solutions, their PL QYs in solid state differ drastically (vide Fig. 3). For instance, the λ_{EMmax} of the two compounds in THF dilute solution are guite similar, while in polycrystalline powder state, the λ_{EMmax} of **FNIa** is found to show ~20 nm bathochromic shift relative to FNIb (647 nm vs 628 nm). In addition, the PL OY of FNIb is about 10 times as high as that of **FNIa** (in polycrystalline powder state, vide Table 1). The red-shifted emission accompanied by drastically lowered PL efficiency of FNIa relative to FNIb suggests the presence of more severe aggregation in its condensed state [50].

3.2.2. AEE property of FNIb

As **FNIb** exhibits strong fluorescence in the solid state, yet shows quite weak PL emission in polar solvents such as dichloromethane, MeCN and DMSO, it should be AEE-active in these high polar media. By adding water to the MeCN solution of FNIb from 0 to 30% (water fraction in volume, f_w), the fluorescence intensity of the sample is found to increase 220-fold, indicative of the AEE activity of FNIb (shown in Fig. 4). As FNIb exhibits both ICT and AEE behaviors, which is analogous to those AIE luminogens based on twisted intramolecular charge transfer (TICT) mechanism [54-57], the AEE phenomenon of FNIb could be tentatively attributed to the effective restriction of the TICT process in condensed state. When f_w is increased to more than 50%, the PL emission spectra of the FNIbdispersed system are found to show red-shifted emission peak together with decreased PL intensity, this may be ascribed to the phase transition of FNIb from amorphous to polycrystalline states, since the λ_{EMmax} of **FNIb** in 50% MeCN/water mixture is quite analogous to that of its polycrystalline powder.

3.2.3. Photophysical properties of host materials and energy transfer between host and guest

As **FNIb** displays much higher PL efficiency than that of **FNIa** in the condensed state, and is AEE-active, it should be a more



Fig. 2. Fluorescence images of FNIa (top) and FNIb (bottom) dissolved in solvents with different polarity (under irradiation at 365 nm).



Fig. 3. Normalized absorption and fluorescence spectra of **FNIa** and **FNIb** in polycrystalline powder state and in 10^{-5} mol L⁻¹ THF solution. Insets show the photographs of the polycrystalline powder sample of **FNIa** (A, B), **FNIb** (C, D) under room light (top) and UV irradiation at 365 nm (bottom).

promising candidate than FNIa as emissive guest to fabricate OLEDs with high doping-level. To evaluate whether Alq₃ and 4CzTNA could act as appropriate host materials for FNIb, the absorption spectrum of FNIb and PL emission spectra of 4CzTNA and Alq3 were recorded in the solid film state (shown in Fig. 5), and the PL spectra and PL QYs of films with FNIb blended in Alq₃ and 4CzTNA at different doping ratios have been measured (vide Fig. 6 and Table 2). Although as illustrated in Fig. 5, the spectral match of $Alq_3/$ FNIb is better than that of 4CzTNA/FNIb, the energy transfer (ET) efficiency between FNIb and Alq3 is much inferior to FNIb/4CzTNA pair, since the emission of Alq₃ host is even discernable at high guest concentration of 6 wt%, and the PL QY of Alq3 blended film is drastically lower than that of **4CzTNA** doped film at ever doping level. That is, **FNIb** and **4CzTNA** could form a more efficient ET pair. Taking into account that the PL QYs of Alg₃ and **4CzTNA** in solid film states are 0.25 [58] or 0.32 [59] and 0.62, respectively, the much enhanced ET efficiency between FNIb and 4CzTNA should not only be attributed to the higher fluorescence efficiency of 4CzTNA, but also be attributed to the better structural similarity of the host/ guest system [42].



Fig. 4. PL spectra of **FNIb** in MeCN/water mixtures with different water fractions. (Concentration of **FNIb**: 10^{-5} mol L⁻¹, $\lambda_{Ex} = 460$ nm). Insets are the photographs of **FNIb** in MeCN/water mixture taken under irradiation at 365 nm.



Fig. 5. Normalized absorption spectra of 4CzTNA, FNIb and PL emission spectra of **4CzTNA** and Alq₃ in solid film state.

