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Tetrahedron

Tetrahedron 64 (2008) 4460–4467

www.elsevier.com/locate/tet

Synthesis and cubic nonlinear optical behavior of phenyl and ferrocenyl-ended resorcinarene-based dendrimers

Irina Victorovna-Lijanova [a], Maria I. Reyes-Valderrama [a], José-Luis Maldonado [b], Gabriel Ramos-Ortiz [b], Klimova Tatiana [c], Marcos Martínez-García [a,*]

[a] Instituto de Química, UNAM, Cd. Universitaria, Circuito exterior, Coyoacán, C.P. 04510, México D.F., Mexico
[b] Centro de Investigaciones en Óptica, A.P. 1-948, 37000 León, Gto., Mexico
[c] Facultad de Química, UNAM, Cd. Universitaria, Circuito interior, Coyoacán, C.P. 04510, México D.F., Mexico

Received 1 February 2008; received in revised form 12 February 2008; accepted 14 February 2008
Available online 20 February 2008

Abstract

Dendrimers were synthesized with phenyl and ferrocenyl-ended groups joined by vinyl moieties. All the dendrons used for dendrimers synthesis had showed trans configuration. This configuration as well as the 'cone' conformation of the resorcinarenes was preserved in the dendrimers, as it was shown by ^{1}H NMR spectroscopy. The chemical structure and purity of the synthesized dendrimers were confirmed by ^{1}H and ^{13}C NMR, FAB+, MALDI-TOF, electrospray mass spectra, and elemental analysis. Cubic nonlinear optical behavior of this first generation of resorcinarene dendrimers was studied. The $\chi^{(3)}$ values estimated from the THG Maker-fringe technique for the phenyl and ferrocenyl-ended resorcinarene dendrimers dispersed in thin solid films are of the order of 10^{-13} and 10^{-12} esu, respectively.

Keywords: Phenyl; Ferrocenyl; π-Conjugated systems; Resorcinarene; Dendrimers; Nonlinear optics

1. Introduction

Luminescent and redox-active multichromophoric dendrimers with a specific architecture are at the center of a large interest for many reasons. They can be used to study photoinduced charge-separation processes and energy migration patterns within the arrays, with the final aim of designing efficient supramolecular systems for energy conversion purposes and/or light information devices.[1] Among various luminescent and redox-active macromolecules, π-conjugated dendrimers and those containing organometallic fragments are particularly attractive[2–5] for the applications above because (i) their size and architecture can be specifically controlled during the synthesis,[4] (ii) they have numerous peripheral end chains surrounding a single core, (iii) the globular shape of dendrimers provides a large surface area that can be decorated with chromophores or organometallic species, thus resulting in a large absorption cross section and enabling efficient capture of photons.[6] Furthermore, both the peripheral chromophores and the core are capable of contributing to the light absorption properties of the entire macromolecule. Dendrimers provide new opportunities for precisely placing some charge-carrier transporting units in a three-dimensional nanoscale construction. Furthermore, recently the nonlinear optical (NLO) properties of several dendrimers have been reported.[7–16] The use of novel nanostructured dendrimer–metal composites for electronic and optical applications is a very important issue for the creation of new devices.[7,8,10,12,15] These compounds belong to the family of organometallic materials, which could possess strong π-electron conjugation, i.e., extended electron delocalization throughout the molecule. Since this is a crucial factor in attaining high optical nonlinearities, it is of great interest to identify and understand the structure–property relation of these compounds. This knowledge will contribute to a rational design of new third-order NLO[9–12,16] materials based on low molecular weight molecules, macromolecules, and polymers.

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* Corresponding author.
E-mail address: margar@servidor.unam.mx (M. Martínez-García).

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doi:10.1016/j.tet.2008.02.050

Here we report the synthesis and cubic NLO behavior of a novel series of ferrocenyl and phenyl ended resorcinarene-based dendrimers with extended π-conjugated systems.

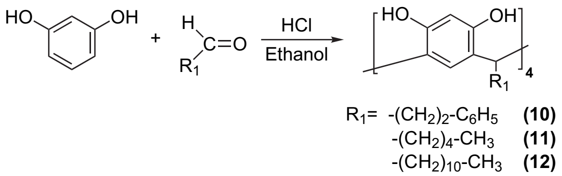
2. Results and discussion

2.1. Synthesis and chemical characterization of dendrons and dendrimers

The synthesis of the two series of dendrimers with vinyl ferrocene and stilbene was carried out applying the convergent Fréchet approach[17] that consists in three steps. The first one is the synthesis of the two conjugated dendrons, which is followed by the selective formation of resorcinarenes bearing three different solubilizing groups and finally the alkylation of the dendrons to the resorcinarenes. Under this order, dendrons containing styryl and ferrocenylvinyl groups were prepared starting from a Heck reaction coupling of the commercially available 3,5-dibromo-benzaldehyde **3** with styrene **1** or vinyl ferrocene **2** in dimethylformamide/triethylamine (1:0.25) using palladium acetate as catalyst (Scheme 1). Both compounds **4** and **5** were obtained in 60% yield. They have *E*-configuration as it was evidenced by the high value (ca. 16 Hz) of the coupling constant for the AB system of the vinylic protons. Aldehydes **4** and **5** were reduced with $LiAlH_4$ in THF to give alcohols **6** and **7** in 90 and 99% yield, respectively, which were converted into chlorides **8** and **9** upon treatment with thionyl chloride and pyridine in dichloromethane. Dendrons **8** and **9** are the first generation dendrons of the stilbene and vinylferrocenyl families (Scheme 1).

The structure of dendrons **8** and **9** was confirmed by ^{1}H NMR spectroscopy. Signals at δ_H 4.63 (dendron **8**) and 4.61 (dendron **9**) corresponded to the methylene protons Ar–CH_2–Cl. Compound **9** showed three signals at δ_H 4.17, 4.32, and 4.59 due to the ferrocenyl groups. The vinylic protons were observed as two doublets at δ_H 7.13 and 7.15 for compound **8** and at δ_H 6.69 and 6.94 for compound **9**. The broad signals for the aromatic protons appear at δ_H 7.23–7.58. The coupling constants of ca. J=15.4–16.8 Hz were observed for all the π-conjugated systems pointing out their trans configuration.

