PAPER www.rsc.org/njc | New Journal of Chemistry

Synthesis, characterization, two-photon absorption, and optical limiting properties of triphenylamine-based dendrimers†

Bin Xu,[a] Honghua Fang,[b] Feipeng Chen,[a] Hongguang Lu,[a] Jiating He,[a]
Yaowen Li,[a] Qidai Chen,[b] Hongbo Sun*[b] and Wenjing Tian*[a]

Received (in Victoria, Australia) 7th August 2009, Accepted 8th September 2009
First published as an Advance Article on the web 6th October 2009
DOI: 10.1039/b9nj00393b

Three π-conjugated dendrimers (**Ph-G0**, **Ph-G1** and **Ph-G2**) bearing triphenylamine moieties have been synthesized through a convergent synthetic strategy without any protection–deprotection chemistry. The linear photophysical properties, two-photon absorption (TPA), and optical limiting behavior of the dendrimers were investigated in solution at room temperature. Linear absorption and emission spectra revealed a bathochromic shift and decreased fluorescence quantum yields with increasing dendrimer generation. A strong cooperative effect in the TPA absorption of these dendrimers was observed. The TPA cross-sections increase gradually with the proportion of triphenylamine units and the maximum value of the TPA cross-section can reach 5690 GM for **Ph-G2**. These triphenylamine-based dendrimers exhibited efficient two-photon optical limiting under femtosecond excitation.

Introduction

π-Conjugated organic molecules with large two-photon absorption (TPA) cross sections have attracted increasing attention due to their versatile applications in optical power limiting, 3D microfabrication, three-dimensional optical data storage, multi-photon pumped lasing, two-photon fluorescent microscopy, two-photon cellular imaging and photodynamic therapy.[1–16] The realization of these technological applications relies greatly on the development of novel organic molecules with large TPA cross-sections. It is known that a large TPA response can be attributed to an extended π-conjugated system and increased charge transfer character within a molecule.[17–19]

Recently, dendrimers have been introduced into the field of organic nonlinear optics and have shown great promise, due to their well-defined and controllable architectures.[20–27] A fundamental advantage of dendrimers over conventional linear polymers in optical applications is mostly associated with the concentration of a large number of chromophores in an ordered and confined geometry which grows exponentially with the generation number.[28–31] In addition, strong intrachromophore interactions, efficient energy transfer, and migration through the structural design of dendritic architecture and formation of delocalized excited states render them to have enhanced nonlinear optical properties in comparison to their linear counterparts.[32–35]

With these advantages in mind, several π-conjugated phenyl cored, nitrogen centered dendritic chromophores have been synthesized and their TPA cross-sections have shown cooperative enhancement with increasing dendrimer generation.[20–22,36] Among them, triphenylamine has been widely used as an electron donating moiety, and has shown promise as a framework for the design of TPA chromophores. Since the central nitrogen atom and the three adjacent carbon atoms are highly coplanar, the triphenylamine unit can maintain uninterrupted conjugation between the central nitrogen lone pair electrons and the dendrimer arms.[38–44] Dendritic molecules or hyperbranched polymers containing such moieties are thus anticipated to show efficient TPA response.[45–48] Meanwhile, the triphenylamine derivatives connected by C=C double bonds can be synthesized by Heck and Wittig–Horner reactions, and integrated into *p*-phenylene vinylene structures which also show interesting nonlinear optical properties.[49–50] On the other hand, most π-conjugated dendrimers containing large numbers of strongly coupled conjugated blocks, which are two-branched systems (dimers) or three-branched systems (trimers), demonstrate the enhanced TPA response beyond simple additive behavior.[34–37] When the branch of the dendrimer are larger than trimer, the enhancement effect of TPA has been reported in stilbenyl dendrimer which can be interpreted in terms of coherent domains extending beyond the trimer configuration.[22] Therefore, with a useful design strategy of dendrimers with larger branches architecture than trimer, a more efficient TPA response may be expected.

In this paper, we report the synthesis, characterization and nonlinear optical properties of novel, strongly coupled, conjugated four-branched dendrimers (Chart 1) based on triphenylamine branches connected by alkene linkers. Fixation of a rigid and planar core, bis(styryl)benzene, into these π-conjugated dendrimers not only enhances the π-conjugation, but also greatly facilitates π-delocalization, since such a structure can severely restrict geometric relaxations from the excited states.[4,51] The synthetic of the triphenylamine-based branches involved an iterative,

---

[a] *State Key Laboratory of Supramolecular Structure and Materials, Jilin University, 2699 Qianjin Avenue, Changchun 130012, P. R. China. E-mail: wjtian@jlu.edu.cn; Fax: +86 431 85193421; Tel: +86 431 85155359*
[b] *State Key Laboratory on Integrated Optoelectronics, Jilin University, 2699 Qianjin Avenue, Changchun 130012, P. R. China. E-mail: hbsun@jlu.edu.cn*

† Electronic supplementary information (ESI) available: Additional images (Fig. S1–S3). See DOI: 10.1039/b9nj00393b

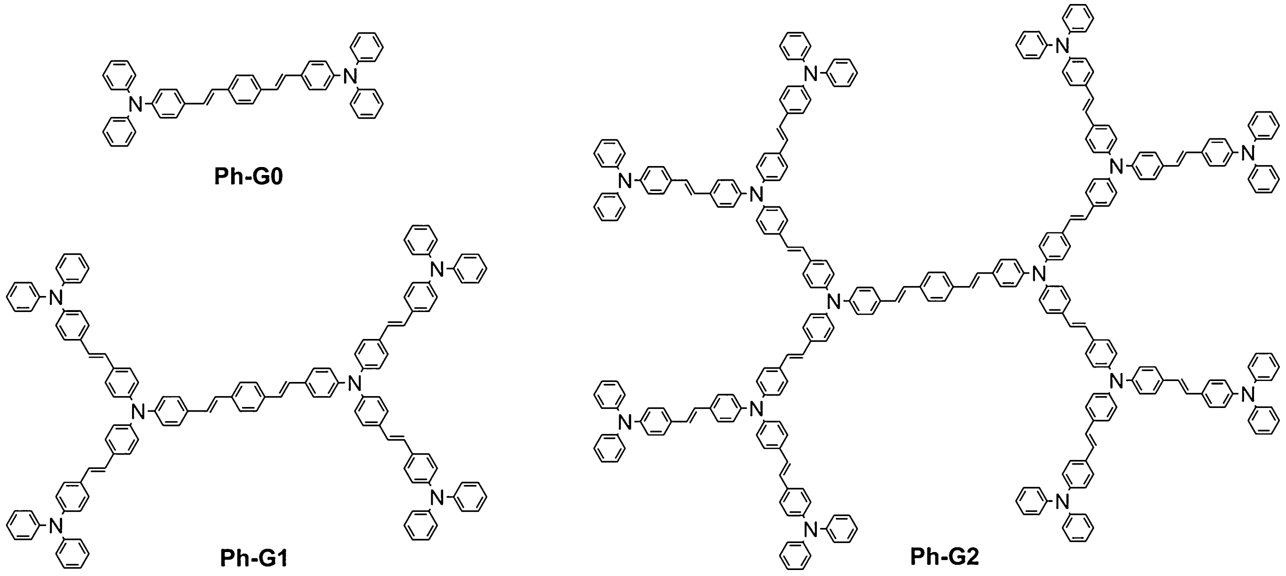


Chart 1 Molecular structures of the dendrimers containing triphenylamine branches (**Ph-G0**, **Ph-G1** and **Ph-G2**).

convergent procedure without protection–deprotection chemistry. The linear and two-photon absorption properties, as well as the one- and two-photon excited fluorescence properties of these dendrimers are reported herein. By systematically tuning the generation of the dendrimers, an attempt to correlate and understand the property-generation relationship is made. The effect of TPA-based optical limiting for dendrimers was demonstrated under femtosecond excitation.

