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# Journal Name

## COMMUNICATION

# Efficient synthesis of π-extended phenazasilines for optical and electronic applications

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**The rhodium-catalyzed synthesis of phenazasilines from readily achievable biarylhydrosilanes is presented. This highly efficient method offers opportunities for preparing π-extended phenazasilines with enhanced optoelectronic properties for device applications in organic electronics.**

Silicon-containing conjugated molecules are an emerging class of optoelectronic materials that have wide-spread applications in organic electronics,[1] owing to their singular optical and electronic properties originated from the particular interactions (σ*→π* conjugation) between Si atom and π-electron system.[2] Silicon-bridged diphenylamines (phenazasilines),[3] benefited from both Si and N atoms in a fused six-member ring, show promising potentials as hole transporting layers in organic light-emitting diodes (OLEDs),[4] DNA straightening and fixing materials,[5] electrochromic molecules,[6] antioxidants,[7] stabilizer,[8] lubricants[9] etc. Impressively, their properties can be effectively tuned by changing substituents on Si or N atoms.[10] However, the synthesis of phenazasilines, either by the extended heating of diphenylsilane with phenothiazine derivatives[11] or by cyclization reactions of 2,2'-dilithiodiarylamine intermediates with dichlorosilanes,[12,13] suffers from the low yield, complicated precursor, and long synthetic route. These synthetic difficulties significantly hinder the studies and applications of phenazasilines, especially in the field of organic electronics, where π-extended phenazasilines either *via* conjugation expansion from the diphenyl wing of phenazasilines or *via* aromatic substitution on Si and N atoms were generally required for high optical and/or electronic activities.[14]

Inspired by the recent studies on the metal-catalyzed double activation of Si-H and C-H bonds with dehydrogenation to generate Si-C bond in the preparation of five-membered Si-ring (silafluorenes),[15] we propose a rhodium-catalyzed synthetic method for the synthesis of the N-containing six-membered Si-ring of phenazasilines (Scheme 1). Started from readily achievable mono-halogen (Br or I) substituted precursors, this new synthetic route to prepare aromatically substituted π-extended phenazasilines is accomplished in two steps with 80~90% overall yield. As an added benefit, the highly rigid (carbazole-fused) phenazasilines that can be hardly prepared in traditional routes were efficiently synthesized in high yields. The obtained π-extended phenazasilines show excellent solubility, ultra-small Stokes shift, high triplet energy, and excellent device performance in phosphorescent OLEDs (PhOLEDs). The method represented here offer a new way for the efficient preparation of optically and electronically active phenazasilines for optoelectronic devices.

The synthetic route for the construction of phenazasiline derivatives was outlined in Figure 1a and Scheme S1. Compared to the classical route developed about 50 years ago,[11, 13] where the key intermediate is highly reactive organometallic reagents such as 2,2'-dilithio derivatives prepared from multi-halogen substituted precursors for cyclization with dichlorosilanes to generate phenazasilines, this route provides an alternative way. Firstly, from the mono-brominated precursors of **2a** and **2b** that facilely prepared by Ullmann reaction,[16] **3a** and **3b** were obtained in high yield (93% for **3a** and 90% for **3b**) after conventional halogen-metal interconversion and Si-C formation.[17] The second step is to treat the stable diarylhydrosilanes of **3a** and **3b** with 0.5 mol% of the rhodium
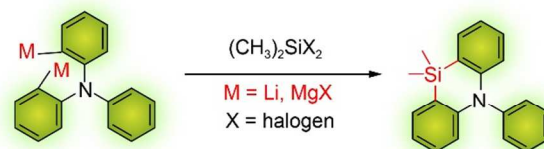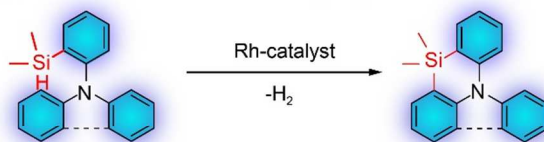


