Synthesis and Carrier-transporting Properties of 5,10-Dihydro-5,5-dimethyl-10,10-diphenyl-1,9-diazasilanthrene

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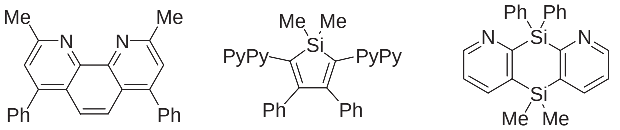
The title compound was synthesized and investigated as an electron-transporting and hole-blocking material for an organic electroluminescent (EL) device. EL efficiency of the phosphorescent device indicated a good performance of the hole-blocking ability of the compound. The maximum external quantum efficiency was recorded as 14.9% at a low current density of 0.03 mA cm^{-2}.

There has been considerable interest in new carrier-transporting materials for the research and development of organic EL devices. These materials are important for effective recombination between electrons and holes at the emitting layers.[1] Various electron-transporting materials with high electron affinities have been synthesized and investigated.[2] In addition, these materials have been employed to perform the hole-blocking function in EL devices using phosphorescent emitters.[3] 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) is one of the most useful substances.[4] Recently, silicon compounds, such as silole, have attracted considerable attention as emitting and carrier-transporting materials.[5] 2,5-Bis(2′,2″-bipyridin-6-yl)-1,1-dimethyl-3,4-diphenylsilole (PyPySPyPy) is well known as an electron-transporting material with a high-electron mobility.[5c,5d] However, silole compounds are not suitable for phosphorescent EL devices because they generally possess small HOMO–LUMO energies.[5a,5b] Therefore, as a new electron-transporting and hole-blocking material, we have synthesized 5,10-dihydro-5,5-dimethyl-10,10-diphenyl-1,9-diazasilanthrene (**1**) with a spiro-shaped structure. In this paper, we report the synthesis and properties of compound **1** and its application to the study of organic EL devices (Chart 1).

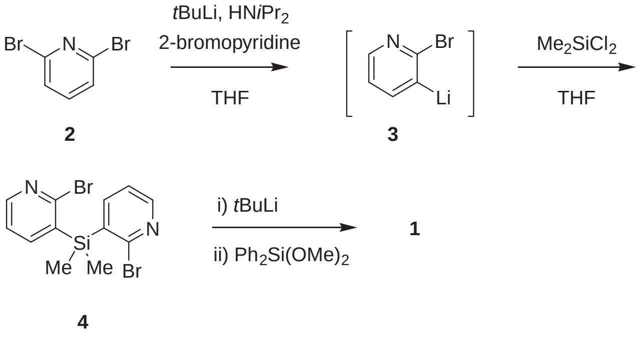


BCP PyPySPyPy **1**

(PyPy = 2,2′-bipyridin-6-yl)

Chart 1.

The synthesis of 5,10-dihydro-1,9-diazasilanthrene derivative **1** is shown in Scheme 1. Compound (**4**) was prepared with a yield of 37% by the silanization of dichlorodimethylsilane with lithium reagent (**3**); this reagent was obtained from 2,6-dibromopyridine (**2**) by a reported method.[6] Compound **1** was synthesized with a yield of 49% by lithiation with *tert*-butyl lithium, followed by silanization with diphenyldimethoxysilane. The product was purified by alumina column chromatography (ethyl acetate) and recrystallization from methanol to obtain colorless crystals.[7] It was sublimated at 210 °C under 10^{-3} Torr for use in an EL device. The absorption maximum of **1** was observed at 268 nm (log ε4.11) in dichloromethane, and it was blue-shifted from those of PyPySPyPy (386 nm)[5c] and BCP (312 nm (sh), 280 nm). The HOMO–LUMO energy of **1** was evaluated by the optical method as 3.9 eV. This value was larger than those of PyPySPyPy (2.7 eV)[5d] and BCP (3.5 eV). The cyclic voltammetry (CV) of **1** in DMF revealed an irreversible reduction wave. The peak potential ($E_{\rm pc}$) was recorded as −2.88 V vs Fc/Fc$^+$. The reduction potential was lower than that of BCP (−2.42 V); this indicates that the electron affinity of compound **1** is low.



Scheme 1.

Differential scanning calorimetry (DSC) was performed to investigate the thermal properties of compound **1**. The measurement revealed a glass transition at 28.6 °C, crystallization at 67.7 °C, and melting at 216.0 °C. The glass-transition temperature is lower than that of PyPySPyPy ($T_{\rm g} = 77$ °C).[5c] A single crystal of **1** obtained by sublimation was selected for X-ray crystallographic analysis.[8] The crystal structure is shown in Figure 1. The 5,10-dihydro-1,9-diazasilanthrene moiety in the crystal is planar. Functional groups, such as methyl and phenyl groups, are located at the top and bottom of the plane. The molecule crystallizes in monoclinic $P2_1/n$ with an independent molecule. Intermolecular N···H–C contact was observed in the crystal. The distance is 2.54 Å, and it is shorter than the sum of van der Waals radii (2.75 Å). The 5,10-dihydro-1,9-diazasilanthrene moieties interact with each other in the solid state.