Experimental

General procedures

All reagents were purchased from Aldrich Chemical Co. and used as received without further purification except for the following. Tetrahydrofuran (THF) was refluxed with sodium and benzophenone, and distilled. *N*,*N*-Dimethylacetamide (DMAc) was dried with CaH_2. The ^{1}H NMR and ^{13}C NMR spectra were recorded on AVANCZ 500 spectrometers and Varian Mercury-300 NMR at 298K by utilizing deuterated $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard. Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry experiments were performed on a Kratos MALDI-TOF mass system, and the spectrum was recorded in the linear or reflect mode with anthracene-1,8,9-triol as the matrices.

Preparation of 4-(bis(4-iodophenyl)amino)benzaldehyde (2). 4-(*N*,*N*-Diphenylamino)benzaldehyde **1** (14.00 g, 51.28 mmol), potassium iodide (11.43 g, 68.85 mmol), and acetic acid (210 mL) were heated to 85 °C, and the solution was allowed to cool. Then potassium iodate (10.97 g, 51.26 mmol) was added and the reaction was heated at 85 °C for 5 h. The solution was allowed to cool to room temperature and poured into ice-water under stirring. The yellow precipitated solid was collected by filtration, and the collected solid was poured into 5% $NaHSO_3$ (100 mL) to clear I_2 and KIO_3. The final filtrated yellow solid was pure compound **2**. ^{1}H NMR (500 MHz $CDCl_3$): δ = 9.85 (1H, s, CHO), 7.71 (2H, d, J = 8.5 Hz, Ar), 7.63 (4H, d, J = 8.5 Hz, Ar), 7.05 (2H, d, J = 8.5 Hz, Ar), 6.89 (4H, d, J = 8.5 Hz, Ar).

Preparation of *N*,*N*-diphenyl-4-vinylaniline (3). 4-(*N*,*N*-Diphenylamino)benzaldehyde **1** (5.46 g, 20 mmol) and methyltriphenylphosphonium bromide (8.57 g, 24 mmol) were dissolved in 100 mL of dry THF. *t*-BuOK (3.36 g, 30 mmol) in 30 mL of dry THF was added slowly dropwise to the resulting solution at 0 °C, then the reaction mixture was warmed to room temperature and stirred under N_2 for 12 h. The reaction mixture was poured into water and extracted with CH_2Cl_2 (3 × 60 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, and concentrated to dryness under vacuum. The crude product was purified by flash column chromatography (petroleum ether–CH_2Cl_2 = 4 : 1) to give (4.12 g, 76%) of product **3** as a white solid. ^{1}H NMR (500 MHz $CDCl_3$): δ = 7.28 (2H, d, J = 8.5 Hz, Ar), 7.23–7.26 (4H, m, Ar), 7.09 (4H, d, J = 8.0 Hz, Ar), 6.98–7.03 (4H, m, Ar), 6.63–6.69 (1H, m, CH), 6.63 (1H, d, J = 16.5 Hz, $CH{=}CH_2$), 5.15 (1H, d, J = 8.5 Hz, $CH = CH_2$).

Preparation of 4-(bis(4-(4-(diphenylamino)styryl)phenyl)amino)benzaldehyde (4). A round-bottomed flask (250 mL) was oven dried and cooled under an N_2 atmosphere. Compound **2** (5.25 g, 10 mmol), compound **3** (7.0 g, 26 mmol), K_3PO_4 (6.5 g, 30 mmol) and $Pd(OAc)_2$ (10 mg) were dissolved in dry DMAc (50 mL). The reaction mixture was heated to 110 °C in an oil bath and stirred for 24 h at this temperature. After being cooled to room temperature, the reaction mixture was poured into the water and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, and concentrated to dryness under vacuum. The crude product was purified by flash column chromatography (petroleum ether–CH_2Cl_2 = 1 : 1) to give (4.47 g, 55%) of product **4** as a yellow solid. ^{1}H NMR (500 MHz $CDCl_3$): δ = 9.83 (1H, s, CHO), 7.71 (2H, d, J = 8.5 Hz, Ar), 7.45 (4H, d, J = 8.5 Hz, Ar), 7.38 (4H, d, J = 8.5 Hz, Ar), 7.25–7.28 (12H, m, Ar), 7.10–7.15 (12H, m, Ar), 7.00–7.06 (8H, m, Ar), 6.96 (2H, d, *J* = 16.5 Hz, Ar), MALDI-TOF MS: Calcd for $C_{59}H_{45}N_3O$ 812.0; found: 812.9. Anal. calcd for $C_{59}H_{45}N_3O$: C, 87.27; H, 5.59; N, 5.17; found: C, 87.14; H, 5.72; N, 5.06%.

Preparation of 4-(4-(diphenylamino)styryl)-*N*-(4-(4-(diphenylamino)styryl)phenyl)-*N*-(4-vinylphenyl)aniline (5). Compound **4** (2.02 g, 2.5 mmol) and methyltriphenylphosphonium bromide (1.1 g, 3 mmol) were dissolved in 50 ml of dry THF. *t*-BuOK (0.45 mg, 4 mmol) in 10 ml of dry THF was slowly added dropwise to the resulting solution at 0 °C, then the reaction mixture was warmed to room temperature and stirred under N_2 for 12 h. The reaction mixture was poured into water and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, and concentrated to dryness under vacuum. The crude product was purified by flash column chromatography (petroleum ether–CH_2Cl_2 = 4 : 1) to give (1.36 g, 67%) of product **5** as a yellow solid. ^1H NMR (500 MHz $CDCl_3$): δ = 7.31–7.39 (12H, m, Ar), 7.10–7.27 (12H, m, Ar), 7.01–7.09 (20H, m, Ar), 6.65–6.71 (1H, m, CH), 6.70 (1H, d, *J* = 17.5 Hz, CH = CH_2), 5.18 (1H, d, *J* = 11.0 Hz, CH=CH_2), MALDI-TOF MS: Calcd for $C_{60}H_{47}N_3$ 809.4; found: 811.4. Anal. calcd for $C_{60}H_{47}N_3$: C, 88.96; H, 5.85; N, 5.19%; found: C, 88.85; H, 6.01; N, 5.07%.

