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Tuning two-photon absorption cross-sections for triphenylamine derivatives†

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A methylene bridge link connecting the *ortho*-positions within the triphenylamine scaffold increases the molecular planarity significantly. The one-photon spectroscopies of bridged triphenylamine molecules show considerable extended conjugation relative to their triphenylamine counterparts, leading to enhanced two-photon absorption (TPA) cross-sections. Various substituents at the scaffold have been prepared and studied. Using a femtosecond laser source Z-scan method, the TPA cross-sections were characterized. The maximum magnitude of the TPA cross-section is ~4800 GM, which is four times that of its triphenylamine counterpart.

Introduction

Two-photon absorption (TPA) has been widely investigated because of its potential applications in optical limiting, 3-D data storage, photodynamic therapy and two-photon fluorescence microscopic bioimaging (TPFM);[1–4] while TPFM is highly dependent on the material's TPA action cross-sections ($\eta\sigma_2$), where σ_2 is the TPA cross-section and η is the fluorescence quantum yield.[5] Within the last two decades, many strategies have been developed for constructing molecules with large TPA cross-sections, which involves increasing π-conjugation length, introducing donor–π-acceptor systems[6] and multipolar and dendritic structures,[7] and improving molecular planarity.[8]

Triphenylamine (**T1** in Chart 1) has been applied as an electron donating function group in the design of TPA chromophores.[9–16] However, due to the large dihedral angle between the phenyl ring plane and the plane of the nitrogen-bonded carbon atoms, the overlap of the p orbital carrying the lone pair of electrons on the nitrogen with the π orbitals of the phenyl rings is relatively poor.[17] To solve this problem, a bridged triphenylamine (**B1** in Chart 1) has been developed as a strong donor framework for electroluminescence and TPA molecules,[18,19] which produce significantly enhanced TPA cross-sections.[20,21] Based on the single crystal diffraction data of **B1**, we found that although the dihedral angle between the phenyl ring and the central N-bonded C plane is dramatically reduced, the central nitrogen atom has a deviation from the plane, which leads to less conjugation than the **T1** molecule.[18] Surprisingly, when the *para*-positions of the three phenyl rings are attached with bulky units, *e.g.* –Br, the central nitrogen atom is suppressed within the 3C plane and the conjugation length is effectively increased.[18,20] Taking advantage of modifying the bridged triphenylamine with bulky units at *para*-positions, a substantial opportunity exists in molecular structure optimization for large TPA cross-sections. Chart 1 shows the structures of triphenylamine based chromophores.

Results and discussion

Triphenylamine was iodinated *via* a typical method under KIO_3 and KI in acetic acid to yield **T2**, followed by a

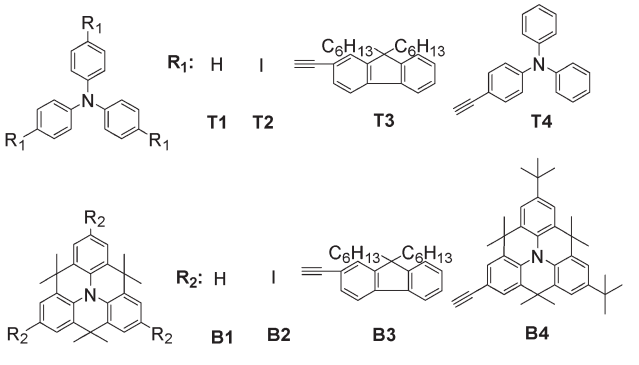

Chart 1 Structures of the **T** and **B** series.

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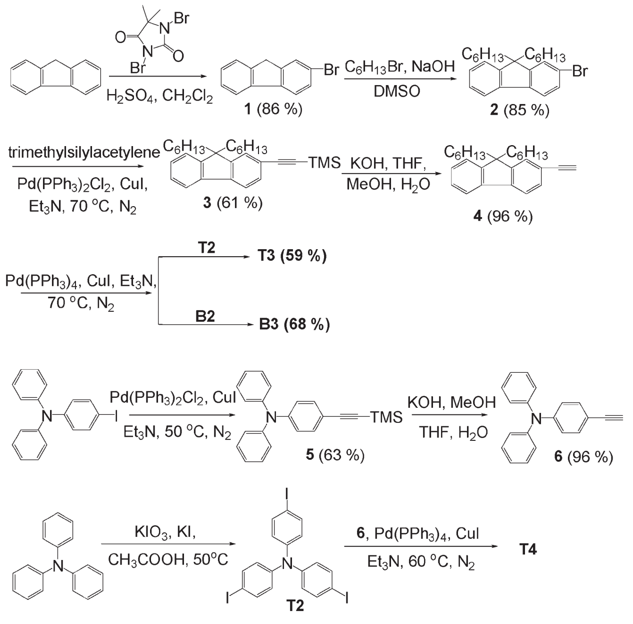

Scheme 1 Synthesis of **T3**, **B3** and **T4**.

