## Accepted Manuscript

Dibenzothiophene, Dibenzofuran and Pyridine Substituted Tetraphenyl Silicon Derivatives Hosts for Green Phosphorescent Organic Light-Emitting Diodes

Lei Ding, Jiang-Nan Wang, Xiang-Yang Liu, Hua Chen, Femi Igbari, Liang-Sheng Liao

PII:	S1566-1199(19)30261-7
PII:	51566-1199(19)30261-7

DOI: 10.1016/j.orgel.2019.05.033

Reference: ORGELE 5268

To appear in: Organic Electronics

Received Date: 10 February 2019

Accepted Date: 18 May 2019

Please cite this article as: Lei Ding, Jiang-Nan Wang, Xiang-Yang Liu, Hua Chen, Femi Igbari, Liang-Sheng Liao, Dibenzothiophene, Dibenzofuran and Pyridine Substituted Tetraphenyl Silicon Derivatives Hosts for Green Phosphorescent Organic Light-Emitting Diodes, *Organic Electronics* (2019), doi: 10.1016/j.orgel.2019.05.033

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



# Dibenzothiophene, Dibenzofuran and Pyridine Substituted Tetraphenyl Silicon Derivatives Hosts for Green Phosphorescent Organic Light-Emitting Diodes

Lei Ding,<sup>1,2,3</sup>\* Jiang-Nan Wang, <sup>2,3</sup> Xiang-Yang Liu,<sup>1</sup> Hua Chen,<sup>1</sup> Femi Igbari,<sup>1</sup> Liang-Sheng Liao<sup>1,3</sup>

<sup>1</sup> Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM) & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215123, P.R. China.

<sup>2</sup> College of Electrical and Information Engineering, Shaanxi University of Science and Technology, Xi'an 710021, P.R. China.

<sup>3</sup> Jiangsu jitri org Optoelectronics Technology Co., Ltd, Suzhou, 215215, China.

\* Corresponding authors.

*E*-mail addresses: *dinglei@sust.edu.cn;* 

Tel: +86-029-86168320

#### Abstract

We report the application of four novel tetraphenyl silicon derivatives as host materials in phosphorescent organic light-emitting diodes (PHOLEDs). The novel derivatives are; 3-(4-((4-(dibenzo[b,d]thiophen-4-yl)phenyl)diphenylsilyl)-phenyl)pyridine (**DBTSiPy3**), 4-(4- ((4-(dibenzo[b,d]thiophen-4-yl)phenyl)diphenyl-

(DBTSiPy4), silyl)phenyl)pyridine 3-(4-((4-(dibenzo[b,d]furan-4-yl)phenyl)diphenylsilyl)phenyl)pyridine (DBFSiPy3) 4-(4-((4-(dibenzo[b,d]furan-4and vl)phenvl)diphenvlsilyl)phenvl)pyridine (DBFSiPv4). They were prepared by the introduction dibenzothiophene (DBT)/dibenzofuran (DBF) and pyridine units into bis(4-bromophenyl)diphenylsilane intermediate. The influences of DBT/DBF and the position of nitrogen atom within the pyridine unit (3- vs 4-position) were studied by theoretical calculations and experimental measurements. To evaluate the electroluminescent (EL) performance of these four materials, (2-phenylpyridine) iridium(III) (Ir(ppy)<sub>3</sub>) based green PHOLEDs were fabricated using the common device structures. DBF substituted materials (DBFSiPy3 and DBFSiPy4) led to efficient green PHOLEDs with notable external quantum efficiencies (EQE) of 22.9 % and 21.9 % respectively.

#### **Keywords:**

Organic light-emitting diodes; Host materials; Tetraphenyl silicon; Triplet energy.

Graphical



Dibenzothiophene, Dibenzofuran and Pyridine Substituted Tetraphenyl Silicon Derivatives Hosts for Green Phosphorescent Organic Light-Emitting Diodes

Lei Ding,<sup>a,b,c\*</sup> Jiang-Nan Wang,<sup>a</sup> Xiang-Yang Liu,<sup>a</sup> Hua Chen,<sup>a</sup> Femi Igbari,<sup>a</sup> Zuo-Quan Jiang<sup>a</sup>, Liang-Sheng Liao<sup>a,c</sup>

a) Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM) & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215123, P.R. China.

b) College of Electrical and Information Engineering, Shaanxi University of Science and Technology, Xi'an 710021, P.R. China.

c) Jiangsu jitri org Optoelectronics Technology Co., Ltd, Suzhou, 215215, China.

\* Corresponding authors

*E*-mail addresses: dinglei@sust.edu.cn (L. Ding)

Tel.: +86-029-86168320; fax: +86-029-86168709;

**Abstract**: We reported the application of four novel tetraphenyl silicon derivatives as host materials in phosphorescent organic light-emitting diodes (PHOLEDs). The novel derivatives are 3-(4-((4-(dibenzo[b,d]thiophen-4-yl)phenyl)diphenylsilyl)-phenyl)pyridine (**DBTSiPy3**), 4-(4- ((4-(dibenzo[b,d]thiophen-4-yl)phenyl)diphenyl-

silyl)phenyl)pyridine 3-(4-((4-(dibenzo[b,d]furan-4-yl)phenyl)-(DBTSiPy4), diphenylsilyl)phenyl)pyridine 4-(4-((4-(dibenzo[b,d]furan-4-(DBFSiPy3) and yl)phenyl)diphenylsilyl)phenyl)pyridine (**DBFSiPy4**). They were prepared by the introduction of dibenzothiophene (DBT)/dibenzofuran (DBF) and pyridine units into bis(4-bromophenyl)diphenylsilane intermediate. The influences of DBT/DBF and the position of nitrogen atom within the pyridine unit (3- vs 4-position) were studied by theoretical calculations and experimental measurements. To evaluate the electroluminescent (EL) performance of these four materials, (2-phenylpyridine) iridium(III) (Ir(ppy)<sub>3</sub>) based green PHOLEDs were fabricated using the common device structures. DBF substituted materials (DBFSiPy3 and DBFSiPy4) led to efficient green PHOLEDs with notable external quantum efficiencies (EQEs) of 22.9% and 21.9%, respectively.

**Keywords**: Dibenzothiophene, Dibenzofuran, Pyridine, Organosilicon derivatives, Host material, Green phosphorescent organic light-emitting diode

#### 1. Introduction

Following the pioneering report on organic light-emitting diodes (OLEDs) in 1987<sup>[1]</sup>, enormous efforts have been made in the development of stable devices which can generate light with high electrical to optical conversion efficiencies<sup>[2-11]</sup>. So far, the realization of high efficiency and long lifetime in OLEDs is still a challenge<sup>[12-14]</sup>. A traditional fluorescent OLED operates by the injection of holes and electrons into the organic materials where they bind to form excitons. According to the spin-statistics, the ratio of singlet and triplet excitons is approximately 1: 3. Consequently, roughly 75% energy is lost due to the nonradiative triplet excitons in fluorescent emitters<sup>[15-20]</sup>. To overcome this spin restriction, phosphorescent emitters

were introduced in 1998<sup>[15,16]</sup>. These materials owe their properties to the possession of heavy transition metals (e.g. Pt and Ir) which are capable of achieving strong intramolecular spin-orbit coupling. Thus, harvesting singlet and triplet excitons can yield phosphorescent organic light-emitting diodes (PHOLEDs) with almost 100% internal quantum efficiency (IQE) <sup>[12-14]</sup>.