In order to investigate the electron-transporting and hole-blocking abilities of compound **1**, a phosphorescent EL device was fabricated; ITO/TPD (50 nm)/Ir(ppy)$_3$:CBP (20 nm)/**1** (30 nm)/LiF (1 nm)/Al (70 nm) (device 1). *N*,*N*′-Diphenyl-

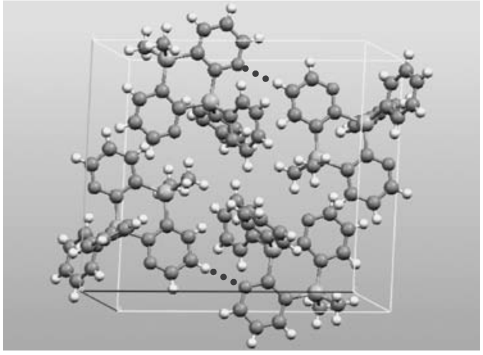


Figure 1. Crystal structure of compound **1**.

N,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD), *fac*-tris(2-phenylpyridine)iridium [Ir(ppy)$_3$], and 4,4′-*N*,*N*′-dicarbazolylbiphenyl (CBP) were used for the hole-transporting layer, emitter, and carrier-combination host, respectively. Compound **1** was used as an electron-transporting layer (ETL). In addition, other EL devices denoted by devices 2 and 3 were examined by using PyPySPyPy and BCP as the ETLs, respectively.

Figure 2a shows the current density–applied voltage characteristics of the EL devices. The current density of device 1 is lower than those of devices 2 and 3 within the measured voltage. In addition, it began to emit at an applied voltage of 4 V. This value was increased to a higher voltage than those observed for devices 2 and 3 (2.6 and 2.8 V, respectively). These results indicated that the electron-transporting ability of compound **1** is poor owing to the presence of 5,10-dihydro-1,9-diazasilanthrene. The emission spectra of devices 1 and 2 were consistent with that of device 3; this implies phosphorescence from the Ir(ppy)$_3$ emitters in the devices. The Commission Internationale de L'Eclairage (CIE) coordinates of devices 1–3 were (0.28, 0.63), (0.26, 0.60), and (0.24, 0.66), respectively.

Figure 2b shows a plot of the variation in the external quantum efficiency versus the current density. Below the current density of 10^2 mA cm^{-2}, the efficiency of device 1 is higher than those of devices 2 and 3; this indicates that more effective recombination occurs at the emitting layer of device 1. This result is attributed to the high hole-blocking ability of compound **1**, which is primarily due to its large HOMO–LUMO energy. Some properties of compound **1** are similar to those of BCP. On the other hand, the EL efficiency of device 2 is very low owing to the poor hole-blocking ability of PyPySPyPy. This is ascribable to its small HOMO–LUMO energy. For device 1, the maximum external quantum efficiency was recorded as 14.9% at a low current density of 0.03 mA cm^{-2}. When a high voltage was applied, the recombination balance between electrons and holes at the emitting layer was disordered because of the poor electron-transporting ability of compound **1**. Improvement in the electron-transporting ability is required to achieve more effective recombination at high voltages.

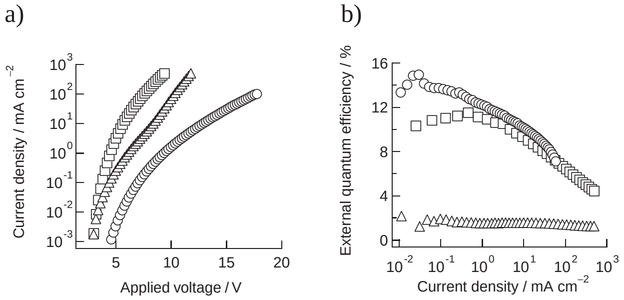


Figure 2. EL properties of ITO/TPD (50 nm)/Ir(ppy)$_3$:CBP (20 nm)/ETL (30 nm)/LiF (1 nm)/Al (70 nm); device 1 (○) ETL = **1**, device 2 (△) ETL = PyPySPyPy, device 3 (□) ETL = BCP: a) current density–applied voltage curves, b) EL efficiency–current density curves.

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7 Data for compound **1**: mp 212–213 °C; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.45 (s, 6H), 7.29–7.36 (m, 8H), 7.68 (dd, 4H, $J = 7.4$, 1.6 Hz), 7.91 (dd, 2H, $J = 7.8$, 1.8 Hz), 8.88 (dd, 2H, $J = 4.8$, 1.8 Hz); ^{13}C NMR (CDCl$_3$, 50 MHz) δ −0.38, 122.8, 127.7, 129.5, 134.0, 136.2, 139.3, 140.3, 150.8, 167.9; MS m/z (%) 394 (M$^+$, 100), 316 (16). Found: C, 73.34; H, 5.50; N, 7.13%. Calcd for $C_{24}H_{22}N_2Si_2$: C, 73.05; H, 5.62; N, 7.10%.

8 X-ray crystallographic data for **1**: $C_{24}H_{22}N_2Si_2$, M_r 394.62, colorless block, monoclinic, space group $P2_1/n$, $a = 8.9833(7)$, $b = 14.462(1)$, $c = 16.709(1)$ Å, $\beta = 97.189(4)°$, $V = 2153.7(3)$ Å^3, $Z = 4$, $D_{\rm calcd} = 1.217$ g cm^{-3}, $F(000) = 832$, $\mu = 1.76$ cm^{-1}. The final values of $R_1 = 0.075$, GOF = 1.76, and max./min. residual electron density 0.48/−0.26 e Å^{-3} were obtained for 4880 unique reflections ($I > 2\sigma(I)$). CCDC 286658.

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