



Carbazol-*N*-yl and diphenylamino end-capped triphenylamine-based molecular glasses: synthesis, thermal, and optical properties



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ABSTRACT

Novel low-molecular-weight amorphous organic glasses based on triphenylamine core end-capped by either di(4-methoxyphenyl)amino or 3,6-dimethoxycarbazol-*N*-yl groups have been synthesized and characterized. The molecules exhibit high glass-transition temperatures (74–151 °C), excellent thermal stability, and are soluble in common organic solvents. Moreover, most of them absorb mainly in UV domain. These star-shaped triphenylamine derivatives are promising hole transporting materials for solid-state dye-sensitized solar cell applications.

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Introduction

Nowadays, dye-sensitized solar cells (DSSCs)¹ have been becoming one of the most promising technologies in the field of renewable energies thanks to their low weight, to the possibility of making large flexible surfaces, and also to their photovoltaic efficiency which are found to be more and more significant.² One of the manufacturing challenges for DSSCs is the need for a robust sealing process that would prevent the liquid electrolyte in the cells from leakage and evaporation. Moreover, the electrolyte, the iodide/triiodide redox couple, is quite corrosive to the metallic electrodes. To overcome these problems, one of the promising solutions is replacing the liquid electrolytes with low-molecular-weight amorphous organic π -conjugated semiconductors to make solid-state DSSCs.³ Despite their tendency to crystallization, small molecules can form stable amorphous materials above ambient temperature if their structures are meticulously designed⁴ and become attractive hole conductors for solid-state DSSCs.⁵ Among them, triphenylamine (TPA) derivatives having pseudo-three-dimensional conjugated architecture constitute an attractive class of material thanks to their interesting properties, including good charge transport, good thermal, and morphological stability.^{6,7} Recently, we have reported a series of star-shaped molecules derived from thieno[3,2-*b*]thiophene unit and TPA core.⁸ Experimental and theoretical investigations have shown that these visible-light-harvesting molecular glasses have suitable characteristics for use

as hole conductor in solid-state DSSCs.⁹ In the present work, we focus on the design and the synthesis of new *p*-type amorphous organic semiconductors based on TPA core with short π -conjugated pathways in each branch. Structurally, each branch of these new symmetrical star-shaped molecules is end-capped by either di(4-methoxyphenyl)amino or 3,6-dimethoxycarbazol-*N*-yl. These electron rich end-capping groups will help to modulate electrochemical properties of targeted compounds. Methoxy groups will enhance pore filling properties of these molecules by (i) rendering them more soluble in organic solvents and (ii) making them more hydrophilic and increasing dye-sensitized TiO₂/hole transporter affinity. Additionally, the presence of methoxy groups in para positions of phenyl rings of the diphenylamino moiety should favor charge transport properties.¹⁰ The structures of these compounds are given in Figure 1.

Results and discussion

The synthetic routes toward different targeted molecules are outlined in Figure 2. All compounds were synthesized from commercially available tris(4-bromophenyl)amine (TPA-Br). Compounds **1–5** were obtained from their respective tribrominated TPA-based cores with either di(4-methoxyphenyl)amine or 3,6-dimethoxycarbazole¹¹ via threefold Pd-catalyzed Buchwald–Hartwig amination.¹² **1** and **2** were synthesized from TPA-Br while **3** and **4** were obtained from tris(4-(5-bromothiophen-2-yl)phenyl)amine **7-Br**.⁸ **1** and **3** were isolated in high yields (95% and 78%, respectively) after purification. However, **2** and **4** were obtained in moderate yields (47% and 25%, respectively). These low yields

