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The Synthesis and One- and Two-Photon Optical Properties of Dipolar, Quadrupolar and Octupolar Donor–Acceptor Molecules Containing Dimesitylboryl Groups

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Abstract: Two series of related donor–acceptor conjugated dipolar, pseudo-quadrupolar (V-shaped) and octupolar molecular systems based on the *p*-dimesitylborylphenylethynylaniline core, namely, 4-(4-dimesitylborylphenylethynyl)-*N*,*N*-dimethylaniline, 4-[4-(4-dimesitylborylphenylethynyl)phenylethynyl]-*N*,*N*-dimethylaniline, 3,6-bis(4-dimesitylborylphenylethynyl)-*N*-*n*-butylcarbazole and tris[4-(4-dimesitylborylphenylethynyl)phenyl]amine, and on the *E*-*p*-dimesitylborylethenylaniline motif, namely, *E*-4-dimesitylborylethenyl-*N*,*N*-di(4-tolyl)aniline, 3,6-bis(*E*-dimesitylborylethenyl)-*N*-*n*-butylcarbazole and tris(*E*-4-dimesitylborylethenylphenyl)amine have been synthesised by palladium-catalyzed cross-coupling and hydroboration routes, respectively. Their absorption and emission maxima, fluorescence lifetimes and quantum yields have been obtained and their two-photon absorption (TPA) spectra and TPA cross-sections have been examined. Of these systems, the octupolar compound tris(*E*-4-dimesitylborylethenylphenyl)amine has been shown to exhibit the largest TPA cross-section among the two series of approximately 1000 GM at 740 nm. Its TPA performance is comparable to those of other triphenylamine-based octupoles of similar size. The combination of such large TPA cross-sections and high emission quantum yields, up to 0.94, make these systems attractive for applications involving two-photon excited fluorescence (TPEF).

Keywords: boron · C−C coupling · hydroboration · luminescence · two-photon absorption

Introduction

In recent years, there has been increasing interest in conjugated molecules containing three-coordinate boron for use in functional materials.[1,2] Three-coordinate boron behaves as a π acceptor because of its vacant p_z orbital, although the fact that boron is more electropositive than carbon makes it a σ donor. However, three-coordinate boron tends to be susceptible to hydrolysis by moisture, including that present in the air, unless protected by bulky groups with *ortho* substitu-

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ents, such as the 2,4,6-trimethylphenyl (mesityl = Mes) or 2,4,6-triisopropylphenyl (triptyl) groups. Experience has shown that two mesityl groups are usually sufficient to confer air stability under typical conditions. Compounds containing only one mesityl group have been reported to show decomposition products after approximately two weeks in solutions exposed to air,[3] whereas compounds with only one triptyl group are reported to be air stable.[4]

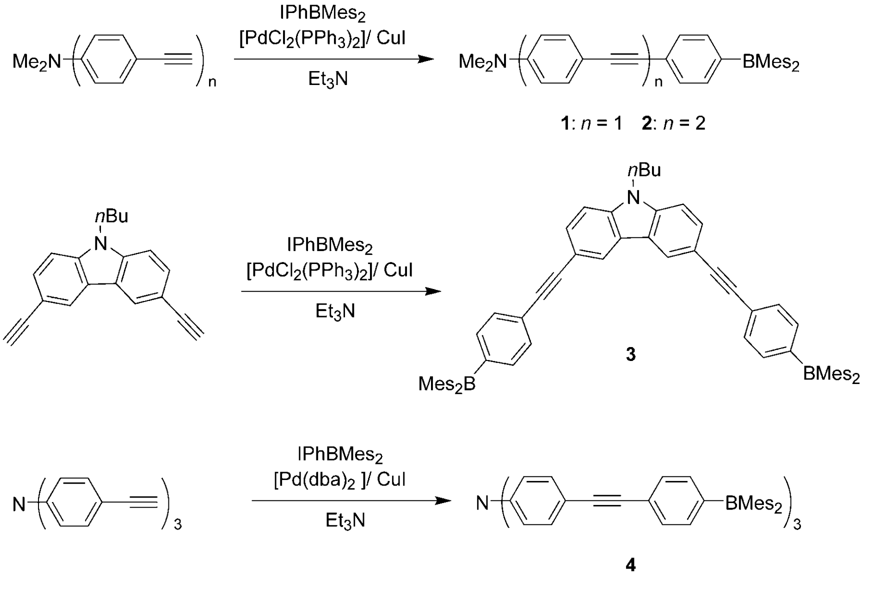
Conjugated molecular materials containing dimesitylboryl ($B(Mes)_2$) groups have been shown to exhibit sizable second- and third-order nonlinear optical (NLO) coefficients.[5,6] Related compounds have been used as efficient electron-transporting and/or emitting layers in organic light-emitting diodes (OLEDs),[7,8] with one such compound being found to produce desirable white-light emission,[9] or as dopants in non-emissive host layers,[10] including a $B(Mes)_2$-substituted 2-phenylpyridyl iridium complex that was found to be an efficient red phosphorescent emitter.[10b] Numerous three-coordinate boron-containing compounds have been shown to be effective colourimetric and luminescent sensors for anions, especially fluoride ions.[11–15] Recently, a number of conjugated molecules with $B(Mes)_2$ side groups were shown to display very large Stokes shifts of up to 195 nm, and high quantum yields both in solution and the solid state, which has been attributed to the lack of close packing.[16] A copper complex with a $B(Mes)_2$-substituted azaindole ligand also has a very large phosphorescence quantum yield in the solid state.[13c] Three-coordinate boron-containing molecules have recently been used to form chiral, metal-containing coordination networks with second harmonic generation (SHG) coefficients up to 35 times that of quartz.[17]

Several molecules containing $B(Mes)_2$ groups have been shown to exhibit large two-photon absorption (TPA) cross-sections up to 1340 GM.[18,19] TPA is defined as the electronic excitation of a molecule induced by simultaneous absorption of two photons. It is the focus of much attention due to its potential applications in laser scanning microscopy,[20] 3D optical data storage,[21] localised photodynamic therapy,[22] microfabrication and optical power limitation.[23] Both experimental findings and theoretical studies have suggested that quadrupolar[24] and octupolar[25,26] molecules exhibit more efficient TPA compared with their dipolar analogues, which has been attributed to intramolecular charge transfer between the ends and the centre of the molecules.

For some time, we have been investigating the molecular and electronic structures, and linear and nonlinear optical properties of conjugated molecules containing $B(Mes)_2$ groups,[6,19] and have recently begun to explore their TPA properties.[19] Herein, we present details of the synthesis and optical properties, including TPA, of a series of dipolar, pseudo-quadrupolar and octupolar molecules containing both amino-based donor groups and dimesitylboryl-based acceptor groups, based on the *p*-dimesitylborylphenyl-ethynylaniline motif, namely, 4-(4-dimesitylborylphenylethynyl)-*N*,*N*-dimethylaniline (**1**), 4-[4-(4-dimesitylborylphenylethynyl)phenylethynyl]-*N*,*N*-dimethylaniline (**2**), 3,6-bis(4-dimesitylborylphenylethynyl)-*N*-*n*-butylcarbazole (**3**) and tris[4-(4-dimesitylborylphenylethynyl)phenyl]amine (**4**), and the *E*-*p*-dimesitylborylethenylaniline motif, namely, *E*-4-dimesitylborylethenyl-*N*,*N*-di(4-tolyl)aniline (**5**), 3,6-bis(*E*-dimesitylborylethenyl)-*N*-*n*-butylcarbazole (**6**) and tris(*E*-4-dimesitylborylethenylphenyl)amine (**7**) to compare and contrast their optical properties.

