**Electronic Supplementary Information (ESI)**

**Tetraphenylnaphthosiline (TPNS): A Potential Building Block for Deep Blue Emitter Featured Aggregation Induced Blue-shifted Emission**

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1. Materials and Measurement

$^1$H and $^{13}$C NMR spectra were recorded with a Bruker AV 500 spectrometer in deuterated CDCl$_3$ using tetramethylsilane (TMS; $h = 0$) as internal reference. High resolution mass spectra (HRMS) were tested using a GCT premier CAB048 mass spectrometer operated in MALDI-TOF mode. UV-visible absorption spectra were measured with a SHIMADZU UV-2600 spectrophotometer. PL spectra were recorded on a HORIBA Flioromax-4 spectrofluorometer. Fluorescence quantum yields were measured using a Hamamatsu absolute photoluminescence quantum yield spectrometer C11347 Quantaurus-QY. The fluorescence lifetimes were determined by the compact fluorescence lifetime spectrometer C11367 of Hamamatsu. Thermogravimetric analysis (TGA) analysis was carried out on a TA TGA Q5000 under dry nitrogen at a heating rate of 20 $^\circ$C min$^{-1}$. Differential scanning calorimetry (DSC) analysis was performed on a DSC Q1000 under dry nitrogen at a heating rate of 10 $^\circ$C min$^{-1}$. Melting point was measured using a INESA WRS-1C melting point apparatus. Single crystal X-ray diffraction was carried out on a Gemini A Ultra diffractometer at 150K. Cyclic
voltammogram (CV) was measured in a solution of tetra-n-butylammonium hexafluorophosphate (Bu4NPF6) (0.1 M) in acetonitrile, using Hg/Hg2Cl2 and platinum wire as reference and counter electrode, respectively, at a scant rate of 50 mV s$^{-1}$. The HOMO and LUMO values are determined from reduction onsets ($E_{re}$) and oxidation onsets ($E_{ox}$) with restore calibration ($E_{rec}$) and oxidation calibration ($E_{oxc}$) [HOMO = -(4.8 + $E_{ox}$ - $E_{oxc}$) (eV); LUMO = -(4.8 + $E_{re}$ - $E_{rec}$) (eV)]. A platinum electrode coated with thin molecule film was used as the working electrode.

2. Synthesis and Characterization

\[
\text{R-Br + R-} \quad \text{Cul, Pd(PPh}_3)_2\text{Cl}_2 \quad \text{Et}_3\text{N, THF} \quad \rightarrow \quad \text{DPA-R}
\]

\[
\text{SiH} \quad \text{Br} \quad \text{Cl} \quad \text{n-BuLi, THF} \quad \rightarrow \quad \text{DPNS}
\]

\[
\text{R} \quad \text{SiH} \quad \text{Br} \quad \text{SiH} \quad \text{Ph} \quad \text{Ph} \quad \text{R} \quad \text{[RuH}_2\text{(CO)(PPh}_3)_3\text{]} \quad \text{toluene, 120°C} \quad \rightarrow \quad \text{TPNS-R}
\]

\[
\text{TPNS-H} \quad \text{TPNS-F} \quad \text{TPNS-M}
\]

**Fig. S1.** Chemical structures and synthetic routes of the TPNS derivatives.

**Naphthalen-1-ylidiphenylsilane (DPNS)**

1-bromonaphthalene (40 mmol, 8.283 g), butyllithium (50 mmol, 2.5 M, 20 mL) in 70 mL tetrahydrofuran were cooled and stirred under nitrogen at -78 °C for 3 h. Subsequently, chlorodiphenylsilane (44 mmol, 9.625 g) and 50 mL tetrahydrofuran was added to the reaction system. When the reaction was completed, the residual butyllithium of system was quenched by 30 mL water. the mixture was extracted with DCM/H$_2$O, the obtained organic layer solution was washed with brine, and dried by
adding anhydrous sodium sulfate. The residents were purified by silica column chromatography using PE as eluent to give pure products. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, $J = 8.0$ Hz, 1H), 7.93 (d, $J = 8.2$ Hz, 1H), 7.87 (d, $J = 7.6$ Hz, 1H), 7.62 – 7.56 (m, 5H), 7.49 – 7.34 (m, 9H), 5.90 (s, 1H).