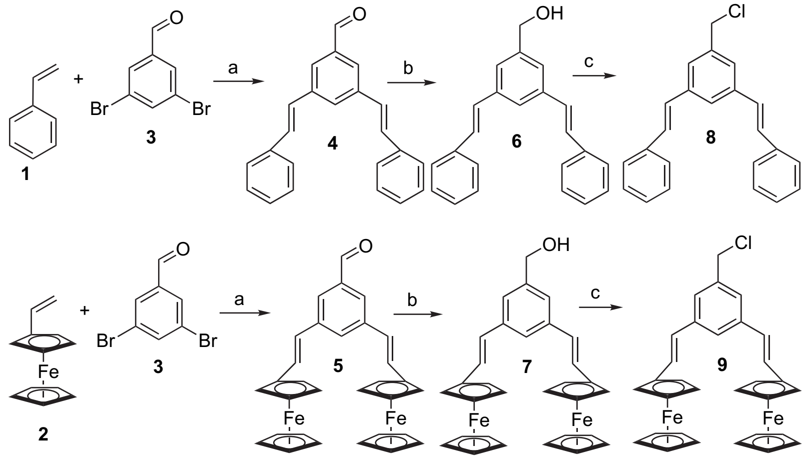
Resorcinarenes **10–12** were obtained from the condensation reaction of resorcinol with three different aldehydes: hydrocinnamaldehyde, hexanal, and dodecanal (Scheme 2). Their chemical structures were confirmed by ^{1}H, ^{13}C NMR, and FAB+ mass spectrometry. The resorcinarenes showed a well resolved triplet at δ_H 4.36, which is attributed to the *rccc* conformation.[18]



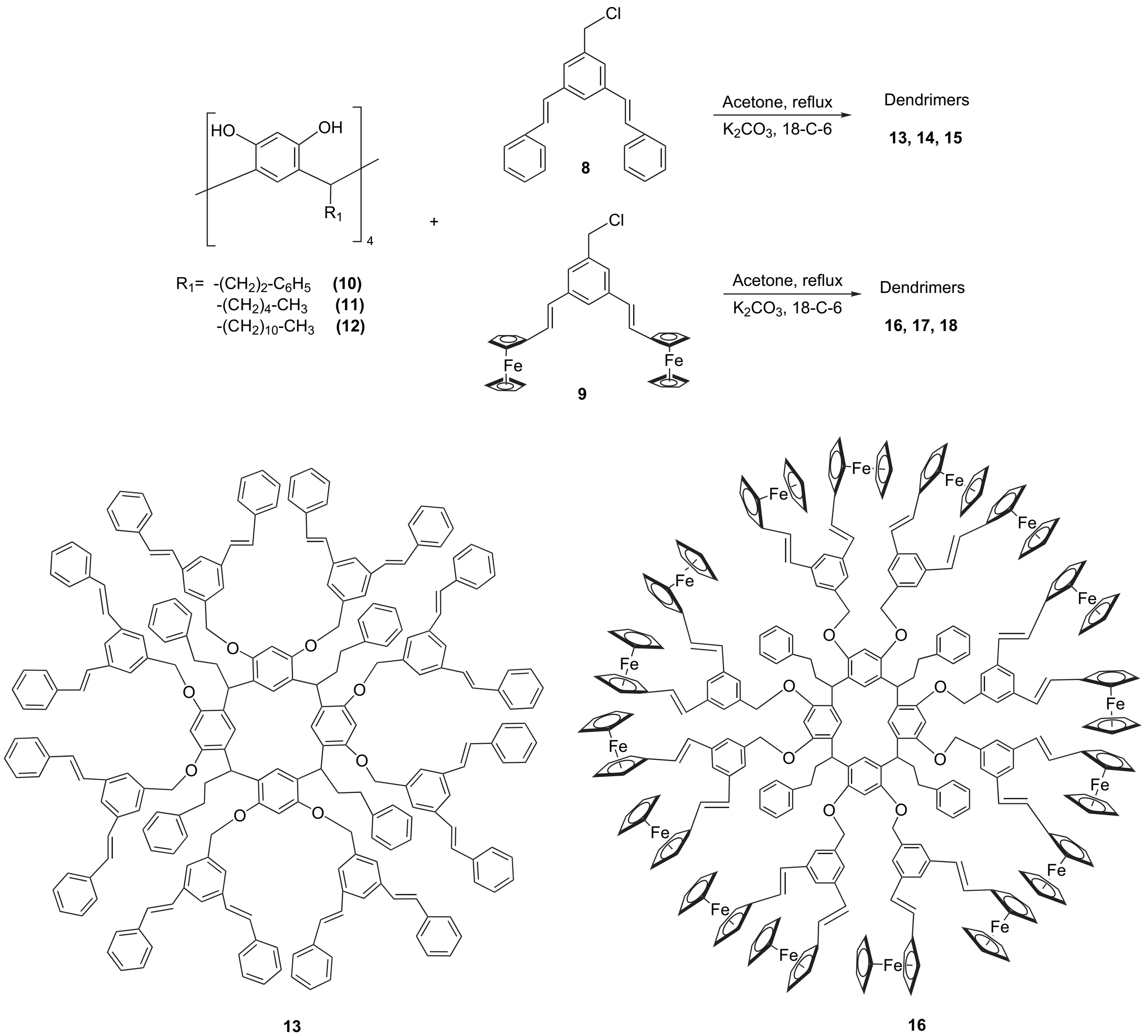
Scheme 2. Synthesis of resorcinarenes **10–12**.

The iterative convergent strategy used for the synthesis of functionalized dendrimers is depicted in Scheme 3. The synthesis of dendrimers involves only one step, an O-alkylation between dendrons **8** or **9** and resorcinarenes **10–12**. The reaction was carried out in acetone and K_2CO_3 at reflux for 7 days and the dendrimers were obtained in good yields.

The ^{1}H NMR spectra of the dendrimers **13–15** showed one triplet at δ_H 5.10, 4.93 and 5.32, respectively, assigned to the methine proton at the resorcinarene bridges. These triplets confirm that the resorcinarene dendrimers have an *rccc* conformation, while that ascribed to the –CH_2–O protons appears as a broad signal at δ_H 4.75, 4.63, and 4.76. For all dendrimers **13–15**, the vinylic protons give two doublets, at δ_H 6.79 and 6.89 both with a couplet constant J=16.2 Hz (Fig. 1a) for dendrimer **13**, at δ_H 6.80 and 6.89 with a couplet constants J=16.2 and 16.1 Hz, respectively, for dendrimer **14**, at δ_H 7.05 and 7.14 with a couplet constants J=16.2 and 16.5 Hz, respectively, for dendrimer **15**. In all cases a broad peak is also observed at δ_H 7.15–7.52 assigned to the aromatic protons. The ^{1}H NMR spectra of dendrimers **16–18** showed the characteristic signals due to the ferrocenyl groups at δ_H 4.13, 4.14,



Scheme 1. Synthesis of dendrons **8** and **9**: (a) $Pd(OAc)_2$/tri-*o*-tolylphosphine, DMF/Et_3N, 120 °C, 24 h; (b) THF, $LiAlH_4$, 0 °C, 4 h; (c) Py, CH_2Cl_2, $SOCl_2$, −10 °C, 7 h.



