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Syntheses and Properties of Novel Quarterphenylene-based Materials for Blue Organic Light-emitting Devices

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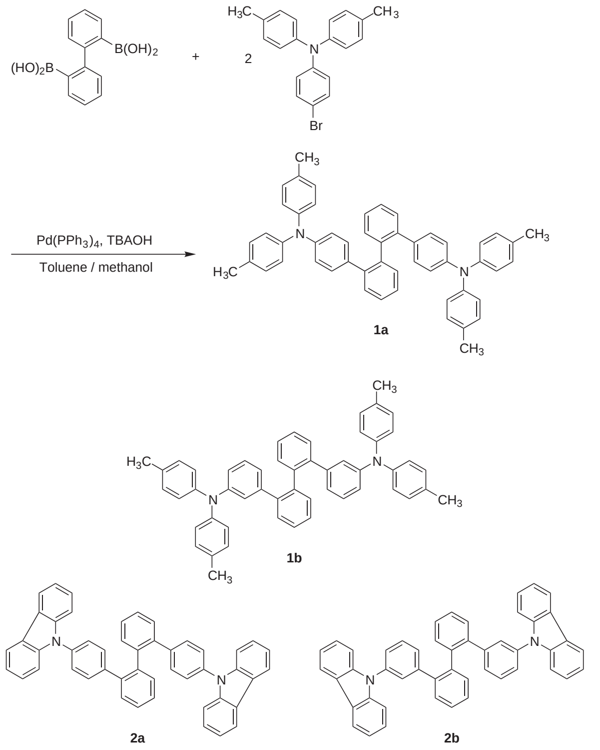
A series of quarterphenylene-based compounds were prepared and investigated as the hole-transport layer and the host materials in organic light-emitting devices (OLEDs). These compounds have wide HOMO–LUMO energy gaps (ca. 3.57 eV) due to the twisted backbone. A maximum external efficiency of 17% was achieved for blue organic light-emitting device using iridium(III)–bis[2-(4,6-difluorophenyl)pyridinate-N,$C^{2'}$]-picolinate (FIrpic) as an emitting material.

Recently, OLEDs using phosphorescent emitters have been intensively investigated because these devices provide high quantum efficiencies. For example, the devices using green-emitting *fac*-tris(2-phenylpyridine)iridium [Ir(ppy)$_3$] exhibited the maximum external quantum efficiency (EQE) of 8.0% in combination with hole-transporting 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (α-NPD), electron-transporting 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), and *N*,*N*′-dicarbazolylbiphenyl (CBP) as a host material.[1] Furthermore, the incorporation of an exciton-blocking layer improved the EQE up to 19.2%.[2] On the other hand, blue OLEDs based on phosphorescent materials such as iridium(III) bis[4,6-di(fluorophenyl)pyridinato-N,$C^{2'}$] picolinate (Firpic) exhibited lower efficiencies compared with the green phosphorescent devices. The OLED, using *N*,*N*′-dicarbazolyl-3,5-benzene (mCP) as a host, exhibited an EQE of 8.0%.[3] Tokito et al. reported that the OLED consisting of 4,4′-bis(9-carbazolyl)-2,2′-dimethylbiphenyl (CDBP) exhibited an EQE of 10.4%.[4] It is considered that the triplet energy transfer from the emitting Firpic to the host or the hole-transport layer prevents efficient phosphorescence from the triplet excited level of Firpic. Therefore, the high triplet energy, or the wide HOMO–LUMO energy gap, of the host and hole-transporting materials are required to achieve high efficiency in blue phosphorescent devices.[4] In this study, we prepared a new series of quarterphenylene-based hole-transporting materials and host materials for blue electrophosphorescent devices.[5]

As shown in Scheme 1, 2,2′-bis(4-ditolylaminophenyl)-1,1′-biphenyl (**1a**) was synthesized by the Suzuki coupling reaction of 2,2′-biphenyldiboronic acid[6] and 4-(*N*,*N*′-ditolylamino)-1-bromobenzene obtained from *p*,*p*′-ditolylamine and 1-bromo-4-iodobenzene.[7] 2,2′-Bis(3-ditolylaminophenyl)-1,1′-biphenyl (**1b**), 2,2′-bis(4-carbazolylphenyl)-1,1′-biphenyl (**2a**), and 1,1′-bis(3-carbazolylphenyl)-2,2′-biphenyl (**2b**) were prepared in the similar manner. All products purified by column chromatography were identified by ^{1}H NMR and elemental analyses.



Scheme 1. Synthesis and chemical structures of **1a**–**2b**.

The thermal properties of these materials were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The electrochemical properties were studied using UV photoelectron spectrometry (AC-1, Riken Keiki Co., Japan) and absorption spectroscopy. The glass transition temperature (T_g), melting temperature (T_m), decomposition temperature (T_d), ionization potential (I_p), electron affinity (E_a), and HOMO–LUMO energy gap (E_g) are summarized in Table 1. The T_g values of the compounds were between 87 and 120 °C. As can be seen from Table 1, the T_g values of **1a** and **1b** having triphenylamine moieties are lower than those of the carbazole-containing compounds (**2a** and **2b**). This is due to the fact that triphenylamine moieties possess nonplaner chemical structures. Since **1b** and **2b** did not show melting points, they form stable amorphous states. From the absorption edges, the HOMO–LUMO energy gaps of the compounds were determined to be

Table 1. Thermal and electrochemical data of **1a**–**2b**

Compound	T_g/°C[a]	T_m/°C[a]	T_d/°C[b]	I_p/eV[c]	E_g/eV[d]	E_a/eV[e]
1a	98	220	434	5.40	3.26	2.14
1b	87	n.d.	424	5.57	3.57	2.00
2a	120	277	472	6.06	3.46	2.60
2b	110	n.d.	460	6.04	3.48	2.56

[a]Determined by DSC measurement. [b]Obtained from TGA analysis. [c]Measured by an AC-1 UV photoelectron spectrometer. [d]Taken as the point of intersection of the normalized absorption spectra. [e]Calculated using I_p and E_g values.

