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A series of modified *bis*(4-(4,5-diphenyl-4*H*-1,2,4-triazol-3-*yl*)phenyl)dimethylsilane (**ST**), **ST-CF**<sub>3</sub>, **ST-Me**, **ST-'Bu**, and **ST-OMe**, were designed and prepared by introducing the electron-withdrawing groups or the electron-donating groups at the 4-position of the end-on phenyl groups on the triazole ring. Systematic investigations of their thermal-, photophysical-, and electron-transporting (ET) properties were successfully carried out. Depending on the electronic characteristics of the substituents at the end-phenyl group on the triazole, their frontier orbital energy levels were controlled while maintaining energy band gaps. Low- temperature photoluminiscence spectra indicate that all the prepared ST moieties maintained high triplet energy states up to 2.85 eV owing to the suppression of electron only device (EOD). The EOD of **ST-'Bu** showed significantly higher current density than the other analogs. Finally, the EL device utilizing **ST-'Bu** as an electron transporting material in phosphorescent organic light-emitting diodes with *bis*[(4,6-di-fluorophenly)-pyridinate-*N*,*C*<sup>2</sup>]picolinate (FIrpic) as a dopant showed an external quantum efficiency of 15.9%.

trapping.<sup>32,33</sup> Therefore,

chelated

## Introduction

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For both displays and solid-state lighting, efficiency is still the crucial factor in the applications of organic light-emitting diodes (OLEDs). The use of phosphorescent emitters is one of the most important strategies to improve the efficiency of OLEDs.1-14 Despite significant achievements in red and green phosphorescent materials, improving efficiency for blue emission seems to be the final obstacle for the commercialization of full colour displays and white light application.<sup>15–19</sup> Obtaining highly efficient blue phosphorescent OLEDs has been difficult, because blue emission is generated from wide-gap excited states.<sup>20</sup> Several blue dopant have been developed,<sup>21-26</sup> for example, iridium (III) bis[(4,6-difluorophenly)-pyridinate-*N*,*C*<sup>2</sup>]picolinate (FIrpic).<sup>27–29</sup> The greenish-blue emission using Firpic exhibited CIE coordinates of (0.16, 0.29). Even though Firpic showed good performance as a blue dopant, another obstacle must be resolved to reach the desired high quality with long lived full-colour display. Because blue phosphorescent emission from Firpic dopant is generated

materials have some drawbacks. For example, PBD and TAZ have relatively low glass-transition temperatures ( $T_g \approx 60-$ 70 °C)<sup>42,43</sup> which results in crystallization over time during device operation. In the case of BAIq, even though this material

metal

Recently, our group<sup>45–47</sup> and others<sup>48–51</sup> developed siliconbased materials as high triplet materials, because silicon atom can block the conjugation, leading to wide band-gap and high

is an efficient ETM for green PHOLEDs, it cannot be used in blue

PHOLEDs because the triplet energy is only 2.2 eV<sup>44</sup> which is

lower than blue phosphorescent dopant materials.

from the relatively high triplet energy ( $E_T = 2.65 \text{ eV}$ ),<sup>27</sup> finding

suitable high-triplet energy materials for host and common layers is indispensable.<sup>30,31</sup> Namely, to achieve the high

quantum efficiency of blue phosphorescent OLEDs, host in the

emissive layer (EML) and common layer materials in hole-

transporting layer (HTL) and electron-transporting layer (ETL)

must possess higher triplet energy levels than those of dopant

In general, the mobility of holes is higher than that of electrons

developing

efficient

bis(2-methyl-8-quinolinato)-4-

electron

(PBD),34,35

in most organic semiconducting materials due to electron

transporting material (ETM) is essential to improve charge

balance in OLED device. Several candidate materials have been

used in PHOLEDs. For example, oxadiazole based ETM, 2-(4-

phenylphenolate (BAIq),<sup>29</sup> azole based ETM, 3-(biphenyl-4-y/)-5-

(4-tert-butylphenyl)-4-phenyl-4H-1,2,4-triazole (t-Bu-TAZ),<sup>36-38</sup>

and benzimidazole based ETM, 1,3,5-tris(N-phenylbenzimidizol-

2-yl)benzene (TPBi)<sup>39–41</sup> have been developed. However, these

biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole

ETM,

materials to confine the triplet energy in dopant material.

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Electronic Supplementary Information (ESI) available: Crystal data and collection parameters for **ST-Bu**, TGA, cyclic voltamograms, device diagram, and EL spectra of the device. CCDC 1445019. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x





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thermal stability. For example, phenyl carbazole units were introduced into silicon atom and the resulting materials were examined as a blue host material.<sup>45</sup> The triplet energy of these silicon-based host materials reached up to 3.0 eV, and fabricated device using silicon based host material showed a better performance than that of the device using mCP (1,3bis(N-carbazolyl)benzene). Another example of silicon based host material is containing 1,3,4-oxadiazole groups and it achieved current efficiency up to 39 cd/A.<sup>48</sup> By the same token, electron-transporting material based on silicon atom was developed for green PHOLEDs by introducing a silicon atom between two 1,8-naphthyridin units.<sup>49</sup> By using this material with Ir(ppy)<sub>3</sub>, 15.4% of maximum external quantum efficiency (EQE) corresponding to 56.2 cd A<sup>-1</sup> of maximum current efficiency was obtained with a maximum power efficiency of 58.9 Im W<sup>-1</sup>. Moreover, triazole units were also introduced into the silicon atom as the electron transporting material.<sup>46</sup> In this case, its triplet energy level was as high as 2.85 eV, and its glasstransition temperature reached up to 115 °C.