1,2-bis(4-fluorophenyl)ethyne (DPA-F)

1-bromo-4-fluorobenzene (20 mmol, 2.402 g), 1-ethynyl-4-fluorobenzene (22 mmol, 3.850 g), Bis(triphenylphosphine)palladium dichloride (1 mmol, 0.702 g) and cuprous iodide (2 mmol, 0.381 g) in a mixture of 30 mL triethylamine and 10 mL tetrahydrofuran were heated and stirred under nitrogen at 80 °C for 8 h. When the reaction was completed, the mixture was extracted with DCM/H$_2$O, the obtained organic layer solution was washed with brine, and dried by adding anhydrous sodium sulfate. The residents were purified by silica column chromatography using PE as eluent to give pure products.

1,2-bis(4-methoxyphenyl)ethyne (DPA-M)

1-bromo-4-methoxybenzene (20 mmol, 2.402 g), 1-ethynyl-4-methoxybenzene (22 mmol, 3.850 g), Bis(triphenylphosphine)palladium dichloride (1 mmol, 0.702 g) and cuprous iodide (2 mmol, 0.381 g) in a mixture of 30 mL triethylamine and 10 mL tetrahydrofuran were heated and stirred under nitrogen at 80 °C for 8 h. When the reaction was completed, the mixture was extracted with DCM/H$_2$O, the obtained organic layer solution was washed with brine, and dried by adding anhydrous sodium sulfate. The residents were purified by silica column chromatography using PE as eluent to give pure products.

1,1,2,3-tetraphenyl-1H-naphtho[1,8-bc]siline (TPNS)

naphthalen-1-ylidiphenylsilane (1.240 g, 4 mmol), 1,2-diphenylethyne (1.068 g, 6 mmol) and carbonyl(dihydrido)tris(triphenylphosphine)ruthenium(II) (0.1832 g, 0.2 mmol) in 8 mL toluene were heated and stirred under nitrogen at 125°C for 20 h. When the reaction was complete, the mixture was extracted with DCM/H$_2$O, the obtained organic layer solution was washed with brine, and dried by adding anhydrous sodium sulfate. The residents were purified by silica column chromatography using PE as eluent to give pure products. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.99 (dt, $J = 7.3$, 3.6 Hz,
1H), 7.92 – 7.77 (m, 2H), 7.63 – 7.43 (m, 5H), 7.37 – 7.24 (m, 8H), 7.21 – 7.05 (m, 5H), 6.91 – 6.79 (m, 3H), 6.69 – 6.57 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.09, 142.24, 141.68, 139.15, 136.74, 136.31, 135.16, 134.75, 133.37, 131.60, 131.31, 130.63, 130.18, 129.80, 129.45, 129.38, 127.72, 127.48, 127.02, 126.16, 125.42, 124.80. HRMS (ESI-TOF, C$_{36}$H$_{26}$Si): m/z 486.1804 [[M+H]$^+$, calcd 487.1880].

2,3-bis(4-fluorophenyl)-1,1-diphenyl-1H-naphtho[1,8-bc]siline (TPNS-F)
naphthalen-1-yldiphenylsilane (1.240 g, 4 mmol), 1,2-bis(4-fluorophenyl)ethyne (1.284 g, 6 mmol) and carbonyl(dihydrido)tris(triphenylphosphine)ruthenium(II) (0.1832 g, 0.2 mmol) in 8 mL toluene were heated and stirred under nitrogen at 125°C for 20 h. When the reaction was complete, the mixture was extracted with DCM/H$_2$O, the obtained organic layer solution was washed with brine, and dried by adding anhydrous sodium sulfate. The residents were purified by silica column chromatography using PE as eluent to give pure products. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (dd, $J$ = 8.2, 1.3 Hz, 1H), 7.90 – 7.78 (m, 2H), 7.63 – 7.43 (m, 5H), 7.38 – 7.23 (m, 8H), 7.09 – 6.98 (m, 3H), 6.93 – 6.82 (m, 2H), 6.68 – 6.40 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 138.99, 138.00, 137.97, 137.39, 137.34, 136.87, 136.23, 134.89, 134.36, 133.96, 133.41, 132.05, 131.97, 131.53, 131.43, 130.71, 130.64, 130.49, 129.62, 129.43, 127.84, 125.54, 125.38, 114.76, 114.54, 114.26, 114.05. HRMS (ESI-TOF, C$_{36}$H$_{26}$F$_2$Si): m/z 522.1615 [[M+H]$^+$, calcd 523.1690].

