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Synthesis and two-photon absorption of triphenylbenzene-cored dendritic chromophores

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Abstract—The synthesis and the characterization of triphenylbenzene-cored dendrimers of first- and second-generation are described. Their absorption, photoluminescence as well as their two-photon absorption properties have been investigated and compared to a quadrupolar counterpart. These molecules combine wide transparency in the visible range and high two-photon absorption cross-sections that increase with the generation, making these dendrimers promising systems for optical power limiting applications.

Two-photon absorption (TPA) has found many applications, such as microfabrication,[1] 3D optical data storage,[2] photodynamic therapy,[3] and two-photon laser scanning fluorescence imaging.[4] TPA has also promising potentialities for optical power limiting.[5,6] Such a nonlinear process offers the possibility of maintaining high transparency in ambient light and achieving efficient and immediate protection against the high intensity delivered by pulsed lasers. Candidate molecules for optical power limiting should exhibit both a high two-photon absorption cross-section (σ_2) and a high transparency at low intensity (i.e. a weak linear absorption). Both one- and two-dimensional push–pull molecules can be endowed with large two-photon absorption cross-sections,[6,7] but often at the expense of reduced transparency in the visible range. For optical power limiting applications, quadrupolar systems are even more attractive than push–pull systems.[6] Molecular engineering of quadrupolar molecules can indeed lead to giant two-photon absorption cross-sections.[8–10] More recently it has been shown that octupolar molecules,[11] branched[12] and multibranched structures[13] can also lead to compounds of interest for multiphoton absorption and optical limitation.

Within this framework, we present the synthesis and the optical properties (absorption, fluorescence and TPA) of a series of molecules of increasing dimensionality and branched character designed in order to investigate and optimize the TPA/transparency trade-off in the visible range (Fig. 1). Quadrupolar (**1**), octupolar (**2**) and dendritic (**3**) molecules bearing solubilizing electron-donating peripheral groups have been synthesized. Our aim was to allow for intramolecular charge transfer to take place from the periphery towards the center of the molecule. Such a phenomenon has been shown to give rise to large optical nonlinear responses in quadrupolar[8,14] and octupolar systems.[15,16] Phenylenevinylene units have been selected as connectors[17,18] to ensure effective electronic conjugation between the 'nodes' while preserving suitable transparency. The triphenylbenzene moiety has been selected as ramification node that maintain large distance between the conjugated connectors, thus preventing sterical hindrances which could hamper electronic conjugation.[16]

The quadrupolar analogue **1** was synthesized by reaction of (1,1′-biphenyl)-4,4′-dicarboxaldehyde (**4**) with 2 equiv. of the phosphonium salt **5**, and subsequent izomerization of the obtained mixture of stereoisomers using a catalytic amount of iodine under illumination (Scheme 1). The octupolar first-generation dendrimer **2** was prepared by reacting the trialdehyde **6** with 3 equiv. of the phosphonium salt **5**.[16] On the other hand, reaction of the same trialdehyde **6** with only 2 equiv. of **5** afforded a mixture containing **2** together with the new dendron **7**. The latter compound was isolated, after isomerization with iodine and light, in a 42% yield. A triple Horner–Wadsworth–Emmons condensation with triphosphonate **8**, using NaH as a base and 18-crown-6 as a solid–liquid phase transfer catalyst[19] (allowing for increase of the conversion rate), finally afforded the second-generation dendrimer **3** (Scheme 1). All these derivatives have been fully charac-

Keywords: two-photon absorption; NLO-phore; dendrimer; photoluminescence; Horner–Wadsworth–Emmons reaction.

