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Branched diphenylsilane derivatives containing electronically isolated indolyl moieties as host materials for blue organic light emitting diodes

R. Zostautiene [a], G. Krucaite [a], J. Simokaitiene [a], J.V. Grazulevicius [a], Y.M. Lai [b], W.B. Wang [b], J.H. Jou [b], S. Grigalevicius [a,*]

[a] *Department of Organic Technology, Kaunas University of Technology, Radvilenu Plentas 19, LT50254 Kaunas, Lithuania*
[b] *Department of Materials Science and Engineering, National Tsing-Hua University, No. 101, Kaungfu Rd., Hsin-Chu 30013, Taiwan, ROC*

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ABSTRACT

Branched diphenylsilane derivatives with pendent indolyl fragments were synthesized and characterized. The compounds show high thermal stability with thermal decomposition starting at temperatures above 367 °C and ability to form glasses with glass-transition temperatures of 53–58 °C. The electron photoemission spectra of the layers of the synthesized compounds showed ionization potentials of ca. 5.85 eV. The derivatives were tested as host materials in phosphorescent OLEDs with iridium(III)[bis(4,6-difluorophenyl)-pyridinato-*N*,C2′]picolinate as the guest. The device with the host derivative containing four electronically isolated indolyl fragments exhibited the best overall performance with maximum current efficiency of about 12 cd/A.

1. Introduction

In phosphor-doped organic light emitting diodes (OLEDs), to reduce quenching associated with relatively long excited-state lifetimes of triplet emitters and triplet–triplet annihilation, triplet emitters of heavy-metal complexes are normally used as emitting guests in a host material, and thus suitable host materials are of equal importance for the phosphorescent devices [1–3]. For electrophosphorescence from triplet guests, it is essential that the triplet level of the host be larger than that of the triplet emitter to prevent reverse energy transfer from the guest back to the host and to effectively confine triplet excitons on guest molecules [4–6]. It was reported earlier that carbazole-, indole- and arylsilane-based derivatives demonstrate rather large triplet energies and are potential host materials for blue electrophosphorescent devices [7–11]. Here, we report on new diphenylsilane-based host materials containing isolated indolyl fragments. These branched and highly soluble compounds could be suitable for the preparation of large area devices by spin coating.

2. Experimental

2.1. Instrumentation

^{1}H NMR spectra were recorded using a Varian Unity Inova (300 MHz) instrument. Mass spectra were obtained on a Waters ZQ 2000 spectrometer. FT-IR spectra were recorded using a Perkin Elmer FT-IR System. UV spectra were measured with a Spectronic Genesys™ 8 spectrometer. Fluorescence (FL) spectra were recorded with a MPF-4 spectrometer.

Differential scanning calorimetry (DSC) measurements were carried out using a Bruker Reflex II thermosystem. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409. The TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 10 °C/min.

The ionization potentials of the layers of the compounds synthesized were measured by the electron photoemission method in air, which was described earlier [12,13]. The measurement method was, in principle, similar to that described by Miyamoto et al. [14].The standard error in the mean to 95% confidence for the values of ionization potential was 0.04 eV [15].

The devices were fabricated on glass substrates and consisted of multiple organic layers sandwiched between the bottom indium tin

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[*] Corresponding author.
E-mail address: saulius.grigalevicius@ktu.lt (S. Grigalevicius).

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oxide (ITO) anode and the top metal cathode (Al). The device structure was ITO/poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) {PEDOT:PSS} (ca. 300 Å)/**DInSi** or **TInSi** doped with **FIrpic** (250 Å)/TPBi/LiF (5 Å)/Al (1500 Å), where the conducting polymer (PEDOT:PSS) was used as the hole-injection layer [16], **DInSi** or **TInSi** doped with the blue phosphorescent iridium(III)[bis(4,6-difluorophenyl)-pyridinato-*N*,*C*2′]picolinate (**FIrpic**) was used as the emitting layer and LiF was used as the electron-injection layer [17]. 1,3,5-Tris(2-*N*-phenylbenzimidazolyl)benzene (TPBi) was used as an electron-transporting layer for the devices.

