Novel Emitting Materials for Organic Electroluminescent Device: 1-Aryl-2,5-di(2-thienyl)pyrrole Derivatives Having an Electron-withdrawing Group

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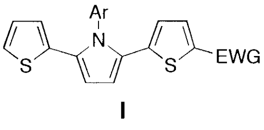
Since 1-aryl-2,5-di(2-thienyl)pyrrole derivatives having an electron-withdrawing group emit strong fluorescence, they could be utilized as an efficient dopant in the emitting layer of an organic EL device. Especially, 1-aryl-2,5-di(2-thienyl)pyrrole having a ketene dithioacetal *S*,*S*-dioxide group showed extremely high performance (the highest luminous efficiency: 5.9 cd/A).

Some organic materials which have high fluorescence efficiency and semiconducting properties have been investigated in the field of electroluminescent (EL) devices because they are expected to show high efficiency, capability to tune the color of light, low operation voltage, fast response time, and so on.[1-8] The usual organic EL devices possess a multi-layered thin-film structure which consists of an emitting layer and carrier (hole or electron) transport layers sandwiched between two electrodes. This is operated by injection of electrons and holes into the organic layers from the cathode and anode, respectively. Since this type of device structure was first demonstrated by Tang and VanSlyke,[9] various organic molecules have been developed for active materials of the emitting layer and carrier transport layers. For a component of the emitting layer, our attention was focused on an organic molecule having an electron-donor site and an electron-acceptor site, which enables the molecule to more easily accept the hole and the electron, respectively. However, few molecules which are utilized as an emitting component were reported in literature.[10]

From this point of view, we introduced an electron-withdrawing group (EWG) into a novel π-system, 1-aryl-2,5-di(2-thienyl)pyrroles which was shown by us to have a significant electron-donating property.[11] Interestingly, the derivatives (**I**) bearing various electron-withdrawing groups (EWG) emitted fluorescence, whose spectra varied depending on the electron-withdrawing strength of the EWG [λem (nm): EWG=COOMe, 471 (sky blue); CHO, 493 (green); PhCO, 523 (light green); NO_2, 582 (yellow)]. In particular, its formyl derivative (**2**), easily prepared according to Scheme 1, exhibited strong fluorescence with a high quantum yield which was independent of the kind of 1-aryl group (Ar=*p*-$MeOC_6H_4$ 0.63; *m*-$CF_3C_6H_4$ 0.53). Noteworthy is that the 5-formyl derivative of 2,2':5',2"-terthiophene emitted fluorescence with a very low quantum yield (0.086). Since the central aryl ring stands perpendicular to the π-system of 2,5-di(2-thienyl)pyrroles,[11] it seems to act as an obstacle to intermolecular interaction and as a result, prevents the formation of an exciplex.[12] This also leads us to expect that an evaporation film of **2** would have good quality. Hence, we applied the compound (**2**) to the emitting component of an organic EL device.



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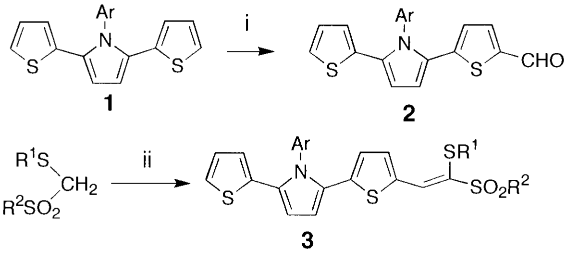

Scheme 1. Reagents and conditions: i, *n*-BuLi, THF, -78 °C then DMF; ii, *n*-BuLi, TMSCl, THF, -78 °C then **2**.

In order to evaluate the characteristics of **2** in the EL device, three device structures ([a] double layer device, [b] doped device, and [c] polymer dispersion device in Table 1) were fabricated using **2** (Ar=*p*-hexyloxyphenyl) as an emitting component. Vacuum evaporation technique was employed for constructing all of the layers except for the emitting layer of the device [c] which was obtained by spin-coating of a mixture of poly(9-vinylcarbazole) (PVK) and **2** (97:3 molar ratio). The emitting layer of the doped device [b] was made by co-deposition of tris(8-hydroxyquinolinate)aluminum (Alq) and **2** in a molar ratio of 99:1. As summarized in Table 1, the doped device [b] showed much higher performance in terms of both luminous efficiency and maximum luminance than the other two.

Table 1. Preliminary results of the performance of three devices

Device Structure	Luminous Efficiency (cd/A)	Maximum Luminance (cd/m^2)
[a] double layer[a]	0.07	178
[b] doped[b]	3.03	16,220
[c] polymer dispersion[c]	2.03	4,682

[a] Mg:Ag (200 nm)/**2** (Ar=*p*-hexyloxyphenyl) (50)/TPD (50)/ITO. [b] Mg:Ag (200)/Alq+**2** (Ar=*p*-hexyloxyphenyl) (99:1) (50)/TPD (50)/ITO. [c] Mg:Ag (200)/Alq (30)/TAZ (20)/PVK +**2** (Ar=*p*-hexyloxyphenyl) (97:3) (50)/ITO.[13]

