

Synthesis and characterization of dendrons and dendrimers skeleton-constructed with azobenzene moiety

Wenquan Zhang, Jianda Xie, Wenfang Shi *

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, PR China

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Abstract

A series of dendrons and dendrimers skeleton-constructed with azobenzene moiety based upon 4-carboxy-4'-(1,2-prop-enediolether)-azobenzene as an AB₂ monomer, via a convergent approach, proceeding in a repeated stepwise growth manner starting from 4-carboxy-4'-(*n*-butylether)-azobenzene as a peripheral monomer, were synthesized, and characterized by NMR, FTIR, and MALDI-TOF-MS analysis. Their regular molecular architecture and thus monodispersed molecular weights were confirmed by GPC. The UV–Vis absorbance and ¹H NMR spectrum study indicated that the azobenzene moieties in CHCl₃ solution took fully *trans*–*cis* isomerization under UV irradiation, and reversely isomerization back to the *trans* by visible light irradiation or by heat.

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1. Introduction

In the past two decades, a new family of polymers with three dimensional molecular architecture and possessing starburst topology has been attracting increasing interest in many fields. The design for novel dendritic polymers with different structure is of considerable significance for various applications [1–5]. To an increasing extent, incorporating functional groups which are sensitive to some specific external stimuli, such as pH [6–9], enzyme [10,11], irradiation [12–15], or temperature [16,17], into the

skeletons of dendrimers will lead to particular applications. Dozens of dendrimers with stimuli-responsive moieties have been designed, where azobenzene is one of the candidates.

Azobenzene group usually undergoes readily induced *trans*–*cis* isomerization under UV light irradiation, leading to large structural change as reflected in the dipole moment, and change in geometry [18]. The reverse isomerization can be realized either thermally or upon irradiation with visible light. The dendrimers with azobenzene moieties in exteriors [19–26] or at cores [27–33] had been developed for “dendritic boxes”, self-assemble, encapsulation, light harvesting, holographic, and nonlinear optical materials. Several dendrimers skeleton-constructed with azobenzene moieties had also been

* Corresponding author. Tel.: +86 551 3606084; fax: +86 551 3606630.

E-mail address: wfshi@ustc.edu.cn (W. Shi).

synthesized and showed rather interesting properties. Yokoyama and co-workers used 4-carboxy-2-nitro-4'-[bis(2-hydroxyethyl)amino]azobenzene as a starting monomer to prepare the dendrons bearing up to 15 azobenzene moieties as branching units. The dendrons in solution existed in cone shape, and the molecular hyperpolarizability increased with increasing the generation [34,35]. Sebastián and co-workers synthesized phosphorus-containing dendrimers bearing azobenzene groups. The influence of the location and crowding of azobenzene chromophores on the photochemical behavior was investigated [36]. McGrath et al. developed benzyl aryl ether dendrimers containing six photochromic azobenzene groups in a single generational shell. Their hydrodynamic volumes were significantly modulated under irradiation [37]. Wang and co-workers synthesized the (benzyl ester) dendrimers containing azobenzene groups in order to obtain "intelligent" polymers with alterable shapes and sizes [38].

Incorporating of azobenzene moieties into the skeletons of dendrimers has been demonstrated to provide interesting properties and possible applications, as well as the contribution to theoretical study on the conformational information of dendrimers using the drastic changes in photochemical and photophysical properties between two isomers of azobenzene. Therefore, design and synthesis of new dendrimers constructed with azobenzene moieties are pursued to fully understand the structure–property correlation and to develop new-style materials. In this paper, the convergent synthesis of up to fourth generation dendrons, and first and second generation dendrimers constructed with azobenzene moieties is described in detail. Their molecular structures were characterized by NMR, FTIR, GPC and MALDI-TOF-MS analysis. The thermal and light responsive properties of the polymers were also investigated.

