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SYNTHESIS AND ELECTRON-TRANSPORTING ABILITY OF 3,6-DIARYL-4,5-DIAZAFLUORENES MODIFIED USING DIRECT ARYLATION

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Abstract –A modification of 4,5-diazafluorene by using direct arylation was performed in order to synthesize a new type of electron-transporting materials in the study of organic electroluminescent (EL) devices. The title compounds possessed high glass transition temperatures over 100 ºC. The phosphorescent EL performance was improved by the increasing electron-transporting ability arising from the extension of the π-electron system.

There has been considerable interest in new carrier-transporting materials with regard to the research and development of organic electroluminescent (EL) devices. These materials are important for the effective recombination between electrons and holes in the emitting layers.[1] Various electron-transporting materials with high electron affinities have been synthesized and investigated.[2] 4,5-Diazafluorene is of interest as an electron-transporting and/or electron-trapping moiety in the study of functional materials.[3–5] Recently, we synthesized 9,9-bis(4-methoxyphenyl)-9*H*-4,5-diazafluorene (**1**) as a new electron-transporting material.[3] A phosphorescent EL device using compound (**1**) demonstrated a high EL efficiency because of its high hole-blocking ability. However, the electron-transporting ability of compound (**1**) was not as high as that of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP).[6] An EL device using both compound (**1**) and PyPySPyPy[7] exhibited a high maximum external quantum efficiency of 18% due to the improved electron injection into the phosphor. On the other hand, the direct arylation and alkylation of the 2,2'-bipyridyl moieties are useful to produce unique building blocks in materials science.[8–10] These reactions have been investigated for substances such as 2,2'-bipyridyl (bipy), 1,10-phenanthroline (phen), and 2,2',6',2''-terpyridine (terpy).[11] Direct arylation is able to introduce two phenyl groups into the substances, and the yields of diphenyl (dp) products have been reported as 35%

(dp-bipy), 70% (dp-phen), and 21% (dp-terpy). In order to improve the electron-transporting ability of compound (**1**), direct arylation was used for the extension of the π-electron system. We examined reactions of compound (**1**) with aryl lithium reagents, and it was followed by its oxidation with manganese dioxide (MnO_2) to obtain 3,6-diaryl-4,5-diazafluorenes (**2**). These compounds possessed high glass transition temperatures and high electron affinities. In this paper, we report the direct arylation of compound (**1**) to produce compounds (**2**) and their applications in the study of phosphorescent EL devices (Chart 1).