Whether Alq₃ or **4CzTNA** is used as a doping matrix, the blending films show maximum PL QYs at the lowest doping-level of 1 wt%, yet their PL QYs are found to decrease just slightly when the doping ratio is increased to as high as 6 wt%, indicative of the alleviated self-quenching characteristics of the guest compound FNIb. Meanwhile, with increased dopant concentration (from 1 wt% to 6 wt%), the λ_{PLmax} red-shifts accordingly. As the PL emission of FNIb is closely related to the polarity of its microenvironment, the red-shifted λ_{PLmax} may stem from the increased polarity arising from the increasing content of FNIb. When the doping level is higher than 6 wt%, the PL QYs of the samples drop drastically, accompanied with bathochromicallyshifted λ_{PLmax} , this should be ascribed to the concentration quenching of FNIb.



Fig. 6. PL emission spectra of the blended films of FNIb in Alq₃ (top) and 4CzTNA (bottom) at doping level of 1 wt%, 3 wt%, 6 wt% and 12 wt%.

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Fluorescence data and PLQYs of 4CzTNA, FNIb , and FNIb blended films (in Alq	3 and
4CzTNA) at 1 wt% 3 wt% 6 wt% 12 wt%	

	Alq ₃		4CzTNA		
	$\lambda_{\rm EMmax} (\rm nm)$	PLQY	$\lambda_{\rm EMmax} (nm)$	PLQY	
4CzTNA	_	_	529	0.617	
FNIb (1%)	609	0.137	594	0.679	
FNIb (3%)	614	0.118	598	0.658	
FNIb (6%)	616	0.086	604	0.614	
FNIb (12%)	623	0.039	605	0.488	
FNIb (100%)	632	0.033	632	0.033	

 $[\]lambda_{\text{EMmax}}$: emission maximum; PLQY: absolute PL quantum yield of the solid film is measured in an integrating sphere under ambient conditions ($\lambda_{Ex} = 400$ nm).

3.3. Thermal and electrochemical properties

The thermal stability of FNIb and 4CzTNA has been investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (diagram shown in ESI, data listed in Table 3). The compounds both exhibit high decomposition temperatures (T_d) of ${>}400\ ^\circ C$ (at 5 wt% loss). According to DSC measurements, in both the two compounds no distinct $T_{\rm g}$ could be identified, but high melting points of >290 °C could be observed. Thus FNIb and 4CzTNA should possess good thermostability, which is highly desirable for applications in OLEDs.

The electrochemical properties of **FNIb** and **4CzTNA** have been investigated by cyclic voltammetry (CV) in degassed 5×10^{-4} mol L^{-1} CH₂Cl₂ solution with Fc/Fc⁺ redox couple as internal standard, and the voltammograms are shown in ESI (data summarized in Table 3). During the anodic scan, the $E_{1/2}^{ox}$ of **FNIb** and **4CzTNA** are determined to be 0.58 V and 0.87 V relative to Fc/Fc⁺, hence by comparison with the Fc/Fc^+ redox couple whose energy level is 4.80 eV in vacuum, the highest occupied molecular orbital (HOMO) energy levels of FNIb and 4CzTNA are calculated to be -5.38 eV and -5.67 eV, respectively. As no reduction wave could be detected due to the limited range available in CH₂Cl₂, the lowest unoccupied molecular orbital (LUMO) energy levels of -3.14 eV and -2.99 eV for FNIb and 4CzTNA are deduced from the HOMO energies and their corresponding optical bandgaps.

3.4. Electroluminescence properties

In order to examine the EL properties of the objective compounds, OLEDs employing FNIb/4CzTNA as the guest/host pair have been fabricated. The configuration of the devices is: ITO/NPB (30 nm)/CBP (2 nm)/**4CzTNA:FNIb** (x wt%) (20 nm)/Bphen (40 nm)/ Mg:Ag (200 nm), where ITO acts as anode, N,N'-diphenyl-N,N'bis(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB) as hole transporting layer (HTL), 4,7-diphenyl-1,10-phenanthroline (Bphen) as electron transporting layer (ETL), FNIb/4CzTNA as light emitting layer (EML), Mg/Ag as cathode. To avoid the formation of an exciplex between NPB and 4CzTNA, a thin layer of 4,4'-bis(9H-carbazol-

Table 3				
Electrochemical a	and thermal	l data of FNI	b and	4CzTNA

Compound	$E_{1/2}^{ox}$ (V) ^{a,b}	$E_{\rm g} ({\rm eV})^{\rm c}$	HOMO (eV) ^d	LUMO (eV) ^e	$T_{d} (^{\circ}C)^{f}$
FNIb	0.58	2.24	-5.38	-3.14	423
4CzTNA	0.87	2.68	-5.67	-2.99	419

Oxidation potential values are determined in 5×10^{-4} mol L⁻¹ CH₂Cl₂ solution.

