

SUPPLEMENTARY MATERIAL**Efficient Synthesis of All-Aryl Phenazasilines for Optoelectronic Applications**

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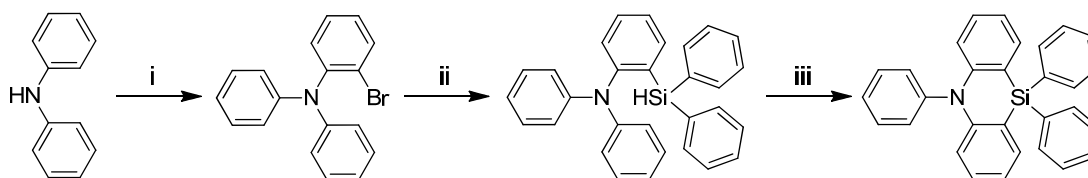
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Table of Contents

1. Materials and Synthesis	2
2. Single Crystal X-ray Analysis	7
3. Thermal Properties	8
4. Electrochemical Properties	9
5. High resolution mass spectrum	10
6. Optical Properties	11
7. Theoretical calculations	12

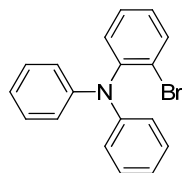
1. Materials and Synthesis

The chemicals and solvents, unless otherwise specified, were purchased from Sigma Aldrich, Acros, or Alfa Aesar, and used without further purification. The manipulations involving air-sensitive reagents were performed under the protection of argon atmosphere. ^1H and ^{13}C -nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Ultra Shield Plus 400 MHz instrument, with $d\text{-CDCl}_3$ as the solvents and tetramethylsilane (TMS) as the internal standard. The quoted chemical shifts are in *ppm* and the *J* values are expressed in Hz. The splitting patterns have been designed as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), and m (multiplet).



Scheme S1: The synthetic route of the all-aryl phenazasiline: (i) 2-bromoiodobenzene, CuI, K_2CO_3 , xylene, 120 °C, 48 h; (ii) *n*-BuLi, chlorodiphenylsilane, THF, -78 °C to room temperature, 12 h; (iii) tetrabutylammonium iodide (TBAI), *tert*-butyl hydroperoxide (TBHP, 5.5 M in decane), benzene, 90 °C, 24 h.

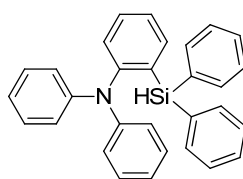
The synthesis of 2-bromo-N,N-diphenylaniline (TPABr)



Diphenylamine (10 g, 59 mmol), 2-bromoiodobenzene (11.43 mL, 89 mmol), copper(I) iodide (7.88 g, 41 mmol) and anhydrous potassium carbonate (16.34 g, 118 mmol) were mixed in xylene (40 mL). The mixture was heated at 120 °C for 2 days, then was cooled to the room temperature and poured into deionized water to end the reaction. The solution was extracted with dichloromethane (DCM) for three times (3×200 mL). The organic phase was separated, collected,

dried, and concentrated *in vacuo*. The resulting residue was further purified by flash column chromatography on silica gel (300-400 mesh) (eluent: petroleum ether (PE)) to afford 2-bromo-N,N-diphenylaniline as a white solid. Yield: 10.05 g (55%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.71 (d, J=8 Hz 1H), 7.44 (t, J=7.6 Hz 1H), 7.29-7.22 (m, 5H), 6.95 (t, J=7.4 Hz 1H), 6.83 (t, J=7.6 Hz 6H). ¹³C NMR (100 MHz, CDCl₃, ppm) 146.98, 145.50, 134.54, 131.67, 129.06, 128.85, 127.29, 123.77, 122.03, 121.98.

