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Efficient Synthesis of All-Aryl Phenazasilines for Optoelectronic Applications

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An efficient metal-free radical-catalyzed intramolecular silylation method has been developed for the preparation of all-aryl phenazasilines, which can be hardly synthesized by traditional synthetic methods. The easily prepared aromatic and rigid phenazasiline exhibits excellent solubility, high thermal stability, and good optoelectronic properties, which are highly attractive for optical and electronic applications in organic electronics. These advances, in the preparation of all-aryl phenazasilines, offer exciting opportunities for sophisticated molecular design and efficient synthesis of optoelectronic molecules based on the phenazasiline.

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Introduction

Phenazasilines, which have a Si-bridged diphenylamine framework containing both Si and N atoms in a fused six-membered ring, are promising candidates for hole-transporting materials, electrochromic molecules, and antioxidants.[1–3] Traditionally, phenazasilines can be synthesized through extended heating of diphenylsilane with phenothiazines or cyclization reactions of 2,2′-dilithiodiarylamine intermediates with dichlorosilanes.[4–5] Unfortunately, these methods commonly require special precursors, which are difficult to prepare, and need long synthetic routes that typically generate low yields. These difficulties, therefore, significantly hinder the further studies and applications of phenazasilines.

To facilitate the application of phenazasilines, concise and efficient synthetic methods are highly desired. Recently, a highly efficient method was developed for the preparation of π-extended phenazasilines by rhodium-catalyzed double activation of Si–H and C–H bonds.[6] This method can give high yields up to 93 %. More importantly, the as-synthesized π-extended phenazasilines exhibited improved optoelectronic properties as indicated by the high external quantum efficiency (up to 11 %) when applied as host materials in blue phosphorescent organic light-emitting diodes (OLEDs).

For practical applications of organic materials in optoelectronic devices, molecules with high thermal stability are generally required to form uniform and amorphous nanofilms under vacuum thermal evaporation conditions.[7] To obtain phenazasilines with high thermal stability, one potential strategy is to replace alkyl groups (e.g. methyl group) with aromatic phenyl substituents on both Si and N atoms in phenazasilines.[8] However, previously reported methods cannot afford the all-alkyl phenazasilines.

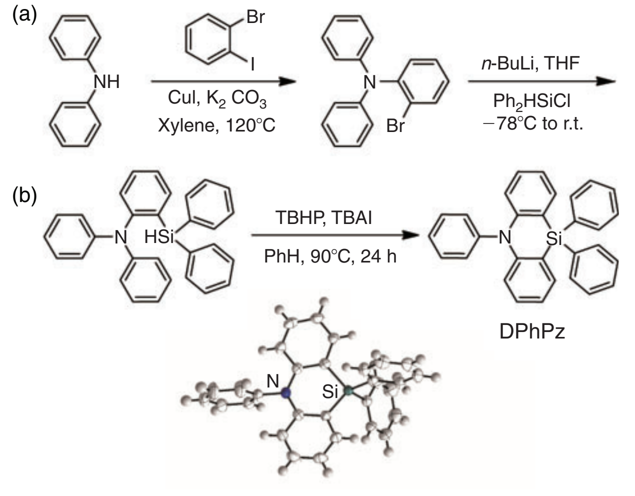
In this study, we established a concise synthetic method for the preparation of a newly designed all-aryl phenazasiline, 5,10,10-triphenyl-5,10-dihydrophenazasiline (**DPhPz**). It should be noted that all-aryl phenazasilines can be hardly obtained by using other synthetic methods such as the facile rhodium-catalytic method. We reasoned that the successful synthesis of the all-aryl phenazasiline proceeds via a radical-mediated catalysis mechanism. Inspiringly, the as-prepared **DPhPz** shows high thermal stability, with a decomposition temperature (T_d) higher than 310°C and a melting point (T_m) above 200°C, however, with photophysical and electrochemical properties similar to those of its alkyl counterpart, 10,10-dimethyl-5-phenyl-5,10-dihydrophenazasiline (**DMePz**). The newly developed metal-free radical-catalytic method could pave the way for the facile and efficient preparation of all-aryl phenazasilines, which are highly attractive owning to their unique photophysical properties for optoelectronic applications.

Results and Discussion

As depicted in Scheme 1a, the synthesis of **DPhPz** starts from diphenylamine and 2-bromoiodobenzene in three steps.

The detailed synthetic procedures and characterizations of the related compounds were described in the Supplementary Material and shown in Figs S1–S4. Notably, this method employed a cheap and commercially available *tert*-butyl hydroperoxide (TBHP) for Si–C bond formation and a small amount of tetrabutylammonium iodide (TBAI) as an initiator. The overall yield of **DPhPz** is 27 %. For the key cyclization reaction in the silylation, the use of aromatic solvents of benzene, chlorobenzene, and toluene produces relatively higher yields of 54 %, 47 % and 41 %, respectively. Single-crystal structure analysis (Scheme 1b and Table S1 in the Supplementary Material) demonstrates that **DPhPz** has a rigid molecular structure with highly planar and π-conjugated diphenylphenazasiline unit to serve as the main functional moiety for optoelectronic properties.