**Scheme 1**. Schematic presentation of the synthesis of phenazasilines: (a) classic route *via* C-M/Si-X coupling; (b) proposed rhodium-catalyzed synthesis *via* Si-H/C-H coupling.

complex (RhCl(PPh₃)₃) and 5 *equiv.* of 3,3-dimethyl-1-butene (a H₂ eliminator) at 135°C in 1,4-dioxane for 24 h. The double activation and subsequent dehydrogenation of Si-H and C-H bonds (Scheme S2) gives Si-C bond for the formation of the desired phenazasiline derivatives (**TPASi** and **PhCzSi**) in high yield (see the SI for the detailed procedure and the characterization data, Figures S1~S8). This two-step route results in the significantly improved synthetic efficiency; the overall yields for **TPASi** and **PhCzSi** reach 87% and 83% respectively.
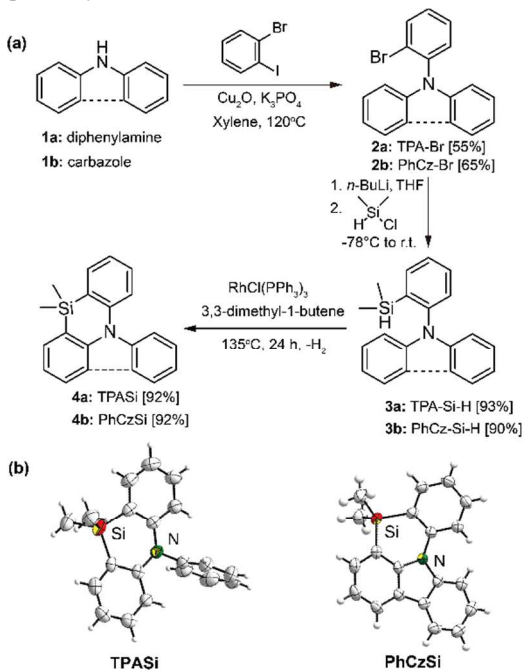


**Figure 1**. (a) Synthetic route for the preparation of phenazasilines; (b) single crystal structures of **TPASi** and **PhCzSi**.

More importantly, besides the advantages of the high yield and easy operation, this route overcomes the difficulties in the preparation of π-extended phenazasilines (**PhCzSi**) with rigid molecular structures that can be hardly synthesized by other routes. The single-crystal structure analysis (Figure 1b) reveals that both of the compounds show the rigid molecular feature with low angles (< 11°) between the planes of phenyl groups (numbered as 1, 2, and 3 in Scheme S3) around N atom (Table S3). Such molecular geometries of **TPASi** and **PhCzSi** are well in line with the *ab initio* density functional theory (DFT) predictions (Scheme S3). When the free phenyl substituent on N atom is forced to be connected to the nearby phenyl of phenazasiline as in **PhCzSi**, the perfect planar phenazasiline in **TPASi** cannot be reserved, because the newly formed carbazole moiety is structurally in competition with phenazasiline; both the planar molecular geometries of phenazasiline and carbazole are slightly distorted, resulting in a slightly bent molecular geometry of **PhCzSi** with a bit torsion of the molecular planes of both phenazasiline (~25°) and carbazole (~10°) (Table S3). This small single molecular structure change, however, leads to significantly different molecular packing structures (Figure S9). An obvious π-π stacking (3.320 Å) is resulted from the larger rigid planar molecular structure of **PhCzSi**, which may have profound effects on its optoelectronic properties.[18]

Despite their high molecular rigidity as indicated by both single crystal X-ray analysis and theoretical predictions, **TPASi** and **PhCzSi** have good solubility in common solvents. Nevertheless, the more rigid carbazole-fused **PhCzSi** exhibits much improved

thermostability than **TPASi** (Figure S10): the decomposition temperature ($T_d$) of **PhCzSi** (246°C) is about 60°C higher than that of **TPASi** (188°C) as revealed by the thermogravimetric analysis (TGA); the melting point ($T_m$) of **PhCzSi** (150°C) is about 40°C higher than that of **TPASi** (110°C) according to the differential scanning calorimetry (DSC) measurements; good amorphous stability of **PhCzSi** film was observed by atomic force microscopy (AFM) before and after annealing at 100°C for 30 min (Figure S11).