The synthesis of 2-(diphenylsilyl)-N,N-diphenylaniline (TPASiH)



To a freshly distilled tetrahydrofuran (THF) solution of 2-bromo-N,N-diphenylaniline (1 g, 3.1 mmol) at -78 °C, a hexane solution of *n*-butyllithium (1.86 mL, 4.65 mmol) was added dropwisely^[1]. After stirred at -78 °C for 1.5 h, chlorodiphenylsilane (3.35 mL, 15.5 mmol) was added into the reaction system. The resulting mixture was subsequently stirred at -78 °C for 0.5 h and at room temperature for 12 h. The reaction solution was quenched with water (150 mL) and extracted with DCM (3×100 mL). The organic layer was collected and dried over Na₂SO₄. The solvent was removed *in vacuo* and the resulting crude product was purified by column chromatography on silica gel (eluent: PE) to give a white solid. Yield: 1.21 g (92%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.428 (td, J₁=8 Hz J₂=1.6 Hz 2H) 7.370 (ddd, J₁=12 Hz J₂=4 Hz J₃=2.4 Hz 5H), 7.320 (dt, J₁=7.2 Hz J₂=2.4 Hz 2H), 7.275-7.236 (m, 3H), 7.179 (td, J₁=7.2 Hz J₂=1.2 Hz 1H), 7.129 (d, J=7.6 Hz 1H), 7.071 (dd, J₁=8.8 Hz J₂=7.2 Hz 2H), 6.853-6.824 (m, 6H), 5.075 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm) 153.55, 148.37, 138.54, 135.66, 133.91, 133.62, 131.70, 129.69, 128.76, 127.77, 125.27, 122.61, 121.61.

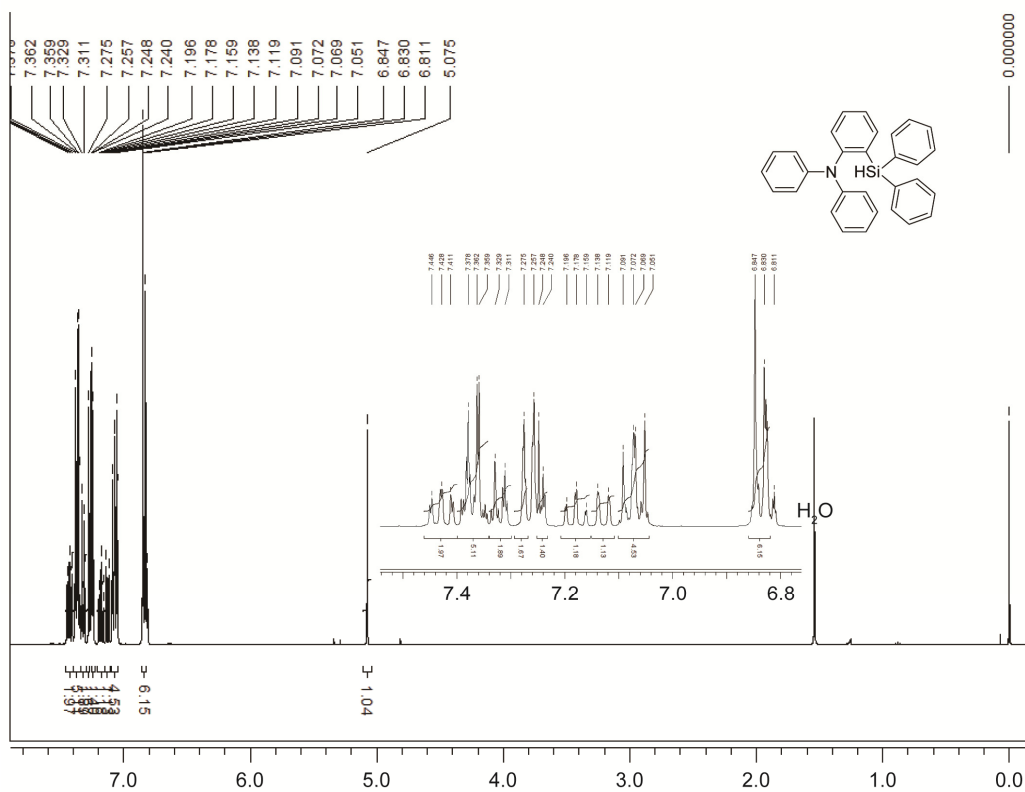


Fig. S1. ¹H NMR spectrum of 2-(diphenylsilyl)-N,N-diphenylamine (TPASiH).

