Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information for:

Spiro-Silafluorene-Phenazasiline Donor based Efficient Blue Thermally Activated Delayed Fluorescence Emitter and its Host Dependent Device Characteristics

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1. Synthesis of the molecule

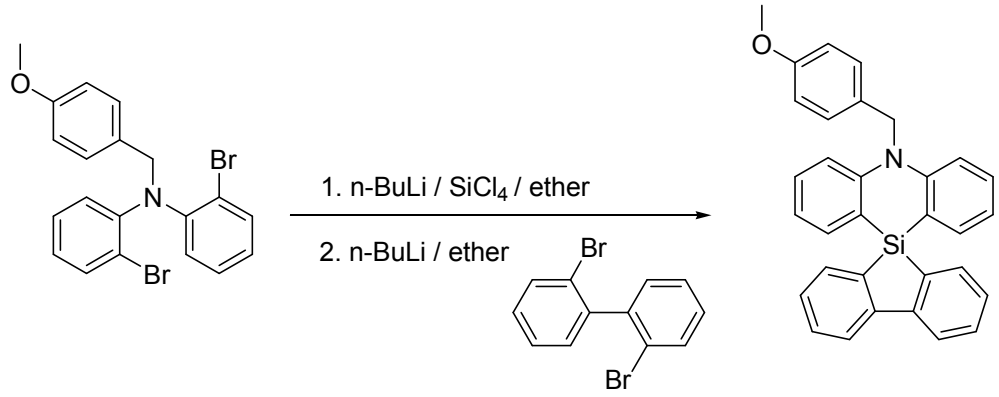
1.1. Materials

All reagents were purchased from Aldrich and TCI. Solvents were dried by using standard procedures. 2-Bromo-N-(2-bromophenyl)-N-(4-methoxybenzyl)aniline was synthesized by reported method. (Chemistry of Materials, 27, 6675-6681; 2015, **DOI:** 10.1021/acs.chemmater.5b02515)

1.2. Instruments

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 300 and Avance 500 spectrometer. A Jeol JMS-700 mass spectrometer was used to obtain the mass spectra of the samples.

1.3. Synthesis and Characterization

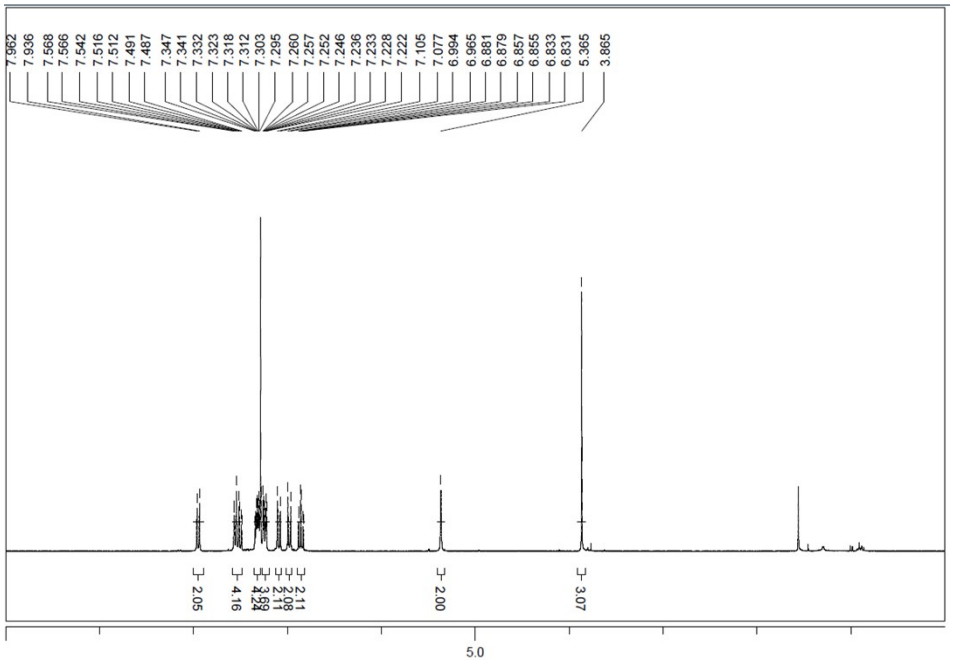


Synthesis of 5'-(4-methoxybenzyl)-5'H-spiro[dibenzo[b,d]silole-5,10'-dibenzo[b,e][1,4]azasiline].

