

# Synthesis of Disilanyl Double-Pillared Bisdibenzofuran with a High Triplet Energy

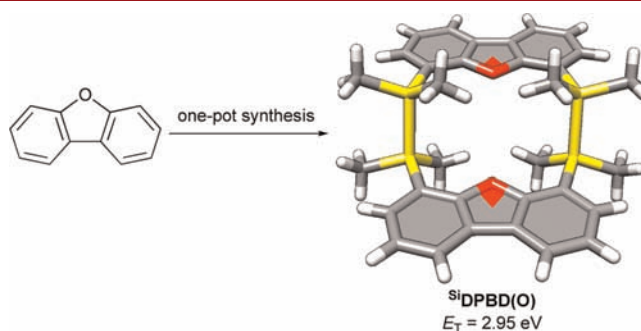
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## ABSTRACT



A double-pillaring strategy for the synthesis of silacyclophanes has been applied to dibenzofuran to create a new cyclophane molecule that links two dibenzofuran molecules through  $\sigma_{\text{SiSi}}-\pi$  conjugation. The performance of disilanyl double-pillared dibenzofuran [<sup>Si</sup>DPBD(O)] in green phosphorescent organic light-emitting diode (OLED) devices was evaluated as both a carrier-transport material and a host material for an Ir-based phosphorescent emitter.

Polycyclic aromatic compounds are attractive materials for organic electronics because their rigid  $\pi$ -conjugated structures possess many of the requisite properties for organic semiconductors, such as a small reorganization energy during transport of the charge carrier. Although the extension of  $\text{sp}^2$ -networks helps to effectively delocalize the charge carrier over a larger  $\pi$ -conjugated system, thus reducing the reorganization energy,<sup>1,2</sup> such a molecular design often becomes an obstacle for optoelectronic devices where additional properties, such as transparency in the visible light region, are required.<sup>3</sup> As a complementary design for optoelectronic applications, we recently introduced a disilanyl double-pillaring strategy for extending conjugated systems and developed a bipolar carrier

transport material from anthracene molecules, disilanyl double-pillared bisanthracene (<sup>Si</sup>DPBA), for use in organic light-emitting diode (OLED) devices.<sup>4</sup>

The double-pillaring method features a  $\sigma_{\text{SiSi}}-\pi$  conjugation that moderately extends the conjugated systems without significantly affecting the optical properties, while also adding thermal stability by creating a large rigid structure with two pillars. Due to the bipolar nature of the charge-carrier transport, <sup>Si</sup>DPBA could also be interesting as a host material for phosphorescent emitters. However, when <sup>Si</sup>DPBA was used as a host material for the emitting layer (EML) with a green emitter, Ir(ppy)<sub>3</sub> (triplet energy ( $E_T$ ) = 2.4 eV),<sup>5</sup> no apparent emission was detected, most likely because the triplet energy level of <sup>Si</sup>DPBA ( $E_T \sim 2.3 \text{ eV}$ ) was slightly too low.<sup>4</sup> Considering that a minor modulation of the HOMO/LUMO energy and the preservation of structural rigidity are characteristic

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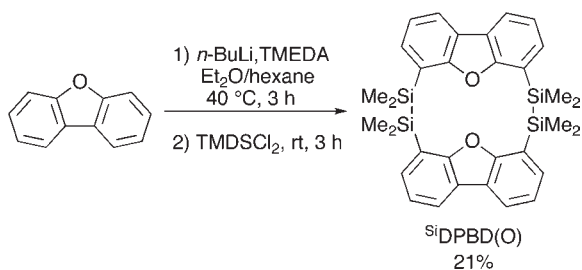
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of the double-pillaring method, we envisioned that this strategy may be of potential interest for the molecular design of host materials with high  $E_T$  values, in which an aromatic molecule with a high energy level for the triplet state would be used for the arene units. From various possible candidates with high  $E_T$  values, we chose dibenzofuran ( $E_T = 3.2$  eV), which was explored recently to produce a few examples of organic materials,<sup>6,7</sup> and synthesized disilanyl double-pillared bisdibenzofuran [<sup>Si</sup>DPBD(O)]. We herein report the synthesis and fundamental properties of this structure and its performance in green phosphorescent OLED devices.<sup>8</sup>