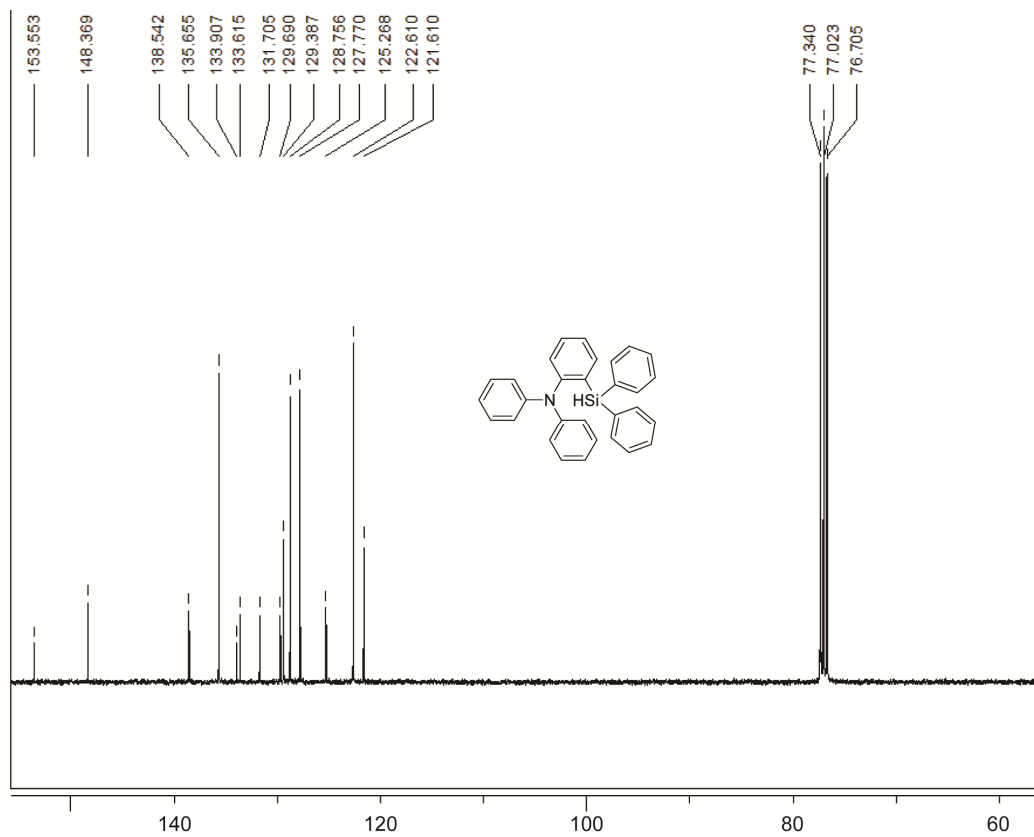
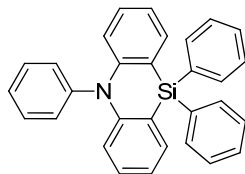


Fig. S2. ¹³C NMR spectrum of 2-(diphenylsilyl)-N,N-diphenylamine (TPASiH).

