Synthesis and Properties of 9,9′-Diaryl-4,5-diazafluorenes.
A New Type of Electron-Transporting and Hole-Blocking Material in EL Device

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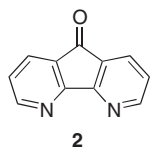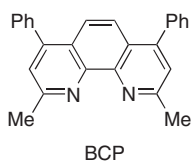Yosuke Matsushita,[†] Shigeki Naka,[†] Hiroyuki Okada,[†] and Hiroyoshi Onnagawa[†]
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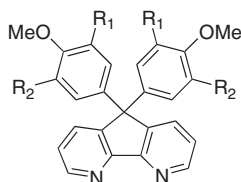
The title compounds were prepared and investigated for electron-transporting and hole-blocking materials in organic electroluminescent (EL) devices. EL efficiencies of the phosphorescent devices indicated high performance of hole-blocking ability in the compounds. A maximum external efficiency of 18% was achieved and a maximum power luminous efficiency was over $45\,Lm\,W^{-1}$.

Studies on carrier-transporting materials have been research subjects of great interest from organic EL devices since effective recombination balance between electrons and holes at emitting layers afford high efficiency and long lifetime of luminescence.[1] A variety of materials with high electron affinity have been synthesized and investigated for electron-transporting layers.[2–7] Recently, electron-transporting materials have been also applied for hole-blocking layers in EL devices using phosphorescent materials such as iridium and platinum complexes to afford high quantum efficiencies.[8–13] 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) is one of the most powerful candidates as an electron-transporting and hole-blocking material and that afforded external quantum efficiencies of 8.0 and 13.7% in combination with *fac*-tris(2-phenylpyridine)iridium [Ir(ppy)$_3$] in 4,4′-*N,N*′-dicarbazolylbiphenyl (CBP) host.[8,9] In this context, we have now prepared 9,9′-diaryl-4,5-diazafluorenes (**1a–c**) as a new type of the materials with high electron affinity due to the bipyridyl moiety and the spiro structure. EL devices fabricated by diazafluorene **1a** and Ir(ppy)$_3$ also demonstrated high external quantum efficiency. We report here the preparation and properties of **1a–c** and the application of **1a** for the EL devices.

4,5-Diazafluoren-9-one (**2**) was obtained by oxidation of 1,10-phenanthroline with KMnO$_4$ in a KOH solution.[14] 9,9′-Diaryl-4,5-diazafluorenes **1a–c** were prepared in 70–90% yields by the Friedel–Crafts reaction[15] of **2** with three types of anisole (10 mol equiv.) in the presence of H$_2$SO$_4$ (10 mol equiv.) at 65 °C. The molecular structures were determined by spectral data and elemental analyses. Compounds **1** were obtained as colorless crystals (**1a**: mp 275–276 °C, **1b**: mp 208–209 °C, **1c**: mp 211–212 °C). The melting point of **1a** is similar to that of BCP (mp 279–283 °C) and those of **1b** and **1c** are slightly lower. The absorption maxima of **1** were observed around 323 and 316 nm in dichloromethane (Table 1) and those were shifted to longer wavelength than those of BCP. Influence of introduction of methoxy groups was not observed in the UV spectra of **1**. According to the absorption edges, the HOMO–LUMO energies of **1** were evaluated as 3.5–3.6 eV. These values are comparable to that of BCP. The cyclic voltammograms (CV) of **1** in DMF showed reversible one-electron redox waves. The half-wave reduction potentials are listed in Table 1. Although the reduction potentials of **1** are slightly lower than that of BCP, it was found that the energy levels of LUMOs are very close to that of BCP. The decrease of electron affinity in compound **1c** is due to substitution of methoxy groups. The MNDO-PM3 calculations indicated that compound **1a** has a lower HOMO energy and a slightly higher LUMO energy than BCP (HOMO/eV: **1a**, −9.37; BCP, −8.80, LUMO/eV: **1a**, −0.77; BCP, −0.81).[16] The results of the UV and CV analyses are consistent with the calculations.

Table 1. Absorption maxima[a] and edges[a] and half-wave reduction potentials[b] of **1a–c**

Compound	λ_{max} (log ε)/nm	λ_{edge}/eV	$E_{1/2}^{red}$/V
1a	324 (4.05), 316 (4.01)	3.6	−2.48
1b	323 (3.96), 316 (3.97)	3.5	−2.48
1c	323 (3.99), 316 (3.98)	3.6	−2.54
BCP	312sh (4.10), 280 (4.63)	3.5	−2.39[c]

[a]In CH$_2$Cl$_2$. [b]0.1 M *n*-Bu$_4$NClO$_4$ in DMF, Pt electrode, scan rate 500 mV s^{-1}, V vs Fc/Fc$^+$. [c]E_{pc} + 0.03 V.