Results and Discussion

Synthesis: As shown in Scheme 1, 4-(4-dimesitylborylphenylethynyl)-*N*,*N*-dimethylaniline (**1**) and 4-[4-(4-dimesitylborylphenylethynyl)phenylethynyl]-*N*,*N*-dimethylaniline (**2**) were synthesised through the Sonogashira cross-coupling of 1-iodo-4-dimesitylborylbenzene[6f] with one equivalent of 4-ethynyl-*N*,*N*-dimethylaniline and 4-(4-ethynylphenylethynyl)-*N*,*N*-dimethylaniline, respectively, using 1 mol % each of $[PdCl_2(PPh_3)_2]$ and CuI in triethylamine, under N_2 at room temperature to give the products in 79 and 81 % yields, respectively. 3,6-Bis(4-dimesitylborylphenylethynyl)-*N*-*n*-butylcarbazole (**3**) was prepared by treatment of two equivalents of 1-iodo-4-dimesitylborylbenzene with 3,6-diethynyl-*N*-*n*-butylcarbazole, using 2 mol % of $[PdCl_2(PPh_3)_2]$ and CuI



Scheme 1. Synthesis of chromophores **1**–**4**.

under identical conditions to give the product in 73 % yield. Note that in all of these reactions, in which the reagents were exposed to strongly basic conditions, no degradation of the dimesitylboryl groups was observed, which shows that only four *ortho*-methyl groups adjacent to the boron atom are required to ensure stability, in contrast to previous Sonogashira cross-coupling reactions involving three-coordinate boron species in which six *ortho*-methyl groups on the boron were employed.[27]

Similar conditions were initially tested for the coupling of three equivalents of 1-iodo-4-dimesitylborylbenzene with tris(4-ethynylphenyl)amine to give tris[4-(4-dimesitylborylphenylethynyl)phenyl]amine (**4**; Scheme 1). However, significant amounts (approximately 10 %) of a diyne side product were detected by MALDI-TOF mass spectrometry, which proved to be inseparable by column chromatography. The diyne arises from oxidative alkyne homocoupling upon reduction of Pd^{II} to Pd^0 during the catalyst initiation step.[28] To obtain pure product, 3 mol % of the Pd^0 complex, $[Pd(dba)_2]$ was used with 6 mol % of PPh_3, thus avoiding the Pd reduction step. This reaction required heating to reflux for one hour to reach completion, and the product was subsequently isolated in 61 % yield.

The vinyl compounds *E*-4-dimesitylborylethenyl-*N*,*N*-di(4-tolyl)aniline (**5**), 3,6-bis(*E*-dimesitylborylethenyl)-*N*-*n*-butylcarbazole (**6**) and tris(*E*-4-dimesitylboryl-ethenylphenyl)amine (**7**) shown in Scheme 2, were prepared by hydroboration of the corresponding terminal alkyne precursors using one, two and three equivalents of dimesitylborane, respectively, in dry THF under N_2 at room temperature to give the products in 67, 83 and 71 % isolated yields, respectively.

Some of these compounds, namely, the dimethylaniline-based compounds **1** and **2**, and the carbazole-containing compounds **3** and **6** undergo discolouration over a period of months if left exposed to the air, which is presumably caused by oxidation of the amino groups. They can be re-purified by filtration through a silica plug with an appropriate solvent system. We were not able to obtain satisfactory carbon analyses for any of the compounds apart from **1** and **5**, because their experimental values were always approximately 1–3 % too low, despite repeated column chromatography and recrystallisation, whereas H and N values were satisfactory for all compounds. This problem may be associated with the formation of ceramic boron carbides during pyrolysis, although we do not understand how this is related to the structure of the compound. Instead we were able to obtain satisfactory accurate mass measurements by using EI SECTOR for **2** and MALDI-TOF techniques for **3**, **4**, **6** and **7**. The experimental *m*/*z* value for the lowest mass isotopomer of **2** was found to be within 9 ppm of its calculated mass, and the highest intensity peaks of the others were each found to be within 8 ppm of the calculated masses for their most abundant combinations of isotopomers.

Optical properties

Linear spectroscopy: The photophysical properties of the series of chromophores, measured in toluene, are presented in Table 1. All of the chromophores show an intense absorption band in the near UV-blue region and emission in the violet-to-blue region.

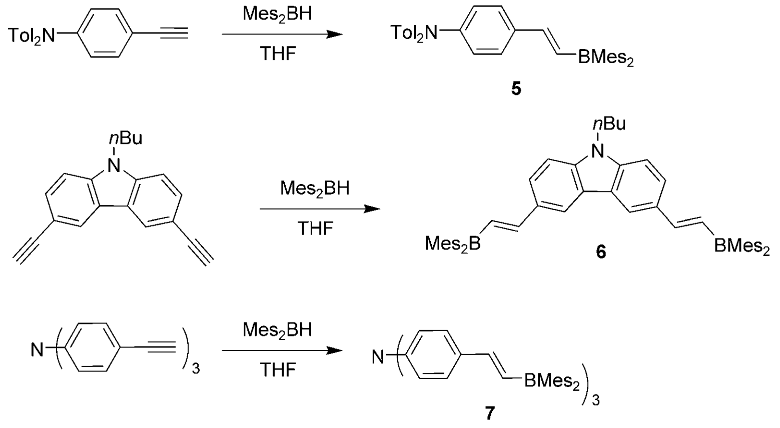
Dipolar phenylene–ethynylene chromophores

Length effect: Interestingly, the UV/Vis absorption maximum λ_{max} for the longer dipolar compound, **2**, is blueshifted by about 20 nm relative to its tolan analogue **1**. This effect has been noted previously for donor–acceptor substituted phenylene–ethynylene oligomers,[29] and is probably a result of statistically poorer donor–acceptor interactions in the ground state of the longer systems due to a number of possible rotameric conformations of the three phenyl rings.[30] Because the barrier to ring rotation in the ground state is small, all twisted conformations

Table 1. Photophysical data for chromophores **1**–**7** in toluene.

	λ_{abs}[a] [nm]	ε[b] $[M^{-1}cm^{-1}]$	λ_{em}[c] [nm]	ϕ[d]	τ[e] [ns]	τ_0[f] [ns]
1	388	35000	462	0.91	1.78	2.0
2	367	47000	466	0.89	1.30	1.5
3	385	58000	417	0.85	1.26	1.5
4	403	84000	448	0.94	1.27	1.4
5	422	34500	489	0.47	1.99	4.2
6	410	47000	431	0.04	0.23	5.8
7	440	85000	480	0.73	2.00	2.7

[a] Experimental one-photon absorption maximum. [b] Experimental molar extinction coefficient. [c] Experimental one-photon emission maximum. [d] Fluorescence quantum yield determined relative to fluorescein in 0.1 N NaOH. [e] Experimental fluorescence lifetime determined by using picosecond domain time-correlated single photon counting. [f] Radiative lifetime derived from fluorescence quantum yield and lifetime values ($\tau_0 = \tau/\phi$).



