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SYNTHESIS AND LUMINESCENT PROPERTIES OF BIS(FLUOREN-9-YLIDENEMETHYL)AROMATICS: GREEN AND RED MATERIALS IN ORGANIC ELECTROLUMINESCENT DEVICES

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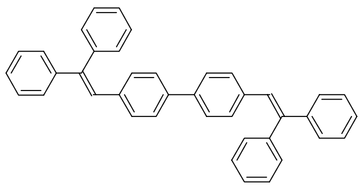
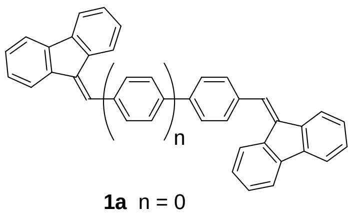
Abstract – Derivatives of 4,4'-bis(2,2-diphenylvinyl)biphenyl (DPVBi) were prepared and investigated for application in green and red fluorescent emitters in organic electroluminescent (EL) devices. Although the green emitter showed yellowish green electroluminescence, a series of π-conjugated compounds revealed the potential for a red-green-blue (RGB) fluorescent system.

The study of luminescent properties and redox behaviors of π-conjugated compounds has attracted considerable research interest in the development of organic EL devices.[1–5] Hence, π-conjugated polymers, such as poly(*p*-phenylenevinylene) (PPV),[1] poly(*p*-phenylene),[2] polyfluorene,[3] and polythiophene,[4] have been investigated. In particular, many derivatives of PPV were prepared and used for emitting or carrier-transporting materials in EL devices. With respect to this, distyrylbenzene derivatives and analogs have also been synthesized and studied as small components of PPV derivatives.[5] It is well known that DPVBi exhibits strong blue fluorescence and has been employed as an EL emitter.[5a] In addition, we recently identified that benzene-fused distyrylbenzene (**1a**)[5b] shows green fluorescence in the solution and its thiophene analog (**2a**) shows red fluorescence. Therefore, we have designed and synthesized DPVBi derivatives (**1b**) and (**2b**) in order to prepare a red-green-blue (RGB) fluorescent system for full color display, and we investigated their luminescent properties and redox behaviors. In this study, we report the electron properties of **1** and **2** and the application of **1b** and **2b** to the EL emitters.

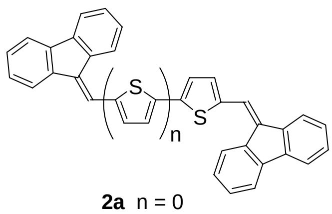
Compounds (**1b**) and (**2b**) were prepared by the Wittig reaction[6] of 9*H*-fluoren-9-ylidenetriphenylphosphorane[7] with the corresponding dicarbaldehydes.[8] These compounds were purified by sublimation under reduced pressures. The structural determination was



DPVBi



1a n = 0
1b n = 1



2a n = 0
2b n = 1

performed by spectral data and elemental analyses.[9] Compounds (**1**) were obtained as yellow crystals (**1a**: mp 220–221 ºC, **1b**: mp 269–270 ºC) and thiophene analogs (**2**) were obtained as red crystals (**2a**: mp 187–188 ºC, **2b**: mp 235–236 ºC). The maxima observed in the absorption and fluorescence spectra of **1** and **2** in dichloromethane are listed in Table 1. The absorption maxima of **1** were observed around 366 nm, while **2a** showed the maximum at 437 nm. The maximum of **2b** is red-shifted by 18 nm from that of **2a**. The emission maxima of **2** are also shifted to longer wavelengths compared to those of **1**. These results indicate that compounds (**2**) possess extended π-conjugation due to the improved planarity of these molecules. The maximum of **1b** is blue-shifted from that of **1a** by adding to the central ring. On the other hand, the emission maximum of **2b** is red-shifted from that of **2a**. Figure 1 displays the fluorescence spectra of **1b**, **2b**, and DPVBi, which occupy green, red, and blue emission regions, respectively.

