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Design and synthesis of stable triarylamines for hole-transport applications[†]

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Abstract—Three new tetrakis(triarylamino)methanes have been designed and synthesized. These triarylamines have been shown to exhibit high glass-transition temperatures and optimal oxidation potential for achieving efficient OLEDs. The *para*-position of the aryl rings is blocked with electron-donating *t*-butyl or methoxy groups, which enhances the radical cation stability of these molecules—a highly desirable quality for hole transporters. \bigcirc 2001 Elsevier Science Ltd. All rights reserved.

Following the seminal report of 4,4'-bis(m-tolyphenylamino) biphenyl (TPD, 1a) as an efficient hole transporter,¹ several triarylamine-based small molecules and polymers have been investigated for applications such as xerography and organic light-emitting diodes (OLEDs).^{2,3} However, the design of triarylamine molecules that possess high stability, while maintaining high efficiency, has been minimal. For example, in a recent study, the ionization potential of TPD was modified by varying the R-group in structure 1.4,5 Upon studying the device property of the polymer versions of these molecules, it was recognized that the F-TPD (1c) exhibited poor stabilities, although its external quantum efficiency was the highest among the TPD derivatives studied.⁶ It was also noted in this study that the TPD derivative that had an electron-donating substituent (MeO-TPD (1b)) exhibited good stability, albeit low efficiency.

The difference in efficiency of these molecules is ascribed to the difference in the oxidation potential of these compounds and the resulting effect on the chargeinjection barrier and charge-recombination energy.^{6,7} As would be expected, F-TPD (1c) and MeO-TPD (1b) exhibited the highest and lowest oxidation potentials, respectively. In the case of 1c, the hole-injection barrier is increased and the hole–electron recombination energy



is decreased, when compared to **1a**. Similarly, the holeinjection barrier is decreased and the hole-electron recombination energy is increased for **1b**.

In organic electroluminescent (EL) materials, the holes and electrons that are generated can be considered to be the radical cations and anions of the charge-transporting molecular species, respectively. Therefore, the difference in the stability of the devices was attributed to the difference in radical cation stability. The mechanism of decomposition of triarylamine radical cations has been well established and is illustrated in Scheme 1.⁸ The difference in stability among **1a–c** was ascribed to the ease of proton removal in compounds that bear an electron-withdrawing group (step 2 of Scheme 1).^{5,9} Note that although the product of the decomposition is also a triarylamine, this transformation impacts the hole-transporting ability of the material for two rea-



Scheme 1.

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[†] This paper is dedicated to Professor Peter Beak on the occasion of his 65th birthday.

sons: (i) the oxidation potential of the product triarylamine is different from that of the starting material. Therefore, the small concentration of the product could act as traps for the charges and reduce the hole-transporting ability of the material. (ii) The formation of protons as by-products could deteriorate the efficiency of the electroluminescent devices through undesirable side reactions.

With these factors in mind, we set out to design triarylamines that exhibit oxidation potentials similar to that of F-TPD (1c), but exhibits much higher radical cation stability. It has been well established that incorporation of electron-donating substituents at the para-position of triarylamines affords stable, often isolable, radical cations.¹⁰ Therefore, we designed triarylamines 2-4, where the para-positions are blocked with electrondonating groups. We particularly targeted electronpara-substituents lack donating that benzylic hydrogens. Thus, this design obviates not only the dimerization pathways through the *para*-position in Scheme 1, but also the possible dimerization through a benzylic position.⁵ It is conceivable that all of the above structural features can be incorporated into a trisubstituted triphenylamine. However, these simpler structures would lack the amorphous nature, a necessary feature for hole-transporting materials.¹¹ Therefore, we envisioned that the tetrahedral architecture in structures 2–4 would also provide the targeted materials with high glass-transition temperatures (T_g) .¹²

