# Carbazole Functionalized Silole: Synthesis, Aggregation-induced Emission, and Electrochemical Polymerization

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A carbazole-functionalized silole, 9,9'-(4,4'-(2,3,4,5-tetraphenyl-1*H*-silole-1,1-diyl)*bis*(4,1-phenylene))bis (9*H*-carbazole) (**BPCTPS**), was prepared through the reaction of dilithium diene with tetrachlorosilane followed by a direct substitution reaction with (4-(9*H*-carbazol-9-yl)phenyl)lithium. Combining the carbazole donor with the silole acceptor resulted in a new type of donor–acceptor (D–A) dyad. Density function theory (DFT) calculations showed that the highest occupied molecular orbital was localized on the carbazole group whereas the lowest unoccupied molecular orbital was localized on the silole group. **BPCTPS** exhibited very weak emission properties in dilute solution but emitted intensely in the aggregated state, revealing that it was an aggregation-induced emission (AIE)-active species. Furthermore, addition of electron donating groups to the silole ring resulted in a slight red shift of both the absorption and emission spectra compared with those of the reference compound hexaphenylsilole (**HTS**). The electrochemical properties of **BPCTPS** were also studied by cyclic voltammetry (CV), which indicated that the compound formed a cross-linked film on the Pt electrode via electropolymerization.

Keywords: Silole, Bipolar compound, Aggregation-induced emission, Electropolymerization

## Introduction

Organic molecules are usually used as films or aggregates<sup>1,2</sup> in applications such as organic light-emitting diodes (OLEDs), field-effect transistors (FETs), and photovoltaics (PVs). However, most of them are highly emissive in dilute solutions but become weakly luminescent in the aggregate form. This phenomenon is known as aggregation-caused quenching (ACQ)<sup>3</sup> and is generally considered as an obstacle in the abovementioned applications. To circumvent this problem, probably the most intriguing approach is based on the aggregation-induced emission (AIE)<sup>4</sup> phenomenon. AIE is the opposite of ACO, and refers to the situation when some nonfluorescent dyes in solution become efficient emitters in their aggregate form. Silole is a typical example of an AIE material.<sup>5</sup> It is nonfluorescent when remains isolated in dilute solutions but becomes strongly fluorescent in the aggregate state. In addition, the crystalline phase of siloles exhibits a much stronger blue-shifted emission than its amorphous phase.<sup>6</sup> This unique phenomenon is due to the presence of a stable lowest unoccupied molecular orbital (LUMO), which is the result of the  $\sigma^* - \pi^*$  interaction between the  $\sigma^*$  orbital of the exocyclic Si–C  $\sigma$ -bonds and the  $\pi^*$  orbitals of the butadiene moiety of the ring.<sup>7</sup> These low-lying LUMO levels of the silole molecule are responsible for its high electron affinity and electron mobility.<sup>8</sup> Furthermore, in the case of silole polymers, it was reported that they can be used to detect chemical vapors, such as the nitro explosive 2,4,6-trinitrotoluene (TNT) and 2,4,6-trinitrophenol (picric acid).<sup>9</sup> Thus, siloles and silole polymers have been widely utilized in several applications,

such as OLEDs,<sup>10</sup> chemo and biosensors,<sup>11</sup> and organic PVs (OPVs).<sup>12</sup>

Carbazole is a well-known electron donor and has been widely used in phosphorescent blue host materials because of its wide bandgap, high triplet energy level, and high hole mobility.<sup>13</sup> Another interesting property of carbazole is that it can be electropolymerized through the extremely reactive sites at its 3 and 6 positions.<sup>14</sup> Thus, the electrochemical preparation of conducting polymers has been investigated as an alternative method to spin-coating. For example, the Advincular<sup>15</sup> and Ma groups<sup>16</sup> have independently reported electrochemically prepared carbazole-based thin films and their applications in OLEDs and OPVs.

Previously, a nonconjugated ethylene bridge was used to introduce carbazole units into the silole acceptor for utilization as a PV active material.<sup>17</sup> It was shown that these donoracceptor (D-A) type dyads are photovoltaically active with high thermal stability. In this study, we used a direct approach to prepare the linked dyad, 9,9'-(4,4'-(2,3,4,5-tetraphenyl-1*H*-silole-1,1-diyl)*bis*(4,1-phenylene))*bis*(9*H*-carbazole) (BPCTPS), which comprises two carbazole units as electron-donating groups and a silole moiety as the electronaccepting group. The photophysical properties of the new compound were investigated by UV-vis absorption and emission spectroscopy. A theoretical study was also performed to explore its optical and electronic properties. Finally, its electrochemical properties were studied by cyclic voltammetry (CV). A highly cross-linked thin film was successfully obtained by CV through the electropolymerization of the two carbazole units.