The luminance and CIE chromatic coordinates of the resulting OLEDs were measured using a Minolta CS-100 luminance meter. A Keithley 2400 electrometer was used to measure the current–voltage (I–V) characteristics. All the devices were characterized without encapsulation and all the measurements were carried out under ambient conditions [18]. The emission area of all the devices was 25 mm^2 and only the luminance in the forward direction was measured.

2.2. Materials

3-(2-Phenylindol-1-ylmethyl)-3-methyloxetane (**1**) was prepared by the reaction of 2-pheny-1*H*-indole with an excess of 3-bromomethyl-3-methyloxetane under basic conditions in the presence of a phase transfer catalyst. The procedure was described earlier [19].

3,3-Bis(chloromethyl)oxetane (**2**), 1*H*-indole (**3**), potassium carbonate, tetrabutylammonium hydrogen sulphate (TBAS), tetrabutylammonium bromide (TBAB) and dichlorodiphenylsilane (**5**) were purchased from Aldrich and used as received.

3,3-Bis(indol-1-ylmethyl)oxetane (**4**) was prepared by the reaction of 3,3-bis(chloromethyl)oxetane (**2**) with an excess of 1*H*-indole (**3**) under basic conditions in the presence of a phase transfer catalyst – TBAS. 1*H*-indole (**3**, 10 g, 85 mmol) and 3,3-bis(chloromethyl)oxetane (4.41 g, 28 mmol) were heated to reflux in ethyl methyl ketone (100 mL). Then powdered potassium carbonate (11.8 g, 85 mmol), potassium hydroxide (14.3 g, 256 mmol) and a catalytic amount of TBAS were added to the mixture, and it was heated under reflux for 24 h. Then the cooled mixture was decanted and the new portion of inorganic materials was added to the solution, and the mixture was again heated under reflux for 24 h. After TLC control the mixture was filtered, the solvent was evaporated and the product was purified by column chromatography with silica gel using hexane/ethyl acetate (vol. ratio 5:1) as an eluent. After crystallization from methanol yield of the product was 53% (4.8 g). Mp: 120–122 °C.

IR (KBr, cm^{-1}): 3119, 3101, 3058 (C–H, Ar); 2957, 2919, 2875 (C–H); 1609, 1574 (C=C, Ar); 1308 (C–N); 1270, 1242, 1090 (C–O–C); 766, 739, 724 (CH=CH).

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.66–7.61 (m, 2H, Ar), 7.19–7.07 (m, 6H, Ar), 6.95 (d, 2H, J = 3.3 Hz, Ar), 6.57 (d, 2H, J = 3.3 Hz Ar), 4.59 (s, 4H, –N–CH$_2$–), 4.33 (s, 4H, –CH$_2$–O–).

MS (APCI$^+$, 20 V), m/z: 317.4 ([M + H]$^+$, 100%), 132.1 (10%).

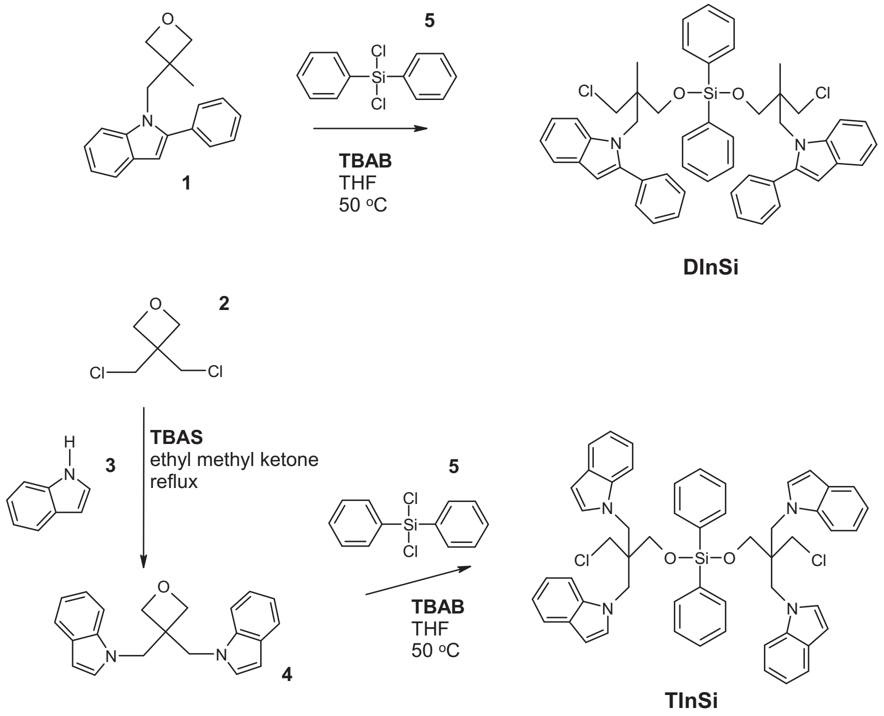
2.2.1. *Di[(1-(2-phenylindol-1-yl)-2-chloromethyl-2-methyl) propoxy]diphenylsilane (**DInSi**)*

