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Bridged Triphenylamine-Based Dendrimers: Tuning Enhanced Two-Photon Absorption Performance with Locked Molecular Planarity

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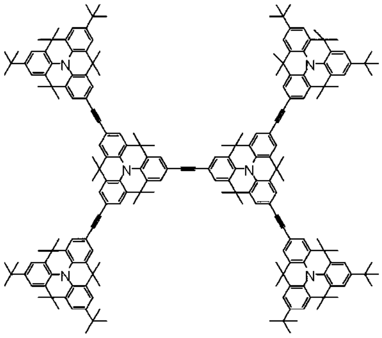
ABSTRACT



Triphenylamine derivatives bridged by methylene units afford a near planar molecular platform in a series of one dimer and two oligomers exhibiting increased structural rigidity compared to that of their parent triphenylamines. This series of dendrimers show significantly enhanced two-photon absorptions that are up to 3-fold that of triphenylamines with similar molecular size and structure.

Organic materials with large two photon absorption (TPA) cross-sections show optical power limiting properties[1] and have potential applications in scanning excitation microscopy,[2] three-dimensional optical data storage,[3] and photodynamic therapy.[4] TPA performance in these applications depends greatly on large TPA coefficients. Design of multipolar[5] and dendritic molecular structures is among several strategies[6] in achieving large TPA cross-sections. This has led to extensive work on building π-conjugated dendritic molecules with π centers and functional groups that possess

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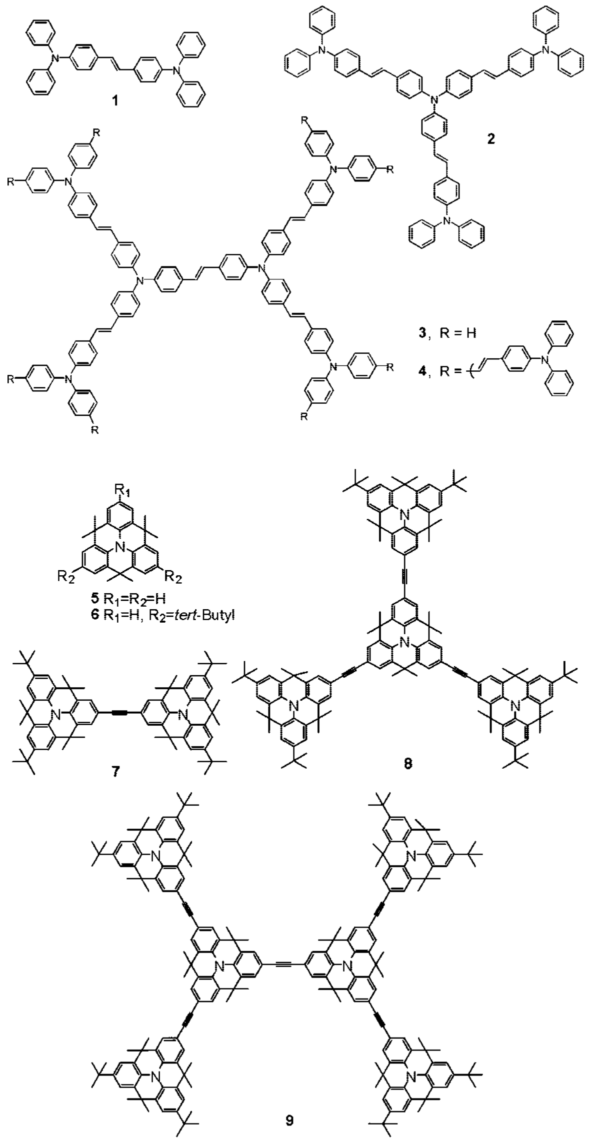
electron-donating and/or electron-withdrawing properties on terminal sites.[7]

Triphenylamine-based molecules **1**−**4** exhibit enhanced nonlinear responses,[8] the three N−C bonds in triphenylamine and its derivatives having been shown[9,10] to be essentially in one common plane. This supports π conjugation through a lone pair of electrons on the nitrogen atom.[11] Extension of π conjugation over the entire molecular framework may, however, be poor as a result of relatively large dihedral angles between the phenyl ring plane and the plane of the N-bonded carbon atoms.[8] Recent research has verified that molecular planarity is an important positive factor for enhancing TPA cross-sections.[12] The methylene units in bridged triphenylamine **5**[13] are expected to hold the three phenyl rings in a locked, planar manner compared to those in triphenylamine. In this work a series of a dimer **7** and two dendrimers **8** and **9** incorporating two to six units of bridged **5** were synthesized. They show TPA cross-sections remarkably higher than their triphenylamine counterparts and hence are more promising models in the field of nonlinear optics.



