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Red non-doped electroluminescent dyes based on arylamino fumaronitrile derivatives

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1. Introduction

Red color is an indispensable component in many applications such as full color organic light-emitting display and anti-counterfeit technology. Usually red fluorescent molecules are either polar, such as electron-donor pyran-containing compounds [1,2], or non-polar but extensively π -conjugated, such as porphyrin-type macrocyclic compounds [3,4]. Many red emitters are highly emissive in solution, e.g. N, N-bis{4-[2-(4-dicyano-methylene-6-methyl-4H-pyran-2-yl) ethylene]phenyl}aniline (BDCM) [5] and 4-(di-cyanomethylene)-8methyl-2-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizin-9-yl) ethenyl]-5,6,7,8-tetrahydro-4H-1-benzopyran (DCMTHBP3) [6]. However, due to the dipole-dipole interaction and extensively delocalized π -conjugation, these red fluorescent materials are prone to aggregation and crystallization in their solid state which leads to concentration quenching [7]. These limit their usage in light-emitting devices only as a dopant. Their optimum dopant concentration is often low and the effective doping range is very narrow [8]. OLEDs based on dopant are more difficult to adapt for mass production in practice than those based on non-doped host emitter. Red fluorescent materials as non-doped host emitters are growingly attractive [9-11].

ABSTRACT

A diarylamine, 2-(phenylamino)-9,9-diethylfluorene and three red fluorescent dyes based on arylamino fumaronitrile derivatives, bis(4-(*N*-(1-naphthyl)phenylamino)-phenyl)fumaronitrile (1-NPAFN, **5a**), bis (4-(*N*-(2-naphthyl)phenylamino)phenyl)-fumaronitrile (2-NPAFN, **5b**) and bis(4-(*N*-(9,9-diethyl-2-fluorenyl)phenylamino)-phenyl)fumaronitrile (EFPAFN, **5c**), were prepared. The red dyes showed strong red photoluminescence upon excitation which centered at around 635, 650, 658 nm for 1-NPAFN, 2-NPAFN and EFPAFN in solid film respectively. Fluorescence concentration quenching of red dyes was suppressed. Thermal stability and energy levels were also measured. Multilayer non-doped electroluminescent devices were fabricated using the red dyes (**5b**, **5c**) as red emitters. Device performance kept relatively constant at a wide current density level in the range of 20–150 mA/cm².

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The first type of nondoping red materials is built with triarylamine units, such as anthracen-9-yl-(8-{4-[anthracen-9-yl-(4-ethylphenyl) amino]-phenyl}-benzo[a]-aceant-hrylen-3-yl)-(4-ethylphenyl)amine (ACEN1) [12] and 3-(N-phenyl-N-p-tolylamino)-9-(N-p-styrylphenyl-*N*-*p*-tolylamino)perylene [(PPA)(PSA)Pe] [9], which enhances the amorphous property and then fluorescent intensity in solid. However, this type of materials normally loses balance on transportation of hole and electron. The second type refers to the fluorophores with donor-acceptor groups having a pair of antiparallel dipoles, such as 2-(4-{1-cyano-2-[4-(4-methoxyphenyl-phenylamino)phenyl]-vinyl} phenyl)-3-[4-(4-methoxyphenyl-phenylamino)phenyl]acrylonitrile (D-CN) [13], bis(4-(N-(1-naphthyl)-phenylamino)phenyl)fumaronitrile (NPA FN) [14], 4,7-bis(5-(3,5-bis-(diphenylamino)phenyl) thien-2-yl)benzo[1,2,5]thiadiazole (btza1) [15], N-methyl-3,4-bis (4-(*N*-(1-naphthy)-phenylamino)phenyl)maleimide (NPAMLMe) [16], 2,3-bis(N, N-1-naphthyl-phenylamino)-N-methylmaleimide (NPAMLI) [17], isophorone dye D-3 with indoline unit as electron donor [18]. Fluorescence concentration quenching in solid can be suppressed due to dipole-dipole interaction. NPAFN [19] is rare material with the bulky and nonplanar arylamino substituents which reduce molecular interactions and PL quenching. Moreover, it shows the property of aggregation-induced emission (AIE) [20], PL emission in solid is much brighter than in solution.