Usually, phosphorescent emitters of doped into suitable host materials to prevent self-aggregation quenching and triplet-involved quenching effects. Such effects include triplet-triplet annihilation (TTA) and triplet exciton-polaron quenching (TPO)<sup>[18,21-23]</sup>. Therefore, the development of highly efficient host materials, requires basic qualities such as good thermal stability, good charge transporting ability, high triplet energy and suitable highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) level<sup>[12-14]</sup>. To realize these qualities, measures such as limited  $\pi$ -conjugation (to realized high triplet energy) and the introduction of electron donor and acceptor (to realize more balanced carrier transport) have been taken<sup>[24-26]</sup>. In this regard, tetraphenyl silvl is a good building block to break the intramolecular  $\pi$ -conjugation as several organosilicon compounds have been reported with ultrahigh triplet energies<sup>[27-31]</sup>. For instance, a series of tetraaryl silicon compounds possessing ultrahigh triplet energies (~3.5 eV) and serving as host materials were reported by Thompson et al<sup>[27]</sup>. Yang et al. also reported a series of organosilicon derivatives with high triplet energies (~2.93 eV)<sup>[30]</sup>. However, their ultrawide energy bandgaps generally aggravated the charge hopping between the adjacent phosphorescent emitters resulting in a relatively higher driving voltage<sup>[26, 32]</sup>.

Therefore, an optimization of carrier transport and recombination in the emitting layer is prerequisite to achieving high device performance. In general, electron transport ability is much lower than hole transport ability for most of the host materials. This could be attributed to the presence of strong electron donors such as aromatic amine derivatives (carbazole and triphenylamine) as the main constituents of such materials<sup>[33-37]</sup>. Hence, achieving highly efficient host materials with improved electron transport capability requires a coupling of electron acceptors such as benzimidazole<sup>[38-41]</sup>, triazine<sup>[42-44]</sup>, oxadiazole<sup>[45]</sup>, phosphine oxide<sup>[4,46,47]</sup> and pyridine<sup>[24-26]</sup> with the electron donor building blocks.

In this article, four novel host materials, **DBTSiPy3**, **DBTSiPy4**, **DBFSiPy3** and **DBFSiPy4** were synthesized with tetraphenyl silicon as  $\pi$ -conjugation interrupter between dibenzofuran (DBF)/dibenzothiophene (DBT) and pyridine (C3- and C4-position) blocks. The silicon bridge suppressed the intramolecular charge transfer from the electron donor to the electron acceptor, yielding molecules with high triplet energies. All of these host materials present high efficiencies in green PHOLEDs with (2-phenylpyridine) iridium(III) (Ir(ppy)<sub>3</sub>) as an emitter. Maximum external quantum efficiencies (EQE) of 22.9 % and 21.9 % and maximum device luminance of 18500 cd/m<sup>2</sup> and 21000 cd/m<sup>2</sup> were achieved for devices fabricated with **DBFSiPy3** and **DBFSiPy4**, respectively.

#### 2. Experimental Section

All chemicals and reagents were commercially sourced and used as received with no further purification. PURE SOLV (Innovative Technology) purification system

was used to purify THF <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained from a Bruker 400 spectrometer at room temperature. Using a direct exposure probe, mass spectra were recorded on a Thermo ISQ mass spectrometer. UV-vis absorption analyses were conducted by using a Perkin Elmer Lambda 750 spectrophotometer. PL and phosphorescent spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was carried out at a heating rate of 10 °C/min under nitrogen, using a TA DSC 2010 unit. Glass transition temperatures  $(T_g)$  were determined from the second heating scan. Thermogravimetric analysis (TGA) was performed at a heating rate of 10 °C/min under nitrogen, using a TA SDT 2960 instrument. The temperature at 5% weight loss served as the decomposition temperature  $(T_d)$ . Ultra-Violet Photoemission Spectroscopy (UPS) was conducted, using an unfiltered He I (21.22 eV) gas discharge lamp and a hemispherical analyzer made by KRATOS ANALYTICAL SHIMADZU GROUP COMPANY. DFT calculations were performed using B3LYP/6-31 G(d) basis set on Gaussian 09.

available Commercially (2-Phenylpyridine) iridium (III)  $(Ir(ppy)_3),$ 1,1-bis[4-[N,N-di(p-tolyl)amino]-phenyl]cyclohexane (TAPC), 1,3,5-tri[(3pyridyl)phen-3-yl]benzene (TmPyPB), dipyrazino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbo-nitrile (HAT-CN) and 8-hydroxyquinolinolatolithium (Liq) were used. Indium-tin oxide (ITO) coated transparent glass substrates were used for the OLEDs fabrication. The conductive ITO layer had a thickness, ca. 100 nm and a sheet resistance, ca. 30  $\Omega$  per square. The substrates were cleaned with

deionized water, acetone and ethanol in succession. They were dried in an oven for 1 hour and subsequently subjected to UV ozone treatment for 30 min. All organic and metal layers were deposited under a vacuum, ca. 10<sup>-6</sup> Torr. Four identical OLED devices, each having an emission area of 0.09 cm<sup>2</sup>, were formed on each substrates. The EL performances of the blue and white devices were evaluated at room-temperature, using a PHOTO RESEARCH SpectraScan PR 655 PHOTOMETER and a KEITHLEY 2400 SourceMeter constant current source.

The synthetic routes of 3-(4-((4-(dibenzo[b,d]thiophen-4-yl)phenyl)diphenylsilyl)phenyl)pyridine (**DBTSiPy3**), 4-(4-((4-(dibenzo[b,d]thiophen-4-yl)phenyl)diphenylsilyl)phenyl)pyridine (**DBTSiPy4**), 3-(4-((4-(dibenzo[b,d]furan-4-yl)phenyl)diphenyl) diphenyl)pyridine (**DBFSiPy3**) and 4-(4-((4-(dibenzo[b,d]furan-4-yl)phenyl)diphenylsilyl)phenyl)pyridine (**DBFSiPy4**) are outlined in **Scheme 1**. We used 1,4-dibromobenzene and dichlorodiphenylsilane as the starting materials to obtain the key intermediate of bis(4-bromophenyl)diphenylsilane in moderate yield. Consequently, good yields of the target products can be obtained via two-step Pd-catalyzed Suzuki–Miyaura coupling reaction of the intermediate with the corresponding boronic acid of dibenzothiophene (DBT), dibenzofuran (DBF) and pyridine (3- and 4-position).

3. Results and Discussion

3.1 Synthesis and Characterization

PURE SOLV (Innovative Technology) purification system was used to purify THF. Commercially available 1,4-dibromobenzene, dichlorodiphenylsilane,

dibenzothiophene-4-boronic acid, *n*-butyl lithium dibenzofuran-4-boronic acid, pyridine-3-boronic and pyridine-4-boronic and other reactants or reagents were used as received.

