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Short communication

'Click' synthesis of starburst triphenylamine as potential emitting material

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ABSTRACT

The efficient synthesis of a starburst triphenylamine, tris(4-(1-(4-(diphenylamino)phenyl)-1H-1,2,3-triazol-4-yl)phenyl)amine, via straightforward 'click coupling' of 4-azido-*N*,*N*-diphenylbenzenamine and tris(4-ethynylphenyl)amine is reported. The reaction was performed in THF using $(PPh_3)_3CuBr$ as catalyst and was accomplished within 6 h in high yield (92%). Both the synthesis and purification steps were greatly simplified in comparison with conventional methods. The optical, electrochemical, and thermal properties of the starburst triphenylamine were examined; the synthesized compound emitted deep blue fluorescence in both solution and the solid state and displayed reversible redox processes. The starburst triphenylamine is a potential hole-transporting material and blue-light-emitting material.

1. Introduction

Over the past years, triarylamines have been widely utilized as crucial components in the development of new electro-optical functional materials and devices due to their unique octupolar configuration, excellent solubility, stability as well as high luminescence and hole-transporting efficiency [1]. In particular, starburst and dendritic triarylamines have recently received growing attention in organic light-emitting diodes (OLEDs) [2,3], organic field-effect transistors (OFETs) [4], organic photovoltaic devices [5,6] for their excellent hole-transporting capability. Starburst triarylamines are also good candidates for organic non-linear materials [7], fluorescence [8] and phosphorescence [9] materials. With regard to the syntheses of starburst and dendritic triarylamines, the conventional Ullmann reactions and the palladium-catalyzed coupling reactions were generally adopted. However, the Ullmann method is notorious for requiring harsh conditions and having very erratic yields. In the palladium-catalyzed coupling reactions, expensive and extremely air-sensitive palladium catalysts and phosphorus ligand are needed. In addition, tedious purification with silica gel chromatography in both approaches is inevitable.

In search of efficient synthesis for starburst triarylamine, we are attracted to the famous Sharpless 'click chemistry', especially the Cu(I)-catalyzed regiospecific formation of 1,2,3-triazoles from azides and terminal acetylenes, being hailed as the cream of the crop [10–13]. The synthetic appeal of this 'click reaction' relies upon its benign reaction conditions, tolerance of oxygen and water, high yields, simple isolation procedure, and almost perfect fidelity in the presence of a wide variety of other functional groups. These appealing features have enabled this reaction to evolve into a powerful synthetic tool which has been successfully exploited in the construction of dendritic [14–18] and linear [19–22] macromolecules or polymers. It is noteworthy that Tang and his coworkers [14] have successfully generated via 'click reaction' the first examples of hyperbranched poly(1,2,3-triazole)s containing triphenylamine groups with good performance of regioregularity and macroscopic processability. However, in these chromophores, the triphenylamine groups are separated by long flexible linkers, which lead to the absence of the properties of classic starburst triarylamine. Herein, we reported the design and synthesis of a starburst triphenylamine by 'click reaction' of acetylene groups terminated triphenylamine core with an azido-attached triphenylamine. In this way, the triphenylamine moieties are held directly via the triazole rings. The absorption, fluorescence, electrochemical, and thermal properties of the material were investigated and it was found that the excellent optical properties of the starburst triarylamine derivatives such as strong luminescence

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intensity and good hole-transporting capability were still retained in the target product.

2. Experimental

2.1. Chemicals and instruments

^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) measurements were performed on a Brücker AM 500 spectrometer. High-resolution mass spectra were done with a HP5989 mass spectrometer. UV–vis spectra were recorded on a Varian Cary 500 spectrophotometer and fluorescence emission spectra were on a Varian Cary Eclipse fluorescence spectrophotometer. Cyclic voltammetry was performed using a Potentiostat/Galvanostat Model K0264 (Princeton Applied Research). Anhydrous CH_2Cl_2 was used as the solvent under inert atmosphere. The starting materials *N*^{1},*N*^{1}-diphenylbenzene-1,4-diamine (**1**) [23] and tris(4-ethynylphenyl)amine (**3**) [24] were synthesized according to the reported procedures.