The synthesis of 5,10,10-triphenyl-5,10-dihydrophenazasiline (DPhPz)



A mixture of 2-(diphenylsilyl)-N,N-diphenylaniline (0.2 g, 0.47 mmol), *tert*-butyl hydroperoxide (0.28 mL, 1.55 mmol), and tetrabutylammonium iodide (1.7 mg, 0.0047 mmol) dissolved in benzene (2 mL) was stirred at 90 °C for 24 h^[2]. After cooling down to room temperature, the reaction mixture was extracted with DCM for three times. The organic layer was collected and dried with Na₂SO₄. After removing the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (eluent: PE/DCM = 30/1) to afford **DPhPz** as white solid. Yield: 0.11 g (54%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.637 (dd, J₁=8 Hz J₂=1.6 Hz 5H) 7.590 (dd, J₁=8 Hz J₂=1.6 Hz 3H), 7.510 (t, J=7.6 Hz 1H), 7.432-7.350 (m, 6H), 7.292 (d, J=7.2 Hz 2H), 7.156 (td, J₁=8.0 Hz J₂=1.6 Hz 2H), 6.922 (t, J=7.2 Hz 2H), 6.410 (d, J=8.4 Hz 2H). ¹³C NMR (100 MHz, CDCl₃, ppm) 150.00, 143.60, 136.09, 135.89, 135.48, 131.39, 130.94, 130.28, 129.54, 128.07, 127.89, 119.85, 117.18, 115.43.

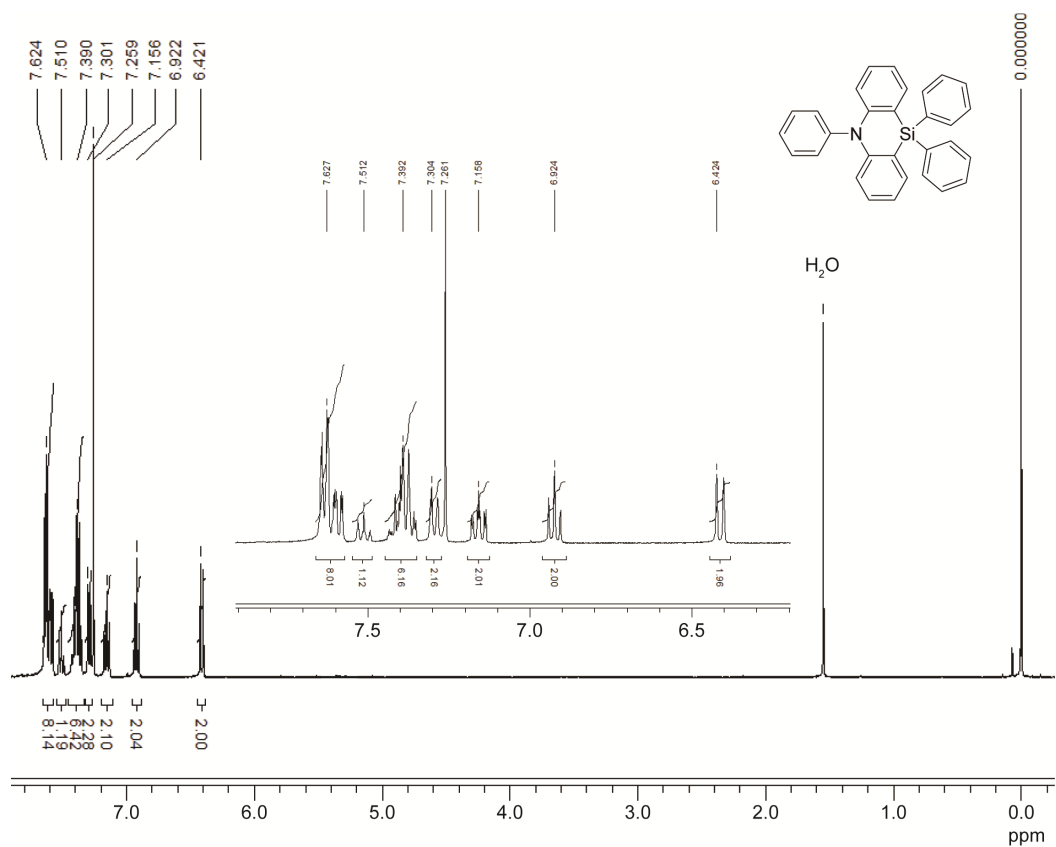


Fig. S3. ^1H NMR spectrum of DPhPz.

