Electronic Supplementary Information (ESI)

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

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Contents

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 ^{o}C min^{-1}. Differential scanning calorimetry (DSC) analysis was performed on a DSC Q1000 under dry nitrogen at a heating rate of 10 ^{o}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/Hg_2Cl_2 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

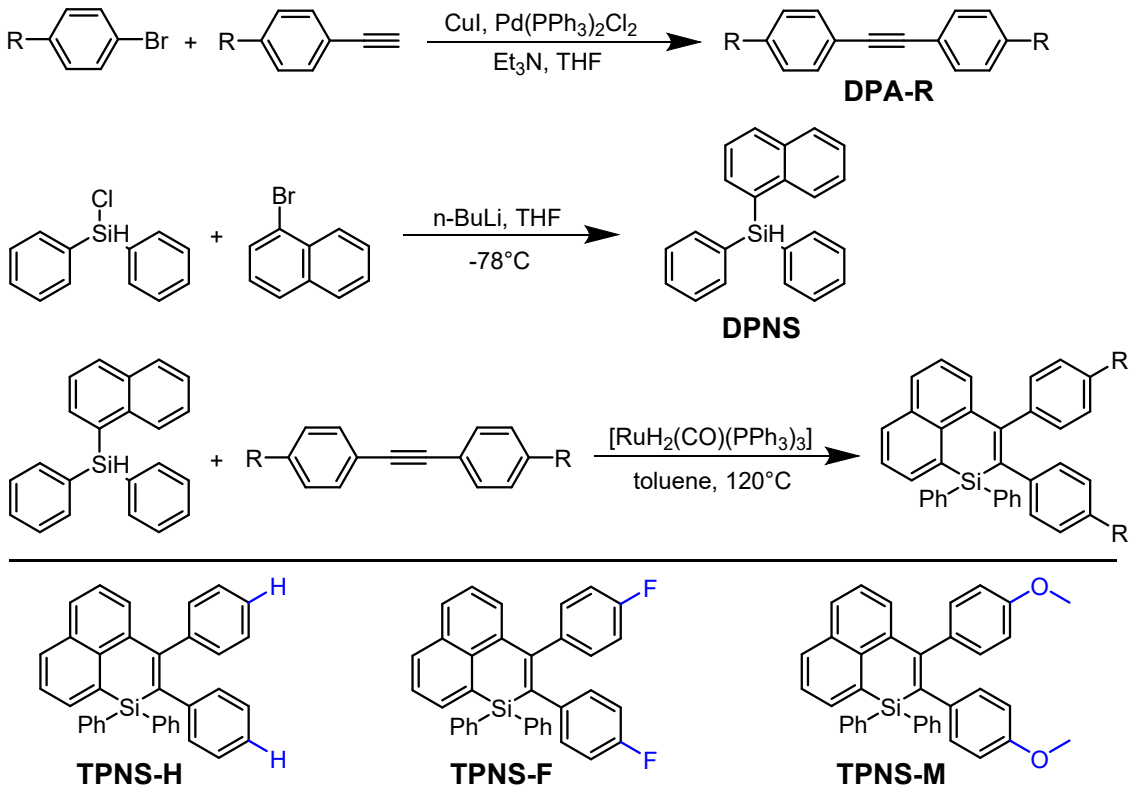


Fig. S1. Chemical structures and synthetic routes of there TPNS derivatives.

Naphthalen-1-yldiphenylsilane (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_2O, 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_2O, 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_2O, 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-yldiphenylsilane (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_2O, 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, $CDCl_3$) δ 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^{o}C for 20 h. When the reaction was complete, the mixture was extracted with DCM/H_2O, 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 8.01 (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, 2H), 6.93 – 6.82 (m, 2H), 6.68 – 6.40 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 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, $C_{36}H_{24}F_2Si$): *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^{o}C for 20 h. When the reaction was complete, the mixture was extracted with DCM/H_2O, 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 7.98 (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, $CDCl_3$) δ 157.73, 156.72, 153.98, 138.65, 136.61, 136.29, 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, $C_{38}H_{30}O_2Si$): *m/z* 546.2015 [$[M+H]^+$, calcd 547.2090].

3. X-Ray Crystallography

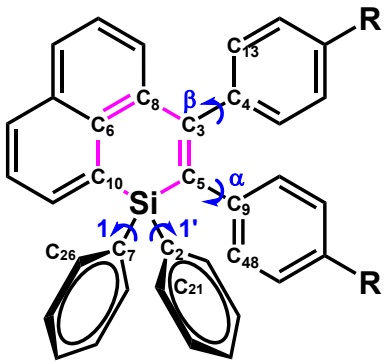
Crystal data for TPNS-H (CCDC). $C_{36}H_{26}Si$, M_W = 486.66, triclinic, P -1, a = 9.1491(3) Å, b = 11.6424(4) Å, c = 13.5780(4) Å, α = 72.151(3)°, β = 88.835(2)°, γ = 72.364(3)°, V = 1307.78(8) Å^3, Z = 2, Dc = 1.236 g cm^{-3}, μ = 0.952 mm^{-1} (CuKα, λ = 1.54184), F(000) = 512, T = 150.00(10) K, $2\theta_{max}$ = 67.078° (98.6%), 12119 measured reflections, 4594 independent reflections (R_{int} = 0.0228), GOF on F^2 = 1.047, R_1 = 0.0369, wR_2 = 0.0932 (all data), Δe 0.253 and -0.349 eÅ^{-3}.