## Experimental

General Procedures. All preparative tasks were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Glassware, syringes, magnetic stirring bars, and needles were dried in a convection oven overnight before use. THF (tetrahydrofuran) and diethyl ether were freshly distilled over sodium and potassium benzophenone. <sup>1</sup>H and <sup>13</sup>C spectra were recorded on a Varian Mercury 300 spectrometer (Palo Alto, CA, USA) operating at 300.1 and 75.4 MHz, respectively. All proton and carbon chemical shifts were measured relative to internal residual benzene from the lock solvent (99.5% CDCl<sub>3</sub>). Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer (Hindley Green, UK). The absorption and photoluminescence (PL) spectra were recorded on a Perkin-Elmer Lambda 2S UV-vis spectrophotometer (Waltham, MA, USA) and a Perkin-Elmer LS fluorescence spectrometer (Waltham, MA, USA), respectively. Diphenylacetylene, lithium, 1,4-dibromobenzene, carbazole, tetrachlorosilane, and n-BuLi in 2.5 M hexane were purchased from Aldrich (St. Louis, MO, USA) and used without further purification. 9-(4-Bromophenyl)-9H-carbazole was prepared according to the literature procedure.<sup>13c</sup>

Synthesis of 1,1'-Dichloro-2,3,4,5-tetraphenylsilole (2). A two-neck round-bottomed flask was charged with diphenylacetylene (4.27 g, 24 mmol) and dry THF (20 mL). Clean lithium shavings (347 mg, 50 mmol) were added at room temperature and the reaction mixture was stirred for 2 h under N<sub>2</sub> atmosphere. The reaction mixture was diluted with an additional 100 mL of THF, followed by an addition of silicon tetrachloride (1.4 mL, 12 mmol) at -78 °C. The reaction mixture was warmed to room temperature and stirred for another 6 h. After the reaction was complete, the solvent and unreacted silicon tetrachloride were evaporated under vacuum and diethylether was then added to precipitate the LiCl salts, which were removed by filtration under N<sub>2</sub> atmosphere. The filtrate was concentrated and recrystallized at -20 °C to produce **2** as a greenish yellow solid. Yield: 2.07 g, 38%.

Synthesis of BPCTPS. To a solution of 9-(4-bromophenyl)-9H-carbazole (1.61 g, 5 mmol) in dry THF (25 mL), n-BuLi in 2.5 M hexane (2.2 mL, 5.5 mmol) was added dropwise at -78 °C. After the resulting mixture was stirred at this temperature for 30 min, diluted 2 (0.91 g, 2 mmol) in THF (10 mL) was added dropwise via a cannula at -78 °C. The mixture was then warmed to room temperature and stirred for an additional 12 h, following which the reaction mixture was poured into distilled water. The crude products were extracted with dichloromethane and washed sequentially with water and brine. The combined organic layers were dried over MgSO<sub>4</sub> and the filtrates were evaporated under reduced pressure. The crude products obtained in this way were purified by flash chromatography over silica gel using ethylacetate/n-hexane 1:10 (v/v) as an eluent to afford BPCTPS as a green solid. Yield: 0.87 g, 30%; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.16 (d, 4H), 7.99 (d, 4H), 7.68 (d, 4H), 7.55 (d, 4H), 7.43 (t, 4H), 7.31 (t,

4H), 6.97–7.15 (m, 12H), 6.84–6.91 (m, 8H). HR-MS (FAB). Calcd. for  $C_{64}H_{44}N_2Si$  (M<sup>+</sup>) *m/z* 868.3274, observed 868.3286. Calcd. for  $C_{64}H_{44}N_2Si$ : C, 88.44; H, 5.10; N, 3.22; Si, 3.23. Found: C, 88.46; H, 5.11; N, 3.21.

Cyclic Voltammetry. The electrochemical polymerization and characterization of BPCTPS were carried out using a BAS 100B electrochemical analyzer (West Lafayette, IN, USA) at room temperature under argon atmosphere after purging for at least 5 min. CV scans were recorded in a solution of dichloromethane containing 0.1 M tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) as supporting electrolyte. A threeelectrode cell system was used, which comprised a platinum disk (diameter 1.6 mm) electrode as the working electrode, a platinum wire as the counter electrode, and Ag/AgNO<sub>3</sub> (0.1 M) as the reference electrode. The number of electrons transferred per molecule was determined by performing a linear sweep voltammetry experiment using a carbon micro-disk electrode. All potential values were calibrated against the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple. The potential values measured in this study were then corrected relative to the saturated calomel electrode (SCE) on the basis of the Fc/ Fc<sup>+</sup> redox potential as 0.58 V vs. that of the SCE, unless otherwise specified.

