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Electronic Supplementary Information

Fluorinated 9,9′-spirobifluorene derivatives as host materials for highly efficient blue organic light-emitting devices

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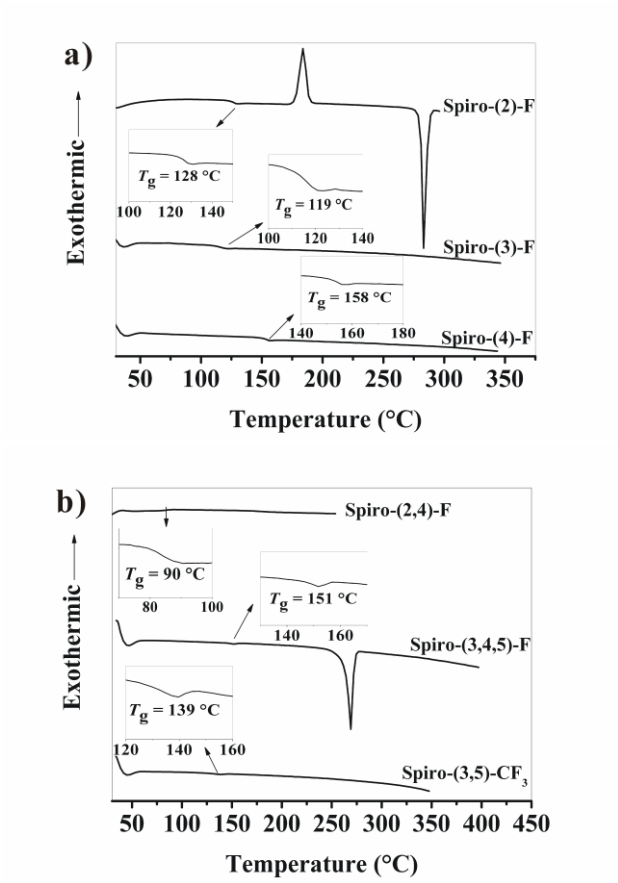

Fig. S1 DSC scans of SFs recorded under nitrogen during the second heating cycle at a scan rate of 10 °C min^{-1}.

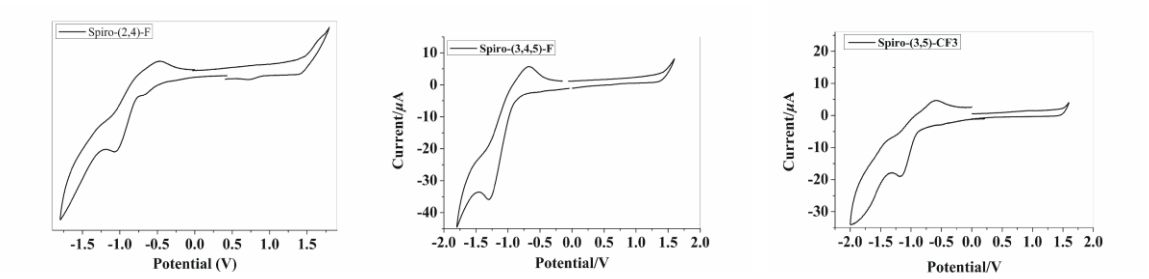

Fig. S2 Cyclic voltammograms of Spiro-(2,4)-F, Spiro-(3,4,5)-F and Spiro-(3,5)-CF_3, in CH_2Cl_2 for oxidation and in CH_3CN for reduction.

Electroluminescent properties

As shown in Fig. S3, the non-doped OLEDs utilizing Spiro-(2)-F, Spiro-(3)-F, Spiro-(4)-F, and Spiro-(2,4)-F as the emitters exhibited blue emissions peaking at ca. 404 nm with Commission Internationale de l'Éclairage (CIE) coordinates in a range of (0.169–0.186, 0.122–0.171), of which the device using Spiro-(3)-F as blue emitter gets excellent CIE coordinates of (0.169, 0.122), almost the same as those of their model compound (Spiro-4Φ) as blue emitter.[1] Spiro-(2)-CF_3-based device

show CIE coordinates of (0.192, 0.153) with peak at ca. 388 nm. However, Spiro-(3,4,5)-F and Spiro-(3,5)-CF_3 devices, compared with other SFs devices, showed a distinct difference in the EL spectra, which displayed a new strong peak at 468 and 460 nm, respectively, and a negligible emission at ca. 388 nm, while others showed no emission in this longer wavelength region. The emission got stronger at the lower energy region can be attributed to the directed charge trapping effect in the EL process other than the PL process.[2,3] In addition, these EL spectra proved to be independent of the applied voltage, suggesting that the EL originates purely from the spirobifluorenes, without exciplex formation.