Scheme 2. Synthesis of chromophores **5**–**7**.

are populated at room temperature, leading to a pronounced blueshift of λ_{max}, whereas the red edge of the absorption band corresponds to the all-coplanar arrangement in which conjugation is maximised. We expect that the lowest energy conformation of the S_1 state is planar, and that the rotation barrier is substantially larger in the excited state, by analogy with closely related symmetric three-ring arylene–ethynylene systems. This is consistent with the slight redshift of the emission band of the longer dipolar compound **2** relative to that of shorter compound **1** that leads, at the same time, to a non-mirror relationship between absorption and emission spectra of chromophore **2** (see the Supporting Information).

Branching and core effect: The branching of dipolar units such as **1** or **5** within three-branched octupolar structures built from a triphenylamine-donating core (giving **4** and **7**, respectively) is examined first. The λ_{max} value for the trigonal octupolar phenylethynyl-based compound **4** is redshifted by 15 nm relative to its dipolar analogue **1**. A similar effect is observed for the octupolar styryl compound **7**, for which λ_{max} is redshifted by 18 nm relative to its dipolar analogue, **5**. This redshift is comparable to that of other three-branched octupolar compounds based on the triphenylamine core.[25c,d] Such behaviour, already observed for different octupolar derivatives based on a triphenylamine core, reveals a noticeable coupling (about 0.1 eV in a simple excitonic scheme)[25d] between the dipolar branches in the ground state. In contrast, the emission bands are only slightly blueshifted for the octupolar derivatives relative to their dipolar counterpart. This must be related to a localisation of the excitation on a dipolar branch prior to emission.[25c,d] We also observed that the branching leads to an increase of the fluorescence quantum yield. The marked increase observed for compound **7** is comparable to that reported for other octupolar compounds derived from a triphenylamine core.[25c,d] Such an effect is of major importance for applications based on photoluminescence, for example, two-photon excited florescence (TPEF) imaging.

Branching of the dipolar units (**1** or **5**) within two-branched V-shaped structures (**3** or **6**) built from a carbazole-donating core leads to quite different behaviour. On one hand, the lowest-energy absorption bands of **3** and **6** are blueshifted, indicating that a simple excitonic picture does not apply. Their absorption spectra have a much larger bandwidth and reveal the presence of different bands, as can be inferred from the non-mirror relationship between absorption and fluorescence spectra (see the Supporting Information). First, for a V-shaped conformation, the doubly degenerate first two excited states are one-photon allowed because of the angle formed between the two branches.[25d] In addition, these charge-transfer absorption bands superimpose on the two carbazole bands located at 34 100 and 29 400 cm^{-1}.[31] Such superimposition is more pronounced for compound **3**, owing to the blueshift with respect to the absorption band of compound **6**. On the other hand, the emission bands show a marked blueshift suggesting that the emitting excited state of the V-shaped compounds must be significantly different from that of their dipolar analogues. Thus, these V-shaped chromophores cannot be seen, even in a first approximation, as the simple gathering of two dipolar monomers. This could well be related to the ring structure of the carbazole unit.

Connector effect—vinylene versus phenylene–ethynylene spacer: Comparison of the absorption and emission data of chromophores **1** and **5** (dipolar type), or **4** and **7** (octupolar type) indicates that replacing a phenylene–ethynylene unit by a vinylene unit induces bathochromic shifts of the absorption and emission maxima in both dipolar and octupolar systems. This can be explained by the fact that insertion of a double bond between the boron atom and the conjugated core leads to a more planar structure allowed by the relief of steric hindrance. However, such structural change also induces a noticeable variation of the fluorescence quantum yields. The fluorescence quantum yields for the phenylethynyl-based molecules **1**–**4** are all above 0.85, whereas those of the vinyl-based molecules are somewhat lower, at 0.47 and 0.73 for **5** and **7**, respectively, and only 0.04 for **6**. The fluorescence lifetimes of all chromophores except **6** are in the 1–2 ns range. In contrast, chromophore **6** has a fluorescence lifetime of 0.23 ns, which, in view of the low quantum yield, can be attributed to a facile non-radiative decay pathway for this compound. The long excited-state lifetimes of the other chromophores provide a major advantage for photoluminescence applications.

The absorption and emission maxima of **1**–**7** were recorded in a range of solvents in addition to toluene, namely, cyclohexane, chloroform, ethyl acetate, THF and DCM. For all of the compounds there is general trend of increasing bathochromic shifts with increased solvent dielectric constant, although the maxima in DCM for certain compounds occur at shorter wavelength than those in less polar THF. The largest solvatochromic shift occurs for **2**, for which the emission maximum shifts by 140 nm on going from cyclohexane to THF. Large, positive solvatochromic shifts in emission tend to be associated with large dipole moments in the excited state. Such dramatic shifts are not observed for any of their absorption maxima; these shifts tend to be much smaller and are not correlated with solvent polarity, indicating that the ground-state dipole moments are relatively small.[6f] The clear positive emission solvatochromic behaviour is observed for all compounds, indicating that emission occurs from a strongly dipolar excited state in all cases. This solvatochromic behaviour can be fitted by simple Lippert–Mataga plots of the Stokes shifts between the absorption and emission maxima (in wavenumbers) versus the solvent polarity parameter F (Figure S2 in the Supporting Information). They show reasonable linear correlations with R^2 values above 0.9 for all of the compounds. Such plots enable an estimate of the change in dipole moment between the ground and excited states to be made, provided that the values of the Onsager cavity radii are known. In view of the somewhat arbitrary nature of the methods used to estimate these radii, especially for rod-shaped molecules, we do not feel that a quantitative treatment would be particularly meaningful. Thus, we present Lippert plots to illustrate the fact that there are significant excited-state dipole moments for all of the compounds, including the trigonal ones, indicating that the excitation localisation occurs on a dipolar subunit in the excited state whatever the structure (including trigonal and quadrupolar derivatives). This phenomenon has already been observed and discussed for octupolar triphenylamine derivatives,[25c] quadrupolar derivatives[32] and other trigonal boron compounds.[31]

Two-photon absorption: Here, we aim to scrutinise the structure–TPA-property relationships. TPA cross-sections, σ_2, have been measured for compounds **1**–**4** (Scheme 1) and **5**–**7** (Scheme 2) in toluene in the femtosecond regime over the range 700–900 nm. Both relative values within the two series (Table 2) and comparison to literature chromophores based on a triphenylamine core (Scheme 3 and Table 3) are discussed. Given the experimental error on the determination of both position and amplitude of TPA maxima, values reported in Tables 2 and 3 have been rounded up for the main first two TPA bands when compared to the experimental data shown in Figures 1–3 and the original papers cited.