1

2

3, R = H

4, R =

5 R_1=R_2=H

6 R_1=H, R_2=*tert*-Butyl

7

8

9

The molecules **7**−**9** were synthesized[14] by Sonogashira couplings. A single crystal of **5** (Figure 1) was grown from hexane. The crystal belongs to the monoclinic system with a space group of $P2_1/c$. There are two independent molecules per asymmetric unit with irregular propeller-like geometries. The central nitrogen atoms are found to have small deviations from the plane of the surrounding carbon atoms with distances of 0.15 and 0.29 Å, respectively. Mean values of the C−N−C bond angle in the two molecules are, however, 118.5° and 119.0°, respectively, corresponding to an sp^2-hybridized nitrogen favoring intramolecular p−π interactions between nitrogen and its adjacent phenyl rings. In addition the dihedral angles between phenyl rings and the plane of

Figure 1. X-ray crystallographic structure of **5** (C = gray; N = dark gray; H atoms are omitted for clarity).

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(14) Synthesis of monomers **5** and **10** is described in Supporting Information.

three central carbon atoms remain small with mean values of 5.9° and 7.6°, respectively, which are much smaller than those in triphenylamine (>43°).[8] The above results clearly show that a bridged triphenylamine molecular framework is a significantly more planar structure compard with that of parent triphenylamine, which is expected to facilitate TPA.

The one-photon absorption and emission spectra of compounds **7**, **8**, and **9** are illustrated in Figure 2. It was observed that an increase in the number of branches from one in compound **7** to three in dendrimer **8** resulted in a red shift from 399 nm for **7** to 411 nm for **8**. The absorptions at the 300−350 nm range correspond to the core bridged triphenylamine moiety in both the dimer and the dendrimer. There is no further red shift observed for λ_{max} at about 400 nm in going from **8** to the larger, more branched, and more conjugated molecule **9**. The onset to absorption is, however, red-shifted for the latter due to its relatively more extended conjugation. All three molecules **7**−**9** emit blue light with wavelengths of 428, 438, and 441 nm, respectively. An extension of conjugation going from **7** to **8** results in a 10-nm red shift in λ_{max}. There is again no appreciable differences in their fluorescence spectra going from **8** to **9**, similar to what was observed in their UV−vis spectra. This indicates that there is little change in conjugation effect in extending the conjugated molelucar framework after the second generation. Fluorescent quantum yield was observed to decrease from 64% for **7** and 53% for **8** to 40% for **9**,[15] possibly because of an increasing probability of intermolecular interaction.

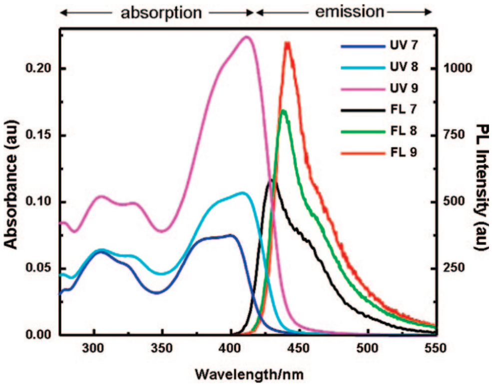

Figure 2. Absorption and emission spectra of **7** ($\varepsilon = 75\,000$ L·mol^{-1}·cm^{-1}), **8** ($\varepsilon = 120\,000$ L·mol^{-1}·cm^{-1}), and **9** ($\varepsilon = 220\,000$ L·mol^{-1}·cm^{-1}) in chloroform (10^{-6} M).

In TPA studies of conformationally mobile porphrins[16] and related examples,[17] the magnitude of TPA cross-section depended on favorable molecular structures that optimize intramolecular charge transfer. The enhancement in electronic interactions derived from extended molecular planarity is strongly correlated to larger TPA cross-sections. The TPA properties of triphenylamine and its derivatives **1**−**9** are summarized in Table 1.

Table 1. Comparison of TPA Properties of Triphenylamine (TPhA) and a Series of Its Derivatives **1**−**9**[a]

compd	MW	N_π[b]	cross-section σ_2 (GM)[c]	σ_2/MW	σ_2/N_π[d]
TPhA	245.32	20	5 (2)	0.02	0.03
1	514.66	42	320 (40)	0.62	1.0
2	1053.34	86	1900 (500)	1.23	2.9
3	1592.02	130	2700[e]	1.70	2.8
4	3746.74	306	4500[e]	1.20	2.0
5	365.51	20	30 (5)	0.08	0.2
7	977.45	44	1300 (300)	1.28	3.9
8	1864.69	92	4800 (500)	2.58	6.8
9	2751.94	140	6100 (1000)	2.22	5.7

[a] TPA cross-sections were calculated from dependences of the nonlinear absorption of solutions on the concentration.[18] [b] N_π: the number of π electrons. [c] 1 GM = 1×10^{-5} cm^4·s·photon^{-1}. [d] Relative values with reference to the value for molecule **1**. [e] The peak values for molecules **3** and **4** are cited from the literature.[18]