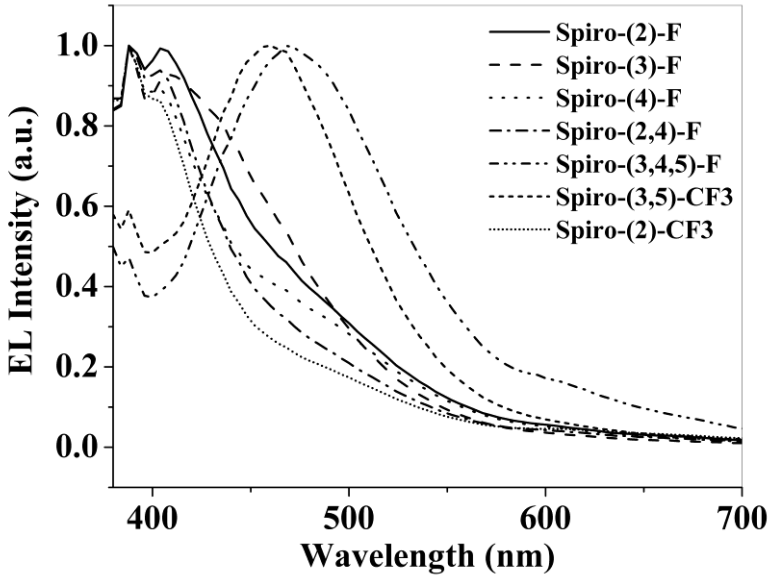

Fig. S3 EL spectrum of non-doped devices at 10 mA cm^{-2}.

The current density–voltage–luminance–efficiency (*J–V–L–η*) measurements of the blue fluorescent OLEDs with SFs as the EMLs were performed under ambient conditions and the results are summarized in Table S1. *J–V–L–η* characteristic of the devices are shown in Fig.S4. The devices with the F-substituted SFs as EML show the turn-on voltages (at which the luminance is 1 cd m^{-2}) of ca. 5.0 V, while with CF_3-substituted SFs Spiro-(3,5)-CF_3 5.8 V and Spiro-(2)-CF_3 6.3 V, respectively. The low turn-on voltages can be explained by the small injection barriers from HTL and EMLs in the devices as well as by the ambipolar transporting property of fluorinated 9,9′-spirobifluorene derivatives. According to the energy level diagram shown in Fig. 6, the energy barrier for hole injection at the interfaces of HTL and various EMLs is only about 0.1–0.3 eV. These small injection barriers enhance hole injection efficiency from the HTL into EML. The blue OLEDs

show the current efficiency in the range of 0.20–0.53 cd A^{-1} at a current density of 20 mA cm^{-2} (Fig. S4). It is noteworthy that there is little roll-off of luminance efficiency as a function of current density in the SFs blue device. For example, the device using Spiro-(2)-F gives the highest efficiency of 0.53 cd A^{-1} at 20 mA cm^{-2} and 0.45 cd A^{-1} at 100 mA cm^{-2}, respectively. Such high efficiencies for the blue OLEDs are consistent with high PL quantum yields of the present fluorinated 9,9′-spirobifluorene derivatives. The high EL efficiencies and low device voltage also indicate rather effective and balanced hole/electron injection into the large-energy-gap blue emitting fluorinated 9,9′-spirobifluorene in the present device structure.