Dipolar derivatives

Length and connector effects: In Figure 1a, the TPA spectrum of dipolar chromophore **1** is compared to that of the longer dipolar compound **2**. The TPA response of **2** is almost twice as large as that of **1** over the whole spectral region investigated (Figure 1a and Table 2). This is consistent with earlier findings,[33] as it shows that extension of the π system by lengthening the phenylene–ethynylene connector is indeed a good way to increase the TPA performance. Surprisingly, whereas the one-photon absorption maximum of **2** is significantly blueshifted with respect to that of **1** (Table 1), the first TPA bands of both chromophores appear at the same position. In fact, the TPA maximum of **2** appears in the vicinity of the red-edge of the absorption previously assigned to the all-coplanar arrangement. This is consistent with the fact that conformations with favoured conjugation yield the largest TPA responses. It also confirms that such connector lengthening allows high fluorescence quantum yields to be maintained (Table 1).[33]

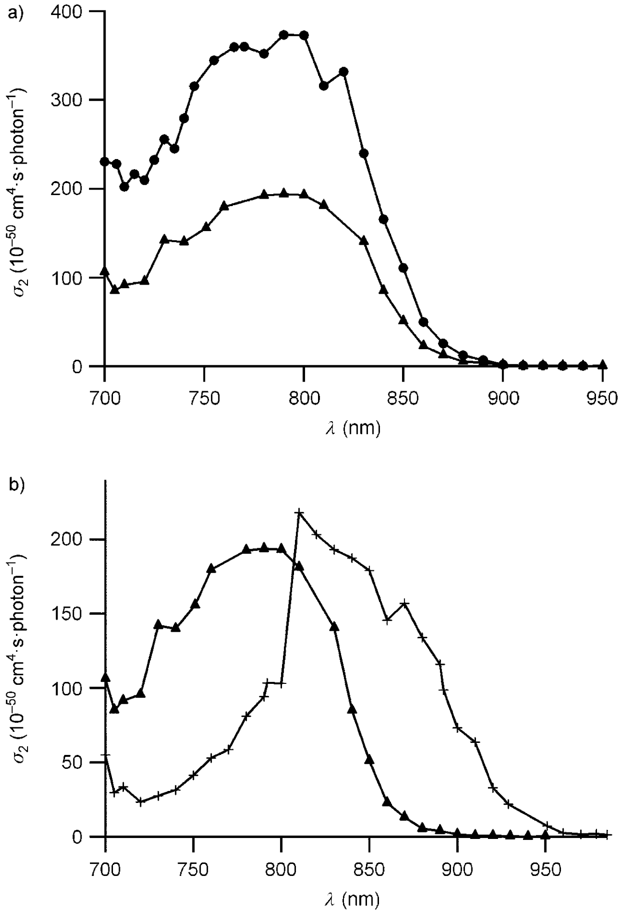
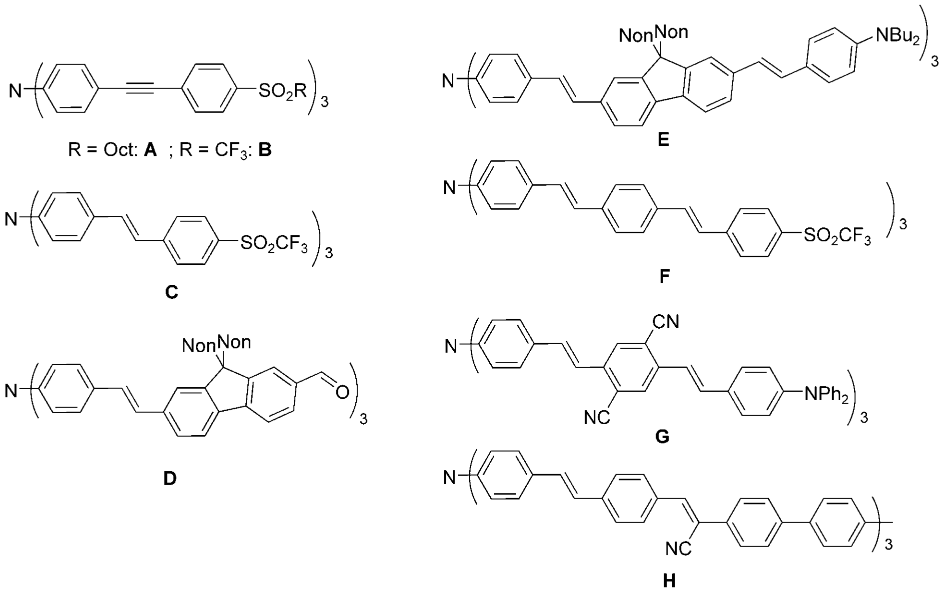


Figure 1. Comparison of TPA spectra in toluene of dipolar compounds: a) **1** (▲) and **2** (●): length effect and b) **1** (▲) and **5** (+): connector effect.



Scheme 3. Structures of reference compounds for comparison to literature chromophores: **A**,[25b] **B**,[25b,35] **C**,[26a] **D**,[26a] **E**,[26b] **F**,[26a] **G**[36a] and **H**.[36b]

Figure 1b compares TPA responses of compounds **1** and **5**, illustrating the connector effect. Both TPA bands are located in the vicinity of twice the one-photon absorption maximum (Table 2) as is expected for dipolar chromophores. The TPA amplitudes are comparable to

Table 2. Two-photon absorption cross-sections (σ_2) for the first two main TPA bands of chromophores **1–7** in toluene.

	$2\ \lambda_{abs}$[a] [nm]	λ_{TPA}^{band1} [nm]	λ_{TPA}^{band1} [nm]	σ_2[b] [GM]		σ_2/N[c] [GM]	
				λ_{TPA}^{band1}	λ_{TPA}^{band2}	λ_{TPA}^{band1}	λ_{TPA}^{band2}
1	780	790	–	~200	–	~200	–
2	744	780	–	~375	–	~375	–
3	774	770	≤700	~350	≥500	~175	≥250
4	806	820	~720	~250	~375	~75	~125
5	844	840	–	~200	–	~200	–
6	820	–	–	<50	~50	<25	~25
7	880	880	740	~200	~1000	~70	~325

[a] λ_{abs} corresponds to the experimental one-photon absorption maximum. [b] TPA cross-sections; $1\,GM = 10^{-50}\,cm^4 s\,photon^{-1}$; TPEF measurements were performed by using a mode-locked Ti:sapphire laser delivering 150 fs pulses at 76 MHz, calibrated with fluorescein. [c] TPA cross-sections normalised for the number of branches (N).

one another and very similar to that of the phenylene–vinylene-based analogue (188 GM; $\Phi = 0.55$, $\lambda_{abs} = 403$ nm),[18b] although the latter values were measured in THF. This shows that varying the connectors from phenylene–ethynylene (**1**) to phenylene–vinylene[18b] to vinylene (**5**) leads to a significant redshift and decrease of fluorescence quantum yields, while maintaining comparable TPA performance.

