

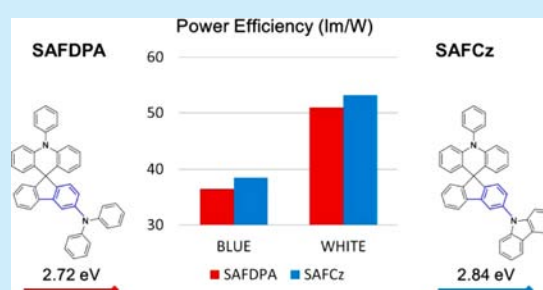
Control of Conjugation Degree via Position Engineering to Highly Efficient Phosphorescent Host Materials

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Supporting Information

ABSTRACT: The C3 meta-position of fluorene is utilized to construct high-triplet energy compounds. Incorporating a spiroacridine structure, two new host materials SAFDPA and SAFCz were facily obtained. Their thermal and photophysical properties are fully investigated. The best efficiencies of 19.4%/21.5% of blue/white devices are achieved by SAFCz.



Conjugated organic compounds with a spiro structure are a series of special functional materials in optoelectronic research.¹ Among these compounds, 9,9'-spirobifluorene (SBF) is the most common building block that has been modified in various ways according to different requirements.² There are two effective methods to modify the physical properties of 9,9'-spirobifluorene: replacing one fluorene ring by acridine or changing the substituted position of fluorene. The former method leads to a new spiro structure spiro[acridine-9,9'-fluorene] (SAF), which had been proven to be a stable unit with improved carrier transportability.³ Compared to the change on the spiro-backbone, the change on the position appears to be less noticeable, but it will remarkably affect the energy levels of spiro-based materials.⁴

The most direct and convenient derivatization position of fluorene is the C2 position, which is a para position. This para substitution of most functional groups will affect both the single and triplet states in a conjugated system.⁵ In some cases, we want to maintain the triplet energy of the spiro backbone, and thus, the para derivatization is not a good option. For the application of host materials in phosphorescent organic lighting diodes (PHOLEDs), the first design principle of conjugated compounds is that the triplet energy of the host must be higher than that of the emitting dopant.⁶ It is noted that most hosts based on C2-substituted spiro-fluorene or its analogues are mostly used in green or red phosphorescent emitter;⁷ by contrast, other series host materials without fluorene block can attain sufficiently high triplet energy and achieve good device efficiency over 20% external quantum efficiency (EQE).⁸

Changing the derivatization position should be an effective way to modulate the energy level of the spiro-backbone. The C4 position as an ortho linkage has been developed to prepare blue host materials, but the device efficiencies are not very high.^{3c,4a-c}

The C3 position as a meta linkage is another option, but the bottleneck for these type materials is the synthesis of the key intermediate 3-bromofluorenone. The yield of traditional synthetic route via bromination then oxidation by KMnO_4 from phenanthrenequinone is low, and the postprocess of the reaction is time-consuming.⁹ Recently, we reported a new method to obtain 3-bromofluorenone via the Pshorr reaction from commercial precursor 2-amino-4-bromobenzophenone in which the bromide atom is pre-substituted.^{4e} On this basis, we could readily prepare spiro blue host materials on the meta position in C–P linking or C–C linking conjugated systems.^{4d,e} In this paper, we use the SAF as the spiro-backbone and diphenylamine or carbazole to form the C–N meta-linking, and the resulting new host materials SAFDPA and SAFCz show good device performance in blue and white PHOLEDs.

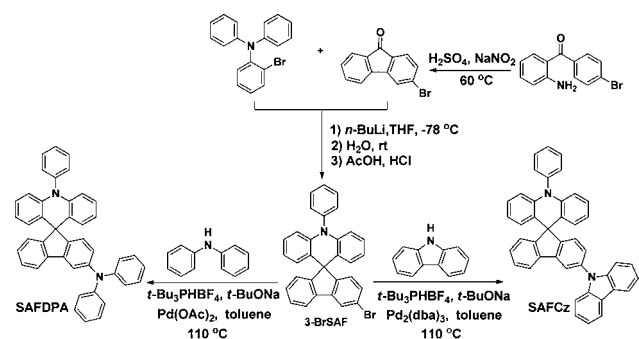
The key intermediate 3-bromofluorenone was prepared via Pshorr reaction with good yield (~80%, see the Supporting Information). Then 2-bromotriphenylamine was treated with *n*-BuLi at -78°C , followed by addition of 3-bromofluorenone/THF to afford the corresponding tertiary alcohol. The SAF core was formed by treating the alcohol with acid. Finally, the host materials were afforded via a Bulchwald–Hartwig C–N coupling reaction with corresponding arylamine (Scheme 1).