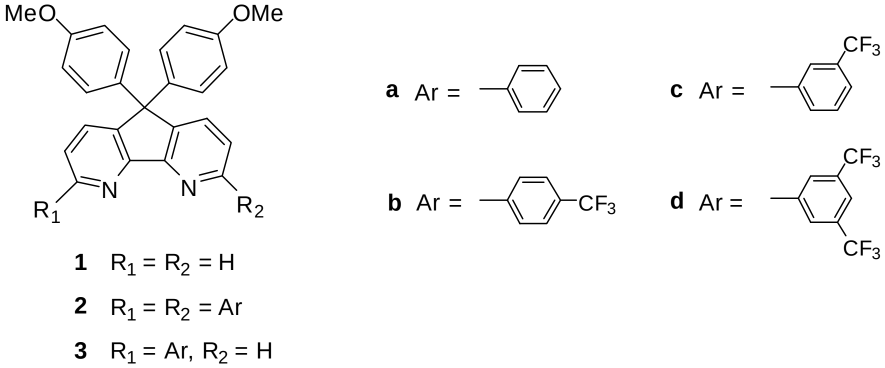

Chart 1

Compound (**1**) reacted with 3.5 molar equiv. of phenyllithium (PhLi) in toluene, and this was followed by an oxidation reaction with MnO_2 to afford compound (**2a**) and monosubstituted compound (**3a**)[12] with yields of 3% and 42%, respectively. A reaction involving 10 molar equiv. of PhLi and compound (**1**) resulted in a similar yield. Thereafter, compound (**2a**) was obtained with a yield of 55% by the direct arylation of **3a** using 1.2 molar equiv. of PhLi. For the purpose of preparing derivatives with high electron affinities, the introduction of trifluoromethyl-substituted phenyl groups was examined. Compounds (**3b**)–(**3d**)[12] were obtained with yields of 43–63% and compounds (**2b**)–(**2c**) were prepared with yields of 32% and 39% by using 1.2 molar equiv. of the corresponding aryllithium reagents. However, compound (**2d**) was not obtained from compound (**3d**) owing to steric hindrance among the 3,5-bis(trifluoromethyl)phenyl groups. Compounds (**2a**)–(**2c**) were purified by sublimation to afford colorless crystals.[13] The UV spectra of compounds (**2a**)–(**2c**) in dichloromethane exhibited absorption bands in the same wavelength region due to the extended π-conjugation. The maxima are summarized in Table 1. These maxima are red-shifted as compared to the maximum of **1**. The HOMO–LUMO energy gaps of **2a**–**2c** were evaluated to be 3.3 eV from the absorption edges. This value is smaller than that of **1**. Cyclic voltammetry (CV) for compounds (**2**) revealed the presence of reversible reduction waves. The half-wave reduction potentials indicate that the introduction of (trifluoromethyl)phenyl groups increased the electron affinities of the diazafluorene moieties.

Table 1. Absorption maxima[a] and half-wave reduction potentials[b] of **2**

Compound	λ_{max} (log ε)/nm	λ_{edge}/eV	$E_{1/2}^{red}$/V
2a	348 (4.32)	3.3	−2.45
2b	347 (4.34)	3.3	−2.32
2c	346 (4.31)	3.3	−2.34
1	324 (4.05)	3.6	−2.48

[a] In CH_2Cl_2. [b] 0.1 M n-Bu_4NClO_4 in DMF, Pt electrode, scanning rate 500 mV s^{-1}, V vs. Fc/Fc^+.

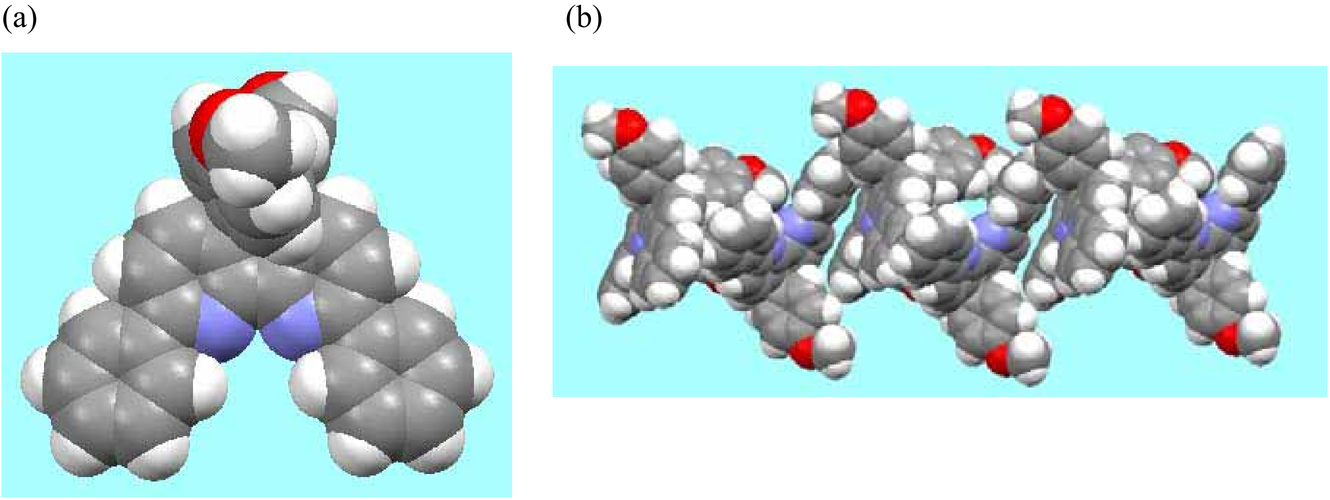

Figure 1. Crystal structure of **2a**: (a) molecular structure; (b) molecular packing.