Branching effect: The TPA spectra normalised for the number of branches of compounds **1**, **3**, **4** and **5–7** are shown in Figure 2a and b, respectively. All chromophores except compound **6** show a first TPA band in the vicinity of twice their one-photon absorption maximum (Table 2 and Figure 2). For all branched chromophores, the corresponding TPA amplitudes are significantly smaller than those observed at the second TPA band that appears on the blue side of the spectra. This is directly related to the selection rules that apply to the first excited states in branched systems for symmetry reasons. The case of chromophores **3** and **6**, which gather two dipolar units through a carbazole moiety, is more complex than that of octupolar derivatives. In fact, as already seen from the linear optical properties, one-photon absorption spectra (see the Supporting Information) extend over the whole spectral region explored for TPA and consist of a superimposition of several transitions, including local carbazole transitions.[31] For chromophores of C_3 symmetry, it is well known that the first excited state, which is doubly degenerate, is mainly one-photon allowed, while the third excited state is one-photon forbidden and shows a much larger TPA activity.[25d,31] This is clearly visible for compounds **4** and **7** from Figure 2 and Table 2.

On the red side of the spectra of both series, the dipolar compounds **1** and **5** show by far the highest responses. This is a clear indication that the branching strategy does not lead to any cooperative enhancement in this spectral region, contrary to what has been reported previously for branched structures based on a triphenylamine core.[25c,d] On the blue side of the spectra, the behaviour within the two series is quite different. Compound **4** shows only little enhancement when compared with three times its dipolar analogue **1**, whereas compound **7** shows a marked increase leading to a cooperative enhancement larger than a factor of ten with respect to the dipolar branch **5**.

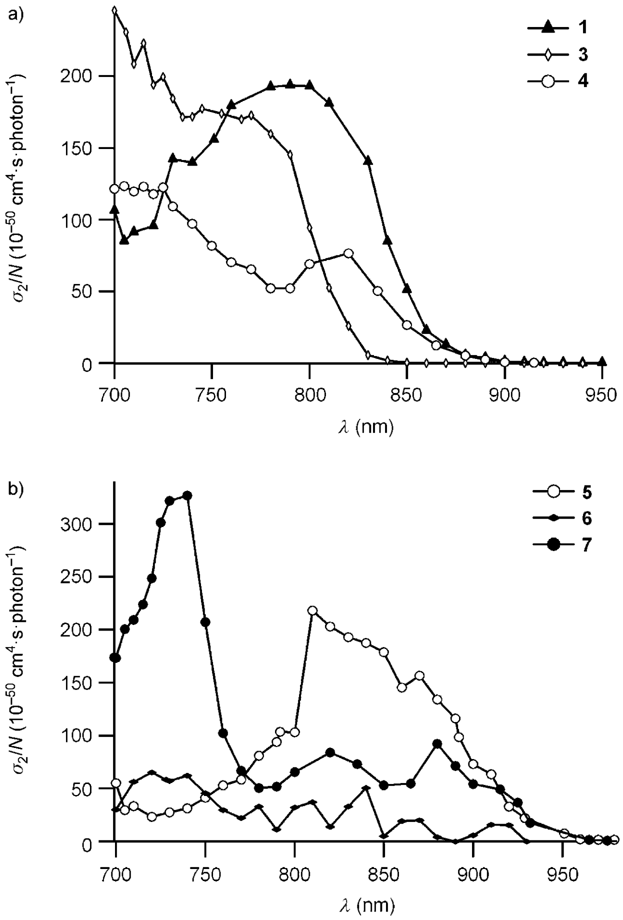


Figure 2. Comparison of the branching effect on TPA spectra normalised for the number of branches (N) in toluene: a) phenylethynyl-based chromophores **1**, **3**, **4** and b) vinylene-based compounds **5**, **6** and **7**.

Effect of the dimesitylboryl end groups—comparison with other electron-withdrawing moieties: To investigate further the structure–TPA relationships, octupolar compounds **4** and **7** are compared to other three-branched chromophores reported in the literature (Table 3). Even though TPA cross-sections are strongly wavelength dependent, we will mainly concentrate on the amplitudes of TPA maxima at the two first bands. TPA performance can be either compared from the absolute TPA cross-section or based on some normalisation criterion that can be manifold and should be chosen depending on the intended application. Data on corresponding dipolar monomers are not available for most of the octupoles reported in the literature, so normalisation using the number of branches is not possible. A first normalisation procedure is based on the molecular weight, so as to obtain a relevant figure of merit for applications such as optical limiting.[25c,d] Alternatively, TPA cross-sections can be normalised for the number of effective electrons according to reference [34].

Figure 3 and Table 3 compare the TPA cross-sections of compound **4** with those reported for two other octupolar chromophores of similar size and which are also based on phenylene–ethynylene spacers and triphenylamine cores (Scheme 3). As a consequence of the redshift of the first excited states, the absolute TPA cross-section increases over the whole spectral region investigated (Figure 3) when replacing the SO_2Oct acceptor moieties (**A**)[25b] with $B(Mes)_2$ terminal groups (**4**). Further substitution by SO_2CF_3 (**B**)[25b,35] results in a comparable band position, while allowing for greater TPA responses in the 700–850 nm range. Both normalisation procedures (molecular weights and effective number of electrons) lead to the same ranking for TPA performance (Table 3): $SO_2Oct < B(Mes)_2 < SO_2CF_3$. Thus, the TPA response of the chromophore **4** is intermediate between that of **A** and **B**, indicating that the dimesitylboryl is a weaker electron-withdrawing unit than the strong trifluoromethylsulfonyl acceptor, but stronger than the octylsulfonyl acceptor.

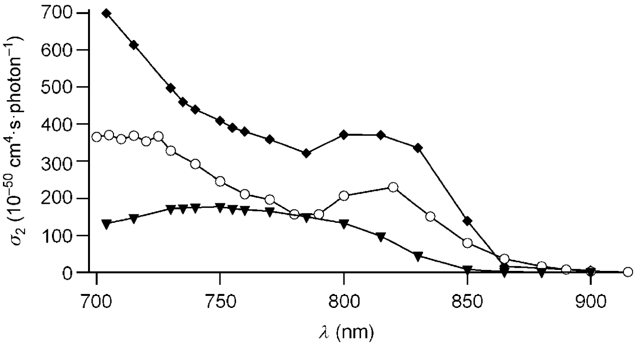


Figure 3. Comparison of TPA spectra of compound **4** (○) with reference chromophores **A**[25b] (▼) and **B**[25b,35] (◆) in toluene: effect of the peripheral acceptor group.

Table 3. Comparison of TPA data for selected reported trigonal compounds built from a triphenylamine core.

	r[a] [nm]	N_{eff}[b] [e]	λ^{band1} [nm]	λ^{band2} [nm]	σ_2^{max}[c] [GM]		σ_2^{max}[c]/MW [GM g^{-1} mol]		σ_2^{max}/N_{eff} [GM e^{-1}]	
					λ^{band1}	λ^{band2}	λ^{band1}	λ^{band2}	λ^{band1}	λ^{band2}
4	1.7	28.4	820	~720	~225	~375	0.17	0.29	8	13
A[25b]	2.2	27.7	775	<740	~150	>150	0.14	–	5	–
B[25b,35]	1.5	27.7	810	705	~400	~700	0.42	0.74	14	25
7	1.5	20.2	880	740	~200	~1000	0.19	0.94	10	50
C[26a]	1.5	27.7	820	740	~425	~1350	0.45	1.42	15	50
D[26a]	1.7	38.1	850	770	~850	~1250	0.51	0.75	22	33
E[26b]	2.9	48.5	860	735	~500	~3700	0.22	1.64	10	76
F[26a]	1.5	41.6	880	800	~1200	~2100	0.96	1.67	29	50
G[36a,37]	2.3	47.4	975	840	~1500	~5000	1.00	3.31	32	105
H[36b]	2.4	52.0	950	800	900	1350	0.75	1.12	17	26

[a] Approximate molecular radius. [b] Effective number of π electrons in the conjugated system defined according to reference [34]. [c] TPA cross-sections (1 GM = 10^{-50} cm^{4}s photon^{-1}) as obtained from TPEF measurements with fs pulses except for compound **G** (obtained with ns pulses) and compound **H** (measured by fs Z-scan).

