Solid-state highly fluorescent diphenylaminospirobifluorenylfumaronitrile red emitters for non-doped organic light-emitting diodes†

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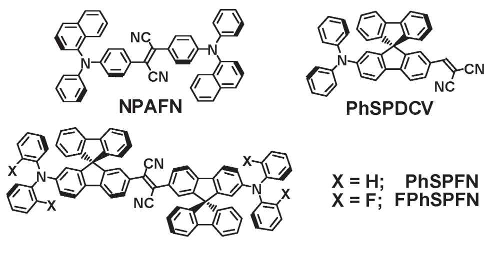
Bright (maximum 11 000 cd m^{-2} and 500 cd m^{-2} at 20 mA cm^{-2}) and efficient (maximum external quantum efficiency of 3.1% at 1 mA cm^{-2}) red (CIE, x = 0.66, y = 0.34) organic light-emitting diodes (OLEDs) employ arylaminospirobifluorene-substituted fumaronitriles as the novel non-dopant red emitter.

Non-doped light-emitting red fluorophores have attracted increasing attention because they are unconventional and could be the materials solution to the troublesome red organic light-emitting diodes (OLEDs), which are largely fabricated by a hard-to-control doping process.[1] Consistent control of the doping process, which requires a low and narrow dopant concentration, is a challenging task for high speed and volume production. With very few exceptions, red fluorophores are flat molecules with extended π-conjugation or they are π-conjugated bearing donor–acceptor substituents with a strong dipole. Such red fluorophores are prone to aggregation and thus fluorescence quenching in the solid state. Red fluorophores with limited solid-state fluorescence quenching are highly desirable but good ones are extremely rare.[1–7]

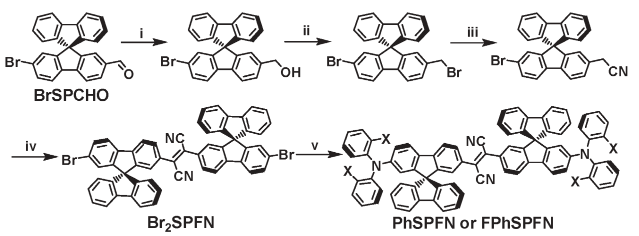
Recently, we have reported fumaronitrile **NPAFN**[3] and spirobifluorene **PhSPDCV**[5] (Scheme 1), two exceptionally good red fluorophores for non-dopant red OLEDs. These two red fluorophores exhibited relatively high solid state fluorescence quantum yields (ϕ_fs) of ~ 20 and 33%, respectively. The antiparallel dipolar arrangement of fumaronitrile and the non-planar bulky π-conjugation of spirobifluorene are two ideal moieties to prevent the molecules from close packing. Such molecules have been demonstrated to form light-emitting materials with limited fluorescence quenching and beneficial to the non-doped red OLEDs. Herein, we report two new red fluorophores, **PhSPFN** and **FPhSPFN** (Scheme 1), bearing a hybrid structure of **NPAFN** and **PhSPDCV**. Their synthesis and photophysical/electrochemical characterization are given. Particularly, we took an '*ortho*-substituent' approach using a diphenylamino electron donor in tuning the fluorescence color and fluorescence quantum efficiency. High performance non-dopant red OLEDs were achieved for the new fumaronitrile red fluorophores and this verified our successful molecular design.



Scheme 1 Chemical structures of **NPAFN**, **PhSPDCV**, **PhSPFN**, and **FPhSPFN**.

PhSPFN or **FPhSPFN** can be efficiently synthesized in five steps from a known starting material **BrSPCHO** (Scheme 2).[5] Two steps of the textbook functional group transformation, aldehyde → alcohol and alcohol → halide, brought **BrSPCHO** almost quantitatively to the benzyl bromide derivative. NaCN nucleophilic substitution converted the functionality of benzyl bromide to benzyl cyanide in moderate 50% isolated yields. The key cyano compound was readily dimerized by sodium methoxide and iodine to form bis(2-bromospirobifluoren-6-yl)fumaronitrile (**Br$_2$SPFN**) in a fashion very similar to the high-yield synthesis of **Br$_2$FN** (bis(4-bromophenyl)fumaronitrile), the synthetic precursor of **NPAFN**.[8] Similar to the synthesis of **NPAFN**, **PhSPFN** and **FPhSPFN** were readily obtained by the Pd-catalysed amination of **Br$_2$SPFN** with diphenylamine and bis(2-fluorophenyl)amine in good to excellent yields, 90 and 73%, repectively.