In this work, three red fluorescent dyes based on arylamino fumaronitrile derivatives, bis(4-(*N*-(1-naphthyl)-phenylamino)phe nyl)fumaronitrile(1-NPAFN, **5a**), bis(4-(*N*-(2-naphthyl)phenylamino)





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phenyl)fumaronitrile (2-NPAFN, **5b**) and bis(4-(*N*-(9,9-diethyl-2-fluorenyl)phenylamino)phenyl)fumaronitrile (EFPAFN, **5c**), were prepared. The steric hindrance and donor-electron behavior from the naphthyl and fluorenyl groups contributed to restricting intermolecular interaction in 2-NPAFN (**5b**) or EFPAFN (**5c**) and emitting strong luminescence in aggregates or solid states. Photoluminescence (PL), thermal stability and energy levels of the materials were investigated. The multilayer electroluminescent devices with 2-NPAFN (**5b**) or EFPAFN (**5c**) as non-doped emitting layers were fabricated and characterized.

2. Experimental

2.1. Materials

Fluorene, Pd(OAc)₂, tris(*tert*-butyl)phosphine (P(*t*-Bu)₃), bis(2-(diphenylphosphino)-phenyl)ether (DPEphos), *N*-phenyl- α -naph-thylamine, *N*-phenyl- β -naphthylamine, Cs₂CO₃, sodium *tert*-butoxide were purchased from Acros Organics. Chemicals and solvents were used as received in the highest commercially available grade unless described otherwise. Diethyl ether, toluene, tetrahydrofuran (THF) was refluxed with sodium and benzophenone, and purified with distillation. Dimethylsulfoxide (DMSO) was purified through distillation at a reduced pressure.

2.2. Synthetic procedures

2.2.1. 9,9-Diethylfluorene (1) [21]

A synthetic procedure to 9,9-diethylfluorene **(1)** was similar to that reported in reference [21], but with a diluted DMSO solution. To a solution of fluorene (50 g, 0.30 mol) in DMSO (500 ml), powdered potassium hydroxide (84 g, 1.5 mol) and potassium iodide (2.4 g, 0.014 mol) were added with mechanical stirring in cold water bath. Bromoethane (64 ml, 0.84 mol) was added over a period of 50 min. The mixture was stirred at 10 °C overnight. It was then diluted with water (800 ml) and extracted with dichloromethane (300 ml, twice). The organic layer was dried over MgSO₄. Volatiles were removed and distilled under reduced pressure to afford pale yellow oil. Yield 57.7 g (86.4%). mp 29–30 °C. MS: 223.03 (M⁺ + 1) (calcd. for C₁₇H₁₈, 222.14).

2.2.2. 2-Bromo-9,9-diethylflurene (2) [22]

To a solution of 9,9-diethylfluorene (20 g, 0.09 mol) in dichloromethane (120 ml), a solution of bromine (5.6 ml) in dichloromethane (30 ml) was added under stirring at room temperature. The mixture kept stirring for 4 h and was washed with water (300 ml), dried and concentrated. The crude product was distilled at $156-163 \ ^{\circ}C/2 \ mm (17.2 \ g, 63.4\%). \ m.p. 52-53 \ ^{\circ}C.$

FT-IR (KBr pellet, cm⁻¹): 2960, 2912, 2873, 2846, 1601, 1570, 1440, 1406, 1375, 1257, 1110, 1060, 1002, 873, 819, 781, 763.

¹H NMR (400 MHz, CDCl₃), δ (ppm):0.30–0.34 (m, 6H), 1.98–2.03 (m, 4H), 7.32–7.34 (s, 3H), 7.44–7.46 (m, 2H), 7.55–7.57 (d, 1H), 7.66–7.68(d, 1H).