#### Preparation of bis(4-bromophenyl)diphenylsilane

1,4-Dibromobenzene (9.91 g, 42 mmol) was placed in a 500 mL Schlenk tube. It was then dissolved in with 150 mL THF under argon. The solution was cooled to -78 °C. *n*-butyl lithium (17.5 mL, 42 mmol, 2.4 M) was added, dropwise, to the solution via a syringe. After 1 hour of reaction at -78 °C, dichlorodiphenylsilane (5.06 g, 20 mmol) in 20 mL THF was added over a period of 30 min. The reaction mixture was allowed to stir for additional 1 hour at -78 °C. The mixture was gradually warmed up to room temperature overnight. Eventually, the reaction was quenched by adding water (5 mL). The resulting mixture was placed into 50 mL of water, and the desired product extracted with EtOAc (3×50 mL). The organic top layer was separated, and dried over sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>). It was then filtered and evaporated under reduced pressure to give a crude product. Using petroleum ether/dichloromethane (5/1, v/v), the crude product was further purified by column chromatography. The final product obtained had a white-powdery appearance (7.15 g, 72.3%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta =$ 7.53-7.50 (m, 8H, Ar-H), 7.47-7.44 (m, 2H, Ar-H), 7.40-7.37 (m, 8H, Ar-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 137.82, 136.23, 133.01, 132.66, 131.22, 130.01,$ 128.11, 124.97 ppm. HRMS (EI): m/z calcd for: 491.9495, found: 491.9849. Anal. Calcd for C<sub>24</sub>H<sub>18</sub>Br<sub>2</sub>Si (%): C 58.32, H 3.67; found: C 58.23, H 3.61.

Preparation of (4-bromophenyl)(4-(dibenzo[b,d]furan-4-yl)phenyl)diphenylsilane

Bis(4-bromophenyl)diphenylsilane (1.98 g, 4 mmol), dibenzo[b,d]furan-4-ylboronic acid (0.85 g, 4 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.23 g, 0.2 mmol) were dissolved with 50 mL THF in under argon. 2 M K<sub>2</sub>CO<sub>3</sub> (THF/H<sub>2</sub>O = 4/1, v/v) was then added. The resulting solution was heated at 70 °C overnight. After cooling to room temperature, the solution was placed into 200 mL of water and the desired product extracted with dichloromethane 3 times. The organic top layer was collected and evaporated. The obtained crude product was purified by column chromatography using petroleum ether/dichloromethane (3/1, v/v) to give the final product as a white powder (1.67 g, 71.6%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.98$  (d, J = 8.0 Hz, 1H, Ar-H), 7.96-7.94 (m, 3H, Ar-H), 7.71 (d, J = 8.0 Hz, 2H, Ar-H), 7.64-7.31 (m, 19H, Ar-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 156.14$ , 153.39, 137.99, 136.65, 136.46, 136.37, 133.57, 133.24, 133.04, 131.15, 129.86, 128.23, 128.04, 127.29, 126.83, 125.42, 125.02, 124.81, 124.13, 123.27, 122.83, 120.68, 119.98, 111.84 ppm. HRMS (EI): m/z calcd for: 580.0858; found: 580.0850. Anal. Calcd for C<sub>36</sub>H<sub>25</sub>BrOSi (%): C 74.35, H 4.33; found: C 74.45, H 4.34

Preparation of (4-bromophenyl)(4-(dibenzo[b,d]thiophen-4-yl)phenyl)diphenylsilane (4-Bromophenyl)(4-(dibenzo[b,d]thiophen-4-yl)phenyl)diphenylsilane was prepared in a similar manner with (4-bromophenyl)(4-(dibenzo[b,d]furan-4-yl)phenyl)diphenylsilane. The final product was obtained as a white powder (72.4%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.18-8.13 (m, 2H, Ar-H), 7.82-7.80 (m, 1H, Ar-H), 7.76 (d, *J*  = 8.0 Hz, 2H, Ar-H), 7.69 (d, J = 7.6 Hz, 2H, Ar-H), 7.61 (d, J = 8.0 Hz, 4H, Ar-H), 7.56-7.39 (m, 14H, Ar-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 141.87, 139.49, 138.43, 137.96, 136.75, 136.59, 136.35, 136.31, 135.70, 133.47, 133.40, 133.17, 131.14, 129.89, 128.06, 127.73, 126.94, 126.84, 125.13, 124.84, 124.40, 122.58, 121.72, 120.67 ppm. HRMS (EI): m/z calcd for: 596.0630; found: 596.0626. Anal. Calcd for C<sub>36</sub>H<sub>25</sub>BrSSi (%): C 72.35, H 4.22; found: C 72.23, H 4.31.

Preparation of 3-(4-((4-(dibenzo[b,d]furan-4-yl)phenyl)diphenylsilyl)phenyl)pyridine (**DBFSiPy3**)

(4-Bromophenyl)(4-(dibenzo[b,d]furan-4-yl)phenyl)diphenylsilane (2.33 g, 4 mmol), pyridin-3-ylboronic acid (0.54 g, 4.4 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.23 g, 0.2 mmol) were dissolved in THF under argon, 2 M K<sub>2</sub>CO<sub>3</sub> (THF/H<sub>2</sub>O = 4/1, v/v) was then added. The resulting solution was heated at 70 °C overnight and was allowed to cool to room temperature. The solution was thereafter placed into 200 mL of water and the desired product extracted by adding dichloromethane. This process was repeated 3 times. The organic layer was separated and evaporated. Using petroleum ether/dichloromethane (2/1, v/v), the obtained crude product was purified via column chromatography. The final product had a white powdery appearance (2.18 g, 94.0%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.90 (d, *J* = 2.0 Hz, 1H, Ar-H), 8.61 (dd, *J* = 4.8, 1.5 Hz, 1H, Ar-H), 8.05-8.78 (m, 5H, Ar-H), 7.76 (dt, *J* = 14.1, 7.1 Hz, 4H, Ar-H), 7.72-7.56 (m, 8H, Ar-H), 7.53-7.32 (m, 10H, Ar-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 156.17,

153.43, 148.73, 148.42, 138.93, 137.71, 137.23, 136.75, 136.48, 136.42, 134.43, 134.30, 133.91, 133.41, 129.84, 128.25, 128.06, 127.32, 126.88, 126.62, 125.51, 125.04, 124.17, 123.65, 123.31, 122.85, 120.72, 119.99, 111.87 ppm. HRMS (EI): m/z calcd for: 579.2018; found: 579.2010. Anal. Calcd for C<sub>41</sub>H<sub>29</sub>NOSi (%): C 84.94, H 5.04, N 2.02; found: C 84.78, H 4.98, N 2.12.

