STRUCTURE OF MATTER AND QUANTUM CHEMISTRY

Synthesis, Photophysical, and Electrochemical Properties of Wide Band Gap Tetraphenylsilane-Carbazole Derivatives: Effect of the Substitution Position and Naphthalene Side Chain¹

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Abstract—Four tetraphenylsilane-carbazole derivatives with wide bandgaps (3.38-3.55 eV) were synthesized. The effects of the substitution position and of the presence of naphthalene groups on the photophysical, electrochemical and thermal properties were investigated. The derivatives exhibited maximum absorption peaks ranging from 293 to 304 nm and maximum emission peaks ranging from 347 to 386 nm. Changing the carbazole substitution position on the tetraphenylsilane did not significantly change the photophysical and electrochemical properties. However, *p*-substituted compounds exhibited higher glass transition temperatures than *m*-substituted compounds. Naphthalene groups with bulky structures had extended the conjugation lengths that red-shifted both the absorption and emission spectra. The LUMO level was decreased, which reduced the optical bandgap and triplet energy level. However, the naphthalene groups significantly improved the thermal stability by increasing the glass transition temperature of the compounds.

Keywords: phosphorescence, tetraphenylsilane, carbazole, naphthalene, organic light emitting diode **DOI:** 10.1134/S0036024416130124

INTRODUCTION

Phosphorescent organic light emitting diodes (PhOLEDs) are currently the focus of intense research. Theoretically, PhOLEDs can generate light from both triplet and singlet excitons, which allows the internal quantum efficiency to reach almost 100% [6, 12, 37, 42, 48]. PhOLEDs have potential for use in large screen displays and for general solid-state lighting. However, efficient host materials with wide bandgaps and triplet energies are still limited and in high demand. Achieving a balance between a high triplet energy host and efficient carrier injection is difficult.

Thus, most synthetic effort and structure-property studies have focused on designing ideal and potential materials for high efficiency OLEDs [5, 19, 38, 39, 42, 47, 52, 56]. Derivatives based on tetraphenylsilane were widely investigated materials because of their wide bandgaps (4.5–5.0 eV). Various studies reported the application of tetraphenylsilane derivatives (either polymers or small molecules) in organic light emitting diodes [1, 4, 6, 8, 10, 11, 16, 18, 21–24, 26, 28, 32–34, 37, 41, 44, 46, 53–55]. However, host materials based on tetraphenylsilane exhibit a high driving voltage due to their deep HOMO levels, which creates a high hole injection barrier and low glass transition temperatures.

The HOMO and LUMO levels for previously reported tetraphenylsilane derivatives were approximately 6.2-6.4 and 2.0 eV, respectively [12, 35]. Previous studies have reported that derivatives based on tetraphenylsilane deposited onto a substrate crystallized due to their glass transition temperature being near room temperature [8]. The poor thermal stability of tetraphenylsilane derivatives has led to various efforts towards designing an ideal host material based on tetraphenylsilane with improved film forming morphological and thermal stability. Methyl, triindole, phosphine oxide and carbazole moieties have been used to increase the glass transition temperature and lower the carrier injection barriers [6, 10, 11, 26, 50]. Carbazole derivatives have been widely studied for their good hole transporting capabilities [3, 7, 12, 31]. The tetraphenylsilane bandgap and carrier injection can also be adjusted using electron-donating carbazole group [1, 6, 10-12, 20, 28, 50]. Electron-rich naphthalene groups have also been extensively studied for light emitting applications [13, 15, 29, 30, 40, 49]. They are used to increase the free volume and thus the solubility, which allows these materials to be solution processed. Bulky naphthalene groups are also good at preserving thermal stability [9, 18, 36]. The energy levels (HOMO and LUMO) for the host materials can also be adjusted using naphthalene groups [15, 18].

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Previous studies have shown that the position and structure of substituent groups affect the photophysical properties and performance [17, 18, 38, 43, 45]. Thus, this paper investigates the effect the carbazole substitution position has on the photophysical, electrochemical and thermal properties of the host materials. Carbazole groups were attached at *p*-position and *m*-position on the two phenyl groups in the tetraphenvlsilane core to obtain bis(4-(9H-carbazol-9yl)phenyl)diphenylsilane (p-CzSi) and bis(3-(9H-carbazol-9-yl)phenyl)diphenylsilane (m-CzSi), respectively. Bis(4-(3,6-di(naphthalen-1-yl)-9H-carbazol-9-yl)phenyl)diphenylsilane (p-NapCzSi)and bis(3-(3,6-di(naphthalen-1-yl)-9H-carbazol-9-yl)phenyl)diphenylsilane (m-NapCzSi) were also synthesized to investigate the effect naphthalene has on the photophysical, electrochemical and thermal properties of the synthesized derivatives were then characterized. The experimental results will be compared to theoretical calculations performed using Gaussian 09.