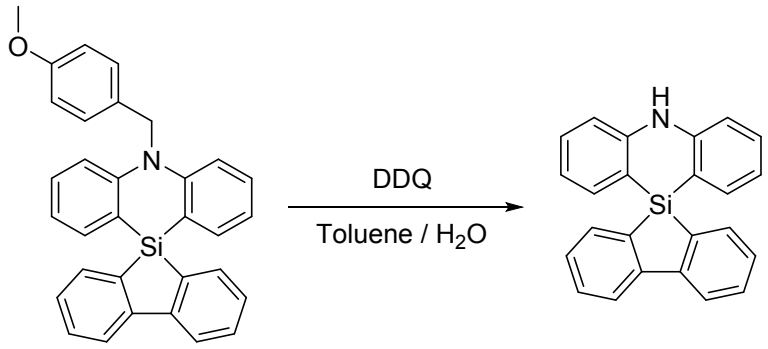
2.5 M *n*-BuLi/hexane (6.22 mL, 15.54 mmol) was added to the mixture of 2-bromo-N-(2-bromophenyl)-N-(4-methoxybenzyl)aniline (3.16 g, 7.06 mmol) and 200 mL of ether at 0 °C. After the mixture was stirred for 30 min at 0 °C, the solution of tetrachlorosilane (0.81 mL, 7.06 mmol) was added to the mixture. The solution was stirred for 4 h at room temperature.

And then 2.5 M *n*-BuLi/hexane (6.22 mL, 15.55 mmol) was added to the mixture of 2,2'-dibromo-1,1'-biphenyl (2.2 g, 7.06 mmol) and 20 mL of ether at -78 °C in another flask. After the mixture was stirred for 1h at -78 °C, this mixture was transferred to the first reaction flask. The solution was extracted by using water and ether. The ether layer was dried by $MgSO_4$, and ether was evaporated. The crude product

was purified by recrystallization using dichloromethane /hexane (1/4). Yield: 2.24 g (67.91 %), ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.96-7.93 (d, 2H), 7.57-7.49 (m, 4H), 7.35-7.30 (m, 4H), 7.26-7.22 (m, 4H), 7.10-7.08 (d, 2H), 6.99-6.96 (d, 2H), 6.88-6.83 (t, 2H), 5.36 (s, 2H), 3.82 (s, 3H).



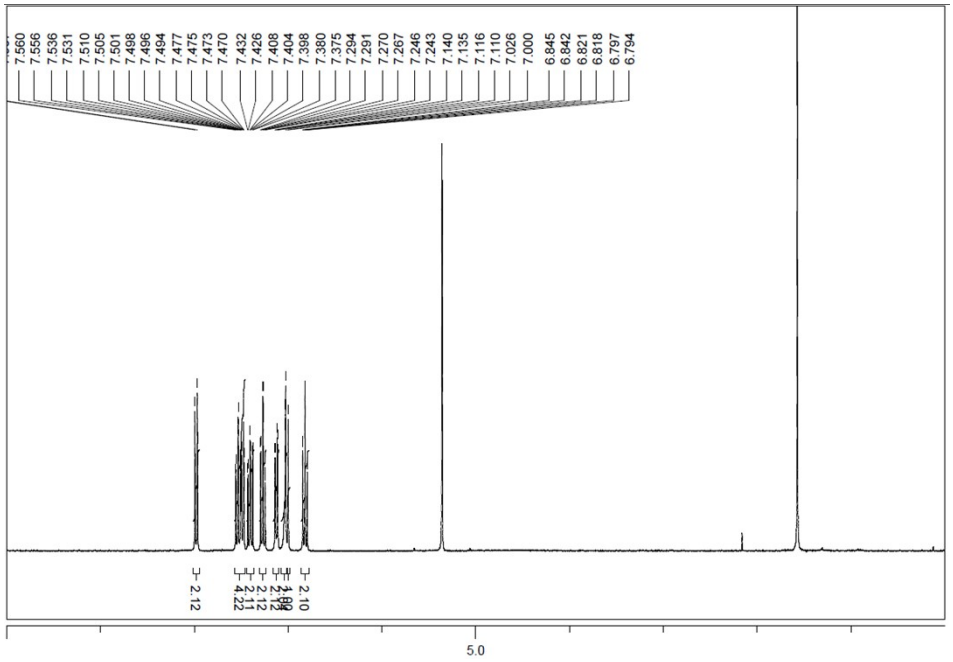
Synthesis Figure 1. ^{1}H-NMR Spectra of 5'-(4-methoxybenzyl)-5'H-spiro[dibenzo[b,d]silole-5,10'-dibenzo[b,e][1,4]azasiline].



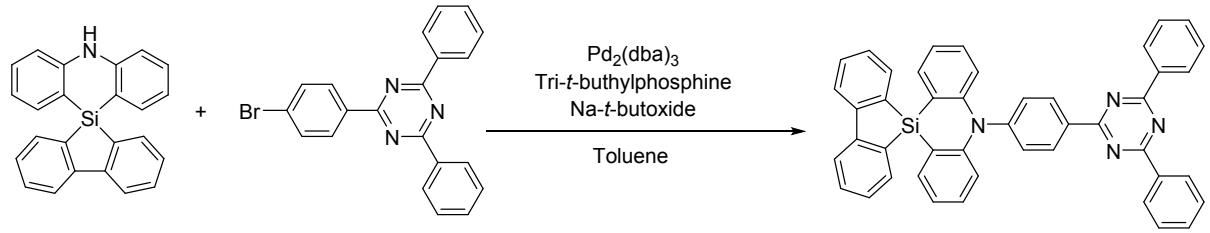
Synthesis of 5'H-spiro[dibenzo[b,d]silole-5,10'-dibenzo[b,e][1,4]azasiline].