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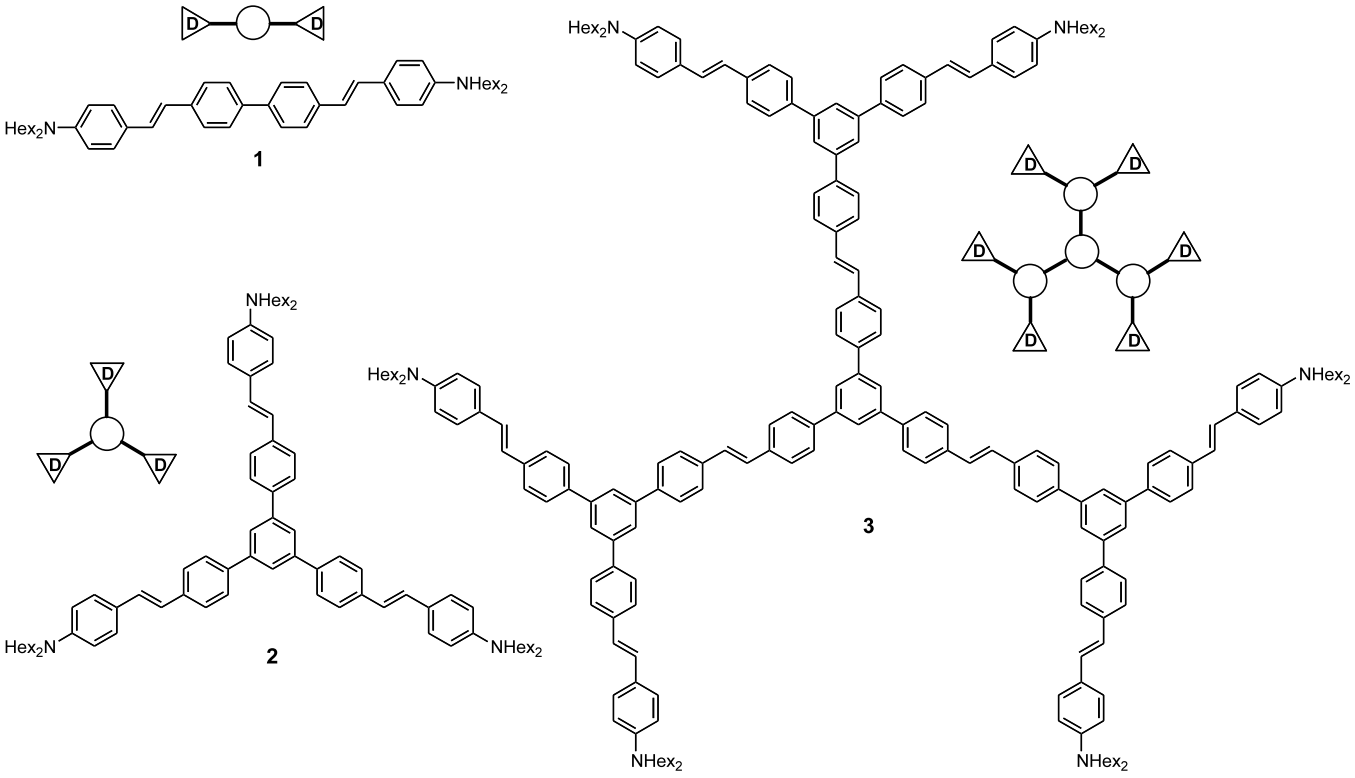
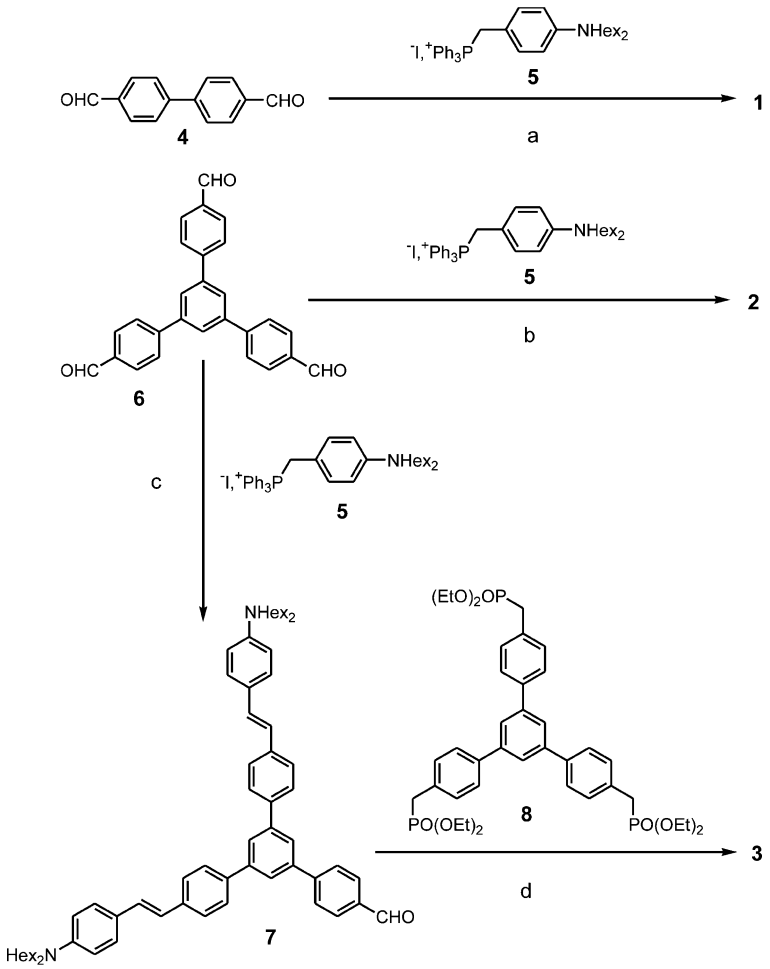