Preparation of 3-(4-((4-(dibenzo[b,d]thiophen-4-yl)phenyl)diphenylsilyl)phenyl)pyridine (**DBTSiPy3**), 4-(4-((4-(dibenzo[b,d]furan-4-yl)phenyl)diphenylsilyl)phenyl)pyridine (**DBFSiPy4**), 4-(4-((4-((dibenzo[b,d]thiophen-4-yl)phenyl)diphenylsilyl)phenyl)pyridine (**DBTSiPy4**)

**DBTSiPy3**, **DBFSiPy4** and **DBTSiPy4** were prepared in a similar manner with **DBFSiPy3**. The final products were obtained as white powders (yield 94.5%, 92.3%, and 91.5% for **DBTSiPy3**, **DBFSiPy4** and **DBTSiPy4**, respectively).

**DBTSiPy3**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.90$  (d, J = 2.1 Hz, 1H, Ar-H), 8.61 (dd, J = 4.8, 1.6 Hz, 1H, Ar-H), 8.26-8.11 (m, 2H, Ar-H), 7.92 (ddd, J = 9.4, 7.9, 5.2 Hz, 1H, Ar-H), 7.87-7.72 (m, 7H, Ar-H), 7.71-7.61 (m, 6H, Ar-H), 7.61-7.40 (m, 10H, Ar-H), 7.38 (ddd, J = 7.9, 4.8, 0.7 Hz, 1H, Ar-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 148.76$ , 148.44, 141.84, 139.54, 138.98, 138.48, 137.21, 136.86, 136.70, 136.47, 136.40, 136.35, 135.75, 134.42, 134.20, 133.82, 133.77, 129.88, 128.09, 127.75, 127.00, 126.89, 126.64, 125.19, 124.45, 123.64, 122.63, 121.77, 120.70 ppm. HRMS

(EI): m/z calcd for: 595.1790; found: 595.1779. Anal. Calcd for C<sub>41</sub>H<sub>29</sub>NSSi (%): C
82.65, H 4.91, N 2.35; found: C 86.11, H 4.93, N 2.50.

**DBFSiPy4**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.68$  (dd, J = 4.6, 1.6 Hz, 2H, Ar-H), 8.03-7.92 (m, 4H, Ar-H), 7.77 (d, J = 7.6 Hz, 4H, Ar-H), 7.72-7.62 (m, 7H, Ar-H), 7.62-7.52 (m, 3H, Ar-H), 7.52-7.40 (m, 8H, Ar-H), 7.36 (td, J = 7.6, 0.8 Hz, 1H, Ar-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 156.17$ , 153.42, 150.34, 148.15, 139.18, 137.76, 137.24, 136.74, 136.47, 135.66, 133.77, 133.26, 129.88, 128.26, 128.08, 127.33, 126.87, 126.44, 125.47, 125.05, 124.16, 123.31, 122.87, 121.68, 120.73, 120.01, 111.86 ppm. HRMS (EI): m/z calcd for: 579.2018; found: 579.2023. Anal. Calcd for C<sub>41</sub>H<sub>29</sub>NOSi (%): C 84.94, H 5.04, N 2.02; found: C 84.83, H 5.00, N 2.04.

**DBTSiPy4**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.68$  (dd, J = 4.5, 1.6 Hz, 2H, Ar-H), 8.25-8.09 (m, 2H, Ar-H), 7.88-7.72 (m, 7H, Ar-H), 7.71-7.63 (m, 6H, Ar-H), 7.61-7.39 (m, 12H, Ar-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 150.34$ , 148.06, 141.85, 139.49, 139.20, 138.43, 137.19, 136.82, 136.63, 136.42, 136.32, 135.71, 135.51, 133.66, 133.59, 129.88, 128.07, 127.73, 126.96, 126.86, 126.43, 125.16, 124.43, 122.59, 121.74, 121.63, 120.68 ppm. HRMS (EI): m/z calcd for: 595.1790; found: 595.1779. Anal. Calcd for C<sub>41</sub>H<sub>29</sub>NSSi (%): C 82.65, H 4.91, N 2.35; found: C 82.66, H 4.93, N 2.45.

#### 3.2 Thermal Analyses

The thermal properties of DBTSiPy3, DBTSiPy4, DBFSiPy3 and DBFSiPy4 were

studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). As shown in **Figure 1**, these materials exhibited good thermal stability. Glass transition temperatures ( $T_g$ ) of 88 °C and 93 °C were obtained for **DBTSiPy3** and **DBTSiPy4** respectively. However, **DBFSiPy3** and **DBFSiPy4** yielded slightly lower  $T_g$  of 86 °C and 88 °C respectively. The negligible difference observed in the  $T_g$  of these materials could be attributed to their similar molecular structures and weights. The thermal decomposition temperatures ( $T_d$ , corresponding to 5% weight loss) of **DBTSiPy3**, **DBTSiPy4**, **DBFSiPy3** and **DBFSiPy4** are 363, 417, 338 and 400 °C respectively. In addition, it is worth noting that 4-Py based materials **DBTSiPy4** and **DBFSiPy4** show relatively higher thermal stability compared to 3-Py based materials **DBTSiPy3** and **DBFSiPy3**.

#### **3.3 Photophysical Properties**

Figure 2 shows the UV-Vis absorption and photoluminescence (PL) spectra of DBTSiPy3, DBTSiPy4, DBFSiPy3 and DBFSiPy4 in dichloromethane at room phosphorescence temperature the (Phos) and spectra measured in 2-methyltetrahydrofuran (2-MeTHF) at 77 K. The detailed data are summarized in Table 1. The absorption spectra of DBT- and DBF-based materials show similar absorption bands. However, the absorption onset and the maximum absorption wavelengths (Abs  $\lambda_{max}$ ) of DBT-based materials are red-shifted by 16 nm relative to the DBF-based materials. The optical band gaps  $(E_g)$  of **DBTSiPy3** and **DBTSiPy4** (3.59 eV) are therefore smaller than **DBFSiPy3** and **DBFSiPy4** (3.77 eV). On the other hand, they possess different PL features. The well-defined PL spectra of

DBF-based materials and the structureless PL spectra of DBT-based materials indicate a difference in their excited states. The peaks at 464 and 460 nm represent the highest vibronic bands of phosphorescence spectra at 77 K for DBT- and DBF-based materials respectively. Therefore, the triplet energies ( $E_T$ ), 2.67 and 2.70 eV were extracted for DBT- and DBF-based materials respectively. Furthermore, the photoluminescence quantum yield (PLQY) of Ir(ppy)<sub>3</sub> (9 wt%) in the **DBTSiPy3**, **DBTSiPy4**, **DBFSiPy3** and **DBFSiPy4** thin films were measured in an integrating sphere to be 0.78, 0.76, 0.85 and 0.80, respectively, which are comparable to the reported results<sup>[48,49]</sup>. The relative high PLQY of DBF based materials would lead to a better device performance.