Sonogashira coupling with 2-ethynyl-9,9-dihexyl-9*H*-fluorene (**4**) to afford **T3**, or coupling with 4-ethynyl-*N*,*N*-diphenylaniline (**6**) to afford **T4** (see Scheme 1). Note that a typical bromination of fluorene has been conducted with bromine or NBS in hot propylene carbonate,[22,23] which will lead to a large amount of 2,7-dibromofluorene or 9-bromofluorene. The presence of 1,3-dibromo-5,5-dimethylhydantoin at ambient condition affords clean bromination without the risk of a hazardous bromine reagent.[24] Using a similar procedure, **B2** and **B3** were synthesized with moderate yields (see details in the ESI†). The core units of bridged triphenylamine (**B1**), and **B4** have been reported elsewhere using mild conditions with a Grignard reagent.[21] The introduction of *tert*-butyl groups at the *para* positions of phenylene rings is to improve the solubility of **B4**, diminishing the probability of aggregation.

The one-photon absorption and emission spectra of **T3**, **B3**, **T4** and **B4** were measured in toluene solutions. The spectra are shown in Fig. 1, and a tabulation of absorption and emission maxima and fluorescence quantum yields (η) is provided in Table 1. Absorption spectra of **T1** and **B1** are shown to illustrate the impact of $-C(CH_3)_2$ linkage on the parent molecules (Fig. 1a). As we found previously, there is deviation of the N atom from the central N-bonded carbon plane in **B1**, resulting in a nitrogen floating above the structure compared to **T1**,[21] while the dihedral angles between the phenyl rings and the central carbon plane decrease significantly. However, we note reverse phenomena when bulky groups are attached at the *para* positions, *i.e.* **B3** and **B4**. As shown in Fig. 1b, **T3** features peak absorption at 385 nm, whereas **B3** exhibits a maximum at 394 nm, which red-shifts by 9 nm, indicating an increase of conjugation length from **T3** to **B3**. Although the parent molecule **B1** has a smaller conjugation length than **T1**, substituting bulky groups at the *para* positions of the three phenylenes increases the conjugation effectively, suppressing the deviation between nitrogen and the central plane of N-bonded C atoms. The emission spectra of **T3** and **B3** a show similar maximum red shift, *i.e.* from 427 nm for **T3** to 437 nm for **B3**. As shown in Fig. 1c, once the periphery groups are replaced by triphenylamine (**T4**) or bridged triphenylamine (**B4**), a magnified variation in both absorption and emission between **T4** and **B4** is observed. There is a large red shift of ~21 nm in maximum wavelength for the absorption spectra from **T4** (390 nm) to **B4** (411 nm), and 13 nm in emission maximum from **T4** (425 nm) to **B4** (438 nm). Interestingly, all four molecules show similar quantum yields (η) of ~0.52–0.60.

