New Si-Based Material with Pyridopyrazine Substituents

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Charge-transporting organic semiconductors are an important class of materials that play crucial roles in electronic and optoelectronic devices such as organic light-emitting devices (OLEDs), thin film transistors, and photovoltaic cells.[1-7] OLEDs, that have organic hole- and electron-transport layers sandwiched between two electrodes, show low driving voltage and bright emission and are of importance for application to full color flat-panel displays and lighting.[8-14] Since electron mobilities in organic materials, in general, are several orders of magnitude lower than hole mobilities, electron-transport materials (ETMs) with high electron mobility are required to further improve OLED performance. To achieve an effective electron injection and transport in an OLED, a high electron affinity to enable efficient electron-injection and a high electron mobility to enhance electron flux, with a high ionization potential. Also, electron transporting materials should have a high triplet energy to confine excitons within the emissive layer. It is also reported that electron transporting organic semiconducting materials develop of fulfilling several requirements, many research groups reported that low molar mass compound or polymeric structure containing π electron deficient heterocyclic moieties such as pyridine, oxadiazole, triazole, triazine, quinoline, or quinoxaline.[15-24]

Recently, we have developed 2,5-bis-(4-triphenylsilanyl-phenyl)-[1,3,4]oxadiazole (BTSO), that functions as good hole blocker and electron transporting layer in the phosphorescent devices.[25]

In this study, we designed bis(4-(2,3-di(pyridin-2-yl)pyrido[2,3-*b*]pyrazin-7-yl)phenyl)diphenyl-silane (DPPDS) with pyridyl-pyridopyrazine, which is composed of tetraphenyl silicone core and high electron attractive π conjugated pyridyl-pyridopyrazine side chains. Silyl groups are well known for their oxidative, thermal and chemical stabilities, low dielectric constants, and good film-forming ability. Moreover, these moieties render a molecule sterical hinderance (bulkyness) in terms of the sp³-hybridized silicon atoms. The tetraphenyl silicone core can give effectively hinder the aggregation and excimer formation. The introduction of pyridines on the 2,3-position of pyridopyrazine can not only enhance electron affinity but also reduce intermolecular interaction of fused pyridopyrazine.

Experimental Details

Measurement. The ^{1}H NMR spectra were recorded using a Bruker Advance 300 spectrometer. The thermal analysis was performed on a TA TGA 2100 thermogravimetric analyzer in a nitrogen on a TA instrument 2100 DSC. The sample was heated at 20 ºC min⁻¹. Differential scanning calorimeter was conducted under nitrogen on a TA instrument 2100 DSC. The sample was heated at 20 ºC min⁻¹ from 0 ºC to 250 ºC. UV-vis absorption studies were carried out using Perkin-Elmer LAMBDA-900 UV/VIS/IR spectrophotometer. The photoluminescence (PL) spectra were measured on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. Cyclic voltammetry (CV) was performed on an EG and G Parc model 273 potentiostat/galvanostat system with a three-electrode cell in a solution of Bu₄NClO₄ (0.1 M) in acetonitrile at a scan rate of 200 mV/s. The polymer films were coated on a square Pt electrode (0.50 cm²) by dipping the electrode into the corresponding solvents and then drying in air. A Pt wire was used as the counter electrode and an Ag/AgNO₃ (0.1 M) electrode was used as the reference electrode.

Synthesis of 4,4'-(Diphenylsilanediyl)bis(4,1-phenylene)diboronic Acid (1). Bis(4-bromophenyl)diphenylsilane (4.2 g, 8.6 mmol) was dissolved in 120 mL of dehydrated diethyl ether with agitation under flow of N₂. *N*-Butyl lithium (2.5 M in hexane, 7.5 mL, 19 mmol) was then added into the solution after cooling to −78 ºC using liquid nitrogen. Triethylborate (8.4 mL, 51 mmol) was added to the reactant solution at −78 ºC, and after 2 h the reaction was allowed to warm to room temperature and left for a further 12 h. Finally, water was added to quench the reaction. The product was extracted be methylenechloride (MC), and then dried over MgSO₄. After the solvent was evaporated, the crude product was filtered and washed with the hexane. Yield: 41% (1.5 g). ^{1}H-NMR (300 MHz, CDCl₃) δ 8.2 (d, 2H), 7.8 (d, 2H), 7.6 (m, 6H), 2.0 (s, 4H). FT-IR (KBr); ν 3428 (O-H str) 3062 (aromatic C-H str), 1106 cm⁻¹ (Si-Ph str).