The thermal properties of the resulting SAFDPA and SAFCz were determined by differential scanning calorimetry (DSC) (see Figure S7, Supporting Information) and thermo gravimetric analysis (TGA) measurements (see Figure S8, Supporting Information). As shown in Table 1, both compounds exhibit good thermal stabilities. The glass-transition temperatures (T_g)

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Scheme 1. Synthetic Routes of the Materials



were measured as 128 and 150 °C for SAFDPA and SAFCz, respectively. This evident enhancement of T_g on carbazole-substituted material compared to its diphenylamine analogue is also observed in other examples,¹⁰ indicating the minor change on the periphery group also could dramatically affect the phase transition in amorphous materials. On the other hand, their thermal decomposition temperatures (T_d , corresponding to 5% weight loss) were observed at 357 °C for SAFDPA and 348 °C for SAFCz, which showed slight difference due to their similar molecular sizes and weights.

Figure 1 shows the UV-vis absorption and room-temperature photoluminescence spectra of SAFDPA and SAFCz in dichloromethane solution, as well as the phosphorescence spectra measured in 2-methyl-THF solution at 77 K. As summarized in Table 1, both materials exhibit an absorption band around ~272 nm, and their PL emission peaks are observed at ~406 nm. The SAFDPA and SAFCz showed completely different phosphorescence spectra, and the corresponding triplet energies were determined as 2.72 eV for SAFDPA and 2.84 eV for SAFCz, respectively, which were calculated from the highest vibronic band at 77 K. The two materials still possess higher E_T levels than common blue phosphorescent dopant, and thus, they can probably serve as good host candidates for blue triplet emitters.

The highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) of SAFDPA and SAFCz were probed by ultraviolet photoelectron spectroscopy (UPS), which is shown in Figure 2. The HOMO levels of SAFDPA and SAFCz were estimated as 5.62 and 5.74 eV, respectively, and the LUMO energy levels of ~2.20 eV were calculated from the HOMO values and optical band gaps. The HOMO levels of the two compounds were also verified by cyclic voltammetry (CV) (see Figure S9, Supporting Information). The measurements were performed in CH_2Cl_2 with ferrocene as the internal reference and the two compounds exhibited reversible oxidation behaviors, and the values were in consistent with the UPS results.

To understand the electronic structure of SAFDPA and SAFCz, density function theory (DFT) calculations were performed at a B3LYP/6-31G(d) level for the geometry optimization. Figure 3 shows that both compounds have similar

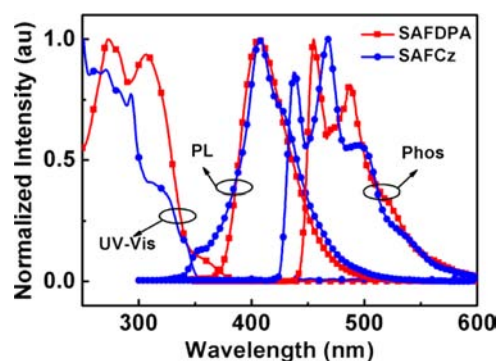


Figure 1. UV-vis absorption in dichloromethane solution and PL spectra in dichloromethane solution at 10^{-5} M. Phosphorescence spectra of these compounds measured in a frozen 2-methyltetrahydrofuran matrix at 77 K.

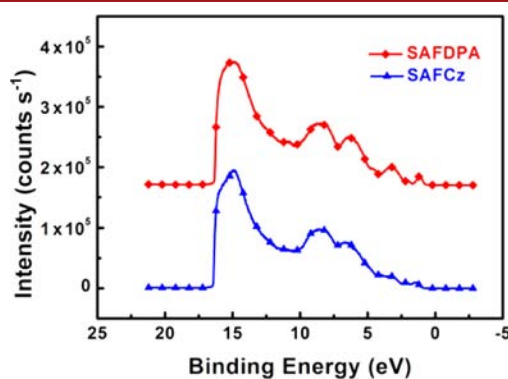


Figure 2. UPS spectrum of SAFDPA and SAFCz.