Crystal data for TPNS-F (CCDC). $C_{36}H_{24}F_2Si$, M_W = 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) Å^3, 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, $2\theta_{max}$ = 67.074° (98.7%), 14034 measured reflections, 4664 independent reflections (R_{int} = 0.0188), GOF on F^2 = 1.066, R_1 = 0.0349, wR_2 = 0.0901 (all data), Δe 0.237 and -0.338 eÅ^{-3}.

Crystal data for TPNS-M (CCDC). $C_{38}H_{30}O_2Si$, M_W = 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) Å^3, 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, $2\theta_{max}$ = 67.684° (98.2%), 13901 measured reflections, 5478 independent reflections (R_{int} = 0.0320), GOF on F^2 = 1.032, R_1 = 0.0475, wR_2 = 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. S_0/S_1 and Δ represent the geometric parameters extracted from the optimized S_0/S_1 states and the modifications between the two states, respectively.



1 - C_{10}-Si-C_7-C_{26}
1'- C_5-Si-C_2-C_{21}
α - Si-C_5-C_9-C_{48}
β - C_8-C_3-C_4-C_{13}

TPNS-H, R = H
TPNS-F, R = F
TPNS-M, R = OCH_3

		TPNS-H			TPNS-F			TPNS-M		
		S_0	S_1	Δ	S_0	S_1	Δ	S_0	S_1	Δ
Soln	Si-C_{10}-C_6-C_8	–5.62	–9.25	3.63	–5.86	–9.86	4.00	–5.81	–11.29	5.48
	Si-C_5-C_3-C_8	–2.19	24.27	26.46	–2.31	23.73	26.04	–2.76	17.75	20.51
	1	74.75	153.78	79.03	75.25	153.09	77.84	76.01	142.06	66.05
	1’	–77.15	–122.15	45.00	–78.39	–121.67	43.28	–78.14	–121.12	42.98
	α	70.43	33.95	36.48	70.37	34.42	35.95	67.05	37.04	30.01
	β	74.25	49.89	24.36	73.67	48.33	25.34	72.07	46.83	25.24
Aggn	Si-C_{10}-C_6-C_8	5.65	5.09	0.56	5.96	6.08	0.12	–4.18	–3.99	0.19
	Si-C_5-C_3-C_8	–0.68	0.91	1.59	–6.41	–9.53	3.12	–9.97	–11.84	1.87
	1	67.27	66.94	0.33	64.59	65.02	0.43	73.13	73.29	0.16
	1’	–75.48	–76.84	1.36	–70.13	–69.94	0.19	–64.25	–64.39	0.14
	α	–80.72	–61.21	19.51	65.82	55.53	10.29	72.22	66.43	5.79
	β	–81.10	–67.83	13.27	84.34	81.75	2.59	80.08	66.82	13.26

Table S2. Optical Properties and Energy Levels of Luminogens Based on TPBSs.

	λ_{abs}[a] (nm)	λ_{em} (nm)		Φ_F[c] (%)		α_{AIE}[d]	τ[e] (ns) [k_r (10^8 s^{-1}), k_{nr} (10^8 s^{-1})]		HOMO/LUMO[g] (eV)	E_g[f] (eV)
		soln[a]	film[b]	soln	film		soln	film		
TPBS-H	330	431	436	1.0	28.2	28.2	1.98 (0.005, 0.50)	3.14 (0.09, 0.23)	−5.73/−2.50	3.23
TPBS-F	330	436	435	1.1	32.7	29.7	2.14 (0.005, 0.46)	2.78 (0.12, 0.24)	−5.64/−2.53	3.11
TPBS-B	341	447	445	1.5	55.2	36.8	1.62 (0.009, 0.61)	3.45 (0.16, 0.13)	−5.61/−2.44	3.17
TPBS-M	341	457	453	1.7	70.3	41.4	1.37 (0.012, 0.46)	4.54 (0.15, 0.06)	−5.38/−2.42	2.96

[a]In THF solution (10^{-5} M). [b]Drop-casted film on quartz plate. [c]Fluorescence quantum yield, determined by a calibrated integrating sphere. [d]Values of AIE effect, calculated by Φ_F (film)/Φ_F (soln). [e]Fluorescence lifetime, measured at room temperature in air; k_r = radiative decay rate ($k_r = \Phi_F/\tau$); k_{nr} = nonradiative decay rate [$k_{nr} = (1 - \Phi_F)/\tau$]. [f]Optical bandgap calculated from the onset of absorption spectrum. [g]Determined by CV measurement in solutions.

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

material	V_{on}[a] (V)	L_{max}[a] (cd m^{-2})	$\eta_{C,max}$[a] (cd A^{-1})	$\eta_{P,max}$[a] (lm W^{-1})	$\eta_{ext,max}$[a] (%)	λ_{EL}[b] (nm)	CIE[b] (x, y)
TPBS-H	2.8	2258	3.15	3.3	3.5	438	(0.155, 0.102)
TPBS-F	2.8	2139	3.28	3.4	3.6	438	(0.154, 0.104)
TPBS-B	2.8	2281	2.89	3.0	3.1	438	(0.154, 0.104)
TPBS-M	2.8	2390	3.13	3.3	3.4	438	(0.154, 0.103)

[a]V_{on} = turn-on voltage at 1 cd m^{-2}; L_{max} = maximum luminance; $\eta_{C,max}$ = maximum current efficiency; $\eta_{P,max}$ = maximum power efficiency; $\eta_{ext,max}$ = maximum external quantum efficiency; [b]λ_{EL} = EL maximum; CIE = Commission Internationale de l’Eclairage coordinates.