EXPERIMENTAL

General

Proton and carbon nuclear magnetic resonance spectroscopy (¹H NMR and ¹³C NMR spectra) were obtained on a Bruker AVANCE III spectrometer using deuterated chloroform as the solvent with tetramethylsilane (TMS) as internal standard. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) measurements were carried out with a Bruker Microflex series spectrometer in order to measure the molecular masses. 2,5-Dihydroxybenzoic acid (DHB) was used as matrix. Differential scanning calorimetry (DSC) measurements were performed on TA Instrument DSC Q20 under dry nitrogen flow, in the temperature range from 25 to 350°C with a heating rate of 10°C/min, followed by cooling to room temperature and subsequent heating at the same rate. UV-Vis absorption spectra were recorded on a 1650 PC spectrophotometer. The photoluminescence (PL) spectra were measured using a Varian Cary 50 Scan UV–Vis spectrophotometer. Phosphorescence spectra at low temperature (77 K) were also measured to calculate the triplet energy. Cyclic voltammetry (CV) measurements were carried out in a conventional three electrode cell using glassy carbon as a working electrode, a platinum wire counter electrode and a Ag/AgCl reference electrode on a computer controlled potentiostat-galvanostat PGSTAT101 at room temperature. CV Measurements of the compounds were carried out in dimethylformamide containing tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) as a supporting electrolyte. The energy levels were calculated using ferrocene as internal standard with value of -4.8 eV below the vacuum level. The HOMO molecular orbital energies were calculated from the onset of oxidation potential using the equation HOMO =

 $-(E_{0x}^{\text{onset}} + 4.8)$. The energy levels of the lowest unoccupied molecular orbitals (LUMOs) were calculated using the HOMO value and optical band gap (E_{s}) obtained from the onset of UV-Vis absorption spectrum. Reagents and solvents were available commercially and used as received. Tetrahydrofuran (THF) is distilled over sodium benzophenone before use.

Theoretical Calculation Studies

The geometrical and electronic calculations were performed using Gaussian 09 program. Optimizations and calculations were carried out using density functional theory (DFT) calculations at the restricted Becke's three parameterized Lee-Yang-Parr exchange functional (B3LYP) using 6-311G(d, p) basis set.

Synthesis

Bis(4-bromophenyl)diphenylsilane (1). Compound 1 was prepared according to modified procedure from the literature [11]. 1,4-Dibromobenzene (4.20 g, 17.8 mmol) was dissolved in 15 mL dry THF under nitrogen atmosphere. The solution was cooled to -78°C. 9.6 mL of n-BuLi (2.0 M in cyclohexane) was added dropwise and stirred for 1 h. Dichlorodiphenylsilane (1.68 mL, 8 mmol) was added slowly at -78° C. The mixture was stirred overnight while allowing the temperature to rise to room temperature. The reaction was then guenched with water and extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate. After the solvent was evaporated, the crude product was purified by recrystallization from ethanol to afford white solid (2.54 g, 64.3%). ¹HNMR (CDCl₃, 400 MHz): δ (ppm) = 7.57–7.52 (m, 8H), 7.48–7.38 (m, 10H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 137.93, 136.32, 134.98, 133.36, 131.14, 129.88, 128.02, 124.82.

Bis(3-bromophenyl)diphenylsilane (2). The procedure for compound 1 was followed to prepare compound 2 from 1,3-dibromobenzene (2.66 mL, 22 mmol) and dichlorodiphenylsilane (2.10 mL, 10 mmol). The crude product was purified by column chromatography using dichloromethane and hexane as eluent to give white powder (1.30 g, 26.2%). 1 H NMR (CDCl₃, 400 MHz): δ (ppm) = 7.56 (s, 2H), 7.51–7.30 (m, 14H), 7.20–7.17 (m, 2H). ¹³C NMR $(CDCl_3, 100 \text{ MHz}): \delta(\text{ppm}) = 138.60, 136.92, 136.29,$ 134.75, 132.99, 132.53, 130.15, 129.80, 128.19, 123.15.