A significant obervation is that for similar numbers of π electron (N_π) in a conjugated molecular framework, the bridged-triphenylamine series always exhibit significantly larger TPA cross-sections (σ_2) than the triphenylamine series. For example, the cross-section of **5** is about 6 times that of parent triphenylamine, and the figures for **7**, **8**, and **9** are about 4, 2.5, and 2.3 times that of **1**, **2**, and **3**, respectively. Although both dendrimers **3** and **4** have relatively more extended conjugated molecular frameworks, their two-photon absorptions are less efficient than those of **8** and **9**. In fact a comparison of their relative efficiency in terms of σ_2/N_π clearly indicate that the **8**/**9** pair is two to three times better. While there is evidence that an ethenyl link may be a relatively better conjugation spacer group than an ethynyl link,[19] our results suggest that improved molecular planarity in the triphenylamine moiety is key to enhanced extended electronic interaction in the entire molecular framework of **7**, **8**, and **9**. This in turn leads to their improved TPA properties. The molecule **8** is the most promising model in our work. Although its σ_2 value is lower than that of **9**, it is synthetically more accessible. A σ_2 value of 4800 GM for a first generation dendrimer such as **8** is considered large for an intrinsic TPA cross-section of molecules of similar sizes. In addition the σ_2/N_π and σ_2/MW values for **8** are most superior among all molecules studied in Table 1.

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(15) Fluorescent quantum yields observed for **7**, **8**, and **9** at 5×10^{-7} M were 80%, 75%, and 56%, respectively.

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To demonstrate that the enhanced TPA properties of **7**−**9** were unlikely to derive from aggregate formation[19] or solvent effects,[20] local molecular environment influences[21] on the optical responses (Figure 3) of **8** were studied.

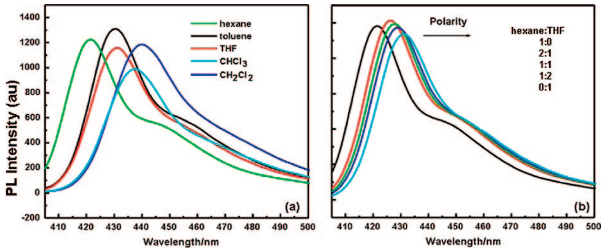
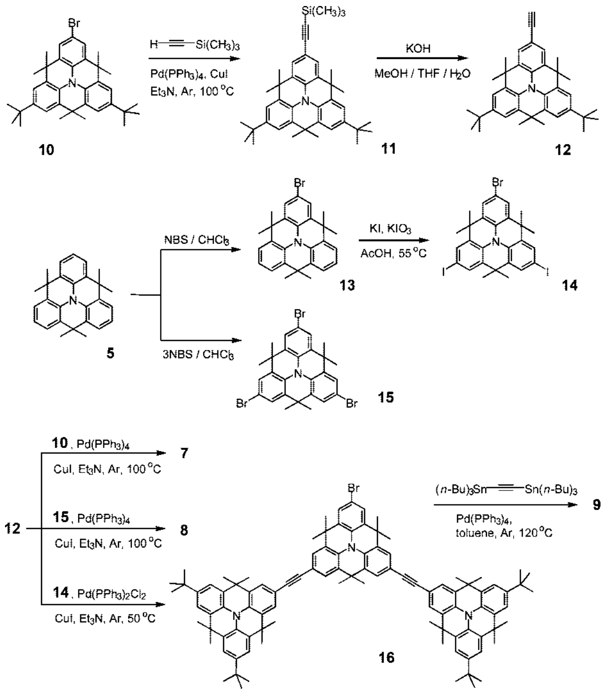


Figure 3. Linear photoluminescence spectra of **8** in (a) various solvents (10^{-6} M) and (b) hexane/THF mixtures.

The fluorescence efficiency (Figure 3a) of **8** in the aprotic solvents studied remained relatively constant (∼65%).[23] A continuous and relatively regular change in red shift and vibronic structure observed in Figure 3b is indicative of nonspecific interactions between **8** and hexane/THF. The relatively constant fluorescence efficiency associated with the above changes indicates that the local molecular environment surrounding **8** involves relatively homogeneous mixture of hexane and THF molecules. The above observations may suggest that there is no significant intermolecular interaction (aggregation) between molecules of **8** in these solvents. This supports our argument that the enhanced TPA performance observed for **7**−**9** was mainly due to their locked molecular planarity.

The molecules **7**−**9** combine high fluorescence quantum yields with large TPA cross-sections (1300−6100 GM). Their locked molecular planarity facilitates TPA. If the degree of molecular planarity is further enhanced by replacing ethynyl with alkenyl linkages, significantly larger σ_2 values could be expected even from low generation dendrimers in the series. This means more desired nonlinear optical properties from relatively smaller dendrimers that are synthetically more accessible.

Scheme 1. Synthesis of Bridged Triphenylamine-Based Dimer **7** and Dendrimers **8** and **9**



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Supporting Information Available: Crystallographic data of **5** and experimental and spectroscopic/elemental data of all compounds prepared. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Compound **8** has poor solubility in protic solvents (e.g., MeOH, EtOH).