On the basis of these preliminary results, two types of EL device were fabricated using **2** as a dopant: [Type A] Mg:Ag (200 nm)/Alq+**2** (99:1) (50)/TPD (50)/ITO and [Type B] Al:Li (200)/Alq+**2** (99:1) (50)/TPD (40)/ITO. All layers were made by vacuum deposition. The performances of the EL devices are summarized in Table 2 (entries 1-5), showing the following dis-

Table 2. The performance of the EL device using 1-aryl-2,5-di(2-thienyl)pyrrole derivative as a dopant

					Maximum Luminance		Luminous Efficiency		EL Peak	Device
Entry	Compd	Ar	R^1	R^2	cd/m^2	V	cd/A	cd/m^2	nm	Structure[a]
1	**2**	*p*-methoxyphenyl	–	–	16,300	18	3.1	605	509	B
2	**2**	*p*-hexyloxyphenyl	–	–	19,000	15	3.1	266	506	A
3	**2**	phenyl	–	–	15,600	15	3.4	162	502	B
4	**2**	*p*-fluorophenyl	–	–	18,000	16	2.6	473	512	B
5	**2**	*m*-(trifluoromethyl)phenyl	–	–	15,000	13	2.6	54	507	B
6	**3**	*p*-methoxyphenyl	Me	Me	20,300	14	4.8	97	546	B
7	**3**	*p*-methoxyphenyl	Me	*p*-Tol	39,500	10	5.9	56	551	B
8	**3**	*p*-hexyloxyphenyl	Me	*p*-Tol	32,000	15	5.8	166	545	B
9	**3**	*p*-methoxyphenyl	*p*-Tol	*p*-Tol	23,800	15	3.5	77	568	C

[a] Type Aand Type B, see text. Type C: Al:Li (200 nm)/Alq+**3** (99:1) (50)/α-NPD (10)/*m*-MTDATA (40)/ITO.[16]

tinct features: (i) the EL peaks appeared at 502-512 nm (no shoulder), shorter wavelength than that (523 nm) of the corresponding non-doped device and (ii) their luminous efficiency is higher than that of the non-doped device (2.0 cd/A), whose emitting layer is composed entirely of Alq, and is affected by the kind of 1-aryl groups, though slightly. From these facts, it is reasonably concluded that the emitting light comes from **2**, which functions as a dopant. To confirm the important role of the aryl group, an EL device employing 1-methyl-2-(5-formyl-2-thienyl)-5-(2-thienyl)pyrrole as a dopant (Type B) was also fabricated. The performance of this device (maximum luminance, 15500 cd/m^2 at 13 V; luminous efficiency, 2.7 cd/A at 254 cd/m^2; EL peak, 510 nm) is comparable to that of the above devices, but a vacuum-deposited film of 1-methyl-2-(5-formyl-2-thienyl)-5-(2-thienyl)pyrrole was unstable.

Since ketene dithioacetal *S,S*-dioxide groups were shown to have high ability to accept a radical[14] and a π-electron,[15] we synthesized the compounds (**3**) having this group as EWG and fabricated an EL device (Type B and Type C) utilizing this compound as a dopant. As seen from Table 2, these devices exhibited orange electroluminescence at 545-568 nm with high luminous efficiency. Surprisingly, the efficiency was variable dependent on a substituent of the ketene dithioacetal *S,S*-dioxide group and, in result, the EL device including **3** (Ar=*p*-methoxyphenyl, R^1=methyl, R^2=*p*-tolyl) gave the best result among those examined here. As Figure 1 depicts the relationship between luminance and applied voltage for the device using **3** (Ar=*p*-methoxyphenyl, R^1=methyl, R^2=*p*-tolyl) as a dopant, high luminance can be realized at lower applied voltage. Noteworthy is that the luminance at 6 V is 1000 cd/m^2. This value is very high in comparison with those for the doped EL devices that have been reported in literature. We can clearly recognize the light from the EL device in full daylight. Although further investigation is necessary to reveal the reason why the ketene dithioacetal *S,S*-dioxide group increases the luminous efficiency of an EL device, the present results will give a new clue to the development of efficient, practical EL devices.

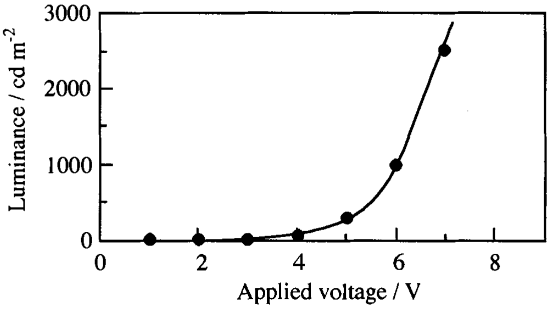

Figure 1. Luminance-voltage characteristic of the EL device using **3** (Ar=*p*-methoxyphenyl, R^1=methyl, R^2=*p*-tolyl) as a dopant.

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TAZ: 3-(biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-4-phenyl-1,2,4-triazole.
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16 α-NPD: *N,N'*-di(1-naphtyl)-*N,N'*-diphenylbenzidine.
m-MTDATA: 4,4',4"-tris(3-methylphenylphenylamino)tri-phenylamine.