Bis(4-(9H-carbazol-9-yl)phenyl)diphenylsilane (p-CzSi). Compound *p*-CzSi was prepared according to procedure from the literature [10, 11]. Compound 1 (0.71 g, 1.43 mmol), carbazole (0.61 g, 3.65 mmol), copper powder (0.40 g, 6.3 mmol), and 18-crown-6 (0.07 g, 0.26 mmol) and K₂CO₃ (1.57 g, 11.4 mmol) were dissolved in 3 mL of anhydrous o-dichlorobenzene under nitrogen atmosphere. The reaction mixture was refluxed for 72 h at 180°C. After cooling to room temperature, the mixture was diluted in dichloromethane and filtered through silica gel. The filtrate was evaporated under reduced pressure to give crude product, which was then purified by column chromatography to give white powdery product (0.355 g, 37.2%). ¹H NMR (CDCl₃, 600 MHz): δ (ppm) = 8.18 (d, 4H, J = 7.7 Hz), 7.88–7.95 (m, 4H), 7.73–7.79 (m, 4H), 7.70 (d, 4H, J = 8.25 Hz), 7.50–7.59 (m, 10H), 7.41–7.49 (m, 4H), 7.30–7.37 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 140.59, 139.26, 137.92, 136.46, 133.58, 133.20, 130.05, 128.21, 126.28, 125.97, 123.58, 120.34, 120.14, 109.91. MALDI-TOF MS (*m*/*z*): calcd. for C₄₈H₃₄N₂Si 666.25, found 666.986.

Bis(*3-(9H-carbazol-9-yl)phenyl)diphenylsilane (m-CzSi)*. Compound *m-CzSi* was prepared according to the procedure reported for *p-CzSi* by using compound *2* (0.50 g, 1.01 mmol) and carbazole (0.38 g, 2.27 mmol). The crude product was purified by column chromatography to give white powder product (0.304 g, 45.1%). ¹H NMR (CDCl₃, 600 MHz): δ (ppm) = 8.13 (d, 4H, *J* = 7.34 Hz), 7.85 (s, 2H), 7.73–7.64 (m, 10H), 7.49–7.43 (m, 6H), 7.35–7.25 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 140.64, 137.52, 136.43, 136.30, 135.06, 134.47, 133.01, 130.11, 129.59, 128.27, 128.22, 125.90, 123.38, 120.23, 119.94, 109.67. MALDI-TOF MS (*m/z*): calcd. for C₄₈H₃₄N₂Si 666.25, found 666.415.

1-Naphthaleneboronic acid (3). 1-Bromonaphthalene (2.1 mL, 15 mmol) was prepared in 20 mL dry tetrahydrofuran under nitrogen and cooled to -78° C in dry ice bath. n-BuLi (2.0 M, 7.5 mL, 15 mmol) was added to the solution dropwise via a syringe. After stirred for 1 h, trimethyl borate (5 mL, 3.0 equiv) was added at -78° C. The reaction was warmed to room temperature and stirred overnight. The reaction mixture was then poured into a mixture of ice and water. The mixture was acidified with 2 N HCl and extracted with chloroform. The organic layer was washed three times with water, dried over sodium sulfate (Na_2SO_4) . The crude product was purified by chromatography using hexane/ethyl acetate as the eluent to obtain white powder (1.338 g, 51.9%). ¹H NMR $(CDCl_3, 400 \text{ MHz}): \delta (ppm) = 9.31 \text{ (d, 1H, } J =$ 8.44 Hz), 8,70 (dd, 1H, J = 6.91, 1.28 Hz), 8.14 (d.)1H, J = 8.07 Hz), 7.89–8.07 (m, 1H), 7.68–7.72 (m, 2H), 7.61 (ddd, 1H, J = 8.04, 6.88, 1.10 Hz). ¹³C NMR $(CDCl_3, 100 \text{ MHz}): \delta (ppm) = 137.74, 133.60, 132.29,$ 130 89, 128.83, 128.11, 126.89, 126.57, 125.17.