 $E_{1/2}^{ox} = 1/2 (E_p^a + E_p^c)$, potential values are reported versus Fc/Fc⁺. E_{gs} are estimated from the onset wavelength of the optical absorption bands.

^d HOMO energy levels are deduced from the equation HOMO = $(-4.8-E_{1/2}^{\alpha})$ eV. ^e LUMO energy levels are obtained from the equation LUMO = HOMO + E_{g} .

^f Temperatures with 5 wt % loss.

9-yl)biphenyl (CBP) is inserted between them. Here, relative high doping levels of 3 wt% and 6 wt% for **FNIb** are used according to the PL QY measurement results, so that a compromise between adequate luminescence sites for carrier recombination and minor concentration quenching could be reached, and devices I and II represent OLEDs with **FNIb** blending ratio of 3 wt% and 6 wt%, respectively. The relative energy level alignment of the devices and the molecular structure of the chemicals used are shown in Fig. 7.

Under driven voltages of 7–13 V, the two devices show analogous EL spectra (vide ESI), thus their EL spectra at 7 V are shown in Fig. 8. The λ_{ELmax} and the CIE coordinates of the two devices are 608 nm and 615 nm, and (0.59, 0.43), (0.60, 0.40), respectively. Compared to the corresponding PL spectra of the host/guest blended films, the λ_{ELmax} of the devices are slightly red-shifted (~10 nm), yet the EL spectra are broadened considerably. Taking into account that the emission color of **FNIb** is closely dependent on the environment polarity, and the EML of the OLEDs is as thin as 20 nm, the carrier recombination may occur not only within the EML, but also at the CBP/EML or EML/Bphen interfaces, which may account for the increased full-width at half maximum (FWHM) of the EL spectra of the devices [60–62].

The current density-voltage-luminance (J-V-L) characteristics of the devices are shown in Fig. 9, and the representative data are summarized in Table 4. The turn-on voltages ($V_{turn-on}$) of device I



Fig. 8. EL spectra of device I, II, III and IV (driven voltage: 7 V).

and II are 5.2 V and 4.1 V, respectively, and in addition to its lower $V_{turn-on}$, device II shows higher current at similar driving voltages (<13 V) relative to device I. The maximum brightness (L_{max}) and current efficiencies (LE_{max}) of devices I and II are 4220 and 6250 cd



Fig. 7. Device configuration and energy band diagram of the OLEDs, and the molecular structures of the compounds used.



Fig. 9. Current density-voltage-luminance (J-V-L) characteristics of devices I, II, III and IV.

 m^{-2} , and 1.74 and 3.13 cd A^{-1} , respectively. Obviously, device II shows much better EL performance. As compared to CBP, Bphen and **4CzTNA**, **FNIb** possesses both higher-lying HOMO and lower-lying LUMO, with increasing concentration of **FNIb**, the holes and electrons should not only be injected into **4CzTNA**, but also be injected directly into **FNIb**, therefore, the better performance of device II may be attributed to the presence of more adequate luminescence sites for carrier recombination in the device [63–65], and the unapparent concentration quenching of **FNIb** even at a high doping-level of 6 wt% as well (Fig. 10).

To evaluate if **4CzTNA** is a better host material than Alq₃ for **FNIb**, a reference device III using Alq₃ as host was also fabricated with a doping level at 6 wt%. The λ_{ELmax} and CIE coordinates of device III are 635 nm and (0.62, 0.38), and the L_{max} and LE_{max} are 1160 cd m⁻² and 0.75 cd A⁻¹, respectively. The absence of emission from Alq₃ in device III suggests effective energy transfer and/or charge carrier trapping on the guests during the EL emission procedure. It is noteworthy that the λ_{ELmax} of device III is much redshifted (19 nm) compared to the λ_{PLmax} of the corresponding blended film, in fact, it is even comparable to the λ_{PLmax} of the neat film of **FNIb** (632 nm). Compared to device II with similar doping-level, the performance of device III is much inferior, suggesting that for **FNIb**, **4CzTNA** is a much better host material than Alq₃.