In this study, we are able to control the frontier orbital energies by introducing trifluoromethyl unit as the electronwithdrawing group and methyl, *tert*-butyl, and methoxy units as the electron-donating groups at the 4-para-position of the endon phenyl group on triazole, as shown in Scheme 1. Central silicon atom effectively breaks the conjugation between two TAZ (3-(biphenyl-4-y/)-5-(4-*tert*-butylphenyl)-4-phenyl-4*H*-1,2,4-triazole) units and thus renders high-triplet energies up to 2.85 eV. Among the series, **ST-<sup>t</sup>Bu** was incorporated into the Firpic-based blue phosphorescent OLEDs, exhibiting and EQE of 15.9% with reduced efficiency roll-off at a high luminance.

#### Experimental

**General Procedures** All the reactions were formed under a dry nitrogen or argon atmosphere using standard Schlenk techniques. THF was freshly distilled over sodium benzophenone. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Varian Mercury 300 spectrometer operating at 300.1 and 75.4 MHz, respectively. All proton and carbon chemical shifts were measured relative to the internal residual benzene from the lock solvent (99.5% CDCl<sub>3</sub>). The elemental analyses were performed using a Carlo Erba Instruments CHNSO EA 1108

analyzer. High-Resolution Tandem Mass Spectrometry (Jeol LTD JMS-HX 110/110A) was performed by the Korean Basic Science Institute. Cyclic voltammetry (CV) was performed in an electrolyte containing 1 mM of the electro-active compounds and 0.1 M tetrabutylammonium perchlorate (TBAP) at room temperature under N<sub>2</sub> atmosphere using a BAS 100B electrochemical analyzer. Platinum, platinum wire, and  $Ag/AgNO_3$  (0.1 M) were used as the working, counter, and reference electrodes, respectively. All the potentials were calibrated to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple. n-BuLi, Benzovl chloride, aniline, PCl<sub>3</sub>, and dimethyldichlorosilane were purchased and used as received. Compounds **1–3** were prepared following literature procedure.52

Synthesis of 4,4'-(dimethylsilanediyl)dibenzohydrazide (4) A 500 mL two-neck round bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with 4,4'-(dimethylsilanediyl)dibenzoate<sup>52</sup> (12.3 g, 37.5 mmol), hydrazine monohydrate (26.3 mL, 750 mmol), and ethanol (100 mL). The reaction mixture was heated to reflux for 24 h and then allowed to cool to room temperature. The reaction mixture was poured into cold water to give a white precipitate. The precipitate was collected by filtration and washed with hexane and small amounts of water to remove the unreacted starting materials. The resulting white solid was dried in a vacuum oven for 24 h to afford the pure product in quantitative yield. <sup>1</sup>H NMR (300.1 MHz, DMSO- $d_6$ ): ( $\delta$ , ppm) 9.78 (NH, s, 2H), 7.78 (Ar-H, d, J = 6.9 Hz, 4H), 7.58 (Ar-H, d, J = 6.9 Hz, 4H), 4.49 (NH<sub>2</sub>, s, 4H), 0.57 (-CH<sub>3</sub>, s, 6H); HRMS (FAB) calcd. for C<sub>16</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>Si: [M]<sup>+</sup> 328.1356, Found: 328.1353; Anal. calcd for C<sub>16</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>Si: C, 58.51; H, 6.14; N, 17.06; O, 9.74; Si, 8.55. Found: C, 58.50; H, 6.13; N, 17.05.

General procedure for the synthesis of ST compound precursors (5a–5d) A 500 mL two-neck round bottomed flask equipped with a magnetic stir bar was charged with 4,4'-(dimethylsilanediyl)dibenzohydrazide, triethylamine (TEA), and *N*-methyl-2-pyrrolidone (NMP). Corresponding 4-benzoyl chloride was slowly added at 10 °C, and then the reaction mixture was stirred overnight at room temperature. The reaction mixture was poured into water to give a precipitate. The precipitate was collected by vacuum filtration and washed with water. The resulting white solid was dried in a vacuum oven for 24 h affording the pure product.

Synthesis of 4,4'-(dimethylsilanediyl)*bis*(*N*'-(4-(trifluoromethyl)*benzoyl*)*benzohydrazide*) (5a) Compound 5a was obtained by the above mentioned procedure by using 4-(trifluoromethyl)*benzoyl* chloride (5 g, 24.0 mmol), 4,4'-(dimethylsilanediyl)dibenzohydrazide (1.97 g, 6.0 mmol), and TEA (1.67 mL, 12 mmol) in NMP (40 mL). Yield: 3.8 g, 94%. <sup>1</sup>H NMR (300.1 MHz, DMSO-*d*<sub>6</sub>): ( $\delta$ , ppm) 10.79 (N*H*, s, 2H), 10.63 (*NH*, s, 2H), 8.12 (Ar-*H*, d, *J* = 7.5 Hz, 4H), 7.84–7.93 (Ar-*H*, m, 8H), 7.70 (Ar-*H*, d, *J* = 6.9 Hz, 4H), 2.69 (-*CH*<sub>2</sub>-, s, 4H), 0.63 (-*CH*<sub>3</sub>, s, 6H); HRMS (FAB) calcd. for C<sub>32</sub>H<sub>27</sub>F<sub>6</sub>N<sub>4</sub>O<sub>4</sub>Si: [M+H]<sup>+</sup> 673.1706, Found: 673.1702; Anal. calcd for C<sub>32</sub>H<sub>26</sub>F<sub>6</sub>N<sub>4</sub>O<sub>4</sub>Si: C, 57.14; H, 3.90; F, 16.95; N, 8.33; O, 9.51; Si, 4.18. Found: C, 57.15; H, 3.89; N, 8.32.