3,6-Diiodocarbazole (4). Carbazole (8.36 g, 50 mmol) was dissolved in boiling acetic acid (200 mL). To the solution, potassium iodide (10.8 g, 50 mmol) was added. The solution was cooled and potassium iodate (21.5 g, 50 mmol) was added. The mixture was refluxed at 80° C for 1 h. The solution was decanted from undissolved potassium iodate and

allowed to cool to room temperature. The crude product separated by filtration and recrystallized from dichloromethane to give brown solid (13.97 g, 66.7%). 1H NMR (CDCl₃, 400 MHz): δ (ppm) = 8.36 (s, 2H), 8.14 (br, s, 1H), 7.71 (dd, 2H, J = 8.50, 1.65 Hz), 7.24 (d, 2H, J = 8.56 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 138.53, 134.83, 129.40, 124.58, 112.70, 82.44.

3,6-Di(naphthalen-1-yl)carbazole (5). Compound 3 (0.89 g, 5.2 mmol) and compound 4 (1.09 g, 2.6 mmol) were dissolved in 25 mL toluene in a round bottom flask under nitrogen. A solution of potassium carbonate (2 M, 6.5 mL) was added to the reaction Tetrakis(triphenylphosphine)palladium(0) mixture. (0.12 g, 0.10 mmol) was added. The reaction mixture was reflux for 24 h under nitrogen. After cooling to room temperature, the reaction mixture was evaporated to remove solvent and extracted with chloroform and then washed with water. The organic layer was evaporated using a rotary evaporator, and the residue was subjected to a column chromatography using hexane/ethyl acetate as the eluent. White powdery product was obtained (0.67 g, 30.7%). ¹H NMR (CDCl₃, 600 MHz): δ (ppm) = 8.30 (s, 1H), 8.22 (s, 2H), 8.03 (d, 2H, J = 8.53 Hz), 7.94 (d, 2H, J = 8.12 Hz), 7.89 (dd, 2H, J = 7.36, 1.44 Hz), 7.62 (d, 4H, J = 1.10 Hz),7.54-7.60 (m, 4H), 7.51 (ddd, 2H, J = 7.98, 6.88, 1.10 Hz), 7.44 (ddd, 2H, J = 8.32, 6.95, 1.24 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 140.93, 139.26, 133.90, 132.35, 132.18, 128.41, 128.24, 127.36, 127.26, 126.34, 125.93, 125.67, 125.42, 123.49, 121.85, 110.39. MALDI-TOF MS (m/z): calcd. for C₃₂H₂₁N 419.17, found 418.905.

Bis(4-(3,6-di(naphthalen-1-yl)-9H-carbazol-9*vl)phenvl)diphenvlsilane (p-NapCzSi).* Compound *p*-*NapCzSi* was prepared according to the procedure reported for p-CzSi from compound 1 (0.17 g, 0.35 mmol) and compound 5 (0.44 g, 0.77 mmol). The crude product was subjected to column chromatography using hexane/ethyl acetate as eluent to give white powder product (0.17 g, 41.5%). ¹H NMR $(CDCl_3, 600 \text{ MHz}): \delta (ppm) = 8.30 \text{ (d, 4H, } J =$ 1.10 Hz, 8.04 (d, 4H), 8.04 (d, 4H, J = 8.44 Hz), 7.94 Hz(d, 4H, J = 8.07 Hz), 7.88-7.91 (m, 4H), 7.86 (d, 4H)J = 8.44 Hz, 7.82 (dd, 4H, J = 7.70, 1.65 Hz), 7.73 (d, 4H, J = 8.25 Hz), 7.63 (dd, 4H, J = 8.44, 1.65 Hz), 7.55-7.60 (m, 14H), 7.51 (t, 4H, J = 7.47 Hz), 7.44(ddd, 4H, J = 8.34, 6.88, 1.28 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 140.75, 140.36, 139.33, 138.11, 136.51, 133.92, 133.54, 133.47, 133.09, 132.15, 130.14, 128.53, 128.28, 127.35, 126.30, 125.98, 125.71, 125.43, 123.72, 121.87, 109.79. MALDI-TOF MS (*m/z*): calcd. for C₈₈H₅₈N₂Si 1171.44, found 1171.938.

Bis(3-(3,6-di(naphthalen-1-yl)-9H-carbazol-9-yl)phenyl)diphenylsilane (m-NapCzSi). Compound m-NapCzSi was prepared according to the procedure for p-CzSi from compound **2** (0.13 g, 0.26 mmol) and

Normalized absorption intensity, a.u.