2.2.3. 2-(Phenylamino)-9,9-diethylfluorene (3) [23,24]

To a three-necked flask aniline (54 mmol), Palladium acetate (0.22 mmol), DPEphos (0.337 mmol), 13.5 g 2-bromo-9,9-diethyl-fluorene (45 mmol) and 18 ml of toluene were added. The mixture was deoxygenated. After stirring for 20 min sodium *tert*-butoxide (6.1 g, 63 mmol) was added in one portion. The flask was purged with nitrogen, and the mixture was heated with stirring to 85 °C for 24 h. The mixture was cooled to room temperature, quenched by the addition of water (45 ml), extracted with dichloromethane (45 ml), and washed with brine. The organic layer was dried over anhydrous MgSO₄, filtered. The solvent was removed under reduced pressure.

The crude product was purified by flash chromatography on silica gel eluting with 1:2 hexanes/dichloro-methane, the solvent was removed in vacuum. A pale white solid was obtained (11.1 g, 78.7%).

FT-IR (KBr pellet, cm⁻¹): 3411, 3045, 2961, 2926, 2872, 2856, 1599, 1506, 1454, 1414, 1374, 1352, 1312, 1263, 1242, 1181, 1137, 1074, 1022, 864, 824, 757, 735, 691, 577, 505, 488, 462, 414.

¹H NMR (400 MHz, CDCl₃), δ (ppm): 0.363–0.399 (6H), 1.937–2.047 (4H), 7.105–7.61 (12H). ¹³C NMR (CDCl₃), δ = 151.4, 149.2, 129.3, 126.7, 125.8, 122.6, 120.5, 120.3, 118.6, 117.2, 117.1, 112.7, 55.8, 32.7, 8.48. MS: 314.3 (M⁺ + 1) (calcd. for C₂₃H₂₃N, 313.4).

2.2.4. Bis(4-bromophenyl)fumaronitrile (4) [25]

A mixture of 4-bromophenylacetonitrile (4.86 g, 24.8 mmol) and iodine (6.35 g, 25 mmol) was purged with N₂ and dry diethyl ether (100 ml) was injected *via* syringe. A solution was cooled to -78 °C. Sodium methoxide (2.84 g, 52.6 mmol) and methanol (40 ml) was added slowly over a period of 30 min and stirred for 40 min. Then the reaction solution was put to ice-water bath with mechanical stirring and kept at 0 °C for a further 4 h. 3–6% hydrochloric acid was added dropwise and the solution was filtered to isolate the precipitate, which was rinsed with cold methanol–water solution. Filtrate was concentrated further and a second crop of product was obtained. A pale yellow solid was given in a yield of more than 90%.

FT-IR (KBr pellet, cm⁻¹): 3096, 2220, 1585, 1488, 1396, 1245, 1074, 1007, 845, 816, 710, 665, 627, 573, 514.

¹H NMR (400 MHz, CDCl₃), δ (ppm):7.67–7.72 (m, 8H).

2.2.5. Bis(4-(N-(substituted)phenylamino)phenyl)fumaronitrile (**5a**, **5b**, **5c**) [15,26]

A mixture of bis(4-bromophenyl)fumaronitrile (0.787 g, 2.03 mmol), *N*-phenyl-substituted amine (4.47 mmol), Cs_2CO_3 (1.95 g, 5.98 mmol), toluene (13 ml) was degassed and purged with N₂. Pd/P (*t*-Bu)₃ catalyst had been prepared previously from Pd(OAc)₂ (0.0135 g, 0.06 mmol), P(*t*-Bu)₃ (0.36 g, 0.178 mmol) and toluene (4 ml) and added in glove box. The reaction mixture was degassed, purged with nitrogen again and heated at 110 °C for 24 h. The mixture was cooled to room temperature, water (30 ml) and dichloromethane (50 ml) were added accordingly. An organic layer was separated and washed with brine, dried over anhydrous MgSO₄ and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using 1:1 light petroleum/ dichloromethane as eluant, affording solid (**5a, 5b, 5c**).

