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Electronic Supplementary Information for

The Study on Two Kinds of Spiro System for Improving the Performance of Host Materials in Blue Phosphorescent Organic Light-Emitting Diodes

Xiang-Yang Liu, Feng Liang, Lei Ding, Shou-Cheng Dong, Qian Li, Lin-Song Cui, Zuo-Quan Jiang,* Hua Chen, Liang-Sheng Liao*

Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of

Functional Nano & Soft Materials (FUNSOM), Soochow University

Suzhou, Jiangsu 215123, China.

Email: zqjiang@suda.edu.cn; lsliao@suda.edu.cn.

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(b) for 3SAFCzPh and 3SFCzPh based devices.

Experimental Section

¹H NMR and ¹³C NMR spectra were recorded on a Bruker 400 spectrometer at room temperature. Mass spectra were recorded on a Thermo ISQ mass spectrometer using a direct exposure probe. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. PL spectra and phosphorescent spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA DSC 2010 unit at a heating rate of 10 °C min⁻¹ under nitrogen. The glass transition temperatures (T_g) were determined from the second heating scan. Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of 10 °C min⁻¹ under nitrogen. Temperature at 5% weight loss was used as the decomposition temperature (T_d). Cyclic voltammetry (CV) was carried out on a CHI600 voltammetric analyzer at room temperature with ferrocenium-ferrocene (Fc⁺/Fc) as the internal standard. Deaerated dichloromethane was used as solvent for oxidation scan with tetrabutylammonium hexafluorophosphate (TBAPF6) (0.1 M) as the supporting electrolyte. The cyclic voltammograms were obtained at scan rate of 0.1 V s⁻¹. Ultra-Violet Photoemission Spectroscopy (UPS) analysis were carried out with an unfiltered He I (21.22 eV) gas discharge lamp and a hemispherical analyzer, which made by KRATOS ANALYTICAL SHIMADZU GROUP COMPANY. DFT calculations were performed using B3LYP/6-31g(d) basis set using Gaussian 09.

Fabrication and measurement of OLED devices

Bis(4,6-(difluorophenyl)pyrudinato-N,C')picolinateiridium(III) (FIrpic), 1,1-bis[4-[N',N'-di(p-tolyl)amino]-phenyl]cyclohexane (TAPC), 1,3,5-tri[(3-pyridyl)phen-3-yl]-benzene (TmPyPB), dipyrazino[2,3-f:2',3'-h]-quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HAT-CN) and 8-hydroxyquinolinolatolithium (Liq) were commercially available.

The OLEDs were fabricated on the indium-tin oxide (ITO) coated transparent glass substrates, the ITO conductive layer having a thickness of ca. 100 nm and a sheet resistance of ca. 30 Ω per square. The substrates was cleaned with ethanol, acetone and deionized water, and then dried in an oven, finally exposed to UV ozone for 30 min. All of the organic materials and metal layers under a vacuum of ca. 10⁻⁶ Torr. Four identical OLED devices were formed on each of the substrates and the emission area of 0.09 cm² for each unit. The EL performances of the blue and white devices were measured with a PHOTO RESEARCH SpectraScan PR 655 PHOTOMETER and a KEITHLEY 2400 SourceMeter constant current source at room temperature.



Scheme S1 Synthetic routes of 3SAFCzPh and 3SFCzPh.

Preparation of 3-Bromofluorenone, 3-BrSAF, 3SAFCzPh and 3SFCzPh.

All chemicals and reagents were used as received from commercial sources without further purification. THF was purified by PURE SOLV (Innovative Technology) purification system.