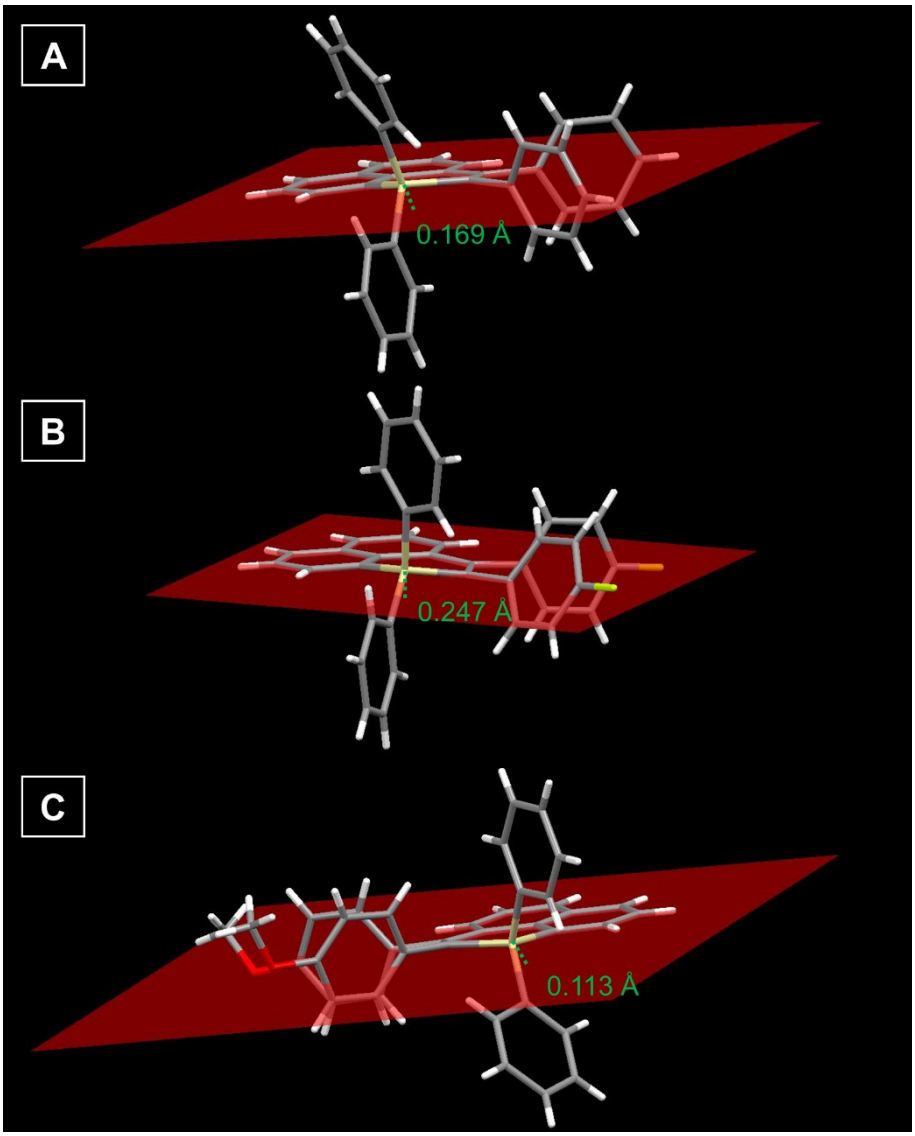


Fig. S1. The distance between the silicon atom and the NS plane of A) TPNS-H, B) TPNS-F and C) TPNS-M.

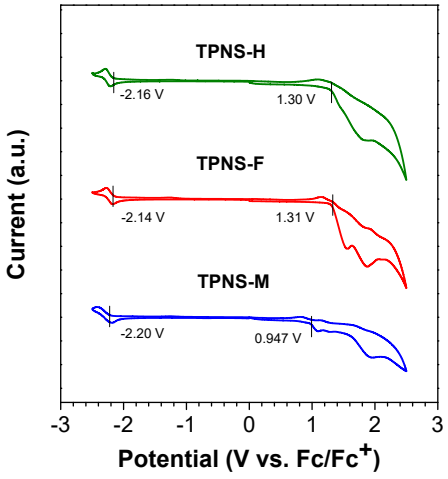


Fig. S2. Cyclic voltammograms curves of TPNS-based compounds.