Synthesis of 7-Bromo-2,3-di(pyridine-2-yl)pyrido[2,3-*b*]pyrazine (2). 7-Bromo-2,3-di(pyridine-2-yl)pyrido[2,3-

b]pyrazine was synthesized by literature method from 1,2-di (pyridine-2-yl)ethandione (2 g, 9.4 mmol) and 5-bromopyridine-2,3-diamime (2.1 g, 11.3 mmol).[26] The crude product was purified by column chromatography (eluent = ethyl acetate), the product was recrystallized from methanol. Yield: 50% (1.7 g). ^{1}H-NMR (300 MHz, CDCl$_3$) δ 9.2 (d, 1H), 8.7 (d, 1H), 8.4-8.2 (m, 3H), 8.0-7.8 (m, 3H), 7.3-7.2 (m, 3H). FT-IR (KBr); ν 3054 (aromatic C-H str), 1627 (C=N str), 1076 cm^{-1} (C-Br str).

Synthesis of Bis(4-(2,3-di(pyridin-2-yl)pyrido[2,3-*b*]-pyrazin-7-yl)phenyl)diphenylsilane (DPPDS). 7-Bromo-2,3-di(pyridine-2-yl)pyrido[2,3-*b*]pyrazine (3.9 g, 10.34 mmol) and 4,4'-(diphenylsilanediyl)bis(4,1-phenylene) di-boronic acid (2 g, 4.7 mmol) were mixed in 50 mL dry toluene. K$_2$CO$_3$ (2.0 M, 20 mL) was added, and mixture was stirred. The mixture was degassed and tetrakis(triphenyl-phosphine)-palladium (0.65 g, 5 mol %) was added in one portion under an atmosphere of N$_2$. The solution was then heated under reflux for 24 h under N$_2$. After the reaction mixture cooled and added to an aqueous solution of HCl (2 N). The resulting mixture was extracted with ethyl acetate (EA), and then dried over MgSO$_4$. After the solvent was evaporated, the crude product was purified by column chromatography (eluent = Ethyl Acetate), the product was recrystallized from hexane. Yield: 53% (2.24 g) ^{1}H-NMR (300 MHz, CDCl$_3$) δ 9.24 (s, 1H), 8.59 (d, 2H), 8.40 (d, 2H), 7.85 (m, 5H), 7.55-7.37 (m, 9H). FT-IR (KBr); ν 3050 (aromatic C-H str), 1585 (C=N str), 1110 cm^{-1} (Si-Ph str). HRMS *m/z* (%): cacld C$_{58}$H$_{38}$N$_{10}$Si 902.3050, found 902.3057 [M+H].

Results and Discussion

Scheme 1 displays the synthetic route of new symmetri-cally pyridopyrazine substituted silicon based material, bis(4-(2,3-di(pyridin-2-yl)pyrido[2,3-*b*]pyrazin-7-yl)phenyl)-diphenyl-silane (DPPDS), as a electron transporting materials. 7-Bromo-2,3-di(pyridine-2-yl)pyrido[2,3-*b*]pyrazine was obtained by 1,2-di(pyridine-2-yl)ethandione and 5-bromo-pyridine-2,3-diamime through the condensation reaction. Synthesis of DPPDS was carried out by Suzuki coupling reaction of 4,4'-(diphenylsilanediyl)bis(4,1-phenylene)di-boronic acid and 7-bromo-2,3-di(pyridine-2-yl)pyrido[2,3-*b*]pyrazine. The structure of DPPDS was confirmed by various spectroscopic analyses such as NMR, IR, and Mass analysis.