In order to investigate the potential of **FNIb** for fabricating more heavily-doped OLEDs, a non-doped device IV with structure of ITO/ NPB (30 nm)/**FNIb** (20 nm)/Bphen (40 nm)/Mg:Ag (200 nm) was also constructed. The λ_{ELmax} of device IV locates at 633 nm, with CIE coordinates of (0.63, 0.37), which is quite analogous to the λ_{PLmax} of the neat film of **FNIb**. The L_{max} and LE_{max} of device IV are 3520 cd m⁻² and 0.55 cd A⁻¹, respectively. In comparison with device I and II, device IV shows higher current at similar driving voltages, indicative of the efficient carrier trapping inside the **FNIb** layer. Although compared to device I and II, the performance of device IV is much poorer, it displays negligible roll-off under a wide range of driving current density of 0–200 mA cm⁻², and its LE_{max} is

EL performance of the OLEDs using FNIb as guest.



Fig. 10. Luminance efficiency-current density characteristics of devices I, II, III and IV.

obtained at relatively high luminance of 1180 cd m^{-2} , indicating that **FNIb** might be a promising guest for fabrication of more heavily-doped OLEDs. Moreover, the *LE* of device IV is even higher than that of device III under current density of >50 mA cm⁻¹, confirming that Alq₃ is not an appropriate doping matrix for **FNIb**.

It should be pointed out that the PL QYs of the **FNIb**-based active layers used here are still not quite satisfied, which may eventually limit the device efficiency. Nevertheless, we believe that the PL QYs can be improved by utilizing other host materials instead of **4CzTNA**. Moreover, the device structure, doping level, and layer thickness used here have not been optimized for either low driven voltage or high efficiency, thus much improved EL performance should be expected after further optimization has been carried out on these issues.

4. Conclusions

By incorporating a diphenylfluorenylamino donor moiety into 7*H*-benzimidazo[2,1-*a*]benzo[*de*]isoquinolin-7-one acceptor segment through an ethenylene bridge, two red D- π -A luminogens have been successfully constructed. One of them (**FNIb**) was found to be AEE-active, which makes it a prospective candidate as a guest to fabricate heavily-doped red OLEDs. In addition, **4CzTNA** bearing naphthalimide acceptor subunit and carbazole donor subunit is also constructed as a new host material for **FNIb**, so that an efficient energy transfer pair of **FNIb/4CzTNA** could be achieved. Using **FNIb/ 4CzTNA** guest/host blending system as emissive layer, an efficient heavily-doped (6 wt%) OLED has been demonstrated, with maximum brightness of 6250 cd m⁻² and current efficiencies of 3.13 cd A⁻¹, respectively. Whereas the analogous OLED employing Alq₃ instead of **4CzTNA** as the host exhibits much inferior EL performance, which may be ascribed to the poor energy transfer

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	$V_{turn-on}^{a}$	$L_{\rm max} ({\rm cd} {\rm m}^{-2})^{ {\rm b}}$	$LE_{\rm max}$ (cd A ⁻¹) ^c	$PE_{\rm max}$ (lm W ⁻¹) ^c	$\lambda_{ELmax} (nm)$	FWHM (nm)	CIE (<i>x</i> , <i>y</i>)
Device I	5.2	4220 (13.9)	1.74 (2.8, 5.5)	0.99 (2.8, 5.5)	608	113	(0.59, 0.43)
Device II	4.1	6250 (14.0)	3.13 (1.2, 4.1)	2.40 (1.2, 4.1)	615	112	(0.60, 0.40)
Device III	5.2	1160 (13.6)	0.75 (4.5, 5.8)	0.41 (4.5, 5.8)	635	126	(0.62, 0.38)
Device IV	4.5	3520 (14.4)	0.55 (1185.6, 10.7)	0.24 (10.0, 5.3)	633	113	(0.63, 0.37)

^a Recorded at 1 cd m^{-2} .

^b Data in parentheses are the corresponding driven voltages (V).

^c Data in parentheses are the corresponding EL brightness (cd m⁻²) and driven voltages (V).

efficiency between Alq₃ and **FNIb**. All these preliminary results suggest that **FNIb** should be a promising guest candidate for fabrication of heavily-doped red OLED, and the design of appropriate host/guest energy transfer pair is of extremely importance with respect to the enhancement of device performance.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.08.021.

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