5'-(4-Methoxybenzyl)-5'H-spiro[dibenzo[b,d]silole-5,10'-dibenzo[b,e][1,4]azasiline] (1.86 g, 3.98 mmol), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.99 g, 4.38 mol), toluene (20 mL) and H_2O (2 mL) were mixed, and refluxed at 80 °C for 14 h. After reaction, the solution was extracted by using ethyl acetate. The crude product was purified by column chromatography using hexane/ethyl acetate (5/1). Yield: 0.5 g (36.18 %).

^{1}H-NMR (300 MHz, CD_2Cl_2) δ = 7.99-7.96 (d, 2H), 7.56-7.50 (t, 2H), 7.50-7.47 (m, 2H), 7.43-7.37 (m, 2H), 7.29-7.24 (t, 2H), 7.14-7.11 (d, 2H), 7.03-7.02 (d, 2H), 7.00 (s, 1H), 6.84-6.79 (t, 2H).

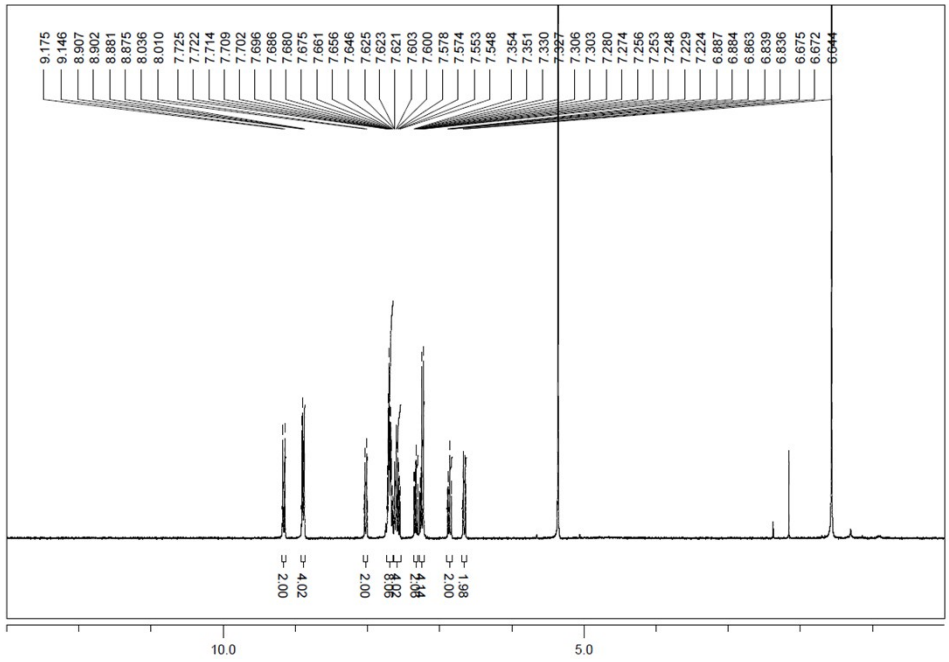


Synthesis Figure 2. ^{1}H-NMR Spectra of 5'H-spiro[dibenzo[b,d]silole-5,10'-dibenzo[b,e][1,4]azasiline].

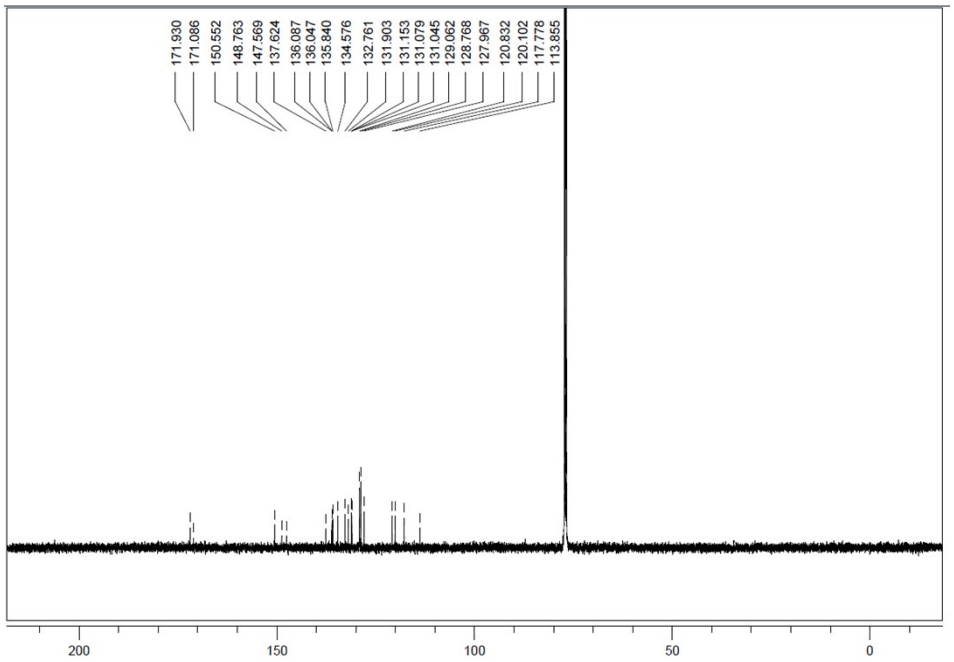


Synthesis of 5'-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-methylphenyl)-5'H-spiro[dibenzo[b,d]silole-5,10'-dibenzo[b,e][1,4]azasiline].