Preparation of 4-(bis(4-(4-(bis(4-(4-(diphenylamino)styryl)phenyl)amino)styryl)phenyl)amino)benzaldehyde (6). A round-bottomed flask (50 mL) was oven dried and cooled under an N_2 atmosphere. Compound **5** (1.6 g, 2 mmol), compound **2** (0.48 g , 0.9 mmol), K_3PO_4 (0.58 g, 2.7 mmol), and $Pd(OAc)_2$ (5 mg) were dissolved in dry DMAc (20 mL). The reaction mixture was heated to 110 °C in an oil bath and stirred for 24 h at this temperature. After being cooled to room temperature, the reaction mixture was poured into the water and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried with $MgSO_4$, and concentrated to dryness under vacuum. The crude product was purified by flash column chromatography (petroleum ether–CH_2Cl_2 = 1 : 1) to give compound **6** as a yellow solid. ^1H NMR (500 MHz $CDCl_3$): δ = 9.83 (1H, s, CHO), 7.71 (2H, d, *J* = 8.5 Hz, Ar), 7.36–7.41 (20H, m, Ar), 7.24–7.27 (12H, m, Ar), 7.14 (2H, d, *J* = 8.5 Hz, Ar), 7.08–7.12 (30H, m, Ar), 6.96–7.05 (32H, m, Ar). MALDI-TOF MS: Calcd for $C_{139}H_{105}N_7O$ 1887.8; found: 1889.0. Anal. calcd for $C_{139}H_{105}N_7O$: C, 88.36; H, 5.60; N, 5.19%; found: C, 88.24; H, 5.77; N, 5.15%.

General reaction procedure for entries Ph-G0, Ph-G1 and Ph-G2. In an oven-dried flask with a stirrer bar, corresponding dendrons with formyl and biphosphonate **7** were dissolved in 20 mL dry THF. The resulting solution was slowly added dropwise to *t*-BuOK (84 mg, 0.75 mmol) in 20 mL of dry THF at 0 °C, then the reaction mixture was warmed to room temperature and stirred under N_2 overnight. The mixture was poured into water and extracted with dichloromethane. The organic phase was washed with water, brine and dried over $MgSO_4$. After removing the solvent, the product was purified by column chromatography using dichloromethane–petroleum ether (1 : 2), giving **Ph-G0**, **Ph-G1** and **Ph-G2**.

Preparation of **Ph-G0**. The resulting dendrimer **Ph-G0** was obtained as a yellow–green powder in a yield of 86%. ^1H NMR (500 MHz $CDCl_3$) δ 7.47 (4H, s, Ar), 7.39 (4H, d, *J* = 8.5 Hz, Ar), 7.26 (8H, t, *J* = 8.0 Hz, Ar), 7.11 (8H, d, *J* = 7.5 Hz, Ar), 7.02–7.08 (10H, m, Ar), 6.99 (2H, d, *J* = 16.5 Hz, CH = CH). MALDI-TOF MS: Calcd for $C_{46}H_{36}N_2$: 616.3; found: 616.3. Anal. calcd for $C_{46}H_{36}N_2$: C, 89.58; H, 5.88; N, 4.54%; found: C, 89.46; H, 5.94; N, 4.48%.

Preparation of **Ph-G1**. The resulting dendrimer **Ph-G1** was obtained as a yellow–green powder in a yield of 53%.^1H NMR (500 MHz $CDCl_3$) δ 7.49 (4H, s, Ar), 7.37–7.43 (20H, m, Ar), 7.25–7.28 (12H, m, Ar), 7.11 (28H, d, *J* = 7.5 Hz, Ar), 6.97–7.07 (32H, m, Ar). MALDI-TOF MS: Calcd for $C_{126}H_{96}N_6$: 1692.7; found: 1693.3. Anal. calcd for $C_{126}H_{96}N_6$: C, 89.33; H, 5.71; N, 4.96%; found: C, 89.21; H, 5.85; N, 4.87%.

Preparation of **Ph-G2**. The resulting dendrimer **Ph-G2** was obtained as a yellow–green powder in a yield of 56%.^1H NMR (500 MHz $CDCl_3$): δ = 7.48 (4H, s, Ar), 7.36–7.42 (48H, m, Ar), 7.24–7.27 (36H, m, Ar), 6.96–7.12 (128H, m, Ar). ^{13}C NMR (75 MHz $CDCl_3$): 122.95, 123.66, 124.24, 124.41, 126.43, 126.66, 126.86, 127.16, 129.45, 131.77, 132.25, 132.44, 146.21, 146.40, 147.10, 147.54. MALDI-TOF MS: Calcd for $C_{286}H_{216}N_{14}$: 3845.7; found: 3846.6. Anal. calcd for $C_{286}H_{216}N_{14}$: C, 89.25; H, 5.66; N, 5.09%; found: C, 89.19; H, 5.72; N, 5.03%.

Linear absorption and emission measurements

Linear absorption spectra for dendrimers in dilute solution were recorded on a UV-3100 spectrophotometer. One-photon excited fluorescence was measured in dilute solutions using an RF-5301PC and 10 mm path-length cuvettes. Fluorescence quantum efficiency at room temperature was determined by a standard method, with quinine sulfate as a reference.