Bis(4-(*N*-(1-naphthyl)phenylamino)phenyl)fumaronitrile (1-NP AFN, **5a**), an orange red solid, 41%.

FT-IR (KBr pellet, cm⁻¹): 3058, 2954, 2921, 2216, 1604, 1587, 1506, 1490, 1393, 1313, 1296, 1271, 1186, 1074, 1010, 827, 800, 775, 754, 696,

¹H NMR (400 MHz, CDCl₃), δ (ppm): 6.89–6.92 (d, 4H), 7.05–7.12 (t, 2H), 7.19–7.24 (m, 4H), 7.27–7.34 (m, 4H), 7.36–7.44 (m, 4H), 7.45–7.54 (m, 4H), 7.58–7.65 (d, 4H), 7.80–7.85 (d, 2H), 7.86–7.94 (m, 4H). Elemental analysis: calcd. for C₄₈H₃₂N₄: C, 86.72; H, 4.85; N, 8.43, found C, 86.41; H, 5.14; N, 8.50.

Bis(4-(*N*-(2-naphthyl)phenylamino)phenyl)fumaronitrile (2-NP AFN, **5b**), a red solid, 78.3%.

FT-IR (KBr pellet, cm⁻¹): 3057, 2958, 2923, 2216, 1627, 1588, 1506, 1489, 1465, 1357, 1296, 1265, 1253, 1188, 1025, 937, 854, 815, 754, 696, 684, 665.

¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.09–7.13 (d, 4H), 7.13–7.18 (m, 4H), 7.19–7.23 (d, 4H), 7.26–7.37 (m, 8H), 7.39–7.46 (m, 4H), 7.65–7.73 (m, 4H), 7.78–7.83 (d, 4H). Elemental analysis: calcd. for C₄₈H₃₂N₄: C, 86.72; H, 4.85; N, 8.43, found C, 86.51; H, 5.11; N, 8.52.

Bis(4-(*N*-(9,9-diethyl-2-fluorenyl)phenylamino)phenyl)fumaronitrile (EFPAFN, **5c**), a red solid, 82.8%.

FT-IR (KBr pellet, cm⁻¹): 3037, 2963, 2921, 2215, 1600, 1589, 1508, 1489, 1451, 1328, 1304, 1265, 1188, 1025, 827, 755, 737, 702.

 ^{1}H NMR (400 MHz, CDCl₃), δ (ppm): 0.339–0.375 (t, 12H), 1.91–1.99 (m, 4H), 7.07–7.17 (m, 10H), 7.18–7.24 (d, 4H), 7.27–7.36 (m, 10H), 7.62–7.67 (m, 4H), 7.68–7.73 (d, 4H).

Elemental analysis: calcd. for C₆₂H₅₂N₄: C, 87.29; H, 6.14; N, 6.57, found C, 87.16; H, 6.28; N, 6.68.

2.3. Measurement

Compounds synthesized were characterized using elemental analysis (Carlo Erba 1106), FT-IR (Shimadzu FT-IR 8400) and ¹H NMR spectroscopy (Bruker DMX-300), respectively. Mass Spectrometry analysis was measured on a Shimadzu LC-MS2010A. Cyclic voltammetry (CV) analyses were carried out by using Zahner Zennium. Thermogravimetric analysis (TGA) was performed on a Netzsch TG-209 under nitrogen flow. UV–vis absorption spectrum was obtained by using GBC Cintra 303 Spectrometer. Photoluminescence (PL) and excitation spectrum were recorded with Perkin Elmer LS-55 luminescence spectrometer.