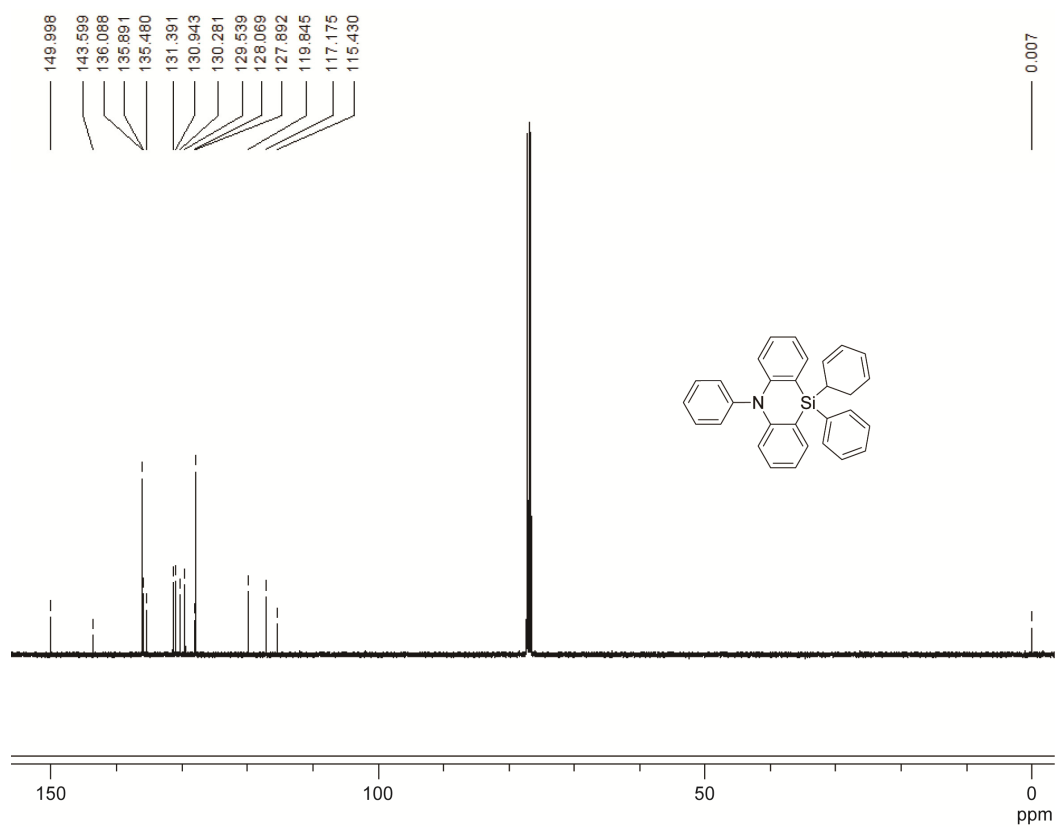


Fig. S4. ^{13}C NMR spectrum of DPhPz.

2. Single Crystal X-ray Analysis

Single crystals of **DPhPz** were grown by slow evaporation of a combined DCM and ethanol solution at room temperature. The single crystal structure data were collected on a Bruker SMART APEX (II)-CCD at 293 K and were analyzed by Mercury 1.4 software. The structure data were summarized in Table S1. The final crystallographic data for molecules have been deposited to the Cambridge Crystallographic Data Centre and are available on request quoting the deposition number CCDC 1431510 for **DPhPz**.