**Electrodeposition.** Cross-linked polymer films were prepared on a Pt disk by oxidative successive scans between 0 and 1.4 V vs. Ag/AgNO<sub>3</sub> at 100 mV/s. After electrochemical polymerization of the film on the Pt electrode, the film was washed several times with pure dichoromethane followed by drying under vacuum for 24 h. CV scans of the film were recorded at scan rates of 100, 50, and 25 mV/s.

**Theoretical Calculations.** Density function theory (DFT) calculations were performed on the platform of the Gaussian 09 package.<sup>18</sup> The ground-state geometry was fully optimized at the DFT level using the B3LYP functional and 6-31G(d,p) basis set for all atoms. Isodensity plots (contour = 0.03 a.u.) of the frontier orbitals were visualized by using the Chem3D Ultra program (Cambridge Soft Corporation, Cambridge, MA, USA). The excitation energies and the oscillator strengths for the lowest 30 singlet–singlet transitions at the optimized geometry of the ground state were obtained through time-dependent DFT (TD-DFT) calculations using the same basis set and functional as used for the ground state.

## **Results and Discussions**

The synthetic route to **BPCTPS** is shown in Scheme 1, and the detailed procedure is described in the Experimental section. The 1,2,3,4-tetraphenylbutadiene-1,4-dianion was generated from diphenylacetylene and Li metal in THF solution and allowed to react with tetrachlorosilane to give 1,1-dichloro-2,3,4,5-tetraphenylsilole (2). The *in situ* reaction of 2 with lith-ium-4-(*N*-carbazolyl)phenyl (1) resulted in the production of the target compound **BPCTPS** in 38% yield after purification by silica gel chromatography using ethylacetate/hexane 1:10 (v/v). The final product displayed the expected signals on



Scheme 1. Synthesis of BPCTPS.



**Figure 1.** (a) Absorption spectrum of **BPCTPS** in THF solution. (b) PL spectra of **BPCTPS** in acetone/water mixed solution with different water fractions ( $f_w$ ).

the <sup>1</sup>H NMR and high-resolution mass spectra (see Supporting Information for <sup>1</sup>H NMR).

Figure 1(a) shows the UV–vis absorption spectrum of **BPCTPS** in THF solution. **BPCTPS** exhibited three absorption bands: those at 298 nm ( ${}^{1}L_{a} \leftarrow {}^{1}A$  transition) and 341 nm ( ${}^{1}L_{b} \leftarrow {}^{1}A$  transition) were characteristic of the carbazole moiety,<sup>19</sup> whereas the lower energy band centered at



Figure 2. A plot of relative emission intensity versus fractions of water in acetone/water mixed solution.

368 nm was attributed to the  $\pi - \pi^*$  transition of the silole unit.<sup>20</sup> Figure 1(b) shows the PL spectrum of BPCTPS in acetone solution. The compound exhibits weak fluorescence centered at 486 nm. However, upon addition of water to the solution, the fluorescence of BPCTPS became increasingly stronger due to growing AIE. This phenomenon was the consequence of increasing levels of aggregation, caused by larger water fractions, in which the silole moieties are insoluble. We also observed a significant bathochromic shift (13 nm) in the solvent mixture with the largest water fraction, which indicated that the excited state of BPCTPS involved a chargetransfer (CT) state. Since the maximum emission of 9methylcarbazole appeared at 364 nm and tailed to 420 nm with significant intensity,<sup>19</sup> the dissipation of carbazole emissions indicated that an intramolecular energy transfer occurred from the carbazole groups to the silole moiety in the excited state of BPCTPS.