2.4. Device fabrications and testing

Compounds 4,4'-bis(N-(1-naphthyl-N-phenylamino)biphenyl) (NPB), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), 1,3,5tris(N-phenyl-benzimidazol-2-yl)benzene (TPBi), LiF and Al were purchased from Acros Organics. NPB was used as hole-transporting layer, BCP as electron-transporting and hole-blocking layer, TPBi as electron-transporting layer, LiF/Al as cathode. 2-NPAFN and EFPAFN were used as the non-doped host emitter in the fabrication of red OLEDs. Indium tin oxide (ITO) glass substrate with a sheet resistance 25 Ω/\Box was (1) cleaned with detergents, deionized water, ethanol and isopropanol in an ultrasonic bath, (2) dried under nitrogen flow, and (3) treated with oxygen plasma for 5 min before use. The threelayer devices with configurations of device A ITO/2-NPAFN or EFPAFN (30 nm)/BCP (10 nm)/TPBi (30 nm)/LiF (0.5 nm)/Al and fourlayer devices with configurations of device B ITO/NPB (40 nm)/ 2-NPAFN or EFPAFN (30 nm)/BCP (10 nm)/TPBi (30 nm)/LiF (0.5 nm)/ Al were fabricated by sequential vacuum deposition of organic materials on pre-treated ITO. Current-voltage characteristic was measured using a Keithley 2410 source meter. Electroluminescence (EL) spectra were measured by using SPEX Fluolog-3 luminescence spectrometer or Acton CCD spectrometry. Device performances were measured at room temperature under ambient atmosphere.

3. Results and discussions

3.1. Synthesis and characterization

Synthetic routes to the three arylamino fumaronitrile derivatives based red dyes and the chemical structures were illustrated in Fig. 1. The diarylamine 2-(phenylamino)-9,9-diethylfluorene was synthesized with an efficient catalyst combination of Pd(OAc)₂/ DPEphos in presence of sodium tert-butoxide as base. For the arylation of primary anilines by aryl bromides, DPEphos was as effective a ligand as rac-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (rac-BINAP) and considerably more effective than 1,1'-bis(diphenylphosphino)ferrocene (DPPF) [23]. Three diarylamines, where were substituted with N-1-naphthyl, or N-2-naphthyl or N-9,9-diethyl-2fluorenyl groups, reacted with bis(4-bromophenyl)fumaronitrile in presence of $Pd(OAc)_2/P(t-Bu)_3$ and cesium carbonate as base to prepare corresponding dyes based on triarylamino fumaronitrile derivatives 1-NPAFN (5a), 2-NPAFN (5b), and EFPAFN (5c), respectively. The bulky and electron-rich P(t-Bu)₃, which accelerated elimination reactions, was widely used in preparation of triarylamines via palladium-catalyzed couplings with high yields [26].

3.2. Thermal stability

Thermal stabilities of 1-NPAFN (**5a**), 2-NPAFN (**5b**), EFPAFN (**5c**) were determined using thermogravimetric analysis (TGA) in nitrogen atmosphere (Fig. 2). Samples were heating up at a rate of 10 °C/min in a temperature range of 25–600 °C with a nitrogen flow. The starts of decompositions of **5a**, **5b** and **5c** were observed at around 409, 428 and 422 °C. The rates of weights remained for the samples were 0% at 485 °C for **5a**, 0% at 491 °C for **5b** and 21% at 473 °C for **5c**. Stabilities were improved for 2-NPAFN (**5b**) and



Fig. 1. A schematic diagram for chemical structures of intermediates and three arylamino fumaronitrile derivatives. Reagents and conditions are: (i) CH₃CH₂Br, KOH, DMSO, cold water bath, over 2.5 h; (ii) Br₂, CH₂Cl₂, rt; (iii) Aniline, Pd(OAc)₂, DPEphos(bis(2-(diphenylphosphino)phenyl)ether), toluene, sodium *tert*-butoxide, purged with nitrogen, 85 °C, 24 h. (iv) l₂, diethyl ether, NaOCH₃, CH₃OH; 30 min at -78 °C; 5 h at 0 °C; (v) *N*-phenyl-α-naphthylamine or *N*-phenyl-β-naphthylamine or *N*-phenyl-9,9-diethyl-2-fluorenylamine), Pd (OAc)₂, P(*t*-Bu)₃, toluene, Cs₂CO₃, 110 °C, 18 h.