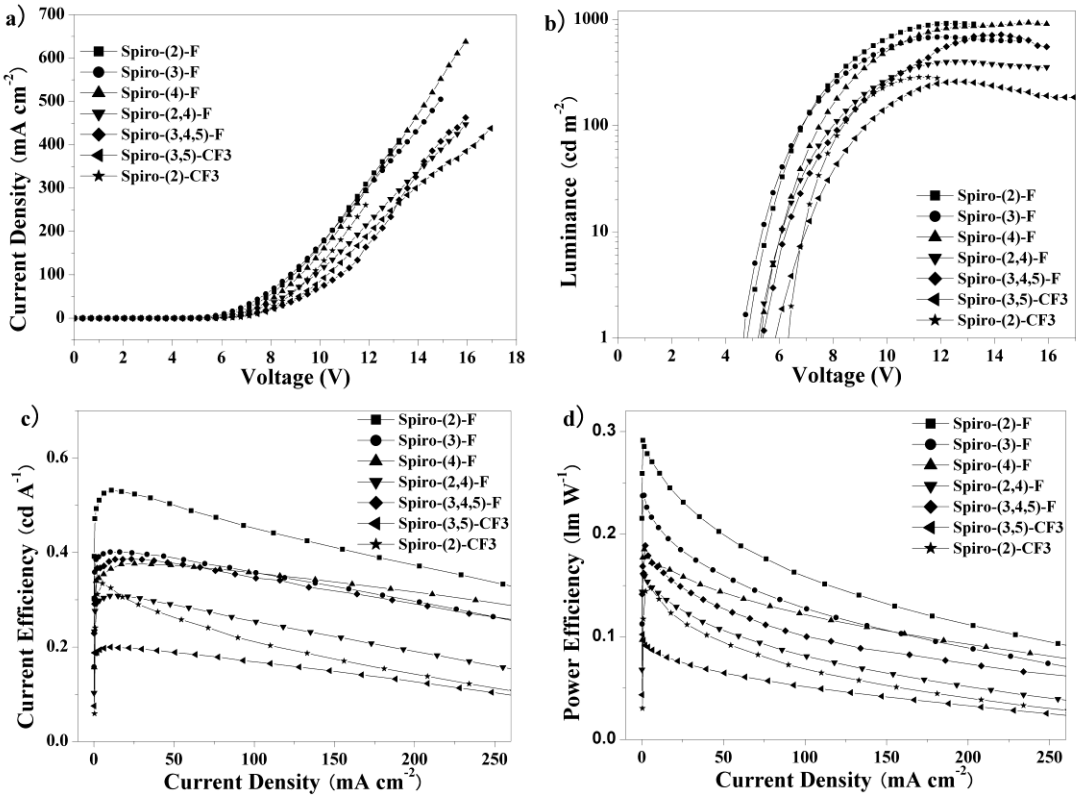

Fig. S4 a) Current density–voltage curves, b) Brightness–voltage curves, c) Current efficiency–current density curves, and d) Power efficiency–current density curves for the devices employing SFs as a non-doped emitter.

Table S1 EL performance of blue devices with a non-doped EML

EML	λ_{max}^{EL} [a] (nm)	V_{on} [b] (V)	L [c] (cd m^{-2})	η_c [c] (cd A^{-1})	η_p [c] (lm W^{-1})	η_c [d] (cd A^{-1})	η_p [d] (lm W^{-1})	CIE (x, y)[a]
Spiro-(2)-F	404	4.8	917	0.53	0.29	0.45	0.16	(0.183, 0.157)
Spiro-(3)-F	408	4.7	682	0.40	0.24	0.36	0.13	(0.169, 0.122)
Spiro-(4)-F	404	5.3	932	0.38	0.19	0.36	0.12	(0.186, 0.171)
Spiro-(2,4)-F	404	5.2	400	0.31	0.16	0.25	0.08	(0.185, 0.145)
Spiro-(3,4,5)-F	468	5.4	720	0.39	0.19	0.35	0.10	(0.199, 0.243)
Spiro-(3,5)-CF_3	460	5.8	259	0.20	0.10	0.17	0.05	(0.171, 0.177)
Spiro-(2)-CF_3	388	6.3	286	0.30	0.15	0.21	0.07	(0.192, 0.153)

[a] Values collected at 10 V. [b] Turn-on voltage at 1 cd m^{-2}. [c] Values collected at a current density of 20 mA cm^{-2}. [d] Values collected at a current density of 100 mA cm^{-2}.

