



# A tetraphenylmethane based starburst triarylamine cluster: spectroscopy, electrochemistry and morphological studies

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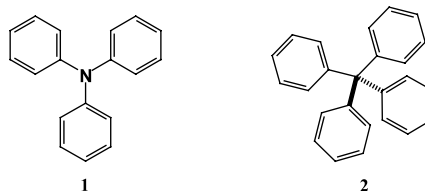
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**Abstract**—While tetraphenylmethane and triphenylamine are crystalline molecules, a starburst hybrid of the two leads to a low band-gap molecular glass which retains the optical and electrochemical properties of the individual components. © 2002 Elsevier Science Ltd. All rights reserved.

There is considerable current interest in low band-gap organic molecules for applications in various electroluminescent (EL) devices.<sup>1–3</sup> Along with their optical and electrical properties, the morphological stability of such compounds plays an important role in determining their potential applications in EL devices. Crystalline compounds or materials having large crystalline domains tend to degrade EL devices.<sup>4</sup> Moreover, they form aggregates or excimer states resulting in diminished emission efficiencies. To circumvent these problems, many studies have focussed on the use of low band-gap amorphous materials in EL devices and indeed, it has been shown recently that amorphous materials when used as the active layer in EL devices can lead to significant improvements in the efficiency of multilayer devices.<sup>5,6</sup> In view of such promise, in recent years, several studies have been directed towards design, synthesis and physical studies of new amorphous molecules.<sup>7</sup>

Shirota and co-workers have systematically developed several starburst triarylamine derivatives that form stable amorphous glasses with glass transition temperatures ( $T_g$ ) much above room temperature.<sup>7</sup> Some of these have been used as efficient hole-transporting components in multilayer EL devices. In an interesting development, Bazan et al. have recently reported a few starburst tetraphenylmethane derivatives which show similar amorphous properties.<sup>8</sup> Notably, both triphenylamine (**1**) and tetraphenylmethane (**2**) and their simple derivatives are highly crystalline materials. Therefore,

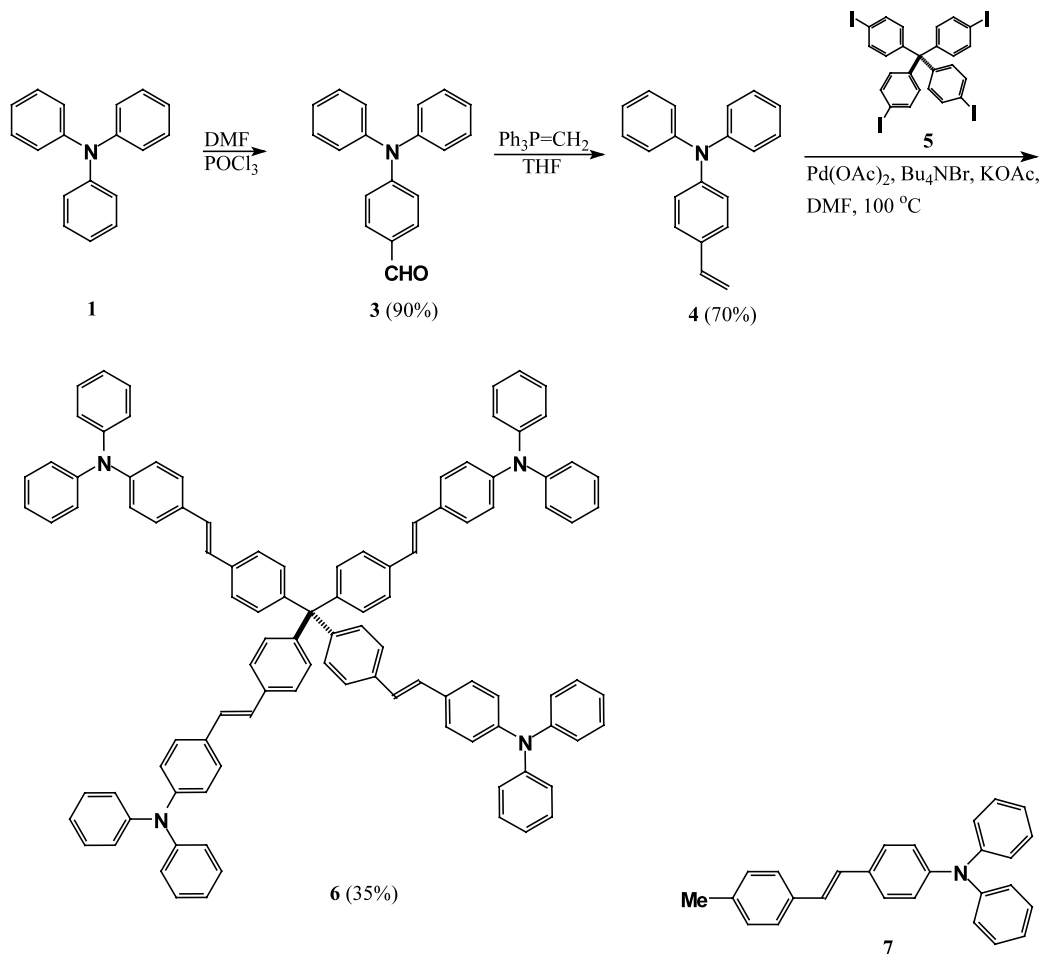
the fact that starburst derivatives of **1** and **2** readily form amorphous glasses must be due to their large molecular volume, non-planar structure and the presence of a large number of conformers which prevent easy crystallization. Based on these arguments, we reasoned that a starburst hybrid comprised of **1** and **2** may also show a stable amorphous state. Moreover, in such a hybrid, the triarylamine moieties would provide means for efficient hole transporting abilities. We therefore embarked on the synthesis and physical studies of a tetraphenylmethane based starburst triphenylamine cluster viz. **6**, the results of which are reported in this letter.