Fig. 1. UV-visible absorption for *p*-*CzSi*, *m*-*CzSi*, *p*-*Nap*-*CzSi* and *m*-*NapCzSi* in dilute dimethylformamide solution.

compound 5 (0.31 g, 0.54 mmol). The crude product was subjected to column chromatography using hexane/ethyl acetate as eluent to give white powder (0.148 g, 48.5%). ¹H NMR (CDCl₃, 600 MHz): δ (ppm) = 8.21 (d, 4H, *J* = 1.28 Hz), 8.05 (s, 2H), 7.96 (d, 4H, *J* = 8.44 Hz), 7.91 (d, 4H, *J* = 8.25 Hz), 7.83–7.86 (d, 8H), 7.80 (dd, 4H, *J* = 7.43, 1.74 Hz), 7.75–7.78 (m, 2H), 7.41–7.57 (m, 26H), 7.38 (td, 4H, *J* = 7.70, 1.10 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 140.68, 140.34, 137.61, 136.71, 136.40, 135.19, 134.42, 133.85, 132.98, 132.08, 130.24, 129.79, 128.45, 128.31, 128.22, 128.18, 127.30, 127.28, 126.25, 125.92, 125.65, 125.39, 123.53, 121.77, 109.52. MALDI-TOF MS (*m*/*z*): calcd. for C₈₈H₅₈N₂Si 1171.44, found 1171.927.

RESULTS AND DISCUSSION

Synthesis

The synthetic routes including intermediates and final products are presented in Scheme 1 and Scheme 2. The synthesis for compounds p-CzSi and *m*-*CzSi* consists of two parts. This synthesis began by reacting dichlorodiphenylsilane with lithiated 1,4-dibromobenzene and 1,3-dibromobenzene to obtain compounds 1 and 2, respectively. The brominated tetraphenylsilane (compounds 1 and 2) was then reacted with carbazole via an Ullmann coupling reaction. Copper powder and 18-crown-6 were used to catalyze the reaction under basic conditions in o-dichlorobenzene. The mixture was then refluxed under nitrogen for 72 h to obtain compounds p-CzSi and *m*-*CzSi* in 37.2 and 45.2% yield, respectively. The carbazole was attached at the p- and m-positions in p-CzSi and m-CzSi, respectively. Compounds p-Nap-CzSi and *m*-NapCzSi were synthesized in three stages. First, 1-naphthaleneboronic acid (compound 3) was obtained by reacting lithiated 1-bromonaphthalene with trimethyl borate. Compound **5** was obtained by reacting compound **3** with iodinated carbazole (compound **4**) via a Suzuki coupling reaction catalyzed with Pd(PPh₃)₄. A white solid powder was obtained as the product with a 30.7% yield. Lastly, compound 5 was reacted with compounds **1** and **2** via an Ullmann coupling reaction to obtain *p*-*NapCzSi* (41.6% yield) and *m*-*NapCzSi* (48.5% yield), respectively. The compounds were fully characterized by ¹H, ¹³C NMR and MALDI-TOF mass spectroscopy. The results were agreed well with the proposed structures. The final products are readily soluble in common solvents such as dichloromethane, chloroform, tetrahydrofurane, and dimethylformamide, which indicates the possibility for solution processing [47].

Photophysical Properties

The photophysical properties of the compounds were analyzed using UV-Vis and fluorescence spectrophotometry. Figure 1 shows the UV-vis electronic absorption spectra for p-CzSi, m-CzSi, p-NapCzSi, and *m*-NapCzSi in a dilute dimethylformamide solution. Table 1 summarizes the photophysical properties of these compounds. Figure 1 shows that the absorption spectra of *p*-CzSi and *m*-CzSi were similar. The tetraphenylsilane compounds containing naphthalene and carbazole moieties (p-NapCzSi and *m*-*NapCzSi*) exhibited similar absorption spectra due to their similar structures. The spectra exhibited a broad absorption band ranging from 260 to 360 nm. Both compounds *p*-*CzSi* and *m*-*CzSi* exhibited a primary maximum main absorption peak at 293 nm which was attributed to the $\pi - \pi^*$ transitions in the tetraphenylsilane core [10, 11, 26, 28]. Shoulder peaks were observed for *p*-*CzSi* at 325 and 339 nm. For *m*-*CzSi*, the shoulder peaks were located at 327.5 and 340 nm. These shoulder peak were attributed to the characteristic $\pi - \pi^*$ transitions of the carbazole unit [3]. The maximum absorption peaks for *p*-Nap-CzSi and m-NapCzSi were red-shifted to 303 and 304 nm, respectively. A small shoulder peak was observed at 354 nm for both *p*-NapCzSi and *m*-Nap-*CzSi*. These results indicate the naphthalene groups red-shifted the absorption peak due to their electron-