Fig. 2. TGA curves of 1-NPAFN (5a), 2-NPAFN (5b), EFPAFN (5c).

EFPAFN (**5c**). It was expected that these dyes might perform better in their device applications.

3.3. Optoelectronic properties

UV—vis absorption spectra of 1-NPAFN (**5a**), 2-NPAFN (**5b**) and EFPAFN (**5c**) in solution were investigated as shown Fig. 3. Absorption from **5a**, **5b** and **5c** peaked at 288, 305 and 326 nm in high energy range and at 471, 487 and 497 nm in low energy range respectively. The replacement of *N*-2-naphthyl and *N*-9,9-diethyl-2-fluorenyl groups to the fumaronitriles extended the π -conjugation and resulted in bathochromic shifts in main absorption wavelength compared to *N*-1-naphthyl in 1-NPAFN (**5a**).

Photoluminescence (PL) of 1-NPAFN (**5a**), 2-NPAFN (**5b**) and EFPAFN (**5c**) in solid and solution were measured and shown in Fig. 4. Emission spectra of 1-NPAFN (**5a**), 2-NPAFN (**5b**) and EFPAFN (**5c**) in THF solution were generally broad and centered at 616, 650 and 657 nm respectively. PL spectra from **5a**, **5b** and **5c** in solid state peaked at 635, 650 and 658 nm respectively, in which emission of **5a** showed a 20 nm bathochromic shift from solution to solid while emissions of **5b** and **5c** were almost unchanged in different media.

The incorporation of N-2-naphthyl and N-9,9-diethyl-2-fluorenyl, bulky and electron-donating groups, in 2-NPAFN (**5b**) and



Fig. 3. UV-vis absorption spectra of 5a, 5b, 5c in a dilute THF solution.



Fig. 4. Emission spectra of 5a, 5b, 5c in solid film and dilute THF solution.

EFPAFN (**5c**) resulted in red shifts in both absorption and emission peaks in solution compared to *N*-1-naphthyl substitute in 1-NPAFN (**5a**). Bulky groups in both **5b** and **5c** contributed to reducing the molecular interaction, which minimized aggregation and hence the shifts in emissions in solid state.

3.4. Electrochemical properties

Energy levels (e.g. HOMO, LUMO) of 1-NPAFN (5a), 2-NPAFN (5b), EFPAFN (5c) (ferrocene shown in the inset) were investigated via redox reactions using cyclic voltammetry (CV) [27] (Fig. 5). Dichloromethane was used as a solvent in presence of tetra-n-butylammonium hexafluorophosphate (TBAPF₄)(0.1 mol/L) as supporting electrolyte. A Hg/Hg₂Cl₂ electrode was used as the reference electrode. A glass carbon rod was used as the working electrode, a platinum wire was used as the counter electrode. Ferrocene was used as a reference material. The first onset oxidation potentials (E_{onset}) were 1.03 eV for 1-NPAFN (5a), 0.95 eV for 2-NPAFN (5b) and 0.87 eV for EFPAFN (5c). As compared to NPAEF (2,7-bis(N-α-naphthyl-Nphenyl-amino)-9,9-diethylfluorine) in our previous work [28], the *E*onset of NPAEF was 0.55 V, which indicated that **5a**, **5b** and **5c** were more difficult to be oxidized. Eonset of the red dyes decreased (1-NPAFN (5a) > 2-NPAFN (5b) > EFPAFN (5c)) in accordance with the increasing of electron-donating ability of the substituent from 1-naphthyl, 2-naphthyl to fluorenyl groups at the nitrogen atoms.