Results and discussion

Synthesis and characterization of dendrimers

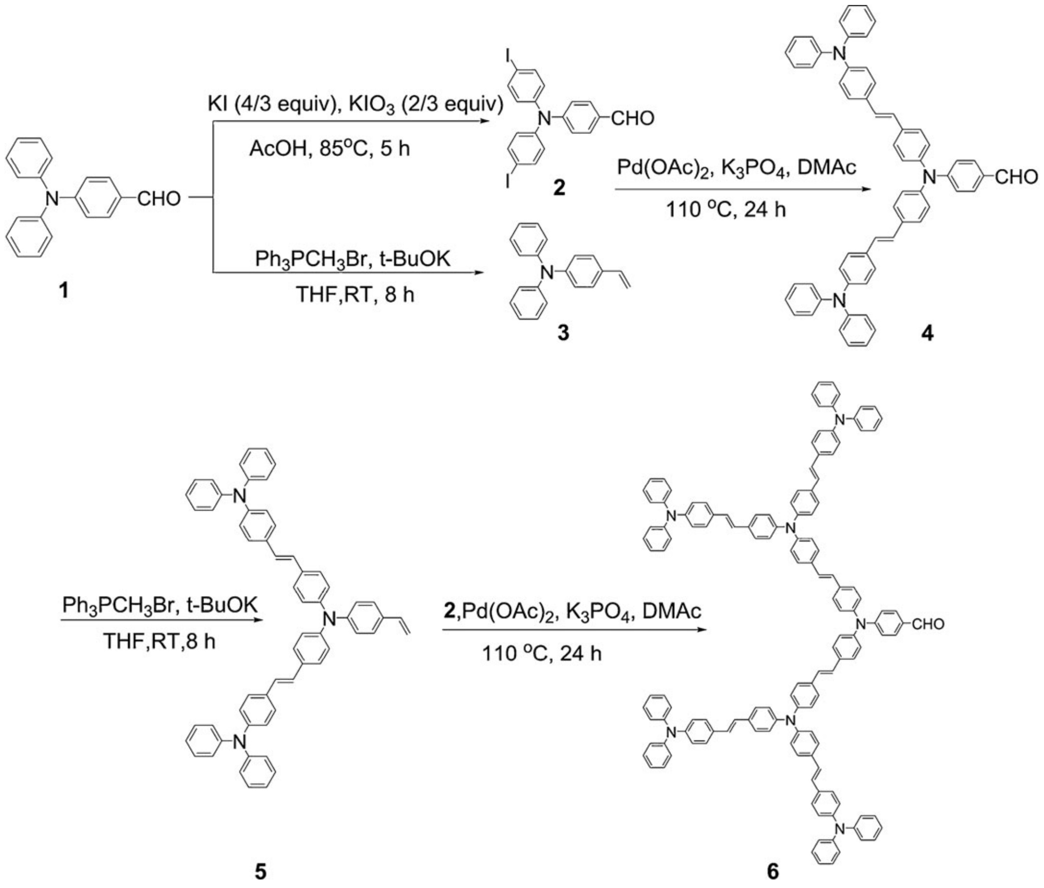
The iterative strategy developed by our group used for the aldehyde-focused dendron synthesis is shown in Scheme 1.[49,50] As illustrated, the two iterative steps for dendron formation involve a simple Wittig reaction[52] followed by a Heck coupling[53] to give a dendron with an aldehyde at its center. The first step in the iterative procedure was the formation of *N*,*N*-diphenyl-4-vinylbenzenamine **3**[54] which was prepared in 76% yield from the reaction of 4-(diphenylamino)benzaldehyde **1**[55] with methyltriphenylphosphonium bromide. The second step in the first cycle of the iterative procedure was the coupling of compound **3** with 4-(bis(4-iodophenyl)amino)benzaldehyde **2**[56] to give the first generation aldehyde-focused dendron **4** in 55% yield. To form the next generation dendron the same two-step procedure was used. Aldehyde **4** was reacted with the methyltriphenylphosphonium bromide to give compound **5** in 67% yield. Compound **3** was then coupled with 4-(bis(4-iodophenyl)amino)benzaldehyde under the above Heck conditions to form the second generation dendron aldehyde **6** in a 51% yield. The targeted dendrimers

Ph-G0,[57] **Ph-G1** and **Ph-G2** were synthesized *via* the typical Wittig–Horner reaction between the core biphosphonate **7** and aldehydes **1**, **4** and **6** in dry tetrahydrofuran in 86%, 53%, 56% yields, respectively, using potassium *tert*-butoxide as base (Scheme 2).

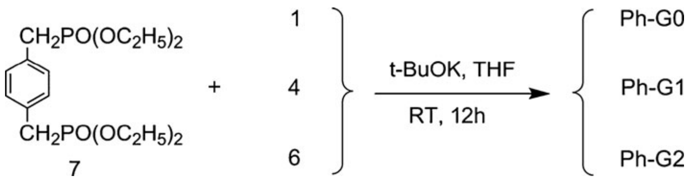
As we anticipated, the targeted dendrimers are soluble in most common organic solvents such as toluene, chloroform, THF, *etc*. All dendrons and dendrimers were characterized by FT-IR, elemental analysis, ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy and MALDI-TOF mass spectrometry. Dendrons **4** and **6** both show a peak at 9.83 ppm in the H NMR spectrum, which confirms the presence of the formyl hydrogen. The disappearance of the aldehyde peak and increased integration values of aromatic protons in the ^{1}H NMR spectra of the **Ph-G0**, **Ph-G1** and **Ph-G2** dendrimers prove the successful coupling reaction between the respective aldehyde focused dendrons (**4** or **6**) and the core reagents (**7**). The coupling constant ($J \sim 16.5$ Hz) of the olefinic protons in the dendrimers indicates that the Heck and Wittig–Horner reaction sequence afforded pure all-*trans* isomers. The all-*trans* isomers of dendrimers **Ph-G0**, **Ph-G1** and **Ph-G2** were further confirmed by the presence of characteristic vibration bands at 958 cm^{-1}, 960 cm^{-1} and 960 cm^{-1} in the FT-IR spectra, respectively.[58] Additional definitive evidence for the dendrimer molecular structures was obtained from MALDI-TOF mass spectra, which revealed only a single intense signal corresponding to the calculated mass of dendrimers **Ph-G1** and **Ph-G2**. (see ESI†)

Linear absorption and emission

The normalized linear absorption and fluorescence spectra for dendrimers **Ph-G0**, **Ph-G1** and **Ph-G2** in toluene are shown in Fig. 1. Linear measurements were performed in dilute toluene solutions ($\sim 10^{-6}$ M). The position of the main peak in both absorption and emission shows a bathochromic shift with increasing dendrimer generation number. All dendrimers show two major absorption bands: the peak at 305 nm is attributed to the absorption of the triphenylamine moiety and remains almost unchanged among the three dendrimers, while the other at long wavelength shows a shift from 411 nm (**Ph-G0**) to 422 nm (**Ph-G2**) which can be assigned to a π–π* transition. A small bathochromic shift in the linear absorption can be observed from **Ph-G0** to **Ph-G1**, and further to **Ph-G2**, which is due to the incremental extension of the conjugation length with increasing dendrimer generation. The crystallographic data on triphenylamine as well as quantum chemical calculations indicate that the three N–C bonds of the triphenylamine group lie in one common plane and further confirm continuity of the π-conjugation all the way through the nitrogen atom within triphenylamine and related molecules.[38,42] Therefore, the systematic shift supports the notion that the triphenylamine moiety serves as a π-electron bridge for extended electron conjugation within the dendrimers. However, after the initial shift of the linear absorption spectra from **Ph-G0** to **Ph-G1**, the absorption maxima remain almost the same, up to the highest dendrimer generation, which indicates that there is



Scheme 1 Synthetic route to compounds **2–7**.



Scheme 2 Synthesis of the dendrimers **Ph-G0**, **Ph-G1** and **Ph-G2**.

little change in the conjugation effect in extending the molecular framework beyond the second generation.

The emission spectra of **Ph-G0**, **Ph-G1** and **Ph-G2** in dilute toluene solutions all displayed similar behaviors. They exhibited emission maxima at 460 nm, 480 nm and 478 nm, respectively. The red shift from **Ph-G0** to **Ph-G1** and **Ph-G2** in the fluorescence spectra is more pronounced than that in the absorption spectra demonstrated that the effective conjugation length significantly improved with increasing generation of the dendrimers. This red shift of fluorescence spectrum with increasing generation number may also suggest that the energy of relaxed electronic states decreases with the size of dendrimer. One explanation for this could be that larger molecules can have a wider distribution of states due to increased branching, allowing greater relaxation of the excited state prior to emission.[59] On the other hand, the emission spectra of dendrimers of a higher generation do not exhibit any further detectable shift, consistent with the absorption spectra. It seems that the saturation value for the energy of the lowest excited state is reached for the number of branch segments in the dendrimer **Ph-G1**. The photophysical characteristics of dendrimers **Ph-G0**, **Ph-G1** and **Ph-G2** are summarized in Table 1.