Figure 1a shows the molecular structure of compound (**2a**) obtained from an X-Ray crystallographic analysis.[14] The molecule has extended π-conjugation with dihedral angles of 13.5° and 15.9° between the diazafluorene moiety and the phenyl groups. The crystal structure is shown in Figure 1b. The molecules are stacked along the *a* axis, and the overlap between the diazafluorene moieties leads to effective electron transport. Differential scanning calorimetry (DSC) was performed in order to investigate the thermal properties of compounds (**2**) (Table 2). Figure 2 shows the DSC profiles of **2b**. The first heating profile exhibits a first melting point of 238.9 °C, a crystallization temperature of 241.8 °C, and a second melting point of 245.0 °C. After cooling, the second heating profile only reveals a glass transition at 130.8 °C, indicating that this compound has a thermal stability comparable to that of the amorphous state. Compound (**2c**) afforded profiles similar to those of compound (**2b**). Since compound (**2a**) exhibited a single melting point, the observations of two melting points for **2b** and **2c** were attributed to the phase transition based on the trifluoromethyl groups. Compounds (**2a**) and (**2b**) possessed high glass transition temperatures over 100 ºC.

Table 2. DSC data for compounds (**2**)

Compound	T_g / ºC	T_{m1} / ºC	T_c / ºC	T_{m2} / ºC
2a	123.8	260.4	–	–
2b	130.8	238.9	241.8	245.0
2c	96.1	204.2	206.5	233.3

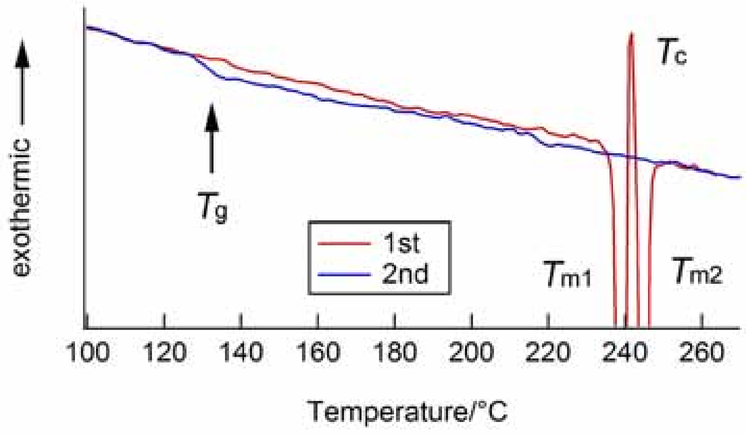

Figure 2. DSC profiles of compound (**2b**).

In order to investigate the electron-transporting properties of compounds (**2**), a phosphorescent EL device using compound (**2b**) was fabricated–ITO/TPD (50 nm)/Ir(ppy)$_3$:CBP (20 nm)/**2b** (30 nm)/LiF (1 nm)/Al (70 nm) (device 1). TPD, Ir(ppy)$_3$, and CBP were used for a hole-transporting layer, an emitter, and a carrier combination host, respectively.^{7} In addition, another EL device denoted as device 2 was examined by using BCP as the electron-transporting layer (ETL). Figure 3 shows a plot of the external quantum efficiency versus the current density. The efficiency of device 1 is higher than that of device 2. This result is attributed to the higher hole-blocking ability of compound (**2b**) as compared to that of BCP. The hole-blocking ability of **2b** resulted in the effective recombination of carriers in the emitting layer. The EL performance of device 1 (1000 cd m^{-2} at 9.4 V) was improved as compared to that of a device using compound (**1**) (1000 cd m^{-2} at 13.4 V), indicating an increasing electron injection to the Ir(ppy)$_3$ emitter. This result is due to the higher electron-transporting ability of compound (**2b**) as well as the increasing electron affinity arising from the π-extension of the diazafluorene moiety modified by direct arylation. The application of compounds (**2a**) and (**2c**) in the study of EL devices is under progress.