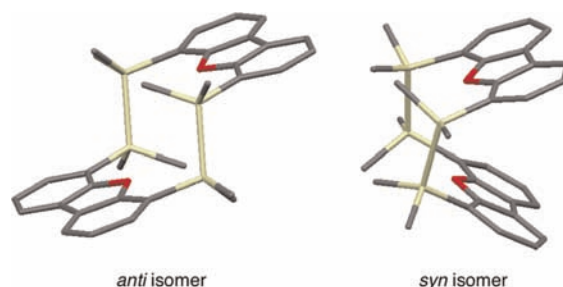
As we demonstrated with 1,8-diidoanthracene for the synthesis of <sup>Si</sup>DPBA, the double-pillaring method can be applied straightforwardly with lithiated arenes.<sup>4</sup> In the case of dibenzofuran, we can also eliminate the halogenation step by subjecting dibenzofuran to direct regioselective lithiation.<sup>9</sup> Thus, dibenzofuran was lithiated selectively at the 4- and 6-positions by butyllithium, and <sup>Si</sup>DPBD(O) was obtained in 21% yield after silylation with dichlorotetramethyldisilane (TMDSCL<sub>2</sub>) (Scheme 1). Although we could not improve the yield by screening other reaction conditions, the desired silacyclophane was obtained in an analytically pure form without the need for chromatographic separation by simply washing and recrystallizing (see the Supporting Information for the details). The yield was most likely reduced by the macrocyclization step, as evidenced by the fact that we obtained oligomeric compounds as byproducts.

**Scheme 1.** Synthesis of <sup>Si</sup>DPBD(O)



Unlike the anthracene congeners,<sup>4a</sup> <sup>Si</sup>DPBD(O) was present in solution as a mixture of *anti* and *syn* conformational isomers (see Figure 1 for the structures). The *anti* isomer was observed as the predominant species regardless of the solvent (*anti/syn* = 77:23 in CDCl<sub>3</sub> and 78:22 in *o*-dichlorobenzene-*d*<sub>4</sub> at 25 °C). In the <sup>1</sup>H NMR spectra, the methyl signals from the silyl groups of the *anti* and *syn* isomers coalesced at 100 °C in *o*-dichlorobenzene-*d*<sub>4</sub>,

which suggested that the two isomers are in equilibrium.<sup>10</sup> The rotation of dimethylsilyl groups was possible, probably due to a larger space that was created by the nonlinear structures of dibenzofuran.<sup>4a</sup> We could not find any appropriate conditions for the separation of the isomers, and the subsequent studies were conducted with the equilibrium mixture.<sup>11</sup>



**Figure 1.** Two isomeric structures of <sup>Si</sup>DPBD(O). The ground-state structures were obtained by geometry optimization at the B3LYP/6-31G(d,p) level of the theory.

In the form of a single crystal, we obtained the pure *anti* isomer from the equilibrium mixture and investigated the structure by X-ray crystallographic analysis (Figure 2). The antiperiplanar alignment of the  $C_{ipso}$ -Si-Si- $C_{ipso}$  moiety was embedded in a step-like structure with the two adjacent dibenzofuran units, and the torsion angles between the Si-Si bonds and the dibenzofuran planes were 86°/99° and 67°/103° for the two molecules. Similar to the anthracene congeners,<sup>4</sup> ubiquitous intermolecular contacts were found in the packing, but the frequency of  $\pi$ -stacking motifs was pronounced (Figure 1c).<sup>12</sup> Thus, the columnar assembly of molecules was supported by  $\pi$ -stacking contacts of 3.49 and 3.54 Å, and the intercolumnar packing was supported by CH- $\pi$  contacts of 2.87 Å.