Figure 1. Series of NLO-phores **1**–**3** of increasing branched-character.



Scheme 1. *Reagents and conditions:* (a) **4** (1 equiv.), **5** (2.4 equiv.), *t*-BuOK, CH_2Cl_2, 20°C, 5 h, then I_2 cat., *hv* (86%); (b) **6** (1 equiv.), **5** (3.3 equiv.), *t*-BuOK, CH_2Cl_2, 20°C, 4 h, then I_2 cat., *hv* (82%); (c) **6** (1 equiv.), **5** (2 equiv.), *t*-BuOK, CH_2Cl_2, 20°C, 24 h, then I_2 cat., *hv* (42%); (d) **8** (1 equiv.), **7** (3.5 equiv.), NaH, THF, 18-crown-6 cat., reflux, 26 h (44%).

Table 1. One- and two-photon photophysical data of molecules **1**–**3** in toluene

Compd	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	$\lambda_{cut\text{-}off}$[a] (nm)	λ_{em} (nm)	Φ[b]	τ[c] (ns)	σ_2[d] (GM)
1	401	83000	455	455	0.81	0.82	757
2	384	131000	433	438	0.36	0.63	407
3	375	360000	432	442	0.37	0.60	798

[a] Wavelength at which the transmittance is 95%.
[b] Fluorescence quantum yield determined relative to fluorescein in 0.1 N NaOH.
[c] Experimental fluorescence lifetime.
[d] TPA cross-section at 755 nm; 1 GM = 10^{-50} cm^4 s $photon^{-1}$; TPEF measurements were performed using a mode-locked Ti:sapphire laser delivering 80 fs pulses at 80 MHz, calibrating with fluorescein.

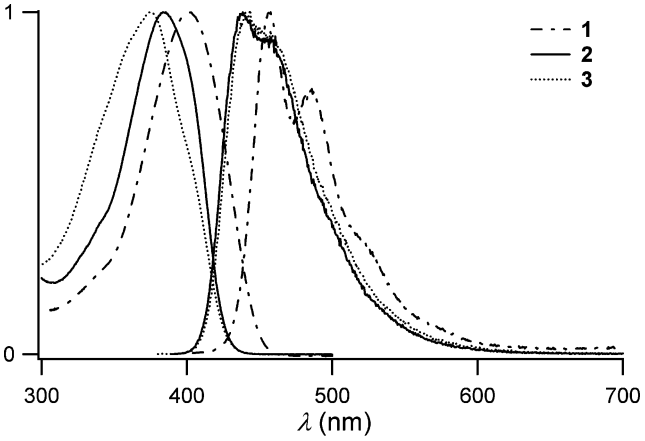


Figure 2. Normalized absorption and fluorescence emission spectra of molecules **1**–**3** in toluene.