In general, all of the dendrimers show large Stokes shifts ranging from 2592 cm^{-1} for **Ph-G0** to 2863 cm^{-1} for **Ph-G1**, indicating that the energy of the emitting states are lower than the Franck–Condon singlet states. The Stokes shifts of the dendrimers increase with the conjugation length, but that of **Ph-G2** is slightly smaller than that of **Ph-G1**. A further increase in the branching of **Ph-G2** has little influence on the Stokes shift, indicating that there is little difference in the excited-state energies between **Ph-G1** and **Ph-G2**. Also, all of the dendrimers **Ph-G0**, **Ph-G1** and **Ph-G2** have relatively high fluorescence quantum yields (η) of 0.78, 0.56 and 0.54 in toluene solutions, respectively, measured against a quinine sulfate standard. There is a gradual decrease of fluorescence quantum yields with an increasing dendrimer generation. From the point of view of molecular structure, due to the large dihedral angle between the phenyl ring plane and the plane of the N-bonded C atoms, higher generation triphenylamine based dendrimers have a greater tendency to adopt twisted configurations than those of lower generation, which might reduce the fluorescence quantum yield due to a higher tendency to nonradiatively decay by geometrical relaxation.[60]

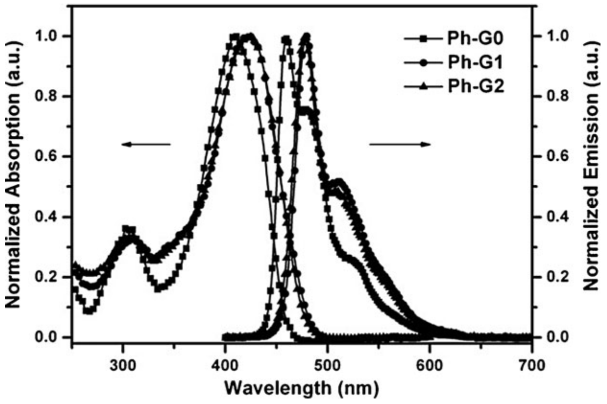


Fig. 1 Linear absorption and emission spectra for dendrimers **Ph-G0**, **Ph-G1** and **Ph-G2** in dilute toluene solution.

Two-photon absorption

The TPA spectra were determined by using pulsed laser light (82 MHz, 120 fs) from 700 nm to 850 nm generated by a mode locked Ti:sapphire laser (Tsunami, Spectra Physics). A spectrum analyzer (AvaSpec-2048) was used to monitor the excitation wavelengths. All data were obtained by the two-photon-excited fluorescence method with fluorescein in pH 11 water as in ref. 12. It is noted that all the results presented here correspond to intrinsic TPA cross-section values measured with the fluorescence method in the femtosecond regime, and thereby prevent contributions from linear nonresonant absorption or from excited-state absorption known to lead to artificially enhanced TPA cross sections when conducted in the nanosecond regime. The measured TPA spectra for the dendrimers are shown in Fig. 2. The TPA cross-section peak values (δ) for the dendrimers **Ph-G0**, **Ph-G1** and **Ph-G2** are 970, 3160, and 5690 GM (1 GM $= 1 \times 10^{-50}$ cm^4 s photon^{-1}), respectively. The TPA cross-section peak value increases by a factor of 3.24 and 5.82 from **Ph-G0** to **Ph-G1** and to **Ph-G2**. The maximum of TPA spectra ($\lambda_{\mathrm{max}}{}^{\mathrm{TPA}}$) of dendrimers **Ph-G1** and **Ph-G2** in Fig. 2 is clearly red-shifted with respect to **Ph-G0**.This shift, as well as a similar red-shift in the linear absorption, suggests either dipole–dipole-type or conjugation-type interaction between the dendrimer's branches. Otherwise, the $\lambda_{\mathrm{max}}{}^{\mathrm{TPA}}/2$ value of the dendrimers is located at a shorter wavelength than the lowest energy of linear absorption maximum (λ_{max}), which is consistent with the prediction that the two-photon allowed states are at a higher energy than the Franck–Condon states.

There is a strong enhancement over simple additive behavior when moving from **Ph-G0** to higher generations (**Ph-G1** or **Ph-G2**). A theoretical study for two-photon absorption of multi-branch structure has revealed that such an enhancement is mainly caused by vibronic coupling. The electronic coupling in the multi-branch molecules, which contain triphenylamine units, is weak, probably because the central amino group is used as the connecting unit, which breaks the conjugation of the whole network.[61] On the other hand, when the extended π-conjugation and the size of the system increase at higher

Table 1 Photophysical characteristics of dendrimers **Ph-G0**, **Ph-G1** and **Ph-G2**

Dendrimer	λ_{abs}/nm	ε_{max}[a]	λ_{em}/nm	Δ[b]/cm^{-1}	η[c]	τ[d]/ns	δ_{max}[e]/GM	$\eta\delta_{max}$[f]	δ_{max}/MW[g]
Ph-G0	411	87 000	460	2592	0.78	0.79	970	760	1.58
Ph-G1	422	182 500	480	2863	0.56	0.94	3160	1770	1.87
Ph-G2	422	490 000	478	2776	0.54	0.62	5690	3080	1.50

[a] In M^{-1} cm^{-1}. [b] Stokes shift. [c] Fluorescence quantum yield in dilute toluene solution, determined by a standard method with quinine sulfate as a reference. [d] Fluorescence lifetime obtained from time-correlated single photon counting (TCSPC). [e] Peak TPA cross-section in 10^{-50} cm^4 s photon^{-1} (GM). [f] The two-photon excited fluorescence (TPEF) action cross section. [g] Maximum TPA cross section per molecular weight.

generations, the density of states will increase, providing more effective coupling channels between the ground and two-photon allowed states, which would in turn increase the TPA cross-section.[26,62]

To understand how the TPA cross section correlates with the chromophores density, the TPA cross-section per unit triphenylamine is calculated and plotted as a function of dendrimer generation. as shown in the inset of Fig. 2. It can be seen from the calculated result that the δ value of dendrimers from **Ph-G0** to **Ph-G2** raise in a proportion of 1 : 3 : 6 by increasing the number of triphenylamine units. This behavior is close to $\delta \propto N$ scaling, namely 1 : 3 : 7 proportion, where N is the number of triphenylamine units. This phenomenon is reminiscent of what has been observed in the case of cooperative enhancement of the TPA cross-section with an increase in branching chromophores, as well as an increase of cross-section in nitrogen centered dendrimers. Furthermore, compared with the 4,4′-bis(diphenylamino)stilbene (BDPAS) series dendrimers which are well-known triphenylamine-based TPA dyes,[21–22] the dendrimers with a bis(styryl)benzene core always exhibit significantly larger TPA cross-sections when the numbers of triphenylamine units in a conjugated molecular framework are similar. This enhancement of TPA cross-section is likely due to the large initial superiority of the bis(styryl)benzene core over a simple ethylene bridge, which could be due to its longer conjugation length and/or the electron accepting ability of the central phenylene ring.[4] Thus, the use of a bis(styryl)benzene unit as the core of the dendrimer may provide a higher TPA response with enhanced emission.