HOMO levels (E_{HOMO}) were therefore calculated to be -5.47 eV for 1-NPAFN (**5a**), -5.39 eV for 2-NPAFN (**5b**) and -5.31 eV for EFPAFN (**5c**) respectively. LUMO levels (E_{LUMO}) of the dyes were estimated in combination with optical band gap, in which the latter was taken from absorption edge (E_g), to be 2.17 eV (571 nm) for 1-NPAFN (**5a**), 2.12 eV (584 nm) for 2-NPAFN (**5b**) and 2.05 eV (606 nm) for EFPAFN (**5c**). E_{LUMO} was calculated according to: $E_{LUMO} = E_{HOMO} + E_g$, i.e. -3.30 eV for 1-NPAFN (**5a**), -3.27 eV for 2-NPAFN (**5b**) and -3.26 eV for EFPAFN (**5c**). It can also be seen from above that incorporation of the group affect more strongly to HOMO level and less to LUMO level. The E_{HOMO} and E_{LUMO} of NPAEF were calculated to be -5.15 and -2.36 eV respectively [28], shifted upwards compared to **5a**, **5b** and **5c**. The changes in energy levels may be related to the electron-withdrawing butenedinitrile group.

3.5. Performance in electroluminescent devices

Electroluminescence of 2-NPAFN (**5b**) and EFPAFN (**5c**) were investigated. They were used as non-doped emitter in multilayer



Fig. 5. The cyclic voltammograms of 1-NPAFN (5a), 2-NPAFN (5b), EFPAFN (5c) (ferrocene shown in the inset) at the concentration 1 × 10⁻³ M in CH₂Cl₂. The scan rate was 50 mV/s.

OLEDs. Four devices were prepared with structures as follows: Device A1: ITO/2-NPAFN (30 nm)/BCP (10 nm)/TPBi (30 nm)/LiF (0.5 nm)/Al; Device B1: ITO/NPB (40 nm)/2-NPAFN (30 nm)/BCP (10 nm)/TPBi (30 nm)/LiF (0.5 nm)/Al; Device A2: ITO/EFPAFN (30 nm)/BCP (10 nm)/TPBi (30 nm)/LiF (0.5 nm)/Al; and Device B2: ITO/NPB (40 nm)/EFPAFN (30 nm)/LiF (0.5 nm)/Al; and Device B2: ITO/NPB (40 nm)/EFPAFN (30 nm)/BCP (10 nm)/TPBi (30 nm)/LiF (0.5 nm)/Al. The HOMO energy levels of 2-NPAFN (-5.39 eV) and EFPAFN

(-5.31 eV) lay much more above that of BCP (-6.7 eV). It formed

a barrier (>1.1 eV) for holes and blocked the holes to migrate from 2-NPAFN or EFPAFN to BCP. In contrast, the LUMO energy levels of 2-NPAFN (-3.27 eV) and EFPAFN (-3.26 eV) were below those of NPB (-2.3 eV) and BCP (-3.2 eV). It is feasible for electron to transport from BCP to the 2-NPAFN or EFPAFN. Hence the recombination took place in the 2-NPAFN or EFPAFN emitting layer.

EL spectra of these devices were measured as shown in Fig. 6. The devices were stable with respect to driving voltage. Emissions



Fig. 6. EL spectra of Device A1, B1, A2 and B2.

from Device A1 and Device B1 had their maxima at around 664 nm and 666 nm, red-shifted ~15 nm compared to its PL emission (650 nm) in the solid state. Emissions from Device A2 and Device B2 peaked at around 680 nm and 677 nm, red-shifted ~ 20 nm compared to its PL emission (658 nm) in the solid film. Both threeand four-layer devices showed pure red EL from 2-NPAFN or EFPAFN, indicating that recombination was located in 2-NPAFN or EFPAFN layer. The difference between PL and EL revealed that there was a certain degree of aggregation formation of 2-NPAFN or EFPAFN providing charge-trapped sites with lower energy. Upon increasing driving voltages, EL spectra were almost unchanged with a slight blue-shift when voltage bias increases from 11 V to 17 V. This is important to provide red non-doped OLEDs with improved performance. Red OLEDs with dopants reported to show color changed with increasing driving voltage [29].