2,3-bis(4-methoxyphenyl)-1,1-diphenyl-1H-naphtho[1,8-bc]siline (TPNS-M)
naphthalen-1-yldiphenylsilane (1.240 g, 4 mmol), 1,2-bis (4-methoxyphenyl) ethyne (1.429 g, 6 mmol) and carbonyl(dihydrido)tris(triphenylphosphine) ruthenium(II) (0.1832 g, 0.2 mmol) in 8 mL toluene were heated and stirred under nitrogen at 125°C for 20 h. When the reaction was complete, the mixture was extracted with DCM/H$_2$O, the obtained organic layer solution was washed with brine, and dried by adding anhydrous sodium sulfate. The residents were purified by silica column chromatography using PE as eluent to give pure products. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (d, $J$ = 8.0 Hz, 1H), 7.82 (dd, $J$ = 15.1, 7.1 Hz, 2H), 7.67 – 7.40 (m, 5H), 7.31 (ddd, $J$ = 20.0, 12.9, 6.3 Hz, 8H), 7.00 (d, $J$ = 8.5 Hz, 2H), 6.73 (d, $J$ = 8.5 Hz, 2H), 6.55 (d, $J$ = 8.6 Hz, 2H), 6.43 (d, $J$ = 8.6 Hz, 2H), 3.76 (s, 3H), 3.63 (s, 3H). $^{13}$C NMR
(101 MHz, CDCl₃) δ 157.73, 156.72, 153.98, 138.65, 136.61, 135.66, 135.02, 134.84, 134.23, 134.06, 133.33, 131.70, 131.37, 131.20, 130.39, 130.03, 129.96, 129.35, 127.68, 125.37, 125.32, 112.98, 112.57, 55.09, 54.91. HRMS (ESI-TOF, C₃₈H₃₀O₂Si): m/z 546.2015 [M+H]⁺, calcd 547.2090.

3. X-Ray Crystallography

Crystal data for TPNS-H (CCDC). C₃₆H₂₆Si, M₆ = 486.66, triclinic, P -1, α = 9.1491(3) Å, b = 11.6424(4) Å, c = 13.5780(4) Å, α = 72.151(3)°, β = 88.835(2)°, γ = 72.364(3)°, V = 1307.78(8) Å³, Z = 2, Dc = 1.236 g cm⁻³, μ = 0.952 mm⁻¹ (CuKα, λ = 1.54184), F(000) = 512, T = 150.00(10) K, 2θmax = 67.078° (98.6%), 12119 measured reflections, 4594 independent reflections (Rint = 0.0228), GOF on F² = 1.047, R₁ = 0.0369, wR₂ = 0.0932 (all data), Δe 0.253 and -0.349 eÅ⁻³.

Crystal data for TPNS-F (CCDC). C₃₆H₂₄F₂Si, M₆ = 522.64, monoclinic, C 1 2/c 1, a = 27.5574(4) Å, b = 9.33100(10) Å, c = 20.8827(3) Å, α = 90°, β = 100.5890(10)°, γ = 90°, V = 5278.29(12) Å³, Z = 8, Dc = 1.315 g cm⁻³, μ = 1.094 mm⁻¹ (CuKα, λ = 1.54184), F(000) = 2176, T = 149.99(10) K, 2θmax = 67.074° (98.7%), 14034 measured reflections, 4664 independent reflections (Rint = 0.0188), GOF on F² = 1.066, R₁ = 0.0349, wR₂ = 0.0901 (all data), Δe 0.237 and -0.338 eÅ⁻³.

Crystal data for TPNS-M (CCDC). C₃₈H₃₀O₂Si, M₆ = 546.71, triclinic, P -1, a = 10.0330(2) Å, b = 12.4401(3) Å, c = 13.7568(3) Å, α = 106.3079(18)°, β = 108.527(2)°, γ = 106.630(2)°, V = 1423.37(6) Å³, Z = 2, Dc = 1.276 g cm⁻³, μ = 0.986 mm⁻¹ (CuKα, λ = 1.54184), F(000) = 576, T = 149.99(10) K, 2θmax = 67.684° (98.2%), 13901 measured reflections, 5478 independent reflections (Rint = 0.0320), GOF on F² = 1.032, R₁ = 0.0475, wR₂ = 0.1228 (all data), Δe 0.282 and -0.451 eÅ⁻³.

4. Additional Data

Table S1. Selected dihedral angles (in deg.) for TPNS and its derivatives in solution (Soln) and aggregation (Aggn) phases. S₀/S₁ and Δ represent the geometric parameters extracted from the optimized S₀/S₁ states and the modifications between the two states, respectively.
Table S2. Optical Properties and Energy Levels of Luminogens Based on TPBSs.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_{\text{Abs}}$ (nm)</th>
<th>$\lambda_{\text{Em}}$ (nm)</th>
<th>$\Phi_\text{l}$ (%)</th>
<th>$\tau$ (ns)</th>
<th>$\text{E}<em>{\text{HOMO}} - \text{E}</em>{\text{LUMO}}$ (eV)</th>
<th>$\eta$ (%)</th>
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<tbody>
<tr>
<td>TPBS-H</td>
<td>330</td>
<td>431</td>
<td>436</td>
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*In THF solution (10⁻³ M). †Drop-casted film on quartz plate. ‡Fluorescence quantum yield, determined by a calibrated integrating sphere.