Table S1. Crystallographic data of **DPhPz**

Compound	DPhPz
Empirical formula	C ₃₀ H ₂₃ NSi
Formula weight g mol⁻¹	425.60
Crystal color	colorless
Wavelength Å	0.71073
Crystal system	triclinic
a, Å	9.622(3)
b, Å	10.571(3)
c, Å	13.943(5)
α, °	79.991(7)
β, °	70.037(6)
γ, °	87.966(6)
volume, Å³	1312.3(7)
Z	2
Density, g cm⁻³	1.292
μ, mm⁻¹	0.314
Tmin, Tmax	0.963,0.969
F(000)	532
hmax, kmax, lmax	12,14,18
Theta_{max}	28.30

3. Thermal Properties

Thermogravimetric analyses (TGA) were conducted on a Shimadzu DTG-60H thermogravimetric analyses under a heating rate of 10 °C/min and a nitrogen flow rate of 50 cm³/min. Differential scanning calorimetry (DSC) analyses were performed on a Shimadzu DSC-60A instrument under a heating rate of 10 °C/min and an nitrogen flow rate of 20 cm³/min. According to the DSC measurements, the melting points of **TPABr** and **TPASiH** are 64 °C and 126 °C, respectively. From TGA curves, the deposition temperatures of the two precursors were found to be 248 °C and 316 °C, respectively.

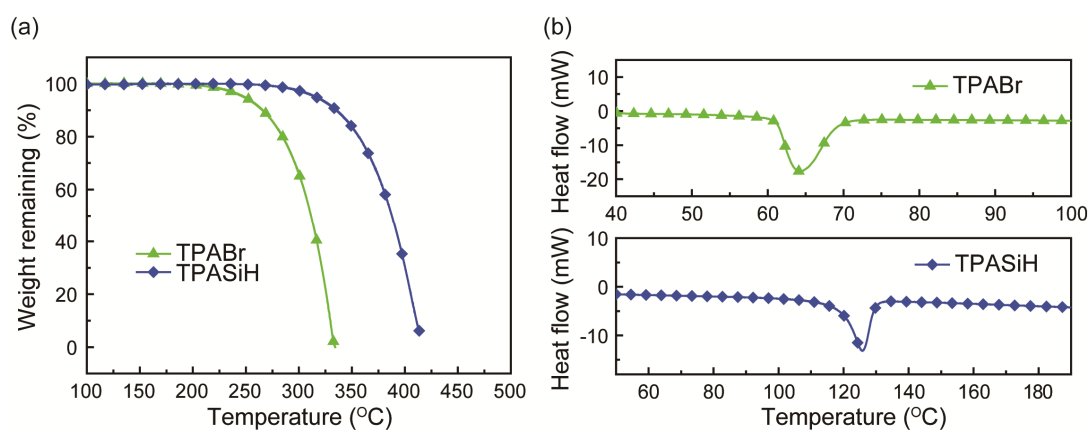


Fig. S5. The (a) TGA and (b) DSC curves of **TPABr** and **TPASiH**.