#### 3.4 DFT Simulation.

In order to have a better understanding of the electronic distributions of **DBTSiPy3**, **DBTSiPy4**, **DBFSiPy3** and **DBFSiPy4**, their frontier molecular orbital (FMO) spatial distributions were simulated by density function theory (DFT) calculations at a B3LYP/6-31G(d) level. As **Figure 3** illustrates, all of these materials have similar highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) distributions. The HOMOs are localized at the DBT and DBF units with Si-phenyl ring acting as a separation group while the LUMOs are distributed on the pyridine part and the phenyl separation group. Therefore, all of these four Si-aryl compounds have similar HOMO/LUMO energy levels, which are -5.72/-1.16 eV, -5.74/-1.32 eV, -5.89/-1.23 eV and -5.92/-1.31 eV for **DBTSiPy3**, **DBTSiPy4**, **DBFSiPy3** and **DBFSiPy4**, respectively. In addition, the lowest triplet energies (*E*<sub>T</sub>s)

of these four **DBTSiPy3**, **DBTSiPy4**, **DBFSiPy3** and **DBFSiPy4** were also evaluated to be 2.87 eV, 2.89 eV, 2.91 eV and 2.97 eV, respectively. The narrow  $E_{\rm T}$  range of **DBTSiPy3**, **DBTSiPy4**, **DBFSiPy3** and **DBFSiPy4** could be attributed to their similar molecular configuration.

#### 3.5 FMO Energy Levels

From the ultraviolet photoemission spectroscopy (UPS) data presented in Figure 4, the HOMO levels of **DBTSiPy3**, **DBTSiPy4**, **DBFSiPy3** and **DBFSiPy4** are estimated as -6.24, -6.38, -6.36 and -6.58 eV respectively. The LUMOs can be calculated as following equation:  $E_{LUMO} = E_g + E_{HOMO}$ . As a result, the LUMO levels are determined as -2.65, -2.79, -2.59 and -2.81 eV for **DBTSiPy3**, **DBTSiPy4**, **DBFSiPy3** and **DBFSiPy4**, respectively.

#### 3.6 Electroluminescent Performances

To investigate the electroluminescent (EL) properties of **DBTSiPy3**, **DBTSiPy4**, **DBFSiPy3** and **DBFSiPy4** host materials, (2-phenylpyridine) iridium (III) (Ir(ppy)<sub>3</sub>) based green phosphorescent OLEDs were fabricated using the following device structure: ITO/HAT-CN (10 nm)/TAPC (55 nm)/Host: 9% Ir(ppy)<sub>3</sub> (20 nm)/TmPyPB (35 nm)/Liq (2 nm)/Al (120 nm). **DBTSiPy3**, **DBTSiPy4**, **DBFSiPy3** and **DBFSiPy4** were doped with 9 % Ir(ppy)<sub>3</sub> to form the emitting layer (EML). To confine the triplet excitons in the EML, 1,1-bis[4-[N',N'-di(p- tolyl)amino]-phenyl]cyclohexane (TAPC) and 1,3,5-tri[(3-pyridyl)phen-3-yl]benzene (TmPyPB) were used as hole transporting layer (HTL)/electron blocking layer (EBL) and electron transporting layer (ETL) /hole blocking layer (HBL), respectively. Furthermore, to achieve efficient carrier

injection, dipyrazino[2,3-f:2',3'-h]-quinoxaline-2,3,6,7,10,11-hexacarbo-nitrile (HAT-CN) and 8-hydroxyquinolinolato- lithium (Liq) were used as hole injection layer (HIL) and electron injection layer (EIL) respectively. The energy diagram and molecular structures can be seen in **Figure 5**. The current density-voltage-luminance (*J*-V-L) characteristics; current efficiency (CE), power efficiency (PE) and EQE as a function as luminance; and the EL spectra are presented in **Figure 6 (a)**, **6 (b)** and **6 (c)**, respectively. The detailed EL performance data are summarized in **Table 2**.

As shown in Figure 6(a), by using 4-Py based materials (DBTSiPy4 and DBFSiPy4) as host, the OLEDs show relatively lowered driving voltage of 3.8 and 4.1 V for  $Ir(ppy)_3$  based devices at 1000 cd/m<sup>2</sup> compared to the devices hosted by 3-Py based materials (DBTSiPv3 and DBFSiPv3). In addition, all of these devices exhibit a maximum luminance of 17500 cd/m<sup>2</sup>. The devices hosted by DBFSiPy4 achieve a maximum luminance above  $21000 \text{ cd/m}^2$ . Figure 6(b) illustrates the efficiencies of the Ir(ppy)<sub>3</sub>-based green devices. High efficiencies of these green devices are achieved. Maximum current efficiencies (CE) of 77.5 cd/A and 74.5 cd/A, power efficiencies (PE) of 65.0 lm/W and 67.4 lm/W and external quantum efficiencies (EQE) of 22.9 % and 21.9 % are respectively reached for DBFSiPy3 and DBFSiPv4 based devices. The devices hosted by DBTSiPv3 and DBTSiPv4 showed relative lower; CE of 58.0 cd/A and 57.5 cd/A, PE of 49.9 lm/W and 56.7 lm/W and EQE of 16.2% and 16.0%, respectively. Moreover, these devices also show relatively flat EQE roll-off, especially for **DBFSiPy4** based device. At 1000 cd/m<sup>2</sup>, the EQE reduce from the maximum value of 21.9% to 21.1 %. At a high brightness of 5000

cd/m<sup>2</sup>, the EQE is still as high as 19.6 %. At 10000 cd/m<sup>2</sup>, the EQE remains above the maximum EQE, with 17.8 % for **DBTSiPy3** and **DBTSiPy4** based devices. The green devices show CIE coordinates of (0.28, 0.64) at 5 mA/cm<sup>2</sup> as expected for a typical Ir(ppy)<sub>3</sub> based device. There are many factors of host materials responsible for OLED performance, such as high  $E_{\rm T}$ , suitable HOMO/LUMO energy level, good and balanced charge transport ability, as well as good thermal property. In this article, taking the very close  $E_{\rm T}$ s, HOMO/LUMO energy levels and thermal properties of four materials into consideration, we ascribe the relative better performance of **DBFSiPy3** and **DBFSiPy4** hosted device to their good and balanced charge transport properties (Figure 7). Moreover, the relative high PLQY of the dopant in host films of **DBFSiPy3** and **DBFSiPy4** also partly account for their better device performance.

#### 4. Conclusion

In conclusion, the design, synthesis and full characterization of four novel organosilicon derivatives, **DBTSiPy3**, **DBTSiPy4**, **DBFSiPy3** and **DBFSiPy4** consisting of DBT, DBF and pyridine units were achieved. Due to suitable linking strategy, these materials exhibit high triplet energy and good thermal stability They were used as host materials in the fabrication of green PHOLEDs with Ir(ppy)<sub>3</sub> as emitter. Green PHOLEDs based on DBF substituted material **DBFSiPy3** and **DBFSiPy4** achieve maximum EQE of 22.9% and 21.9% respectively. This notable device performance demonstrates the great potential of tetraphenyl silicon derivatives in constructing bipolar host materials for PHOLEDs.

Acknowledgement

We appreciate the financial support from the National Natural Science Foundation of China under Grant No 61076066, 21572152, 61575136 and the Innovation Project of Science and Technology Plan Projects of Shaanxi Province under Grant No 2011KTCQ01-09. Key research and development plan of Shaanxi Province (2017ZDCXL-GY-06-03), Special scientific research plan of Shaanxi Provincial Education Department (17JK0095), Jiangsu Youth Foundation Project (BK20180288), Sixty-second grants from China Post Doctoral Science Fund(7131700918).