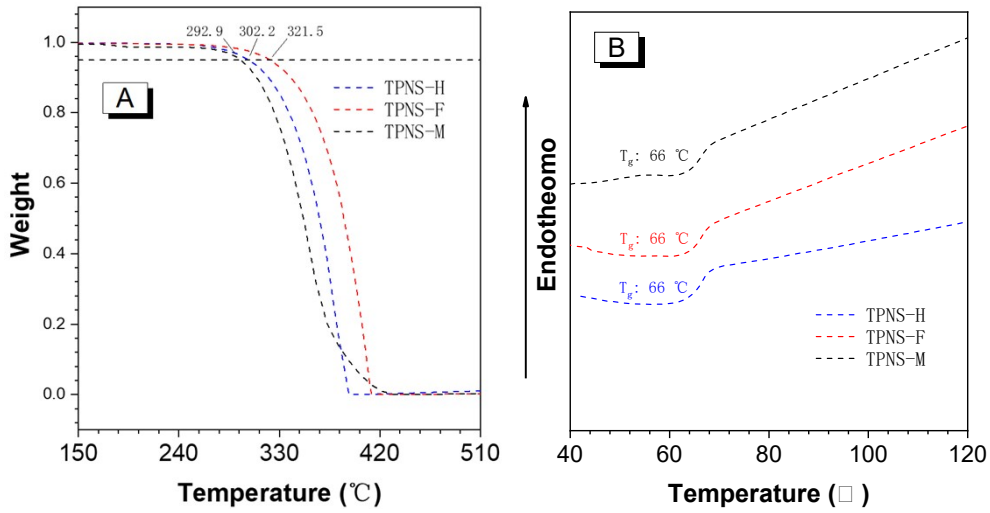


Fig. S3. A) TGA and B) DSC curves of these new TPNS derivatives recorded under nitrogen at a heating rate of 10 °C min^{-1}.

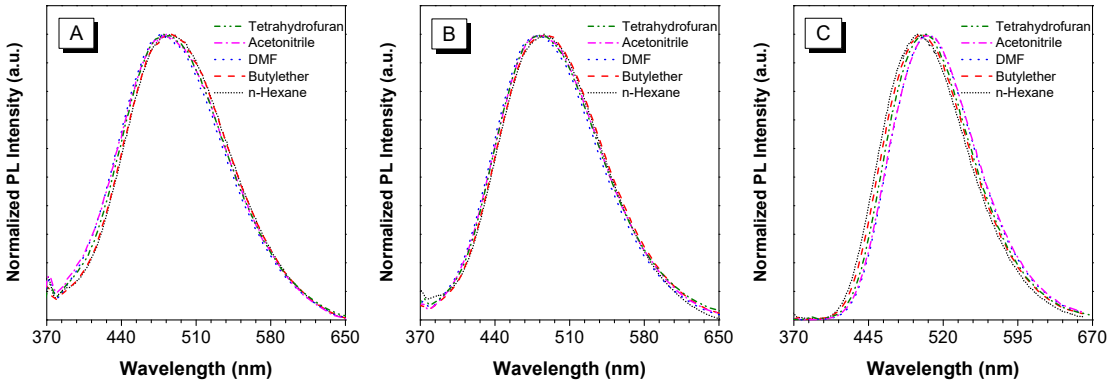


Fig. S4. PL spectra of A) TPNS-H, B) TPNS-F and C) TPNS-M fluorogens in solvents with different polarity.

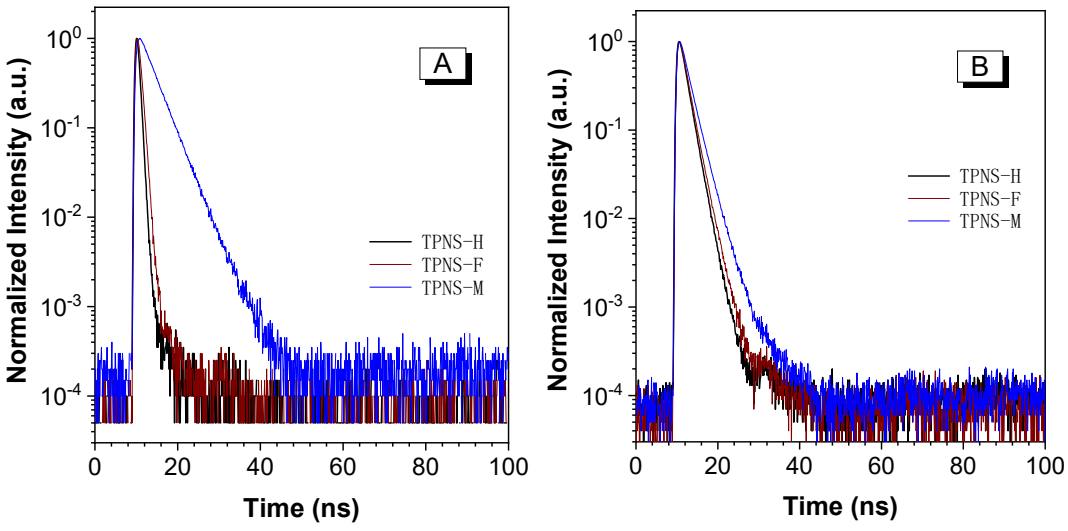


Fig. S5. The transient photoluminescence decay curves (A) in THF solutions (10^{-5}

M) and (B) in neat films.