The vinylene-based octupole **7**, which shows the largest TPA cross-sections of the two novel series, is compared in Table 3 to six three-branched compounds (Scheme 3) all based on a triphenylamine branching centre and among the best TPA chromophores reported in the literature.[25a,26a,b,36a,b] Compounds **C**, **F** and **7** are of similar size and the relative ranking depends on the choice for the normalisation criterion. Whereas normalisation for the number of effective electrons shows similar effective cross-sections at the TPA peak (band 2), normalisation for the molecular weight leads to significantly poorer responses for the $B(Mes)_2$ derivatives. This difference is related to the fact that over half of the molecular weight of compound **7** is attributable to the mesityl groups, which are required for stability and applications. Over the whole 700–950 nm range, chromophore **D**, which bears a formyl end group, shows larger absolute TPA cross-sections than compound **7** (Table 2) with comparable fluorescence quantum yields.[25a] Whilst these trends remain for the first TPA band in both normalisation schemes, compound **7** shows a better normalised TPA cross-section at the maximum of the second TPA band. Thus, depending on the desired application (broadband versus single wavelength), one chromophore surpasses the other. Finally, three other reference octupoles (**E**,[26b] **G**[37] and **H**[36b]), which are significantly larger than chromophore **7**, show comparatively higher absolute and normalised TPA cross-sections at both band maxima (Table 2). These comparisons suggest a route towards enhanced TPA responses, both TPA amplitude and TPA broadening, through the synthesis of extended analogues of **7** with longer conjugated arms.

Conclusion

We have designed and investigated two novel series of dimesitylboryl-based fluorophores. It is shown that dipolar, V-shaped and octupolar compounds containing both amino and dimesitylboryl groups can be synthesised by hydroboration and palladium-catalyzed cross-coupling, even in the presence of strong bases, such as triethylamine, as solvents. Investigation of their TPA properties revealed interesting structure–TPA features. Comparison of the two novel dipolar chromophores to their phenylene–vinylene analogue showed that substitution of vinylene by phenylene–ethynylene leads to comparable TPA responses and allows for significant blueshift (transparency in the visible range) and increase of fluorescence quantum yields. Elongation by introduction of an additional phenylene–ethynylene connector leads to a twofold increase in the TPA amplitude over the whole spectral region investigated without marked decrease of the fluorescence quantum yield. This confirms previous findings on quadrupolar chromophores based on phenylene–ethynylene and phenylene–vinylene spacers.[33] The elongated dipolar compound presents a TPA maximum significantly redshifted with respect to twice the one-photon maximum. This may be related to a larger TPA oscillator strength for the all-coplanar conformation that favors conjugation.

The branching strategy that has been shown to be very successful for improved TPA properties[25c,d] has been investigated for V-shaped and octupolar dimesitylboryl derivatives. Use of the carbazole connecting centre to build V-shaped derivatives prevents qualitative analysis in terms of simple models, such as the excitonic model. This may result from sizable conjugation related to the central ring of the carbazole unit. Furthermore, the carbazole connecting centre is not effective in enhancing TPA responses. The branching effect in the two octupolar compounds with dimesitylboryl end groups and triphenylamine branching centres is quite different. Whereas the phenylene–ethynylene derivative does not present any cooperative enhancement with respect to its monomeric analogue over the whole spectral range investigated, the vinylene derivative does so in the blue part of the spectrum. Interestingly, the former nicely satisfies the level splitting predicted within the excitonic scheme, whereas the latter does not because its TPA state is significantly blueshifted by 40 nm. Such deviation was already observed for other three-branched systems, also based on triphenylamine cores, which showed marked enhancement on the blue side of the TPA spectra.[25c,d] Surprisingly, the TPA broadening observed in the latter compounds is not observed here.

Further comparison to related triphenylamine-based three-branched systems shows that both novel octupolar dimesitylboryl derivatives lead to TPA peaks comparable to those observed for compounds of similar size. It is also shown that the respective ranking depends on the normalisation criterion chosen, and this must be selected by considering the desired application. Comparison to larger branched chromophores reported in the literature suggests that elongated analogues of such octupolar dimesitylboryl-based fluorophores should provide improved TPA properties, thanks to TPA enhancement and broadening. Finally, all novel chromophores except one display relatively long excited-state lifetimes and high fluorescence quantum yields, which are both significant advantages for photoluminescence applications.

Experimental Section

Synthesis: All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques or in an Innovative Technology System 1 glove box. Triethylamine was dried and deoxygenated by heating at reflux over CaH_2 under nitrogen, and THF was dried and deoxygenated by passage through columns of activated alumina and BASF-R311 catalyst under argon pressure using an Innovative Technology SPS-400 solvent purification system. Dimesitylborane was prepared by treating dimesitylboron fluoride with $LiAlH_4$ in dry monoglyme.[38] 1-Iodo-4-dimesitylborylbenzene was prepared according to the literature method.[6f] (Note: this compound was prepared from 1,4-diiodobenzene and not 1-bromo-4-iodobenzene as shown incorrectly in Scheme 1 of reference [6f]). 4-Ethynyl-*N*,*N*-dimethylaniline,[39] 4-ethynyl-*N*,*N*-di(4-tolyl)-aniline,[40] 3,6-diethynyl-*N*-*n*-butylcarbazole[41] and tris(4-ethynylphenyl)-amine[42] were prepared according to literature procedures. The synthesis of 4-(4-ethynylphenylethynyl)-*N*,*N*-dimethylaniline will be reported in detail in a forthcoming paper on extended linear arylene ethynylenes.[43] NMR spectra were obtained by using Varian Mercury 200 and 400 (^{1}H: 200, 400 MHz) or Bruker Avance 400 (^{13}C{^{1}H}: 100 MHz) spectrometers. All spectra were recorded in $CDCl_3$. Chemical shifts are reported relative to tetramethylsilane and are referenced to residual proton or carbon resonances in $CDCl_3$. Mass spectra were recorded on Waters Micromass LCT (ESI), Applied Biosystems Voyager DE STR (MALDI-TOF) spectrometers. Higher resolution MS were carried out by using an Autoflex Tof/Tof (Bruker Daltonic GmBH) instrument fitted with a 337 nm N_2 laser, with positive ions measured using a reflectron for improved accuracy and resolution, sample solutions (1 mg mL^{-1}; compounds **3** and **6** in DCM, compound **7** in THF) were mixed with matrix in a ratio of 1:9 dithranol (50 mg mL^{-1}) in DCM. HRMS was performed on a Thermo–Finnigan LTQ FT ICR MALDI-TOF spectrometer by using a 1 mg/5 mL sample solution in THF/methanol (1:1 v/v) mixed with matrix in a ratio of 1:9 DCTB (50 mg mL^{-1}) in DCM. Accurate mass EI SECTOR MS was performed by using a Finnigan MAT 95XP spectrometer at the EPSRC National Mass Spectrometry Service Centre, Swansea. Elemental analyses were performed on an Exeter CE 440 Analyzer by Ms. J. Dostal at Durham University. Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected.