Synthesis of 4,4'-(dimethylsilanediyl)bis(N'-(4methylbenzoyl)benzohydrazide) (5b) Compound 5b was obtained by the above mentioned procedure by using 4methylbenzoyl chloride (9.4 g, 60.9 mmol), 4,4'-(dimethylsilanediyl)dibenzohydrazide (5 g, 15.2 mmol), and TEA (4.24 mL, 30.5 mmol) in NMP (100 mL). Yield: 10.0 g, 92%. <sup>1</sup>H NMR (300.1 MHz, DMSO-*d*<sub>6</sub>): (δ, ppm) 10.48 (NH, s, 2H), 10.43 (NH, s, 2H), 7.91 (Ar-H, d, J = 7.8 Hz, 4H), 7.83 (Ar-H, d, J = 8.4 Hz, 4H), 7.69 (Ar-H, d, J = 8.4 Hz, 4H), 7.29–7.34 (Ar-H, m, 4H), 2.69 (-CH2-, s, 4H), 0.63 (-CH3, s, 6H); HRMS (FAB) calcd. for C<sub>32</sub>H<sub>33</sub>N<sub>4</sub>O<sub>4</sub>Si: [M+H]<sup>+</sup> 565.2271, Found: 565.2269; Anal. calcd for C<sub>32</sub>H<sub>32</sub>N<sub>4</sub>O<sub>4</sub>Si: C, 68.06; H, 5.71; N, 9.92; O, 11.33; Si, 4.97. Found: C, 68.04; H, 5.70; N, 9.93.

Synthesis of 4,4'-(dimethylsilanediyl)*bis*(*N*'-(4-tertbutylbenzoyl)benzohydrazide) (5c) Compound 5c was prepared following the by above mentioned procedure by using 4-tert-butylbenzoyl chloride (22.1 mL, 113.4 mmol), 4,4'-(dimethylsilanediyl)dibenzohydrazide (9.3 g, 28.3 mmol), and TEA (7.90 mL, 56.7 mmol) in NMP (200 mL). Yield: 22.2 g, 93%. <sup>1</sup>H NMR (300.1 MHz, DMSO-*d*<sub>6</sub>): ( $\delta$ , ppm) 10.48 (N*H*, s, 2H), 10.43 (N*H*, s, 2H), 7.85–7.95 (Ar-*H*, m, 6H), 7.69 (Ar-*H*, d, *J* = 8.4 Hz, 4H), 7.47–7.55 (Ar-*H*, m, 6H), 2.69 (-*C* $H_2$ -, s, 4H), 1.31 (C(*C* $H_3$ ), s, 18H), 0.62 (-*C* $H_3$ , s, 6H); HRMS (FAB) calcd. for C<sub>38</sub>H<sub>45</sub>N<sub>4</sub>O<sub>4</sub>Si: [M+H]<sup>+</sup> 649.3210, Found [M+H]<sup>+</sup>: 649.3207; Anal. calcd for C<sub>38</sub>H<sub>44</sub>N<sub>4</sub>O<sub>4</sub>Si: C, 70.34; H, 6.83; N, 8.63; O, 9.86; Si, 4.33. Found: C, 70.36; H, 6.84; N, 8.62.

4,4'-(dimethylsilanediyl)bis(N'-(4-Synthesis of methoxybenzoyl)benzohydrazide) (5d) Compound 5d was prepared by the same procedure using 4-methoxybenzoyl (5.42 mL, 36.5 4,4'chloride mmol). (dimethylsilanediyl)dibenzohydrazide (3 g, 9.13 mmol), and TEA (2.54 mL, 18.3 mmol) in NMP (60 mL). Yield: 4.9 g, 90%. <sup>1</sup>H NMR (300.1 MHz, DMSO-*d*<sub>6</sub>): (δ, ppm) 10.45 (NH, s, 2H), 10.36 (NH, s, 2H), 7.90 (Ar-H, d, J = 12.9 Hz, 8H), 7.68 (Ar-H, d, J = 6.9 Hz, 4H), 7.05 (Ar-H, d, J = 7.5 Hz, 4H), 3.83 (OCH<sub>3</sub>, s, 6H), 2.69 (-CH<sub>2</sub>-, s, 4H), 0.62 (-CH<sub>3</sub>, s, 6H); HRMS (FAB) calcd. for  $C_{32}H_{33}N_4O_6Si$ : [M+H]+: 597.2169, Found: 597.2167; Anal. calcd for C<sub>32</sub>H<sub>32</sub>N<sub>4</sub>O<sub>6</sub>Si: C, 64.41; H, 5.41; N, 9.39; O, 16.09; Si, 4.71. Found: C, 64.40; H, 5.42; N, 9.40.

**General procedure for the synthesis of ST compounds** A 250 mL two-neck round bottomed flask (**A**) equipped with a magnetic stir bar was charged with the ST compound precursors and *o*-dichlorobenzene. Another 250 mL two-neck round bottomed flask (**B**) equipped with a magnetic stir bar and a

reflux condenser was charged with  $\operatorname{aniling}_{W \land AAA} d_{\operatorname{Onl}AE}$  dichlorobenzene. Flask **B** was cooled dow to  $\operatorname{C}^{3}$  and  $\operatorname{PCl}^{3}$  was added dropwise. Then, the solution in flask **A** was slowly decanted to flask **B** under N<sub>2</sub> atmosphere. The reaction mixture was heated to 180 °C for 18 h, which allowed colour change to orange. The reaction mixture was cooled to room temperature and poured into water and then neutralized with 1 N NaOH aqueous solution, resulting in the formation of the orange precipitate. The precipitate was collected by filtration and dried in a vacuum oven for 24 h. The crude product was purified by silica gel flash column chromatography to afford the final product as white solids.