Since both **PhSPFN** and **NPAFN** are nearly nonfluorescent in solution, we took **FPhSPFN** for solution fluorescence in order to probe the intramolecular charge-transfer (ICT) nature of such a donor–acceptor-substituted fluorophore. **FPhSPFN** exhibits solvatochromic behavior similar to that of **PhSPDCV** in various solvents: 558 nm in hexanes, 611 nm in 1,4-dioxane, and 647 nm in



Scheme 2 *Reagents and conditions:* i) NaBH$_4$, THF, RT, 2 h (99%); ii) PBr$_3$, dichloromethane, RT, 1 h (99%); iii) NaCN, DMSO, 80 °C, 12 h (50%); iv) 3 M NaOMe, I$_2$, ether, THF, −78 °C, 30 min (96%); v) diphenylamine or bis(2-fluorophenyl)amine, Cs$_2$CO$_3$, Pd(OAc)$_2$, P(t-Bu)$_3$, *o*-xylene or toluene, 120 °C, 12 h (90% for **PhSPFN**; 73% for **FPhSPFN**).

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chloroform. However, the extent of the solvatochromic shifting of **FPhSPFN** is relatively small in comparison with the 500–624 nm of **PhSPDCV** in the same three solvents.[5] This can be rationalized by the fact that **FPhSPFN** has a smaller dipole moment than **PhSPDCV** both in ground and excited states due to the antiparallel aligned intramolecular dipole of **FPhSPFN**. Both **PhSPFN** and **FPhSPFN** can be identified as authentic red or deep red fluorophores because they exhibit solid-state red fluorescence $\lambda_{\max}^{f}$ in the long wavelength of 685 and 646 nm, respectively. These wavelengths of solid-state fluorescence are relatively long compared with 616 nm of orange–red **NPAFN**. The long $\lambda_{\max}^{f}$ of both **PhSPFN** and **FPhSPFN** is mainly attributed to the longer π-conjugation of the spirobifluorene moiety than that of a benzene ring of **NPAFN**. On the other hand, comparing **FPhSPFN** with **PhSPFN**, the shorter $\lambda_{\max}^{f}$ of **FPhSPFN** than **PhSPFN** is due to the '*ortho*-substituent effect' of the diphenylamino electron donor causing a hypochromic shift of the fluorescence, which was first reported by us.[9] Such an effect also helps in preventing close contact of the molecules (because of the orthogonal conformation of the diphenylamino moiety which is enforced by sterically hindered *ortho*-substituents) in the solid state, which greatly intensifies solid-state fluorescence. Similar to **NPAFN**, **PhSPFN** shows virtually no fluorescence in solution ($\phi_f \sim 0\%$ in dichloromethane) but it is strongly fluorescent in the solid state ($\phi_f \sim 34\%$) (Fig. 1).‡ Such fluorescence behavior can be attributed to the easily exchangeable multiple conformations of the nonplanar arylamino functionality that facilitate the non-radiative decay of the excited **PhSPFN**. In the solid state, the exchanges between multiple conformations are largely forbidden due to the spatial congestion of molecular stacking in the solid state. These are also known to be the consequence of aggregation-induced emission, AIE.[10] Our rationale gets support herein from the fact that **FPhSPFN**, with restricted rotation of bis(2-fluorophenyl)-amine, exhibits enhanced fluorescence not only in the solid state but also in solution: red fluorescence $\lambda_{\max}^{f}$ of 658 nm with ϕ_fs of 13% in dichloromethane and 646 nm with ϕ_fs of 46% in the solid state (see Fig. 1 and Table 1). It is worth noting that solid state ϕ_fs 46% of **FPhSPFN** is uncommonly high compared with other known red fluorophores (Table 1). It is higher than the 33–34% of **PhSPFN** or **PhSPDCV** as well as the ~ 40% of **NPAFN**. **PhSPDCV** and **NPAFN** are known to be two of the most efficient red fluorophores for non-dopant-based red OLEDs.