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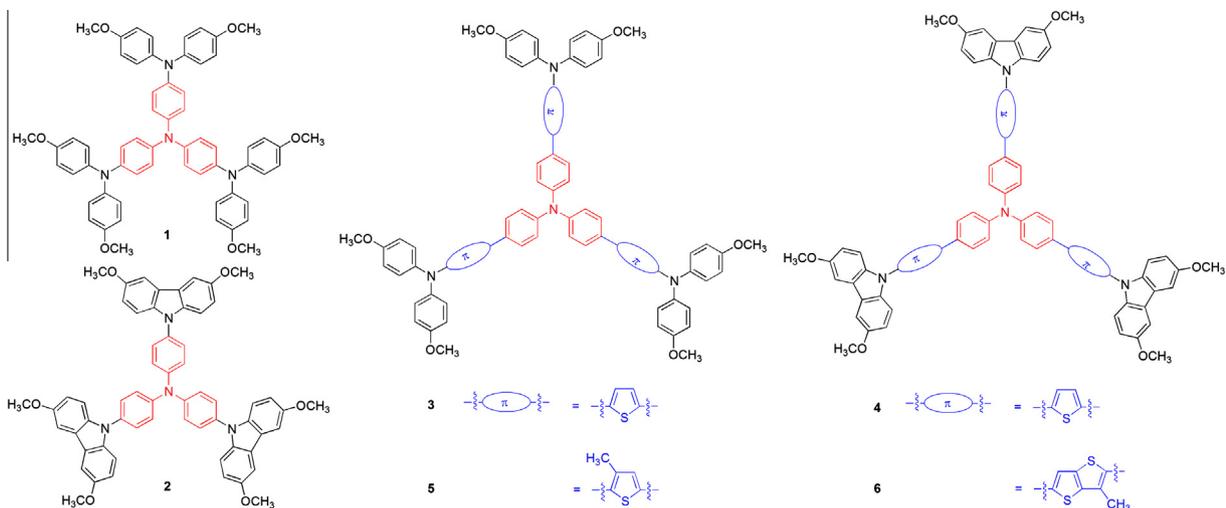


Figure 1. Molecular structures of compounds 1-6.