The equation to calculate the RMSD value

$$\mathrm{RMSD} = \sqrt{\frac{1}{\mathrm{N}} \sum_{i}^{\mathrm{natom}} \left[\left(x_i - x_i' \right)^2 + \left(y_i - y_i' \right)^2 + \left(z_i - z_i' \right)^2 \right]}.$$

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

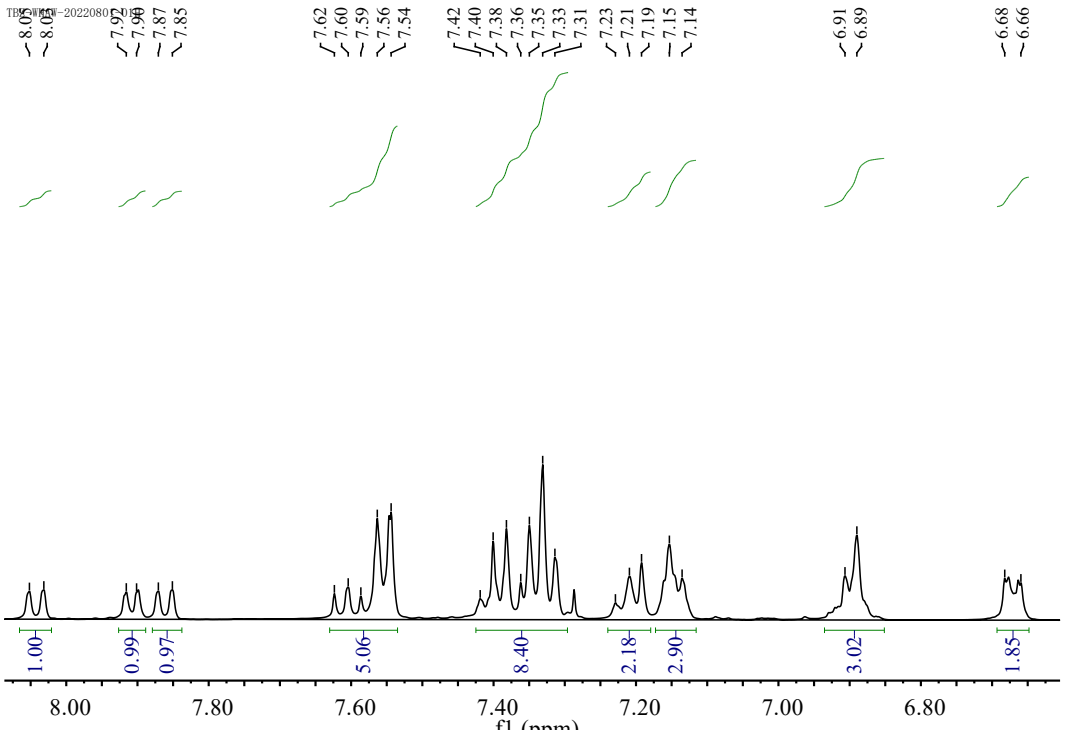


Fig. S7. ^{1}H NMR of TPNS-H in $CDCl_3$.

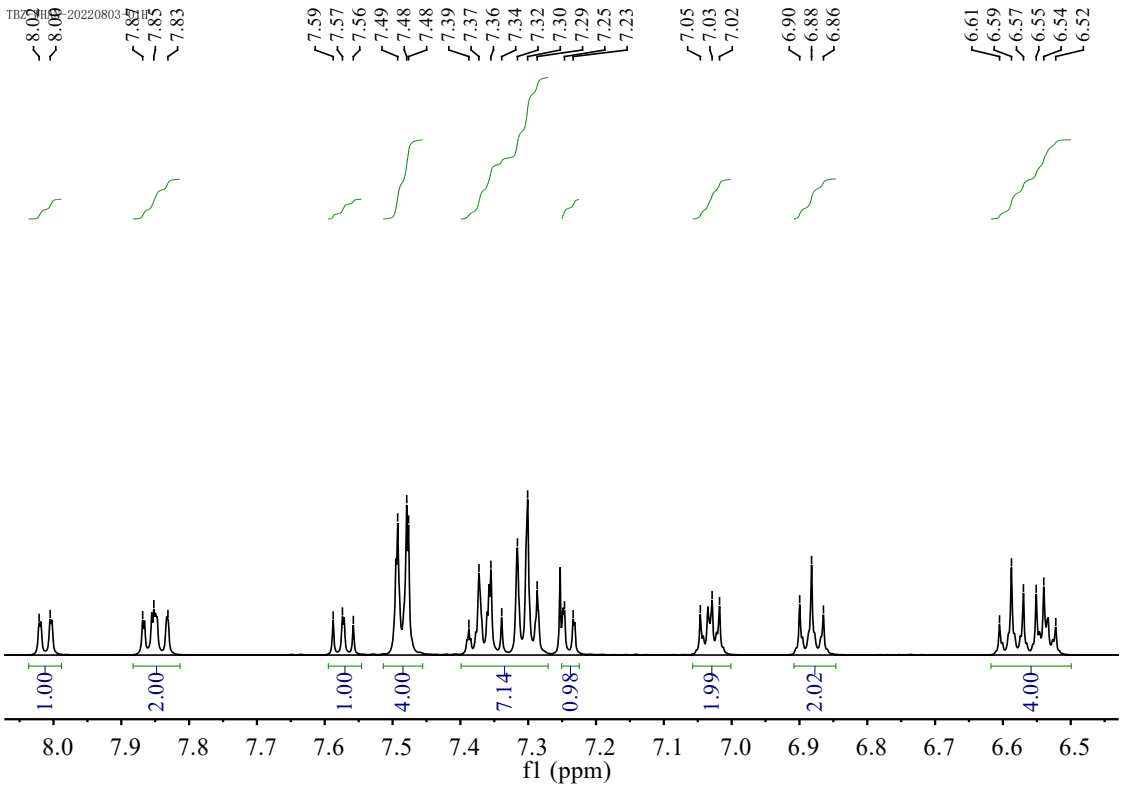


Fig. S8. ^{1}H NMR of TPNS-F in $CDCl_3$.