## Bis(4-(4-phenyl-5-(4-(trifluoromethyl)phenyl)-4H-1,2,4-

triazol-3-y/)phenyl)dimethylsilane, ST-CF3 This compound was prepared by the above mentioned procedure by using the following materials: flask A: 4,4'-(dimethylsilanediyl)bis(N'-(4-(trifluoromethyl)benzoyl)benzohydrazide) (7.7 g, 10.0 mmol) and o-dichlorobenzene (50 mL), flask B: aniline (10.7 mL, 117.5 mmol), PCl<sub>3</sub> (2.1 mL, 23.5 mmol), and o-dichlorobenzene (50 mL). The crude product was purified by silica gel flash column chromatography using THF: dichloromethane = 1:5 (v:v) as an eluent to afford the product as a white solid. Yield: 3.3 g, 42%. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>): (δ, ppm) 7.57 (Ar-H, s, 8H), 7.54 (Ar-H, s, 2H), 7.51 (Ar-H, s, 2H), 7.49-7.48 (Ar-H, m, 1H), 7.46 (Ar-H, s, 1H), 7.42 (Ar-H, d, J = 2.70 Hz, 6H), 7.24 (Ar-H, s, 3H), 7.21 (Ar-*H*, s, 3H), 0.51 (-C*H*<sub>3</sub>, s, 6H); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): (δ, ppm) 154.92, 153.55, 140.57, 134.64, 134.40, 130.56, 129.18, 128.06, 127.85, 126.61, 125.70, 125.66, 125.60, 125.55, -2.64; HRMS (FAB) calcd. for C<sub>44</sub>H<sub>33</sub>F<sub>6</sub>N<sub>6</sub>Si: [M+H]<sup>+</sup> 787.2440, Found 787.2438; Anal. calcd for C<sub>44</sub>H<sub>32</sub>F<sub>6</sub>N<sub>6</sub>Si: C, 67.16; H, 4.10; F, 14.49; N, 10.68; Si, 3.57. Found: C, 67.18; H, 4.11; N, 10.67.

#### Bis(4-(4-Phenyl-5-p-tolyl-4H-1,2,4-triazol-3-

y/)phenyl)dimethylsilane, ST-Me This compound was also prepared by the above mentioned procedure by using the following materials: flask A: 4,4'-(dimethylsilanediyl)bis(N'-(4methylbenzoyl)benzohydrazide) (5.5 g, 10.0 mmol) and odichlorobenzene (50 mL), flask B: aniline (10.9 mL, 120 mmol), PCl<sub>3</sub> (2.1 mL, 24.0 mmol), and o-dichlorobenzene (50 mL). The crude product was purified by silica gel flash column chromatography using THF:dichloromethane = 1:5 (v:v) as an eluent to afford the product as a white solid. Yield: 2.8 g, 41%. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>): (δ, ppm) 7.50-7.49 (Ar-H, m, 1H), 7.48-7.46 (Ar-H, m, 2H), 7.45-7.44 (Ar-H, m, 2H), 7.42-7.41 (Ar-H, m, 1H), 7.38 (Ar-H, s, 8H), 7.32 (Ar-H, s, 2H), 7.29 (Ar-H, s, 2H), 7.18 (Ar-H, t, J = 1.48 Hz, 2H), 7.16 (Ar-H, t, J = 1.83 Hz, 2H), 7.11 (Ar-H, s, 2H), 7.08 (Ar-H, s, 2H), 2.32 (Ar-CH<sub>3</sub>, s, 6H), 0.49 (-CH<sub>3</sub>, s, 6H); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): (δ, ppm) 134.27, 130.26, 129.36, 128.87, 127.97, 127.79, 21.41, -2.79; HRMS (FAB) calcd. for  $C_{44}H_{39}N_6Si$ : [M+H]<sup>+</sup> 679.3005, Found: 679.3002; Anal. calcd for  $C_{44}H_{38}N_6Si$ : C, 77.84; H, 5.64; N, 12.38; Si, 4.14. Found: C, 77.83; H, 5.53; N, 12.36.

#### Bis(4-(5-(4-tert-Butylphenyl)-4-phenyl-4H-1,2,4-triazol-3-

**yl)phenyl)dimethylsilane, ST-**<sup>t</sup>**Bu.** This compound was also prepared by the above mentioned procedure by using the following materials: flask **A**: 4,4'-(dimethylsilanediyl)*bis*(*N*'-(4-(*tert*-butyl)benzoyl)benzohydrazide) (8.0 g, 12.2 mmol) and o-dichlorobenzene (50 mL), flask **B**: aniline (13.4 mL, 147.5 mmol),

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PCl<sub>3</sub> (2.57 mL, 29.5 mmol), and *o*-dichlorobenzene (50 mL). The crude product was purified by silica gel flash column chromatography using THF:dichloromethane = 1:10 (*v*:*v*) as an eluent to afford the product as a white solid. Yield: 5.0 g, 54%. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>): ( $\delta$ , ppm) 7.51-7.50 (Ar-*H*, m, 1H), 7.50-7.47 (Ar-*H*, m, 2H), 7.46-7.45 (Ar-*H*, m, 2H), 7.43-7.42 (Ar-*H*, m, 1H), 7.38-7.37 (Ar-*H*, m, 8H), 7.35 (Ar-*H*, t, *J* = 1.80 Hz, 3H), 7.30 (Ar-*H*, t, *J* = 2.55 Hz, 3H), 7.29-7.28 (Ar-*H*, m, 2H), 7.21 (Ar-*H*, t, *J* = 1.50 Hz, 2H), 7.18 (Ar-*H*, t, *J* = 1.86 Hz, 2H), 1.28 (-CH<sub>3</sub>, s, 18H), 0.49 (-CH<sub>3</sub>, s, 6H); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): ( $\delta$ , ppm) 155.04, 154.66, 153.10, 139.83, 135.58, 134.31, 130.22, 129.94, 128.54, 128.14, 127.98, 127.83, 125.60, 124.05, 34.95, 31.33, -2.48; HRMS (FAB) calcd for C<sub>50</sub>H<sub>50</sub>N<sub>6</sub>Si: (*C*, 78.70; H, 6.60; N, 11.01; Si, 3.68. Found: C, 78.75; H, 6.62; N, 11.00.