Table 1 Fluorescence wavelength and fluorescence quantum yield of various red fluorophores

	Solution		Solid	
	$\lambda_{\max}^{f}$/nm	ϕ_f (%)	$\lambda_{\max}^{f}$/nm	ϕ_f (%)
NPAFN	—[a]	0[a]	616	40
PhSPDCV	624[b]	70[b]	633	33
PhSPFN	—[a]	0[a]	686	34
FPhSPFN	658[a]	13[a]	646	46
NPAMLMe[c]	683[b]	~ 0[b]	651	~ 15
DCM1[d]	627[d]	60[d]	650	~ 5
Nile Red[e]	~ 580[b]	33[b]	—	0
TPP[f]	658[f]	~ 11[f]	—	0

[a] In dichloromethane. [b] In chloroform. [c] 2,3-Bis-(1-naphthylphenylamino)-*N*-methylmaleimide.[2] [d] 4-(Dicyanomethylene)-2-methyl-6-[4-(dimethylaminostyryl)-4*H*-pyran] in acetonitrile.[11] [e] 9-Diethylaminobenzo[*a*]phenoxazin-5-one.[12] [f] 5,10,15,20-Tetraphenylporphyrin in benzene.[13]

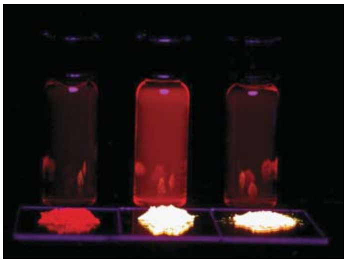

Fig. 1 Fluorescence images of **PhSPFN** (left), **FPhSPFN** (center), and **NPAFN** (right) in solution (dichloromethane) and in the solid state.

Regarding material molecular energy levels, **FPhSPFN** has a HOMO energy level of 5.79 eV in the solid state based on the determination of a low-energy photo-electron spectrometer (Riken-Keiki AC-2) (Fig. S1 top, ESI†). This energy level is about 0.11 eV lower than the 5.68 eV of **PhSPFN** due to the strongly electron-withdrawing fluoro substituent on the diphenylamino electron donor. Based on the on-set absorption energy of the materials in the thin film state, LUMO energy levels of **PhSPFN** and **FPhSPFN** are quite close to each other and there is only 0.02 eV difference in energy (Fig. S1 bottom, ESI†). Electrochemically in solution state, **FPhSPFN** has the oxidation potential of 0.69 V, which is about 0.31 V lower than the ~ 1.00 V of **PhSPFN**, although the difference in the reduction potential of the two fumaronitrile red fluorophores is much smaller (~ 0.1 V) (Fig. 2).

Interestingly, cyclic voltammograms of both **PhSPFN** and **FPhSPFN** show only one electrooxidation process but two or three electroreduction processes (Fig. 2). Cyclic voltammetry results indicate that each molecular half (diphenylaminospirobifluorene moiety) of the dipolar **PhSPFN** or **FPhSPFN** is not effectively π-conjugated with the other but each shares a common electron acceptor, the fumaronitrile moiety. This common fumaronitrile can accommodate a multiple number of reducing electrons. Such results also provide indirect evidence of antiparallel alignment of the intramolecular dipoles of these dipolar red fluorophores.

Both **PhSPFN** and **FPhSPFN** were adopted as non-doped red emitters in red OLEDs: ITO/NPB (30 nm)/**PhSPFN** or **FPhSPFN** (30 nm)/BCP (20 nm)/TPBI (30 nm)/LiF (1 nm)/Al (150 nm). Herein, NPB denotes the hole-transporting layer of 1,4-bis(1-naphthylphenylamino)biphenyl, BCP denotes the hole-blocking

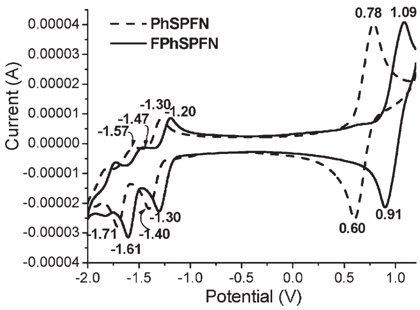

Fig. 2 Cyclic voltammograms of **PhSPFN** and **FPhSPFN** in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate at a scan rate of 100 mV s^{-1}. Determined potential was relative to Ag/AgNO$_3$ reference electrode.

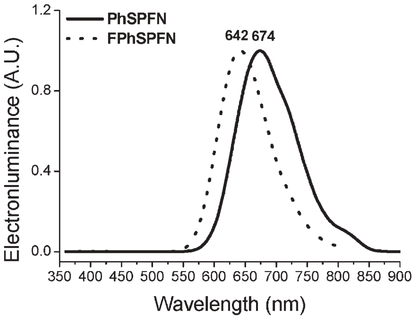

Fig. 3 EL spectra of **PhSPFN** and **FPhSPFN** OLEDs.