In designing our starburst hybrid **6**, a stilbenoid unit was chosen as the linker between **1** and **2**. This, we thought, would impart structural rigidity as well as a strong fluorescence property to the cluster. The synthesis of **6** is shown in Scheme 1. Thus, monoformylation of triphenylamine with  $\text{POCl}_3/\text{DMF}$  gave the aldehyde **3** (90%) which upon Wittig olefination led to *p*-diphenylamino styrene (**4**) in 70% yield. A fourfold Heck reaction of **4** with *tetra*-(*p*-iodo)phenylmethane (**5**)<sup>9,10</sup> under Jeffery's phase transfer conditions ( $\text{Pd}(\text{OAc})_2$ ,  $\text{Bu}_4\text{NBr}$ ,  $\text{KOAc}$ ,  $\text{DMF}$ ,  $100^\circ\text{C}$ )<sup>8a,11</sup> then produced the starburst cluster **6** (35%) after purification by preparative thin layer chromatography over silica gel. The product was characterized by its spectral data ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) and elemental analysis.<sup>12</sup>

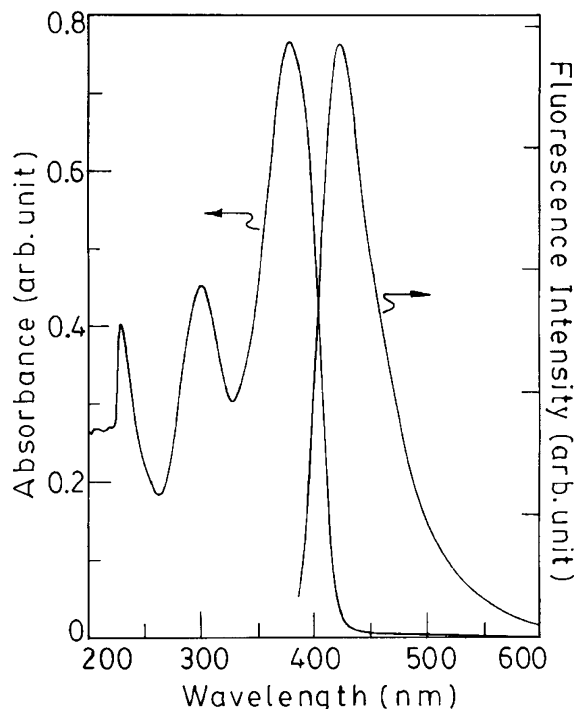
**Keywords:** triarylamine; tetraphenylmethane; molecular glass.

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Scheme 1.

