Readily synthesised arylamino fumaronitrile for non-doped red organic light-emitting diodes

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Bright (maximum 10034 cd m⁻², 455 cd m⁻² at 20 mA cm⁻²) and efficient (maximum 2.4% at 4 mA cm⁻²) red (λ_{max}^{el} 634–636 nm) organic light-emitting diodes employ arylamino-substituted fumaronitrile as the novel host emitter, which is readily prepared and easily purified.

Organic light-emitting diode (OLED)-based displays have started entering the market of consumer electronics, which has been dominated for the past three decades by the liquid-crystal display (LCD).¹ Small OLED displays can be found in some name-brand car stereos, mobile phones, electric shavers, and digital cameras. Red OLEDs are an indispensable component in full colour displays. However, due to their chemical structure. red light-emitting materials have to be used as dopants in OLED fabrication.²⁻⁴ This is because fluorophores showing red emission either have extended π -conjugation or bear donoracceptor polar substituents. Both types of red fluorophore are prone to crystallization in the solid state and hence are highly concentration quenching. Realistically, OLEDs based on dopant emitters are more difficult to adapt for mass production processes than those based on non-doped host emitters, considering the reproducibility of the optimum doping level that requires careful manufacture control.4

Satisfactory non-doped pure red OLEDs are extremely rare.^{3–5} Herein, we report a new red fluorophore, NPAFN (bis(4-(N-(1-naphthyl)phenylamino)phenyl)fumaronitrile), suitable for high performance non-doped red OLEDs. Significantly, NPAFN can be easily prepared in a simple two-step procedure (Scheme 1) with overall isolated yield >45%. Moreover, the whole preparation process can be performed without chromatography, which is an advantage for mass production. This is probably one of the first red fluorophores, either as a red dopant or a non-doped host emitter, having such convenient accessibility. Synthetically, the starting material 4-bromophenylacetonitrile used in the synthesis of NPAMLMe (N-methyl-3,4-bis(4-(N-(1-naphthyl)phenylamino)phenyl)maleimide), one of the first novel non-doped red OLED materials discovered by us, is also used in the two-step preparation of NPAFN (Scheme 1).⁴ Slight but critical modification of the synthetic procedure of NPAMLMe can lead to the easy preparation of dibromo-substituted fumaronitrile Br₂FN (bis(4bromophenyl)fumaronitrile). By controlling the concentration of 4-bromophenylacetonitrile to ca. 0.25 M (near the saturation point) and 2 equiv. of the base (NaOCH₃) in the reaction, the product Br₂FN was obtained in almost quantitative yield (>90%).^{6,7} The beauty of the **Br₂FN** synthesis was that the analytically pure product could be isolated by simple suction



Scheme 1 Reagents and conditions: i, I₂ (1 equiv.) in diethyl ether, NaOCH₃ (2.1 equiv.) in CH₃OH, 30 min at -78 °C, 4 h at 0 °C, then 3% HCl_(aq) (90% by filtration); ii, *N*-phenyl-1-naphthylamine (2.2 equiv.) in toluene, Pd(OAC)₂ (3%), P(*t*-Bu)₃ (9%), Cs₂CO₃ (3 equiv.), 110 °C, 24 h (50% by sublimation).

filtration of the reaction solution. The second step in the preparation of NPAFN involved the Pd-catalysed amination of Br_2FN . The reaction conditions were modified from those reported by Yamamoto et al. in the high-yield synthesis of triarylamine from diarylamine.8 However, the common base, sodium or potassium tert-butoxide, used in the reaction caused undesired reaction of the cyano group of NPAFN. Other bases, such as sodium hydroxide and sodium hydride, also failed to yield reasonable amounts of NPAFN. After several attempts, we found Cs_2CO_3 could accomplish the amination of $Br_2F\hat{N}$ in forming NPAFN with the most satisfactory result. In the isolation of NPAFN, we encountered purification problems if column chromatography was used. NPAFN seems to isomerise easily into its Z-isomer upon contact with silica gel or aluminium oxide. The purification problem was solved by subjecting the product mixture to train sublimation, the process we used for the purification of other OLED materials, before the device fabrication. The desired NPAFN was isolated cleanly from other reaction side products by sublimation (at 10^{-5} Torr, with the zone temperatures set at 310, 190, and 150 °C).

NPAFN is unusual because it is brightly fluorescent but only in the solid state. The fluorescence of **NPAFN** is virtually invisible in common organic solvents. The solution fluorescence of **NPAFN** was barely observed in nonpolar solvents such as benzene ($\lambda_{max}^{em} = 586$ nm) and hexane ($\lambda_{max}^{em} =$ 545–560 nm). This may be due to the easily exchangeable multiple conformations of the nonplanar benzene and naphthalene rings of the molecule. The twin dipolar nature also contributes to the non-radiative relaxation of **NPAFN** in the excited state. However, a full understanding of the unusual fluorescence properties remains to be developed.⁹ In the solid state, bright orange-red fluorescence with λ_{max}^{em} at 616 nm was detected for **NPAFN** (see Fig. 1 for the photoluminescence, PL, spectrum).

Nevertheless, the strong solid-state fluorescence observed for **NPAFN** is reflected in the thermal analysis data. In differential scanning calorimetry (DSC) thermograms (Fig. 2), the glass transition temperature (T_g) around 109 °C was detected for **NPAFN** in either heating or cooling cycles (10 °C/min). It is notable that the melting temperature (260 °C) occurs only in the first heating cycle and no exothermic crystallization signal appears regardless of repeated heating and cooling of **NPAFN**.