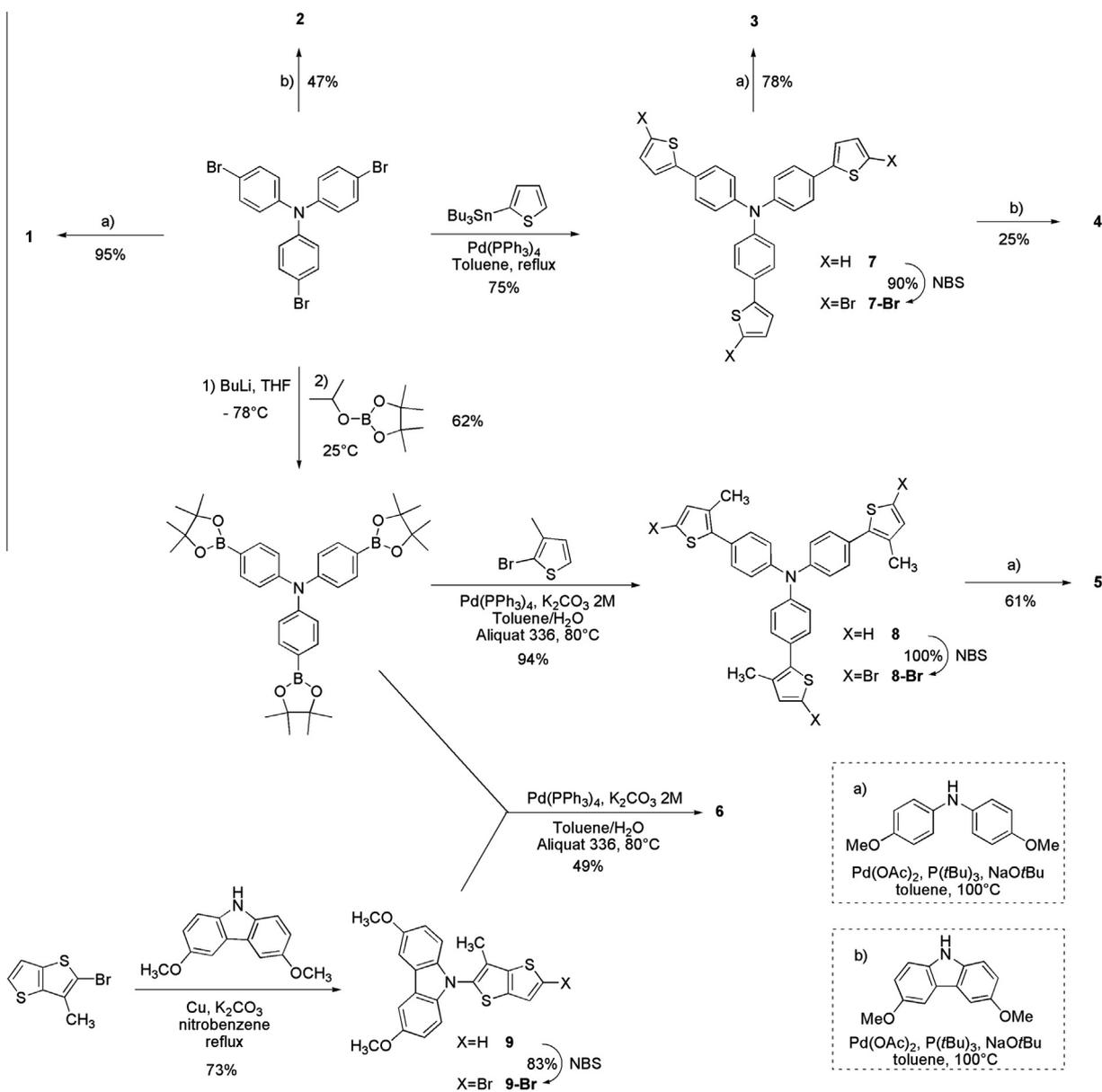


Figure 2. Synthetic routes toward compounds 1-6.

Table 1
Thermal and optical properties of compounds **1–6**

Compound	MW g/mol	λ_{\max} nm	λ_{onset} nm	ϵ (λ_{\max}) L mol ⁻¹ cm ⁻¹	E_{gopt}^c eV	T_{g}^d °C	T_{d}^e °C
1	927.09	354 ^a	400	41000	3.10	—	437
2	921.05	338 ^a	396	37000	3.13	—	439
3	1173.47	406 ^b	449	85000	2.76	99	428
4	1167.42	382 ^b	430	70000	2.88	134	426
5	1215.54	382 ^b	435	55000	2.85	74	313
6	1377.76	392 ^b	434	94000	2.86	151	424

^a In 1,2-dichlorobenzene.^b In THF.^c $E_{\text{gopt}} = hc/\lambda_{\text{onset}}$.^d determined from DSC analyses at heating rate: 20 °C/min.^e determined from TGA analyses at heating rate: 20 °C/min.

are consequence of incomplete multiple cross-coupling reactions leading to crude products containing complex mixtures of mono- and di-coupling derivatives. In case of **5**, the desired product was obtained from tris(4-(5-bromo-2-methylthiophen-2-yl)phenyl)amine **8-Br** with di(4-methoxyphenyl)amine in good yield (61%). A stille coupling between 2-tributylstannylthiophene and **TPA-Br** gave **7** (75% yield) which was then brominated leading to tris(4-(5-bromothiophen-2-yl)phenyl)amine **7-Br**⁷ in good yield (90%). The treatment of tris(4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane)phenyl)amine¹³ with 2-bromo-3-methylthiophene¹⁴ under Suzuki cross-coupling conditions afforded tris(4-(3-methylthiophen-2-yl)phenyl)amine **8** in high yield (94%). **8** was then brominated before being converted into targeted compound **5**.

Compound **6** was constructed in a different way starting from 2-bromo-3-methylthieno[3,2-*b*]thiophene which was prepared as described for its analogues.¹⁵ The copper-catalyzed Ullmann N-arylation conditions¹⁶ were then used to link 2-bromo-3-methylthieno[3,2-*b*]thiophene and 3,6-dimethoxycarbazole yielding **9** (73% yield), which was subsequently treated with NBS providing **9-Br**. The final molecule **6** was then achieved through a threefold Suzuki coupling between **9-Br** and tris(4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane)phenyl)amine and isolated in moderate yield (49%). Except **1** and **2**, all other compounds have good solubility in common organic solvents, such as dichloromethane, chloroform, tetrahydrofuran, (di)chlorobenzene, and toluene.

