

Triarylamines Designed to Form Molecular Glasses. Derivatives of Tris(*p*-terphenyl-4-yl)amine with Multiple Contiguous Phenyl Substituents

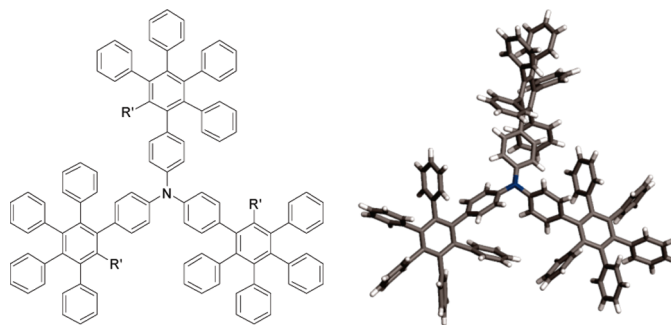
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ABSTRACT



The principles of crystal engineering can be used in a contrary way to help devise molecules that resist crystallization and form long-lived glasses. This can be achieved by making structural changes that thwart established patterns of crystallization. In using this strategy to block the crystallization of triarylamines, we have found that the introduction of methylpentaphenyl groups is particularly effective, presumably because they inhibit efficient molecular packing and normal intermolecular interactions.

The characteristic optoelectronic properties of triarylamines are widely exploited in modern technology.¹ Properties of particular importance are the typically low oxidation potentials of triarylamines, the stability of their delocalized radical cations, the reversibility of their oxidation, high charge-carrier mobilities, efficient fluorescence, and the ease of tuning behavior by making rational structural alterations.¹ As a result, triarylamines can serve as critical components in a broad range of molecular optoelectronic devices,¹ including light-emitting diodes, field-effect transistors, and solar cells, as well as in advanced materials for xerography, two-photon absorption,² and photorefraction.³

Many of these applications require using triarylamines within amorphous films. Such films simplify fabrication, favor trans-

parency and flexibility, and avoid discontinuities created at the intersection of individual crystalline domains. In principle, crystallization can be suppressed by employing polymeric triarylamines; however, this approach foregoes the advantages of working with materials composed of small molecules, including their well-defined compositions, increased volatility, straightforward purification, and rigorous structural characterization. For these reasons, learning how to engineer simple triarylamines that resist crystallization is an important objective.

Small molecules tend to crystallize readily, but certain compounds can form long-lived amorphous phases with high glass-transition temperatures (T_g). Shirota and others have presented valuable general guidelines for the design of mol-

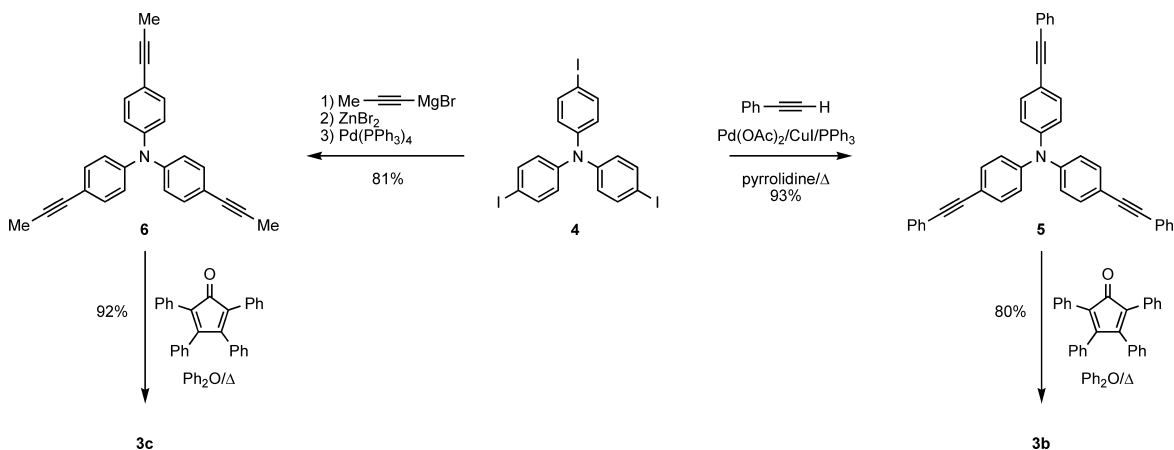
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Scheme 1