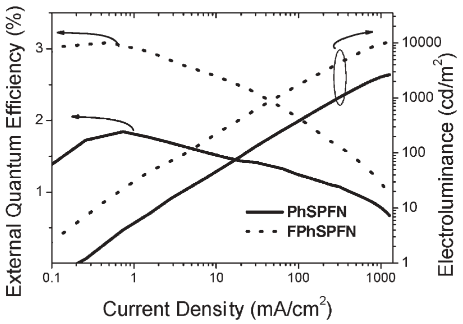

Fig. 4 Current density dependency of EL intensity and EL efficiency of **PhSPFN** and **FPhSPFN** OLEDs.

layer of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, and TPBI is the electron-transporting layer of 2,2′,2″-(1,2,5-phenylene)tris(1-phenyl-1*H*-benzimidazole).[2] These devices were fabricated by sequential thermal vacuum-deposition of organic materials on pre-treated ITO (indium tin oxide)-coated glass. Electroluminescence (EL) spectra with $\lambda_{\max}{}^{\mathrm{EL}}$ at 642 and 674 nm were observed for **PhSPFN** and **FPhSPFN** OLEDs, respectively (Fig. 3). Compared with the standard red (0.64, 0.33) of NTSC (National Television System Committee), these EL spectra correspond to 1931 CIE (Commission Internationale de l'Eclairage) chromaticity coordinates of saturated red (0.67, 0.30) and red (0.66, 0.34) for **PhSPFN** and **FPhSPFN** OLEDs, respectively.

From a practical point of view, **PhSPFN** is not satisfactory because of its inferior performance and its saturated red EL which is partially beyond the visible range of a human being. The intensity of EL reached 2600 and 10 100 cd m^{-2} for **PhSPFN** and **FPhSPFN** OLEDs, respectively. At a low current density of 20 mA cm^{-2}, saturated red **PhSPFN** OLED is pretty dim with an EL intensity of a mere 90 cd m^{-2}, much less than the required 200 or 300 cd m^{-2} for flat panel displays. In contrast, at a current density of 20 mA cm^{-2}, **FPhSPFN** red OLED has electroluminance as high as 500 cd m^{-2}, which is significantly brighter than the 390 cd m^{-2} of **NPAFN** OLED and surpasses the required standard for practical usage. Red **FPhSPFN** OLED is one of the brightest non-dopant red OLEDs and comparable with previous **PhSPDCV** OLEDs.[5] Whereas saturated red **PhSPFN** OLED performed poorly in terms of EL efficiency (less than 1.8%), red **FPhSPFN** OLED exhibited external quantum efficiency (EQE) of 2.5% at 20 mA cm^{-2}, which is a slight drop from the maximum EQE of 3.1% at ~ 1 mA cm^{-2} (Fig. 4). Such an efficiency performance of **FPhSPFN** is also much better than that of the previously reported orange–red **NPAFN** (maximum EQE 2.4% and 2.1% at 20 mA cm^{-2}). The superior performance of **FPhSPFN** OLED can be largely attributed to its high ϕ_fs (low fluorescence quenching) in the solid state, which, in turn, is due to the bulging molecular structure (spirobifluorene) and the '*ortho*-substituent' of the nonplanar diphenylamino electron donor.

In summary, we have synthesized and characterized two novel red fluorophores **PhSPFN** and **FPhSPFN** for the highly demanding non-dopant red OLEDs. They are compounds which are structurally modified from the previously known non-planar **PhSPDCV** and they can be considered as better fluorophores than the previously known orange–red **NPAFN**. Whereas **PhSPFN** is a saturated red fluorophore, **FPhSPFN** is highly fluorescent showing satisfactory non-dopant-based red EL brightly and efficiently.

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Notes and references

‡ The fluorescence quantum yields of the red-emitting fluorophores were determined by the integrating-sphere method described by de Mello *et al.* on solution samples or on thermal vacuum-deposited thin-film samples.[5,14] Solid-state fluorescence quantum yields of **NPAFN** have been determined by the same measurement as before and a lower fluorescence quantum yield of 20% was observed for a solid powder sample.[8]

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