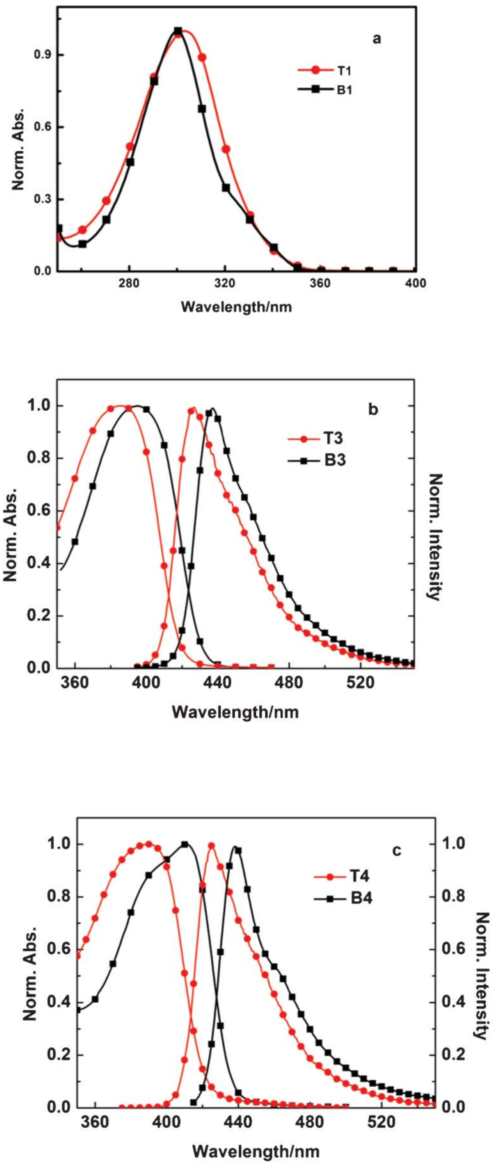

Fig. 1 Normalized absorption spectra of **T1** and **B1** (a), absorption and emission spectra of **T3** and **B3** (b), **T4** and **B4** (c), concentration: 5 μM in toluene, emission spectra were recorded when excited with the maximum absorption wavelength.

Table 1 One-photon photophysical of **T3**, **T4**, **B3** and **B4** in toluene

Compound	λ_{abs}/nm	λ_{em}/nm	η^a
T3	385	427	0.55
B3	394	437	0.60
T4	390	425	0.52
B4	411	438	0.53

[a] Determined using quinine sulfate in 0.1 M H_2SO_4 as the standard, quantum yield (η) = 0.55.

The studies of the molecular conformation effect on TPA have revealed that the magnitude of the TPA cross-section depends on favorable molecular structures that optimize intramolecular charge transfer.[25–28] An extended molecular planarity resulting from the enhanced electronic interaction suggests a strong correlation to larger TPA cross-sections, which has been highlighted in our previous studies.[21] A tabulation of TPA cross-sections is provided in Table 2. All results were obtained by a femtosecond Z-scan method, with a light intensity of about 70 GW cm^{-2} at a repetition rate of 250 Hz. A wavelength of 650 nm, also the only wavelength we used, was chosen as we found the maximum TPA absorption for triphenylamine derivatives at this wavelength.[16,20,21] This wavelength is significantly lower than the doubled wavelength (~800 nm). Similar findings have been observed in our and other groups' earlier work,[20,21,29,30] attributed to the fact that a higher excited energy state with larger probability is populated, as compared with one-photon excitation.[31]

Compared with the triphenylamine series, the bridged triphenylamine series exhibits significantly larger TPA cross-sections for similar numbers of pi electrons (N_π). We observed strong photo darkening in **T3**, which may result in an overestimated TPA cross-section value. However, **B3** (1350 GM, 1 GM = 1 × 10^{-50} cm^4 s per photon) displays a larger cross-section relative to **T3** (1100 GM). This result indicates the improved molecular planarity in the triphenylamine core unit to be the only contribution to the increase of the cross-section, which is in agreement with the red shift in the absorption and emission spectra (Fig. 1). Another impressive increase is that the cross-section of **B4** is over 4 times that of **T4**. In fact, the comparison of their relative efficiencies in terms of σ_2/N_π clearly suggests the enhancement. Note that **B4** has four bridged triphenylamine moieties, which leads the magnitude of the cross-section to be superior to that of **T4**. Interestingly, the introduction of iodine atoms at the phenylene *para* positions of **B1** makes the cross-section increase from 30 GM to 110 GM. This result gives us confidence that the planar bridged triphenylamine, combined with polar or multipolar units, would be an efficient strategy for building up molecules with large TPA cross-sections.

Table 2 TPA properties of **T3**, **T4**, **B3** and **B4** in toluene

	M_w	N_π	Cross-section σ_2 (GM)^a	σ_2/N_π	$\eta\sigma_2$
T1	245.32	20	5(2)	0.25	—
B1	365.51	20	30(5)	1.5	—
T2	623.0	20	22(3)	1.1	—
B2	743.2	20	110(40)	5.5	—
T3	1314.95	68	1100 (100)	16.2	605
B3	1435.14	68	1350 (120)	19.9	810
T4	1047.29	92	1200(200)	13.0	624
B4	1864.69	92	4800(500)	52.2	2544

[a] Numbers in parentheses represent the uncertainty.