Scheme 3. Synthesis of resorcinarene dendrimers **13–18**.

and 4.47 and due to the CH_2–O at δ_H 4.14. One broad signal at δ_H 4.70 was assigned to the methine groups CH, and two broad signals at δ_H 7.07–7.46 were assigned to the aromatic protons. For the dendrimers **16–18** in all the cases four sets of signals for the vinylic protons were observed: at δ_H 6.56, 6.68, 6.87, 6.91 with a couplet constants J=15.6, 15.9, 15.6, 16.2 Hz for the dendrimer **16**, at δ_H 6.69, 6.71, 6.90, 6.94 with a couplet constants J=16.5, 15.9, 15.6, 15.6 Hz for the dendrimer **17** (Fig. 1b), at 6.69, 6.73, 6.87, 6.91 with a couplet constants J=16.2, 15.9, 15.6, 15.9 Hz for the dendrimer **18**. The four set of signals two small and two bigger for the vinylic protons in the ferrocenyl terminating dendrimers could be due to the presence two types of conformations the boat C_{2v} and the crown C_{4v} symmetry and their slow interconvertion. This resorcinarene dendrimers behavior also was reported by Ueda and co-workers.[18] Similar results were observed in the ^{1}H NMR spectra of resorcinarene when it has bulky substituents.[18]

The structures of dendrimers **13–18** were also confirmed by ^{13}C NMR, IR, and electrospray, MALDI-TOF mass spectrometry. It was found that all the dendrimers have an expected molecular weight. The MALDI-TOF mass spectra of dendrimer **15** and electrospray mass spectra of **18** are shown in Figure 2.

2.2. Linear and third-order nonlinear optical characterization

In this work, the cubic NLO response for the series of phenyl and ferrocenyl-ended resorcinarene dendrimers (compounds **13–18**) was estimated through the use of third-harmonic generation (THG) Maker-fringes technique.[19] This technique was chosen to measure $\chi^{(3)}$ because it allows measuring pure electronic NLO effects (important for high bandwidth photonic applications). Figure 3 shows the linear

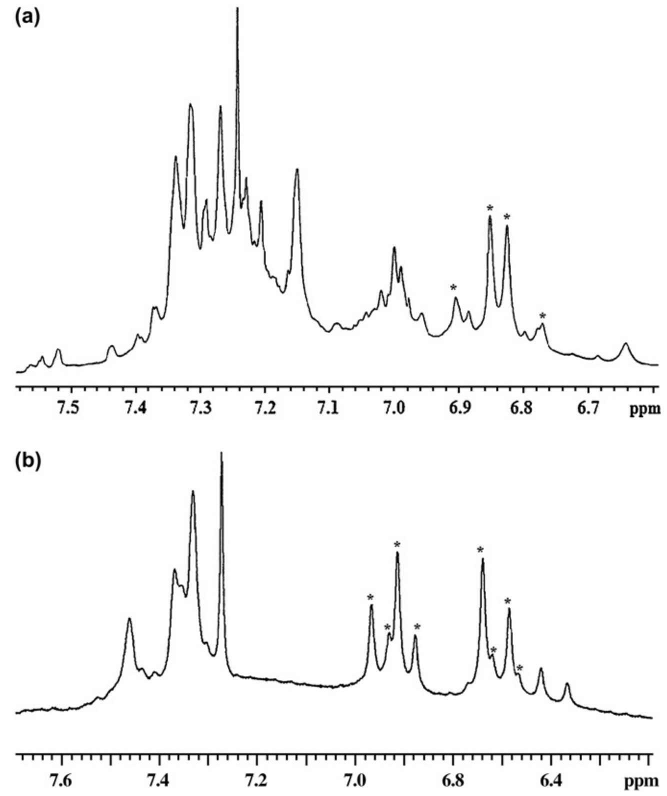


Figure 1. Aromatic portion of the ^1H NMR spectrum of dendrimers **13** (a) and **17** (b) in $CDCl_3$ at room temperature. The vinylc groups are indicated by stars.

absorption (absorption coefficient) of the dendrimers doped into solid polystyrene (PS) films at a loading level of 30 wt % (weight percent). Sample thickness was between 140 nm and 1.6 μm.

The films show a broad absorption band with maxima around 300–312 nm. These compounds exhibit high transparency in the visible and IR wavelength regions. Figure 4 shows the so called THG Maker-fringe patterns for the compound **16** doped into PS film (sample thickness: 144 nm). As reference, the figure also includes the THG patterns measured from the fused silica substrate alone (thickness: 1 mm). These data were obtained at the fundamental near infrared wavelength of 1200 nm (THG signal at 400 nm). From these data it is estimated that the third-order nonlinear susceptibility of the polymer film doped with compound **16** is of the order of 10^{-12} esu at such fundamental wavelength. Table 1 shows $\chi^{(3)}$ values for the compounds studied. We could not prepare good quality samples with dendrimer **15** and so, the corresponding $\chi^{(3)}$ value is not reported.