3-(2-Phenylindol-1-ylmethyl)-3-methyloxetane (**1**, 1 g, 3.6 mmol) and TBAB (0.06 g, 0.18 mmol) of were dissolved in THF (3 mL), and dichlorodiphenylsilane (**5**, 0.42 g,1.63 mmol) was added. The reaction mixture was stirred at room temperature for 30 min. Then the temperature was raised to 50 °C and the mixture was stirred for 48 h. The reaction was stopped after TLC control. The product was separated by column chromatography with silica gel using hexane/ethyl acetate (vol. ratio 2:1) as an eluent. Yield of the amorphous product was 0.8 g (60%).

IR (KBr, cm^{-1}): 3419 (O–H); 3052, 3028 (C–H, Ar); 2951, 2926, 2872 (C–H); 1605, 1592 (C=C, Ar); 1347, 1316 (C–N); 1127, 1117, 1075 (C–O); 767, 750, 741, 719, 670 (CH=CH).

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.62–7.26 (m, 24H, Ar), 7.16–7.06 (m, 4H, Ar), 6.5 (s, 2H, Ar), 4.54–4.32 (m, 4H, Cl–CH$_2$–), 3.36 (s, 4H, –N–CH$_2$–), 3.16–3.02 (m, 4H, CH$_2$–O–), 0.51 (s, 6H, –CH$_3$).

MS (APCI$^+$, 20 V), m/z: 807,5 ([M]$^+$, 100%), 810,5 ([M + 3]$^+$, 50%), 811,5 ([M + 4]$^+$, 30%).



Scheme 1. Synthesis of **DInSi** and **TInSi**.

Elemental analysis for $C_{50}H_{48}Cl_2N_2O_2Si$ % Calc.: C 74.33, H 5.99, N 3.47; % Found: C 74.25, H 5.84, N 3.39.

2.2.2. Di[(1-chloro-2,2-bis(indol-1-ylmethyl))propoxy] diphenylsilane (**TInSi**)

3,3-bis(indol-1-ylmethyl)oxetane (**4**, 1 g, 3.2 mmol) and TBAB (0.05 g, 0.16 mmol) were dissolved in THF (5 mL) and dichlorodiphenylsilane (**5**, 0.36 g, 1.4 mmol) was added. The reaction mixture was stirred at room temperature for 30 min. Then the temperature was raised to 50 °C and the mixture was stirred for 24 h. The reaction was stopped after TLC control. The product was separated by column chromatography with silica gel using hexane/ethyl acetate (vol. ratio 5:1) as an eluent and crystallized from the eluent mixture of solvents. Yield of the product was 0.4 g (32%).

IR (KBr, cm^{-1}): 3102, 3072, 3051 (C—H, Ar); 2946, 2929, 2887 (C—H); 1611, 1592 (C═C, Ar); 1337, 1311 (C—N); 1131, 1118, 1090, 1052 (C—O); 788, 767, 740, 699 (CH═CH).