2. Experimental details

2.1. General

The NMR spectra were recorded on a Bruker 300 MHz spectrometer using appropriate solvents. The elemental analysis was carried out on a the Elementar Vario EL-III instrument. The FTIR spectra were recorded with a Nicolet MAGNA-IR 750 spectrometer (Nicolet Instrument Corp., USA). The Nujol Mull technique was utilized to prepare

the samples. The molecular weights were determined by a Waters gel permeation chromatography (GPC) system equipped with a refractive index detector, using THF as an eluent (elution rate: 1 ml/min). The MALDI-TOF-MS spectra were recorded on a Bruker Daltonics BIFLEX™ III time-of-flight mass spectrometer equipped with a nitrogen laser (337 nm) using DHB as a matrix and NaI as a cationization agent. The differential scanning calorimetry (DSC) was carried out with a Shimadzu DSC-60 equipment. All the samples were heated at 10 °C/min from 20 to 140 °C under nitrogen for the first scan, then cooled to 20 °C at 10 °C/min, and immediately heated at 10 °C/min from 20 to 170 °C for the second scan. The UV–Vis spectra were measured on a Shimadzu UV-2401pc ultraviolet–visible spectrometer in CHCl₃ solution. The excitation light of Shimadzu Fluorescence Spectroscopy RF-5301PC was tuned to the appropriate wavelength in order to investigate the light-responsive properties of samples.

4-Aminobenzoic acid, 3-chloro-1,2-propanediol and 2-methoxyethoxymethyl (MEM) chloride were purchased from Aldrich. Thionyl chloride was distilled before use. All other reagents and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd., and used as received.

2.2. Synthesis

2.2.1. 4-Carboxy-4'-hydroxy-azobenzene (CHA)

The synthesis of CHA was performed according to the previous literature [39]. 4-Aminobenzoic acid (21.12 g (0.154 mol)) was first dissolved in 300 ml of sodium hydroxide (6.16 g, 0.154 mol) aqueous solution with 11.2 g (0.162 mol) sodium nitrite, and then slowly added into 250 ml of hydrochloric acid solution (5 mol L⁻¹) previously added 2.12 g (0.031 mol) sodium nitrite at 5–10 °C. The reactants were continuously stirred for 30 min. Then urea (2 g, 0.033 mol) was added to react with excessive sodium nitrite at 0 °C. The obtained diazonium solution was slowly added into an alkaline solution of phenol (14.50 g, 0.154 mol) with pH 7–8 adjusted by a sodium hydroxide solution at 5–10 °C, and stirred for 30–40 min. Then the pH value was adjusted to around 3 using hydrochloric acid solution, leading to the snuffcolored precipitate formed. This precipitate (CHA) was filtered, washed with distilled water, and finally dried (35.4 g, yield 95%).

¹H NMR (300 MHz, DMSO-*d*₆): δ = 7.00 (d, Ar–H, 2H, *ortho* to OH), 7.89 (t, Ar–H, 4H, *ortho*

to N), 8.11 (d, Ar–H, 2H, *ortho* to –COOH), 10.49 (–OH).

^{13}C NMR (75 MHz, DMSO- d_6): δ = 116.01 (*o*-ArC to OH), 122.03 (*m*-ArC to OH), 125.26 (*m*-ArC to –COOH), 130.41 (*o*-ArC to –COOH), 131.69 (ArC next to –COOH), 145.30 (*p*-ArC to OH), 154.58 (*p*-ArC to –COOH), 156.62 (ArC next to –OH), 166.67 (ArCOOH).

Anal. Calc. for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_3$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.65; H, 4.18; N, 11.37%.

2.2.2. 4-Carboxy-4'-(*n*-butylether)-azobenzene (CBA)

CHA (15.0 g (0.062 mol)) was dissolved in 22.0 g (0.161 mol) *n*-butyl bromide solution with 150 g cyclohexanone and 50 g K_2CO_3 as a catalyst under stirring, and reacted under nitrogen atmosphere at 80 °C for 4 h, and at 120 °C for 4 h. Then K_2CO_3 was removed by filtration and the solvent was evaporated under vacuum. The dark red ceraceous intermediate product, 4-(*n*-butylcarboxylate)-4'-(*n*-butylether)-azobenzene (BBA), was obtained after recrystallization from acetone. BBA was further hydrolyzed by KOH solution in methanol, and carefully washed with acetone, yielding a yellow powder, named CBA (12.4 g, yield 67%) as a peripheral monomer.

