Silicon-based carbazole and oxadiazole hybrid as a bipolar host material for phosphorescent organic light-emitting diodes

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A B S T R A C T

A silicon-based bipolar compound, 2-(4-((4-(9H-carbazol-9-yl)phenyl)dimethylsilyl)phenyl)-5-phenyl-1,3,4-oxadiazole (COHS), was designed and prepared as a host material for phosphorescent organic light-emitting diodes (OLEDs). The conjugated analogue of COHS, 2-(4′-(9H-carbazol-9-yl)biphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (COH), was also prepared to investigate their structure—property relationships. Thermal-, photophysical- and electrochemical properties as well as their single-crystal X-ray structures were studied for COHS and COH. The central silicon atom in COHS successfully disconnected the electronic communication between the carbazole and oxadiazole groups, resulting in relatively high triplet energy of ca. 2.71 eV, which were capable of hosting green phosphorescent emitters. DFT calculations were conducted to investigate the electronic structures of COHS and COH, and the results showed good correlation to experimental results. Finally, COHS and COH were used as a bipolar host material for a green phosphorescence organic light-emitting diode (PHOLED) devices with Ir(ppy)$_3$ (tris[2-phenylpyridinato-C^2,N]iridium(III)) as a dopant. The resulting device with COHS (device I) showed higher performance than the device with COH (device II), exhibiting high efficiencies and low-efficiency roll-off. Device I achieved maximum external quantum efficiencies (EQE) of 15.8%, whereas device II exhibited a relatively lower EQE of 13.0%.

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1. Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have been deemed potential candidates for flat-panel displays and solid-state lighting sources because the heavy-metal phosphors can theoretically achieve 100% internal quantum efficiency by harvesting both electronically generated singlet and triplet excitons [1]. To avoid efficiency roll-off induced by concentration quenching and triplet—triplet annihilation, the heavy-metal phosphors are normally homogeneously dispersed into a host matrix [2,3]. Therefore, developing host materials with great performance is of equal importance to the dopant material for achieving high performance in a PHOLED device.

In general, an appropriate host material is required to satisfy several conditions. First, the triplet energy level (ET) of the host material should be higher than that of the dopant material to facilitate total energy transfer from the host to the phosphorescent emitter and confine the triplet exciton within the emitting layer [4].

To achieve this, several strategies have been suggested for the development of host materials with limited π-conjugation. For example, 1) both silicon [5—8] or sp^3—hybridized carbon [9] atoms were introduced into a host material to block the π-conjugation, and 2) changing the interconnection between aromatic functional groups to the meta position, rather than ortho or para positions, to increase the distortion of the backbone structure [10—12]. Second, the desired host materials should have a high glass transition temperature (T$_g$) that can enhance the thermal and morphological stability, extending the operational lifetime of the device. Another requirement is that it should has proper carrier transport properties. If charge hopping occurs in the emission layer, the charge recombination zone would decrease and the exciton will be generated on the surface between the hole-transporting or electron-transporting layer, resulting in a decrease in device efficiency [13]. In addition, charge and exciton accumulation at interfaces may cause efficiency roll-off and device degradation owing to triplet—triplet annihilation [14]. Therefore, it is crucial that the host material possesses efficient and balanced charge transport properties. For this reason, electron acceptors such as benzimidazole [15—17], phosphine oxide [18—21], triazine [22—25],

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oxadiazole [26–28], and electron donors such as carbazole [29,30], triarylamine [31], and dibenzothiophene [32,33] were introduced to modify the bipolar carrier abilities of host materials; however, because of possible charge delocalization between the hole and electron-transport moieties, this type of material usually exhibits a relatively small energy band gap and low E_T. Therefore, it is imperative that the bipolar host materials possess weak donor-acceptor interactions to retain a high E_T. Thus, the first strategy mentioned above which incorporating silicon atom can be applied in designing a bipolar host material.

Carbazoles, possessing the advantage of high triplet energies up to 3 eV [34], have been mostly used as building blocks for the design of host materials. One commonly used host for phosphorescent emitters is 4,4′-bis(9-carbazolyl)-biphenyl (CBP); however, owing to the presence of a biphenyl group in the molecule, this material has a triplet energy of 2.56 eV [35], relatively lower than dopant materials for green or blue OLED applications.

Oxadiazole derivatives are among the most widely investigated electron-transporting materials for OLEDs because of their relatively high electron affinities. For example, the oxadiazole moiety, 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxdiazole (PBD), showed an electron affinity of 2.16 eV and was first used as an electron-transporting material in a bilayer OLED [36]; however, vacuum-evaporated amorphous PBD thin films have low stability (T_g = 60 °C) and crystallize during device operation. Therefore, enhancement of thermal and morphological stability of the oxadiazole moieties is still required.

In this study, we have prepared 2-(4-((4-(9H-carbazol-9-yl)phenyl)dimethylsilyl)phenyl)-5-phenyl-1,3,4-oxadiazole (**COHS**), a bipolar host material comprising carbazole and oxadiazole units. A silicon atom was introduced between the two units to disconnect their electronic communication and enhance their thermal properties. To investigate the role of the silicon atom, its analogous compound, 2-(4′-(9H-carbazol-9-yl)biphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (**COH**), was also prepared. Single-crystal X-ray molecular structures for both compounds were determined and the thermal-, photophysical- and electrochemical properties of these compounds were systematically investigated. Thereafter, green PHOLEDs using **COHS** and **COH** as bipolar host materials with Ir(ppy)$_3$ as a dopant material were fabricated and their efficiencies were reported.