Several properties of <sup>Si</sup>DPBD(O) were found that would be desirable for optoelectronic applications. First, the compound was thermally stable, with a glass transition temperature ( $T_g$ ) of 171 °C and a decomposition temperature ( $T_d$ , with a weight loss of less than 5%) of 309 °C. Notably, the  $T_g$  value was much higher than that of both dibenzofuran (43 °C)<sup>13</sup> and a standard OLED host material (62 °C for 4,4'-bis(9-dicarbazoly)-2,2'-biphenyl (CBP)).<sup>14</sup> Second, the compound was transparent in the visible light region, with an absorption edge ( $\lambda_{abs}$ )

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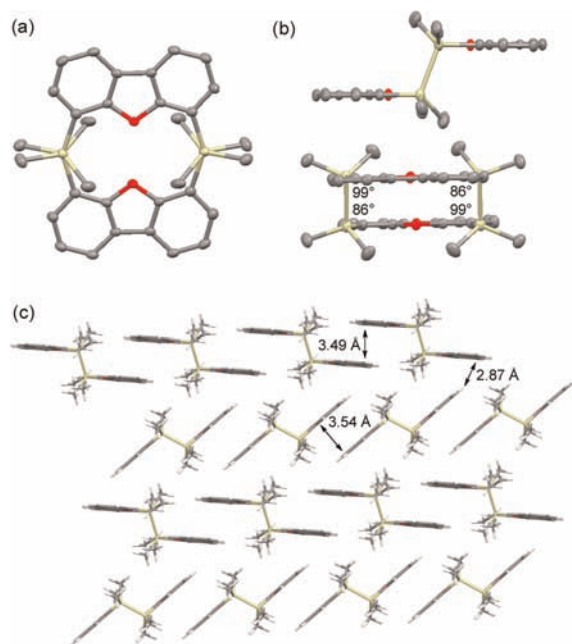
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**Figure 2.** Structures of  $\text{SiDPBD(O)}$  determined by X-ray crystallographic analysis. (a) ORTEP diagram viewed perpendicular to the dibenzofuran plane. (b) ORTEP diagram viewed along the dibenzofuran plane. (c) Packing structure of  $\text{SiDPBD(O)}$ . C gray, Si yellow, O red, H white. In a and b, a representative molecule among two geometries is shown with the thermal ellipsoids drawn at 50% with hydrogen atoms omitted for clarity.

at 316 nm in cyclohexane (Figure S7). As expected, the extension of the conjugation through  $\sigma_{\text{SiSi}}-\pi$  overlaps was moderate<sup>4,15</sup> when compared with dibenzofuran ( $\lambda_{\text{abs}} = 303$  nm). Third, the structural change at the excited state is small, as indicated by a small Stokes shift of 6 nm ( $\lambda_{\text{em}} = 322$  nm; Figure S8). Finally, the compound has a high triplet energy with an  $E_{\text{T}}$  value of 2.95 eV, as revealed by the phosphorescent signal at 420 nm in 2-methyltetrahydrofuran ( $-196$  °C (77 K), delay time 2 ms; Figure S9). The  $E_{\text{T}}$  value was comparable to the parent dibenzofuran ( $E_{\text{T}} = 3.2$  eV)<sup>7</sup> and larger than that of CBP ( $E_{\text{T}} = 2.56$  eV),<sup>16</sup> which confirmed the viability of the double-pillaring method for the design of a material with a high triplet energy.

Finally, we evaluated the performance of  $\text{SiDPBD(O)}$  as a host material for the EML of green phosphorescent OLED devices using  $\text{Ir(ppy)}_3$  as the emitter ( $E_{\text{T}} = 2.4$  eV). The device was fabricated as follows: ITO (indium tin oxide; 100 nm)/PEDOT:PSS (poly(ethylenedioxy)thiophene:polystyrene sulfonate; 20 nm)/ $\alpha$ -NPD ( $N,N'$ -diphenyl- $N,N'$ -bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine; 20 nm)/EML with 6%  $\text{Ir(ppy)}_3$  (40 nm)/BCP (bathocuproine; 10 nm)/ $\text{Alq}_3$  (tris(8-hydroxyquinoline)aluminum; 30 nm)/LiF (0.5 nm)/Al (110 nm) (see the Supporting Information for