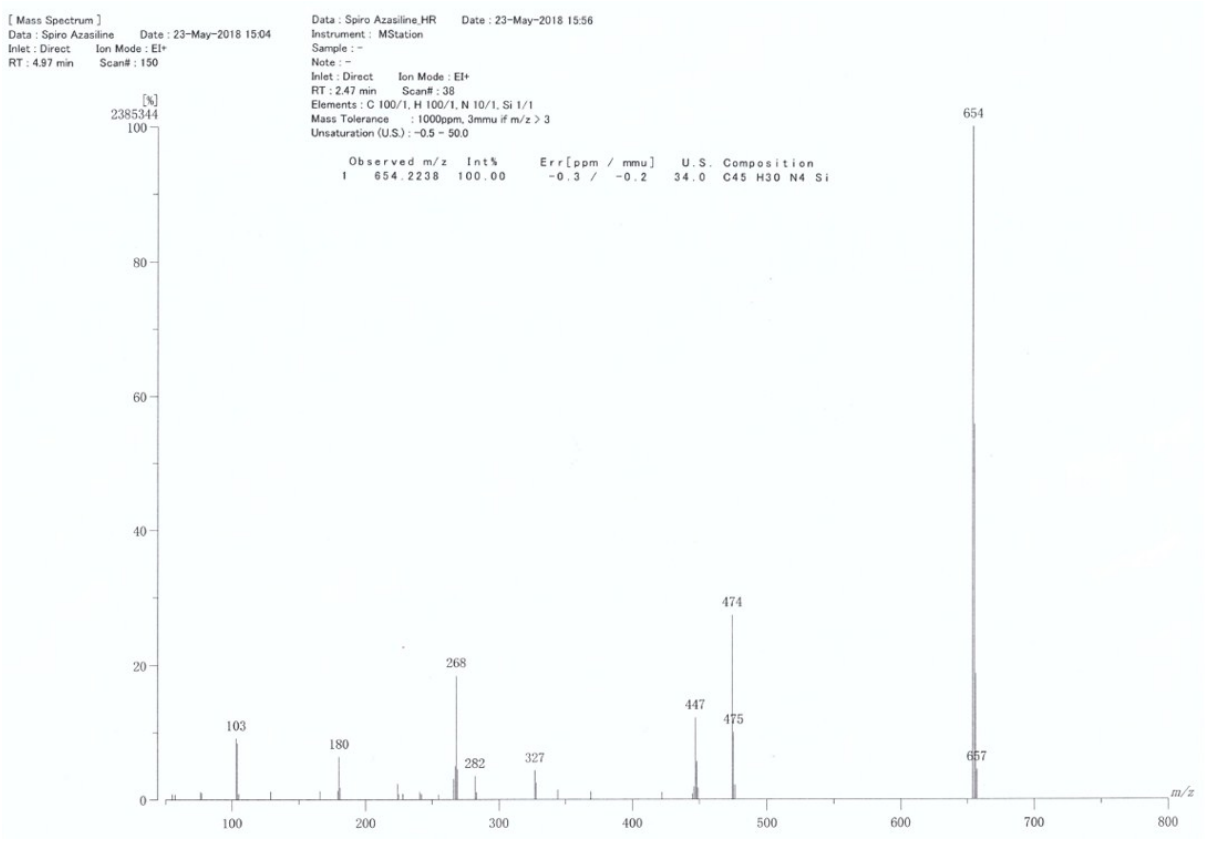
5'H-spiro[dibenzo[b,d]silole-5,10'-dibenzo[b,e][1,4]azasiline] (0.4 g, 1.15 mmol) and 2-(4-bromo-3-methylphenyl)-4,6-diphenyl-1,3,5-triazine (0.45 g, 1.15 mmol) were mixed in dry toluene (5.75 mL). Na-*t*-butoxide (0.33 g, 3.45 mmol), tri-*t*-buthylphosphine (0.02 g, 0.115 mmol) and tris(dibenzylideneacetone)dipalladium(0) (0.05 g, 0.058 mmol) was added and stirred for 10 h at 90 °C. The reaction mixture was extracted with dichloromethane and dried over anhydrous $MgSO_4$. The product was purified by a column with hexane and dichloromethane (Hex : MC = 3:1). Yield : 0.47 g, (62.35 %) ^{1}H-NMR (300 MHz, CD_2Cl_2) δ = 9.17-9.14 (d, 2H), 8.90-8.87 (m, 4H), 8.03-8.01 (d, 2H), 7.72-7.64 (m, 8H), 7.62-7.54 (m, 4H), 7.35-7.30 (t, 2H), 7.28-7.22 (m, 4H), 6.88-6.83 (t, 2H), 6.67-6.64 (d, 2H). ^{13}C-NMR (500 MHz, $CDCl_3$) δ = 171.93, 171.08, 150.55, 148.76, 147.57, 137.62, 136.09, 136.05, 135.84, 134.58, 132.76, 131.90, 131.15, 131.08, 131.05, 129.06, 128.77, 127.97, 120.83, 120.10, 117.78, 113.85. HRMS (EI) m/z $C_{45}H_{30}N_4Si$ Cacld: 654.2240, Found: 654.2238 (M+, 100%).