From our measurements it is evident that for this series of dendrimers, the cubic susceptibilities $\chi^{(3)}$ are clearly improved with the addition of the ferrocenyl-ended group **16**–**18**. Previously, $\chi^{(3)}$ values of the order of 10^{-10}–10^{-12} esu were reported for some others dendrimers.[12,14] However, in these works[12,14] different NLO techniques were used such as degenerate four wave mixing (DFWM),[12] Z-scan, and self-phase modulation.[14] Also, in the last reference, samples were tested in solution and a femtosecond laser system was used for the excitation. For some particular dendrimers with CdS quantum

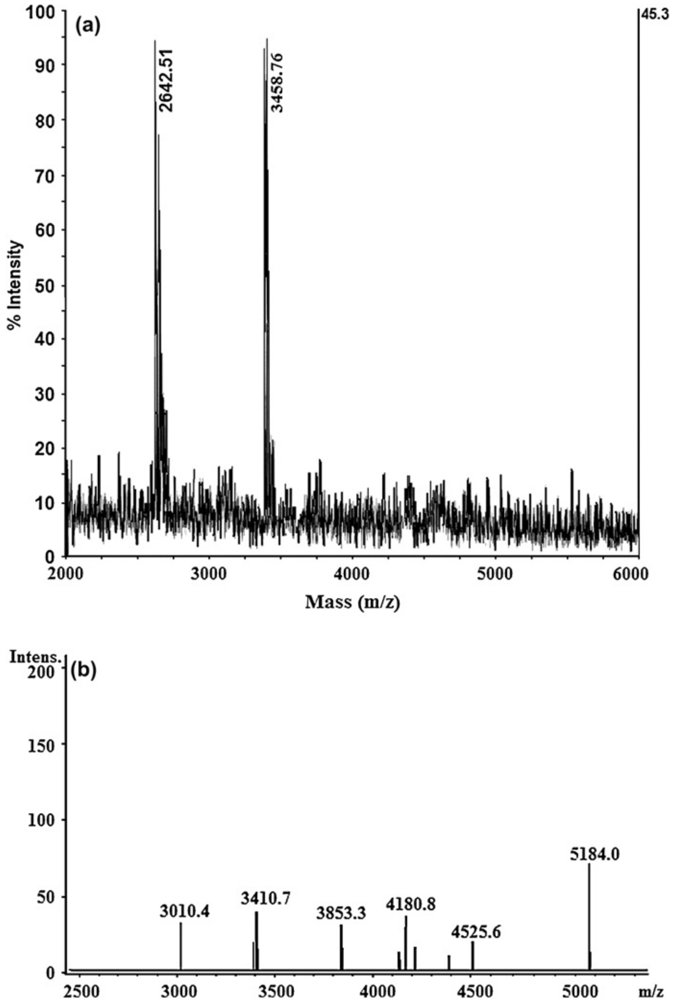


Figure 2. MALDI-TOF and electrospray mass spectra of phenyl **15** (a) and ferrocenyl **18** (b) ended resorcinarene dendrimers.

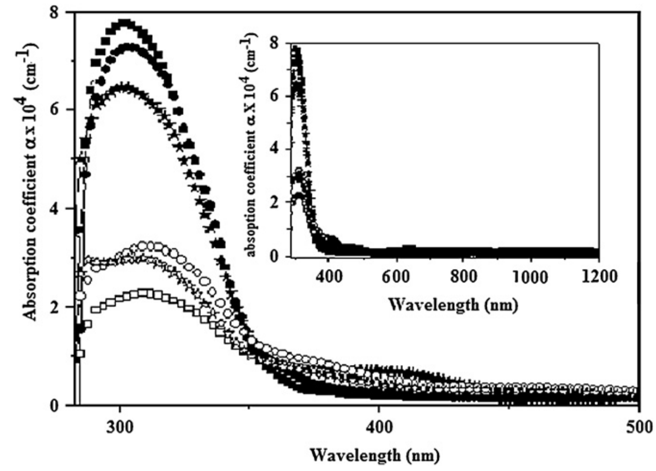


Figure 3. Optical linear absorption coefficient of polymer films doped with phenyl and ferrocenyl-ended resorcinarene dendrimers; **13** (filled squares), **14** (filled circles), **15** (filled stars), **16** (open circles), **17** (open squares), and **18** (open stars). The inset shows the transparency of these films in the visible and infrared wavelength region.

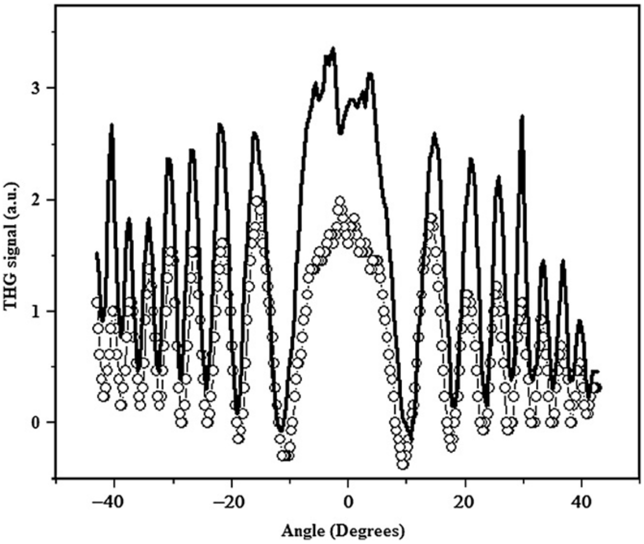


Figure 4. THG Maker-fringe patterns for 144-nm thin polymer film doped with 30 wt % of compound **16** (solid line) and for a 1-mm thick substrate without a film deposited on it (open circles). The fundamental wavelength is 1200 nm.

Table 1
$\chi^{(3)}$ values for dendrimers **13–18**

Sample (30 wt % into PS)	(10^{-12} esu)[a]
13	0.55
14	0.50
15	—
16	2.6
17	2.3
18	1.9

Fundamental wavelength: 1200 nm.
[a] $\chi^{(3)}$ for fused silica=3.1×10^{-14} esu.

dots, $\chi^{(3)}$ of the order of 10^{-9} esu was obtained by Z-scan technique with a picosecond laser system.[16]

Because of the above reasons it is difficult to compare the $\chi^{(3)}$ absolute values obtained in the present work employing the THG Maker-fringe technique for solid dendrimers-containing polymer films with others reported in the literature. However, the results obtained in the present study for the two series of resorcinarene dendrimers (Table 1) clearly show a great improvement in $\chi^{(3)}$ values when adding the phenyl and ferrocenyl-ended dendrimers with the ethylphenyl resorcinarene cores **13** and **16**, respectively, showed for the series of ferrocenyl ended dendrimers in comparison with phenyl ended ones. In addition, for both series studied, the best $\chi^{(3)}$ values inside each series this were obtained for the dendrimers with the ethylphenyl resorcinarene cores (**13** and **16**, respectively). This could be due the presence of four more phenyl group in these dendrimers.