Optical properties of synthesized compounds (**1–6**) were examined in dilute solutions. UV–vis absorption spectra were given in the [Supplementary data](#) and related data are summarized in [Table 1](#). Compounds **1** and **2** have the shortest λ_{\max} of absorption (354 and 338 nm, respectively) in this group due to limited conjugation in the molecular structures. The insertion of π -bridges between TPA core and end-capping groups increases the delocalization of π electrons in the targeted molecules. As a consequence, the structure of these new compounds involves a bathochromic shift in comparison with **1** and **2**. For instance, the insertion of a thiophene unit as π -bridge in **3** and **4** causes a shift of 52 nm (vs **1**) and 32 nm (vs **2**), respectively, ([Table 1](#)). Adding a methyl moiety on the thiophene in the adjacent position of phenyl-thiophene bond in compound **5** causes higher deviation from planarity in comparison with **3** resulting in a hypsochromic shift of 24 nm. Replacement of the thiophene in **4** by more conjugated π -bridge, thienothiophene in **6**, causes a slightly bathochromic shift (10 nm vs **4**). Obviously, on the same TPA-based core, diphenylamino end-capping group causes bathochromic shift in comparison with its analogue carbazol-*N*-yl one (**1** vs **2**: $\Delta\lambda_{\max} = 16$ nm; **3** vs **4**: $\Delta\lambda_{\max} = 24$ nm).

The corresponding optical band gaps, which were determined from the edge of the absorption bands, are summarized in [Table 1](#). With the absence of π -bridge in the molecular structures, **1** and **2** have the largest optical gaps with values of 3.10–3.13 eV. These values decreased to 2.76–2.86 eV when π -bridges were

inserted. Simultaneously, the molar extinction coefficients were doubled in accordance with the increasing of conjugation lengths. The high ϵ values of these compounds (70,000–94,000 L mol⁻¹ cm⁻¹) can be reasoned as a combined effect of high molecular weights and of the presence of multi conjugated branches in each molecule.

Thermal behaviors of six synthesized compounds were then investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under argon atmosphere. The temperatures corresponding to 5% weight loss (T_{d}) and the glass transition temperatures (T_{g}) were summarized in [Table 1](#). Synthesized compounds showed significant thermal stability with T_{d} values in the range of 420–440 °C in most cases. The T_{d} of **5** is 313 °C which is significantly lower than that of **3** (428 °C). This can be attributed to the presence of a methyl moiety on the thiophene ring in the α -position of phenyl-thiophene bond. Methyl moieties cause steric hindrance and thus decrease thermal stability of corresponding compound. However, the thermal stability of all compounds is good enough for the applications in optoelectronic devices. Glass forming properties of **1–6** were then investigated by DSC. In our experiments, no glass transition was detected in the range of 0–200 °C for compounds **1** and **2**. Other compounds (**3–6**) exhibit glass transition temperatures (T_{g}) ranging from 74 to 151 °C and their DSC curves were shown in [Figure S2](#) in the [Supplementary data](#). Compound **3** exhibits the glass transition at 99 °C. The introduction of a methyl moiety on the thiophene significantly decreases its T_{g} (74 °C). Structurally, **3** differs from **4** by their end-capping moieties. The replacement of di(4-methoxyphenyl)amino in **3** by more rigid 3,6-dimethoxycarbazol-*N*-yl in **4** significantly increases the corresponding T_{g} (134 °C vs 99 °C). When 3-methylthienothiophene was used as π -conjugated bridge (compound **6**) in place of thiophene (in **4**), the rigidity increased leading to higher T_{g} (151 °C vs 134 °C of **4**, [Table 1](#)). The compounds **3–6** were obtained as amorphous materials as confirmed by DSC.

Conclusions

In summary, synthesis, thermal, and optical properties of novel di(4-methoxyphenyl)amino and 3,6-dimethoxycarbazol-*N*-yl end-capped triphenylamine-based molecular glasses were investigated in detail. The synthetic routes allowed the preparation of highly soluble compounds using short multistep syntheses starting from tris(4-bromophenyl)amine in relatively good yields. Thanks to their high glass transition temperatures (T_{g} varies from 74 to 151 °C), such low-molar-weight compounds are able to stay in amorphous state allowing the realization of a thin film with good contact with the nanostructured inorganic layer. Moreover, most of them absorb mainly in UV domain. These properties make them being promising candidates for solid-state dye-sensitized solar cell applications.

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Supplementary data

Supplementary data (full experimental detail, DSC curves and UV–vis spectra of compounds **1–6**) associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2013.05.152>.

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