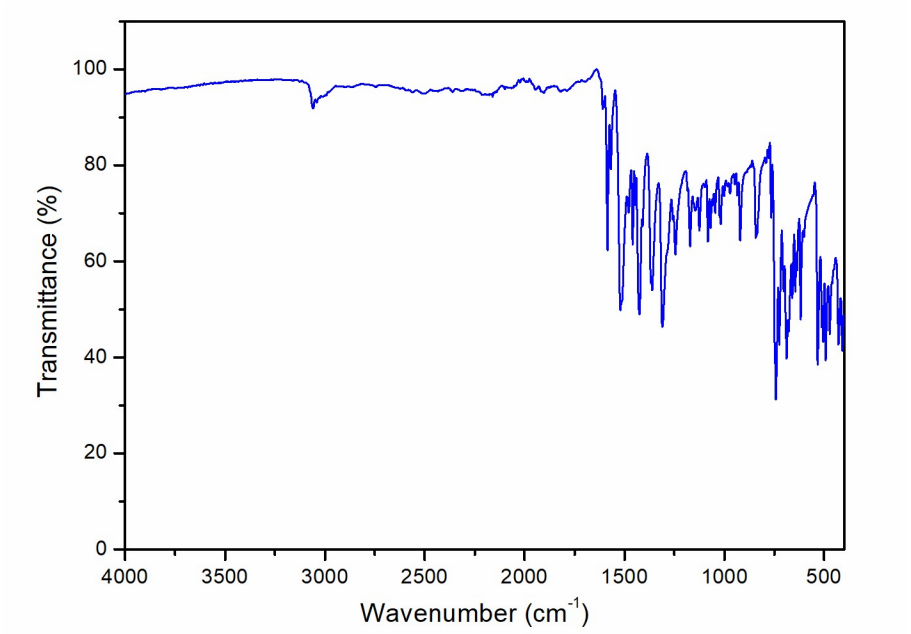
Synthesis Figure 3. ^{1}H-NMR Spectra of 5'-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-methylphenyl)-5'H-spiro[dibenzo[b,d]silole-5,10'-dibenzo[b,e][1,4]azasiline].



Synthesis Figure 4. ^{13}C-NMR Spectra of 5'-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-methylphenyl)-5'H-spiro[dibenzo[b,d]silole-5,10'-dibenzo[b,e][1,4]azasiline].



Synthesis Figure 5. EI Mass Spectra of 5'-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-methylphenyl)-5'H-spiro[dibenzo[b,d]silole-5,10'-dibenzo[b,e][1,4]azasiline].



Synthesis Figure 6. FT-IR spectrum of SAzTrz.

Synthesis Table 1. Element Analysis of SAzTrz

	Sample(mg)	Nitrogen(%)	Carbon(%)	Hydrogen(%)	Sulfur(%)
Sample 1	2.149	8.1569	82.494	4.5425	N.D
Sample 2	2.361	8.2224	82.595	4.4755	N.D
Sample 3	2.512	8.1621	81.943	4.4407	N.D

2. Supplementary Table and Figures

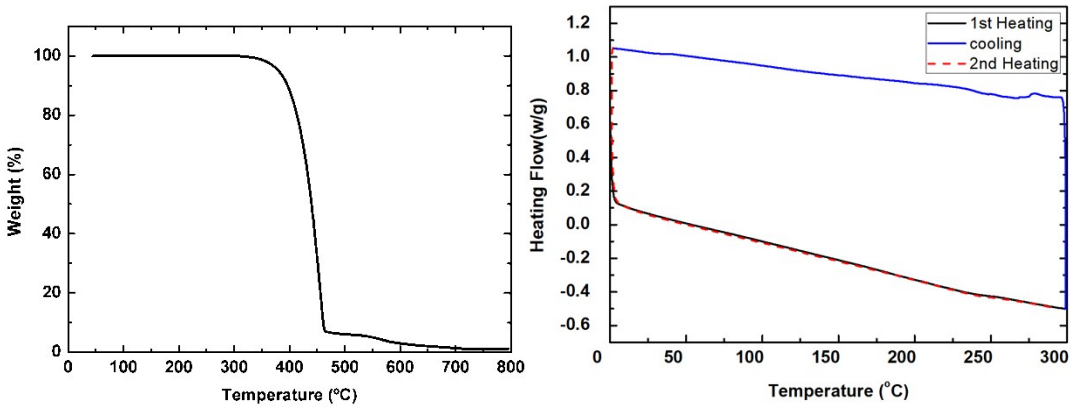


Figure S1. Thermogravimetric analysis (TGA) and differencial scanning calorimetry (DSC) of SAzTrz.