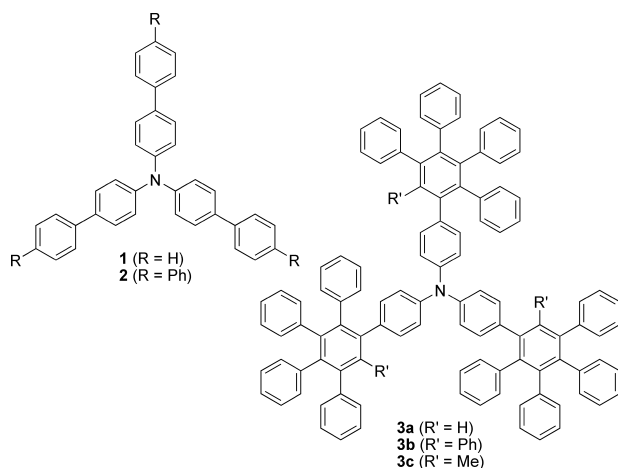


ecules likely to yield long-lived glasses.⁴ Among the key features are nonplanar molecular structures that adopt multiple conformations and inhibit effective packing. In addition, recent efforts to design molecular glasses have underscored the effectiveness of turning to the “dark side” of crystal engineering and making shrewd structural alterations that thwart established patterns of crystallization, without necessarily changing other properties of interest.⁵ To test these strategies in an area of established practical importance, we have prepared new triarylamines designed to form glasses with high values of T_g .

Triphenylamine itself is known to crystallize readily instead of forming a molecular glass, even when molten samples are cooled rapidly.⁶ In contrast, tris(biphenyl-4-yl)amine (**1**) and tris(*p*-terphenyl-4-yl)amine (**2**) both form glasses ($T_g = 76$ and 132 °C, respectively), possibly in part because they can adopt more conformations than triphenylamine.⁶ This behavior allows triarylamine **2** to serve as a modestly effective blue emitter in thin-film molecular electroluminescent devices.⁷

Analysis of the reported structure of triarylamine **1** shows that (1) the triphenylamino core adopts a nonplanar, propeller-shaped conformation and (2) multiple intermolecular $\pi\cdots\pi$ and C–H $\cdots\pi$ aromatic interactions are present.^{8,9} As summarized in a recent study of the structures of hexaphenylbenzene, pentaphenylbenzene, methylpentaphenylbenzene, and related compounds,¹⁰ simple arenes can be modified by attaching multiple contiguous phenyl substituents to create complex nonplanar topologies that disfavor extensive $\pi\cdots\pi$ and C–H $\cdots\pi$ aromatic interactions. Applied to triarylamines **1** and **2**, such structural alterations should weaken molecular association, impede molecular movement, and hinder efficient packing,¹⁰ thereby enhancing the predisposition to form glasses.⁴ Indeed, substituted triarylamine **3a** has been shown to produce a long-lived glass ($T_g = 202$ °C) and to serve as an effective hole transporter in electroluminescent devices.¹¹

To provide a deeper understanding of structural features that can inhibit the crystallization of triarylamines, we synthesized fully substituted derivatives **3b,c** and studied their behavior. As summarized in Scheme 1, triarylamine **3b** was prepared in 74% overall yield from tris(4-iodophenyl)amine (**4**)¹² by Sonogashira coupling with phenylethyne to give intermediate **5**, followed by heating with excess tetraphenylcyclopentadienone to effect a 3-fold Diels–Alder reaction and elimination of CO. Similarly, analogue **3c** was obtained in 75% overall yield from compound **4** by Negishi coupling



The principles of crystal engineering can be used to design related triarylamines predisposed to form molecular glasses.

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with 1-propynylzinc bromide to give intermediate **6**,¹³ followed again by heating with excess tetraphenylcyclopentadienone. Thermogravimetric analysis (TGA) of triaryl- amines **3b,c** (Figure 1) confirmed their expected high thermal

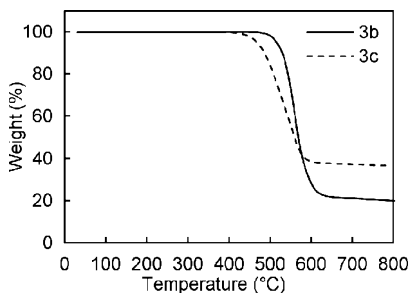


Figure 1. Analyses of triaryl amines **3b,c** by TGA, conducted under N₂ at a heating rate of 10 °C/min.

stability, and no loss of weight was noted below 460 °C for compound **3b** or below 400 °C for analogue **3c**. Study of triarylamine **3c** by differential scanning calorimetry (DSC) revealed a well-defined glass transition (T_g = 207 °C), followed by an exotherm caused by crystallization and an endotherm at 395 °C associated with melting (Figure 2).

