

A Novel Pyrazoline-based Starburst Amorphous Molecular Material

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Abstract: A pyrazoline-containing starburst molecule, 4,4',4''-tris[(1,3-diphenyl-4,5-dihydro-1H-pyrazol-5-yl)]-triphenylamine (Tris-5-DPP), was synthesized in a facile way, which can form amorphous thin films with glass transition temperature as high as 136 °C.

Keywords: Starburst molecule, pyrazoline, amorphous thin film.

Amorphous organic thin films with high charge carrier (hole or electron) mobility have found wide applications in optoelectronic devices such as organic solar cells^{1,2}, dye-sensitized nanocrystalline semiconductor solar cells³, and organic light-emitting diodes (OLEDs)⁴⁻⁹. In such applications the thermal and morphological stabilities of the amorphous thin films are highly desired properties for achieving long term durability of the devices. These properties strongly depend on the steric structures of the molecules forming the films. As a result, functional molecular materials with the capability of forming stable amorphous thin films, namely amorphous molecules, draw much attention recently, and “starburst molecules” constitute a main part among the amorphous molecules developed so far⁵⁻⁹. Owing to the highly branched and global-like structure along with the high molecular weight and large molecular size, starburst molecules have low tendency of crystallization and therefore can easily form amorphous thin films, having high glass transition temperature (T_g , generally higher than 100 °C), which renders the molecules “frozen” so firmly that it does not recrystallize during the operation of device at elevated temperatures.

1, 3, 5-Triaryl-2-pyrazoline compounds have been applied in OLEDs as hole transporting materials due to their good hole-transporting and film-forming abilities^{10,11}. We recently synthesized a phenanthrene-substituted pyrazoline, 1, 3-diphenyl-5-(9-phenanthryl)-4, 5-dihydro-1H-pyrazole (DPPhP)¹², which formed an amorphous thin film with T_g as high as 96 °C *via* vacuum deposition. The electroluminescent device, using DPPhP as hole transporting layer, exhibited improved brightness and efficiency compared with the device using N,N'-di-1-naphthyl-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (α -NPD) which is the most prevalent hole transporting material ($T_g = 98$ °C) used in OLEDs¹³ to transport holes. In view of the device durability, however, it is necessary to further increase the T_g of pyrazoline-based hole transporting molecules, and herein we

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reported on a facile synthesis of pyrazaoline-containing starburst compound, 4, 4', 4''-tris[(1,3-diphenyl-4,5-dihydro-1H-pyrazol)-5-yl]-triphenylamine (Tris-5-DPP), which show T_g up to 136 °C.

Tris-5-DPP was synthesized following the procedures shown in **Scheme 1**. According to the literature¹⁴, three equivalent acetophenone in 95% ethanol reacted with one equivalent tri(4-formylphenyl)amine (**I**) for 24 h at room temperature in the presence of a base to give intermediate **II** in 63 % yield. Then **II** was refluxed with excess phenylhydrazine in ethanol, followed by column chromatography on silica gel and recrystallization from THF/EtOH to give pure Tris-5-DPP in 25% yield, identified with ¹H NMR (CDCl₃, 300 MHz, δ ppm): 3.10-3.19 (q, 3H, $J = 7.0$ Hz, 17.1Hz), 3.75-3.86 (q, 3H, $J = 12.6$ Hz, 17.1Hz), 5.18-5.25 (q, 3H, $J = 7.1$ Hz, 12.0Hz), 6.80 (t, 3H, $J = 6.6$ Hz), 6.96 (d, 6H, $J = 8.2$ Hz), 7.00-7.40 (m, 27H), 7.72 (d, 6H, $J = 7.1$ Hz) and MS (m/z 905 (M^+)).

Scheme 1 The synthetic route of Tris-5-DPP

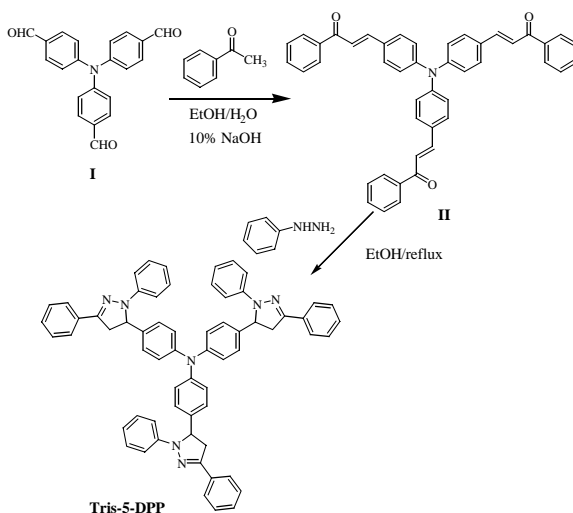
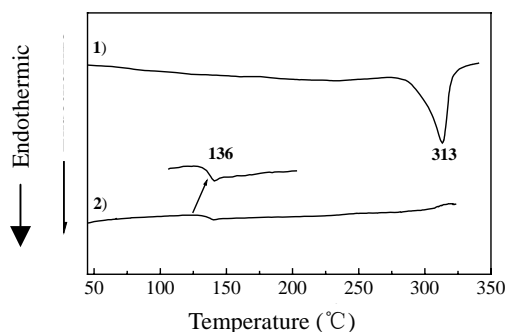