#### Reference

[1] C.-W. Tang, S.-AV anSlyke, Organic electroluminescent diodes, Appl. Phys. Lett, 51(1987), 913-915.

[2] J Kido, M Kimura, Multilayer white light-emitting organic electroluminescent device, Science, 267(1995), 1332-1334.

[3] L.-S Cui, Y.-M Xie, Y.-K Wang, C Zhong, Y.-Li Deng, X.-Y Liu, Z.-Q Jiang, L.-S Liao, Pure Hydrocarbon Hosts for ≈100% Exciton Harvesting in Both Phosphorescent and Fluorescent Light-Emitting Devices, Adv Mater, 27(2015), 4213-4217.

[4] L Ding, S.-C Dong, Z.-Q Jiang, H. Chen, L.-S Liao, Orthogonal molecular structure for better host material in blue phosphorescence and larger OLED white lighting panel, Adv. Funct. Mater, 25(2015), 645-650.

[5] X.-Y Liu, F Liang, L Ding, S.-C Dong, Q. Li, L.-S Cui, Z.-Q Jiang, H Chen, L.-S Liao, The study on two kinds of spiro systems for improving the performance of host materials in blue phosphorescent organic light-emitting diodes, J. Mater. Chem. C, 3(2015), 9053-9056.

[6] M Romain, D Tondelier, B Geffroy, A Shirinskaya, O Jeannin, R.-B. Joëlle, C Poriel. Spiro-configured phenyl acridine thioxanthene dioxide as a host for efficient PhOLEDs. Chem. Commun, 51(2015), 1313-1315.

[7] M Kim, J.-Y Lee, Engineering the Substitution Position of Diphenylphosphine Oxide at Carbazole for Thermal Stability and High External Quantum Efficiency Above 30% in Blue Phosphorescent Organic Light-Emitting Diodes, Adv. Funct. Mater, 24(2014), 4164-4169.

[8] C.-W Lee, J.-Y Lee, Structure–Property Relationship of Pyridoindole-Type Host Materials for High-Efficiency Blue Phosphorescent Organic Light-Emitting Diodes, Chemistry of Materials, 26(2014), 1616-1621.

[9] X.-Y Liu, F Liang, L.-S Cui, X.-D. Yuan, Z.-Q Jiang, L.-S Liao, Effective Host Materials for Blue/White Organic Light-Emitting Diodes by Utilizing the Twisted Conjugation Structure in 10-Phenyl-9,10-Dihydroacridine Block, Chemistry an Asian Jounal, 10(2015), 1402-1409.

[10] X.-Y Liu, F Liang, L Ding, Q Li, Z.-Q Jiang, L.-S Liao, A new synthesis strategy for acridine derivatives to constructing novel host for phosphorescent organic light-emitting diodes, Dyes and Pigments, 126(2016), 131-137.

[11] X.-Y Liu, F Liang, Y Yuan, L.-S Cui, Z.-Q Jiang, L.-S Liao, An effective host material with thermally activated delayed fluorescence formed by confined conjugation for red phosphorescent organic light-emitting diodes, Chem. Commun, 52(2016), 8149-8170.

[12] L.-X Xiao, Z.-J Chen, B Qu, J.-X Luo, S. Kong, Q.-H Gong, J.-J Kido, Recent Progresses on

Materials for Electrophosphorescent Organic Light-Emitting Devices, Adv Mater, 23(2011), 926-952.

[13] Y.-T Tao, C.-L Yang, J.-G Qin, Organic host materials for phosphorescent organic light-emitting diodes. Chemical Society Reviews, 40(2011), 2943-2970.

[14] K.-S Yook, J.-Y Lee, Organic Materials for Deep Blue Phosphorescent Organic Light-Emitting Diodes. Adv Mater, 24(2012), 3169-3910.

[15] Y.-G. Ma, H.-Y, Zhang, J.-C. Shen, C.-M. Che, Electroluminescence from triplet metal—ligand charge-transfer excited state of transition metal complexes, Synth Met, 94(1998), 245-248.

[16] M.-A Baldo, D.-F O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S.-R. Forrest, Highly efficient phosphorescent emission from organic electroluminescent devices, Nature, 395(1998), 151-154.

[17] M-A Baldo, D-F O'Brien, M.-E Thompson, S.-R. Forrest, Excitonic singlet-triplet ratio in a semiconducting organic thin film. Physical Review B covering condensed matter and materials physics, 60(1999), 14422.

[18] M-A Baldo, S Lamansky, P-E Burrows, M-E Thompson, S.-R. Forrest, Very high-efficiency green organic light-emitting devices based on electrophosphorescence, Appl Phys Lett, 75(1999), 4-6.

[19] Adachi C, Baldo M-A, Forrest S-R, M-E Thompson, High-efficiency organic electrophosphorescent devices with tris(2-phenylpyridine)iridium doped into electron-transporting materials, Appl Phys Lett, 77(2000),904-906.

[20] Y Sun, N.-C Giebink, H Kanno, B Ma, M.-E. Thompson, S.-R. Forrest, Management of singlet and triplet excitons for efficient white organic light-emitting devices, Nature, 440(2006), 908-912.

[21] W.-Y Wong, C.-L Ho, Heavy metal organometallic electrophosphors derived from multi-component chromophores, Coordination Chemistry Reviews, 253(2009), 1709-1758.

[22] W.-Y Wong, C.-L Ho, Functional metallophosphors for effective charge carrier injection/transport: new robust OLED materials with emerging applications, J. Mater. Chem, 19(2009), 4457-4482.

[23] C.-L Ho, W.-Y Wong, Charge and energy transfers in functional metallophosphors and metallopolyynes, Coordination Chemistry Reviews, 257(2013): 1614-1649.

[24] S.-J Su, H Sasabe, T Takeda, J Kido, Pyridine-Containing Bipolar Host Materials for Highly Efficient Blue Phosphorescent OLEDs, Chemistry of Materials, 8(2009), 1691-1693.

[25] S.-J Su, C Cai, J Kido, RGB Phosphorescent Organic Light-Emitting Diodes by Using Host Materials with Heterocyclic Cores: Effect of Nitrogen Atom Orientations. Chemistry of Materials, 23(2011), 274-284.

[26] S-J Su, C Cai, J Kido, Three-carbazole-armed host materials with various cores for RGB phosphorescent organic light-emitting diodes, J. Mater. Chem, 28(2012), 24959 -25506.

[27] X Ren, J Li, R.-J Holmes, P.-I Djurovich, S.-R. Forrest, M.-E Thompson, Ultrahigh Energy Gap
Hosts in Deep Blue Organic Electrophosphorescent Devices, Chemistry of Materials, 16(2004),
4743-4747.

[28] H Chen, Z.-Q Jiang, C.-H Gao, M.-F Xu, S.-C Dong, L.-S Cui, S.-J Ji, L.-S Liao, Silicon-Based Material with Spiro-Annulated Fluorene/Triphenylamine as Host and Exciton-Blocking Layer for Blue Electrophosphorescent Devices, Chemistry A European Journal, 19(2013), 11791-11797.