In order to optimize the molecular structure fully, a theoretical calculation using the PM3 parameterization in the Hyper Chem 5.0 program (Hypercube) was carried out for the characterization of the three-dimensional structure. Figure 1 shows the stereo structure of DPPDS from the cal-culative analyses. The 4 substituents, which are two pyrido-pyrazine substituted benzenes and two benzenes, located in
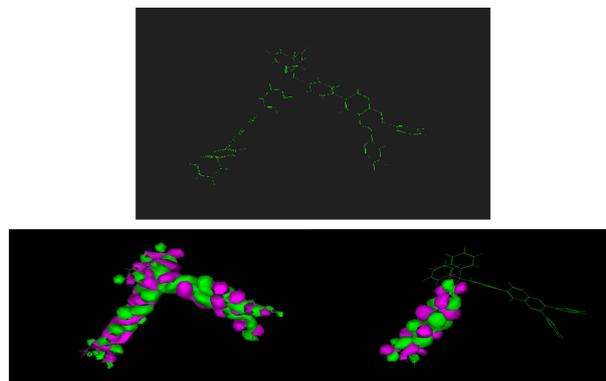
Figure 1. 3-Dimesional molecular configuration, and HOMO and LUMO electron densities of DPPDS.
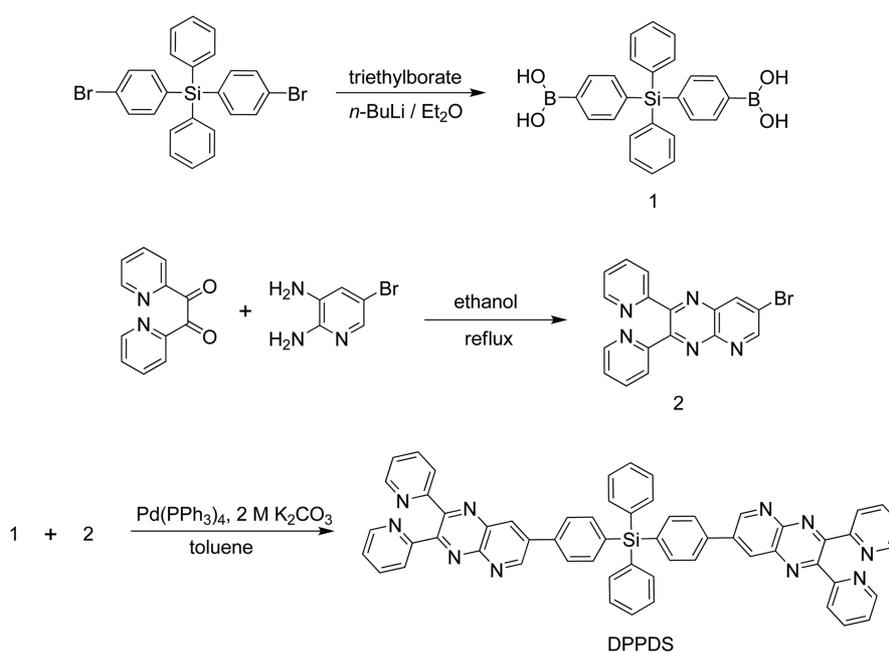
Scheme 1. Synthetic scheme of DPPDS.
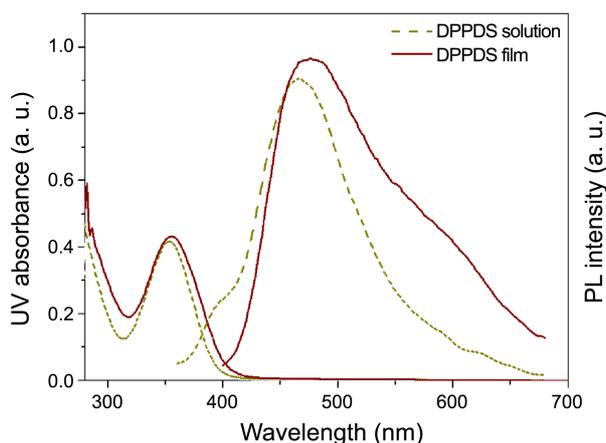
Figure 2. UV-visible absorption and PL spectra of DPPDS.

angular point of tetrahedron silicone core. The theoretical calculation of the three-dimensional structure suggests that it has a non-coplanar structure with inhibited intermolecular interaction. The electron densities of HOMO and LUMO of DPPDS are also shown in Figure 1. The electron density of LUMO is localized in pyradopyrazine.

Figure 2 exhibits the UV-visible absorption and photo-luminescent spectra (PL) of DPPDS both in chloroform solution and in thin films. UV-visible absorption and photo-luminescent spectra (PL) of DPPDS were measured both in 10^{-5} M in chloroform and in thin films. The absorption maximum was observed at 353 nm for solution and 355 nm for film. The optical band gap was 3.06 eV, which was obtained from the UV-absorption onset (405 nm). Shoulder peak around 600 nm in PL spectra of the film may be due to interaction between pyridopyrazine polar group.