2.2. 4-Azido-N,N-diphenylbenzenamine (2)

A suspension of compound **1** (0.5 g, 1.92 mmol) in concentrated hydrochloric acid (0.4 ml) and water (5 ml) was cooled at 0–5 °C and diazotized with a solution of sodium nitrite (0.14 g, 2.03 mmol) in water (2 ml). After being allowed to stand for a quarter, the resulting solution was treated dropwisely with sodium azide (0.15 g, 2.31 mmol) in water (2 ml), stirred for 1 h at 0–5 °C. The precipitated product was collected by filtration, washed with cold water and dried to a constant weight in a vacuum oven at room temperature to give compound **2** as a white solid (0.38 g, 70%). ^{1}H NMR ($CDCl_3$, ppm): δ_H 7.23–7.26 (4H), 7.05–7.09 (6H), 6.89–6.92 (2H). ^{13}C NMR ($CDCl_3$, ppm): δ_c 148.3, 145.6, 134.8, 129.9, 126.2, 124.6, 123.5, 120.5. HRMS *m*/*z* calcd for $C_{18}H_{14}N_4$: 286.1218, found: 286.1219. IR (KBr) 2097.58 cm^{-1} (–N=N=N).

2.3. Tris(4-(1-(4-(diphenylamino)phenyl)-1H-1,2,3-triazol-4-yl)phenyl)amine (TM)

Compound **2** (0.123 g, 0.43 mmol), compound **3** (0.038 g, 0.12 mmol), *N*,*N*-diiso-propylethylamine (0.06 ml, 0.36 mmol), and $Cu(PPh_3)_3Br$ (0.022 g, 0.024 mmol) were dissolved in THF (35 ml) and stirred at 30–35 °C for ca. 6 h. The reaction mixture was then cooled to 0 °C. The precipitated product was collected by filtration and recrystalized from C_2H_5OH/CH_2Cl_2 to furnish compound **TM** as a white solid (0.12 g, 92%). ^{1}H NMR (DMSO-*d*$_6$, ppm): δ_H 9.13 (s, 3H), 7.85 (dd, 12H, $J = 7.0$ Hz, 6.9 Hz), 7.14 (dd, 12H, $J = 6.9$ Hz, 7.6 Hz). ^{13}C NMR (DMSO-*d*$_6$, ppm): δ_c 149.7, 149.0, 148.9, 148.8, 133.0, 131.9, 128.8, 127.4, 126.7, 126.3, 125.9, 125.2, 123.4, 120.9. HRMS *m*/*z* calcd for $C_{78}H_{58}N_{13}$: 1176.4938, found: 1176.4935.

3. Results and discussion

3.1. Synthesis

Fig. 1 outlines the synthesis of the target starburst triphenylamine molecule, tris(4-(1-(4-(diphenylamino)phenyl)-1H-1,2,3-triazol-4-yl)phenyl)amine (**TM**). Diazotization of **1** followed by