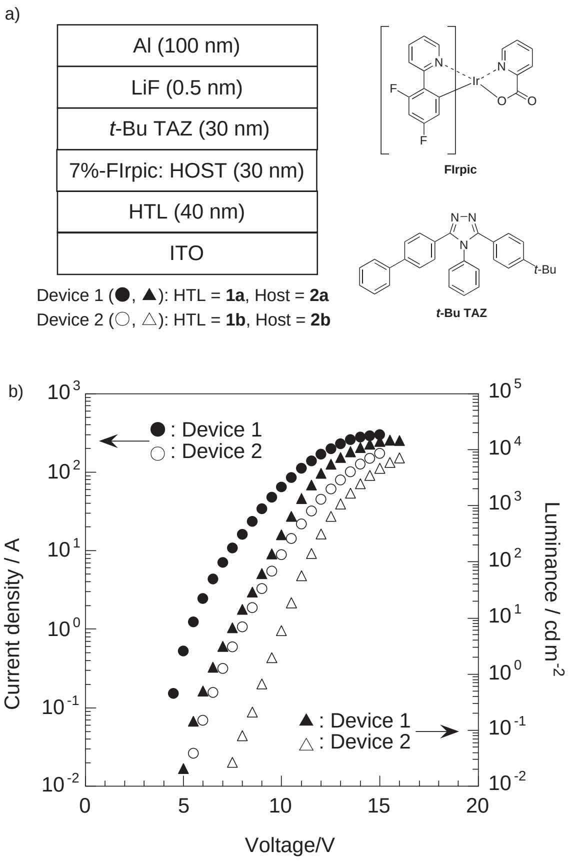


Figure 1. Characteristics of OLEDs: a) EL device structures, b) current density–voltage–luminance curves.

3.26 to 3.57 eV. These values are greater than those of conventional OLED materials such as α-NPD and CBP, which is due to the twisted structures of the quarterphenylene backbone. The I_p values of **1a** and **1b** were 5.40 and 5.57 eV, respectively. These I_p values are almost the same as that of α-NPD, and hence, **1a** and **1b** are expected to function as hole-transporting materials in OLEDs.

We fabricated the blue phosphorescent OLEDs using these materials. **1a** and **1b** were used as the hole-transport layer (HTL), and **2a** and **2b** were used as the host materials in the emitting layer. 3-(4-Biphenylyl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole (*t*-Bu TAZ) was used as the electron-transport layer. All organic layers were successively formed by vacuum deposition at 10^{-6} Torr. The device architecture was described in Figure 1a. Figure 1b shows the current density–voltage and luminance–voltage characteristics of the OLEDs using **1a** and **2a** (Device 1) and **1b** and **2b** (Device 2), respectively. The turn-on voltage of Device 1 is lower than that of Device 2. Because the I_p value of **1a** is smaller than that of **2a**, the barrier height for the hole injection should be smaller for **1a**. The luminance reaches 18300 cd/m^2 at an applied voltage of 15.0 V for Device 1.

Table 2. The maximum power efficiencies, current efficiencies, and external quantum efficiencies of the blue emitting device

Device	Maximum external quantum efficiency/%	Maximum luminance efficiency/cd A^{-1}	Maximum power efficiency/lm W^{-1}
1	14.5	32.5	21.6
2	16.5	36.0	17.3

The maximum power efficiencies, current efficiencies, and external quantum efficiencies of the devices were summarized in Table 2. The high external quantum efficiencies of 14.5–16.5% and the high maximum power efficiencies of 17.3–21.6 lm/W indicate that the triplet energy transfer from FIrpic to the host or the HTL is effectively prevented.

In summary, novel quaterphenylene-based hole-transport materials and host materials for OLED were prepared. The FIrpic-based blue phosphorescent OLEDs with these materials exhibited high performance.

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7 To a solution of tetra(*n*-butyl)ammonium hydroxide (TBAOH) (19.0 mL; 1.0 M; 19 mol) in methanol were added toluene (30 mL), 4-(*N*,*N*′-ditolylamino)-1-bromobenzene (4.00 g, 11.4 mmol), 2,2′-biphenyldiboronic acid (1.50 g, 6.20 mmol), and tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) (34 mg, 0.029 mmol). The mixture was refluxed with stirring under N_2 for 48 h. The solvent was removed on a rotary evaporator and the residue was dissolved in chloroform. The solution was washed with 5% HCl and brine, dried over anhydrous $MgSO_4$, and filtered. The solvent was evaporated and purified by column chromatography on silica gel using a mixture of chloroform and hexanes (vol ratio = 1/3) as eluent. The yield was 0.93 g (22%). ^{1}H NMR ($CDCl_3$): δ7.43–7.38 (m, 2H), 7.33–7.28 (m, 4H), 7.21–7.16 (m, 2H), 6.98–6.86 (m, 16H), 6.70–6.64 (d, 4H), 6.52–6.46 (d, 4H), 2.28–2.20 (s, 12H).

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