In order to investigate electron-transporting and hole-blocking ability of the diazafluorene derivatives, EL devices using **1a** were fabricated as shown in Figure 1a. *N,N*′-Diphenyl-*N,N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD), Ir(ppy)$_3$, and CBP were used for a hole-transporting layer, an emitter, and a carrier combination host, respectively. For the cathode, an Al electrode with a LiF buffer layer was employed. Four types of electron-transporting layer (ETL) were examined (devices 1–4). The ETL of device 1 was composed of only compound **1a**. The ETLs of devices 2 and 3 were formed in the combination of **1a** with tris(8-hydroxyquinoline)aluminum (Alq$_3$) and 2,5-bis(bipyridyl)-1,1′-dimethyl-3,4-diphenylsilole (PyPySPyPy),[17] respectively. BCP was employed for the ETL of device 4 as a reference.

Figure 1b shows current-voltage (*J-V*) characteristics in the EL devices. The current density of device 1 is lower than that of

device 4 in the range of the applied voltage, indicating that the electron-transporting ability of **1a** is inferior to that of BCP. The current density of the EL device is slightly improved in devices 2 and 3. All of the devices began to emit at an applied voltage of 3 V. The emission spectra from devices 1–3 were coincident with that from device 4, implying phosphorescence from the Ir(ppy)$_3$ emitters in the devices. Devices 1–4 had the Commission Internationale de L'Eclairage (CIE) coordinates of (0.28, 0.64), (0.29, 0.51), (0.27, 0.61), and (0.24, 0.66), respectively.

a)

ITO/TPD (500 Å)/4.8%-Ir(ppy)$_3$:CBP (200 Å)/ETL (300 Å)/LiF (10 Å)/Al (700 Å).

   device 1 (○) : ETL = **1a** (300 Å)
   device 2 (□) : ETL = **1a** (100 Å) + Alq$_3$ (200 Å)
   device 3 (△) : ETL = **1a** (100 Å) + PyPySPyPy (200 Å)
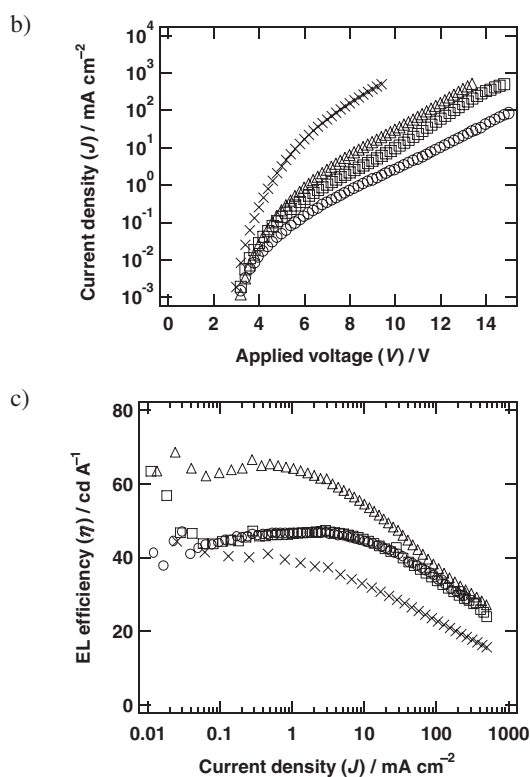   device 4 (×) : ETL = BCP (300 Å)

b)

c)

Figure 1. EL devices fabricated by Ir(ppy)$_3$ and **1a**: a) EL structures, b) current density-applied voltage curves, c) EL efficiency-current density curves.

Figure 1c shows external EL efficiency (η) on the current density (J). The efficiency of device 1 is higher than that of device 4 within the measured current density, indicating more effective recombination at the emitting layer of device 1. Compound **1a** is superior to BCP as a hole-blocking material. The EL efficiency of device 2 is not different from that of device 1. On the other hand, significant increase of the efficiency was observed in device 3. Thus, the efficiency is 1.5 times higher than that of device 4. A maximum external efficiency reached

to 18% in device 3 and this value is close to the theoretical limit about 20% from simple classical optics.[18] In addition, the maximum power luminous efficiency of device 3 was over $45\,\mathrm{Lm\,W^{-1}}$ although the device was driven at the relatively high voltage.

In summary, we designed and prepared 9,9′-diaryl-4,5-diazafluorenes **1** as electron-transporting and hole-blocking materials. The EL devices using **1a** indicated the high performance of hole-blocking ability in comparison to BCP. Improvement of the electron-transporting ability is expected to provide higher performance of phosphorescent EL devices. EL devices with compounds **1b**, **c** are currently under study.

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