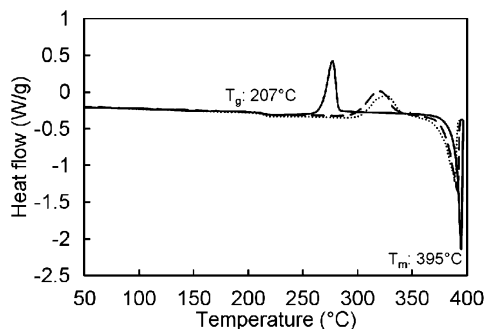


Figure 2. Analysis of triarylamine **3c** by DSC, using a heating rate of 10 °C/min. A cycle of three heating runs is shown, with the first, second, and third runs represented by solid, dashed, and dotted lines, respectively.

Closely similar behavior was shown by partially substituted derivative **3a**.¹¹ Unexpectedly, however, fully substituted analogue **3b** showed no glass transition upon heating, and DSC revealed only a broad endotherm at 260 °C that may be associated with a change of phase.¹⁴

Analysis by powder X-ray diffraction confirmed that triaryl amines **3b** and **3c** can form amorphous films.¹⁴ Moreover, methyl-substituted compound **3c** proved to remain amorphous even after being heated for 1 h at a temperature (230 °C) above its T_g . In contrast, similar heating of triarylamine **3b** induced crystallization.

To better understand these differences, we attempted to grow crystals of triaryl amines **3b,c** suitable for structural study by X-ray diffraction. Repeated attempts to crystallize compound **3c** were unsuccessful, but we found that crystals of analogue **3b** could be grown under carefully defined conditions involving very slow evaporation of solutions in THF. The crystals proved to belong to the monoclinic group *Pn* and to have the approximate composition **3b**·13 THF.¹⁴ A significant fraction of the volume of the crystals (49%) is accessible to guests,^{15,16} which envelop molecules of triaryl- amine **3b** almost completely.¹⁴ The high percentage of guests and the absence of $\pi\cdots\pi$ and C–H $\cdots\pi$ aromatic interactions between molecules of compound **3b** provide clear evidence that normal crystallization has been thwarted.

As expected, the central triphenylamino core of compound **3b** adopts a nonplanar, propeller-shaped conformation. In addition, the average interaryl torsional angles between the three fully substituted aromatic rings and their substituents (66.5°, 73.5°, and 75.1°) are similar to the averages observed in the structures of hexaphenylbenzene (79.3°) and related compounds.^{10,17} In contrast, a much smaller average angle is expected in partially substituted analogue **3a**, as found in two structures of pentaphenylbenzene itself (60.5° and 59.5°).¹⁰ Moreover, studies of compounds closely related to pentaphenylbenzene have demonstrated rapid angular movement around the bonds linking the peripheral phenyl substituents to the central aromatic ring, even in the solid state.¹⁸ As a result, significant conformational mobility is allowed, whereas fully substituted analogues have less liberty and more persistent shapes.¹⁹

Together, these structural data help rationalize the behavior of triaryl amines **3a–c** and provide useful guidelines for designing other molecules that can form long-lived glasses. In particular, our observations show that interaryl torsional angles in fully substituted aromatic rings with multiple contiguous phenyl groups (such as those in triaryl amines **3b,c**) are normally much larger than those in analogues that are only partially substituted (such as in triarylamine **3a**). In turn, larger torsional angles can promote the formation of glasses in two ways: (1) by introducing a higher degree of nonplanarity, thereby inhibiting efficient packing and (2) by more effectively obstructing the formation of normal intermolecular $\pi\cdots\pi$ and C–H $\cdots\pi$ aromatic interactions, thereby leading to lower degrees of association. Although triaryl- amine **3b** does not in fact show a glass transition, its structure provides abundant signs of inefficient molecular packing,

(15) We estimate the percentage of volume accessible to guests by using the PLATON program.¹⁶ PLATON calculates the accessible volume by allowing a spherical probe of variable radius to roll over the van der Waals surface of the network. PLATON uses a default value of 1.20 Å for the radius of the probe, which is an appropriate model for small guests such as water.