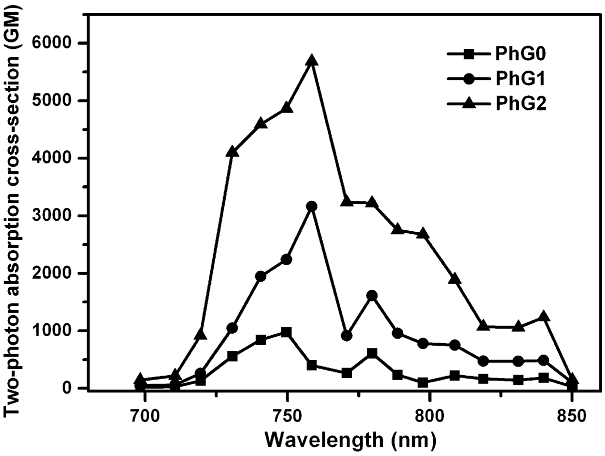


Fig. 2 TPA spectra for dendrimers **Ph-G0**, **Ph-G1** and **Ph-G2** in toluene. The TPA cross-sections were determined by using the two-photon excited fluorescence method relative to fluorescein.

Two-photon excited (TPE) fluorescence

The TPE fluorescence spectra of dendrimers **Ph-G0**, **Ph-G1** and **Ph-G2** in toluene are shown in Fig. 3. The pump source for two-photon excitation as well as TPA cross-section measurements was a focused ultra-short pulsed laser beam from a Ti:sapphire laser oscillator/amplifier system. This beam was focused by an f = 12 cm lens with the solution sample in a fluorimeter cuvette with four optically clear windows placed at a fixed distance of ~12 cm from the focusing lens. Under these conditions, the intensity for two-photon excitation was in an excitation regime where the fluorescence signal showed a quadratic dependence on the intensity of the excitation beam, as expected for two-photon induced emission. For example, as shown in Fig. 4, the log–log plots show slopes of 1.91, 1.93, and 1.95 for dendrimers **Ph-G0**, **Ph-G1** and **Ph-G2**. The collection of the TPE fluorescence signal was performed by using a CCD-array spectrometer (iDus CCD Spectroscopic CCD Camera, Andor) in conjunction with a fiber coupler head. Similarly to their linear emission in toluene, **Ph-G1** and **Ph-G2** exhibit a red-shifted emission compared to that of **Ph-G0**. From Fig. 1 and 3, one may find that the TPE fluorescence spectra for the three generation dendrimers in toluene are essentially the same as their linear fluorescence spectra, confirming that both emissions are from the same excited state.

The values of $\eta\delta_{max}$, the two-photon excited fluorescence (TPEF) action cross section, increase in the order of **Ph-G0** < **Ph-G1** < **Ph-G2**. The smaller $\eta\delta_{max}$ value for **Ph-G0** is attributed to the much smaller δ_{max} value. For applications that require strong TPA such as optical limiting, 3D micro-fabrication or strong TPEF for bioimaging, molecules with large TPA cross section per molecular weight (δ_{max}/MW) are needed.[1,19] To compare relative TPA properties per unit mass, we calculate δ_{max}/MW values of these dendrimers. The results show that δ_{max}/MW values of these dendrimers are larger than 1.5, indicating that these dendrimers may be useful for such practical applications.[19]

TPA-based optical limiting

For some laser-based applications such as optical communication, optical fabrication, and manufacturing, the intensity or energy stability of the utilized laser beam is very important because random intensity or power fluctuation may be troublesome for these applications. Optical power limiting, the optical analog to an electrical surge protector, is important for the protection of optical sensors and eyes from sudden exposure to high incident intensities.[18] However, materials with a strong and efficient nonlinear absorption response as a function of

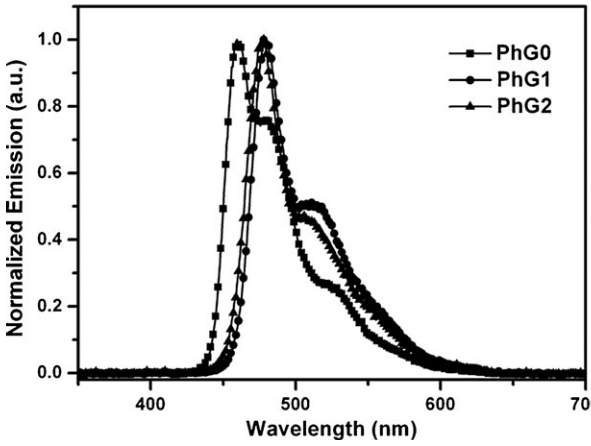


Fig. 3 Two-photon excited fluorescence (TPEF) spectra for dendrimers **Ph-G0**, **Ph-G1** and **Ph-G2** in toluene.

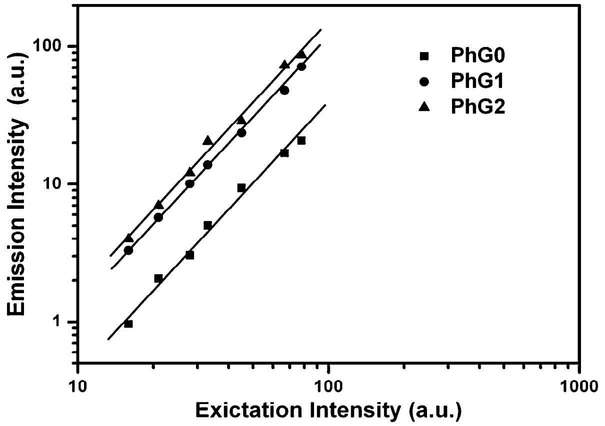


Fig. 4 Dependence of the peak intensity of TPE fluorescence intensity *versus* the input laser intensity at 800 nm for all three dendrimers in toluene.

incident intensity could be one of the approaches to reducing such fluctuation and stabilizing the pulsed laser signals, and are thus of great interest for optical power limiting. Two photon optical power limiting was investigated for **Ph-G1** and **Ph-G2** in CH_2Cl_2 under femtosecond excitation. Nonlinear optical transmission measurements were performed using a 10 mm quartz cuvette with molecular concentrations $\sim 10^{-3}$ M, with a Ti:sapphire laser oscillator/amplifier system generating output pulses of 120 fs duration and 800 nm wavelength. The measured input and output intensity data for **Ph-G1** and **Ph-G2** are plotted in Fig. 5. The plots display a typical optical limiting curvature in which the output energy levels off at higher input energies because of the nonlinear optical properties of the dendrimers. When the input energy increases from 0.51 to 14.95 μJ (an increase of about 29.3 times), the transmitted energy changed from 0.45 to 5.85 (an increase of 13.0 times) for **Ph-G1** and from 0.44 to 4.5 (an increase of 10.2 times) for **Ph-G2**. These are typical optical limiting behaviors based on a TPA mechanism. The results suggest that this series of dendrimers would provide better optical limiting performance with increasing generation due to an enhanced two photon response. The optical limiting properties of **Ph-G1** and **Ph-G2** under femtosecond excitation are comparable to the efficiency of multibranched triphenylamine-based chromophores in the femtosecond regime.[63,64]