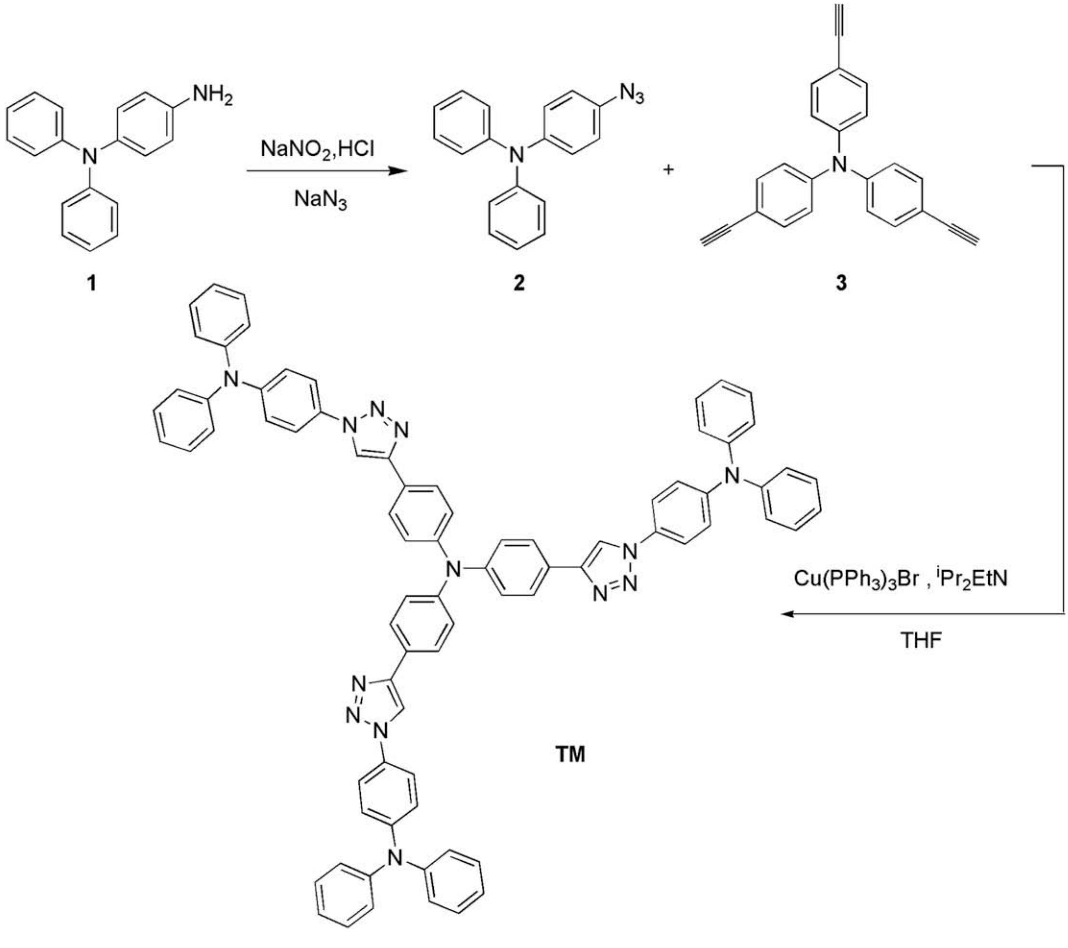

Fig. 1. Synthetic route for **TM**.

reaction with sodium azide led to 4-azido-*N*,*N*-diphenylbenzenamine (**2**) in good yield. Compound **2** was precipitated during the reaction and separated by simple filtration. Afterwards, the 'click reaction' of **2** and **3** in THF at temperature around 30–35 °C for about 6 h afforded **TM** as precipitation, collected by filtration in high yield of 92%. It was found that the reaction of **2** and **3** did not proceed smoothly at room temperature, while a little higher temperature facilitated the reaction to accomplish in a short time. Over the past years, it has been found that many 'click' reactions often proceeded better in water than in an organic solvent [10]. In our work, since both **2** and **3** are insoluble in water, the copper catalyzed reaction was performed in THF and an organo-soluble Cu(I) species, $(PPh_3)_3CuBr$, was used. Such slight modification of the reaction conditions led to the same degree of efficiency and near quantitative yields as was demonstrated previously [16]. The product **TM** obtained from the 'click reaction' initiated by $Cu(PPh_3)_3Br$ exhibits a strong singlet peak at 9.13 ppm in ^{1}H NMR spectrum in DMSO-d_6, which was ascribed to C═C**H**–N in the triazole rings (see Fig. 2).

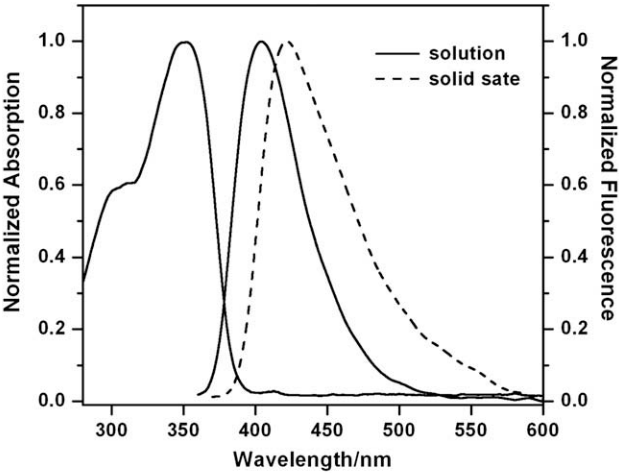

Fig. 3. Normalized absorption and fluorescence spectra (excitation wavelength: 350 nm) of **TM** in CH_2Cl_2 solution (5×10^{-6} M) and solid state.

3.2. Optical properties

The optical properties of the **TM** were measured by UV–vis absorption and fluorescence spectroscopies in CH_2Cl_2 solution and solid state, as shown in Fig. 3. **TM** shows an intense absorption at 350 nm, with a shoulder at around 305 nm. UV irradiation of **TM** in CH_2Cl_2 solution under ambient conditions resulted in bright, deep blue fluorescence ($\lambda_{max} = 405$ nm, excited at 350 nm). Fluorescence quantum yield is as high as 74% (measured in CH_2Cl_2 using (7,12-diphenyl)benzo[*k*]fluoranthene in cyclohexane ($\Phi_F = 1$) as a standard). Moreover, in solid state, **TM** still shows strong blue fluorescence at 421 nm, and the full width at half-maximum of the emission is as narrow as 69 nm. The strong and deep blue emission in solid state, which should be profited from the non-planar structure of starburst triphenylamine configuration, makes **TM** a highly-needed potential deep blue emitter in OLED.