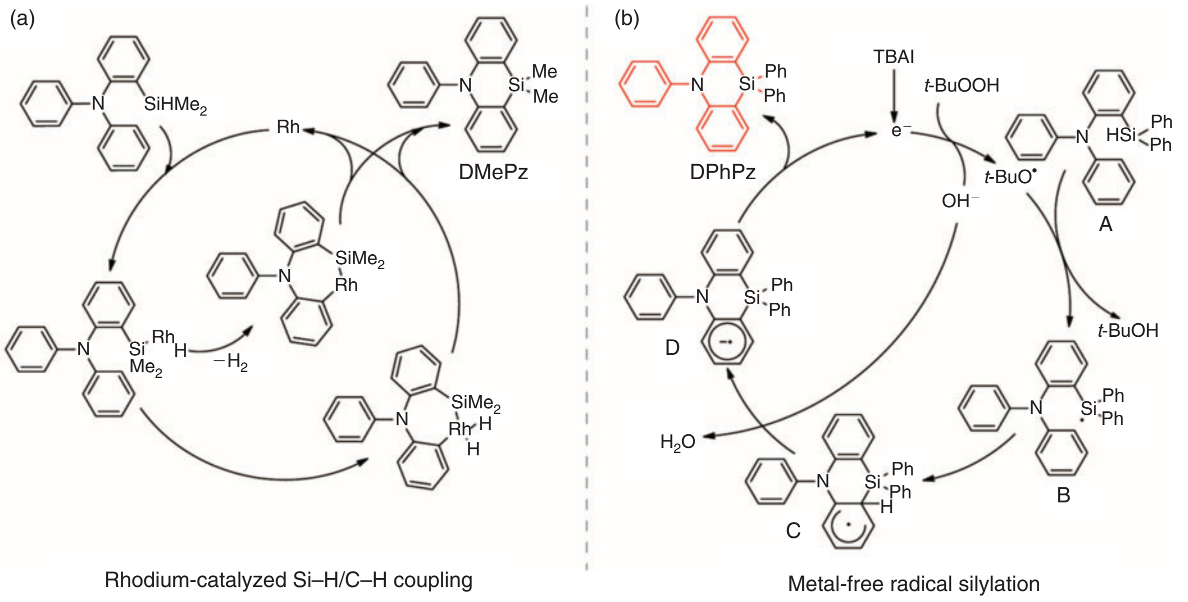
To elucidate the mechanism of the newly developed synthetic method for the synthesis of all-aryl phenazasilines, we compared our newly developed reaction with the previously reported rhodium-catalyzed approach. In fact, the rhodium-catalyzed approach can generate **DMePz** in high yield (Scheme 2a).[6] However, the attempts to extend this synthetic method to the preparation of **DPhPz** failed, probably because of the large spatial hindrance of diphenyl substituents towards the bulky rhodium catalyst of $RhCl(PPh_3)_3$, which significantly blocks the catalytic cycling reaction.[9–10] Meanwhile, inspired by the intramolecular radical silylation of 2-diphenylsilylbiaryls via base-promoted homolytic aromatic substitution for preparing a five-membered Si-ring of 9-silafluorene,[11] we propose that the synthesis of **DPhPz** follows a radical-catalyzed silylative cross-dehydrogenative coupling mechanism (Scheme 2b). In the initiation step, an electron transfers from the iodide of TBAI to TBHP, subsequently generating a hydroxyl anion along with a *tert*-butoxyl radical. The resulting *tert*-butoxyl radical then abstracts the H atom from silane **A** to give the corresponding Si-centred radical **B** and cyclohexadienyl radical **C**. The acidic proton in **C** gets deprotonated by the hydroxyl anion to give the radical anion **D**. Finally, liberation of the electron from **D** produces target product of **DPhPz** and the liberated electron then serves as the catalyst for the next reaction cycle.



Scheme 1. (a) Synthetic route and (b) single-crystal structure of **DPhPz** (CCDC 1431510).

We then characterized the thermal stability of as-prepared **DPhPz**. As expected, **DPhPz**, with a high molecular weight, has a significantly improved thermal stability with T_d up to 313°C and T_m of 218°C (Fig. S6, Supplementary Material) when compared with its alkyl counterpart, **DMePz** ($T_d = 191$°C and $T_m = 111$°C). These results confirm the success in designing thermal stable phenazasilines via all-aryl substitution strategy. On a separate note, similarly to **DMePz**, the all-aryl phenazasiline, **DPhPz**, has good solubility in common solvents.