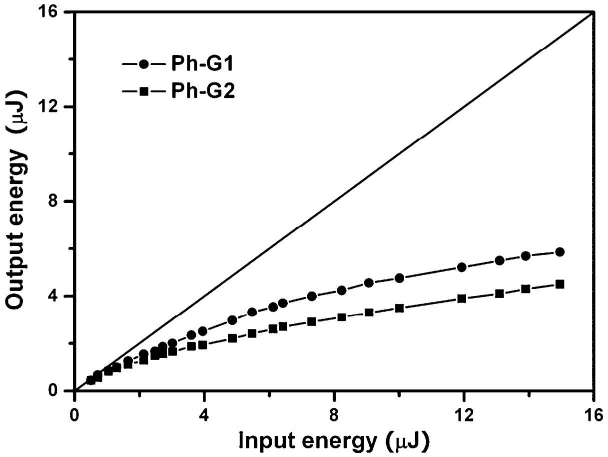


Fig. 5 Output energy as a function of the input energy for **Ph-G1** and **Ph-G2** in CH_2Cl_2 under femtosecond excitation at 800 nm, in 10 mm quartz cuvettes with concentrations $\sim 10^{-3}$ M.

Thus, if we use dendrimers as a two-photon absorbing medium to stabilize the input laser, we would expect that more than a two-fold reduction in laser fluctuation could be achievable, which suggests dendrimers **Ph-G1** and **Ph-G2** may be useful for the development of new multifunctional organic materials for two-photon based optical limiting.

Conclusions

A novel series of triphenylamine-based dendrimers **Ph-G0**, **Ph-G1** and **Ph-G2** have been synthesized and characterized. Their linear and nonlinear optical properties were investigated. Linear absorption and emission spectra revealed a bathochromic shift with increasing dendrimer generation number, whereas their fluorescence quantum yields decrease with increasing generation. Investigation of the TPA properties of these dendrimers reveals a strong cooperative effect and their TPA cross section values increase with increasing the generation, as well as the π-conjugation lengths. Moreover, the TPA cross-sections values increase gradually with the proportion of triphenylamine units and the maximum value of the TPA cross-section can reach 5690 GM for **Ph-G2**. The effect of two-photon optical limiting behaviors for these dendrimers was demonstrated in CH_2Cl_2 under femtosecond excitation. The high TPA cross section and two-photon optical limiting abilities of **Ph-G1** and **Ph-G2** suggest that triphenylamine-based dendrimers are a highly suitable class of two-photon absorbing materials in a number of nonlinear optical applications.

Acknowledgements

This work was supported by the National Basic Research Program of China (973 program, 2009CB623605), the Natural Science Foundation of China (Grant No. 50673035), the Program for New Century Excellent Talents in Universities of China Ministry of Education, the 111 Project (Grant No. B06009) and the Graduated Innovation Fund of Jilin University (No. 20080109).