Fig. 1 EL spectra of OLED device, with NPB (thin solid line) and without NPB (dotted line). The PL spectrum of **NAPFN** solid film (thick solid line), which was prepared by vacuum deposition, was taken by using 420 nm as the excitation energy.



Fig. 2 DSC thermograms of **NPAFN** with sequential heating and cooling. The signal of the first heating thermogram is reduced two-fold to be accommodated in the figure and the cooling thermograms are enlarged twofold for clarity.

The DSC characteristics imply there is no strong contact of **NPAFN** molecules in the solid state and **NPAFN** shows limited tendency to crystallize.

The bright solid-state fluorescence renders NPAFN quite possible to be used as the non-doped host emitter in the fabrication of red OLEDs. Two OLED devices with configurations ITO/NPB(40 nm)/NPAFN(30 nm)/BCP(10 nm)/TPBI (30 nm)/MgAg and ITO/NPAFN(50 nm)/BCP(10 nm)/TPBI (30 nm)/MgAg were fabricated by sequential vacuum deposition of organic materials on pre-treated ITO (indium tin oxide)-coated glass.¹⁰ Despite the difference of the NPB layer, red electroluminescence (EL) of the both OLED devices became visible at the about the same driving voltage between 3 and 4 V. The EL of the OLED had emission maxima (λ_{max}^{el}) around 634 and 636 nm (Fig. 1), although the spectra were broadened and redshifted (+18–20 nm) compared with the PL of the solid film. Usually, such a difference between PL and EL indicates there is a certain degree of aggregation formation of NPAFN providing charge-trapped sites with lower energy.11 Nevertheless, both EL spectra corresponded to coordinates (x = 0.64, y = 0.36) of the 1931 CIE (Commission Internationale de l'Eclairage) chromaticity diagram, indicative of a red EL comparable with (x = x)0.64, y = 0.33) of the National Television System Committee (NTSC) standard red colour. The intensity of EL reached 10034 cd m^{-2} and 9359 cd m^{-2} for the devices with and without NPB, respectively, as the maximum values recorded at 14.5 V and over 1000 mA cm⁻² (Fig. 3). These are the two brightest nondoped red OLEDs reported so far. More practical, at a low current density of 20 mA cm⁻², the device without NPB still emitted red EL with intensity as high as 392 cd m^{-2} , which is bright enough for active-matrix-driven OLED displays. Moreover, at a current density of 20 mA cm⁻² (about 6.9 V), the device reached 1.8% external quantum efficiency (or 2.0 cd A^{-1} photometric efficiency or 0.9 lm W^{-1} power efficiency). The performance of the device without NPB is even better at low current density. The external quantum efficiency was as high as 2.4% (or 2.5 cd A^{-1} photometric efficiency or 1.7 lm W^{-1} f power efficiency) at 4.5 V and 4 mA cm⁻². At 20 mA cm^{-2} (about 5.7 V), the device emitted red EL with intensity 455 cd m^{-2} , brighter than the device containing the NPB layer.



Fig. 3 EL intensity and external quantum efficiency of OLED, ITC/NPB(40 nm)/NPAFN(30 nm)/BCP(10 nm)/TPBI(30 nm)/MgAg (solid line) and ITC/NPAFN(50 nm)/BCP(10 nm)/TPBI(30 nm)/MgAg (dotted line).

Performance-wise, the non-doped red OLED reported here is comparable with a previously reported non-doped red OLED based on **NPAMLMe**.⁴ However, the synthesis and purification of the red material **NPAFN** is even more convenient than those of **NPAMLMe**. This makes **NPAFN** more commercially significant than **NPAMLMe** to be employed in the fabrication of non-doped red OLEDs.

In summary, we have developed a new red fluorophore NPAFN as a rare host emitter in non-doped red OLEDs. NPAFN is weakly emissive in solution but highly fluorescent in the solid state and its photophysics are worth further exploration. The easy synthesis and purification of NPAFN make nondoped red OLEDs more feasible than ever. The performance of the NPAFN-based red OLED is comparable with or better than most fluorophore-based, dopant or non-doped red OLEDs, although there is plenty of room for improvement. Conceivable tests including the thickness of the NPAFN and BCP layers, different hole-blocking and electron-transporting materials other than BCP and TPBI, respectively, are underway. For the material itself, the diarylamino moieties of NPAFN can be easily replaced with various readily available substituents through synthesis and the fluorescence and amorphous properties can thus be optimised.

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Notes and references

† Characterization data of **NPAFN**: An orange red solid with red fluorescence purified from train sublimation once. ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.94 (d, 2H, J = 8.1Hz), 7.91 (d, 2H, J = 8.5Hz), 7.87 (d, 2H, J = 8.3Hz), 7.61 (d, 4H, J = 9.1Hz), 7.56–7.47 (m, 4H), 7.45–7.39 (m, 4H), 7.33–7.27 (m, 4H), 7.25–7.21 (m, 4H), 7.10 (t, 2H, J = 7.3Hz), 6.92 (d, 4H, J = 9.1Hz). ¹³C NMR (100 MHz, CD₂Cl₂): δ (ppm) 151.5, 147.0, 142.6, 140.0, 131.6, 130.4, 130.1, 129.2, 128.2, 128.1, 127.4, 127.0, 124.8, 124.7, 124.6, 124.2, 121.5, 119.0, 118.2. FAB-MS: calcd MW 664; m/z = 664. Anal. Found (calcd) for C₄₈H₃₂N₄: C 86.61(86.72), H 4.80(4.85), N 8.23(8.43)%.

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