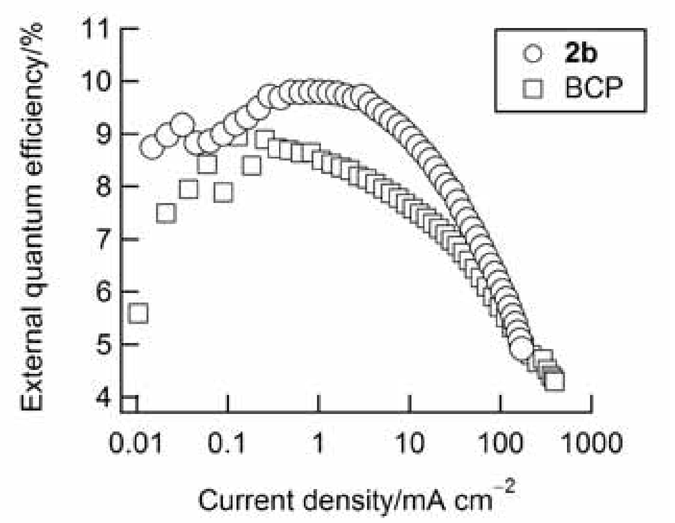

Figure 3. EL efficiency–current density curves; device 1 with **2b** (○), device 2 with BCP (□).

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REFERENCES AND NOTES

1. a) C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913. b) C. Adachi, S. Tokito, T. Tsutsui, and S. Saito, *Jpn. J. Appl. Phys.*, 1988, **27**, L713.
2. a) A. P. Kulkarni, C. J. Tonzola, A. Babel, and S. A. Jenekhe, *Chem. Mater.*, 2004, **16**, 4556. b) G. Hughes and M. R. Bryce, *J. Mater. Chem.*, 2005, **15**, 94.
3. K. Ono, T. Yanase, M. Ohkita, K. Saito, Y. Matsushita, S. Naka, H. Okada, and H. Onnagawa, *Chem. Lett.*, 2004, **33**, 276.
4. Z. Liu, F. Wen, and W. Li, *Thin Solid Films*, 2005, **478**, 265.
5. K.-T. Wong, R.-T. Chen, F.-C. Fang, C. Wu, and Y.-T. Lin, *Org. Lett.*, 2005, **7**, 1979.
6. H. Nakada, Eur. Patent 564224 (1993) (*Chem. Abstr.*, 1994, **120**, 204088r).
7. 2,5-Bis(2',2''-bipyridin-6-yl)-1,1-dimethyl-3,4-diphenylsilole (PyPySPyPy); *N*,*N*'-diphenyl-*N*,*N*'-bis-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD); *fac*-tris(2-phenylpyridine)iridium [Ir(ppy)$_3$]; 4,4'-bis(carbazol-9-yl)-1,1'-biphenyl (CBP).
8. a) C. O. Dietrich-Buchecker and J. P. Sauvage, *Tetrahedron Lett.*, 1983, **24**, 5091. b) G. Bidan, B.

Divisia-Blohorn, M. Lapkowski, J.-M. Kern, and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1992, **114**, 5986.

9. T. Yamamoto, K. Anzai, T. Iijima, and H. Fukumoto, *Macromolecules*, 2004, **37**, 3064.
10. J. J. Moore, J. J. Nash, P. E. Fanwick, and D. R. McMillin, *Inorg. Chem.*, 2002, **41**, 6387.
11. C. O. Dietrich-Buchecker, P. A. Marnot, and J. P. Sauvage, *Tetrahedron Lett.*, 1982, **23**, 5291.