terized by NMR, HRMS and elemental analysis.[20] The ^1H and ^{13}C NMR spectra confirm their high symmetry. In addition, their *all-E* stereochemistry was derived from the values of the ^3J coupling constants between vinylic protons ($J \sim 16$ Hz).

The absorption and photoluminescence characteristics (including fluorescence quantum yields and fluorescence lifetimes) of the series of NLO-phores **1**–**3** are gathered in Table 1. As illustrated in Figure 2, octupole **2** and dendrimer **3** exhibit an intense absorption band in the UV-blue region, but maintain very good transparency in the remaining range of the visible region. The maximum and the cut-off wavelengths of octupole **2** are blue-shifted by 17 nm and 22 nm, respectively, compared to the corresponding quadrupole **1**. The dendrimer **3** is even more blue-shifted, providing evidence that ramification has a positive effect on transparency. Interestingly, dendrimers **2** and **3** exhibit much lower fluorescence quantum yield and shorter lifetime than the quadrupolar compound **1**. On the other hand, we observe that both dendritic molecules **2** and **3** exhibit similar photoluminescence (PL) properties (emission maximum, fluorescence quantum yield and lifetime), indicating that increasing the generation does not affect the PL properties.

The TPA cross-sections (σ_2) were determined in 10^{-4} M toluene solutions at 755 nm by investigating their two-photon-excited fluorescence (TPEF). This procedure provides the TPEF cross-section ($\sigma_2\phi$) from which the corresponding σ_2 value is derived. The σ_2 values for **2** and **3** were found to be of 407 and 798 GM, respectively, which corresponds to *12 and 23 times that of the standard fluorophore fluorescein*, respectively. Interestingly, we observe that the second-generation dendritic molecule **3** shows a TPA cross-section twice that of its first-generation (octupolar) analogue **2** yet being more transparent. Indeed molecule **3** shows slightly higher TPA cross-section than model quadrupolar derivative **1** while having a significantly blue-shifted absorption band. With such an interesting compromise between linear transparency in the visible range, fluorescence quantum yields and TPA cross-sections, dendrimer **3** hold promise for optical power limiting applications. The PL properties also suggest the dendritic molecules to be of interest for a variety of applications including nonlinear optical imaging of biological structures,[10] as well as in material science.