^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.58–7.48 (m, 10H, Ar), 7.43 (t, 6H, J = 7,5 Hz, Ar), 7.3 (t, 2H, J = 7,5 Hz, Ar), 7.04–6.9 (m, 10H, Ar), 6.44–6.35 (m, 6H, Ar), 4.18 (s, 8H, $-N-CH_2-$), 3.6 (s, 4H, $Cl-CH_2-$), 3.35 (s, 4H, $-CH_2-O-$).

MS ($APCI^+$, 20 V), m/z: 887,4 ($[M+H]^+$, 90%), 888,3 ($[M+2]^+$, 50%).

Elemental analysis for $C_{54}H_{50}Cl_2N_4O_2Si$ % Calc.: C 73.20, H 5.69, N 6.32; % Found: C 73.31, H 5.62, N 6.43.

3. Results and discussion

The synthesis of derivatives containing isolated indolyl and diphenylsilane fragments was carried out by the synthetic route shown in Scheme 1. Oxetane **1** was prepared by the reaction of 2-pheny-1*H*-indole with an excess of 3-bromomethyl-3-methyl-oxetane under basic conditions as described earlier [19]. The derivative **1** was treated with dichlorodiphenylsilane (**5**) to yield the diphenylsilane containing two electronically isolated 2-phenylindolyl moieties (**DInSi**). 3,3-Bis(indol-1-ylmethyl)oxetane (**4**) was prepared by the reaction of 3,3-bis(chloromethyl)oxetane (**2**) with an excess of 1*H*-indole (**3**) under basic conditions in the presence of a phase transfer catalyst TBAS. Oxetane **4** was treated with dichlorodiphenylsilane (**5**) in the presence of TBAB to yield the branched derivative **TInSi** containing four electronically isolated indolyl fragments.

The newly synthesized derivatives were identified by IR and ^1H NMR spectroscopy and mass spectrometry. The data were found to be in good agreement with the proposed structures. The derivatives were soluble in common organic solvents, such as acetone, chloroform or THF at room temperature. Transparent thin films of these materials were prepared by spin coating from solutions.

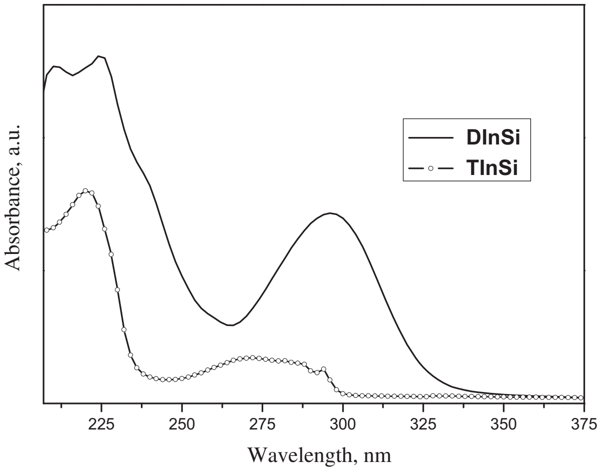


Fig. 2. UV absorption spectra of dilute THF solutions of **DInSi** and **TInSi**.

The behavior under heating of **DInSi** and **TInSi** was studied by DSC and TGA. Both these derivatives demonstrate high thermal stability. The temperatures at which initial loss of mass was observed ($T_{5\%}$) are 367 °C for **DInSi** and 371 °C for **TInSi**. **DInSi** was amorphous in nature. When the sample of **DInSi** was heated, T_g was observed at 53 °C and no peaks due to crystallization and melting appeared. Cooling down and repeated heating revealed only the glass transition again. **TInSi** was obtained as crystalline material by re-crystallization from solution, however it readily formed glass when the molten sample was cooled on standing in air or with liquid nitrogen. The DSC thermograms of **TInSi** are shown in Fig. 1. When the crystalline sample was heated, the endothermic peak due to melting was observed at 189 °C. When the molten sample of **TInSi** was cooled down and heated again, the glass-transition phenomenon was observed at 58 °C and on further heating no peaks due to crystallization and melting appeared.