3. Conclusions

The first generation of resorcinarene dendrimers with phenyl and ferrocenyl-ended groups joined by vinyl moieties was synthesized by convergent building method with good yields. All dendrons showed trans configuration, and this was preserved in the dendrimers, as well as the cone conformation of the resorcinarene core as it was observed by ^{1}H NMR spectroscopy. The chemical structure and purity of the synthesized dendrimers have been confirmed by ^{1}H and ^{13}C NMR, FAB+, MALDI-TOF and electrospray mass spectra, and elemental analysis. The $\chi^{(3)}$ values estimated from the THG Maker-fringe technique for our synthesized molecules are of the order of 0.5×10^{-12} esu for the phenyl ended resorcinarene dendrimers and this nonlinearity is increased in about a factor of five when the phenyl group is substituted by a ferrocenyl group.

4. Experimental section

4.1. Materials and equipments

Solvents and reagents were purchased as reagent grade and used without further purification. Acetone was distilled over calcium chloride. Tetrahydrofuran was distilled from sodium and benzophenone. Column chromatography was performed on Merck silica gel 60 Å (70–230 mesh). ^{1}H and ^{13}C NMR were recorded on a Varian-Unity-300 MHz with tetramethylsilane (TMS) as an internal reference. Infrared (IR) spectra were measured on a spectrophotometer Nicolet FT-SSX. Elemental analysis was determined by Galbraith Laboratories, INC Knoxville. FAB+ mass spectra were taken on a JEOL JMS AX505 HA instrument. Electrospray mass spectra were taken on a Bruker Daltonic, Esquire 6000. MALDI-TOF mass spectra were taken on a Bruker Omni FLEX. The nonlinear optical measurements were performed in solid state (solid films) using the guest (molecule)–host (polymer) approach. Mixtures of polystyrene (PS) and dendrimer 70:30 wt % ratio, respectively, were dissolved in dichloromethane. The solid films were deposited on fused silica substrates (1 mm-thick) by using the spin coating technique. The prepared films had typical thickness between 100 and 500 nm with good optical quality. Absorption spectra of spin-coated films were obtained with a spectrophotometer (Perkin–Elmer Lambda 900). Sample thickness was measured by using a Dektak 6M profiler.

4.2. Synthesis of dendrons

A mixture of **1** or **2** (3.8 mmol), **3** (1.89 mol), Pd(OAc)$_2$ (1.3 mmol), and tri-*o*-tolylphosphine POT (3.28 mmol) in Et$_3$N/DMF 1:5 (120 mL) was stirred under N$_2$ at 120 °C for 24 h. After cooling, the resulting mixture was filtered and the solvents evaporated. The crude product was purified by column chromatography (SiO$_2$, hexane).

4.2.1. (E)-3,5-Distyrylbenzaldehyde **4**

Yield 5.4 g (60%), white powder, mp 125–127 °C, UV CH$_2$Cl$_2$ (nm): 242, 311. IR (KBr, cm^{-1}): 3443, 3025, 2809, 2738, 1695 (C═O), 1590, 1449, 1143, 966, 884, 743, 694, 528. ^{1}H NMR (300 MHz, CDCl$_3$) δ_H (ppm): 7.13 (d, 2H, CH═, J=16.5 Hz), 7.23 (d, 2H, CH═, J=16.5 Hz), 7.27–7.45 (m, 4H, Ar), 7.35 (t, 2H, Ar, J=1.6 Hz), 7.54–7.60 (m, 4H, Ar), 7.87 (t, 2H, Ar, J=2.0 Hz), 7.92 (s, 1H, Ar), 10.09

(s, 1H, HC═O). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm): 126.2 (CH═), 126.7 (Ar), 127.0 (CH═), 128.2 (Ar), 128.8 (Ar), 130.2 (Ar), 130.7 (Ar), 136.6 (Ar_{ipso}), 137.2 (Ar_{ipso}), 138.7 (Ar), 192.2 (C═O). MS (*m/z*): 310. Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85%. Found: C, 89.10; H, 5.86%.

4.2.2. *(E)-3,5-(Divinylferrocenyl)benzaldehyde* ***5***

Yield 0.8 g (60%), red powder, mp 159–162 °C, UV $CHCl_3$ (nm): 458, 314, 248. IR (KBr, cm^{-1}): 3085, 2928, 2806, 1693, 1632, 1589, 1303, 1103, 962, 813, 487. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): 4.16 (s, 10H, C_5H_5), 4.32 (s, 4H, C_5H_4), 4.50 (s, 4H, C_5H_4), 6.75 (d, 2H, ═CH, *J*=16.2 Hz), 7.02 (d, 2H, ═CH, *J*=15.9 Hz), 7.65 (s, 2H, Ar), 7.79 (s, 1H, Ar), 10.05 (s, 1H, O═C–H). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm): 67.0 (C_5H_4), 69.2 (C_5H_5), 69.3 (C_5H_4), 82.5 (Ar_{ipso}), 124.3 (Ar), 124.6 (═CH), 128.9 (Ar), 129.1 (═CH), 137.1 (Ar_{ipso}), 139.1 (Ar_{ipso}), 192.6 (O═C–H). MS (*m/z*): 526. Anal. Calcd for $C_{31}H_{26}Fe_2O$: C, 70.72; H, 4.94; Fe, 21.29%. Found: C, 70.72; H, 4.49; Fe, 21.27%.

Lithium aluminum hydride (97%, 15.2 mmol) was dissolved in 50 mL of dry THF. To this emulsion, 6.4 mmol of **4** or **5** dissolved in 15 mL of dry THF was added dropwise using an addition funnel. The reaction was carried at 0 °C for 4 h. After this time, 10 mL of water was added and the reaction mixture was filtered in Celite®. The solvent was evaporated and the residue was dissolved in dichloromethane. The resulting solution was dried with sodium sulfate, filtered and the product was vacuum dried, and purified by column chromatography (Al_2O_3, hexane).

4.2.3. *(E)-3,5-(Distyrylphenyl)methanol* ***6***

Yield 1.8 g (90%), white powder, mp 130–132 °C, UV CH_2Cl_2 (nm): 241, 302. IR (KBr, cm^{-1}): 3370, 3025, 2883, 1595, 1493, 1449, 1029, 961, 750, 693. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): 4.75 (s, 2H, CH_2), 5.18 (s, 1H, OH), 7.15 (s, 2H, CH═), 7.16 (s, 2H, CH═), 7.23–7.44 (m, 10H, Ar), 7.51 (d, 2H, Ar, *J*=1.5 Hz), 7.55 (t, 1H, Ar, *J*=1.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm): 65.2 (CH_2–OH), 124.0 (Ar), 124.2 (Ar), 126.5 (Ar), 127.7 (CH═), 128.1 (CH═), 128.7 (Ar), 129.2 (Ar), 137.1 (Ar_{ipso}), 138.0 (Ar_{ipso}), 141.6 (Ar). MS (*m/z*): 312. Anal. Calcd for $C_{23}H_{20}O$: C, 88.46; H, 6.41%. Found: C, 88.49; H, 6.38%.

