This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Efficient synthesis of π-extended phenazasilines for optical and electronic applications

Huanhuan Li, Yang Wang, Kai Yuan, Ye Tao, Runfeng Chen*, Chao Zheng, Xinhui Zhou, Junfeng Li, Wei Huang*

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, owing to their singular optical and electronic properties originated from the particular interactions (σ*→π* conjugation) between Si atom and π-electron system. Silicon-bridged diphenylamines (phenazasilines), 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), DNA straightening and fixing materials, electrochromic molecules, antioxidants, stabilizer, lubricants etc. Impressively, their properties can be effectively tuned by changing substituents on Si or N atoms. However, the synthesis of phenazasilines, either by the extended heating of diphenylsilane with phenothiazine derivatives or by cyclization reactions of 2,2'-dilithiodiarylamine intermediates with dichlorosilanes, 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.

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), 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 phenazasline derivatives was outlined in Figure 1a and Scheme S1. Compared to the classical route developed about 50 years ago, 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, 3a and 3b were obtained in high yield (93% for 3a and 90% for 3b) after conventional halogen-metal interconversion and Si-C formation. The second step is to treat the stable diarylhydrosilanes of 3a and 3b with 0.5 mol% of the rhodium catalyst (Scheme 1a).

(a) Classical synthetic route: C-M/Si-X coupling

(b) This work: Si-H/C-H coupling

Scheme 1. Schematic presentation of the synthesis of phenazasilines: (a) classical route via C-M/Si-X coupling; (b) proposed rhodium-catalyzed synthesis via Si-H/C-H coupling.
The single-crystal structure analysis (Figure 1b) reveals that both of the molecular structures that can be hardly synthesized by other routes. Despite their high molecular rigidity as indicated by both single crystal X-ray analysis and theoretical predictions, 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 phenazasilene as in PhCzSi, the perfect planar phenazasilene in TPASi cannot be reserved, because the newly formed carbazole moiety is structurally in competition with phenazasilene; both the planar molecular geometries of phenazasilene and carbazole are slightly distorted, resulting in a slightly bent molecular geometry of PhCzSi with a bit torsion of the molecular planes of both phenazasilene (~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. 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 amorhous 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 phenazasilenes 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 is 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.

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 from the newly formed aromatic phenazasilene 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. Additional new broad 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 phenazasilene in aggregated states.

The electrochemical properties of the phenazasilenes 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 levels were identified (Figure 2c). The introduction of Si-bridge generally leads to the lower LUMO (decreased ~0.10 eV) due to particular π-π* interaction between the silyl group and π-electron system, when comparing TPA with TPASi and PhCz with PhCzSi. The π-extended system usually has low bandgap, which is in accord with the observation that the most rigid phenazasilene 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 phenazasilenes. 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 phenazasilene of PhCzSi, indicating the effective extending of the π-conjugation in these phenazasilenes.

The charge mobility of the phenazasilenes was assessed by the relaxation and reorganization energies via DFT calculations to...
provide a qualitative investigation of their charge-transport rates at a single molecule level. 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 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,C2'] picolinate (FIRpic), which is a famous blue phosphorescent emitter, suggests the potential of these phenazasilines as host materials for FIRpic-based blue PhOLEDs.

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, 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 electronic 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.

This study was supported in part by National Natural Science Foundation of China (21274065, 21304049, 21001065, 61136003, and 51173081), The Ministry of Education of China (No. IRT11148), Natural Science Foundation of Jiangsu Province (BK2011751, BM2012010), Natural Science Foundation of the Jiangsu Higher Education Institutions of China (12KJB150017), A project funded by the priority academic program development of Jiangsu higher education institutions (PAPD, YX03001), the National Basic Research Program of China (973 Program) (2012CB933301, 2012CB723402, and 2014CB648300), and the Program for Postgraduates Research Innovations in Universities of Jiangsu Province (CXXZ11_0412 and CXXZZ12_0455).

Notes and references

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.