donating character [47]. The optical bandgaps (E_g^{opt}) determined from the absorption spectra onset are shown in Table 1. The optical bandgaps calculated for *p*-*CzSi* and *m*-*CzSi* were 3.55 and 3.54 eV, respectively [6, 10, 11, 28]. The calculated optical bandgaps for compounds *p*-*NapCzSi* and *m*-*NapCzSi* significantly decreased to 3.38 eV. The naphthalene groups reduced the optical bandgap by approximately 0.17 eV.

The photoluminescence (PL) spectra of the compounds in dilute solutions are shown in Fig. 2. Upon excitation, the emission spectra were similar between p-CzSi and m-CzSi, while the spectra for p-NapCzSi



Scheme 1. Synthetic routes to compounds *p*-*CzSi* and *m*-*CzSi*. Reagents and conditions: *a*, *n*-BuLi, dry THF, -78° C, and 1,4-dibromobenzene; *b*, *n*-BuLi, dry THF, -78° C, and 1,3-dibromobenzene; and *c*, copper, 18-crown-6, K₂CO₃, *o*-dichlorobenzene (*o*-DCB), and 180^{\circ}C.

and *m*-*NapCzSi* were also similar due to similarity of their structure. The maximum emission peaks for *p*-*CzSi* and *m*-*CzSi* were located at 347 and 349 nm, respectively. The maximum emission peaks for *p*-*Nap*-*CzSi* and *m*-*NapCzSi* were red-shifted to 386 and 385 nm, respectively. Shoulder peak were observed for *p*-*CzSi* and *m*-*CzSi* at 364 nm. The naphthalene group may have extended the conjugated backbone, increased the electron density and thus red-shifted the emission peak [47]. The calculated Stokes shift calculated for *p*-*CzSi* and *m*-*CzSi* were 54 and 56 nm, respectively. Compounds *p*-*NapCzSi* and *m*-*NapCzSi* exhibited an 82 nm Stokes shift, which is 27 nm higher than for *p*-*CzSi* and *m*-*CzSi*.

The triplet energy (E_T) is an essential requirement for an ideal host. This energy should be greater than that of the phosphorescent guest to prevent back transferring from the guest to the host. The low temperature phosphorescent spectrum was used to measure the triplet energy. The triplet energy calculated from the *p*-*CzSi* and *m*-*CzSi* from triplet emission peaks were 2.94 and 2.91 eV, respectively [10, 11, 28]. The triplet energy for *p*-*NapCzSi* and *m*-*NapCzSi* were both 2.21 eV. The triplet energy was significantly reduced upon inclusion of the



Scheme 2. Synthetic routes to compounds p-NapCzSi and m-NapCzSi. Reagents and conditions: (a) n-BuLi, dry THF, -78° C, and B(OMe)₃; (b) KI, KIO₃, acetic acid, reflux, and 2 h; (c) Pd(PPh₃)₄, K₂CO₃ 2 M, toluene, 90°C, and overnight; and (d) copper, 18-crown-6, K₂CO₃, o-DCB, and 180°C.

naphthalene groups in the derivatives. The substituent position on the tetraphenylsilane core did not significantly change the spectral features. This may be because the substituents position does not drastically change the vibrational structure and configuration structural changes between the ground and excited states [25, 51].

Electrochemical Properties

The redox behavior of these compounds in dimethylformamide was studied via cyclic voltammetry to determine the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies. This information is crucial for examining the charge injection barriers and device

Compound	Photophysical properties								
	λ^{a}_{abs} (nm)	λ_{edge}^{a} (nm)	λ_{em}^{a} (nm)	Stoke shift (nm)	$E_{g}^{\text{opt b}}$ (eV)	$E_{\rm T}^{\rm c}$ (eV)			
p-CzSi	293, 325, 339	349.5	347, 362	54	3.55	2.94			
m-CzSi	293, 327.5, 340	350.0	349, 364	56	3.54	2.91			
p-NapCzSi	304	366.5	386	82	3.38	2.21			
m-NapCzSi	303	366.5	385	82	3.38	2.21			

Table 1. Photophysical properties for *p*-CzSi, *m*-CzSi, *p*-NapCzSi, and *m*-NapCzSi

^a Recorded in dimethylformamide at r. t.