The photophysical properties of the π-extended phenazasilines were investigated by UV-Vis absorption and photoluminescence (PL) spectra in both dilute dichloromethane (DCM) and thin solid film (Figure 2a and 2b) in comparison with that of triphenylamine (**TPA**) and 9-phenyl-carbazole (**PhCz**). Considering that **TPASi** is formed by connecting the nearby two phenyls in **TPA** with a silicon bridge to extend the molecular planarity and the π-conjugation, the newly emerged absorption bands of **TPASi** in both dilute solution and aggregated solid film provide a clear evidence of this π-extension. Similarly, **PhCzSi** can be assumed to be structurally derived from **PhCz** also *via* Si-bridging. The obvious red-shift of the π-π* transition absorption band of carbazole moieties[19] at around 330 and 340 nm in **PhCz** to around 340 and 355 nm in **PhCzSi** clearly supports the extended π-system after the Si-bridging.[20]

This red-shift in absorption spectrum due to Si-bridging is in accordance with the red-shifted PL band of **PhCzSi** (370 nm) compared to that of **PhCz** (349 and 365 nm). However, **TPASi** shows a blue-shifted PL regardless of the π-extension of **TPA** *via* Si-bridging, which may be because of the localized emission[21] from the newly formed aromatic phenazasiline moiety. The absorption and emission spectra of **TPASi**, **PhCz**, and **PhCzSi** in solution are quite close, leading to very small Stokes shifts (~15 nm) due to their rigid molecular geometries before and after photo-excitation.[22] Small variations of their UV and PL spectra in solvents with different polarities (Figure S12) further confirm the rigidity of these molecules.[19] The increased rigidity results in much increased photoluminescene quantum yield (PYQL) in **PhCzSi** (37%) compared to that in **TPASi** (8%). In contrast to the similar absorption spectra in dilute solution and solid film, their PL spectra were significantly different (Figure 2b). Additional new broad emission bands of **TPASi** (429 nm) and **PhCzSi** (~489 nm) appear in solid films, indicating the possible formation of excimers owing to the enhanced molecular interactions of the π-extended phenazasiline in aggregated states.[23]

The electrochemical properties of the phenazasilines were investigated by cyclic voltammetric (CV) measurements. From the onset voltage of the irreversible oxidation wave of **TPASi** and **PhCzSi** at 0.67 and 0.85 V, their HOMO energy levels were determined to be at -5.43 and -5.61 eV respectively, according to the reference energy level of ferrocene[24] (Figure S13). Combined with the optical bandgap results, the frontier molecular orbital energy levers were identified (Figure 2c). The introduction of Si-bridge generally leads to the lower LUMO (decreased ~0.10 eV) due to particular σ*→π* interaction between the silyl group and π-electron system,[20] when comparing **TPA** with **TPASi** and **PhCz** with **PhCzSi**. The π-extended system usually has low bandgap,[25] which is in accord with the observation that the most rigid phenazasiline of **PhCzSi** has the lowest optical bandgap. The DFT calculations well predict the same changing trends of HOMO, LUMO, and bandgap upon the structural modifications in phenazasilines. Notably, the calculated iso-surface of the frontier orbitals distributes on the whole molecular plane; the delocalized distribution is of the most obvious in the most rigid phenazasiline of **PhCzSi**, indicating the effective extending of the π-conjugation in these phenazasilines.