^1H NMR (300 MHz, DMSO- d_6): δ = 0.95 (t, –CH₃, 3H), 1.46 (m, –CH₂CH₃, 2H), 1.75 (m, –CH₂CH₂CH₃, 2H), 4.10 (t, –CH₂CH₂CH₂CH₃, 2H), 7.15 (d, Ar–H, 2H, *ortho* to O), 7.91 (m, Ar–H, 4H, *ortho* to N), 8.10 (d, Ar–H, 2H, *ortho* to –COOH).

^{13}C NMR (75 MHz, DMSO- d_6): δ = 13.66 (–CH₃), 18.68 (–CH₂CH₃), 30.62 (–CH₂CH₂CH₃), 67.81 (–OCH₂CH₂CH₂CH₃), 115.15 (*o*-ArC to –OCH₂CH₂CH₂CH₃), 122.22 (*m*-ArC to –OCH₂CH₂CH₂CH₃), 125.02 (*m*-ArC to –COOH), 130.58 (*o*-ArC to –COOH), 132.05 (ArC next to –COOH), 146.13 (*p*-ArC to –OCH₂CH₂CH₂CH₃), 154.52 (*p*-ArC to –COOH), 162.11 (ArC next to –OCH₂CH₂CH₂CH₃), 166.66 (ArCOOH).

Anal. Calc. for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3$: C, 68.44; H, 6.08; N, 9.39. Found: C, 68.18; H, 6.04; N, 9.28%.

2.2.3. 4-Carboxy-4'-(1,2-propanediolether)-azobenzene (CPA)

15.0 g (0.062 mol) CHA was dissolved in 17.0 g (0.154 mol) 3-chloro-1,2-propanediol solution in 150 g cyclohexanone with 50 g K_2CO_3 and 0.5 g potassium iodide as catalysts, reacted under nitrogen atmosphere at 80 °C for 4 h, and then at

120 °C for 4 h with stirring. After cyclohexanone was removed by filtration, the resultant product was hydrolyzed for 10 h by adding 200 ml of water. The pH value was carefully adjusted to about 3 using a hydrochloric acid solution. Finally, a salmon pink product, named CPA as AB₂ monomer, was collected by filtration and recrystallized from dioxane (14.4 g, Yield 73%).

^1H NMR (300 MHz, DMSO- d_6 , ppm): δ = 3.48 (d, –O–CH₂–CH(OH)–CH₂–OH, 2H), 3.84 (m, –O–CH₂–CH(OH)–CH₂–OH, 1H), 4.02 and 4.14 (m, –O–CH₂–CH(OH)–CH₂–OH, 2H), 7.16 (d, Ar–H, 2H, *ortho* to O), 7.93 (m, Ar–H, 4H, *ortho* to N), 8.12 (d, Ar–H, 2H, *ortho* to –COOH).

^{13}C NMR (75 MHz, DMSO- d_6): δ = 62.51 (–O–CH₂–CH(OH)–CH₂–OH), 69.79 (–O–CH₂–CH(OH)–CH₂–OH), 70.16 (–O–CH₂–CH(OH)–CH₂–OH), 115.25 (*o*-ArC to O), 122.24 (*m*-ArC to O), 125.03 (*m*-ArC to –COOH), 130.60 (*o*-ArC to –COOH), 132.15 (ArC next to –COOH), 146.20 (*p*-ArC to O), 154.52 (*p*-ArC to –COOH), 162.23 (ArC next to O), 166.72 (ArCOOH).

Anal. Calc. for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_5$: C, 60.75; H, 5.10; N, 8.86. Found: C, 61.13; H, 5.12; N, 8.61%.

2.2.4. CPA-MEM

CPA (10.0 g (0.0316 mol)) was reacted with 2-methoxyethoxymethyl (MEM) chloride (3.94 g, 0.0316 mol) in the presence of triethylamine (4.78 g, 0.0474 mol) in 100 ml of THF for 4 h at 0 °C under stirring. The formed white salt was removed by filtration. The filtrate solution was concentrated under reduced pressure until the total bulk of about 50 ml reached, then poured into 500 ml of water, and extracted out by adding 200 ml of CHCl_3 . The CHCl_3 solution was washed with water (3 × 500 ml), dried over Na_2SO_4 and evaporated under reduced pressure, yielding an orange powder, named CPA-MEM (yield 92%) as a protected AB₂ monomer.