References

1 B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I. Y. S. Lee, D. McCord-Maughon, J. Q. Qin, H. Röckel, M. Rumi, X. L. Wu, S. R. Marder and J. W. Perry, *Nature*, 1999, **398**, 51.
2 C. N. LaFratta, J. T. Fourkas, T. Baldacchini and R. A. Farrer, *Angew. Chem., Int. Ed.*, 2007, **46**, 6238–6258.
3 M. Albota, D. Beljonne, J.-L. Bredas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Rockel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu and C. Xu, *Science*, 1998, **281**, 1653.
4 M. Rumi, J. E. Ehrlich, A. A. Heikal, J. W. Perry, S. Barlow, Z. Hu, D. McCord-Maughon, T. C. Parker, H. Roeckel, S. Thayumanavan, S. R. Marder, D. Beljonne and J.-L. Bredas, *J. Am. Chem. Soc.*, 2000, **122**, 9500.
5 G. S. He, G. C. Xu, P. N. Prasad, B. A. Reinhardt, J. C. Bhatt and A. G. Dillard, *Opt. Lett.*, 1995, **20**, 435.
6 C. W. Spangler, *J. Mater. Chem.*, 1999, **9**, 2013.
7 D. A. Parthenopoulos and P. M. Rentzepis, *Science*, 1989, **245**, 843.
8 T. C. Lin, S. J. Chung, K. S. Kim, X. P. Wang, G. S. He, J. Swiatkiewica, H. E. Pudavar and P. N. Prasad, *Adv. Polym. Sci.*, 2003, **161**, 157.
9 W. Denk, J. H. Strickler and W. W. Web, *Science*, 1990, **248**, 73.
10 S. Kim, T. Y. Ohulchanskyy, H. E. Pudavar, R. K. Pandey and P. N. Prasad, *J. Am. Chem. Soc.*, 2007, **129**, 2699.
11 P. T. C. So, C. Y. Dong, B. R. Masters and K. M. Berland, *Annu. Rev. Biomed. Eng.*, 2000, **2**, 399.
12 C. Xu and W. W. Webb, *J. Opt. Soc. Am. B*, 1996, **13**, 481.
13 L. Ventelon, S. Charier, L. Moreaux, J. Mertz and M. Blanchard-Desce, *Angew. Chem., Int. Ed.*, 2001, **40**, 2098.
14 J. Yoo, S. K. Yang, M. Y. Jeong, H. C. Ahn, S. J. Jeon and B. R. Cho, *Org. Lett.*, 2003, **5**, 645.
15 C. Y. Chen, Y. Tian, Y. J. Cheng, A. C. Young, J. W. Ka and A. K. Y. Jen, *J. Am. Chem. Soc.*, 2007, **129**, 7220–7221.
16 Y. Tian, C. Y. Chen, Y. J. Cheng, A. C. Young, N. M. Tucker and A. K. Y. Jen, *Adv. Funct. Mater.*, 2007, **17**, 1691.
17 Y. Tian, C. Y. Chen, C. C. Yang, A. C. Young, S. H. Jang, W. C. Chen and A. K. Y. Jen, *Chem. Mater.*, 2008, **20**, 1977–1987.
18 G. S. He, L. S. Tan, Q. Zheng and P. N. Prasad, *Chem. Rev.*, 2008, **108**, 1245.
19 H. M. Kim and B. R. Cho, *Chem. Commun.*, 2009, 153–164.
20 S. Chung, K. S. Kim, T. C. Lin, G. S. He, J. Swiatkiewicz and P. N. Prasad, *J. Phys. Chem. B*, 1999, **103**, 10741.
21 M. Drobizhev, A. Karotki and A. Rebane, *Opt. Lett.*, 2001, **26**, 1081.
22 M. Drobizhev, A. Karotki, Y. Dzenis, A. Rebane, Z. Suo and C. W. Spangler, *J. Phys. Chem. B*, 2003, **107**, 7540.
23 J. L. Hua, B. Li, F. S. Meng, F. Ding, S. X. Qian and H. Tian, *Polymer*, 2004, **45**, 7143–7149.
24 L. Porrès, O. Mongin, C. Katan, M. Charlot, T. Pons, J. Mertz and M. Blanchard-Desce, *Org. Lett.*, 2004, **6**, 47.
25 F. Terenziani, C. L. Droumaguet, C. Katan, O. Mongin and M. Blanchard-Desce, *ChemPhysChem*, 2007, **8**, 723–734.
26 W. J. Yang, D. Y. Kim, C. H. Kim, M. Y. Jeong, S. K. Lee, S. J. Jeon and B. R. Cho, *Org. Lett.*, 2004, **6**, 1389.
27 Q. Zheng, G. S. He and P. N. Prasad, *Chem. Mater.*, 2005, **17**, 6004–6011.
28 J. M. J. Frechet and D. Tomalia, *Dendrimers and Other Dendritic Polymers*, Wiley, Chichester, 2001.
29 J. S. Moore, *Acc. Chem. Res.*, 1997, **30**, 402–413.
30 J. N. G. Pillow, M. Halim, J. M. Lupton, P. L. Burn and I. D. W. Samuel, *Macromolecules*, 1999, **32**, 5985–5993.
31 A. Adronov, S. L. Gilat, J. M. J. Frechet, K. Ohta, F. V. R. Neuwahl and G. R. Fleming, *J. Am. Chem. Soc.*, 2000, **122**, 1175–1185.
32 T. Goodson, III., *Annu. Rev. Phys. Chem.*, 2005, **56**, 581.
33 T. Goodson, III., *Acc. Chem. Res.*, 2005, **38**, 99–107.
34 O. Varnavski, X. Yan, O. Mongin, M. Blanchard-Desce and T. Goodson, III., *J. Phys. Chem. C*, 2007, **111**, 149–162.
35 G. Ramakrishna, A. Bhaskar, P. Bauerle and T. Goodson, III., *J. Phys. Chem. A*, 2008, **112**, 2018–2026.
36 Y. Wang, G. S. He, P. N. Prasad and T. Goodson, III., *J. Am. Chem. Soc.*, 2005, **127**, 10128–10129.
37 M. I. Ranasinghe, O. P. Varnavski, J. Pawlas, S. I. Hausk, J. Louie, J. F. Hartwig and T. Goodson, III., *J. Am. Chem. Soc.*, 2002, **124**, 6520–6521.
38 X. M. Wang, D. Wang, G. Y. Zhou, W. T. Yu, Y. F. Zhou, Q. Fang and M. H. Jiang, *J. Mater. Chem.*, 2001, **11**, 1600–1605.
39 J. M. Lupton, I. D. W. Sameul, P. L. Burn and S. Mukamel, *J. Phys. Chem. B*, 2002, **106**, 7647–7653.
40 H. J. Lee, J. Sohn, J. Hwang, S. Y. Park, H. Choi and M. Cha, *Chem. Mater.*, 2004, **16**, 456–465.
41 P. Wei, X. Bi, Z. Wu and Z. Xu, *Org. Lett.*, 2005, **7**, 3199–3202.
42 R. Sander, V. Stumpflen, J. H. Wendorff and A. Greiner, *Macromolecules*, 1996, **29**, 7705–7708.
43 Z. Fang, T. Teo, L. Cai, Y. Lai, A. Samoc and M. Samoc, *Org. Lett.*, 2009, **11**, 1–4.
44 Z. Fang, X. Zhang, Y. Lai and B. Liu, *Chem. Commun.*, 2009, 920–922.
45 Z. Li, A. Qin, J. W. Y. Lam, Y. Dong, Y. Dong, C. Ye, I. D. Williams and B. Z. Tang, *Macromolecules*, 2006, **39**, 1436–1442.
46 A. Qin, J. W. Y. Lam, H. Dong, W. Lu, C. K. W. Jim, Y. Dong, M. Haussler, H. H. Y. Sung, I. D. Williams, G. K. L. Wong and B. Z. Tang, *Macromolecules*, 2007, **40**, 4879–4886.
47 Y. Jiang, Y. Wang, J. Hua, S. Qu, S. Qian and H. Tian, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 4400–4408.
48 Q. Zhang, Z. Ning and H. Tian, *Dyes Pigm.*, 2009, **81**, 80–84.
49 H. Xia, J. He, B. Xu, S. Wen, Y. Li and W. Tian, *Tetrahedron*, 2008, **64**, 5736.
50 H. Xia, J. He, P. Peng, Y. Zhou, Y. Li and W. Tian, *Tetrahedron Lett.*, 2007, **48**, 5877.
51 Q. Zheng, S. K. Gupta, G. S. He, L. Tan and P. N. Prasad, *Adv. Funct. Mater.*, 2008, **18**, 2770–10.
52 M. Lehmann, B. Schartel, M. Hennecke and H. Meier, *Tetrahedron*, 1999, **55**, 13377.
53 Q. Yao, E. P. Kinney and Z. J. Yang, *J. Org. Chem.*, 2003, **68**, 7528.
54 H. Detert and O. Sadovski, *Synth. Met.*, 2003, **138**, 185.
55 G. N. Tew, M. U. Pralle and S. I. Stupp, *Angew. Chem., Int. Ed.*, 2000, **39**, 517.
56 Z. Ning, Z. Chen, Q. Zhang, Y. Yan, S. Qian, Y. Cao and H. Tian, *Adv. Funct. Mater.*, 2007, **17**, 3799.
57 R. S. Tewari, N. Kumari and P. S. Kendurkar, *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.*, 1977, **15**, 753.
58 R. Beavington, M. J. Frampton, J. M. Lupton, P. L. Burn and I. D. W. Samuel, *Adv. Funct. Mater.*, 2003, **13**, 211.
59 M. Drobizhev, A. Rebane, C. Sigel, E. H. Elandaloussi and C. W. Spangler, *Chem. Phys. Lett.*, 2000, **325**, 375–382.
60 X. Wang, P. Yang, B. Li, W. Jiang, W. Huang, S. Qian, X. Tao and M. Jiang, *Chem. Phys. Lett.*, 2006, **424**, 333–339.
61 P. Macak, Y. Luo, P. Norman and H. Agren, *J. Chem. Phys.*, 2000, **113**, 7055.
62 S. K. Lee, W. J. Yang, J. J. Choi, C. H. Kim, S. J. Jeon and B. R. Cho, *Org. Lett.*, 2005, **7**, 323–326.
63 K. D. Belfield, M. V. Bondar, F. E. Hernandez and O. V. Przhonska, *J. Phys. Chem. C*, 2008, **112**, 5618–5622.
64 T. C. Lin, G. S. He, Q. Zheng and P. N. Prasad, *J. Mater. Chem.*, 2006, **16**, 2490.