2. Experimental

2.1. General information

All the experimental procedures were carried out under a dry nitrogen or argon atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled freshly over sodium benzophenone. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Fourier 300 MHz spectrometer, which was operated at 300.1 and 75.4 MHz, respectively. ^{1}H and ^{13}C NMR chemical shifts were measured in CDCl$_3$ and referenced to relative peaks of CHCl$_3$ (7.26 ppm for ^{1}H NMR) and CDCl$_3$ (77.16 ppm for ^{13}C NMR). The elemental analyses were performed using a Carlo Erba Instrument CHNS−O EA 1108 analyzer. The HR-MS analysis was performed by high sensitive LC/MS/MS$_n$ (n = 10) spectrometer (Thermo Fisher Scientific, LCQ Fleet Hyperbolic Ion Trap MS/MS$_n$ Spectrometer).

Cyclic voltammetry (CV) was performed in an electrolytic solution prepared using 0.1 M tetrabutyl ammonium hexafluorophosphate (NBu$_4$PF$_6$) at room temperature under an atmosphere of argon. For this purpose, CHI600E was used. Glassy carbon, platinum wire, and Ag/AgNO$_3$ (0.1 M) were used as working, counter, and reference electrodes, respectively. All the potentials were calibrated to the ferrocene/ferrocenium (Fc/Fc$^+$) redox

couple. 1,4-Dibromobenzene, carbazole, benzhydrazide, 4-benzoyl chloride, sodium bicarbonate, copper sulfate, potassium carbonate, phosphorus oxychloride, bis(pinacolato)diboron, potassium acetate, 1,4-dibromo-2,5-dimethylbenzene, [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) complex with dichloromethane, tetrakis(triphenylphosphine)palladium(0), n-BuLi (2.5 M solution in n-hexane), dimethyldichlorosilane, and sodium carbonate were purchased from Aldrich or TCI and used without further purification. The starting materials, 2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole (DPO-Br) [37], 9-(4-bromophenyl)carbazole (PC−Br) [5], 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2′-yl)phenyl)-9H-carbazole (PC-BE) [38] were prepared according to the previously reported procedures.

2.2. Synthesis

2.2.1. 2-(4-((4-(9H-carbazol-9-yl)phenyl)dimethylsilyl)phenyl)-5-phenyl-1,3,4-oxadiazole (COHS)

9-(4-bromophenyl)carbazole (PC−Br) (2.13 g, 6.6 mmol) in diethyl ether (40 mL) was stirred at 0 °C under dry argon atmosphere and treated with a solution of n-BuLi (2.9 mL, 2.5 M in n-hexane, 7.3 mmol). The resulting mixture was kept at 0 °C for 1 h, and then dichlorodimethylsilane (6.6 mL, 54.9 mmol) was added slowly. The reaction temperature was warm to room temperature and the reaction mixture was stirred for overnight. After the reaction, LiCl salts were filtered by canuula and reaction solvent and excess dichlorodimethlysilane in filtrate were removed under reduced pressure and stored in Ar atmosphere. In another flask, 2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole (DPO-Br) (2.22 g, 7.4 mmol) in dry THF (40 mL) was prepared and a 2.5 M solution of n-BuLi in n-hexane (2.9 mL, 7.3 mmol) was added dropwise at −78 °C. After stirring for 30 min, the previously prepared 9-[4-(chlorodimethylsilyl)phenyl]-9H-carbazole (PCS) in THF (10 mL) was added slowly at −78 °C. After addition, the reaction temperature was warm to room temperature and the reaction mixture was stirred for overnight. The reaction mixture was quenched by addition of distilled water, extracted with dichloromethane and washed with water. The combined organic layers were dried over MgSO$_4$ and filtered. The filtrate was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography using ethyl acetate/n-hexane (v/v = 1:4) as an eluent. The resulting white solid was dissolved in dichloromethane and evaporated slowly to give single crystals. Yield: 36%; ^{1}H NMR (300 MHz, CDCl$_3$, δ): 8.18–8.13 (m, 6H), 7.76 (t, J = 15.9 Hz, 4H), 7.6–7.53 (m, 5H), 7.48–7.38 (m, 4H), 7.31−7.26 (m, 2H), 1.58 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, δ): 142.9, 140.6, 138.8, 136.6, 135.7, 134.9, 131.8, 129.1, 126.9, 126.3, 126.1, 125.9, 124.5, 123.9, 123.4, 120.3, 120.0, 109.8, −2.46. HRMS: calculated for C$_{34}$H$_{27}$N$_3$OSi: 521.1923, Found: 521.1931. Elemental analysis: calculated for C$_{34}$H$_{27}$N$_3$OSi: C, 78.28; H, 5.22; N, 8.05, Found: C, 78.29; H, 5.23; N, 8.03.

2.2.2. 2-(4′-(9H-carbazol-9-yl)biphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (COH)

A mixture of 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2′-yl)phenyl)-9H-carbazole (PC-BE) (1.49 g, 4.0 mmol), 2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole (DPO-Br) (1.33 g, 4.4 mmol), tetrakis(triphenylphosphine)palladium (0.46 g, 0.4 mmol), and Na$_2$CO$_3$ (1.71 g, 16.0 mmol) in tetrahydrofuran (THF)/H$_2$O (v:v = 21 mL:7 mL) was stirred at 70 °C for overnight under argon atmosphere. After cooling to room temperature, the mixture was poured into distilled water and extracted with dichloromethane. The combined organic layers were dried over MgSO$_4$ and evaporated under reduced pressure. The crude product was purified by recrystallization in dichloromethane/n-hexane to