^b Optical bandgaps were determined from the absorption edge of the normalized absorption spectra.

^c Triplet energy was calculated from the first emission peak in the low temperature PL spectra (77 K).

optimization. The cyclic voltammograms are shown in Fig. 3, and the data are summarized in Table 2. An irreversible, single-electron oxidation peak was observed during the anodic sweeping shown in Fig. 3 in the range of 1.37 to 1.50 V. The irreversible oxidation peak was attributed to unstable electrochemical properties due to the formation of new species formed during the anodic sweep [2, 51]. The oxidation peak for *p*-*CzSi* occurred at 1.50 V, which is slightly higher than for m-CzSi (1.40 V). The oxidation peaks for *p*-*NapCzSi* and *m*-*NapCzSi* are observed at 1.37 V. Assuming that the HOMO energy for the ferrocence standard is 4.8 eV with respect to the zero vacuum level, the HOMO and LUMO can be calculated based on the oxidation potentials onset (E_{ox}^{onset}) and optical bandgaps (E_{g}^{opt}). The HOMO and LUMO energy levels were estimated using the empirical formulas: HOMO = $-(E_{ox}^{onset} + 4.8)$ and LUMO = HOMO + E_{g}^{opt} . The HOMO levels calculated for *p*-*CzSi*, m-CzSi, and m-NapCzSi using the onset potential shown in Table 1 were both -6.05 eV. The HOMO





Fig. 2. Photoluminescence spectra for *p*-*CzSi*, *m*-*CzSi*, *p*-*NapCzSi*, and *m*-*NapCzSi* in dilute dimethylformamide solution.

level determined for *p*-*NapCzSi* was -6.04 eV. No significant changes were observed in the HOMO regardless of the substituent position or presence of naphthalene. The LUMO levels calculated for *p*-*CzSi* and *m*-*CzSi* were -2.50 and -2.51 eV, respectively. These LUMO levels decreased significantly in the presence of naphthalene for *p*-*NapCzSi* (-2.65 eV) and *m*-*Nap-CzSi* (-2.67 eV).

Thermal Properties

The thermal properties for these compounds were evaluated via differential scanning calorimetry (DSC) under a nitrogen atmosphere. From Fig. 4 it can be seen that all of the compounds were stable up to 350° C with no melting point. These results imply that the compounds were in amorphous state, as desired for PhOLED devices. The glass transition temperature (T_g) was observed for p- C_zSi , m- C_zSi , p- $NapC_zSi$, and m- $NapC_zSi$ at 120, 90, 205, and 172°C, respectively. The glass transition temperature for p- C_zSi agrees well with the literature data [6, 10, 11]. The glass transition temperature may increase with the increasing rigidity,



Fig. 3. Oxidation cyclic voltammograms of *p*-*CzSi*, *m*-*CzSi*, *p*-*NapCzSi*, and *m*-*NapCzSi* in dimethylformamide solution containing 0.1 M TBAPF₆.

Compound	Experimental						Theoretical			
	$E_{\rm ox}^{\rm peak}$ (V)	$E_{\rm ox}^{\rm onset}$ (V)	HOMO ^a (eV)	LUMO ^b (eV)	E_{g}^{opt} (eV)	$E_{\rm T}^{\rm c}$ (eV)	HOMO ^d (eV)	LUMO ^d (eV)	E_{g}^{calcd} (eV)	$E_{\mathrm{T}}^{\mathrm{d}}$ (eV)
p-CzSi	1.50	1.25	-6.05	-2.50	3.55	2.94	-5.62	-1.23	4.39	2.87
m-CzSi	1.40	1.25	-6.05	-2.51	3.54	2.91	-5.52	-1.19	4.33	2.87
p-NapCzSi	1.37	1.24	-6.04	-2.65	3.38	2.21	-5.49	-1.33	4.16	2.22
m-NapCzSi	1.37	1.25	-6.05	-2.67	3.38	2.21	-5.41	-1.28	4.13	2.23

 Table 2. Electrochemical properties of p-CzSi, m-CzSi, p-NapCzSi, and m-NapCzSi

^a Calculated from the oxidation potential onset using HOMO = $-(E_{ox}^{onset} + 4.8)$.

^b LUMOs were calculated from the HOMO and bandgap (E_{g}^{opt}).