Preparation of 3-Bromofluorenone:



2-amino-4-bromobenzophenone (10 g, 36.21 mmol) was stirred into 100 mL water, and then 20 mL sulfuric acid was added and stirred over 30 min at room temperature. The solution was cooled to 0 °C and 20 mL sodium nitrite solution (3.7 g, 54.32 mmol) was added dropwise under stirred. After 1 h reaction at 0 °C, the mixture was gradually warmed up to room temperature overnight. Filtered and washed with absolute ethyl alcohol, and dried under vacuum to give 3-bromofluorenone as light yellow power resulting in 8.1 g light yellow solid (86%).^[1]

Preparation of 3'-bromo-10-phenyl-10H-spiro(acridine-9,9-fluorene) (3-BrSAF):



2-Bromotriphenylaime (5 g, 15.4 mmol) was dissolved in 100 mL THF in a 500 mL Schlenk tube under argon and cooled to -78 °C, *n*-butyl lithium (6.5 mL, 15.5 mmol, 2.4 M) was added dropwise via a syringe. After 1 h reaction at -78 °C, 3-bromofluorenone (4 g, 15.4 mmol) in 80 mL THF was added over a period of 30 min. The resulting mixture was allowed to stir for 1 hour at -78 °C, the mixture was gradually warmed up to room

temperature overnight. The reaction was quenched by water (5 mL). Put the mixture into 50 mL water, the product was extracted with EtOAc (3×50 mL). Then the organic layer was separated, dried over sodium sulfate (NaSO₄), filtered and evaporated under reduce pressure to afford the crude product as a light yellow soild or oil (7.5 g), which was directly used in the next reaction without further purification.

The crude product was dissolved in 100 mL acetic acid (HOAc) under 80 °C and 10 mL hydrochloric acid (HCl) was added dropwise under stirred. The mixture was reaction overnight at 80 °C. After the reaction cooling to room temperature, filtered and washed with absolute ethyl alcohol, and dried under vacuum to give 3'-bromo-10-phenyl-10H-spiro(acridine-9,9-fluorene) (3-BrSTF) as white powder (7.0 g, ~93%).^[2] MS m/z: 486.42. Anal. calcd for $C_{31}H_{20}BrN$ (%): C 76.55, H 4.14, N 2.88; found: C 76.48, H 4.32, N 3.72.

Preparation of 3-bromo-9,9'-spirobifluorene (3-BrSF):



3-BrSF was prepared in a similar method with 3-BrSF. The result to afford a white power (80%).^[1] MS m/z: 395.33. Anal. calcd for $C_{25}H_{15}Br$ (%): C 75.96, H 3.82; found: C 76.08, H 3.89.

Preparation of 10-phenyl-3'-(9-phenyl-9H-carbazol-3-yl)-10H-spiro(acridine-9,9'fluorene) (3SAFCzPh):



3'-bromo-10-phenyl-10H-spiro(acridine-9,9-fluorene) (3-BrSAF) (3 g, 6.2 mmol), 9phenyl-9H-carbazol-3-ylboronic acid (2.2 g, 7.4 mmol) and $Pd(PPh_3)_4$ (0.07 g, 0.06 mmol) were dissolved in THF under argon, and then 2 M K_2CO_3 (THF/Water = 4/1, v/v) was added. The resulting solution was heated at 70 °C overnight. After the reaction solution cooled to room temperature, put it into 200 mL water, and extracted with dichloromethane for 3 times. The organic layer was collected and evaporated. The crude product was purified by column chromatography using petroleum ether/ dichloromethane (2/1, v/v) to afford the final product as a white powder (3.7 g, 92%). ¹H NMR (400 MHz, $CDCl_3$): $\delta = 8.19$ (t, J = 12.1 Hz, 2H), 8.06 (d, J = 24.2 Hz, 1H), 7.90 (s, 1H), 7.84 (d, J = 12.1 Hz, 2H), 8.06 (d, J = 24.2 Hz, 1H), 7.90 (s, 1H), 7.84 (d, J = 12.1 Hz, 2H), 8.06 (d, J = 24.2 Hz, 1H), 7.90 (s, 1H), 7.84 (d, J = 12.1 Hz, 2H), 8.06 (d, J = 24.2 Hz, 1H), 7.90 (s, 1H), 7.84 (d, J = 12.1 Hz, 2H), 8.06 (d, J = 24.2 Hz, 1H), 7.90 (s, 1H), 7.84 (d, J = 12.1 Hz, 2H), 8.06 (d, J = 24.2 Hz, 1H), 7.90 (s, 1H), 7.84 (d, J = 12.1 Hz, 2H), 8.06 (d, J = 24.2 Hz, 1H), 7.90 (s, 1H), 7.84 (d, J = 12.1 Hz, 1H), 7.84 (d, J 7.5 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.70 (td, J = 7.6, 5.7 Hz, 3H), 7.62–7.35 (m, 11H), 7.35-7.21 (m, 4H), 6.99-6.87 (m, 2H), 6.64-6.53 (m, 2H), 6.47 (d, J = 7.7 Hz, 2H), 6.37 (d, J = 7.7 Hz, 3Hz, 3Hz,(d, J = 8.3 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 156.69$, 156.19, 143.21, 141.31, 141.00, 140.89, 139.90, 139.64, 138.94, 138.21, 131.13 (d, J = 8.5 Hz), 130.27, 128.69, 128.48, 127.70 (d, J = 2.8 Hz), 127.55, 127.29, 126.25, 126.08, 125.99, 125.92, 125.85, 125.80, 124.54, 123.39, 120.58, 120.34, 119.96, 118.57, 114.69, 109.85, 56.68 ppm. MS m/z: 648.33. Anal. Calcd for C₄₉H₃₂N₂ (%): C 90.71, H 4.97, N 4.32; found: C 90.79, H 4.94, N 4.38.