Table 1. Absorption and emission maxima of **1** and **2**

Compound	λ_{abs}/nm (log ε)^a	λ_{em}/nm^a	λ_{EL}/nm
1a	366 (4.39)	504	–
1b	367 (4.60)	472	565
2a	437 (4.46)	546	–
2b	455 (4.64)	565	627, 613
DPVBi	350 (4.77)	442	479, 452

^{a}In CH_2Cl_2.

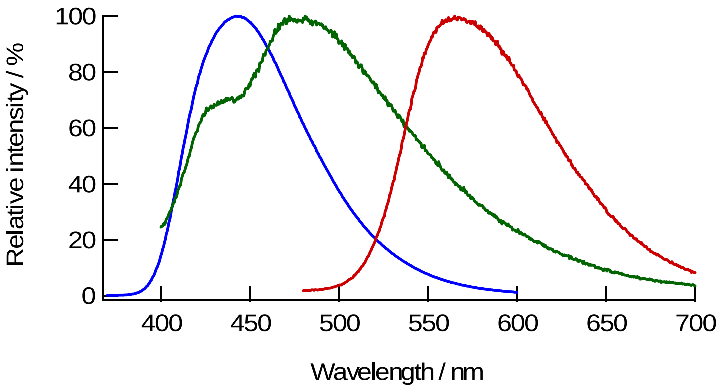


Figure 1. Fluorescence spectra of **1b** (green), **2b** (red), and DPVBi (blue).

The cyclic voltammetry (CV) of **1** and **2** in dichloromethane showed irreversible oxidation waves and reversible or irreversible reduction waves (Table 2). The oxidation potentials of **1** are similar to that of DPVBi. The reduction potentials of **1** were observed around −2.0 V vs Fc/Fc^+. These results indicate that the fluorene moieties lead to the lower LUMO energies. In addition, the oxidation potentials of **2** are lower than those of **1**, indicating that the HOMO energies of **2** are based on the thiophene moieties. Compounds (**1**) and (**2**) are amphoteric redox systems.

Table 2. CV data of **1** and **2**[a]

Compound	E_{pa}^{ox}/V[b]	$E_{1/2}^{red}/V$
1a	+0.98	−1.89
1b	+1.11	−2.06[c]
2a	+0.78	−1.73
2b	+0.55	−1.75
DPVBi	+0.91	–

[a] 0.1 M n-Bu_4NBF_4 in CH_2Cl_2, Pt electrode, scanning rate 100 mV s^{-1}, V vs Fc/Fc^+. [b] Irreversible wave. [c] Calculated as E_{pc}^{red} + 0.03 V.

A single crystal of **1b** obtained by recrystallization from AcOEt–CH_2Cl_2 was selected for X–Ray crystallographic analysis.[10] The crystal structure is shown in Figure 2. The biphenyl moiety in the crystal is planar, and it twists with the dihedral angle of 59.0° from the plane of the two fluoren-9-ylidene groups. The molecule crystallizes in triclinic $P-1$. Intermolecular C–H···π contacts were observed between the biphenyl and fluoren-9-ylidene groups to form a molecular stacking. Since DPVBi has diphenylvinyl groups instead of fluoren-9-ylidene groups, similar C–H···π contacts were not formed. The planar and rigid structure of a fluoren-9-ylidene group led to the intermolecular C–H···π contacts, resulting in a molecular aggregation.

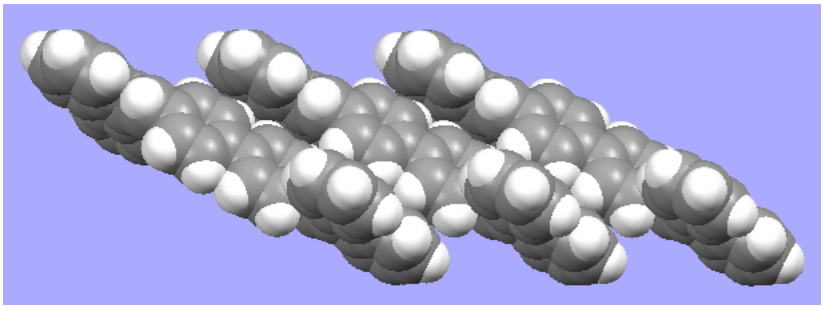


Figure 2. Molecular packing of compound (**1b**).