^1H NMR (300 MHz, DMSO- d_6 , ppm): δ = 3.24 (s, –CH₃, 3H), 3.47–3.52 (m, –O–CH₂–CH(OH)–CH₂–OH and –CH₂OCH₃, 4H), 3.82–3.85 (m, –O–CH₂–CH(OH)–CH₂–OH and –CH₂CH₂OCH₃, 3H), 4.01 and 4.14 (m, –O–CH₂–CH(OH)–CH₂–OH, 2H), 7.16 (d, Ar–H, 2H, *ortho* to O), 7.93 (m, Ar–H, 4H, *ortho* to N), 8.17 (d, Ar–H, 2H, *ortho* to –COOH).

^{13}C NMR (75 MHz, DMSO- d_6): δ = 58.07 (–CH₃), 62.48 (–O–CH₂–CH(OH)–CH₂–OH), 69.14 (–CH₂CH₂OCH₃), 69.77 (–O–CH₂–CH(OH)–CH₂–OH), 70.15 (–O–CH₂–CH(OH)–CH₂–OH), 70.98

($-\text{CH}_2\text{OCH}_3$), 89.92 (ArCOOCH₂), 115.23 (*o*-ArC to O), 122.21 (*m*-ArC to O), 125.00 (*m*-ArC to $-\text{COO}$), 130.58 (*o*-ArC to $-\text{COO}$), 130.73 (ArC next to $-\text{COO}$), 146.19 (*p*-ArC to O), 154.50 (*p*-ArC to $-\text{COO}$), 162.21 (ArC next to O), 164.74 (ArCOO).

Anal. Calc. for C₂₀H₂₄N₂O₇: C, 59.40; H, 5.98; N, 6.93. Found: C, 59.22; H, 5.86; N, 6.99%.

2.2.5. Dendron G-1-COOH

CBA (8.34 g (0.028 mol)) was dissolved in 50 ml of CH₂Cl₂, followed by the addition of SOCl₂ (9.0 g, 0.075 mol) dropwise under stirring. The reaction was carried out for 4 h at room temperature, and at 40 °C for another 4 h under reflux condition till the reactant became a clear homogeneous solution. Then CH₂Cl₂ and SOCl₂ were evaporated under vacuum carefully. The resulted red CBA acyl chloride was dissolved in 50 ml of CH₂Cl₂.

CPA-MEM (5.66 g (0.014 mol)) was dissolved in 60 ml of pyridine in the presence of 4-dimethylaminopyridine (DMAP) (0.05 g) at 50 °C. Then the above prepared CBA acyl chloride solution was added dropwise into CPA-MEM solution, and stirred for 8 h. After CH₂Cl₂ was removed by distillation, the reaction was continuously carried out for 8 h at 80 °C. The reaction solution was poured into 200 ml of water after the removal of the formed white pyridine salt by filtration, and extracted out by adding 100 ml of CHCl₃, then washed with water (3 × 200 ml), dried over Na₂SO₄ and concentrated under reduced pressure. MEM segment was subsequently removed from CPA-MEM in a 2–5% hydrochloric acid/THF solution at below 5 °C. The reaction mixture was then poured into water (200 ml), yielding a yellowish precipitate. The filtrated product was further purified by column chromatography (silica gel, CHCl₃ and EtOAc/petroleum ether (2:1) as eluents in turn), to obtain the first generation of dendron G-1-COOH (10.08 g, Yield: 81%).

¹H NMR (300 MHz, CDCl₃): δ = 1.00 (t, $-\text{CH}_3$, 6H), 1.54 (m, $-\text{CH}_2\text{CH}_3$, 4H), 1.82 (m, $-\text{CH}_2-\text{CH}_2\text{CH}_3$, 4H), 4.07 (t, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 4H), 4.52 (d, Ar-O-CH₂-CH(O)-CH₂-O, 2H), 4.87 (m, Ar-O-CH₂-CH(O)-CH₂-O, 2H), 5.88 (m, Ar-O-CH₂-CH(O)-CH₂-O, 1H), 7.02 (d, Ar-H, 4H, *ortho* to O in CBA moiety), 7.13 (d, Ar-H, 2H, *ortho* to O in CPA moiety), 7.91 (m, Ar-H, 12H, *ortho* to N), 8.18 (m, Ar-H, 6H, *ortho* to $-\text{COO}$).