Current density—voltage and luminance—voltage characteristics of the devices were given in Fig. 7. At a fix current density of 20 mA/ cm², corresponding driving voltages for Device A1, B1, A2 and B2 were 10.7, 14.0, 12.2 and 13.2 V respectively. At a given voltage, the current density of the four-layer device (Device B1, Device B2) was lower than that of the three-layer device (Device A1, Device A2).

Maximum luminances of Device A1, B1, A2 and B2 were measured to be 650, 1420, 1290 and 3370 cd/m^2 respectively at operating voltages between 20 and 21 V. Turn-on voltages of the devices were defined as the voltage needed to deliver a brightness of 1 cd/m^2 , which were 8V, 6.1V, 8.4V and 5.9V for Devices A1, B1, A2 and B2 respectively. Device B1 and B2 containing NPB as hole

injection layer performed better. Their luminance maxima were higher than those from Device A1 and A2 at same operating voltage.

Current efficiency or luminance efficiency (LE) and power efficiency (PE) vs current density characteristics of Device A1, B1, A2 and B2 were given in Fig. 8. Maxima of current efficiency and power efficiency were 0.18 cd/A and 0.057 lm/W for Device A1. 1.34 cd/A and 0.42 lm/W for Device B1. 0.51 cd/A and 0.11 lm/W for Device A2, 2.27 cd/A and 0.72 lm/W for Device B2 respectively. Device B1 and B2 improved both brightness and efficiency, indicating a better balance in charge injection with NPB hole injection layer, which ensured the recombination occurred within the emitting layer. A red EL was achieved with high intensity. This demonstrated the material property played an important role in determining the performance of the device. The steric hindrance in the naphthyl and fluorenyl groups restricted intermolecular interaction, where steric hindrance and donor-electron behavior were more effective for EFPAFN than that of 2-NPAFN. This suppressed fluorescence concentration quenching in solid state, which contributed to the high brightness and efficiency.

More interestingly devices A1 and A2 appeared to have constant current or power efficiencies when current density was varying in the rage of 20–150 mA/cm². The current efficiency and power efficiency of four devices exhibited a small decline even when current density increased to 150 or 300 mA/cm². These characteristics primarily indicated that the dyes were promising candidates for efficient red non-doped light-emitting materials.



Fig. 7. Current density and luminance vs voltage characteristics.



Fig. 8. Current efficiency and power efficiency vs current density characteristics.

4. Conclusions

Diarylamine 2-(phenylamino)-9,9-diethylfluorene were synthesized by Pd(OAc)₂/DPEphos. Three novel red dyes based on arylamino fumaronitrile derivatives, 1-NPAFN, 2-NPAFN and EFPAFN, as red organic non-doped electroluminescent materials in the presence of $Pd(OAc)_2/P(t-Bu)_3$ were prepared. Thermal decomposition temperatures of 1-NPAFN, 2-NPAFN, EFPAFN were determined at about 409, 428, 422 °C respectively. Photoluminescent emissions from 1-NPAFN, 2-NPAFN, EFPAFN centered at 616, 650, 657 nm in THF solution and at 635, 650, 658 nm in solid state. HOMO and LUMO energy levels were -5.47, -3.30 eV for 1-NPAFN, -5.39, -3.27 eV for 2-NPAFN and -5.31, -3.26 eV for EFPAFN. Threelayered (A1, A2) and four-layered (B1, B2), with additional NPB layer, electroluminescent devices were fabricated using 2-NPAFN and EFPAFN as non-doped emitting layers. All devices emitted red with peak luminance 650-1420 cd/m² for 2-NPAFN and 1290-3370 cd/ m² for EFPAFN. EFPAFN material and four-layered devices improved device performance. Additionally, devices with 2-NPAFN as emitting layer showed a relatively constant efficiency within the current density range of $20-150 \text{ mA/cm}^2$ and with almost no color changes. The results were exciting towards red organic non-doped lightemitting devices.

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