#### Bis(4-(5-(4-Methoxyphenyl)-4-phenyl-4H-1,2,4-triazol-3-

yl)phenyl)dimethylsilane, ST-OMe This compound was also prepared by the above mentioned procedure by using the following materials: flask A: 4,4'-(dimethylsilanediyl)bis(N'-(4methoxybenzoyl)benzohydrazide) (8.1 g, 13.6 mmol) and odichlorobenzene (50 mL), flask B: aniline (14.86 mL, 163.0 mmol), PCl<sub>3</sub> (2.8 mL, 32.6 mmol), and o-dichlorobenzene (50 mL). The crude product was purified by silica gel flash column chromatography using THF:dichloromethane = 1:4 (v:v) as an eluent to afford the product as a white solid. Yield: 6.1 g, 63%. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>): (δ, ppm) 7.54-7.53 (Ar-H, m, 1H), 7.52-7.20 (Ar-H, m, 2H), 7.48-7.47 (Ar-H, m, 2H), 7.46-7.45 (Ar-H, m, 1H), 7.39 (Ar-H, t, J = 4.35 Hz, 12H), 7.21 (Ar-H, t, J = 1.41 Hz, 2H), 7.19 (Ar-H, t, J = 3.30 Hz, 2H), 6.84 (Ar-H, t, J = 3.00 Hz, 2H), 6.80 (Ar-H, t, J = 2.55 Hz, 2H), 3.80 (-OCH<sub>3</sub>, s, 6H), 0.50 (-CH<sub>3</sub>, s, 6H); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): (δ, ppm) 160.81, 154.97, 154.53, 151.72, 139.80, 135.97, 135.56, 134.31, 130.43, 130.22, 129.89, 128.45, 128.10, 127.96, 127.86, 125.72, 119.40, 114.08, 55.46, 34.43, 31.79, 30.52, 22.86, 21.39, 14.32, -2.49; HRMS (FAB) calcd. for C<sub>44</sub>H<sub>39</sub>N<sub>6</sub>O<sub>2</sub>Si: [M+H]<sup>+</sup> 711.2904, Found: 711.2901; Anal. calcd for C44H38N6O2Si: C, 74.34; H, 5.39; N, 11.82; O, 4.50; Si, 3.95. Found: C, 74.33; H, 5.38; N, 11.84.

Crystal Structure Determination Single crystal of ST-tBu was sealed in glass capillaries under argon and mounted on the diffractometer. The preliminary examination and data collection were performed using a Bruker SMART CCD detector system single-crystal X-ray diffractometer equipped with a sealed-tube X-ray source (50 kV × 30 mA) using graphitemonochromated Mo K<sub>rad</sub> ( $\lambda$  = 0.71073 Å). The preliminary unit cell constants were determined using a set of 45 narrow-frame  $(0.3^{\circ} \text{ in } \omega)$  scans. A double-pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. The SMART software package was used for data collection, and SAINT was used for frame integration.<sup>53</sup> The final cell constants were determined by a global refinement of the xyz centroids of the reflections harvested from the entire data set. Structure solution and refinement were carried out using the SHELXTL-PLUS software package.54

Absorption, Emission, and Phosphorescence The absorption and photoluminescence spectra were recorded using a SHIMADZU UV-3101PC UV-VIS-NIR scanning



Figure 1. (a) Single crystal structure of ST-'Bu. Hydrogens were omitted for clarity and (b) crystal packing of ST-'Bu in a unit cell.

spectrophotometer and a VARIAN Cary Eclipse fluorescence spectrophotometer, respectively. The triplet energies were determined at the maximum of the first vibronic transition of the phosphorescence spectra. The samples dissolved in 2-MeTHF were frozen in liquid nitrogen at 77 K. The samples were excited using a 1 ns pulsed nitrogen laser (GL-3300, Photon Technology International) at a repetition rate of 10 Hz. Luminance light was allowed to pass through a monochromator (Oriel instruments) and Photomultiplier photomultiplier tube (Oriel instruments). The signal was obtained using a gated boxcar Integrator System (SR 250, Stanford research System). The detection window was set to 15  $\mu$ s, and the delay was set to 0.2 ms from the rigging edge of the laser. For the transient photoluminescent decay measurements, a nitrogen laser (GL-3300, PTI) was used as the excitation light source, and the phosphorescence light was passed through a monochromator (Oriel 77200), to which a photomultiplier tube (Oriel 77346) was attached at the exit slit.

**Thermal Property** Thermal property of the synthesized materials was measured by differential scanning calorimetry (Perkin-Elmer/Pyris Diamond DSC). A heating rate of 10 °C/min was used after the first melting of the compound, followed by a rapid cooling to room temperature at a rate of 40 °C/min.

**DFT calculations** The derivatives were theoretically calculated using the *Gaussian 09* package.<sup>55</sup> The ground-state geometries of compounds were optimized using the B3LYP density functional theory (DFT) and 6/31G (d,p) basis set. The contours of electron density were plotted using Chem3D ver.10.<sup>56</sup>

**OLED Devices** The OLED devices were fabricated on glass substrates pre-coated with a 150 nm ITO layer having a sheet resistance of 10  $\Omega$ /square. The ITO glass was pre-cleaned using a conventional solvent cleaning method. The ITO surface was cleaned again with a UV ozone treatment immediately before



Figure 2. DSC diagrams for ST-CF<sub>3</sub>, ST-Me, ST-<sup>t</sup>Bu, and ST-OMe.

depositing the hole injecting layer (HIL). The organic, Liq, and Al layers were deposited sequentially onto the substrate without breaking the vacuum. The current–voltage characteristics of OLEDs were measured using a source measure unit (Keithley 2635B). The electroluminescence spectra, luminance, and CIE coordinates were measured using a spectro-radiometer (Konica Minolta CS-2000). Assuming Lambertian emission, the external quantum efficiency (EQE) was calculated from the luminance, current density, and electroluminescence spectrum.

