

# Crystal structure of 9,9'-(4,4'-(silinane-1,1-diyl)bis(4,1-phenylene))bis(9*H*-carbazole) and its photophysical and electrochemical properties

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## ABSTRACT

The title compound 9,9'-(4,4'-(silinane-1,1-diyl)bis(4,1-phenylene))bis(9*H*-carbazole) (**6-bisCz**) has been designed and prepared to investigate its crystal structure and photophysical and electrochemical properties. **6-bisCz** is crystallized in the centrosymmetric space group  $P-1$ . Interestingly, the asymmetric unit contains two molecules ( $Z' = 2$ ), and hence, the entire cell contains four units ( $Z = 4$ ). The central silicon atom was arranged in pseudo-tetrahedral geometry defined by the two *ipso*-carbon atoms of the phenyl groups and two carbon atoms in the endocyclic hexyl ring, with average bond angles of  $104.5(1)^\circ$  and  $108.5(1)^\circ$ , respectively. UV/Vis absorption and photoluminescence spectra showed that the central silicon atom successfully disconnected electronic communication between the two peripheral phenyl-carbazole units, yielding similar absorption and emission spectra to an unsubstituted carbazole monomer. The influence of the central silicon atom between the two phenylcarbazole units is also simulated by density functional theory calculations. Finally, electrochemical properties of **6-bisCz** were investigated, and the analysis shows that an electropolymerized film was successfully formed during the electrochemical process.

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## 1. Introduction

Silicon-based compounds have been introduced as hole transporting materials in organic light-emitting diodes (OLEDs) owing to their advantageous properties such as wide energy band gaps and enhanced morphologies arising from their tetrahedral geometries [1]. Because of these unique properties, they have been widely used in optoelectronic materials [2–5]. For example, a silicon atom has been incorporated into phenylcarbazole groups, successfully tuning their photophysical properties to achieve higher triplet energies and wider energy band gaps [6].

Carbazole is one of the most useful compounds in OLEDs because of its chemical stability, inherent electron donating nature, moderately high oxidative potential, high triplet energy level, and planarity and rigidity. Further, carbazole exhibits unique electrochemical properties in electrochemistry. It is well known that carbazole can be electropolymerized through extremely reactive sites at the 3, 6, and 9 positions [7]. Electrochemical polymerization

of carbazole proceeds through an electron transfer–chemical reaction–electron transfer (ECE) mechanism, which starts with the oxidation of the monomer to the corresponding unstable cation-radicals such as 9,9'- and 3,3'-bicarbazyls, followed by fast dimerization. The Previous work has reported on luminescent luminescent thin films of conjugated polymers using a carbazole precursor and their applications in organic solar cells and OLEDs [8–13]. Carbazole end-capped carbosilane dendrimers have also been applied to the fabrication of homogeneous films by electropolymerization [14].

In this work, 9,9'-(4,4'-(silinane-1,1-diyl)bis(4,1-phenylene))bis(9*H*-carbazole) (**6-bisCz**) was designed and its crystal structure was elucidated. The effects of the central silacyclohexyl ring on the photophysical and electrochemical properties were also investigated.

## 2. Experimental

### 2.1. Synthesis and crystallization

9-(4-Bromophenyl)-9*H*-carbazole (**Br-Cz**) was prepared in

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modest yields by a mono-substitution reaction between carbazole and dibromobenzene proceeding via Ullmann condensation [6]. Direct lithiation of **Br-Cz**, followed by nucleophilic substitution with 1,1-dichlorosilane, which was prepared according to literature methods [15], afforded **6-bisCz** in 72% yield as a white solid. After purification, a single crystal of **6-bisCz** was obtained through slow evaporation. The detailed experimental procedure is shown below.

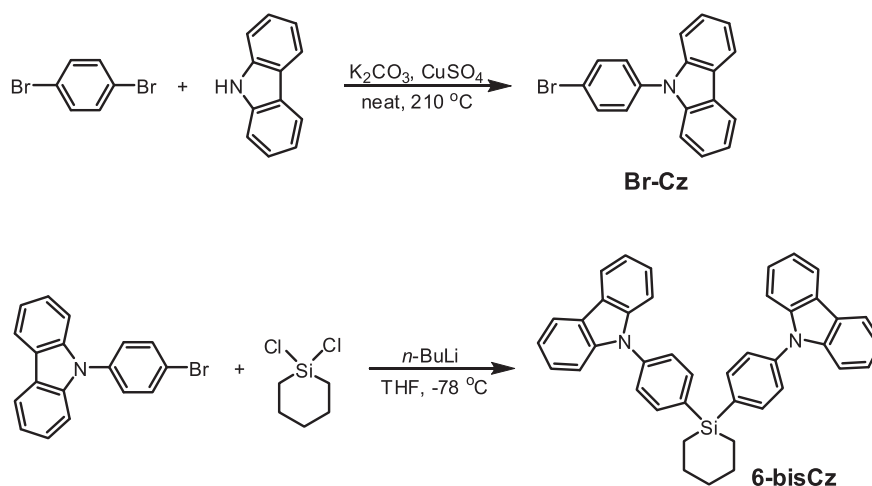
**9,9'-(4,4'-(Silinane-1,1-diyl)bis(4,1-phenylene))bis(9H-carbazole) (6-bisCz)** Under nitrogen atmosphere, *n*-butyllithium (*n*-BuLi) in 2.5 M hexane (2.2 mL, 5.5 mmol) was added dropwise to a solution of 9-(4-bromophenyl)-9H-carbazole (1.61 g, 5 mmol) in dry THF (25 mL) at  $-78^{\circ}\text{C}$ . After stirring for 30 min, 1,1-dichlorosilane (0.38 g, 2.3 mmol) was added slowly to the mixture, maintaining it at  $-78^{\circ}\text{C}$ . The reaction was then allowed to