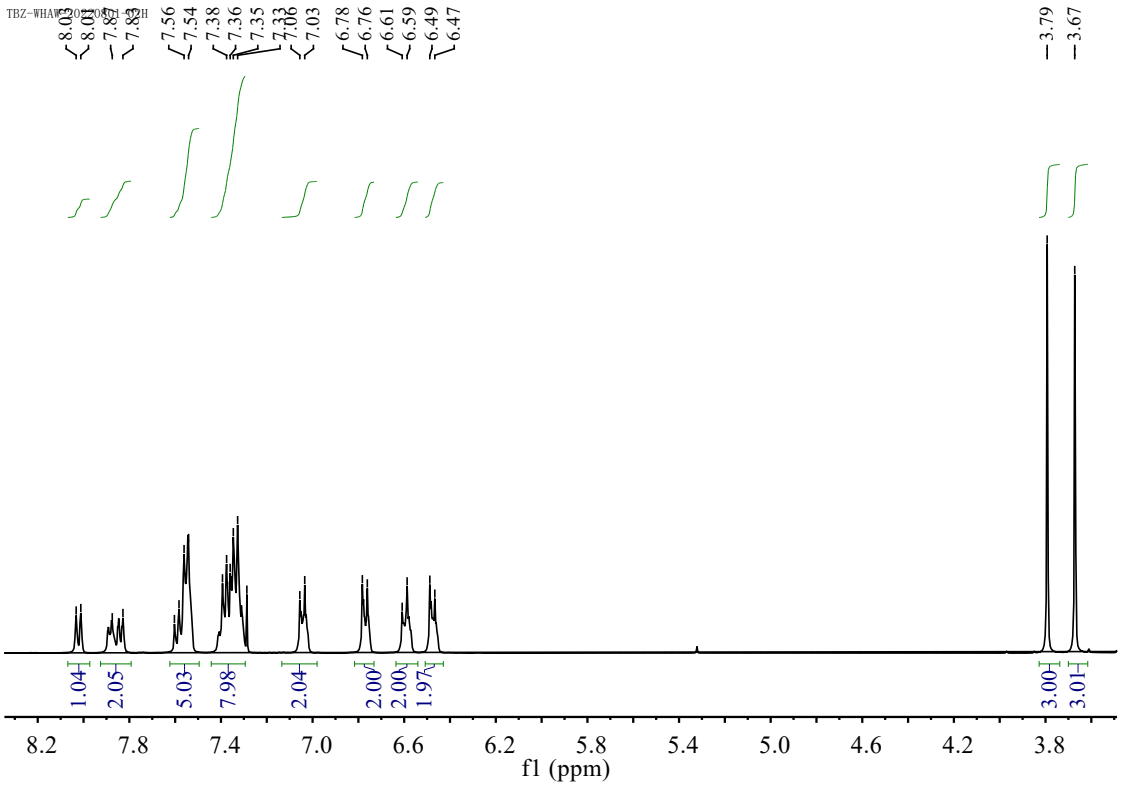


Fig. S9. ^{1}H NMR of TPNS-M in $CDCl_3$.

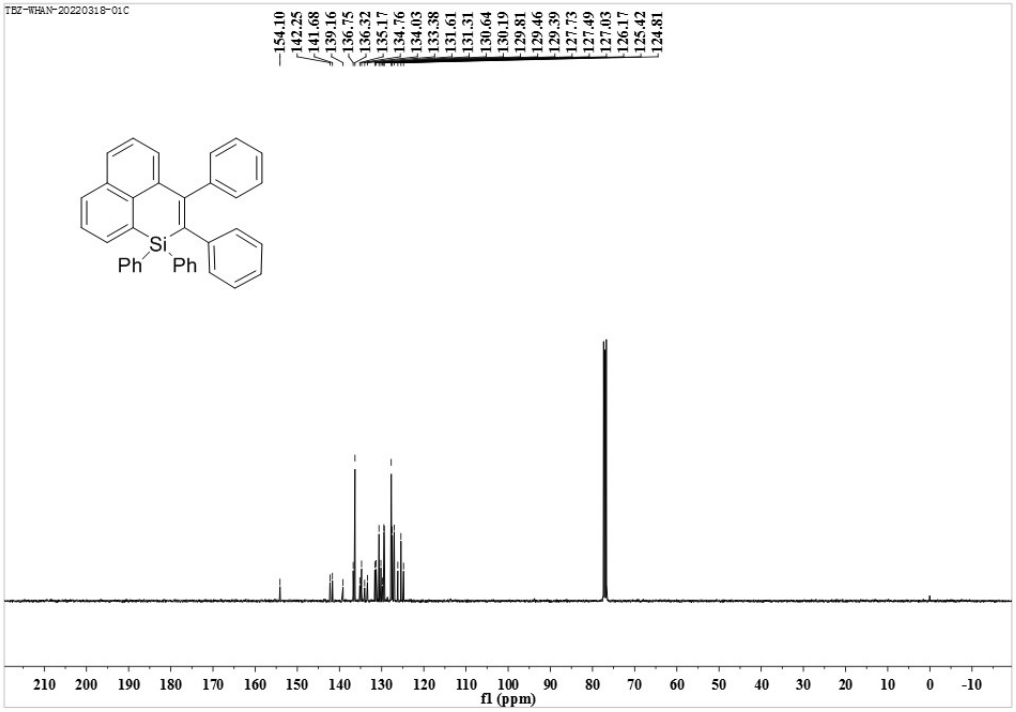


Fig. S10. ^{13}C NMR of TPNS-H in $CDCl_3$.