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20. *Selected data for*:
Quadrupole **1**: mp 147–148°C; ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.59 and 7.53 (AA′XX′, $J=8.6$ Hz, 8H), 7.39 and 6.62 (AA′XX′, $J=8.8$ Hz, 8H), 7.08 (d, $J=16.2$ Hz, 2H), 6.90 (d, $J=16.2$ Hz, 2H), 3.28 (m, 8H), 1.59 (m, 8H), 1.32 (m, 24H), 0.91 (t, $J=6.4$ Hz, 12H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 147.8, 138.7, 137.2, 128.8, 127.8, 126.8, 126.3, 124.4, 123.1, 111.6, 51.0, 31.7, 27.3, 26.8, 22.7, 14.1; HRMS (LSIMS$^+$, mNBA) calcd for $C_{52}H_{72}N_2$ ($M^{+\bullet}$) m/z 724.5696, found 724.5694. Anal. calcd for $C_{52}H_{72}N_2$ (725.15): C, 86.13; H, 10.01; N, 3.86. Found: C, 85.81; H, 10.03; N, 3.78.
Dendrimer **2**: ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.79 (s, 3H), 7.68 and 7.58 (AA′XX′, $J=8.5$ Hz, 12H), 7.41 and 6.63 (AA′XX′, $J=8.8$ Hz, 12H), 7.11 (d, $J=16.2$ Hz, 3H), 6.93 (d, $J=16.2$ Hz, 3H), 3.29 (t, $J=7.5$ Hz, 12H), 1.60 (m, 12H), 1.32 (m, 36H), 0.91 (t, $J=6.0$ Hz, 18H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 147.8, 141.9, 139.1, 137.9, 129.8, 129.1, 127.8, 127.4, 126.3, 124.4, 123.0, 111.6, 51.0, 31.9, 27.2, 26.8, 22.8, 14.0; HRMS (LSIMS$^+$, mNBA) calcd for $C_{84}H_{111}N_3$ ($M^{+\bullet}$) m/z 1161.8778, found 1161.8778. Anal. calcd for $C_{84}H_{111}N_3$ (1162.83): C, 86.76; H, 9.62; N, 3.61. Found: C, 86.51; H, 9.83; N, 3.54.
Dendrimer **3**: mp 154°C; ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.84 (s, 3H), 7.81 (m, 9H), 7.78–7.62 (m, 30H), 7.68 and 7.58 (AA′XX′, $J=8.3$ Hz, 24H), 7.41 and 6.63 (AA′XX′, $J=8.8$ Hz, 24H), 7.11 (d, $J=16.1$ Hz, 6H), 6.93 (d, $J=16.1$ Hz, 6H), 3.29 (t, $J=7.3$ Hz, 24H), 1.58 (m, 24H), 1.32 (m, 72H), 0.91 (t, $J=6.5$ Hz, 36H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 147.8, 141.9, 141.6, 140.2, 140.0, 139.0, 137.5, 136.4, 130.2, 129.0, 128.4, 128.3, 127.9, 127.5, 127.4, 127.1, 126.4, 124.4, 123.1, 111.6, 51.1, 31.7, 27.2, 26.8, 22.7, 14.0; ES$^+$-MS (CH_2Cl_2/MeOH) m/z 1506.5 ([M+2H]$^{2+}$), 1004.3 ([M+3H]$^{3+}$), 753.5 ([M+4H]$^{4+}$); HRMS (ES$^+$, CH_2Cl_2/MeOH) calcd for $C_{222}H_{260}N_6$ ([M+2H]$^{2+}$) m/z 1505.0265, found 1505.0273. Anal. calcd for $C_{222}H_{258}N_6$ (3010.55): C, 88.57; H, 8.64; N, 2.79. Found: C, 88.18; H, 8.62; N, 2.52.
Dendron **7**: ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.01 and 7.87 (AA′XX′, $J=8.3$ Hz, 4H), 7.88 (t, $J=1.8$ Hz, 1H), 7.80 (d, $J=1.8$ Hz, 2H), 7.68 and 7.58 (AA′XX′, $J=8.5$ Hz, 8H), 7.41 and 6.63 (AA′XX′, $J=8.8$ Hz, 8H), 7.12 (d, $J=16.0$ Hz, 2H), 6.93 (d, $J=16.0$ Hz, 2H), 3.29 (t, $J=7.7$ Hz, 8H), 1.60 (m, 8H), 1.32 (m, 24H), 0.91 (m, 12H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 191.8, 147.8, 147.2, 142.2, 140.7, 138.5, 137.9, 135.3, 130.3, 129.3, 127.8, 127.3, 126.4, 125.5, 124.6, 124.3, 122.8, 111.6, 51.0, 31.7, 27.2, 26.8, 22.7, 14.0; IR (KBr) ν 1696 cm^{-1}; HRMS (LSIMS$^+$, mNBA) calcd for $C_{65}H_{80}N_2O$ ($M^{+\bullet}$) m/z 904.6271, found 904.6264. Anal. calcd for $C_{65}H_{80}N_2O$ (905.37): C, 86.23; H, 8.91; N, 3.09. Found: C, 86.19; H, 9.01; N, 2.99.