The charge mobility of the phenazasilines was assessed by the relaxation and reorganization energies *via* DFT calculations to
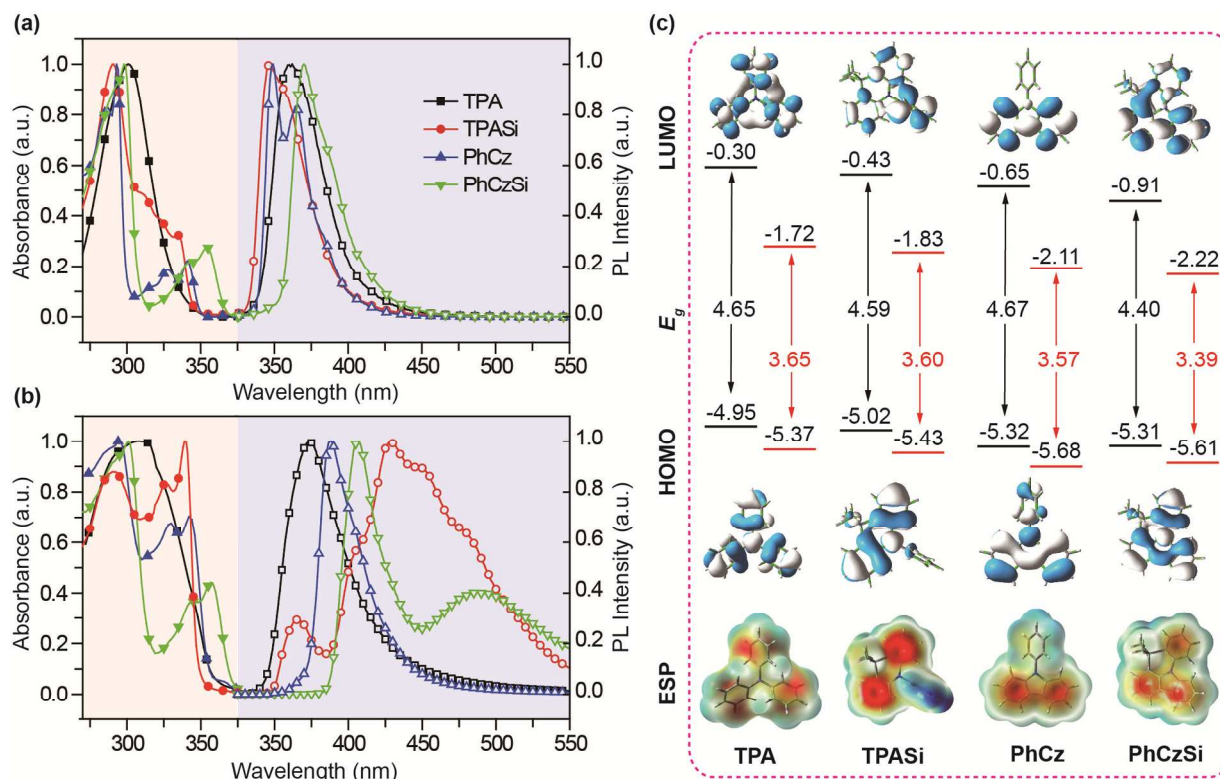
**Figure 2.** UV-Vis absorption (solid symbol) and PL (hollow symbol) spectra **(a)** in DCM ($1.3\times10^{-6}$ mol L$^{-1}$) and **(b)** in thin film. PL was excited at the absorption peak around 300 nm; **(c)** DFT calculated (in black) and experimental (in red) HOMO, LUMO, and bandgap ($E_g$) energy levels (in eV) as well as the isosurfaces of HOMO, LUMO, and electrostatic potential (ESP).

provide a qualitative investigation of their charge-transport rates at a single molecule level[16] (Table S4). Compared to the widely used excellent hole transport units of **TPA** and **PhCz**, the π-extended phenazasilines (**TPASi** and **PhCzSi**) also exhibit high hole and



**Figure 3**. (a) Current density (J)-luminance -voltage curves of the device of ITO/MoO$_x$/TAPC/PhCzSi: FIrpic/TmPyPB /LiF/Al, inset: the device structure; (b) EL spectra under varied voltages, insets: the efficiencies-luminance curves.

electron transport rates with close relaxation and reorganization energy values, suggesting the good electronic properties of these π-extended phenazasilines. The molecular packing structure (Figure S9d) of **PhCzSi** revealed by its single crystal structure analysis also support the good charge transport mobility of the rigid conjugated compound, which preserve intermolecular π-π stacking as conducting channels for charge carriers.