warm to room temperature and was stirred overnight. The reaction mixture was poured into water, extracted with dichloromethane (50 mL  $\times$  2), and subsequently washed with water and brine. The combined organic layers were dried over  $\text{MgSO}_4$  and filtered. The filtrate was dried under reduced pressure and the residue was subjected to column chromatography (ethyl acetate/hexane,  $v/v = 1/1$ ) to afford pure **6-bisCz** in 72% yield as a white solid. The resultant white solid was dissolved in a solution of dichloromethane/*n*-hexane and evaporated slowly to obtain a single crystal of **6-bisCz**, which was suitable for X-ray analysis.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.16 (d, 4H,  $J_{\text{H-H}} = 7.8$  Hz), 7.85 (d, 4H,  $J_{\text{H-H}} = 8.4$  Hz), 7.63 (d, 4H,  $J_{\text{H-H}} = 8.4$  Hz), 7.51 (d, 4H,  $J_{\text{H-H}} = 8.1$  Hz), 7.42 (t, 4H,  $J_{\text{H-H}} = 7.5$  and 1.2 Hz), 7.30 (t, 8H,  $J_{\text{H-H}} = 8.1$  and 1.2 Hz), 1.85–1.98 (m, 2H), 1.59–1.71 (m, 2H), 1.37 (t, 2H,  $J_{\text{H-H}} = 6.6$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  140.7, 138.8, 136.1, 135.8, 126.4, 126.0, 123.5, 120.4, 120.1, 110.0, 30.0, 24.5, 11.7.

**Table 1**  
Crystal data and structure refinement for **6-bisCz**.

Crystal data	
Identification code	<b>6-bisCz</b>
Empirical formula	$\text{C}_{41}\text{H}_{34}\text{N}_2\text{Si}$
Formula weight	582.79
Temperature	233(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P-1$
Unit cell dimensions	$a = 9.9970(4)$ Å, $\alpha = 79.651(1)^{\circ}$ $b = 16.6745(7)$ Å, $\beta = 88.921(1)^{\circ}$ $c = 21.3595(9)$ Å, $\gamma = 89.119(1)^{\circ}$
Volume	$3501.7(3)$ Å <sup>3</sup>
Z, Calculated density	4, 1.105 Mg/m <sup>3</sup>
Absorption coefficient	$0.096$ mm <sup>-1</sup>
$F(000)$	1232
Crystal size	$0.170 \times 0.120 \times 0.090$ mm
Theta range for data collection	$0.969-28.355^{\circ}$
Limiting indices	$-13 \leq h \leq 13$ , $-22 \leq k \leq 22$ , $-28 \leq l \leq 28$
Reflections collected/unique	48660/17414 [ $R_{\text{int}} = 0.0741$ ]
Completeness to $\theta = 25.242$	100.0%
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	17414/0/794
Goodness-of-fit on $F^2$	1.006
Final R indices [ $I > 2\sigma(I)$ ]	$R_1^a = 0.0583$ , $wR_2^b = 0.1447$
R indices (all data)	$R_1^a = 0.1676$ , $wR_2^b = 0.2017$
Extinction coefficient	0.0003(3)
Largest diff. peak and hole	0.243 and $-0.375$ e. Å <sup>-3</sup>

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c||$  (based on reflections with  $F_o^2 > 2\sigma F_o^2$ ).  
<sup>b</sup>  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ ;  $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$ ,  $P = [\max(F_o, 2, 0) + 2 F_c^2] / 3$  (also with  $F_o^2 > 2\sigma F_o^2$ ).



**Scheme 1.** Synthesis procedure and chemical structure of **6-bisCz**.

## 2.2. NMR

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Fourier 300 MHz spectrometer operated at 300.1 and 75.4 MHz, respectively.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts were measured in  $\text{CDCl}_3$  and referenced to the relative peaks of  $\text{CHCl}_3$  (7.26 ppm for  $^1\text{H}$  NMR) and  $\text{CDCl}_3$  (77.16 ppm for  $^{13}\text{C}$  NMR), respectively.

## 2.3. UV/Vis absorption and fluorescence

The absorption and photoluminescence spectra were recorded on a Shimadzu UV-2450 UV/VIS/NIR scanning spectrophotometer and a Varian Cary Eclipse fluorescence spectrophotometer, respectively.

## 2.4. Cyclic voltammetry

Cyclic voltammetry (CV) was performed in an electrolytic solution prepared with 0.1 M tetrabutylammonium tetrafluoroborate ( $\text{TBABF}_4$ ) at room temperature under an argon atmosphere using CHI600E electrochemical analyzer (CH Instruments, Inc.). Copolymer-coated platinum, platinum wire, and reference electrodes, respectively. Electrical potentials were calibrated to the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox couple.

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