To evaluate the performance of the fluorinated 9,9′-spirobifluorene derivatives as hosts, organic light-emitting devices were fabricated by using the well known blue emitter, BCzVBi, as the guest. To optimize the concentration of the dopant, Spiro-(2)-CF_3 was initially selected as the host in concentration-dependent experiments, with the dopant amount ranging from 1 to 22 vol%. Devices with the structure of indium tin oxide (ITO)/molybdenum trioxide (MoO_3) (1 nm)/4,4',4''-Tris(carbazol-9-yl)-triphenylamine (TcTa) (40 nm)/Spiro-(2)-CF_3:x% BCzVBi (20 nm)/1,3,5-Tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi) (40 nm)/LiF (1 nm)/Al (100 nm) (x = 1, 3, 5, 7, 10, 15, 22) were firstly fabricated. TcTa and TPBi were used as the hole- and electron-transporting materials, respectively; BCzVBi doped into Spiro-(2)-CF_3 was used as the emitting layer; MoO_3 and LiF served as the hole- and electron-injecting layers, respectively. Fig. S5 shows the current efficiency–voltage (η–V) characteristics for the devices. Up to 10 vol%, as the dopant concentration increases, the current efficiency is gradually enhanced. Device with a 10 vol% doping ratio exhibits a maximum current efficiency of 4.03 cd A^{-1} at 6 V. When the doping ratio reaches 22 vol%, the maximum current efficiency is decreased to 2.19 cd A^{-1} at 8 V due to concentration quenching.

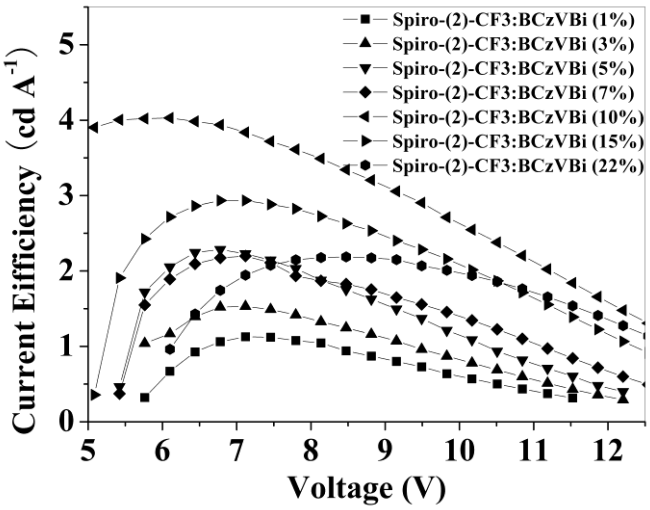

Fig. S5 Current efficiency versus voltage curves for devices ITO/MoO_3 (1 nm)/TcTa (40 nm)/Spiro-(2)-CF_3:x% BCzVBi (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm) (x = 1, 3, 5, 7, 10, 15, 22).

To investigate the device operation stability, the lifetime of non-doped and BCzVBi-doped Sprio-(3)-F devices was measured as the operational half lifetime ($t_{1/2}$) under an initial luminance of 2000 cd m^{-2} at a constant current (see Fig. S6). The lifetime of the blue host material DPVBI was compared. The non-doped Sprio-(3)-F device was better than that of DPVBI device. The improved thermal stability of Sprio-(3)-F may improve the lifetime of the device. It can be seen from Figure S6 that the BCzVBi-doped Sprio-(3)-F device exhibited better stability, which showed a lifetime (0.34 h) that was approximately 3 times longer than that of the DPVBI device (0.12 h).

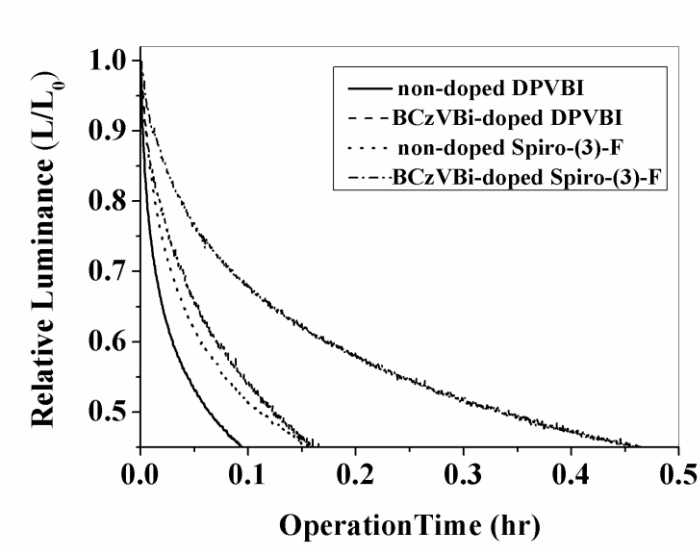

Fig. S6 Device life-time of non-doped and BCzVBi-doped OLEDs (initial luminance is 2000 cd m^{-2} and device is operated with constant current).

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