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Improved performance of organic light-emitting diodes using advanced hole-transporting materials

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ABSTRACT

A new class of aryl amine derivatives, which contains phenylnaphthyldiamine core, has been synthesized and examined as a hole-transporting material (HTM) for organic light-emitting diodes (OLEDs). These phenylnaphthyldiamine derivatives possess high radical cation stabilities and high morphologic stabilities relative to their biphenyldiamine analogs. Theoretical experiments and OLED device fabrication were carried out to study their better hole-transporting properties. The electroluminescent devices with the phenylnaphthyldiamine derivatives **HTM 2**–**4** as the hole-transporting layer were more efficient than that with the biphenyldiamine **HTM 1**.

1. Introduction

Since the first report of multi-layered OLEDs [1], many studies have focused on improving device efficiency and enhancing the durability of OLEDs. For the fabrication of highly stable OLEDs, specific optical and electronic properties, such as fluorescence, energy levels, charge mobility, etc., and high morphologic stability are required [2–5]. The electrochemical stability of materials used in OLED is very important to improve the device properties. Also, the thermal stability of hole-transporting material is one of the significant factors of the device durability. Under thermal stress, most organic glass transition materials tend to turn into the thermodynamically stable crystalline state, which leads to device failure [6,7]. It is known that an amorphous thin film with a high glass transition temperature (T_g) is more stable to heat damage [8–12]. In general, high thermal stability, especially high T_g above 100 °C, good hole-transporting ability, and excellent film formability are essentially needed for the hole-transporting materials. Various triarylamine derivatives have been utilized as hole-transporting materials (HTMs) because of their good film forming capabilities as well as good hole-transporting abilities [4,12,13].

Recently, considerable efforts have been devoted to the development of new amorphous triarylamines possessing high morphologic stability [14–19]. We have already reported that the device employing thermally stable hole-transporting materials showed high efficiencies [20,21]. However, we think that these hole-tansporting materials cannot meet high efficiency and long life-time simultaneously. In this paper, we will discuss how to modify the structure of HTMs in order to increase their radical cationic stabilities. In addition, device performance with these modified molecules will be discussed.

The radical cation is one of important reactive intermediate in organic molecules and it can be obtained by loss of single electron from neutral molecules. The chemical structures of common radical cation species are shown in Fig. 1.

Both hole and charge are not necessary to be localized together on one atom and they can be delocalized over the whole molecule. In fact, the delocalization of the unpaired electron in conjugated system can lead to stable radical cations such as the Wurster salt. This compound is isolable and the chemical structure including its resonance forms are shown in Scheme 1 [22]. Aryl amine moieties are thought to be a main core structure in HTMs because amine atom is relatively easy to lose one electron and the resulting radical cation can be stabilized by resonance effect of adjacent aryl substituent. It is worth to note that the Wurster salt mentioned above is stabilized by two factors. One is a resonance effect by aryl substituents and the other is stabilized by counter ion, perchlorate.

However, there is no such stabilization by counter anion in OLED devices. The stability of radical cation mainly depends on its adjacent substituent. Therefore the HTMs stabilized by their substituents are one of important factors to improve the OLED performance.

There are several factors contributing to the stability of radicals. Those are hyperconjugation, resonance, hybridization, captodative

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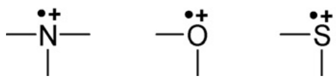
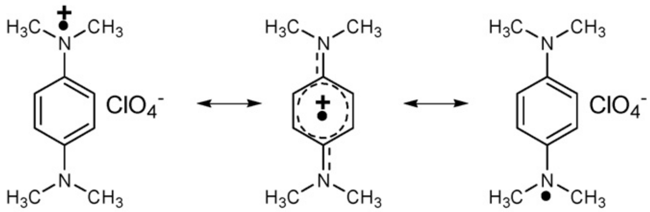
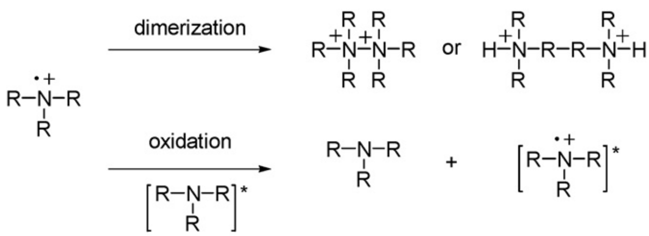


Fig. 1. The common radical cation species.



Scheme 1. The possible resonance forms of Wurster salt.



Scheme 2. Dimerization vs oxidation reaction.

effect, and steric effect [23]. Among them resonance and steric effect are important in aryl aminyl radical cations. These aminyl radical cations can be reactive and there are many possible reactions such as fragmentation, dimerization, disproportionation, and, oxidation. However, the first three reactions are not favorable in OLED device because these give rise to change of the original HTMs via formation or cleavage of σ bond. It is thought to be one of plausible reasons for OLED degradation. However, the oxidation is desirable in OLED device because this single electron transfer process between adjacent molecules results in a hole-transporting process, a fundamental reaction of HTMs. Fragmentation and disproportionation reaction is relatively less important in solid state because the interactions between each radical cations are small but the interactions between a molecule and solvent are strong in solution. In contrast, the dimerization and the oxidation reaction are more important in solid state owing to their strong interaction between radical cation each other. The following Scheme 2 summarizes the important reactions in OLED device.