### **Results and discussion**

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Synthesis and Structural Characterization The target ST compounds were prepared as illustrated in Scheme 1, and the detailed procedures are given in the experimental section. The tetrahedral silicon structure was initialized by the Grignard reaction between *p*-tolylmagnesium bromide and dimethyldichlorosilane in a quantitative yield. Treatment of 1 with KMnO<sub>4</sub> results in oxidation to afford 2, followed by the condensation reaction with methanol to give 3 in 95% yields. Important intermediate, silylbenzohydrazide moiety (4), was prepared quantitatively by the reaction of 3 with excess amounts of hydrazine monohydrate under reflux condition. Then, it was treated with various substituted benzoyl chloride in the presence of triethylamine as a base yielding the precursors 5a-5d in quantitative yields. Finally, the condensation reaction of 5 with aniline in the presence of phosphorus trichloride at 180 °C afforded the final products in moderate yields (41-63%). Final products, ST-CF<sub>3</sub>, ST-Me, ST-<sup>t</sup>Bu, and ST-OMe were further purified by train sublimation. All the compounds were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR, high-resolution mass spectrometry, and elemental analysis.

Among them, the solid-state molecular structure of **ST-<sup>t</sup>Bu** was determined by single-crystal X-ray crystallography using suitably grown crystals in dichloromethane/*n*-hexane. Figure 1a shows the molecular structure of a single crystal for **ST-<sup>t</sup>Bu**. Tables S1–S3 in the electronic supplementary Information (ESI) summarizes the structural parameters, bond lengths, and angles determined by the X-ray structural studies. **ST-<sup>t</sup>Bu** was crystallized in the monoclinic crystal system using the *C2/c* 



spectra of **ST-CF**<sub>3</sub>, com disposes a the three methyl bon atom in the the phenyl ring In contrast, the

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Figure 3. UV-Vis absorption and normalized PL emission spectra of ST-CF<sub>3</sub>, ST-Me, ST-<sup>t</sup>Bu, and ST-OMe in 10  $\mu$ M THF solution.

space group at  $R_1$  = 0.0559. The silicon atom disposes a tetrahedral geometry, which is defined by the three methyl groups [1.850(3) Å (averaged)] and one ipso-carbon atom in the phenyl ring [1.885(2) Å]. The triazole ring and the phenyl ring substituted at 2-position are tilted by 41.09(8)°. In contrast, the phenyl ring at 1-position (C17-C18-C19-C20-C21-C22) is twisted further to 59.56(7)°. The crystal packing structure of ST-tBu is shown in Figure 1b. As noted from the crystal packing diagram shown in Figure 1b, two different intermolecular interaction motifs are present in the middle molecule when three packed molecules are considered. One is hydrogen bonding between the hydrogen atom of phenyl ring and the nitrogen atom of triazole ring with the bond distance of 2.614 Å. The other is  $\pi$ –  $\pi$  interaction between the phenyl groups to which *tert*-butyl groups are substituted. tert-Butyl groups encourage spatial overlap of the two adjacent phenyls falling their closest plan-toplan distance into ca. 4.18 Å. Those two types of interactions come into play alternately in one molecule to another sidewise. So, driving force for the molecular packing in **ST-**<sup>t</sup>**Bu** comes from hydrogen bonding and intermolecular  $\pi - \pi$  interaction. In particular, enhanced intermolecular  $\pi - \pi$  interactions seem to be the prime reason for the higher mobility in the context of facile electron-hopping process among adjacent molecules in close proximity.

**Thermal Properties** The thermal properties of **ST** compounds were analysed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere and are summarized in Table 1. All the compounds exhibited high thermal decomposition temperatures (T<sub>d</sub>) in the range 352–474 °C (Figures S2–S5 in the ESI) and high glass transition temperatures (T<sub>g</sub>) in the range of 97–131 °C (Figure 2), which are substantially higher than general electron transporting materials such as 3-(4'*-tert*-butylphenyl)-4-phenyl-5-(4"-biphenyl)-1,2,4-triazole (TAZ, T<sub>g</sub> ~ 70 °C)<sup>43,57</sup> and as high as 1,3,5-tris(1-phenyl-1*H*-benzo[d]imidazol-2-yl)benzene (TPBi, T<sub>g</sub> = 124 °C).<sup>58</sup> High thermal stabilities, in particular, having high T<sub>g</sub> are desirable in phosphorescence OLEDs, because they can Published on 20 April 2016. Downloaded by University of California - San Diego on 20/04/2016 17:22:09

Гak	ole 1. Physical p	roperties of S	ST compounds, ST	-CF₃, ST-Me, ST-¹l	Bu, and ST-OMe	in THF solution			View Artic	le Online						
								DOI:	10.1039/C6TC	5TC00017G						
	Comp.	<i>T</i> <sub>g</sub> (°C)	λ <sub>abs</sub> (nm) <sup>a</sup>	λ <sub>em</sub> (nm) <sup>a</sup>	<i>E</i> <sub>T</sub> (eV) <sup><i>b</i></sup>	$E_{\rm red}$ (V) <sup>a</sup>	HOMO (eV) <sup>c</sup>	LUMO (eV) <sup>d</sup>	E <sub>g</sub> (eV)							
	ST-CF₃	123	276	354	2.83	-2.44	-6.95	-3.03	3.92	_						
	ST-Me	97	275	362	2.85	-2.64	-6.78	-2.83	3.95							
	ST- <sup>t</sup> Bu	131	276	364	2.85	-2.66	-6.75	-2.81	3.94							
	ST-OMe	110	279	372	2.84	-2.68	-6.67	-2.79	3.88	_						