^c The triplet energy was calculated from the first emission peak for the low temperature PL spectra (77 K).

^d Calculated from the theoretical simulations.

intermolecular interactions and molecular backbone symmetry. The glass transition temperatures for the *p*-substituted compounds were higher than for the *m*-substituted ones. This may be explained by stronger intermolecular interactions in *p*-substituted compounds [9]. The presence of naphthalene moieties also significantly improved the glass transition temperature and thermal stability (>70%). The naphthalene group in *p*-NapCzSi and *m*-NapCzSi increased the bulkiness and molecular interactions and thus increase the glass transition temperature [18, 36]. A glass transition temperature was only barely seen for *p*-NapCzSi and *m*-NapCzSi due to their small heat capacity and crystallinity [27].

Theoretical Calculations

Theoretical molecular orbital calculations were performed for the studied compounds to characterize their optimized geometries, orbital energies, and electron densities for HOMO and LUMO states of each molecule. Density functional theory (DFT) calculations were performed using Gaussian 09 program with a restricted Becke's three parameterized Lee-Yang-Parr exchange functional (B3LYP) using a 6-311G basis set. Figure 5 shows the optimized molecular structures for these compounds. The molecules exhibited a non-coplanar twisted conformation due to the large torsional angle between the carbazole and tetraphenylsilane core. Such a non-planar structural feature is beneficial to PhOLED applications by preventing excessive intermolecular interactions against quenching and suppressing crystallization to establish a uniform amorphous film in the device [14, 27].

The calculated HOMO and LUMO energy levels are listed in Table 2. Figure 6 summarizes the experimental and theoretical HOMO and LUMO energy levels for these compounds and their corresponding molecular orbital distribution. Comparing the experimental and theoretical results shows that the calculated HOMO and LUMO levels are higher than the experimental results. The theoretical results indicate



Fig. 4. DSC curves for p-CzSi, m-CzSi, p-NapCzSi and m-NapCzSi measured at a heating rate of 10°C/min under nitrogen.

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Fig. 5. Optimized three-dimensional geometry for (a) p-CzSi, (b) m-CzSi, (c) p-NapCzSi, and (d) m-NapCzSi via DFT calculations using a B3LYP model with a 6-311G as the basis set.



Fig. 6. HOMO and LUMO energy levels for *p*-*CzSi*, *m*-*CzSi*, *p*-*NapCzSi*, and *m*-*NapCzSi* and their corresponding molecular orbital distributions.

the HOMO and LUMO levels for the *m*-substituted compounds shift slightly upwards compare to *p*-substituted compounds. In contrast, the experimental results yielded no significant change in energy levels upon changing the substituent position. The theoretical data predicted the HOMO and LUMO energy levels would narrow in the presence of a naphthalene group. The theoretical calculations predicted much higher bandgaps than those determined experimentally. However, the theoretical triplet energies were similar to the experimental results. The difference in experimental and theoretical results may be attributed to simulated orbital of the HOMO and LUMO energies being an estimate of the transition energy [47].

Figure 6 shows the HOMO electrons populations were uniformly dispersed over the carbazole unit, and carbazole is well known to be an electron-donating group [1]. Upon excitation, electron population for the LUMO level was localized over the phenyl unit in the tetraphenylsilane core. Thus, the π - π * transitions for both tetraphenylsilane and carbazole are thought yield the absorption and emission properties.

CONCLUSIONS

In conclusion, four wide bandgap derivatives based on tetraphenylsilane-carbazole were successfully synthesized. Their photophysical, electrochemical and thermal properties were investigated. The results indicate that the substituents position did not significantly affect the photophysical and electrochemical properties of the derivatives. However, higher glass transition temperatures were observed for *p*-substituted compounds compared with to *m*-substituted compounds. Incorporating bulky naphthalene groups increased the glass transition temperature by increasing intermolecular interactions. The presence of naphthalene moieties in substituents extended the conjugation length and red-shifted both the absorption and photoluminescence bands. The optical bandgap decreased as the LUMO levels decreased. However, no significant changes were observed in the HOMO level. Theoretical molecular orbital calculations for these compounds yielded calculated HOMO and LUMO energy levels that were slightly higher than the experimental results. However, the calculated triplet energies were nearly identical to the experimental results. The electroluminescence properties of these derivatives will be investigated to determine their potential for hole-transporting or host materials in PhOLEDs.

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