4.2.4. *(E)-3,5-((Divinylferrocenyl)phenyl)methanol* ***7***

Yield 3.3 g (99%), red powder, mp 173–175 °C, UV $CHCl_3$ (nm): 455, 312, 265, 243. IR (KBr, cm^{-1}): 3329, 2926, 1592, 1451, 1169, 1136, 808, 718, 690. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): 2.49 (s, 1H, –OH), 4.17 (s, 10H, C_5H_5), 4.32 (s, 4H, C_5H_4), 4.51 (s, 4H, C_5H_4), 4.73 (s, 2H, C–OH), 6.69 (d, 2H, ═CH, *J*=15.5 Hz), 6.93 (d, 2H, ═CH, *J*=15.4 Hz), 7.33 (s, 2H, Ar), 7.42 (s, 1H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm): 65.4 (C–OH), 67.0 (C_5H_5), 69.3 (C_5H_4), 69.5 (C_5H_4), 83.1 (Ar_{ipso}), 122.7 (Ar), 125.4 (═CH), 125.9 (Ar), 127.5 (═CH), 132.9 (Ar_{ipso}), 143.6 (Ar_{ipso}). MS (*m/z*): 528. Anal. Calcd for $C_{31}H_{28}Fe_2O$: C, 70.45; H, 5.30; Fe, 21.21%. Found: C, 70.43; H, 5.33; Fe, 21.19%.

Compound **6** or **7** (14.0 mmol), pyridine 1 mL (14.0 mmol), and 1.45 mL (14.0 mmol) of $SOCl_2$ were dissolved in 100 mL of dry CH_2Cl_2, then this mixture was cooled to −10 °C. The reaction was carried out in nitrogen atmosphere in ice bath for 7 h. After this period, the solvent was evaporated and the resulting oil was dry supported and purified in a silica gel (60–240 pore size) column using a mixture of hexane/dichloromethane (2:1) as eluent.

4.2.5. *(E)-1-(Chloromethyl)-3,5-distyrylbenzene* ***8***

Yield 4.1 g (95%), yellow-brown powder, mp 106–108 °C, UV $CHCl_3$ (nm): 242, 302. IR (KBr, cm^{-1}): 3026, 2924, 2953, 1596, 1493, 1450, 1261, 1155, 960, 750, 691. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): 4.63 (s, 2H, CH_2–Cl), 7.13 (d, 2H, CH═, *J*=16.4 Hz), 7.15 (d, 2H, CH═, *J*=16.6 Hz), 7.23–7.52 (m, 10H, Ar), 7.55 (t, 2H, Ar, *J*=2.5 Hz), 7.58 (t, 1H, Ar *J*=1.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm): 46.1 (CH_2–Cl), 124.7 (Ar), 125.6 (Ar), 126.5 (Ar), 127.8 (CH═), 129.6 (Ar), 136.9 (Ar_{ipso}), 138.1 (Ar_{ipso}), 138.2 (Ar). MS (*m/z*): 330. Anal. Calcd for $C_{23}H_{19}Cl$: C, 83.50; H, 5.79%. Found: C, 83.56; H, 5.78%.

4.2.6. *(E)-1-(Chloromethyl)-3,5-divinyl-diferrocenylbenzene* ***9***

Yield 2.9 g (39%) as a red powder, $T_{decomp.}$ 178–190 °C, UV $CHCl_3$ (nm): 447, 312, 272, 242. IR (KBr, cm^{-1}): 3360, 3059, 3010, 2925, 1707, 1567, 1448, 1216, 1167, 1106, 1138, 810, 757. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H (ppm): 4.17 (s, 10H, C_5H_5), 4.32 (s, 4H, C_5H_4), 4.59 (s, 4H, C_5H_4), 4.61 (s, 2H, CH_2–Cl), 6.69 (d, 2H, ═CH, *J*=15.5 Hz), 6.93 (d, 2H, ═CH, *J*=15.4 Hz), 7.33 (s, 2H, Ar), 7.42 (s, 1H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm): 46.2 (H_2C–Cl), 66.8 (C_5H_5), 69.1 (C_5H_4), 69.2 (C_5H_4), 83.1 (Ar_{ipso}), 122.7 (Ar), 125.27 (═CH), 125.5 (Ar), 127.7 (═CH), 132.8 (Ar_{ipso}), 143.3 (Ar_{ipso}). MS (*m/z*): 547. Anal. Calcd for $C_{31}H_{27}ClFe_2$: C, 68.13; H, 4.94; Fe, 20.51%. Found: C, 68.13; H, 4.94; Fe, 20.48%.

The resorcinarenes were obtained in agreement with reference.[8]

4.3. *Synthesis of dendrimers*

A mixture of 1 mmol of the respective dendron **8** or **9**, potassium carbonate (21.2 mmol), and 18-crown-6 (0.56 g, 2.12 mmol) in dry acetone (80 mL) was heated to reflux and stirred vigorously in nitrogen atmosphere for 20 min. The compounds **10–12** (0.0125 mmol) dissolved in dry acetone (40 mL) were added dropwise and the reaction was continued for 7 days. The mixture was allowed to cool and the precipitate was filtered. The filtrate was evaporated to dryness under reduced pressure. The residue dissolved in diethyl ether was washed with an aqueous solution of 5% Na_2CO_3 (three times). The organic layer was dried and evaporated to dryness and the dendrimers were purified using the following procedure: the dendrimer was dissolved in CH_2Cl_2, then methanol was added producing the precipitation of the dendrimer back. This procedure was repeated three times.