In the following set of experiments, we studied the optoelectronic properties of the stable all-aryl phenazasiline. Structurally, **DPhPz** is formed by connecting the nearby two phenyls in triphenylamine (**TPA**) with a silicon bridge, thus exhibiting an extended molecular planarity and π-conjugation. Such a π-system extension is evidenced by the emerging red-shifted absorption bands in both dilute DCM and thin solid film (Fig. 1a, b) when compared with that of **TPA**. The molar absorptivity of **DPhPz** can be up to 10^4 M^{-1} cm^{-1} (Fig. S9,



Rhodium-catalyzed Si–H/C–H coupling

Metal-free radical silylation

Scheme 2. Proposed mechanisms for (a) rhodium-catalyzed synthesis of **DMePz** and (b) radical-catalyzed synthesis of **DPhPz**.

Supplementary Material). Due to the high rigid molecular structure, the absorption and emission peaks of **DPhPz** in solution are quite close with very small Stokes shifts (~15 nm); these features are very similar to those of **DMePz**.[12] The enhanced UV absorption around 310–340 nm of **DMePz** in solid film may be due to the smaller spatial hindrance of methyl substitutions when compared with that of the bulky phenyl groups in **DPhPz**, leading to stronger intermolecular interactions in **DMePz** film. Contrary to the sharp and slightly shifted photoluminescence (PL) spectra in solution, broad PL spectra, with additional emission bands, were observed in the thin solid film state. The red-shifted broad PL spectra in the film state are probably due to the strong molecular interactions of the rigid phenazasilines in aggregated states with apparent excimer emission.[13–15] Particularly, in the all-aryl phenazasiline film formed by **DPhPz**, the intermolecular interactions are even stronger than those in **TPA** and **DMePz** films, leading to a more suppressed single molecular emission at ~360 nm. Taken together, the UV-visible absorption and PL spectra of **DMePz** and **DPhPz** are quite similar, suggesting the limited influence of peripheral aromatic substituents on the electronic structure of the rigid phenazasilines (Table 1).

Subsequently, the electrochemical properties of the optically active all-aryl phenazasiline were investigated by cyclic voltammetry (CV).[16] From the onset voltages of the oxidation wave of **DMePz** (0.67 V) and **DPhPz** (0.76 V) (Fig. S7, Supplementary Material), the HOMO energy levels were determined to be at –5.43 and –5.55 eV, correspondingly, on the basis of the reference energy level of ferrocene under identical CV conditions. Taking into account the optical band gaps (${}^{\mathrm{opt}}E_g$) from the onset absorption spectra in the film state, the LUMO energy levels can be determined. As listed in Table 1, the HOMO and LUMO of **DPhPz** are very close to those of **DMePz**, with a small variation of smaller than 0.1 eV, indicating the limited effects of peripheral substituents of Si on the electrochemical properties of phenazasilines.

Density functional theory (DFT) calculations were further performed to understand the optoelectronic properties of the obtained all-aryl phenazasiline theoretically.[17,18] Compared with **DMePz**, **DPhPz** exhibits slightly lower predicted HOMO and LUMO energy levels, which is well in line with the experimental results (Fig. 1c). The DFT calculations also reveal that the peripheral phenyl substituents of Si have a very small contribution to the HOMO and LUMO isosurfaces, offering theoretical insights on the intrinsic mechanism for their limited influence on absorption and PL spectra as well as frontier orbital energy levels. In addition, the DFT-predicted triplet energies of **DPhPz** and **DMePz** are also very similar, with high values of >3.1 eV (Table 1). Such a high triplet energy of **DPhPz** with