the details).<sup>4,17</sup> The performance of  $\text{SiDPBD(O)}$  as a host material was compared with CBP as a reference, and the representative characteristics for the external quantum efficiency (EQE) and the driving voltage were evaluated. Green phosphorescence from the Ir emitter was detected from device A, in which  $\text{SiDPBD(O)}$  was loaded as the host material (Table 1), and an EQE of 4.6% was recorded at the driving voltage of 6.1 V. This observation confirmed that the triplet energy of  $\text{SiDPBD(O)}$  was high enough to avoid quenching the emission of  $\text{Ir(ppy)}_3$ , unlike the anthracene congener.<sup>4</sup> However, the performance of device B, in which CBP was used as the reference host, was better and yielded a higher EQE of 10.7% at 6.6 V.

**Table 1.** Performance of OLEDs Operated at a Constant Current Density of 2.5  $\text{mA}/\text{cm}^2$

device	HTL	EML host	ETL	V	EQE (%)
A	$\alpha$ -NPD	$\text{SiDPBD(O)}$	$\text{Alq}_3$	6.1	4.6
B	$\alpha$ -NPD	CBP	$\text{Alq}_3$	6.6	10.7
C	$\alpha$ -NPD	CBP	$\text{SiDPBD(O)}$	14.1	7.2
D	$\text{SiDPBD(O)}$	CBP	$\text{Alq}_3$	9.3	0.2

The poorer performance of  $\text{SiDPBD(O)}$  could be ascribed to the unipolarity of the carrier transport. Although device C, in which  $\text{SiDPBD(O)}$  was used as an electron transport material, emitted green phosphorescence, device D, in which  $\text{SiDPBD(O)}$  was used as a hole transport material, afforded negligible emission. We further determined the charge-carrier mobilities from the current density–voltage ( $J$ – $V$ ) characteristics in the space-charge limited current (SCLC) region of an electron-only thin film device (0.66 MV/cm).<sup>18</sup> The electron mobility of  $\text{SiDPBD(O)}$  was comparable to that of  $\text{Alq}_3$  ( $2.15 \times 10^{-5}$  vs  $7.25 \times 10^{-5}$   $\text{cm}^2/(\text{V}\cdot\text{s})$ ), whereas the hole mobility was 5 orders of magnitude lower than that of  $\alpha$ -NPD ( $1.10 \times 10^{-8}$  vs  $1.52 \times 10^{-2}$   $\text{cm}^2/(\text{V}\cdot\text{s})$ ). The anthracene congener,  $\text{SiDPBA}$ , showed similar superiority for electron transport (SCLC mobility:  $1.1 \times 10^{-6}$   $\text{cm}^2/(\text{V}\cdot\text{s})$  for electrons,  $7.8 \times 10^{-8}$   $\text{cm}^2/(\text{V}\cdot\text{s})$  for holes at 0.3 MV/cm).<sup>4</sup> Although we do not understand the mechanism and electronics of this preference, the disilanyl linkers seem to accelerate the electron transport.

In summary, we synthesized a molecule with a high thermal stability and a high triplet energy through a concise synthetic operation from dibenzofuran. As demonstrated by the high  $E_{\text{T}}$  value of  $\text{SiDPBD(O)}$ , the structural rigidity acquired by the two disilanyl pillars helps the step-like molecule inherit favorable properties

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from the parent aromatic molecules for electronic applications. Further refinement of the device performance may thus be possible by fine-tuning the parent structure. Together with the previous example based on anthracene,<sup>4</sup> this study may call for further applications of the double-pillaring strategy for the design of organic materials.<sup>19</sup>

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**Supporting Information Available.** Synthetic procedures, characterizations including copies of the NMR spectra, physical properties including isomerization analysis and photophysical spectra, theoretical data and device evaluations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The authors declare no competing financial interest.