3-(9,9'-spirobifluorene-6-yl)-9-phenyl-9H-carbazole was prepared in a similar manner with 3SAFCzPh. The final product can be afforded as a white powder (90%). ¹H NMR (400 MHz, CDCl₃): δ = 8.41 (d, *J* = 1.5 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.15 (d, *J* = 1.4 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 2H), 7.71 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.63–7.58 (m, 4H), 7.49–7.36 (m, 8H), 7.31 (ddd, *J* = 7.9, 5.5, 2.6 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 3H), 6.82 (t, *J* = 7.1 Hz, 3H), 6.76 (d, *J* = 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 149.22, 148.86, 147.14, 142.42, 141.82 (d, *J* = 11.3 Hz), 141.37, 140.40, 137.67, 133.62, 129.92, 127.81 (dd, *J* = 22.3, 5.5 Hz), 127.52, 127.30, 127.08, 126.14, 125.61, 124.15 (t, *J* = 10.4 Hz), 123.90, 123.49, 120.39, 120.09, 120.07, 120.00, 118.91 (d, *J* = 8.7 Hz), 109.98 (d, *J* = 12.3 Hz), 65.76 ppm. MS m/z: 557.59. Anal. calcd for C₄₃H₂₇N (%): C 92.61, H 4.88, N 2.51; found: C 92.58, H 4.95.



Fig. S1 ¹H NMR spectrum of 3SAFCzPh.



Fig. S2 ¹³C NMR spectrum of 3SAFCzPh.



Fig. S3 ¹H NMR spectrum of 3SFCzPh.



Fig. S4 ¹³C NMR spectrum of 3SFCzPh.

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Table S1 Summary of the physical properties of 3SAFCzPh and 3SFCzPh.

Host	Abs λ_{max}^{a}	$PL \; \lambda_{max}{}^a$	$T_{\rm g}^{\ \rm b}$	$T_{\rm d}^{\rm c}$	E_{g}^{d}	$E_{\mathrm{T}}^{\mathrm{e}}$	HOMO ^f	LUMOg
	[nm]	[nm]	[°C]	[°C]	[eV]	[eV]	[eV]	[eV]
3SAFCzPh	259	415	151	386	3.54	2.81	-5.69	-2.42
3SFCzPh	269	388	140	433	3.31	2.70	-5.79	-2.48

^aMeasured in toluene solution at room temperature. ^b T_g : Glass transition temperature. ^c T_d : Decomposition temperature. ^d E_g : Band gap energies were calculated from the corresponding absorption onset in toluene solution. ^e E_T : Measured in 2-MeTHF glass matrix at 77 K. ^fHOMO levels were calculated from UPS date. ^gThe LUMO level of 3SFCzPh was calculated from the HOMO and E_g ; the LUMO level of 3SAFCzPh was estimated according to the DFT calculation results of 3SFCzPh and 3SAFCzPh and the LUMO level of 3SFCzPh.

Fig. S10 Calculated HOMO/LUMO distribution at ground state (S_0) and triplet state (T_1) of 3SAFCzPh and 3SFCzPh.

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Notes and references

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