UV absorption spectra of dilute THF solutions of **DInSi** and **TInSi** are presented in Fig. 2. The comparison of UV spectra of these derivatives with that of other compounds containing electronically isolated indolyl or 2-phenylindolyl moieties [19] shows that the spectra are very similar. This observation confirms that an interaction between chromophores is not observed in dilute solutions of

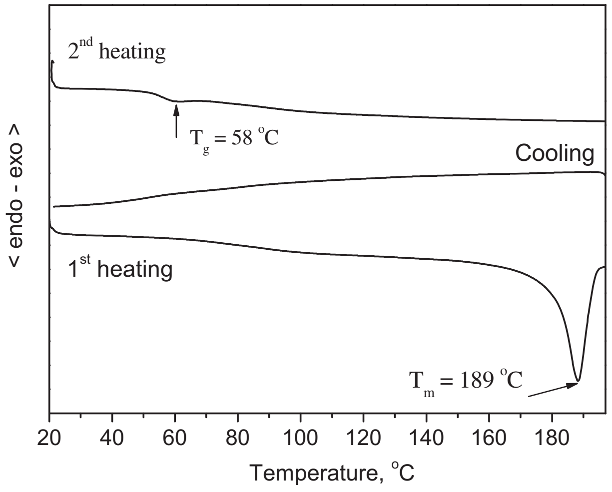


Fig. 1. DSC curves of **TInSi**.

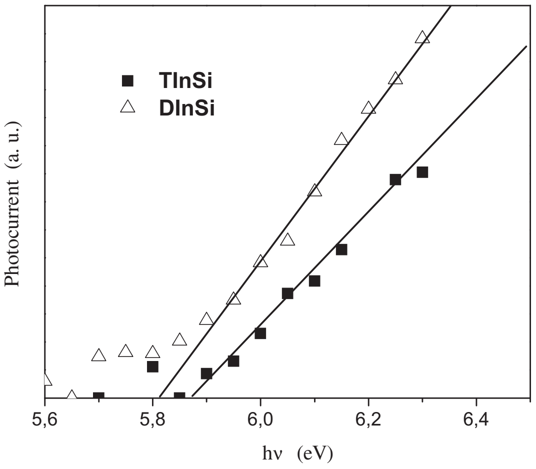


Fig. 3. Electron photoemission spectra of layers of **DInSi** and **TInSi**.

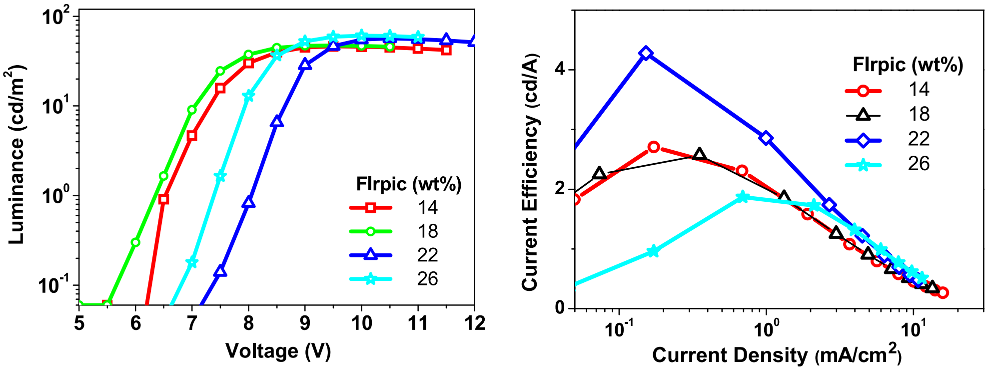


Fig. 4. OLED characteristics of devices containing **DInSi** as the host: luminance–voltage characteristics and current efficiencies versus current density.