Figure 1 DSC curves of Tris-5-DPP



1) crystalline Tris-5-DPP was heated; 2) Tris-5-DPP glass obtained by cooling the melt was heated (heating rate: 10 °C/min)

Figure 1 shows the differential scanning calorimetry (DSC) curves of Tris-5-DPP. The crystalline sample of Tris-5-DPP melted at 313°C, which is much higher than the melting point (T_m) of DPPhP (242°C). After rapid cooling, a glassy state formed. When heated again, the sample in glassy state underwent phase change at 136°C (T_g , also much higher than that of DPPhP at 96°C), transforming to a super-cooled liquid state. Till the melting temperature of 313°C, no exothermic peak resulting from the sample crystallization was observed, suggesting Tris-5-DPP has low crystallization tendency. In contrast, crystallization occurred (at 153°C) for DPPhP when its glassy state was heated above T_g ¹². The higher T_g and T_m and lower crystallization tendency of Tris-5-DPP may be ascribed to the enlarged molecular size as well as the non-planar, highly branched molecular structure, which suppresses molecular diffusion and regular packing. The non-planar feature of triphenylamine unit has been well utilized in preparation of amorphous molecules⁵⁻⁹. An amorphous thin film, observed by atomic force microscopy (AFM), can also formed by casting concentrated solution of Tris-5-DPP in chloroform (1×10^{-3} mol/L) at the surface of sheet mica, which was very flat with average roughness (Ra) of about 1 nm (**Figure 2**).

Redox potentials were measured by cyclic voltammetry using a three electrode configuration on an EG&G Instruments Potentiostat/Galvanostat Model 283. The working electrode was a platinum wire, while a platinum wire and a saturated calomel electrode (SCE) served as counter and reference electrodes, respectively. A 0.1 mol/L solution of Bu_4NBF_4 in acetonitrile was used as the supporting electrolyte and was flushed with N_2 prior to the measurements. The onset oxidation potential of Tris-5-DPP is 0.66 V (*vs* SCE), while 0.53 and 0.78 V for DPPhP and α -NPD, respectively¹². Accordingly, the HOMO energy levels *vs* vacuum are respectively -5.40, -5.27, and -5.52 eV for Tris-5-DPP, DPPhP, and α -NPD by taking -4.74 eV as the energy of SCE *vs* vacuum¹². The intermediate HOMO level between the two known hole transporting materials makes Tris-5-DPP well match the work function of ITO anode (-5.4 eV after oxygen plasma treatment)¹⁵, and therefore facilitates hole injection from ITO anode to Tris-5-DPP layer.

Figure 2 An AFM image of Tris-5-DPP film on sheet mica surface

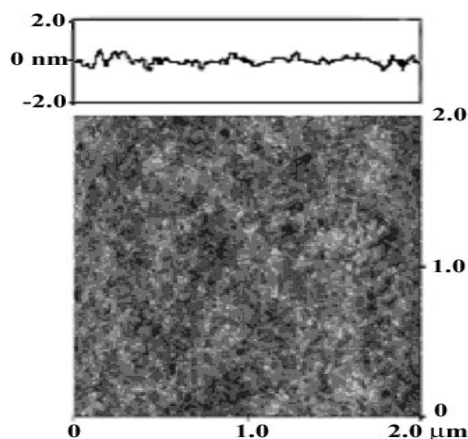
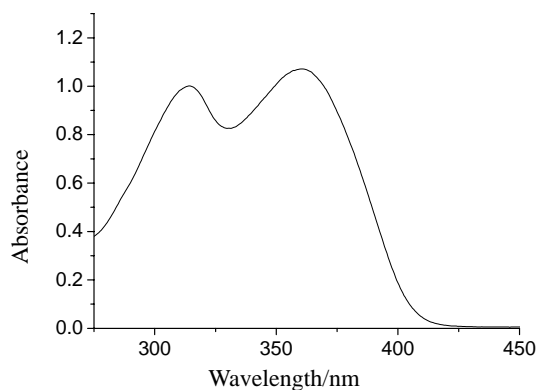


Figure 3 The absorption spectrum of Tris-5-DPP in THF (1.9×10^{-5} mol/L)

In summary, the high T_g , the low crystallization tendency, the suitable oxidation potential, the transparency in visible region (absorption bands locate below 400 nm, **Figure 3**), and the ease of preparation make the starburst Tris-5-DPP to possess potential application in OLEDs as hole transporting material. The electroluminescent device study based on Tris-5-DPP is in progress.

Acknowledgments

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