



Multi-triphenylamine-substituted carbazoles: synthesis, characterization, properties, and applications as hole-transporting materials

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ABSTRACT

A series of triphenylamine-substituted carbazoles, namely **TnC** ($n = 2-4$), are synthesized and characterized. By increasing the number of triphenylamine substituents, we are able to reduce the crystallization and improve the thermal stability of the molecule. Their thermal properties and abilities as hole-transporting layers in Alq3-based OLED, especially **T4C** having four triphenylamine substituents, are greater than both the common hole-transporters, *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB) and *N,N'*-bis(3-methylphenyl)-*N,N'*-bis(phenyl)benzidine (TPD). A green light-emitting device with a luminance efficiency as high as 5.07 cd/A is achieved.

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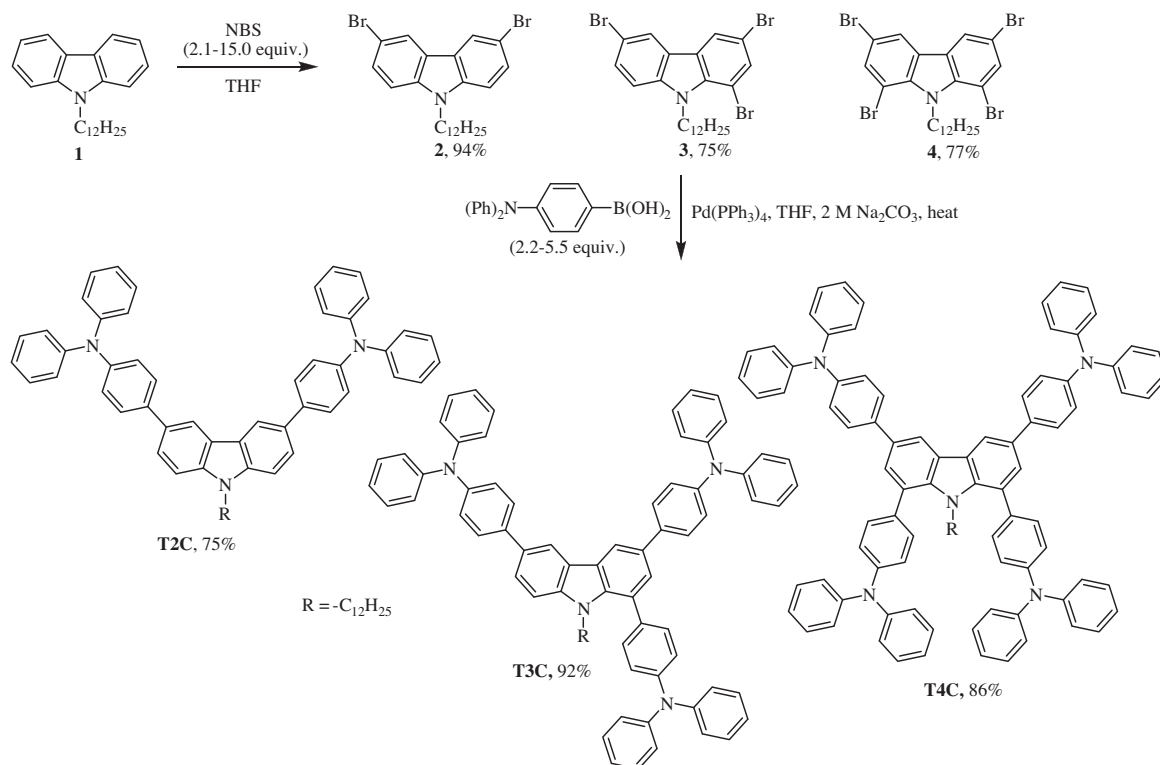
Since the pioneering work on the first organic light-emitting diodes (OLEDs) by Tang in 1987,¹ OLEDs have attracted significant attention from the scientific community due to their potential for future flat-panel displays and lighting applications.² The past decade has seen great progress in both device fabrication techniques and material development.^{3,4} One of the key developments is the use of hole-transporting layers (HTLs) for hole injection from the anode into the light-emitting layer providing significant improvements in the performance of devices.⁵ As a result, many new hole-transporting materials (HTMs) have been developed.⁶⁻⁸ In particular, low-molecular weight amorphous materials have received interest as HTM candidates due to their easy purification by vapor deposition or column chromatographic techniques, and uniformly thin films can be processed simply by coating techniques. The most commonly used amorphous hole-transporting materials (AHTMs) are triarylamine derivatives such as *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB) and *N,N'*-bis(3-methylphenyl)-*N,N'*-bis(phenyl)benzidine (TPD), which demonstrate excellent hole-transporting properties. However, their low thermal and morphological stability usually leads to their degradation.⁹ In order to achieve highly efficient and long lifetime

devices, an AHTM with high mobility, a high glass transition temperature (T_g), a stable amorphous state, and good thin film forming ability are desirable. To optimize all these requirements, many efforts have been devoted to the synthesis of new AHTMs.^{6,10} Carbazole derivatives containing a peripheral diarylamine,¹¹ additional carbazole,¹² bis(4-*tert*-butylphenyl)carbazole,¹³ and dipyrrenyl units¹⁴ were also reported to exhibit good thermal and morphological stability. Recently, we synthesized a series of aromatic compounds with peripheral triphenylamine-carbazole units possessing high T_g (121–185 °C) values, and found that the OLED devices based on the resulting carbazole compounds were promising in terms of device performance and stability.¹⁵ Undoubtedly, it is very attractive to explore and develop new carbazole derivatives that meet the requirements as AHTMs for OLEDs, and which can be synthesized using simple and low-cost methods. Our design involved multiple substitution of the carbazole ring with triphenylamine moieties. With this molecular architecture, compounds should exhibit amorphous hole-transporting ability.