3.3. Theoretical calculation

To gain insight into the geometrical and optical properties of **TM**, we performed DFT and time-dependent DFT (TDDFT) calculations, using the Gaussian 03 program package [25]. The ground-state geometry of **TM** optimized by hybrid density functional theory (B3LYP) with 6-31G* basis set is presented in Fig. 4. The dihedral angles formed between the triazole rings and benzene rings are about 27 degrees and the whole molecule takes a non-planar configuration, which helps to impede the π–π stacking interaction in solid state to some extent. Fig. 5 illustrates the calculated spatial distributions of the HOMO, LUMO and LUMO + 1 levels of **TM**. HOMO is the highest occupied molecular orbital; LUMO is the lowest unoccupied molecular orbital; LUMO + 1 is the next lowest unoccupied molecular orbital. As can be seen clearly, HOMO is a π orbital concentrated on the central triphenylamine moiety; LUMO and LUMO + 1 are of π* character distributed on the arms. Judging from TDDFT calculation, the absorption band observed around 350 nm is resulted from two major transitions: HOMO → LUMO and HOMO → LUMO + 1, that is, π–π* transition from the electron-donating triphenylamine core to the electron-accepting triazole moieties. In addition, the band around 305 nm originates from the n–π* transition that is characteristic of the triphenylamine moiety.

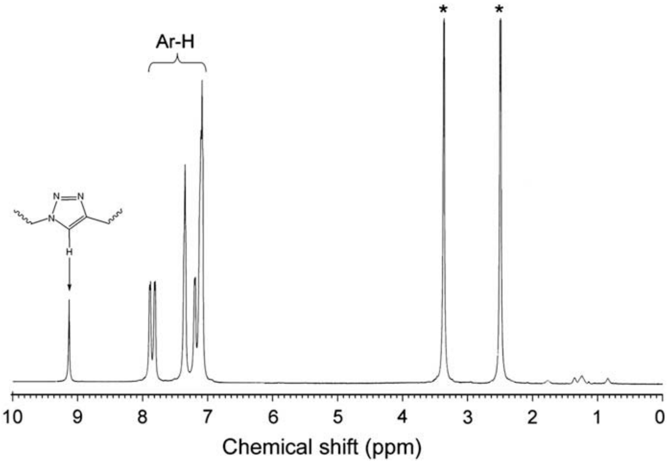

Fig. 2. ^{1}H NMR spectrum of DMSO-d_6 solution of **TM** measured at room temperature. The solvent and water peaks are marked with asterisks.

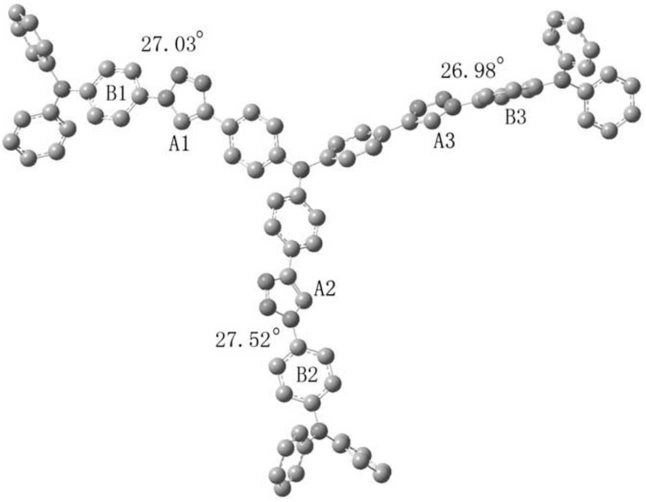

Fig. 4. Optimized ground-state geometry of **TM** with B3LYP/6-31G* in gas phase. Note: A and B represent the triazole ring and benzene ring, respectively.