12. Elemental analyses for compounds (**3**). **3a**: Anal. Calcd for $C_{31}H_{24}N_2O_2$: C, 81.56; H, 5.30; N, 6.14. Found: C, 81.58; H, 5.23; N, 6.32. **3b**: Anal. Calcd for $C_{32}H_{23}N_2O_2F_3$: C, 73.27; H, 4.42; N, 5.34. Found: C, 73.37; H, 4.24; N, 5.54. **3c**: Anal. Calcd for $C_{32}H_{23}N_2O_2F_3$: C, 73.27; H, 4.42; N, 5.34. Found: C, 73.27; H, 4.33; N, 5.31. **3d**: Anal. Calcd for $C_{33}H_{22}N_2O_2F_6$: C, 66.89; H, 3.74; N, 4.73. Found: C, 66.81; H, 3.53; N, 4.67.
13. Data for compounds (**2**). **2a**: white solid. mp 271–272 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.76 (s, 6H, Me), 6.80 (d, 4H, J = 8.8 Hz), 7.18 (d, 4H, J = 8.8 Hz), 7.41-7.54 (m, 6H), 7.76 (d, 2H, J = 8.0 Hz), 7.82 (d, 2H, J = 8.0 Hz), 8.23 (d, 4H, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 55.2, 59.6, 113.9, 120.6, 127.4, 128.6, 128.9, 129.0, 134.1, 135.9, 139.1, 145.3, 157.6, 157.9, 158.7. IR (KBr) 1605, 1570, 1508, 1460, 1373, 1292, 1250, 1179, 1024, 829, 747, 693 cm^{-1}. MS (EI) *m/z* 532 (M^+, 100). Anal. Calcd for $C_{37}H_{28}N_2O_2$: C, 83.43; H, 5.30; N, 5.26. Found: C, 83.52; H, 5.24; N, 5.29. **2b**: white solid. mp 251–252 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.77 (s, 6H, Me), 6.81 (d, 4H, J = 8.9 Hz), 7.17 (d, 4H, J = 8.9 Hz), 7.76-7.90 (m, 8H), 8.33 (d, 4H, J = 8.2 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 55.3, 59.9, 114.0, 121.1, 124.2 (q, J = 272.1 Hz), 125.6 (q, J = 3.6 Hz), 127.6, 128.9, 130.9 (q, J = 32.3 Hz), 134.4, 135.5, 142.3, 146.3, 156.5, 157.6, 158.9. IR (KBr) 1616, 1570, 1510, 1458, 1325, 1254, 1177, 1125, 1071, 1034, 1015, 822, 596 cm^{-1}. MS (EI) *m/z* 668 (M^+, 100). Anal. Calcd for $C_{39}H_{26}N_2O_2F_6$: C, 70.06; H, 3.92; N, 4.19. Found: C, 70.05; H, 3.86; N, 4.16. **2c**: white solid. mp 209–210 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.78 (s, 6H, Me), 6.81 (d, 4H, J = 8.8 Hz), 7.17 (d, 4H, J = 8.8 Hz), 7.62-7.73 (m, 4H), 7.79 (d, 2H, J = 8.1 Hz), 7.88 (d, 2H, J = 8.1 Hz), 8.45 (m, 4H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 55.3, 59.9, 114.1, 121.1, 124.2 (q, J = 3.7 Hz), 124.2 (q, J = 272.5 Hz), 125.8 (q, J = 3.6 Hz), 128.9, 129.2, 130.8, 131.1 (q, J = 30.5 Hz), 134.6, 135.4, 139.7, 146.3, 156.6, 157.4, 158.9. IR (KBr) 1607, 1574, 1510, 1337, 1298, 1256, 1175, 1130, 1073, 1030, 837, 808, 700 cm^{-1}. MS (EI) *m/z* 668 (M^+, 100). Anal. Calcd for $C_{39}H_{26}N_2O_2F_6$: C, 70.06; H, 3.92; N, 4.19. Found: C, 70.32; H, 3.81; N, 4.24.
14. X-Ray crystallographic data for **2a**: $C_{37}H_{28}N_2O_2$, M_r = 532.64, colorless prism, monoclinic, space group *C2/c*, a = 29.868(6), b = 9.729(2), c = 19.917(4) Å, β = 103.446(4)°, V = 5628(1) $Å^3$, Z = 8, D_{calcd} = 1.257 g cm^{-3}, $F(000)$ = 2240, μ = 0.78 cm^{-1}. The final values of R_1 = 0.086, GOF = 1.38, and max./min. residual electron density 0.27/−0.25 e $Å^{-3}$ were obtained for 6387 unique reflections ($I > 2\sigma(I)$). CCDC 603473.