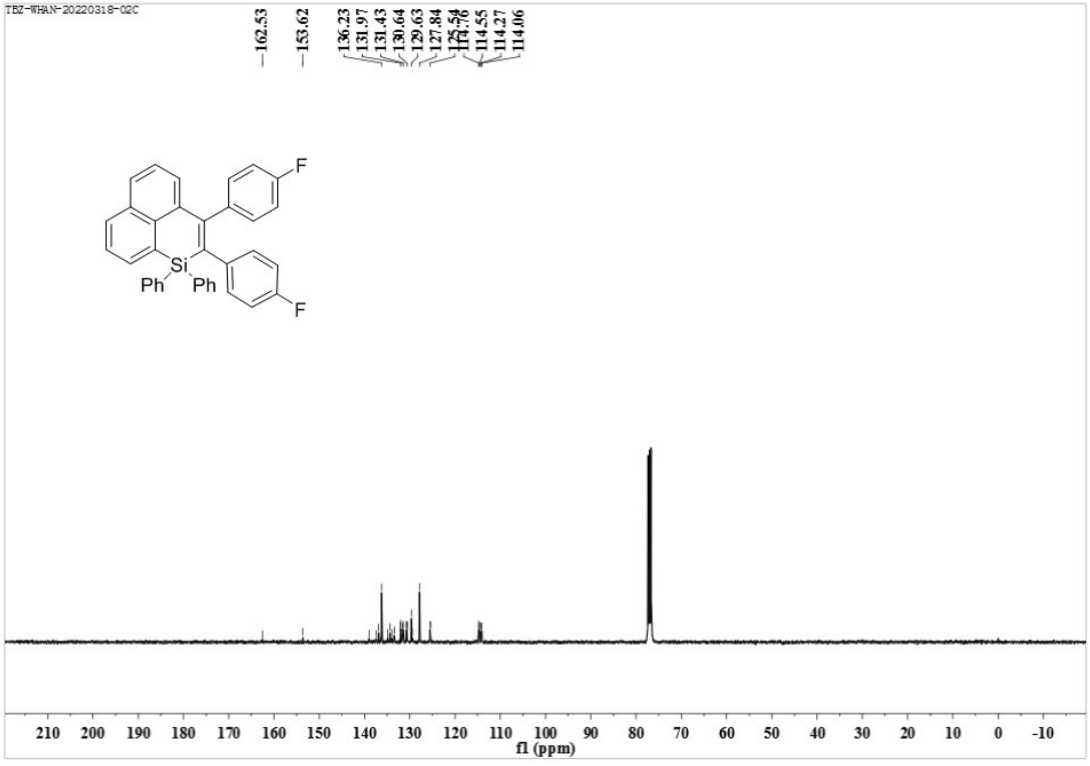


Fig. S11. ^{13}C NMR of TPNS-F in $CDCl_3$.

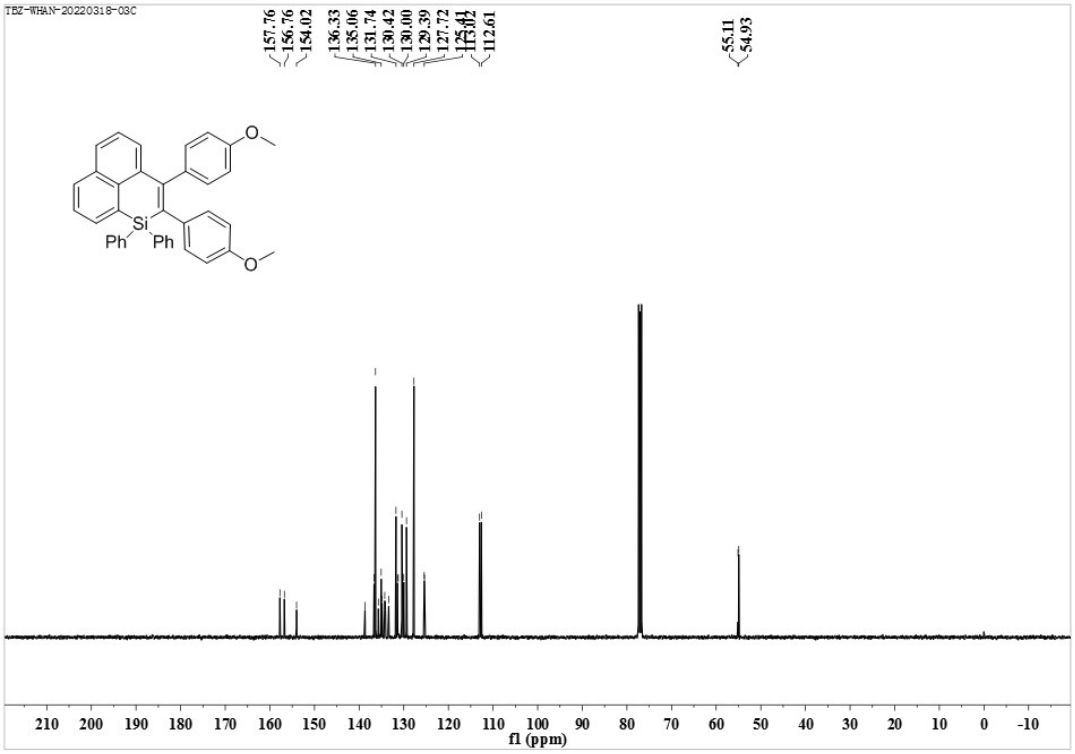


Fig. S12. ^{13}C NMR of TPNS-M in $CDCl_3$.