The triarylamines were synthesized using the palladiumcatalyzed carbon-nitrogen bond-forming methodo- $\log y^{13,14}$ or by Ullmann coupling.¹⁵ The aniline 5 or 6 was treated with the aryl bromide 7 or 8 in the presence of sodium tert-butoxide and catalytic amounts of $Pd_2(dba)_3$ and DPPF, to afford the diarylamines 9–11 in 72-98% yields, as shown in Scheme 2. Treatment of excess 9 and 10 with tetrakis(4-iodophenyl)methane¹⁶ (12) under the above reaction conditions afforded products 2 and 3 in 9% and 48% yield, respectively. However, reaction of the diarylamine 11 with 12 did not afford the product 4 under the same conditions. The reason for the difference in yields with varying substituents in the diarylamines is not apparent to us at this time. To achieve the targeted tetrakis(triarylamine) product 4, we treated the diarylamine 11 with 12 under



Ullmann reaction conditions. The product **4** was obtained in 24% yield.

Cyclic voltammetry studies were carried out on the triarylamines 2-4 to determine their oxidation potential. The electrochemical studies were performed in 0.1 M solution of (Bu₄N)PF₆ in THF with a glassy carbon electrode as the working electrode. All potentials are reported with respect to ferrocene/ferrocenium, which was used as the internal standard. The $E_{1/2}$ of 272, 351, and 440 mV were observed for the tetrakis(triarylamines) 2, 3, and 4, respectively. The oxidation waves of the compounds 2-4 were fully reversible, compared to the irreversible oxidation waves observed with triphenylamine itself (see Fig. 1). These results were taken to indicate that the stability of the radical cations of the triarylamines increases with the incorporation of electron-donating groups. Note that the first oxidation potentials of TPD (1a) and F-TPD (1c) are at 269 and 371 mV, respectively. The oxidation potential of the tetrakis(triarylamine) 2 at 272 mV is essentially the same potential observed for the commonly used TPD (1a). The oxidation potential of the compound 3 compares very well with that of the more efficient, but less stable hole-transport material, F-TPD (1c). The presence of electron-donating groups in 3 to stabilize the radical cation is promising to afford stable and efficient electroluminescent devices.







Figure 1. Electrochemical comparison of triphenylamine and compound 2.

In order to further confirm that blocking the *para*-position enhanced the chemical stability of the radical cations of the designed triarylamines, radical cations of **3** and triphenylamine were also chemically generated by reaction with SbCl₅. The stabilities of these radical ions were compared by monitoring the absorption spectra of these radical cations (Fig. 2). In the case of triphenylamine, the peak that belongs to the triphenylamine radical cation (658 nm) decayed rapidly with time, while the peak at 484 nm increased with time. The latter peak corresponds to the absorption spectra of the monocation of N, N, N', N'-tetraphenylbenzidine,⁵ which is the decomposition product of triphenylamine (Scheme 1). These results suggest that the benzidine product is immediately formed even in dilute solutions.



Figure 2. Change in the absorption spectra of the radical cation solutions of Ph_3N and 3.

Since the oxidation potential of the benzidine derivative is much lower than that of triphenylamine, it could be oxidized by the radical cation of triphenylamine. This transformation could also be due to the reaction of any unreacted SbCl₅ with the benzidine product. In the case of **3**, a slight increase in the radical cation peak at 720 nm was observed over time. These results suggest that the radical cation of **3** is significantly more stable than those of TPD⁵ or Ph₃N. The small increase in absorption is ascribed to the slow reaction between the triarylamine and SbCl₅, since the reaction was carried out with extremely dilute solutions to facilitate observation by absorption spectroscopy.

The tetrahedral molecular architecture was also chosen in the system to provide amorphous materials that have high glass-transition (T_g) and high recrystallization temperatures to prevent failures associated with joule heating at device interfaces.¹¹ The T_g of **2**, **3**, and **4** were measured to be 169, 145, and 185°C, respectively, as measured using differential-scanning calorimetry (DSC). These glass-transition temperatures are superior to those observed for the TPD derivatives **1**, which were around 50°C.⁴

In summary, we have designed and synthesized a new series of triarylamine derivatives that exhibit high radical cation and thermal stabilities. In addition, the preliminary electrochemical investigations suggest that the redox potentials of these compounds are also suitable to provide high efficiency in electroluminescent devices. Efforts are underway to collaboratively study the holetransporting ability of these triarylamines in electroluminescent devices.

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