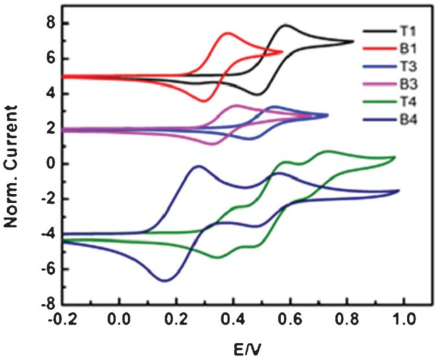

Fig. 2 Cyclic voltammograms spectra. 1 mM solution in CH_2Cl_2 with 0.1 mM n-Bu_4NPF_6 at a scan rate of 100 mV s^{-1}; 1 mm diameter planar Pt electrode at 293 ± 5 K.

The electrochemical behaviour of **T3**, **B3**, **T4** and **B4** (1 mM in CH_2Cl_2) was examined by cyclic voltammetry (CV) and square wave voltammetry (SWV) and the spectra are presented in Fig. 2. **T1** and **B1** are presented for comparison. **T1** displays a one-electron oxidation process at 0.535 V *vs.* Fc/Fc$^+$, while **B1** displays a one-electron oxidation process at 0.340 V *vs.* Fc/Fc$^+$. We have revealed that **B1**'s oxidized form, *i.e.* the radical cation, is more stable than that of **T1** due to the stabilization from the –C(CH_3)$_2$ linkages.[18] We note that both **T3** and **B3** show only a one-electron oxidation process, which is identical to **T1** and **B1**, respectively. The reason is that the fluorene moiety has a higher oxidative potential (>1 V),[32] which is not observed in the scan range. **T4** displays a one-electron oxidation, followed by a two-electron oxidation and then another one-electron oxidation at intervals of 160 mV. As presented in Fig. 3, the presence of ethynyl conjugated linkages allows **T4** to stabilize its monocation through more effective and extended conjugation, which is identical to that proposed by us previously.[18] In contrast, **B4** displays a three-

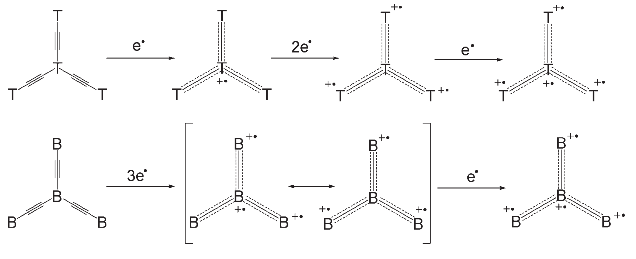

Fig. 3 Oxidation process of **T4** (upper) and **B4** (lower) up to tetracation.

Table 3 Approximate formal potentials (E_0) and number of electrons transferred during the oxidations

	E_0/V^{a,b}			
	Process 1	Process 2	Process 3	Process 4
T1	0.535 (1)			
B1	0.340 (1)			
T3	+0.510 (1)			
B3	+0.375 (1)			
T4	+0.375 (1)	+0.535 (2)	+0.695 (1)	
B4	+0.230 (3)	+0.530 (1)		

[a] Peak potential *vs.* Fc/Fc+ to the nearest 5 mV measured by square wave voltammetry and assuming electrochemical reversibility.
[b] Number of electrons associated with each process are given in parentheses.

electron oxidation followed by a one-electron oxidation, represented in Fig. 3. A summary of the formal oxidation potentials measured by SWV is given in Table 3. Compared with the **T** series, the **B** series shows 140–200 mV less for the first oxidation attributed to the stabilization of radical cations, as shown in **B1** and **T1**.

Conclusions

In summary, we synthesize both triphenylamine and bridged triphenylamine based triads. Their one-photon and two-photon photophysical properties are discussed. Due to the enhanced planarity of the triphenylamine moiety, extended conjugation has been found in both **B3** and **B4**, which provide larger two-photon absorption cross-sections than **T3** and **T4**. Together with the studies of oxidation under cyclic voltammetry conditions, an over 150 mV lower oxidation potential in **B** series affirms the stabilization of radical cations by the planar structures. This shows potential in electroluminescent applications as well as the considerable TPA performance for bridged triphenylamine.

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