4-(4-Dimesitylborylphenylethynyl)-*N*,*N*-dimethylaniline (1): 1-Iodo-4-dimesitylborylbenzene (0.45 g, 1.00 mmol), 4-ethynyl-*N*,*N*-dimethylaniline (0.15 g, 1.00 mmol), [$PdCl_2(PPh_3)_2$] (0.007 g, 0.01 mmol) and CuI (0.002 g, 0.01 mmol) were added to a 250 mL Schlenk flask, which was evacuated and purged with nitrogen three times. Triethylamine (~100 mL) was added by cannula under nitrogen. The reaction was stirred at room temperature overnight. The solvent was removed in vacuo and the residue was filtered through a 3 cm silica plug, eluting with a hexane/DCM (5:1 v/v) mixture. The filtrate was evaporated and the residue was recrystallised from hexane to give a pale-yellow solid (0.37 g, 79 %). M.p. 164–166 °C; ^{1}H NMR (200 MHz): $\delta = 7.47$ (s, 4H), 7.43 (m, 2H), 6.83 (s, 4H), 6.67 (m, 2H), 3.00 (s, 6H), 2.32 (s, 6H), 2.02 ppm (s, 12H); ^{13}C NMR (100 MHz): $\delta = 150.3$, 141.7, 140.9, 138.7, 136.2, 132.9, 130.6, 128.2, 127.7, 111.8, 109.8, 93.2, 87.9, 40.2, 23.4, 21.2 ppm; MS (ESI): *m*/*z*: 469 [M^+]; elemental analysis calcd (%) for $C_{34}H_{36}BN$: C 86.98, H 7.73, N 2.98; found: C 86.81, H 7.77, N 3.26.

4-[4-(4-Dimesitylborylphenylethynyl)phenylethynyl]-*N*,*N*-dimethylaniline (2): 1-Iodo-4-dimesitylborylbenzene (0.45 g, 1.00 mmol), 4-(4-ethynylphenylethynyl)-*N*,*N*-dimethylaniline (0.24 g, 1.00 mmol), [$PdCl_2(PPh_3)_2$] (0.007 g, 0.01 mmol) and CuI (0.002 g, 0.01 mmol) were added to a 250 mL Schlenk flask which, was evacuated and purged with nitrogen three times. Triethylamine (~100 mL) was added by cannula under nitrogen and the reaction was stirred at room temperature overnight. The solvent was removed in vacuo and the residue was filtered through a 3 cm silica plug, eluting with a hexane/DCM (4:1 v/v) mixture. The filtrate was evaporated and the residue was recrystallised from hexane to give the product as a bright-yellow solid (0.46 g, 81 %). M.p. 198–200 °C; ^{1}H NMR (200 MHz): $\delta = 7.50$ (s, 4H), 7.48 (s, 4H), 7.43 (m, 2H), 6.83 (s, 4H), 6.67 (m, 2H), 3.00 (s, 6H), 2.32 (s, 6H), 2.02 ppm (s, 12H); ^{13}C NMR (100 MHz): $\delta = 150.3$, 140.9, 138.9, 136.1, 132.8, 131.6, 131.2, 131.0, 128.4, 126.5, 124.4, 121.8, 111.8, 109.7, 93.0, 91.5, 91.2, 87.3, 40.2, 23.4, 21.2 ppm; MS (EI) *m*/*z* calcd for $C_{42}H_{40}{}^{10}BN$: 568.3285; found: 568.3280; elemental analysis calcd (%) for $C_{42}H_{40}BN$: C 88.56, H 7.08, N 2.46; found: C 85.37, H 7.02, N 2.43.

3,6-Bis-(4-dimesitylborylphenylethynyl)-*N*-*n*-butylcarbazole (3): 1-Iodo-4-dimesitylborylbenzene (0.90 g, 2.00 mmol), 3,6-diethynyl-*N*-*n*-butylcarbazole (0.27 g, 1.00 mmol), [$PdCl_2(PPh_3)_2$] (0.014 g, 0.02 mmol) and CuI (0.004 g, 0.02 mmol) were added to a 250 mL Schlenk flask, which was evacuated and purged with nitrogen three times. Triethylamine (~ 50 mL) was added by cannula under nitrogen. The reaction was stirred at room temperature overnight. The solvent was removed in vacuo and the residue was filtered through a 3 cm silica plug, eluting with a hexane/DCM (5:1 v/v) mixture. The filtrate was evaporated and the residue was recrystallised from hexane to give the product as an off-white solid (0.67 g, 73 %). M.p. 270–272 °C (dec.); ^{1}H NMR (200 MHz): $\delta = 8.30$ (s, 2H), 7.67 (m, 2H), 7.54 (m, 8H), 7.38 (m, 2H), 6.83 (s, 8H), 4.29 (t, ^3J(H,H) = 7.2 Hz, 2H), 2.31 (s, 12H), 2.03 (s, 24H), 1.83 (m, 2H), 1.36 (m, 2H), 0.93 ppm (t, ^3J(H,H) = 7.2 Hz, 3H); ^{13}C NMR (100 MHz): $\delta = 145.3$, 141.5, 140.8, 140.5, 138.7, 136.2, 130.9, 129.8, 128.2, 127.2, 124.3, 122.4, 113.6, 109.0, 93.0, 88.3, 43.1, 31.0, 23.4, 21.2, 20.5, 13.8 ppm; MS (MALDI-TOF) *m/z* calcd for $C_{68}H_{67}B_2N$: 919.548; found: 919.555; elemental analysis calcd (%) for $C_{68}H_{67}B_2N$: C 88.79, H 7.34, N 1.52; found: C 87.00, H 7.49, N 1.47.

Tris-[4-(4-dimesitylborylphenylethynyl)phenyl]amine (4): 1-Iodo-4-dimesitylborylbenzene (1.35 g, 3.00 mmol), tris(4-ethynylphenyl)amine, (0.32 g, 1.00 mmol), triphenylphosphine (0.015 g, 0.06 mmol), $[Pd(dba)_2]$ (0.017 g, 0.03 mmol) and CuI (0.006 g, 0.03 mmol) were added to a 100 mL Schlenk flask, which was evacuated and purged with nitrogen three times. Triethylamine (~100 mL) was added by cannula under nitrogen. The reaction was stirred at room temperature overnight, followed by heating to reflux for 1 h. The solvent was removed in vacuo, and the residue was filtered through a 3 cm silica plug, eluting with a petroleum ether (40–60 °C)/DCM (5:1 v/v) mixture. The filtrate was evaporated under reduced pressure and residual solvent was removed in vacuo, by using a heat gun, to give the product as a pale-yellow solid (0.79 g, 61 %). M.p. > 300 °C; ^{1}H NMR (200 MHz): $\delta = 7.44$ (m, 18H), 7.07 (m, 6H), 6.83 (s, 12H), 2.30 (s, 18H), 2.01 ppm (s, 36H); ^{13}C NMR (100 MHz): $\delta =$ 146.8, 141.6, 140.9, 138.8, 136.2, 133.0, 131.0, 128.2, 126.7, 124.1, 117.9, 91.4, 89.8, 23.4, 21.2 ppm; HRMS (MALDI) *m/z* calcd for $C_{96}H_{91}{}^{10}B_3N$: 1287.7534; found: 1287.7555 $[M+H]^+$.