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(14) See the Supporting Information for details.

such as the inclusion of guests. Analogue **3c** may be assisted in its ability to form long-lived glasses by its lower symmetry. In general, our results suggest that the introduction of alkylpentaphenyl groups and related fully substituted unsymmetric aryl units may be an especially effective strategy for inducing the formation of glasses, primarily by inhibiting efficient molecular packing and normal intermolecular aromatic interactions. The low conformational mobility of fully substituted arenes with multiple contiguous phenyl groups does not appear to make them inherently less apt to form glasses than more mobile analogues with partial substitution, as demonstrated by the similar behavior of triarylamines **3a** and **3c**.

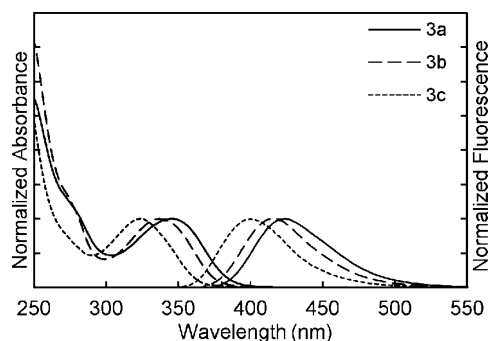


Figure 3. Normalized absorption and emission spectra of solutions of triarylamines **3a–c** in CH_2Cl_2 .

It is important to note that altering the structure of tris(*p*-terphenyl-4-yl)amine (**2**) to create highly substituted derivatives **3a–c** does not greatly change the optoelectronic properties of individual molecules. Absorption and emission spectra of compounds **3a–c** are shown in Figure 3. In all cases, two distinct absorption bands are observed, one attributed to the π – π^* transition of phenyl rings (<300 nm) and the other assigned to absorption of the triphenylamino core (300–400 nm). Among triarylamines **3a–c**, conjugation between the core and the highly substituted periphery appears to be greatest in partially substituted compound **3a**, which is expected to have the smallest average interaryl torsional angles and shows the most red-shifted absorption (λ_{max} ($\log \epsilon$) = 345 nm (3.2) in CH_2Cl_2). Fully substituted analogues

3b and **3c** have maxima at 337 nm (3.0) and 324 nm (3.0), respectively, whereas simpler triarylamines such as triphenylamine, tris(biphenyl-4-yl)amine (**1**), and tris(*p*-terphenyl-4-yl)amine (**2**) absorb at 299 nm (4.5), 345 nm (4.7), and 361 nm (4.9), respectively, in THF.⁶ Bandgaps calculated from the absorption spectra of compounds **3a**, **3b**, and **3c** have similar values (3.1, 3.2, and 3.4 eV, respectively). Our data reveal that compounds **3a–c** achieve a degree of π -conjugation, despite their twisted conformations. It is noteworthy that the compound incorporating methylpentaphenyl groups (**3c**) shows the most blue-shifted absorption and emission. Similarly, the absorption of methylpentaphenylbenzene is blue-shifted relative to that of hexaphenylbenzene.¹⁴

Our results confirm that the principles of crystal engineering can be used in a contrary way to help guide the design of molecules that resist crystallization and form long-lived glasses. In particular, we have developed a detailed understanding of the crystallization of hexaphenylbenzene and related arenes with multiple contiguous phenyl groups,¹⁰ and we have applied this understanding to the problem of devising triarylamines able to form amorphous thin layers of potential use in molecular optoelectronic devices. Our observations suggest that methylpentaphenyl substituents may be particularly effective in inhibiting crystallization, both by enforcing highly nonplanar topologies that pack poorly and by interfering with normal molecular association induced by $\pi \cdots \pi$ and $\text{C–H} \cdots \pi$ aromatic interactions.

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Supporting Information Available: Experimental procedures, spectroscopic data for all new compounds, analysis of compounds **3b,c** by DSC, and additional crystallographic details, including powder X-ray diffractograms, ORTEP drawings, and structural data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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