¹³C NMR (75 MHz, CDCl₃): δ = 13.96 ($-\text{CH}_3$), 19.35 ($-\text{CH}_2\text{CH}_3$), 31.18 ($-\text{CH}_2\text{CH}_2\text{CH}_3$), 63.35

($-\text{O}-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2-\text{O}$), 66.75 ($-\text{O}-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2-\text{O}$), 68.28($-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 70.60 ($-\text{O}-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2\text{O}$), 114.96 (*o*-ArC to O in CBA), 115.21 (*o*-ArC to O in CPA), 122.60 (*m*-ArC to O in CBA), 122.76 (*m*-ArC to O in CPA), 125.41 (*m*-ArC to $-\text{COO}$), 130.48, 130.58, 130.88, 131.03, 131.34 (ArC next and *ortho* to $-\text{COO}$), 147.01 (*p*-ArC to $-\text{O}$ in CBA), 147.64 (*p*-ArC to O in CPA), 155.80 (*p*-ArC to $-\text{COO}$ in CPA), 155.89 (*p*-ArC to $-\text{COO}$ in CBA), 161.40 (ArC next to O in CPA), 162.59 (ArC next to O in CBA), 165.56, 165.87 (ArCOO in CBA), 166.23 (ArCOO in CPA).

Anal. Calc. for C₅₀H₄₈N₆O₉: C, 68.48; H, 5.52; N, 9.58. Found: C, 68.64; H, 5.42; N, 9.31%.

2.2.6. Dendron G-2-COOH to G-4-COOH

The second to fourth generation of dendrons, G-2-COOH G-3-COOH and G-4-COOH, were synthesized via the similar procedures as described above for G-1-COOH preparation. The reaction times were, however, further prolonged to 32 h, 54 h and 96 h, respectively. The dendrons were also purified by column chromatography using the same eluents, obtaining lower yields of about 65%, 44% and 27%, respectively.

¹H NMR (300 MHz, CDCl₃) for G-2-COOH: δ = 1.00 (t, $-\text{CH}_3$, 12H), 1.52 (m, $-\text{CH}_2\text{CH}_3$, 8H), 1.81 (m, $-\text{CH}_2\text{CH}_2\text{CH}_3$, 8H), 4.06 (t, $-\text{CH}_2-\text{CH}_2\text{CH}_2\text{CH}_3$, 8H), 4.50 (d, Ar-O-CH₂-CH(O)-CH₂-O, 6H), 4.85 (m, Ar-O-CH₂-CH(O)-CH₂-O, 6H), 5.86 (m, Ar-O-CH₂-CH(O)-CH₂-O, 3H), 6.99 (d, Ar-H, 8H, *ortho* to O in CBA moiety), 7.10 (d, Ar-H, 6H, *ortho* to O in CPA moiety), 7.91 (m, Ar-H, 28H, *ortho* to N), 8.18 (m, Ar-H, 14H, *ortho* to $-\text{COO}$).

¹³C NMR (75 MHz, CDCl₃) for G-2-COOH: δ = 13.95 ($-\text{CH}_3$), 19.34 ($-\text{CH}_2\text{CH}_3$), 31.03 ($-\text{CH}_2\text{CH}_2\text{CH}_3$), 63.37 ($-\text{O}-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2-\text{O}$), 66.74 ($-\text{O}-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2-\text{O}$), 68.27 ($-\text{OCH}_2-\text{CH}_2\text{CH}_2\text{CH}_3$), 70.58 ($-\text{O}-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2\text{O}$), 114.95 (*o*-ArC to O in CBA), 115.20 (*o*-ArC to O in CPA), 122.60 (*m*-ArC to O in CBA), 122.69 (*m*-ArC to O in CPA), 125.40 (*m*-ArC to $-\text{COO}$), 130.46, 130.58, 130.87, 131.02, 131.27 (ArC next and *ortho* to $-\text{COO}$), 147.00 (*p*-ArC to $-\text{O}$ in CBA), 147.61 (*p*-ArC to O in CPA), 155.73 (*p*-ArC to $-\text{COOH}$), 155.88 (*p*-ArC to $-\text{COO}-\text{C}$), 161.43 (ArC next to O in CPA), 162.58 (ArC next to O in CBA), 165.54, 165.81 (ArCOO-C), 166.21 (ArCOOH).