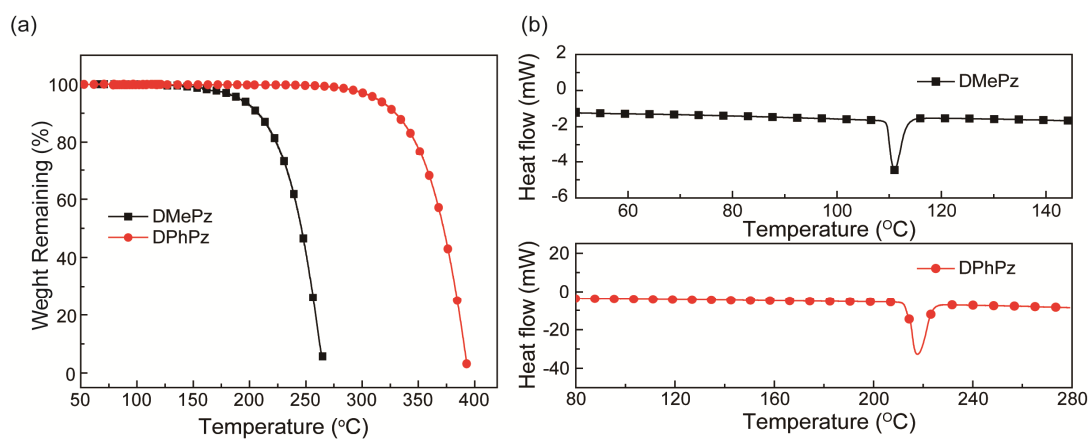


Fig. S6. The (a) TGA and (b) DSC curves of **DMePz** and **DPhPz**.

4. Electrochemical Properties

The highest occupied molecular orbital (HOMO) of **DPhPz** were measured by cyclic voltammetry (CV). The CV measurements were performed at room temperature on a CHI660E system in a typical three-electrode cell with a working electrode (glass carbon), a reference electrode (Ag/Ag^+ , referenced against ferrocene/ferrocenium (FOC)), and a counter electrode (Pt wire) in an acetonitrile solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) at a sweeping rate of 100 mV/s. The acetonitrile was purified and dried according to standard procedures. The **DMePz** and **DPhPz** thin film were prepared by drop casting the DCM solution (~ 5 mg/mL) onto the surface of glass carbon electrode. Then, this electrode served as the working electrode in the following electrochemical measurements. The electrochemical experiments were kept under the protection of dry nitrogen atmosphere.

The HOMO energy levels were estimated based on the reference energy level of ferrocene (-4.8 eV):

$$E_{\text{HOMO}} = -[E_{\text{onset}} - (0.04) + 4.8],$$

where the value of 0.04 V is the onset oxidative voltage of FOC vs Ag/Ag^+ and E_{onset} is the oxidative onset voltage of **DMePz** or **DPhPz**^[3].

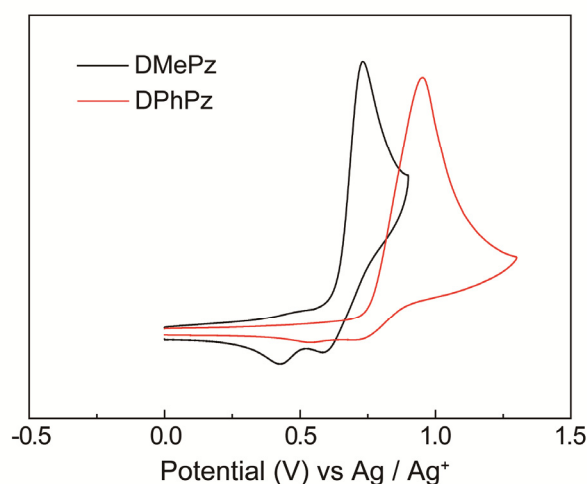


Fig. S7. Cyclic voltammograms of **DMePz** (black) and **DPhPz** (red) thin solid films.

5. High resolution mass spectrum

High resolution mass spectrum of **DPhPz** was recorded on a LCT Premier XE (Waters)

HRMS spectrometry.

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

46 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0-48 H: 0-100 N: 0-3 Si: 0-1

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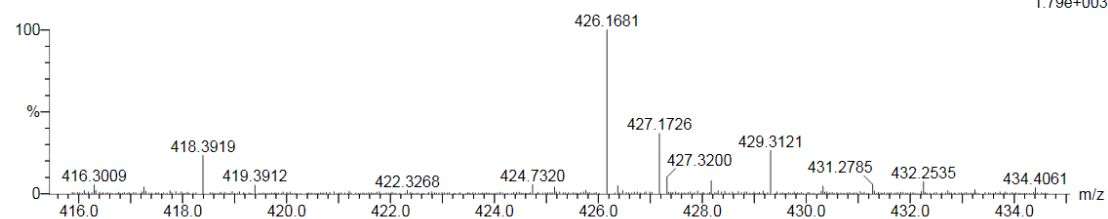
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TH-ZP-6-XS-6 39 (1.283) Cm (29:41)