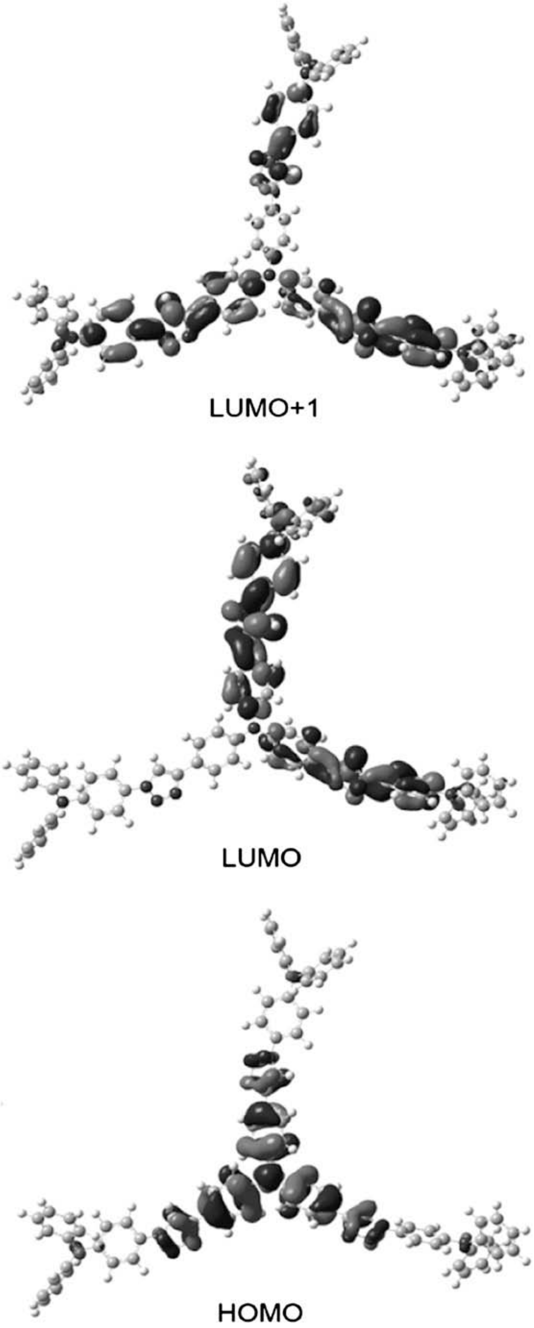

Fig. 5. Calculated spatial distributions of the HOMO, LUMO and LUMO + 1 levels of **TM**.

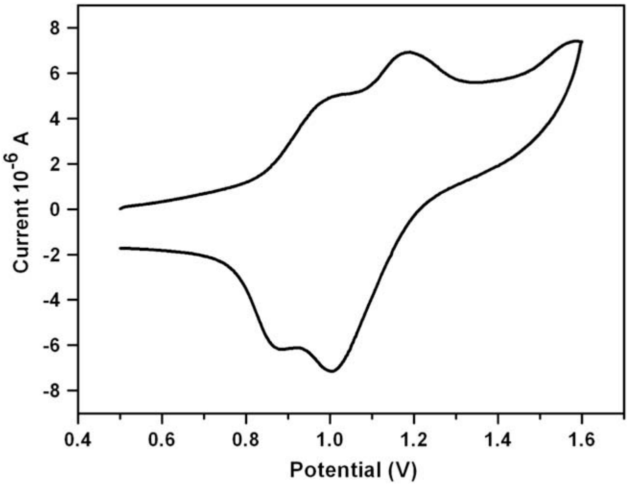

Fig. 6. Oxidative cyclic voltammetry plot measured in CH_2Cl_2 solution.

3.4. *Electrochemistry*

The electrochemical behavior of **TM** was examined by a cyclic voltammetry technique on a Pt disk electrode in CH_2Cl_2 with TBAHFP (tetra (*n*-butyl) ammonium hexafluorophosphate, 0.1 M) as the supporting electrolyte and saturated Ag/AgCl as the reference electrode (Fig. 6). The oxidation potential shows two reversible redox processes, indicating that **TM** has favorable hole-transporting capability. The HOMO value of **TM** was calculated to be 5.24 eV based on the first oxidation potential and by comparison with ferrocene (4.8 eV). The HOMO energy level is almost the same as that of NPB (5.20 eV), indicative of comparable hole-transport capacity to NPB [26]. Furthermore, **TM** demonstrates a modest melting point of 240 °C. Therefore, **TM** has the general characteristic of the starburst triarylamine, which makes it a promising candidate as a hole-transport material for optical electronic devices.

4. Conclusion

In this study, we designed and synthesized a starburst triphenylamine **TM** by ‘click coupling’ of 4-azido-*N*,*N*-diphenylbenzenamine (**2**) and tris(4-ethynylphenyl)amine (**3**). The synthetic strategy is straightforward and benefits from high yield and facile purification without tedious silica gel chromatography. Compound **2** is a novel triphenylamine derivative, which lends a new way for the functionalization of materials with triphenylamine by ‘click reaction’. **TM** emits deep blue fluorescence in both solution and solid state. It shows two reversible redox processes, suggesting a good hole-transporting capability. The overall results proved that **TM** is a potential hole-transporting material and blue-light-emitting material.

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