Figure 2 shows the magnitude of AIE as a function of the volume fraction of water. The onset of AIE was observed at 16%, and the maximum enhancement was achieved at 66% in the acetone/water mixed solvent system. Interestingly, even though the presence of increasing amounts of water would be expected to promote aggregation, a dramatic decrease in the

AIE effect was observed for larger water fractions, possibly due to the resulting lower solubility of **BPCTPS**. Apart from this, the excited singlet state might be partially quenched by energy dissociation, because the CT process is favored by the aggregated phase.<sup>17</sup>

The observed photophysical properties were further investigated by conducting quantum chemical calculations for **BPCTPS** using the B3LYP/6-31G(d,p) level of theory. Figure 3 shows selected molecular orbitals and the calculated absorption spectrum for **BPCTPS**. In Figure 3(a), it can be seen that the highest occupied molecular orbital (HOMO) is mainly located on the electron-donating phenyl carbazole (PC) unit. It is well known that a low-lying LUMO in silole results from unique orbital interactions between the  $\sigma^*$  orbital of the exocyclic Si–C  $\sigma$ -bonds and the  $\pi^*$  orbital of the butadiene moiety.<sup>7</sup> As shown in Figure 3(a), the LUMO is mainly localized on the C–Si–C and C–C bonds of the silole moiety in **BPCTPS**.

TD-DFT methods are useful for assigning and understanding the absorption spectra.<sup>21</sup> Therefore, a TD-DFT calculation was conducted, and the selected oscillation strength (f) and electronic transitions are displayed in Figure 3(b). The calculated HOMO and LUMO energy levels of **BPCTPS** were



Figure 3. (a) Selected molecular orbitals and (b) computed absorption spectrum for **BPCTPS**.

-5.36 and -1.77 eV, respectively, giving rise to a HOMO– LUMO bandgap ( $E_g$ ) of 3.59 eV. As shown in Figure 3(b), the TD-DFT transition energies for the first excited states corresponded qualitatively to the experimental values. The lowest energy absorption can be described as predominantly HOMO  $\rightarrow$  LUMO in nature (39%), with an  $n-\pi^*$  transition from the electron-donating PC units to the electron-accepting silole unit as well as a HOMO-2  $\rightarrow$  LUMO (32%)  $\pi-\pi^*$  transition within the butadiene fragment of the silole ring.

The electrochemical behavior of **BPCTPS** was determined by CV at room temperature in presence of 0.1 M TBABF<sub>4</sub> as supporting electrolyte in anhydrous dichloromethane under N<sub>2</sub> at various scan rates (details of the electrodes are provided in the Experimental section). It was found that **BPCTPS** exhibited irreversible oxidation and reduction waves, as observed for other silole derivatives.<sup>22</sup> From the first oxidation onset potential, the HOMO energy level of **BPCTPS** was estimated to be ~ -5.53 eV (calibrated using a ferrocene, 4.8 eV below the vacuum level) and the LUMO energy level was calculated to be -2.04 eV from the absorption edge of the optical absorption spectra of **BPCTPS**. Hence, there was a good correspondence between the experimental and calculated values.

Carbazole can be electropolymerized on transparent conducting oxides (TCOs), such as indium tin oxide (ITO), through its extremely reactive sites at the 3 and 6 positions.<sup>14</sup> Therefore, we carried out the electropolymerization of **BPCTPS** on a Pt disk by using CV. The electropolymerization of BPCTPS became apparent after five repeated scans, after which an increase in both the anodic and cathodic peak currents was observed during continuous CV scans (see Figure 4). The formation of the deposited film was confirmed by immersing the electropolymerized electrode into a 0.1 M dichloromethane solution of TBABF<sub>4</sub> electrolyte and measuring the current at scan rates of 100, 50 and 25 mV/s (Figure 4(b)). The peak currents were proportional to the scan rates, and the difference between the anodic and the cathodic peak potentials were not changed, which is a typical property of a film deposited on an electrode.<sup>23</sup>

#### Conclusions

We have prepared a silole dyad, **BPCTPS**, consisting of two PC units as electron donors and a silole unit as an electron acceptor. **BPCTPS** exhibited AIE when water was added to a solution of the compound. A dramatic decrease in the AIE, together with a significant bathochromic shift, was observed for larger water fractions (>70%), indicating that the excited state of **BPCTPS** involved a CT state. Furthermore, an electrodeposited film was successfully formed by electropolymerization using CV. The electrochemical preparation of TCO substrates is widely applied in organic electronics, such as in OLEDs and OPVs; therefore, an investigation of the application of **BPCTPS** in organic electronics has been currently undertaken in our laboratory.



**Figure 4.** (a) CV of 0.5 mM **BPCTPS** on Pt electrode in dichloromethane solution containing 0.1 M TBABF<sub>4</sub> with V = 100 mV/s during five cycles. (b) Typical CVs of deposited film in dichloromethane solution with V = 100, 50, and 25 mV/s.

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**Supporting Information.** <sup>1</sup>H NMR spectrum of **BPCTPS** is available in the online version of this article.

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