4.3.1. Dendrimer **13**

Yield 0.40 g (91%), brown-red powder, mp >300 °C, UV–vis CH_2Cl_2 (nm): 241.5, 301.5. IR (KBr, cm^{-1}): 3429, 3025, 2925, 2861, 1943, 1798, 1597, 1494, 1452, 1376, 1294, 1180, 1105, 959, 749, 692, 534. ^1H NMR (300 MHz, $CDCl_3$) δ_H (ppm): 2.38 (br, 8H, CH_2), 2.77 (br, 8H, CH_2), 4.75 (m, 16H, CH_2–O), 4.78 (t, 4H, CH, *J*=7.0 Hz), 6.64 (s, 4H, Ar), 6.79 (d, 16H, CH=, *J*=16.2 Hz), 6.89 (d, 16H, CH=, *J*=16.2 Hz), 6.99 (s, 4H, Ar), 7.14–7.52 (m, 124H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm): 35.0 (CH), 36.3 (CH_2), 37.1 (CH_2), 70.0 (CH_2–O), 70.8 (CH_2–O), 123.5 (Ar), 124.7 (Ar), 125.3 (Ar), 126.5 (CH=), 127.0 (Ar), 127.5 (Ar), 128.1 (Ar), 128.2 (Ar), 128.6 (Ar), 128.8 (Ar), 129.2 (Ar), 137.0 (Ar_{ipso}), 137.4 (Ar_{ipso}), 137.9 (Ar), 142.5 (Ar_{ipso}), 155.2 (Ar–O). Electrospray (*m*/*z*): 3260. Anal. Calcd for $C_{244}H_{200}O_8$: C, 89.89; H, 6.18%. Found: C, 89.90; H, 6.17%.

4.3.2. Dendrimer **14**

Yield 0.60 g (91%), brown powder, mp >300 °C, UV–vis CH_2Cl_2 (nm): 242.5, 302, 391. IR (KBr, cm^{-1}): 3430, 3026, 2924, 2853, 1780, 1703, 1596, 1494, 1456, 1173, 1107, 961, 750, 694. ^1H NMR (300 MHz, $CDCl_3$) δ_H (ppm): 0.68 (t, 12H, CH_3, *J*=4.5 Hz), 1.23 (br, 16H, CH_2), 2.02 (br, 16H, CH_2), 4.63–4.87 (m, 16H, CH_2–O), 4.93 (m, 4H, CH), 6.65 (s, 4H, Ar), 6.80 (d, 16H, CH=, *J*=16.2 Hz), 6.89 (d, 16H, CH=, *J*=16.1 Hz), 6.96 (s, 4H, Ar), 7.15–7.5 (br, 104H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm): 14.0 (CH_3), 22.7 (CH_2), 32.3 (CH_2), 34.6 (CH), 69.9 (CH_2–O), 123.5 (Ar), 124.0 (Ar), 124.7 (Ar), 126.5 (Ar), 127.5 (CH=), 128.2 (Ar), 128.5 (Ar), 137.1 (Ar_{ipso}), 137.4 (Ar_{ipso}), 138.0 (Ar_{ipso}), 155.1 (Ar–O). Electrospray (*m*/*z*): 3121. Anal. Calcd for $C_{232}H_{208}O_8$: C, 89.19; H, 6.71%. Found: C, 89.20; H, 6.71%.

4.3.3. Dendrimer **15**

Yield 0.36 g (85%), brown powder, mp >300 °C, UV–vis CH_2Cl_2 (nm): 242.5, 301.5. IR (KBr, cm^{-1}): 3446, 3055, 3025, 2860, 1623, 1596, 1495, 1453, 1400, 1279, 1180, 1110, 1020, 959, 832, 749, 692. ^1H NMR (300 MHz, $CDCl_3$) δ_H (ppm): 0.87 (br, 12H, CH_3), 1.23 (br, 56H, CH_2), 1.68 (s, 8H, CH_2), 2.07 (m, 16H, CH_2), 4.76–5.25 (m, 16H, CH_2–O), 4.72 (s, 4H, CH), 6.42 (br, 4H, Ar), 7.05 (d, 16H, CH=, *J*=16.2 Hz), 7.13 (br, 4H, Ar), 7.14 (d, 16H, CH=, *J*=16.5 Hz), 7.27–7.61 (m, 104H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm): 14.0 (CH_3), 22.6 (CH_2), 29.3 (CH_2), 29.7 (CH_2), 31.9 (CH), 70.0 (CH_2–O), 112.0 (Ar), 118.0 (Ar), 124.3 (Ar), 126.5 (CH=), 127.5 (Ar), 127.7 (Ar), 128.0 (Ar), 128.6 (Ar), 130.2 (Ar), 136.8 (Ar_{ipso}), 137.1 (Ar_{ipso}), 138.1 (Ar), 138.8 (Ar_{ipso}), 155.3 (Ar–O). Electrospray (*m*/*z*): 3458. Anal. Calcd for $C_{256}H_{256}O_8$: C, 88.85; H, 7.46. Found: C, 88.85; H, 7.44%.

4.3.4. Dendrimer **16**

Yield 0.33 g (92%), brown powder, mp >300 °C, UV $CHCl_3$ (nm): 454, 311, 233. IR (KBr, cm^{-1}): 3368, 3090, 3025, 2894, 1702, 1631, 1591, 1497, 1452, 1408, 1351, 1284, 1246, 1185, 1107, 1048, 1000, 959, 830, 756, 696, 488. ^1H NMR (300 MHz, $CDCl_3$) δ_H (ppm): 2.47 (br, 8H, CH_2), 2.6 (br, 8H, CH_2), 4.13 (br, 16H, CH_2–O–), 4.14 (s, 80H, C_5H_5), 4.47 (s, 32H, C_5H_4), 4.47 (s, 32H, C_5H_4), 4.68 (br, 4H, CH), 6.56 (s, 4H, Ar), 6.68 (d, 8H, =CH, *J*=15.9 Hz), 6.71 (d, 8H, =CH, *J*=15.9 Hz), 6.85 (s, 4H, Ar), 6.91 (d, 8H, =CH, *J*=16.2 Hz), 7.30 (br, 36H, Ar), 7.46 (br, 8H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm): 29.1 (–CH_2), 66.8 (C_5H_4), 69.1 (C_5H_5), 69.9 (O–CH_2), 83.1 (C_{ipso}), 122.5 (Ar), 124.1 (Ar), 125.6 (CH=), 127.1 (CH=), 127.3 (Ar), 128.8 (Ar_{ipso}), 138.3 (Ar_{ipso}), 141.6 (Ar_{ipso}). Electrospray (*m*/*z*): 4984. Anal. Calcd for $C_{308}H_{246}Fe_{16}O_8$: C, 74.15; H, 5.29; Fe, 17.97%. Found: C, 74.16; H, 5.27; Fe, 17.99%.