Organic EL devices using **1b**, **2b**, and DPVBi as fluorescent emitters (EM) were fabricated, as shown in Figure 3a. *N*,*N*'-Diphenyl-*N*,*N*'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were used as the hole- and electron-transporting layers, respectively. An Al electrode with a LiF buffer layer was employed as the cathode. Figure 3b exhibits current density vs voltage (*J*–*V*) characteristics in the EL devices. The current density of device 2 is higher than those of devices 1 and 3. This result may be related to the amphoteric redox property of **2b** in the CV study. Devices 1–3 began to emit at applied voltages of 3.8, 3.0, and 3.6 V, respectively. Figure 3c demonstrates the external quantum efficiency (η) against the current density (*J*). Although the efficiency of devices 1 and 2 is almost constant within the measured current density, the values are lower by approximately one order of magnitude than that of device 3. This may be attributed to the molecular aggregation as explained in the X-Ray crystallographic analysis.

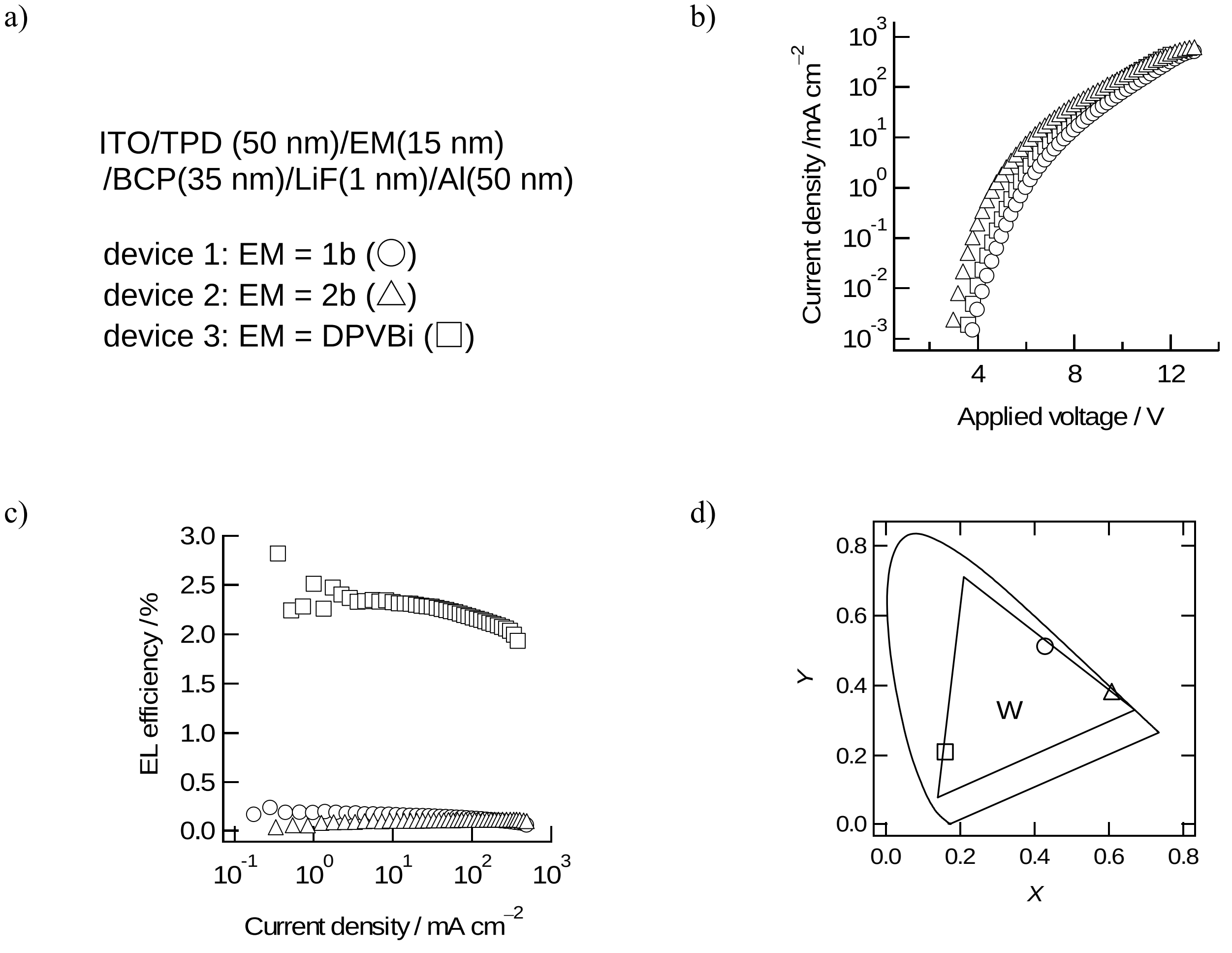


Figure 3. EL characteristics: a) structures of devices 1–3, b) current density (*J*)–applied voltage (*V*) curves, c) external quantum efficiency (η)–current density (*J*) curves, d) CIE coordinates.

The EL spectra from devices 1–3 were observed with the emission maxima listed in Table 1. The EL maxima move to longer wavelengths from the maxima observed in the fluorescence spectra due to the molecular aggregation. Since the red-shift of **1b** (93 nm) is larger than those of **2b** and DPVBi (62, 37 nm), the Commission Internationale de L'Eclairage (CIE) coordinates of device 1 are in the