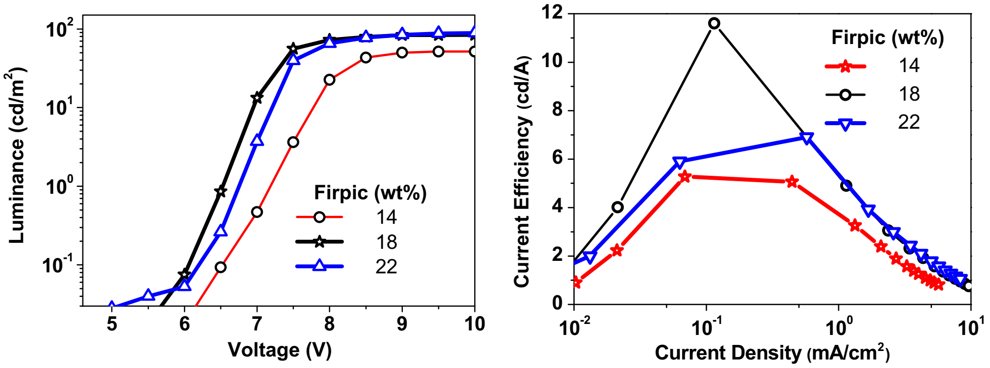


Fig. 5. OLED characteristics of devices containing **TInSi** as the host: luminance–voltage characteristics and current efficiencies versus current density.

DInSi and **TInSi**. The λ_{max} of **DInSi** is red shifted in comparison with that of **TInSi** due to the phenyl ring attached to the 2nd position of indole core.

Ionization potentials (I_p) of thin amorphous layers of the derivatives were determined from electron photoemission spectra of the layers (Fig. 3). The I_p values of the layers of **DInSi** and **TInSi** are close to 5.85 eV. As it could be expected from the UV absorption spectroscopy data, the I_p values for films of the synthesized derivatives are similar to that of other derivatives containing electronically isolated indole rings [19].

To evaluate the performance of derivatives **DInSi** and **TInSi** as hosts, phosphorescent OLEDs were fabricated by using the blue emitter **FIrpic** as the guest. The structure of the multilayer devices is described in the experimental section. In both devices of **DInSi** and **TInSi**, the electroluminescence was found to originate only from **FIrpic** at different bias voltages. No host and doped transport molecular emission was visible from the devices, indicating an energy transfer or charge transfer from the hosts to the guest as well as the sufficient injection of both holes and electrons into the emitting layer.

The host **DInSi** was used in concentration-dependent experiments with the dopant amount ranging from 14 to 26 wt%. Fig. 4 shows the luminance–voltage characteristics and curves of current efficiency versus current density for the devices. These OLEDs exhibit turn-on voltages of 5.5–7.2 V and current efficiencies of 1.9–4.2 lm/W. The device containing 22 wt% of **FIrpic** as the guest exhibits the highest current efficiency of 4.2 lm/W.

The host **TInSi** was also used in concentration-dependent experiments with the dopant amount ranging from 14 to 22 wt%. Fig. 5 shows the luminance–voltage characteristics and current efficiencies versus voltage for the devices. Up to 18 wt%, as the **FIrpic** guest concentration increases, the efficiency of the device is gradually increased. Device with an 18 wt% doping ratio exhibits a maximum current efficiency of ~12 cd/A. The maximum luminance of the device exceeds 90 cd/m^2. When the doping ratio reaches 22 wt%, the maximum current efficiency is decreased due to concentration quenching and triplet–triplet annihilation. The characteristics of the devices containing **TInSi** host are promising also in comparison to the well known host: 4,4′-bis(9-carbazolyl)-2,2′-biphenyl (CBP)-based devices [4]. It should be pointed out that these characteristics were obtained in non-optimized test devices under ordinary laboratory conditions. The device performance may be further improved by an optimization of the layer thicknesses and processing conditions.

In conclusion, branched derivatives containing a diphenylsilane core and pendent indolyl moieties were synthesized from indole-based oxetanes and dichlorodiphenylsilane. The derivatives show sufficient thermal stability and form homogeneous amorphous films with glass-transition temperatures of 53–58 °C. The compounds were tested as host materials in phosphorescent OLEDs with iridium(III)[bis(4,6-difluorophenyl)-pyridinato-*N*,C2′]picolinate as the guest. The device with the host derivative containing four electronically isolated indolyl fragments exhibited the best overall performance with maximum current efficiency of about 12 cd/A.

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