<sup>a</sup>Measured in THF. <sup>b</sup>Measured in 2-MeTHF. The HOMO and LUMO levels were determined using the following equations: <sup>c</sup>E<sub>HOMO</sub>(eV) = *E*<sub>LUMO</sub>-*E*<sub>g</sub>.<sup>d</sup>*E*<sub>LUMO</sub>(eV) = -e(*E*<sub>red</sub>(V vs Fc/Fc<sup>+</sup>) + 4.74 eV + 0.73 eV); Correction value of 0.73 V was used from TAZ (reported value of E<sub>LUMO</sub> = -2.7 eV).<sup>57</sup>



Figure 4. Phosphorescence spectra of ST-moieties and TAZ measured in 2-MeTHF at 77 K.

prevent morphological changes and suppress aggregation upon heating.

Photophysical Properties Figure 3 shows the electronic absorption and fluorescence spectra of the ST compounds in THF solution. All the compounds showed maximum absorptions in the range of 275–279 nm, which are assigned to the  $\pi$ – $\pi$ \* electronic transition of the triazole heterocycle ring. The Hammett parameters of substituents do not affect their absorption properties. In contrast, spectral shifts in emission correspond well to the electronic perturbation of the substituents, as summarized in Table 1. ST-CF<sub>3</sub> showed hypsochromic shifted emission at 354 nm, whereas ST-OMe showed bathochromic shifted emission at 372 nm because of the lower energy gap. Figure 4 shows the phosphorescence spectra of ST-moieties measured in 2-MeTHF at 77 K. The phosphorescence peaks of the ST-moieties are in the similar range 434-438 nm. The energy gap of the triplet levels, estimated from the phosphorescence peaks of ST-CF<sub>3</sub>, ST-Me,  $ST^{-t}Bu$ , and  $ST^{-}OMe$  were obtained at  $E_{T1} = 2.83$ , 2.85, 2.85, and 2.84 eV, respectively, as listed in Table 1. They showed much higher triplet levels compared to that of TAZ ( $E_{T1} = 2.70 \text{ eV}$ )<sup>43</sup> because of the suppression of electron delocalization by the silicon atom, whereas TAZ contains only organic biphenyl group at the end-on position. Because the energy gap of the triplet levels of the ST-moieties are higher than that of deep blue dopant, for example, FIrpic ( $E_{T1} = 2.65 \text{ eV}$ ),<sup>27</sup> the **ST** series are expected to preferentially confine the triplet excitons of Firpic.



Figure 5. Reduction potential ( $E_{onset}$ , V vs Fc/Fc<sup>+</sup>) vs Hammett parameter ( $\sigma$ ) for ST-CF<sub>3</sub>, ST-Me, ST-<sup>t</sup>Bu, and ST-OMe.

Electrochemical Properties To investigate the electrochemical properties of ST-CF<sub>3</sub>, ST-Me, ST-<sup>t</sup>Bu, and ST-OMe, cyclic voltammetry (CV) was performed by utilizing a three-electrode cell system: platinum disk electrode was used as the working electrode, whereas a platinum wire and Ag/AgNO<sub>3</sub> were used as the counter and reference electrodes, respectively. As shown in Figure S6 in the ESI, irreversible reduction waves appeared at  $E_{pc} = -2.44$ , -2.64, -2.66, and -2.68 V (versus Fc/Fc<sup>+</sup>) for compounds ST-CF<sub>3</sub>, ST-Me, ST-<sup>t</sup>Bu, and ST-OMe, respectively. A linear plot of reduction potential (Eonset) versus Hammett parameter (o), for ST-CF<sub>3</sub>, ST-Me, ST-<sup>t</sup>Bu, and ST-OMe with the known Hammett parameters<sup>59</sup> indicates that there is indeed a strong dependency of the reduction potential on the nature of the electron-withdrawing or the electron-donating ability at the 4-position of the end-on phenyl groups on the triazole, as shown in Figure 5. Using redox potentials, the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in compounds ST-CF<sub>3</sub>, ST-Me, ST-<sup>t</sup>Bu, and ST-OMe were estimated as -6.95/-3.03, -6.78/-2.83, -6.75/-2.81, and -6.67/-2.79 eV, respectively, as listed in Table 1. With increasing electron withdrawing capability of the triazole units, the energy levels of LUMO were lowered, indicating that the electron injection from a metallic cathode could be improved for high-performance blue OLEDs.

**Theoretical Calculations** To gain insight into the electronic states of ST compounds, DFT calculations were carried out using the TD-DFT/B3LYP/6-31G(d,p) method with the *Gaussian 09* package.<sup>55</sup> All the **ST** compounds showed a very similar HOMO and LUMO distributions. The calculated electron contour plots



Figure 6. Spatial distributions for the frontier orbitals of compounds ST-CF<sub>3</sub>, ST-Me, ST-'Bu, and ST-OMe.

of the molecular orbitals are shown in Figure 6. The HOMOs and LUMOs of the ST compounds are distributed mainly over the triazole and two phenyl groups at 3- and 5-positions of the triazole ring. Because of the symmetrical molecular structure of the **ST** compounds, the HOMO and HOMO–1 orbitals are energetically degenerated, and their distributions are same but positioned at different branches. The LUMO and LUMO+1 orbitals also show similar phenomenon, but there were very small distributions on the phenyl group at 4-position of the triazole ring. Since the major electronic distributions of the LUMO levels are on the triazole unit for all the compounds, efficient electron transfer properties of **ST** compounds are expected.