Therefore HTMs have to be modified to increase the stability of aminyl radical cation which can result in minimizing the cleavage of σ bond in molecules. Furthermore resonance effect and steric factor have to be considered to minimize the dimerization reaction in solid state. Common molecules having hole-transporting properties are shown in Fig. 2.

In this paper, three novel HTMs were designed and synthesized in order to compare OLED performance and we focus on these hole-transporting materials with enhanced EL properties.

2. Experimental

Tetrahydrofurane and toluene were dried from $LiAlH_4$ and CaH, respectively. All other solvents were used as received from commercial sources without further purification. Tris(dibenzylideneacetone)dipalladium(0), tri-*tert*-butylphosphine, tetrakis (triphenylphosphine) palladium(0), sodium *tert*-butoxide, potassium carbonate, *n*-butyllithium, triisopropylborate, bromobenzene, 1-bromonaphthalene and 4-bromobiphenyl were used as purchased.

2.1. General procedure for the synthesis of phenylnaphthyldiamine derivatives

All reactions were carried out under nitrogen atmosphere in sealed reaction vessels and were heated in an oil bath.

2.1.1. 1-Bromo-4-(4-bromo-phenyl)-naphthalene **2**

Lithiation of 1,4-dibromonaphthalene (50 mmol, 14.3 g) in dry THF (120 mL) with *n*-BuLi (2.5 M hexane solution, 55 mmol, 22 mL, −78 °C) for 1 h, followed by quenching with $B(Oi\text{-}Pr)_3$ (100 mmol, 23 mL) at −78 °C. After being stirred for 5 h at room temperature, the reaction mixture was poured into 10% HCl solution. The organic phase was separated and dried over anhydrous $MgSO_4$. The concentrated residue was purified by recrystallization with diethyl ether and normal hexane to gave 4-bromo-1-naphthylboronic acid **1** (9.16 g, 73%). The Suzuki-coupling of the boronic acid **1** (10 mmol, 2.5 g) with 1-bromo-4-iodobenzene (15 mmol, 4.24 g) was carried out in the 2:1 mixture of THF and H_2O (30 mL) in the presence of K_2CO_3 (50 mmol, 6.9 g) and catalytic amount of $Pd(PPh_3)_4$ (0.04 mol%, 693 mg). The reaction mixture was heated under reflux until 4-bromo-1-naphthylboronic acid **1** was consumed. After cooling to room temperature, the organic phase was separated and dried over anhydrous $MgSO_4$. The concentrated residue was purified by column chromatography on silica to give 1-bromo-4-(4-bromo-phenyl)-naphthalene **2** (2.17 g, 65%).

2.1.2. Phenylnaphthyldiamine derivatives ***HTM 2–4***

Iodomethane (220 mmol, 14 mL) was added dropwise into the solution of 2-bromofluorene (100 mmol, 27.3 g) in THF (300 mL) in the presence of KO*t*-Bu (280 mmol, 31.4 g) at 0 °C. After further 10 h at room temperature, the reaction mixture was poured into water and the organic phase was separated and dried over anhydrous $MgSO_4$. The concentrated residue was purified by column chromatography on silica to give dimethylated compound **3** in 80% yields. The Pd-catalyzed amination reaction of resulting 2-bromo-9,9-dimethyl-9H-fluorene **3** (30 mmol, 8.19 g) with aniline (36 mmol, 3.35 g) was performed by using catalytic amount of $Pd_2(dba)_3$ (0.02 mol%, 550 mg) and $P(t\text{Bu})_3$ (0.02 mol%, 121 mg) in the presence of NaO*t*-Bu (45 mmol, 4.32 g) in dry toluene (100 mL). The reaction mixture was heated for 3 h at 85 °C. After cooling, the reaction mixture was poured into water and extracted with diethyl ether. The organic phase was dried over anhydrous $MgSO_4$ and then the volatile was removed. The purification of residue by column chromatography on silica gave (9,9′-dimethyl-9H-fluoren-2-yl)-phenyl-amine **4a** (7.88 g, 92%). **4b** and **4c** were synthesized by using corresponding amines, 1-naphthylamine and 4-aminobiphenyl, respectably (Scheme 3).

The phenylnaphthyldiamine derivatives **HTM 2**–**4** were prepared by using the same reaction condition of Pd-catalyzed amination reaction with dibromide **2** (10 mmol, 3.62 g) and arylamine derivatives **4a**–**4c** (22 mmol) in good yields. The biphenyldiamine analog, **HTM 1** known for the hole-transporting material in OLED [24], was synthesized in similar way using 4,4′-dibromobiphenyl.

2.1.2.1. ***HTM 1****.* Yellow solid, yield = 6.85 g (95%). mp 264 °C, ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.63 (d, 2H), 7.57 (d, 2H), 7.48 (d, 4H), 7.38 (d, 2H), 7.30 (dt, 3H), 7.27–7.22 (m, 7H), 7.17 (d, 8H), 7.06 (dd, 2H), 7.01 (dt, 2H), 1.42 (12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 155.1, 153.5, 147.8, 147.1, 146.9, 138.9, 134.6, 134.2, 129.2, 127.2, 126.9, 126.4, 124.2, 124.0, 123.4, 122.7, 122.4, 120.6, 119.4, 118.7. HRMS calcd. for $C_{54}H_{44}N_2$ [M+H] 721.3583, found [M+H] 721.3584.