4.3.5. Dendrimer **17**

Yield 0.50 g (78%), brown powder, mp >300 °C, UV $CHCl_3$ (nm): 449, 311, 246. IR (KBr, cm^{-1}): 3358, 3094, 3010, 2924, 2858, 1707, 1633, 1593, 1499, 1468, 1454, 1410, 1376, 1351, 1285, 1248, 1218, 1173, 1108, 1043, 1026, 1001, 961, 931, 835, 819, 754. ^1H NMR (300 MHz, $CDCl_3$) δ_H (ppm): 0.87 (br, 12H, CH_3), 1.25 (br, 32H, CH_2), 4.14 (br, 80H, C_5H_5, 16H, CH_2–O), 4.29 (br, 64H, C_5H_4), 4.73 (br, 4H, CH), 6.62 (br, 4H, Ar), 6.69 (d, 8H, =CH, *J*=16.5 Hz), 6.71 (d, 8H, =CH, *J*=15.9 Hz), 6.90 (d, 8H, Ar, *J*=15.6 Hz), 6.94 (d, 8H, Ar, *J*=15.6 Hz), 7.29 (br, 4H, Ar), 7.35–7.64 (br, 16H, Ar), 7.46 (br, 8H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm): 14.1 (CH_3), 22.6 (CH_2), 28.0 (CH_2), 32.1 (–CH_2), 66.9 (C_5H_4), 69.2 (C_5H_5), 70.0 (O–CH_2), 83.2 (Fc_{ipso}), 122.5 (Ar), 124.1 (Ar), 125.7 (Ar), 127.4 (CH=), 127.2 (Ar), 129.3 (CH=), 131.9 (Ar_{ipso}), 138.5 (C_{ipso}), 140.5 (Ar_{ipso}). Electrospray (*m*/*z*): 4849. Anal. Calcd for $C_{296}H_{272}Fe_{16}O_8$: C, 73.25; H, 5.60; Fe, 18.47%. Found: C, 73.25; H, 5.62; Fe, 18.46%.

4.3.6. Dendrimer **18**

Yield 0.56 g (83%), brown powder, mp >300 °C, UV $CHCl_3$ (nm): 453, 311, 235. IR (KBr, cm^{-1}): 3380, 3090, 3027, 2920, 2855, 1706, 1631, 1591, 1497, 1459, 1410, 1352, 1287, 1246, 1183, 1107, 1047, 1001, 958, 819, 697, 488. ^1H NMR (300 MHz, $CDCl_3$) δ_H (ppm): 0.85 (br, 12H, CH_3), 1.22 (br, 56H, CH_2), 1.25 (br, 8H, CH_2), 2.18 (br, 8H, CH_2), 2.63 (br, 8H, CH_2), 4.10 (br, 80H, C_5H_5, 16H, O–CH_2), 4.29 (br, 32H, C_5H_4), 4.46 (br, 32H, C_5H_4), 4.74 (br, 4H, CH), 6.60 (br, 4H, Ar), 6.69 (d, 8H, =CH, *J*=16.2 Hz), 6.73 (d, 8H, =CH, *J*=15.9 Hz), 6.87 (d, 8H, Ar, *J*=15.6 Hz), 6.91 (d, 8H, =CH, *J*=15.9 Hz), 7.09 (br, 4H, Ar), 7.33 (br, 16H, Ar), 7.38 (br, 8H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C (ppm): 14.1 (CH_3), 22.6 (CH_2), 29.7 (CH_2), 31.9 (CH_2), 66.8 (C_5H_4), 69.2 (C_5H_5), 70.0 (O–CH_2), 83.1 (Fc_{ipso}), 122.5 (Ar), 122.8 (Ar), 125.6 (Ar), 127.0 (Ar), 127.4 (C=), 131.3 (C=), 131.9 (Ar_{ipso}), 138.5 (Ar_{ipso}), 145.5 (Ar_{ipso}). Electrospray (*m*/*z*): 5185. Anal. Calcd for $C_{320}H_{320}Fe_{16}O_8$: C, 74.05; H, 6.17; Fe, 17.28%. Found: C, 74.03; H, 6.19; Fe, 17.30%.

4.4. THG Maker-fringe measurements

The nonlinear optical behavior of the synthesized dendrimers was studied in solid state (solid films) using the guest (molecule)–host (polymer) approach. Ratios of 70:30 wt % of polystyrene (PS) and the dendrimers were dissolved in chloroform.

The solid films were deposited on fused silica substrates (1 mm-thick) by using the spin coating technique. The prepared films had thickness between 140 nm and 1.6 μm with good optical quality showing negligible light scattering at visible and NIR wavelengths. Absorption spectra of spin-coated films were obtained with a spectrophotometer (Perkin–Elmer Lambda 900). Sample thickness was measured by using a Dektak 6M profiler.

THG Maker-fringes setup is reported elsewhere.[20,21] Briefly, it consisted of a Nd-YAG laser-pumped optical parametric oscillator (OPO) that delivered pulses of 8 ns at a repetition rate of 10 Hz. A fundamental wavelength of 1200 nm (idler beam) was used. The output of the OPO system was focused into the films with a 30-cm focal length lens to form a spot with a radius of approximately 150 μm. Typical energies in our measurements were set at 1 mJ per pulse at sample position (corresponding to peak intensities of ~0.18 GW/cm^2). The third-harmonic beam, as a bulk effect, emerging from the films was separated from the pump beam by using a color filter and detected with a PMT and a lock-in amplifier. The THG measurements were performed for incident angles in the range from −40° to 40° with steps of 0.270°. The entire experiment was computer-controlled.

In the Maker-fringes technique, the third-harmonic peak intensity $I^{3\omega}$ from the substrate–film structure is compared to one produced from the substrate alone. Then, the nonlinear susceptibility $\chi^{(3)}$ in a film of thickness L_f is determined from:[22]

$$\chi^{(3)} = \chi_s^{(3)} \frac{2}{\pi}\left(\frac{L_{c,s}}{L_f}\right)\left(\frac{I_f^{3\omega}}{I_s^{3\omega}}\right)^{1/2} \qquad (1)$$

where $\chi_s^{(3)}$ and $L_{c,s}$ are the nonlinear susceptibility and coherence length, respectively, for the substrate at the fundamental wavelength. In our calculation we considered $\chi_s^{(3)} = 3.1 \times 10^{-14}$ esu and $L_{c,s}$=9 μm for the fused silica substrate.[20,21] In any case, our samples satisfied the condition $L_f \ll L_{c,s}$ in which the Eq. 1 is valid.

Acknowledgements

This work was supported by the DGAPA (IN209106). We would also like to thank Nieves Z.S.M., Rios O.H., Velasco L., Huerta S.E., Patiño M.M.R., and Peña Gonzalez M.A., for technical assistance.

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