***E*-4-Dimesitylborylethenyl-*N*,*N*-di(4-tolyl)aniline (5)**: A solution of dimesitylborane (0.08 g, 0.30 mmol) in dry THF (20 mL) was added dropwise to a solution of 4-ethynyl-*N*,*N*-di(4-tolyl)aniline (0.10 g, 0.30 mmol) in dry THF (10 mL) and the reaction mixture was stirred for seven days at room temperature under N_2. The solvent was evaporated under reduced pressure with diethyl ether added to assist in the removal of residual THF. The residue was filtered through a 3 cm silica plug, eluting with a hexane/DCM (5:1 v/v) mixture, and the filtrate was evaporated to give the pure product as a bright-yellow solid (0.11 g, 67 %). M.p. 234–236 °C (dec.); ^{1}H NMR (400 MHz) $\delta = 7.39$ (m, 2H), 7.21 (m, 1H), 7.10 (m, 5H), 7.02 (m, 4H), 6.94 (m, 2H), 6.83 (s, 4H), 2.31 (s, 6H), 2.29 (s, 6H), 2.19 ppm (s 12H); ^{13}C NMR (100 MHz): $\delta = 152.9$, 149.8, 144.6, 140.6, 138.1, 133.5, 130.3, 130.0, 129.2, 128.1, 125.4, 120.9, 23.3, 21.2, 20.9 ppm; MS (MALDI): *m/z*: 547 $[M^+]$; elemental analysis calcd (%) for $C_{40}H_{42}BN$: C 87.74, H 7.73, N 2.56; found: C 87.23, H 7.77, N 2.58.

3,6-Bis-(*E*-dimesitylborylethenyl)-*N*-*n*-butylcarbazole (6): A solution of dimesitylborane (0.53 g, 2.10 mmol) in dry THF (25 mL) was added dropwise to a solution of 3,6-diethynyl-*N*-n-butylcarbazole (0.27 g, 1.00 mmol) in dry THF (15 mL) and the reaction mixture was stirred for three days at room temperature under N_2. The solvent was evaporated under reduced pressure with diethyl ether added to assist in the removal of residual THF. The residue was filtered through a 3 cm silica plug, eluting with a hexane/DCM (9:1 v/v) mixture, and the filtrate was evaporated to give the pure product as a yellow solid (0.64 g, 83 %). M.p. 221–223 °C (dec.); ^{1}H NMR (400 MHz): $\delta =$ 8.21 (s, 2H), 7.75 (m, 2H), 7.46–7.37 (m, 6H), 6.85 (s, 8H), 4.29 (m, 2H), 2.33 (s, 12H), 2.24 (s, 24H), 1.83 (m, 2H), 1.36 (m, 2H), 0.94 ppm (t, $^3J(H,H) = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz): $\delta =$ 154.3, 141.8, 140.5, 138.1, 134.9, 129.5, 128.1, 126.2, 124.6, 123.2, 121.2, 109.2, 43.0, 31.0, 23.3, 21.2, 20.4, 13.8 ppm; MS (MALDI-TOF) *m/z* calcd for $C_{56}H_{63}B_2N$: 771.516; found: 771.512; elemental analysis calcd (%) for $C_{56}H_{63}B_2N$: C 87.15, H 8.23, N 1.81; found: C 85.30, H 7.94, N 1.76.

Tris-(*E*-4-dimesitylborylethenylphenyl)amine (7): A solution of dimesitylborane (0.80 g, 3.20 mmol) in dry THF (75 mL) was added dropwise to a solution of tris(4-ethynylphenyl)amine (0.32 g, 1.00 mmol) in dry THF (25 mL) and the reaction mixture was stirred for seven days at room temperature under N_2. The solvent was evaporated under reduced pressure, with diethyl ether added to assist in the removal of residual THF. The residue was filtered through a 3 cm silica plug, eluting with a hexane/DCM (3:1 v/v) mixture, and the filtrate was evaporated to give the pure product as a bright-yellow solid (0.76 g, 71 %). M.p. > 250 °C; ^{1}H NMR (200 MHz): $\delta =$ 7.45 (m, 6H), 7.30 (m, 3H), 7.10 (m, 9H), 6.83 (s, 12H), 2.30 (s, 18H), 2.20 ppm (s, 36H); ^{13}C NMR (100 MHz): $\delta =$ 151.9, 148.0, 142.3, 140.6, 138.3, 133.0, 129.4, 128.2, 124.3, 23.6, 21.2 ppm; HRMS (MALDI) *m/z* calcd for $C_{78}H_{84}B_3N$: 1067.691; found: 1067.685; elemental analysis calcd (%) for $C_{78}H_{84}B_3N$: C 87.72, H 7.94, N 1.31; found: C 86.59, H 7.89, N 1.06.

Optical experiments

Optical absorption and emission spectroscopy: All photophysical properties were measured using freshly prepared solutions of the chromophores in air-equilibrated toluene at room temperature (298 K). UV/Vis absorption spectra were recorded on a Jasco V-570 spectrophotometer. Steady-state and time-resolved fluorescence measurements were performed on dilute solutions (approximately 10^{-6} M; optical density < 0.1) contained in standard 1 cm quartz cuvettes using an Edinburgh Instruments (FLS920) spectrometer in photon-counting mode. Emission spectra were obtained for each compound under excitation at the wavelength of the absorption maximum. Fluorescence quantum yields were measured according to literature procedures by using fluorescein in 0.1 N NaOH as a standard (quantum yield $\Phi = 0.90$).[44,45] The lifetime values were obtained from the reconvolution fit analysis (Edinburgh F900 analysis software) of decay profiles obtained by using the FLS920 instrument under excitation with a nitrogen-filled nanosecond flashlamp. The quality of the fits was evidenced by the reduced χ^2 value ($\chi^2 < 1.1$).

Two-photon absorption: Two-photon excited fluorescence spectroscopy was performed by using a mode-locked Ti:sapphire laser generating a 76 MHz train of pulses with a duration of 150 fs and a time-averaged power of several hundreds of mW (Coherent Mira 900 pumped by a 5 W Verdi). Absolute values for the two-photon excitation action cross-sections $\sigma_2\Phi$ were obtained according to the method described by Xu and Webb, using 10^{-4} M fluorescein in 0.01 M NaOH(aq) as a reference,[46] applying corrections for the refractive index of the solvent.[47]

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