[29] J-J Lin, W.-S Liao, H.-J Huang, A Highly Efficient Host/Dopant Combination for Blue Organic Electrophosphorescence Devices, Adv. Funct. Mater, 18(2008), 485-491.

[30] M.-S Lin, L.-C Chi, H.-W Chang, Y.-H Huang, K-C Tien, C.-C Chen, C.-H Chang, C.-C Wu, A Chaskar, S.-H Chou, H.-C Ting, K.-T Wong, Y.-H Liu, Y Chi, A diarylborane-substituted carbazole as a universal bipolar host material for highly efficient

electrophosphorescence devices, J. Mater. Chem, 22(2012), 870-876.

[31] S Gong, N Sun, J Luo, C Zhong, D.-D Ma, J Q, C.-L Yang, Highly Efficient Simple-Structure Blue and All-Phosphor Warm-White Phosphorescent Organic Light-Emitting Diodes Enabled by Wide-Bandgap Tetraarylsilane-Based Functional Materials, Adv. Funct. Mater, 24(2014), 5710-5718.
[32] R.-J Holmes, B.-W D'Andrade, S.-R Forrest, X. Ren, J. Li, and M. E. Thompson, Efficient, deep-blue organic electrophosphorescence by guest charge trapping, Appl Phys Lett, 83(2003), 3818-3820.

[33] P.-I Shih, C.-L Chiang, A.-K Dixit, C.-K Chen, M.-C Yuan, R.-Y Lee, C.-T Chen, EW-G Diau,C.-F Shu, Novel Carbazole/Fluorene Hybrids: Host Materials for Blue Phosphorescent OLEDs, Org.Lett, 8(2006), 2799-2802.

[34] M-H Tsai, Y-H Hong, C.-H Chang, H.-C Su, C.-C Wu, A. Matoliukstyte, J. Simokaitiene, S. Grigalevicius, C.-P. Hsu, 3-(9-Carbazolyl)carbazoles and 3,6-Di(9-carbazolyl)carbazoles as Effective Host Materials for Efficient Blue Organic Electrophosphorescence, Adv Mater, 19(2007), 862-866.
[35] H Fukagawa, K Watanabe, T Tsuzuki, Highly efficient, deep-blue phosphorescent organic light emitting diodes with a double-emitting layer structure, Appl Phys Lett, 93(2008), 133312-133314.
[36] K Brunner, A Brunner, H B€orner, Jolanda. Bastiaansen, Nicole M. M. Kiggen, and M. W. Langeveld, Carbazole Compounds as Host Materials for Triplet Emitters in Organic Light-Emitting Diodes: Tuning the HOMO Level without Influencing the Triplet Energy in Small Molecules, J. Am. Chem. Soc, 126(2004), 6035-6042.

[37] Z Jiang, Y Chen, C Yang, Y Cao, Y.-T Tao, J.-Q Qin, D.-G Ma, A Fully Diarylmethylene-Bridged Triphenylamine Derivative as Novel Host for Highly Efficient Green Phosphorescent OLEDs, Org. Lett, 11(2009), 1503-1506.

[38] C.-H Chen, W.-S Huang, M.-Y Lai, W.-C Tsao, J.-T Lin, Y.-H Wu, T.-H Ke, L.-Y Chen, C.-C
Wu, Benzimidazole/Amine-Based Ambipolar Compounds for Electroluminescent Applications:
Single-Layer, Blue, Fluorescent OLEDs, Hosts for Single - Layer, Phosphorescent OLEDs, Adv.
Funct. Mater, 19(2009), 2661-2670.

[39] S-Y Takizawa, V-A Montes, P Anzenbacher, Phenylbenzimidazole-Based New Bipolar Host Materials for Efficient Phosphorescent Organic Light-Emitting Diodes. Chemistry of Materials, 21(2009), 2452-2458.

[40] Z Ge, Hayakawa T, S Ando, M Ueda, T Akiike, H Miyamoto, T Kajita, M Kakimoto, Solution-Processible Bipolar Triphenylamine-Benzimidazole Derivatives for Highly Efficient Single-Layer Organic Light-Emitting Diodes, Chemistry of Materials, 20(2008), 2532-2537.

[41] Z Ge, T Hayakawa, S Ando, M Ueda, T Akiike, Hi Miyamoto, T Kajita, M Kakimoto, Spin-Coated Highly Efficient Phosphorescent Organic Light-Emitting Diodes Based on Bipolar Triphenylamine-Benzimidazole Derivatives, Adv. Funct. Mater, 18(2008), 584-590.

[42] H-F Chen, S-J Yang, Z-H Tsai, W.-Yi Hung, T.-C Wang and K-T Wong, 1,3,5-Triazine derivatives as new electron transport-type host materials for highly efficient green phosphorescent OLEDs, J. Mater. Chem, 19(2009), 8112-8118.

[43] H Inomata, K Goushi, T Masuko, T Konno, T Imai, H Sasabe, J.-J. Brown, C Adachi, High-Efficiency Organic Electrophosphorescent Diodes Using 1,3,5-Triazine Electron Transport Materials, Chemistry of Materials, 16(2004), 1285-1291.

[44] Rothmann M-M, Haneder S, Da Como E, T Konno, T Imai, H Sasabe, J.-J. Brown, and C Adachi, Donor-Substituted 1,3,5-Triazines as Host Materials for Blue Phosphorescent Organic Light-Emitting Diodes, Chemistry of Materials, 22(2010), 2403-2410.

[45] M-K Leung, C-C Yang, J-H Lee, H.-H. Tsai, C.-F. Lin, C.-Y. Huang, Y.-O Su, C.-F Chiu, The Unusual Electrochemical and Photophysical Behavior of 2,2'-Bis(1,3,4-oxadiazol-2-yl)biphenyls, Effective Electron Transport Hosts for Phosphorescent Organic Light Emitting Diodes, Org. Lett, 9(2007), 235-238.

[46] A.-B Padmaperuma, L.-S Sapochak, P.-E Burrows, New Charge Transporting Host Material forShort Wavelength Organic Electrophosphorescence: 2,7-Bis(diphenylphosphineoxide)-9,9-dimethylfluorene, Chemistry of Materials, 18(2006), 2389-2396.

[47] P.-A Vecchi, A.-B Padmaperuma, H Qiao, L.-S Sapochak, P.-E. Burrows, A Dibenzofuran-Based Host Material for Blue Electrophosphorescence, Org. Lett, 8(2006), 4211-4214.
[48] Y. Kawamura, K. Goushi, J. Brooks, J. J. Brown, H. Sasabe, C. Adachi, 100% phosphorescence quantum efficiency of Ir(III) complexes in organic semiconductor films Appl. Phys. Lett, 86(2005), 071104.

[49] S.-J. Su, T. Chiba, T. Takeda, J. Kido, Pyridine-Containing Triphenylbenzene Derivatives with High Electron Mobility for Highly Efficient Phosphorescent OLEDs Adv. Mater, 20(2008), 2125-2130.



Scheme 1. Synthetic routes to DBTSiPy3, DBTSiPy4, DBFSiPy3 and DBFSiPy4.