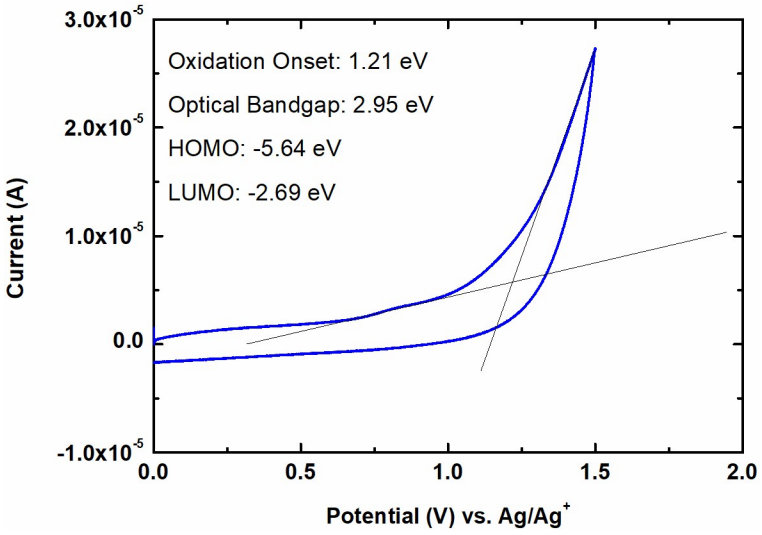


Figure S2. Cyclic Voltammetry curve of SAzTrz.

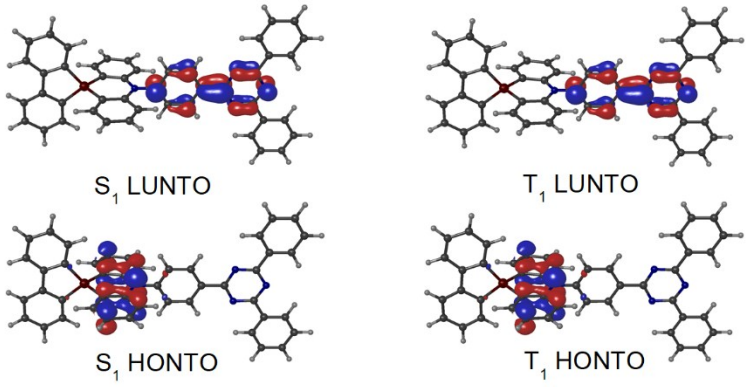


Figure S3. Optimized S_1 state geometry and natural transition orbitals of $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ of SAzTrz.

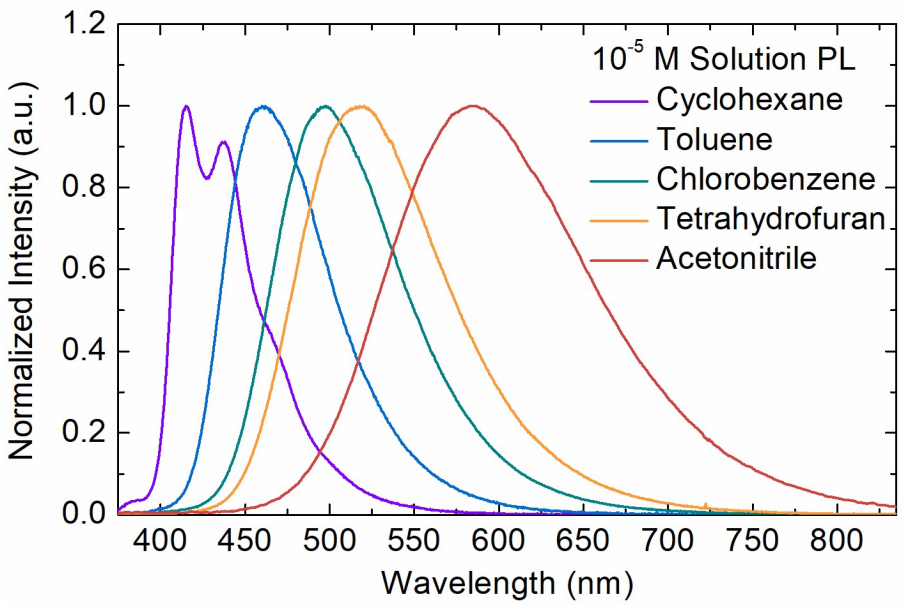


Figure S4. Solvatochromism of SAzTrz.