The electrochemical behavior of DPPDS was investigated by cyclic voltammetry (CV) (Figure 3). CV was measured with three electrodes electrochemical cell in a 0.1 M Bu_4NClO_4 solution in anhydrous acetonitrile at room temperature under nitrogen with a scanning rate of 200 mV/s. A
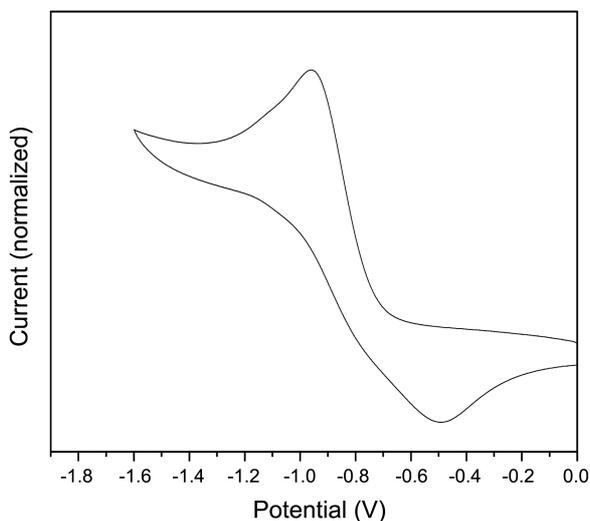
Figure 3. Cyclic voltammetry of DPPDS.
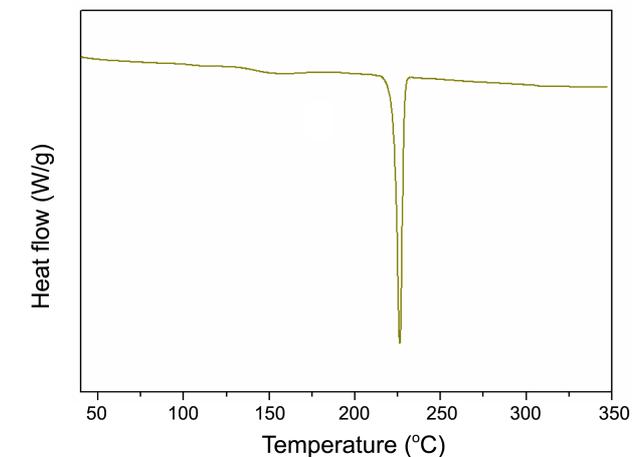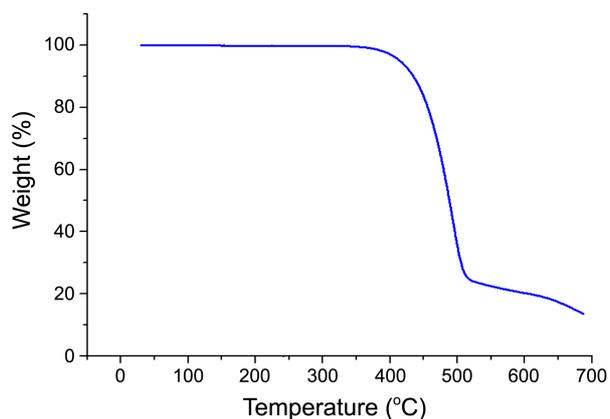
Figure 4. Thermogravimetric analysis (TGA) curve and differential scanning calorimetry (DSC) curve of DPPDS.

platinum working electrode and an $Ag/AgNO_3$ (0.1 M) reference electrode were used. The reduction onset potentials were measured to be 0.74 V with reversible cathodic reduction. The corresponding LUMO energy level was calculated to be −3.66 eV. The result indicates that the electron accepting property of the DPPDS is higher than those of well-known electron transporting materials such as Alq_3 −2.9 eV.[27] According to the UV edge of band gap energy (3.06 eV) and LUMO (−3.66 eV), the energy value of the highest occupied molecular orbital (HOMO) was estimated to be −6.72 eV. The reversible cathodic reduction, deep HOMO and deep LUMO level of DPPDS suggest that it will be good electron transporting material as well as good hole blocking material in EL device.

The thermal properties of DPPDS were studied by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in a nitrogen atmosphere (Figure 4). TGA of DPPDS exhibited 5% weight loss at 437 °C. The glass transition was observed at 150 °C. DPPDS with the symmetrically pyridopyrazine substituted tetrahedral silicone skelecton showed good thermal stability.

From the theoretical calculation, optical property, thermal stability and electrochemical properties, DPPDS is good candidate material for electron transporting material as well as hole blocking material for OLED.

Conclusion

We have designed and synthesized symmetric pyridopyrazine substituted silicon based material, bis(4-(2,3-di(pyridin-2-yl)pyrido[2,3-*b*]pyrazin-7-yl)phenyl)diphenyl-silane (DPPDS), as electron-transporting material for OLEDs. The bulky, sterically hindered tetrahedron molecular skeleton of tetraphenyl silyl group hindered close packing and crystallization. The pyridopyrazine with bipyridyl was efficient electron affinity group. Thus, it shows low lying HOMO and LUMO level. DPPDS is good candidate material for electron transporting material as well as hole blocking material for OLED.

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