Figure 1. Differential scanning calorimetry (DSC, left) and thermogravimetric analysis (TGA, right) curves of DBTSiPy3, DBTSiPy4, DBFSiPy3 and DBFSiPy4.



Figure 2. UV-Vis absorption, PL and Phos spectra of DBTSiPy3, DBTSiPy4, DBFSiPy3 and DBFSiPy4.



Figure 3. HOMO/LUMO distributions and molecular structure of DBTSiPy3, DBTSiPy4, DBFSiPy3 and DBFSiPy4.



Figure 4. UPS spectra of DBTSiPy3, DBTSiPy4, DBFSiPy3 and DBFSiPy4.

Host	Abs $\lambda_{max}{}^a$	$PL \; \lambda_{max}{}^a$	$T_{\rm g}{}^{\rm b}$	$T_{\rm d}^{\rm c}$	$E_{g}{}^{d}$	$E_{\mathrm{T}}^{\mathrm{e}}$	HOMO <sup>f</sup> /eV	LUMO <sup>g</sup> /eV
	/nm	/nm	∕°C	∕°C	/eV	/eV		
DBTSiPy3	278	356	88	363	3.59	2.67	-6.24	-2.65
DBTSiPy4	266	356	93	417	3.59	2.67	-6.38	-2.79
DBFSiPy3	254	333, 346	86	338	3.77	2.67	-6.36	-2.59
DBFSiPy4	254	333, 346	88	400	3.77	2.70	-6.58	-2.81
<sup>a</sup> Measured in toluene solution at room temperature. ${}^{b}T_{g}$ : Glass transition temperature. ${}^{c}T_{d}$ :								
Decomposition temperature. ${}^{d}E_{g}$ : Band gaps calculated from the corresponding absorption								
onset. <sup>e</sup> E <sub>T</sub> : Measured in 2-MeTHF glass matrix at 77 K. <sup>f</sup> HOMO levels calculated from UPS								

Table 1. Physical Properties of DBTSiPy3, DBTSiPy4, DBFSiPy3 and DBFSiPy4.

data. <sup>g</sup> LUMO levels calculated from the HOMO and  $E_{\rm g}$ .



Figure 5. Molecular structures and representative energy level diagram of the materials.



**Figure 6**. (a) Current density-voltage-luminance (*J*-V-L) characteristics; (b) current efficiency (CE), power efficiency (PE) and external quantum efficiency (EQE) versus luminance curves for Ir(ppy)<sub>3</sub>-based devices and (c) EL spectra at 5 mA/cm<sup>2</sup>.



**Figure 7.** Hole- and electron only device based on DBFSiPy3 and DBFSiPy4. Device con figuration: Hole only device: ITO/MoO<sub>3</sub>(10 nm)/Host (30 nm)/MoO<sub>3</sub>(10 nm)/Al(100 nm) Electron only device: ITO/Liq(2 nm)/Host(30 nm)/TmPyPB(35 nm)/Liq(2 nm)/Al(100 nm), Host=DBFSiPy3 and DBFSiPy4.

	Uest		$\Box \eta_{ ext{CE}}^{c}$	$\Box  \eta_{ m PE}{}^{\sf c}$	EQE°	CIE <sup>d</sup>
Device	1105t	[V]	[cd A <sup>-1</sup> ]	[lm W <sup>-1</sup> ]	[%]	[x, y]
G1	DBTSiPy3	4.2	58.0, 55.2, 47.7	49.9, 39.9, 26.1	16.2, 15.3, 13.3	0.28, 0.64
G2	DBTSiPy4	3.8	57.5, 54.7, 48.6	56.7, 45.4, 29.4	16.0, 15.1, 13.2	0.28, 0.64
G3	DBFSiPy3	4.4	77.5, 70.9, 54.9	65.0, 52.8, 28.5	22.9, 22.0, 16.5	0.28, 0.64
G4	DBFSiPy4	4.1	74.5, 74.6, 60.5	67.4, 53.5, 31.8	21.9, 21.1, 17.8	0.28, 0.64

<sup>a</sup> The notation 1-4 in devices G1-G4 indicates the corresponding devices fabricated with DBTSiPy3, DBTSiPy4, DBFSiPy3 and DBFSiPy4 as the host respectively. Device configuration: G1-G4: ITO/HAT-CN (10 nm)/TAPC (55 nm)/Host: 9% Ir(ppy)<sub>3</sub> (20 nm)/TmPyPB (35 nm)/Liq (2 nm)/Al (120 nm). <sup>b</sup> Voltages at 1000 cd/m<sup>2</sup>, <sup>c</sup> Efficiencies in the order of the maxima, at 1000 cd/m<sup>2</sup> and at 10000 cd/m<sup>2</sup>, <sup>d</sup> Commission International de Ieelaiage coordinates measured at 5 mA/cm<sup>2</sup>.

Scheme 1. Synthetic routes to DBTSiPy3, DBTSiPy4, DBFSiPy3 and DBFSiPy4.

Figure 1. Differential scanning calorimetry (DSC, left) and thermogravimetric analysis (TGA,

right) curves of DBTSiPy3, DBTSiPy4, DBFSiPy3 and DBFSiPy4.

Figure 2. UV-Vis absorption, PL and Phos spectra of DBTSiPy3, DBTSiPy4, DBFSiPy3 and DBFSiPy4.

Figure 3. HOMO/LUMO distributions and molecular structure of DBTSiPy3, DBTSiPy4, DBFSiPy3 and DBFSiPy4.

Figure 4. UPS spectra of DBTSiPy3, DBTSiPy4, DBFSiPy3 and DBFSiPy4.

Figure 5. Molecular structures and representative energy level diagram of the materials.

Figure 6. (a) Current density-voltage-luminance (J-V-L) characteristics; (b) current efficiency

(CE), power efficiency (PE) and external quantum efficiency (EQE) versus luminance curves for

 $Ir(ppy)_3$ -based devices and (c) EL spectra at 5 mA/cm<sup>2</sup>.

**Figure 7.** Hole- and electron only device based on DBFSiPy3 and DBFSiPy4. Device con figuration: Hole only device: ITO/MoO<sub>3</sub>(10 nm)/Host (30 nm)/MoO<sub>3</sub>(10 nm)/Al(100 nm) Electron only device: ITO/Liq(2 nm)/Host(30 nm)/TmPyPB(35 nm)/Liq(2 nm)/Al(100 nm), Host=DBFSiPy3 and DBFSiPy4.

Table 1. Physical Properties of DBTSiPy3, DBTSiPy4, DBFSiPy3 and DBFSiPy4.

Table 2. Electroluminescence characteristics of the devices

- Four novel tetraphenyl silicon derivatives were designed with high triplet energy.
- All of these materials showed high glass transition temperatures and thermal decomposition temperatures.
- The Ir(ppy)<sub>3</sub> based PHOLEDs hosted by DBFSiPy3 and DBFSiPy4 exhibited high EQEs of 22.9% and 21.9% respectively.
- The way of modifying tetraphenyl silicon block still has further potential to develop a wide variety of derivatives for optoelectronic applications.