Table S3. EL Performance of Blue OLEDs Based on Luminogens Based on TPBSs.

<table>
<thead>
<tr>
<th>Material</th>
<th>$V_{\text{on}}$ (V)</th>
<th>$I_{\text{max}}$ (cd m⁻²)</th>
<th>$\eta_{\text{Lum}}$ (cd A⁻¹)</th>
<th>$\eta_{\text{CIE}}$ (lm W⁻¹)</th>
<th>$\eta_{\text{ff}}$ (lum W⁻¹)</th>
<th>$\eta_{\text{p}}$ (lum W⁻¹)</th>
<th>$\eta_{\text{ext}}$ (lum W⁻¹)</th>
<th>$\lambda_{\text{EM}}$ (nm)</th>
<th>CIE* (x, y)</th>
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<tr>
<td>TPBS-H</td>
<td>2.8</td>
<td>2238</td>
<td>3.15</td>
<td>3.3</td>
<td>3.3</td>
<td>3.5</td>
<td>438</td>
<td>(0.155, 0.102)</td>
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<td>TPBS-F</td>
<td>2.8</td>
<td>2139</td>
<td>3.28</td>
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<td>3.6</td>
<td>438</td>
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<tr>
<td>TPBS-B</td>
<td>2.8</td>
<td>2281</td>
<td>3.28</td>
<td>3.0</td>
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<td>3.1</td>
<td>438</td>
<td>(0.154, 0.104)</td>
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<tr>
<td>TPBS-M</td>
<td>2.8</td>
<td>2390</td>
<td>3.30</td>
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<td>3.4</td>
<td>438</td>
<td>(0.154, 0.103)</td>
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* $V_{\text{on}}$ = turn-on voltage at 1 cd m⁻²; $I_{\text{max}}$ = maximum luminance; $\eta_{\text{Lum}}$ = maximum current efficiency; $\eta_{\text{ff}}$ = maximum power efficiency; $\eta_{\text{ext}}$ = maximum external quantum efficiency; $\lambda_{\text{EM}}$ = EL maximum; CIE = Commission Internationale de l’Eclairage coordinates.
**Fig. S1.** The distance between the silicon atom and the NS plane of A) TPNS-H, B) TPNS-F and C) TPNS-M.

**Fig. S2.** Cyclic voltammograms curves of TPNS-based compounds.
Fig. S3. A) TGA and B) DSC curves of these new TPNS derivatives recorded under nitrogen at a heating rate of 10 °C min⁻¹.

Fig. S4. PL spectra of A) TPNS-H, B) TPNS-F and C) TPNS-M fluorogens in solvents with different polarity.

Fig. S5. The transient photoluminescence decay curves (A) in THF solutions (10⁻⁵
M) and (B) in neat films.

The equation to calculate the RMSD value

$$\text{RMSD} = \sqrt{\frac{1}{N} \sum \left[ (x_i - x'_i)^2 + (y_i - y'_i)^2 + (z_i - z'_i)^2 \right]}.$$ 

$^1$H and $^{13}$C NMR Spectra of TPNS derivatives

$^1$H NMR of TPNS-H in CDCl$_3$.

Fig. S7. $^1$H NMR of TPNS-H in CDCl$_3$. 
Fig. S8. $^1$H NMR of TPNS-F in CDCl$_3$.

Fig. S9. $^1$H NMR of TPNS-M in CDCl$_3$. 
Fig. S10. $^{13}$C NMR of TPNS-H in CDCl$_3$.

Fig. S11. $^{13}$C NMR of TPNS-F in CDCl$_3$. 
Fig. S12. $^{13}$C NMR of TPNS-M in CDCl$_3$.

The high-resolution mass spectrometry of TPNS derivatives

**Elemental Composition Report**

**Single Mass Analysis**

- Tolerance = 10.0 PPM
- DBE: min. = -1.5, max. = 50.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1471 formula(s) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:

- C: 36-36
- H: 26-150
- N: 0-16
- O: 0-23
- Si: 0-1
- K: 0-1

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Fig. S13. The mass spectrometry of TPNS-H.
Fig. S14. The mass spectrometry of TPNS-F.

Fig. S15. The mass spectrometry of TPNS-M.