The high-resolution mass spectrometry of TPNS derivatives

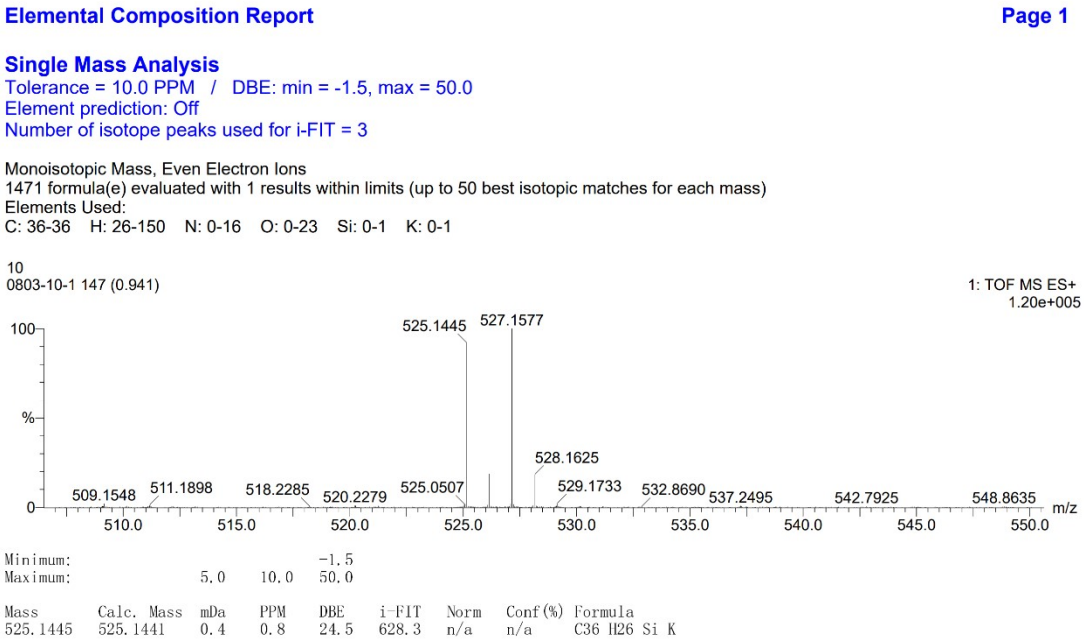


Fig. S13. The mass spectrometry of TPNS-H.

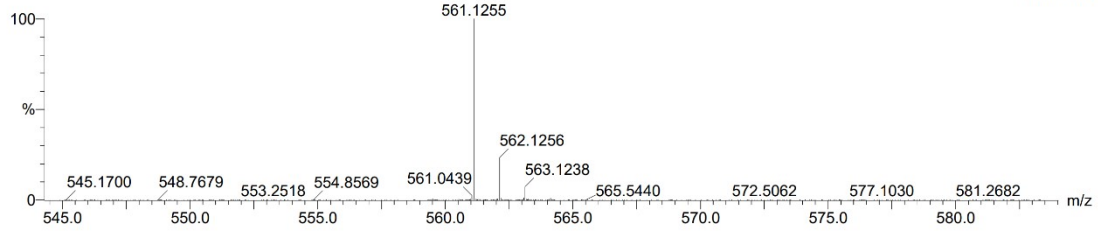
Elemental Composition Report **Page 1**

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
1476 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 36-36 H: 20-150 N: 0-16 O: 0-23 Si: 0-1 K: 0-1 F: 2-2

10
0803-10-2 144 (0.917)

1: TOF MS ES+
1.18e+005



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
561.1255	561.1252	0.3	0.5	24.5	592.2	n/a	n/a	C36 H24 Si K F2

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

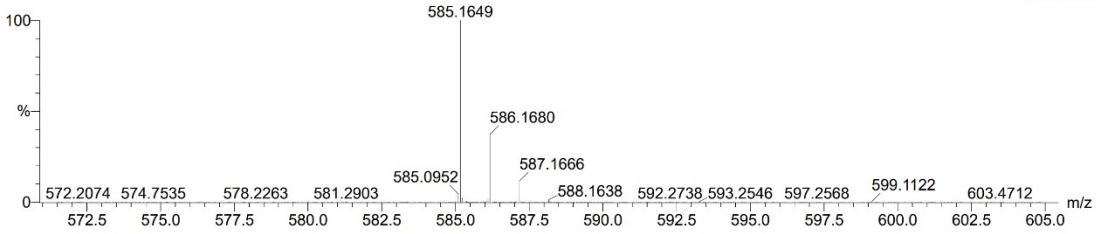
Elemental Composition Report **Page 1**

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
182 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 38-38 H: 20-150 N: 0-16 O: 0-2 Si: 0-1 K: 0-1

10
0803-10-3 122 (0.786)

1: TOF MS ES+
8.08e+005



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
585.1649	585.1652	-0.3	-0.5	24.5	813.7	n/a	n/a	C38 H30 O2 Si K

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