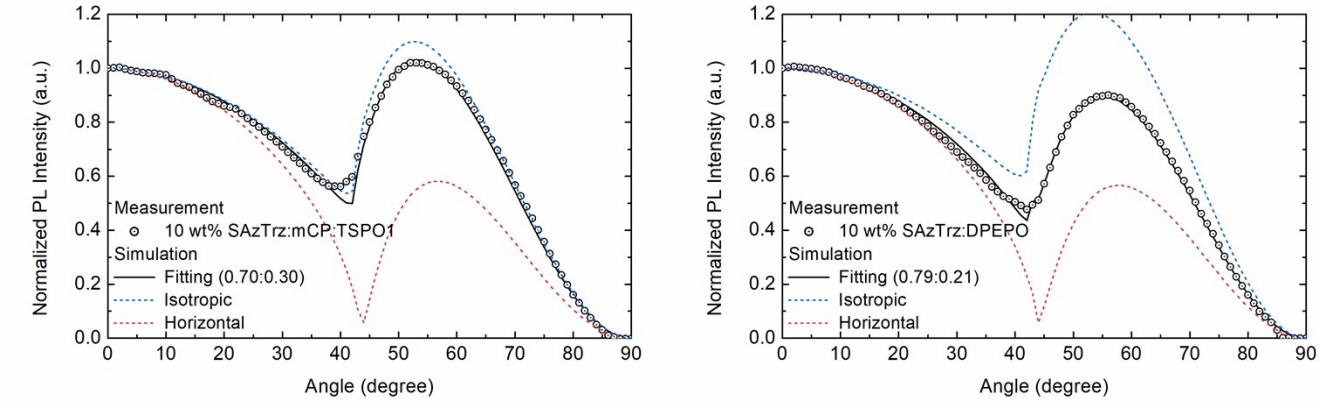


Figure S5. Angle-Dependent PL intensity of p-polarized light from 10 wt% SAzTrz: mCP:TSPO1 and 12 wt% SAzTrz:DPEPO 30 nm films at the wavelength of PL peak of each film.

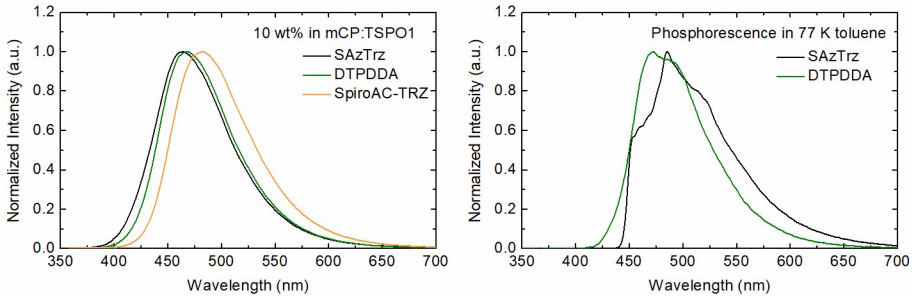


Figure S6. PL spectra of SAzTrz, DTPDDA, and SpiroAC-TRZ in 10 wt% mCP:TSPO1 film and phosphorescence of SAzTrz and DTPDDA in 77 K toluene.

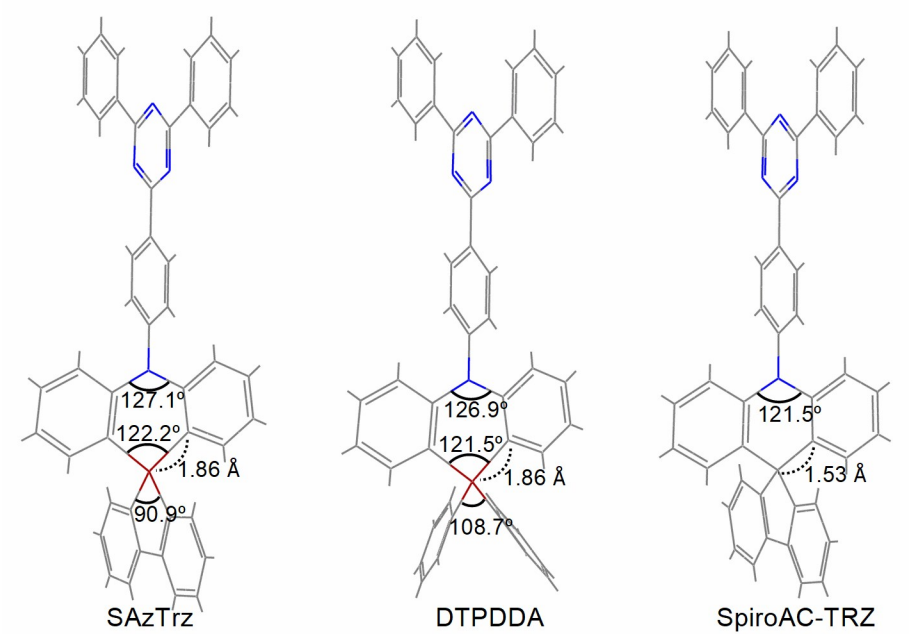


Figure S7. Bond angles and length of SAzTrz, DTPDDA, and SpiroAC-TRZ at optimized S_0 geometry.