Electron-only devices (EODs) To compare the electrontransport properties of ST compounds, electron-only devices (EODs) containing each compound were fabricated. Figure 7 shows the current density-voltage (J-V) characteristics of EODs with the structures of ITO (150 nm)/Al (50 nm)/ST (100 nm)/Liq (1 nm)/Al (150 nm). Under the same voltage, the EOD containing ST-<sup>t</sup>Bu showed significantly higher current densities compared to other compounds, ST-CF<sub>3</sub>, ST-Me, and ST-OMe. Murgatroyd et al. presented the space charge limited current (SCLC) model, which is characterized by field dependent mobility;<sup>60,61</sup> the electron mobilities (µ) of ST-CF<sub>3</sub>, ST-Me, ST-<sup>t</sup>Bu, and ST-OMe, which were estimated by this model, were found to be 9.52 X 10^-5, 1.62 X 10^-5, 2.65 X 10^-4, and 3.93 X 10^-5  $\rm cm^2/Vs$ at 0.5 MV/cm, respectively. The ST-tBu compound showed the highest electron mobility among ST compounds. We believe there are two factors related to the enhanced electron mobility on ST-<sup>t</sup>Bu: one is related to electronic effect stemming from the tert-Bu group and the other is associated with the molecular aggregation in the solid states. As can be seen in the Hammett plot of Figure 5, ST-<sup>t</sup>Bu lies in the electron donating side second to the **ST-OMe**. Also, as noted in the crystal packing structure, ST-<sup>t</sup>Bu exhibits hydrogen bonding as well as  $\pi-\pi$  interactions between adjacent molecules among repeating molecules in the crystal packing. We believe higher mobility of ST-tBu is due to synergistic effect of those two factors.

**PHOLEDs performances** To examine **ST-'Bu** as an electrontransporting material, PHOLEDs was fabricated with the structure of ITO (150 nm)/HATCN (10 nm)/TAPC (85



**Figure 7.** (a) J-V characteristics of electron-only devices (EODs) for **ST-CF**<sub>3</sub>, **ST-Me, ST-'Bu**, and **ST-OMe**. Devices were fabricated with the following structures: ITO (150 nm)/AI (50 nm)/**ST** (100 nm)/Liq (1 nm)/AI (150 nm) and (b) the J-V characteristics were fitted to SCLC with field dependent mobility. J = (9/8) $\varepsilon_0\varepsilon_r(E^2/L)\mu_0\exp(0.89\beta\sqrt{E})$ , where J is the current density;  $\varepsilon_0\varepsilon_r$  is the dielectric constant; E is the electric field; L is the film thickness;  $\mu_0$  is the zero-field carrier mobility; and  $\beta$  is the Poole Frenkel factor. The values of  $\mu_0$  and  $\beta$  were calculated by assuming  $\varepsilon_r$  is equal to 3. The field dependent mobility was calculated using Poole Frenkel equation:  $\mu(E) =$  $\mu_0 \exp(\beta\sqrt{E})$ .

nm)/mCBP:FIrpic 8% (30 nm)/**ST-**<sup>t</sup>**Bu** (5 nm)/ **ST-**<sup>t</sup>**Bu**:Liq 50% (25 nm) /Liq (1 nm)/AI (150 nm), where HAT-CN is dipyrazino[2,3f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile, TAPC is 4,4'-cyclohexylidene-*bis*[*N*,*N*-*bis*(4-

methylphenyl)benzenamine], mCBP is 3,3-di(9*H*-carbazol-9y/)biphenyl. The chemical structures and energy level diagram of the used materials are shown in Figure S7. The current density–voltage–luminance (J–V–L) characteristics, current efficiency vs. current density, power efficiency vs. current density, and EQE vs. current density are shown in Figure 8. The performances of the devices are summarized in Table 2. Overall, the PHOLED device using **ST-tBu** as an electron-transporting layer showed peak external electroluminescent (EL) quantum and power efficiencies of  $\eta_{ext} = 15.9\%$  and  $\eta_p = 17.9$  lm/W.

#### Conclusions

In this study, a series of modified *bis*(4-(4,5-diphenyl-4*H*-1,2,4-triazol-3-*yl*)phenyl)dimethylsilane (**ST**), **ST-CF**<sub>3</sub>, **ST-Me**, **ST-**<sup>t</sup>**Bu**,

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Figure 8. (a) J-V-L characteristics, (b) current efficiency-current density curves, (c) power efficiency-current density curves, and (d) EQE-current density curves of device.

2. EL performances of the device with ST- <sup>t</sup> Bu as a ETM										
Device	Turn on (V) -	Power efficiency (lm/W)		Current efficiency (cd/A)		EQE (%)		CIE		
		max	400 nits	max	400 nits	max	400 nits	at 400 nits		
ST-tBu	4.29	17.87	10.97	30.05	26.82	15.92	14.05	(0.14, 0.31)		

Device configuration: ITO (150 nm)/HATCN (10 nm)/TAPC (85 nm)/mCBP:FIrpic 8% (30 nm)/ST-\*Bu (5 nm)/ ST-\*Bu:Liq 50% (250 nm) /Liq (1 nm)/AI (150 nm).

and ST-OMe, were designed and prepared as electrontransporting materials. Their energy band gaps were successfully tuned depending on the Hammett parameters. All the compounds showed the triplet levels of > 2.83 eV, which are much higher compared to that conventional electrontransporting material, TAZ ( $E_{T1}$  = 2.70 eV), because of the suppression of electron delocalization by silicon centre. Among the series, ST-<sup>t</sup>Bu exhibited highest thermal stability with T<sub>g</sub> at 131 °C. Furthermore, the fabricated EOD of ST-<sup>t</sup>Bu showed most efficient electron-transporting capability among the series. Finally, in the PHOLED devices using ST-tBu as an electrontransporting material, a maximum EQE and maximum power efficiency of 15.9% and 17.9 lm/W, respectively, were achieved. These results suggest that the materials in the ST series can be used as potential blue phosphorescence electron-transporting materials.

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