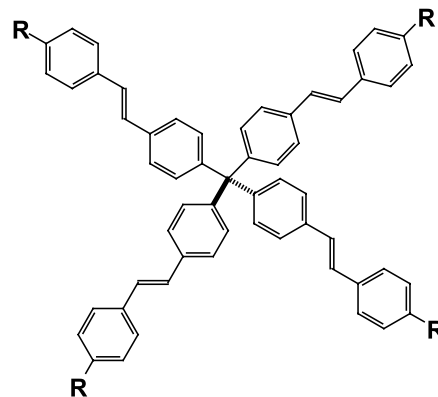
The solution optical properties of **6** recorded in  $\text{CH}_2\text{Cl}_2$  are shown in Fig. 1. The absorption maximum was found at 378 nm with a high molar absorptivity ( $\epsilon_{\text{max}} 1.52 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) whereas the emission maximum was found at 423 nm with some red tailing up to 600 nm. Compared to tetra-stilbenylmethane,<sup>8a</sup> both these maxima are considerably red shifted ( $\Delta\lambda_{\text{max(abs)}} = 56 \text{ nm}$ ;  $\Delta\lambda_{\text{max(ems)}} = 44 \text{ nm}$ ) due to increased charge delocalization in the styryl triarylamino chromophore of **6**. In fact, the absorption and emission maxima of **6** match very well with those reported for tetra-(styrylstilbenyl)methane<sup>8a</sup> indicating similar delocalization efficiencies in diphenylamino stilbenes and distyryl benzene chromophores. Interestingly, the absorption maximum of **6** is also red shifted from that of the model chromophore arm **7**<sup>13</sup> ( $\lambda_{\text{max}} 366 \text{ nm}$ ) suggesting a small degree of homoconjugation through the central tetrahedral carbon of **6**. Moreover, the molar absorptivity of **6** is much greater than the fourfold value of **7** ( $\epsilon_{\text{max}} 21\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ), indicating constructive excitonic coupling between the four stilbenoid arms in **6**. The band-gap energy ( $E_g$ ) of **6**, estimated from the onset of the absorption curve, was calculated to be 2.91 eV, which is comparable to those reported by Shirota et al. for other triarylamino clusters.<sup>7</sup>

Figure 1. Absorption and fluorescence spectra of **6** in  $\text{CH}_2\text{Cl}_2$ .

Cyclic voltammetric (CV) studies on **6** (Pt anode,  $\text{CH}_2\text{Cl}_2$ ,  $\text{Bu}_4\text{NClO}_4$  as supporting electrolyte) produced a reversible oxidation wave ( $E_{1/2}=1.00$  V versus SCE) due to the peripheral triarylamine moieties. The oxidation takes place at a higher potential than those reported for common triarylamine derivatives, presumably due to charge delocalization from the triarylamine groups to the conjugated styryl double bonds. This, in turn, lowers the HOMO level of **6**, which is also reflected in its optical properties mentioned above. Interestingly, **6** showed only one redox wave in the vicinity of 1.00 V, suggesting that all the four triarylamine units in **6** are electrochemically equivalent. It thus appears that the central  $sp^3$ -carbon of **6** causes a total disruption in conjugation in the molecule and does not allow any electronic communication whatsoever between the peripheral triarylamine units.<sup>14</sup> It may also be noted that the four triarylamine moieties in **6** are rigidly held by the stilbenoid linkages and hence are placed at a maximum distance apart, despite which they show only one redox wave. Therefore, during CV scanning, the molecule must undergo fast rotational changes so that all four triarylamine ends are able to reach the electrode within the electrochemical time scale. A second oxidation peak (irreversible) was also found for **6** at 1.23 V (versus SCE) due to oxidation of the stilbene units.

Thermal studies on **6** were carried out by differential scanning calorimetry (DSC). The results showed a step transition at 165°C which we have assigned as the glass transition temperature ( $T_g$ ). It may be noted that the individual arm **7** had a distinct melting endotherm at 145°C and showed no signs of glass formation. Therefore, as proposed by Bazan et al.,<sup>8a</sup> bringing together four stilbenoid units to a central tetrahedral junction dramatically alters the morphological properties of the composite (crystalline→amorphous). Perhaps the rigid tetrahedral arrangement of the chromophores does not encourage any intermolecular  $\pi$ -stacking interactions and hence, such molecules show an amorphous morphology. However, we note that tetrahedral composites comprised of small stilbenoid arms e.g. tetra-stilbenylmethane (**8**, mp 275°C) are crystalline materials.<sup>8a,15</sup> Therefore, unless the individual stilbenoid units are sufficiently large, the above strategy does not necessarily give rise to amorphous states. An overall increase in molecular volume either via extended conjugation as shown by Bazan et al. for **9** ( $T_g=190^\circ\text{C}$ )<sup>8a</sup> or via functionalization with bulky, conformationally mobile triarylamines as shown here for **6**, appears to be necessary to provide an amorphous character to centrally tetrahedral stilbenoid composites.

In summary, we have shown that crystalline molecules viz. tetraphenylmethane and triphenylamine when held together by a covalent linkage provide an amorphous character to the hybrid while retaining their individual optical and electrochemical properties. Based on these design elements, we are exploring the synthesis of other small molecular weight molecular glasses for optoelectronic applications.



**8**: R = H (crystalline)

**9**: R =  $\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{Bu}^1-p$  (amorphous)

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15. Tetrakis(4-*t*-butylstilbenyl)methane is also a crystalline material (unpublished work).