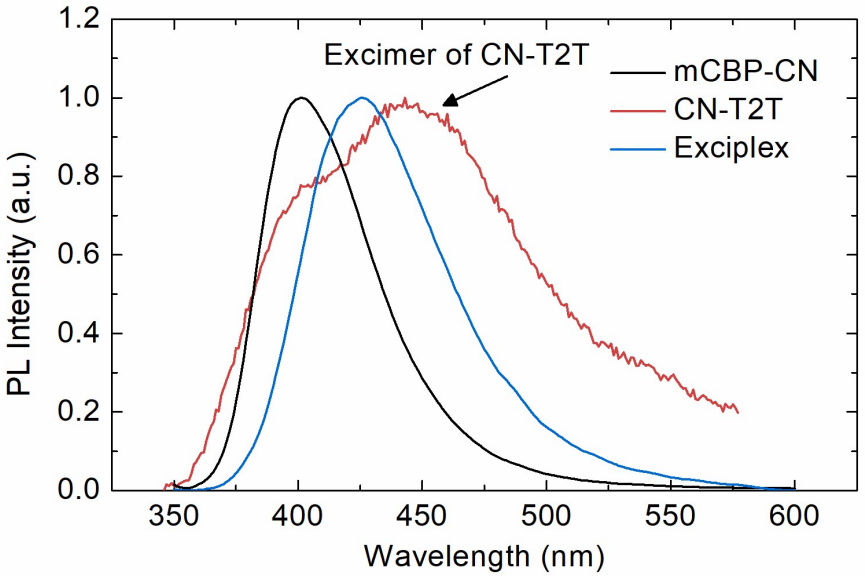


Figure S8. PL spectra of mCBP-CN, CN-T2T, and the exciplex.

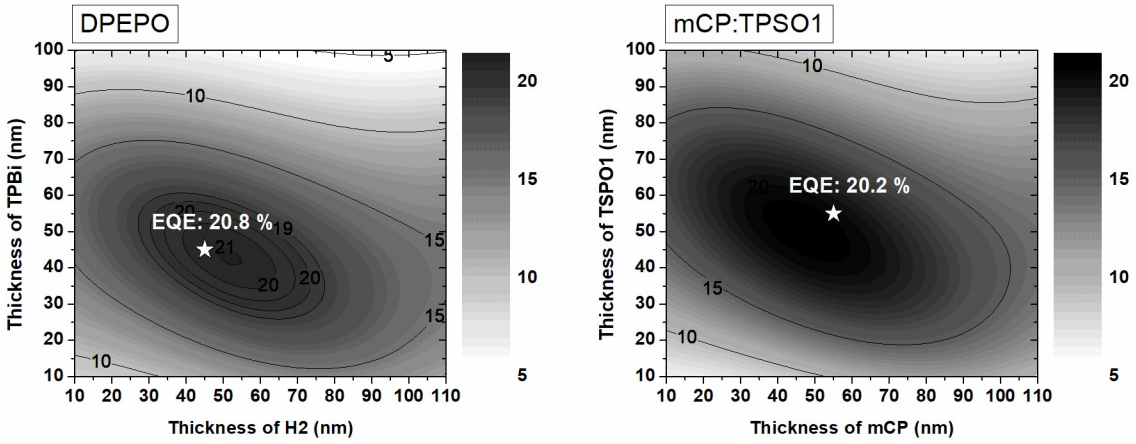


Figure S9. EQE simulation of DPEPO and mCP:TSPO1 host device.

Table S1. Photophysical properties of SAzTrz, DTPDDA, and SpiroAC-TRZ. (10^{-5} M toluene solution for a and 10 wt% in mCP:TSPO1 film for b-g)

Material	$Peak_{sol}$[a] (nm)	$Peak_{film}$[b] (nm)	ΔE_{ST}[c] (eV)	PLQY[d] (%)	Φ_p[e] (%)	Φ_d[f] (%)	Θ[g] (%)
SAzTrz	458	465	0.25	65	11	89	70
DTPDDA	465	468	0.16	70	19	81	66
SpiroAC-TRZ	486	483	0.07	98	20	80	71

Table S2. EL device characteristics of SAzTrz, DTPDDA, and SpiroAC-TRZ. [a]maximum EQE of real device. [b]Calculated maximum EQE by optical simulation based on PLQY and Θ of the emitters . [c]Estimated RISC efficiency. [d]PL quantum yield. [e]Horizontal ratio of emitting dipole orientation.

Material	Host	EQE_{max}[a] (nm)	$EQE_{max,cal}$[b] (nm)	Φ_{RISC}[c] (%)	PLQY[d] (%)	Θ[e] (%)
SAzTrz	DPEPO	20.6	20.8	~100	68	79
SAzTrz	mCP:TSPO1	8.2	20.2	~20	65	70
DTPDDA[43]	mCP:TSPO1	22.3	22.0	~100	70	66
SpiroAC-TRZ[8]	mCP-CN	36.7	38.3	~100	100	83