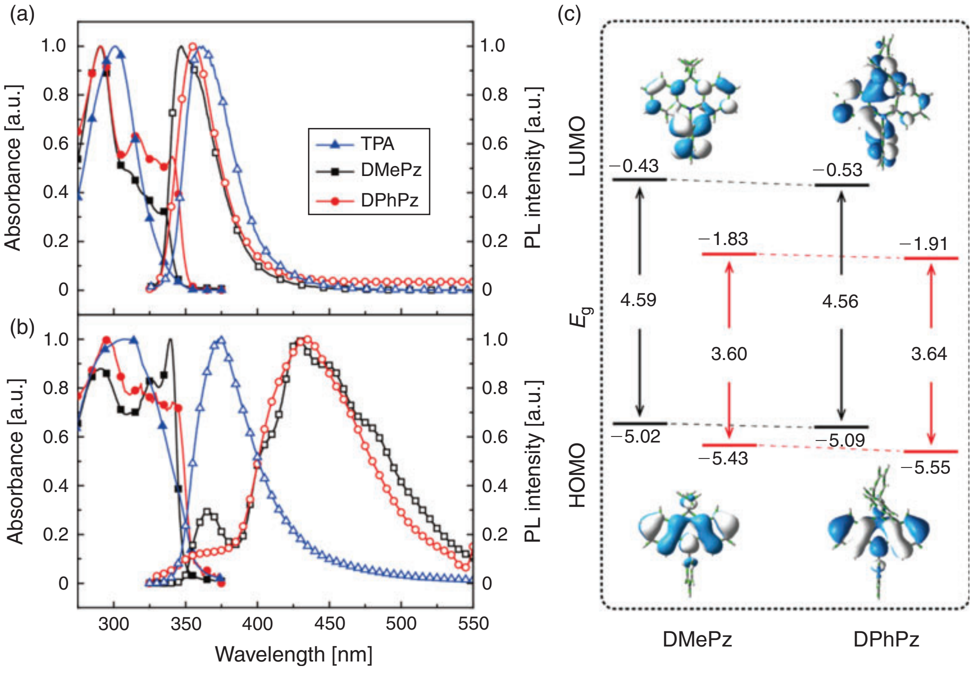


Fig. 1. UV-visible absorption (closed markers) and photoluminescence (opened markers, excited at 300 nm) spectra of **TPA**, **DMePz**, and **DPhPz** measured in (a) DCM (1.3×10^{-6} mol L^{-1}) and (b) in thin film. (c) DFT-calculated (in black) and experimentally determined (in red) HOMO, LUMO, and band gap (E_g) energy levels (in eV) as well as the frontier orbital isosurfaces of **DMePz** and **DPhPz**.

Table 1. Physical, optical, and electrochemical properties of DMePz and DPhPz

${}^{\mathrm{cal}}E_g$, calculated bandgap; ${}^{\mathrm{cal}}E_T$, calculated lowest triplet energy level

Comp.	T_d/T_m [°C]	λ_{abs} [nm]		${}^{\mathrm{opt}}E_g$ [eV]	λ_{em} [nm]		CV [eV]		DFT [eV]			
		DCM	Film		DCM	Film	HOMO	LUMO	HOMO	LUMO	${}^{\mathrm{cal}}E_g$	${}^{\mathrm{cal}}E_T$
DMePz	191/111	290, 312, 335	290, 325, 339	3.60	346	363, 429	−5.43	−1.83	−5.02	−0.43	4.59	3.15
DPhPz	313/218	291, 316, 341	296, 329, 341	3.64	356	360, 438	−5.55	−1.91	−5.09	−0.53	4.56	3.13

significantly improved thermal stability indicates the great potential of the all-aryl phenazasiline as high-performance host materials for blue phosphorescent OLEDs.[19–21]

Conclusion

In summary, an efficient transition-metal-free intramolecular radical silylation method has been developed, for the first time, to prepare all-aryl phenazasilines with excellent optoelectronic properties. The novel synthetic process is important for overcoming the difficulties of rhodium-catalyzed Si–H/C–H coupling in the synthesis of spatially hindered phenazasilines. Compared with alkyl phenazasiline of **DMePz**, the obtained all-aryl phenazasiline, **DPhPz**, shows excellent solubility and significantly improved thermal stability with almost identical optical and electronic properties, highlighting the bright future of optoelectronically active all-aryl phenazasilines in organic electronics.

Experimental

*General Procedure for the Preparation of 5,10,10-Triphenyl-5,10-dihydrophenazasiline (**DPhPz**)*

*2-Bromo-*N,N*-diphenylaniline*

A mixture of 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) in xylene (40 mL) were heated at 120°C for 2 days, followed by cooling to room temperature. The resulting reaction mixture was then poured into deionized water to quench the reaction and extracted with DCM for three times. The organic phase was collected, dried, and concentrated under vacuum. The resulting residue was further purified by flash column chromatography on silica gel to afford 2-bromo-*N*,*N*-diphenylaniline as a white solid.

*2-(Diphenylsilyl)-*N,N*-diphenylaniline*

To a freshly distilled 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 dropwise.[6] The resulting mixture was stirred at –78°C for 1.5 h, followed by the addition of chlorodiphenylsilane (3.35 mL, 15.5 mmol). The reaction was subsequently kept at –78°C for 0.5 h and at room temperature for 12 h, quenched with water, and extracted with DCM. The organic layer was collected and dried, and the solvent was removed under vacuum. The resulting crude product was purified by column chromatography on silica gel to give a white solid.

*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) were stirred at 90°C for 24 h.[11] After cooling to room temperature, the reaction mixture was extracted with DCM for three times. The organic layer was collected and dried. After removing the solvent, the crude product was purified by column chromatography on silica gel to afford **DPhPz** as a white solid.

Supplementary Material

Experimental details and ^{1}H NMR and ^{13}C NMR spectra of **DPhPz** are available on the Journal's website.

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