The lowest triplet states ($T_1$) of the π-extended phenazasilines were measured from the 0-0 transition bands of their low-temperature (77 K) time-resolved phosphorescence spectra (Figure S14). To our delight, both the experimental measurements and theoretical predictions indicate that the increase of the π-extension *via* Si-bridging does not lead to the lower $T_1$ energies ($E_{T1}$), because $T_1$ is dominated by either **TPA** or **PhCz** unit in the π-extended phenazasilines, according to the spin density distributions (Figure S15). The higher $T_1$ than that of iridium(III) [bis(4,6-difluorophenyl)-pyridinato-N,C$^{2'}$] picolinate (FIrpic), which is a famous blue phosphorescent emitter, suggests the potential of these phenazasilines as host materials for FIrpic-based blue PhOLEDs.[26]

In light of the high optical and electronic properties of the π-extended phenazasilines (Table S5), especially the high-lying $T_1$ energy levels, we fabricated blue PhOLED devices using **PhCzSi** ($E_{T1}$=2.9 eV) as the host material and FIrpic as the guest under the following device configuration (Figure S16): ITO/MoO$_x$ (10 nm)/TAPC (25 nm)/**PhCzSi**: FIrpic (20 nm)/TmPyPB (35 nm)/LiF(1 nm)/Al(100 nm). In the device, MoO$_x$ and LiF served as the hole- and electron-injecting materials; FIrpic doped in PhCzSi with the doping level of 10% was used as the emitting layer; TAPC [1,1-bis{(di-4-tolylamino)phenyl} cyclohexane] and TmPyPB [1,3,5-tri(m-pyrid-3-ylphenyl)benzene)] act as the hole- and electron-transporting materials, respectively. The preliminary device results of the blue PhOLED showed the highest current efficiency (CE) of
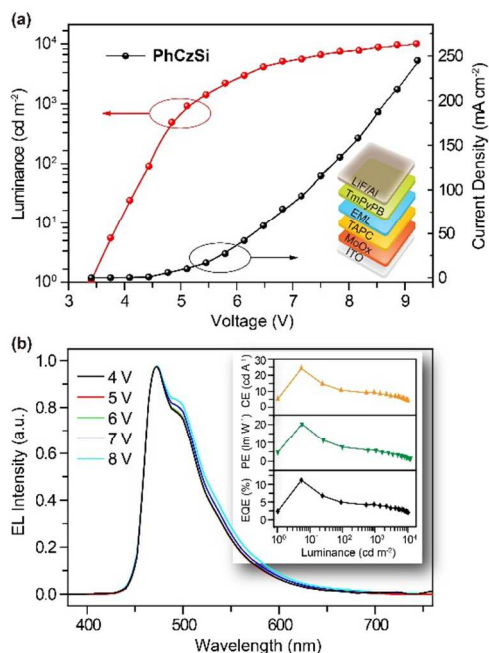
24.2 cd/A, power efficiency (PE) of 20.3 lm/W, and external quantum efficiency (EQE) of 11.2% with stable electroluminescence (EL) spectrum under the various voltages during the operation of the device (Figure 3). The first attempt to use phenazasilines as host materials for PhOLEDs is exciting to afford a high EQE of the blue PhOLED device (over 10%) that is still achievable in a relatively small number of host materials,[27] suggesting bright future of the π-extended phenazasilines for optical and electronic applications.

In summary, we have succeeded in extending the rhodium-catalyzed Si-H/C-H coupling to nitrogen-containing substrates, offering a new route for the highly efficient synthesis of phenazasilines, especially of the π-extended phenazasilines. The obtained phenazasilines exhibit excellent solubility and unique optical and elec-tronic properties. For the first time, the preliminary blue PhOLED device based on phenazasilines as host material was fabricated; the high device performance with high CE (24.2 cd/A), PE (20.3 lm/W) and EQE (11.2%) highlights the great potential of the optoelectronically active phenazasilines in organic electronics.

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