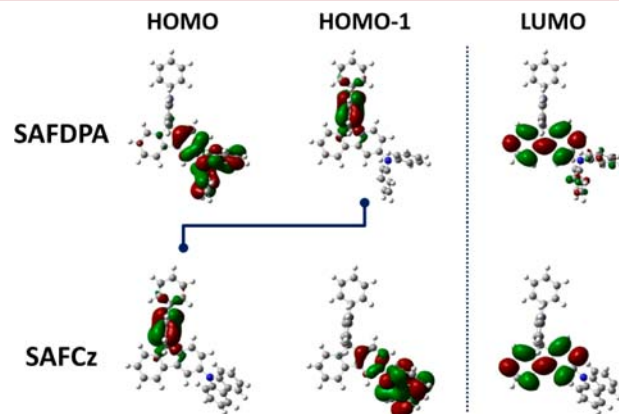


Figure 3. Optimized geometry and HOMO/LUMO and HOMO-1 spatial distributions of SAFDPA and SAFCz.

LUMO distributions which are mainly localized at the fluorene moiety. This fact can also explain well why both compounds

Table 1. Physical Properties of SAFDPA and SAFCz

compd	T_g^a (°C)	T_m^a (°C)	T_d^a (°C)	$\lambda_{\text{max,abs}}^b$ (nm)	$\lambda_{\text{max,pl}}^b$ (nm)	λ_{ph}^c (nm)	E_g^d (eV)	E_T^e (eV)	HOMO/LUMO ^f (eV)
SAFDPA	128	268	357	273	406	455	3.42	2.72	5.62/2.20
SAFCz	150	290	348	271	407	437	3.54	2.84	5.74/2.20

^a T_g : glass transition temperatures. T_m : melting temperatures. T_d : decomposition temperatures, measured by DSC and TGA. ^bMeasured in dichloromethane solution at room temperature. ^cMeasured in 2-MeTHF glass matrix at 77 K. ^d E_g : band gap energies were estimated from the optical absorption edges of UV-vis absorption spectra. ^e E_T : triplet energy were estimated from the onset peak of the phosphorescence spectra. ^fHOMO and LUMO were calculated from UPS and the optical band gap from the absorption spectra.

have nearly identical LUMO levels. Their HOMO distributions, however, are quite different from each other. In SAFDPA, there are two “triphenylamine” subunits, but the spiro rigidity make the external phenyl ring twisted and other two phenyl rings of acridine linking to the spiro-carbon nearly coplanar. Thus, the conjugation on the spiro triphenylamine actually delocalizes on “diphenylamine”, which is smaller than that of normal triphenylamine at the meta position where the conjugation delocalizes over the entire triphenylamine, and thus, we observed the HOMO of SAFDPA is localized at the appending triphenylamine part. Its HOMO-1 is localized at the spiro-triphenylamine with Ph–N–Ph distribution, accordingly. In SAFcz, the rigidity of the carbazole unit also makes itself twisted; thus, the conjugation of carbazole is less likely to delocalize to the neighboring phenyl ring on the fluorene unit. In addition, the nitrogen atom of carbazole is embedded in a five-membered ring, while the spiro-triphenylamine forms a six-membered ring, indicating the nonbonding electrons on the latter nitrogen could participate in the conjugation more easily. Therefore, the HOMO of SAFcz is localized at the spiro-triphenylamine with Ph–N–Ph distribution, which is similar to the HOMO-1 of SAFDPA. This theoretical understanding agrees well with the measured results that SAFDPA has a higher HOMO. On the other hand, time-dependence DFT was utilized to simulate the natural transition orbitals (NTOs) using the optimized structures of the S_0 state. Figure S10 (Supporting Information) illustrates the spatial distribution of the lowest and highest NTOs of the host materials. The NTOs of both molecules mainly locate on the fluorene ring, but in SAFDPA, another obvious distribution of NTO to appending DPA moiety can also be observed. This enlarged delocalization means that the SAFDPA possesses relatively lower triplet energy.

To investigate the electroluminescent properties of SAFDPA and SAFcz as host materials, blue PHOLEDs using iridium(III) bis(4,6-(difluorophenyl)pyridinato-N,C')picolinate (FIrpic) as emitting dopant were fabricated with a simple configuration of: ITO/HAT-CN (10 nm)/TAPC (45 nm)/host: FIrpic (8%, 20 nm)/TmPyPB (50 nm)/Liq (2 nm)/Al (120 nm) (host = SAFDPA for device A; host = SAFcz for device B). 1,1-bis[4-[N,N'-di(*p*-tolyl)amino]phenyl]cyclohexane (TAPC) was used as hole-transporting layer and electron-blocking layer. 1,3,5-Tri[(3-pyridyl)phen-3-yl]benzene (TmPyPB) was employed as the electron-transporting layer and hole-blocking layer. 1,4,5,8,9,11-Hexaazatriphenylene-hexacarbonitrile (HAT-CN) and 8-hydroxyquinolinolitolithium (liq) served as the hole- and electron-injecting layers, respectively. Figure 4 shows *J-V-L* characteristics and external quantum efficiencies of blue devices. All devices show sky-blue emission (see Figure S11, Supporting Information) with CIE coordinates of (0.16, 0.38). The device A reached maximum data of 39.0 cd/A for current efficiency (CE), 36.5 lm/W for power efficiency (PE, see Figure S11, Supporting Information) and 17.9% for EQE. The efficiencies of device A were slightly lower than those of device B, in which 42.1 cd/A for CE, 38.5 lm/W for PE, 19.4% for EQE were achieved.