1: TOF MS ES+

1.79e+003



Minimum:

Maximum: 300.0 50.0 -1.5 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
426.1681	426.1678	0.3	0.7	20.5	134.4	0.0	C30 H24 N Si

Fig. S8. The high resolution mass spectrum (HRMS) of **DPhPz**.

6. Optical properties

Ultraviolet/visible (UV/Vis) spectra were recorded on a SHIMADZU UV-3600 UV/Vis-NIR spectrophotometer, while fluorescence spectra were obtained using a RF-5301PC spectrofluorophotometer with a Xenon lamp as light source. The drop-cast films were prepared by casting solutions of the compounds on quartz substrates. The molar extinction coefficients (molar absorptivity, ϵ) of **DPhPz** were measured at the concentration of 10^{-5} M in CH_2Cl_2 .

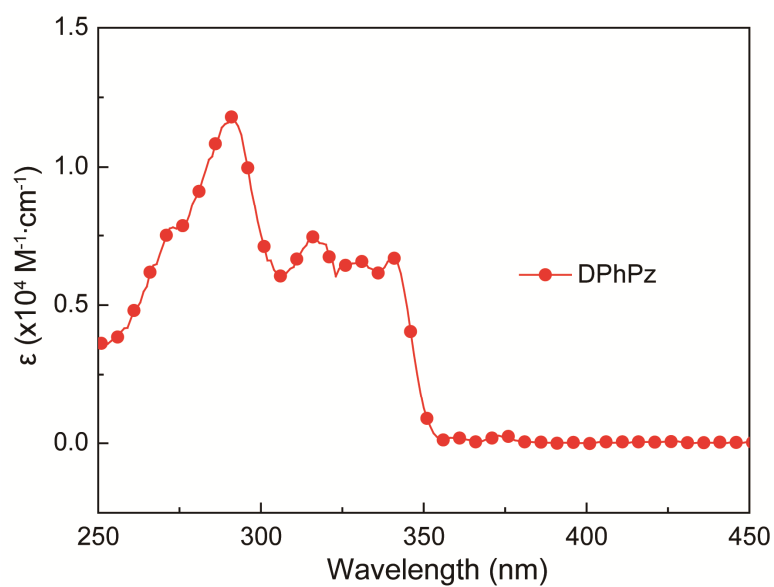


Fig. S9. The molar absorptivity (ϵ) of **DPhPz** in CH_2Cl_2 .

7. Theoretical calculations

The density functional theory (DFT) computations were carried out using Gaussian 09 program package for structure optimizations and vibrational analyses. The ground state (S_0) of the molecule was optimized by the Becke's three-parameter exchange functional along with the Lee Yang Parr's correlation functional (B3LYP) using 6-31G (d) basis sets; the optimized stationary point was further characterized by harmonic vibrational frequency analysis to ensure that real local minima were found. The lowest triplet excited state (T_1) molecules were optimized by the unrestricted formalism (UB3LYP) / 6-31G(d). The triplet energy (adiabatic $S_0 \rightarrow T_1$ excitation) was calculated by the difference of the total energy of the S_0 and T_1 states. The various property parameters of the all-aryl phenazasilines, such as the highest occupied molecular orbital (HOMOs), the lowest unoccupied molecular orbital (LUMOs) energies, energy gap (E_g), and triplet energy (3E_g) were derived from the computed results according to literature publications^[4].

References:

- [1] H. Li, Y. Wang, K. Yuan, Y. Tao, R. Chen, C. Zheng, X. Zhou, J. Li, W. Huang, *Chem. Commun.* **2014**, 50, 15760.
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