Herein, we report on a simple synthesis of multi-triphenylamine substituted carbazoles (**TnC**, $n = 2-4$), and their physical and photo-physical properties. Investigations on their abilities to act as hole-transporting layers in OLEDs are also reported. Scheme 1 outlines the synthesis of the triphenylamine functionalized carbazoles. We began with the synthesis of 3,6-dibromo-*N*-dodecylcarbazole (**2**),

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Scheme 1. Synthesis of triphenylamine substituted carbazoles **TnC**.

1,3,6-tribromo-*N*-dodecylcarbazole (**3**), and 1,3,6,8-tetrabromo-*N*-dodecylcarbazole (**4**) by bromination of *N*-dodecylcarbazole (**1**) with NBS.¹⁶ A solution of **2** in THF was treated with NBS (2.1–15.0 equiv) in small portions in the absence of light to yield bromides **2–4** in moderate to good yields (75–94%). Subsequently, coupling of these multibromo-*N*-dodecylcarbazoles **2–4** with 4-(diphenylamino)phenylboronic acid (2.2–5.5 equiv) in the presence of Pd(PPh₃)₄ as the catalyst and aqueous Na₂CO₃ as the base in THF at reflux afforded 3,6-bis[4-(diphenylamino)phenyl]-*N*-dodecylcarbazole (**T2C**), 1,3,6-tri[4-(diphenylamino)phenyl]-*N*-dodecylcarbazole (**T3C**), and 1,3,6,8-tetrakis[4-(diphenylamino)phenyl]-*N*-dodecylcarbazole (**T4C**) as white solids in good yields (75–92%). The structures of the products were characterized unambiguously by ¹H NMR and ¹³C NMR spectroscopy as well as high-resolution mass spectrometry.¹⁷ Noticeably, the ¹H NMR spectra of **TnC** showed that the chemical shifts of the dodecyl protons were shifted to low frequency as the number of triphenylamine substituents on the carbazole increased. This is due to a shielding effect resulting from the ring current produced by the surrounding 1- and 8-triphenylamine substituents. For example, the chemical shift of –NCH₂– protons of **T2C** (4.34 ppm) was shifted to 4.00 and 3.70 ppm in **T3C** and **T4C**, respectively. These compounds showed good solubility in most organic solvents.

To gain insight into the geometrical and electronic properties of these multisubstituted carbazoles, quantum chemistry calculations were performed using the TDDFT/B3LYP/6-31G(d) method.¹⁸ The optimized structures of the **TnCs** revealed that the phenyl rings attached to the carbazole of each triphenylamine were twisted out of the plane of the carbazole, forming bulky substituents around the carbazole, especially in **T4C** (Fig. 1). This would facilitate the formation of amorphous materials. In all cases, π -electrons in the HOMO orbitals were delocalized only over the carbazole and two triphenylamine substituents at the 3- and 6-positions [3,6-bis[4-(diphenylamino)phenyl]carbazole backbone], and no electrons at the triphenylamine moieties at the 1 and

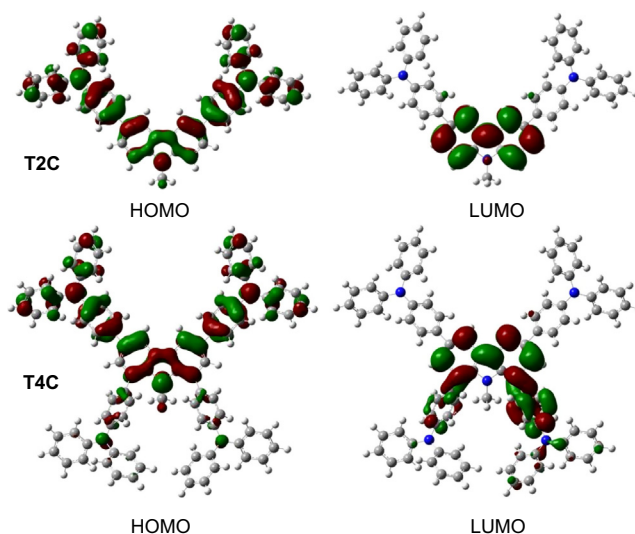


Figure 1. HOMO and LUMO orbitals of **T2C** and **T4C** calculated by the TDDFT/B3LYP/6-31G(d) method.

8-positions. In the LUMO orbitals, the excited electrons were delocalized over the carbazole plane and the phenyl ring of the triphenylamine substituents at the 1,8-positions. This suggests that substitution of the carbazole at the 1- or 8-positions with triphenylamine only affected the LUMO of the molecule, while the HOMO remained nearly untouched.

The solution UV–vis absorption spectra of **TnC** showed absorption bands at 320–328 nm corresponding to the π – π^* electronic transition of the π -conjugated 3,6-bis[4-(diphenylamino)phenyl]carbazole backbone (Fig. 2a). With **T3C** and **T4C**, absorption bands at lower wavelengths (284–296 nm) were observed, which were identical to the absorption peak of a triphenylamine

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