Finally, to further evaluate the performance of SAFDPA and SAFcz as the single host for all phosphor white PHOLEDs. The devices configuration is ITO/HAT-CN (10 nm)/TAPC (45 nm)/host: FIrpic: PO-01 (8 wt %, 0.5 wt %, 20 nm)/TmPyPB (50 nm)/Liq (2 nm)/Al (120 nm) (host = SAFDPA for device C; host = SAFcz for device D). FIrpic and iridium(III) bis(4-phenylthieno[3,2-*c*] pyridinato-N,C2') acetylacetonate (PO-01) were codoped into the hosts SAFDPA and SAFcz as emitting layer. As illustrated in Figure S12 (Supporting Information),

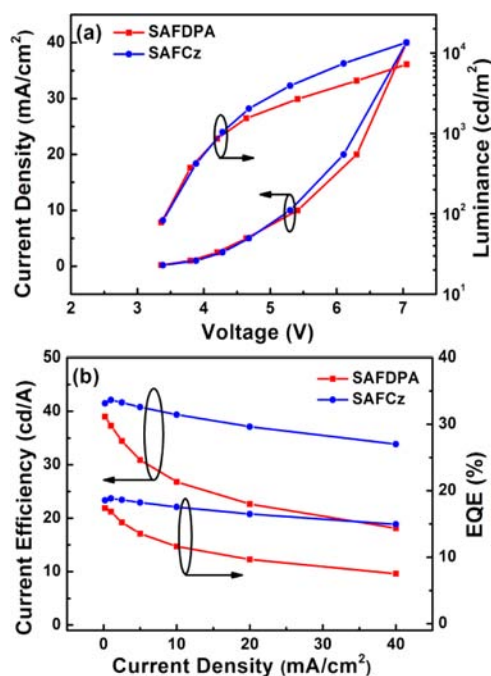


Figure 4. (a) Current density–voltage–luminance characteristics. (b) External quantum efficiency versus current density curves.

device C hosted by SAFDPA exhibits the best performance with a current efficiency of 56.6 cd/A and EQE of 19.9%; while device D hosted by SAFcz exhibited 60.2 cd/A, and 21.5%. The color rendering indexes (CRI) of two white PHOLEDs are 47. The detailed device performances are summarized in Table 2 and Table S2 (Supporting Information).

Table 2. Summary of OLED Performances

device	$\eta_c/\eta_p/\eta_{ext}/V^{2a}$ (cd/A/lm/W/ %/V)	$\eta_{c,max}/\eta_{p,max}/\eta_{ext,max}^b$ (cd/A/lm/ W/ %/V)
blue/A	34.4/25.7/15.8/4.2	39.0/36.5/17.9/3.4
blue/B	41.6/30.6/19.2/4.3	42.1/38.5/19.4/3.4
white/C	56.6/45.7/18.6/3.9	56.6/51.0/19.9/3.4
white/D	60.2/43.6/21.5/4.3	60.2/53.2/21.5/3.0

^aCurrent efficiency (η_c), power efficiency (η_p), external quantum efficiency (η_{ext}), voltage (V) at 1000 cd/m². ^bMaximum current efficiency ($\eta_{c,max}$), maximum power efficiency ($\eta_{p,max}$), maximum external quantum efficiency ($\eta_{ext,max}$).

In conclusion, we have designed and synthesized two new spiro-based materials SAFDPA and SAFcz. By a suitable synthetic route, we can effectively afford the target compounds via meta-linkage. In this case, C–N derivatization is used to design blue hosts with high E_T and further proves the generality of this position engineering. Finally, the best performances of 42.1 cd/A/38.5 lm/W/19.4% of the blue device and 60.2 cd/A/53.2 lm/W/21.5% of the white device were achieved by host SAFcz.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis, NMR, EL, and references. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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