yellowish green region. Devices 1–3 had CIE coordinates of (0.43, 0.51), (0.61, 0.38), and (0.16, 0.21), respectively (Figure 3d). However, these results indicated that the DPVBi derivatives have potential application as an RGB fluorescent system. The optimization of the RGB fluorescent system and improvement of the EL efficiency are currently under study.

ACKNOWLEDGEMENTS

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9. Data for **1b** and **2b** as follows. **1b**: ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.10 (t, 2H, J = 7.6 Hz), 7.33 (t, 2H, J = 7.6 Hz), 7.34 (t, 2H, J = 7.6 Hz), 7.39 (t, 2H, J = 7.6 Hz), 7.73 (m, 12H), 7.80–7.82 (m, 6H). MS m/z (rel intensity) 506 (M$^+$, 100), 252 (36). Found: C, 95.01; H, 5.35%. Calcd for $C_{40}H_{26}$: C, 94.83; H, 5.17%. **2b**: ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.24 (t, 2H, J = 7.8 Hz), 7.30 (d, 2H, J = 3.8 Hz), 7.32 (t, 2H, J = 7.5 Hz), 7.36–7.38 (m, 4H), 7.42 (d, 2H, J = 3.8 Hz), 7.56 (s, 2H), 7.71 (d, 2H, J = 7.3 Hz), 7.74 (d, 2H, J = 7.5 Hz), 7.75 (d, 2H, J = 7.6 Hz), 8.31 (d, 2H, J = 7.8 Hz). MS m/z (rel intensity) 518 (M$^+$, 100), 258 (19). Found: C, 83.40; H, 4.10%. Calcd for $C_{36}H_{22}S_2$: C, 83.36; H, 4.28%.
10. X-Ray crystallographic data for **1b**: $C_{40}H_{26}$, M_r = 506.65, yellow prism, triclinic, space group $P-1$, a = 7.589(1), b = 9.0987(9), c = 11.063(2) Å, α = 66.19(2)°, β = 76.07(2)°, γ = 65.07(2)°, V = 631.4(2) Å^3, Z = 1, D_{calcd} = 1.332 g cm^{-3}, $F(000)$ = 266, μ = 0.75 cm^{-1}. The final values of R_1 = 0.071, GOF = 1.29, and max./min. residual electron density 0.21/−0.24 e Å^{-3} were obtained for 2802 unique reflections ($I > 2\sigma(I)$). CCDC 296446.