Anal. Calc. for $C_{116}H_{108}N_{14}O_{21}$: C, 68.49; H, 5.35; N, 9.64. Found: C, 68.71; H, 5.28; N, 9.50%.

1H NMR (300 MHz, $CDCl_3$) for G-3-COOH: δ = 0.99 (– CH_3 , 24H), 1.51 (– CH_2CH_3 , 16H), 1.80 (– $CH_2CH_2CH_3$, 16H), 4.04 (– $CH_2CH_2CH_2CH_3$, 16H), 4.49 (Ar–O– CH_2 –CH(O)– CH_2 –O, 14H), 4.84 (Ar–O– CH_2 –CH(O)– CH_2 –O, 14H), 5.86 (Ar–O– CH_2 –CH(O)– CH_2 –O, 7H), 6.98 (Ar–H, 16H, *ortho* to O in CBA moiety), 7.09 (Ar–H, 14H, *ortho* to O in CPA moiety), 7.90 (Ar–H, 60H, *ortho* to N), 8.17 (Ar–H, 30H, *ortho* to –COO).

^{13}C NMR (75 MHz, $CDCl_3$) for G-3-COOH: δ = 13.94 (– CH_3), 19.33 (– CH_2CH_3), 31.16 (– $CH_2CH_2CH_3$), 63.33 (–O– CH_2 –CH(O)– CH_2 –O), 66.74 (–O– CH_2 –CH(O)– CH_2 –O), 68.26 (–OCH $_2$ – $CH_2CH_2CH_3$), 70.58 (–O– CH_2 –CH(O)– CH_2 O), 114.94 (*o*-ArC to O in CBA), 115.20 (*o*-ArC to O in CPA), 122.59 (*m*-ArC to O in CBA), 122.76 (*m*-ArC to O in CPA), 125.40 (*m*-ArC to –COO), 130.46, 130.57, 130.87, 131.02, 131.28 (ArC next and *ortho* to –COO), 147.01 (*p*-ArC to –O in CBA), 147.63 (*p*-ArC to O in CPA), 155.80 (*p*-ArC to –COOH), 155.88 (*p*-ArC to –COO–C), 161.40 (ArC next to O in CPA), 162.57 (ArC next to O in CBA), 165.56, 165.86 (Ar–COO–C), 166.23 (Ar–COOH).

Anal. Calc. for $C_{248}H_{228}N_{30}O_{45}$: C, 68.50; H, 5.28; N, 9.66. Found: C, 68.60; H, 5.22; N, 9.56%.

1H NMR (300 MHz, $CDCl_3$) for G-4-COOH: δ = 0.98 (– CH_3 , 48H), 1.50 (– CH_2CH_3 , 32H), 1.79 (– $CH_2CH_2CH_3$, 32H), 4.04 (– $CH_2CH_2CH_2CH_3$, 32H), 4.47 (Ar–O– CH_2 –CH(O)– CH_2 –O, 30H), 4.84 (Ar–O– CH_2 –CH(O)– CH_2 –O, 30H), 5.85 (Ar–O– CH_2 –CH(O)– CH_2 –O, 15H), 6.98 (Ar–H, 32H, *ortho* to O in CBA moiety), 7.08 (Ar–H, 30H, *ortho* to O in CPA moiety), 7.90 (Ar–H, 124H, *ortho* to N), 8.17 (Ar–H, 62H, *ortho* to –COO).

^{13}C NMR (75 MHz, $CDCl_3$) for G-4-COOH: δ = 13.93 (– CH_3), 19.32 (– CH_2CH_3), 31.16 (– $CH_2CH_2CH_3$), 63.32 (–O– CH_2 –CH(O)– CH_2 –O), 66.74 (–O– CH_2 –CH(O)– CH_2 –O), 68.25 (–OCH $_2$ – $CH_2CH_2CH_3$), 70.57 (–O– CH_2 –CH(O)– CH_2 O), 114.94 (*o*-ArC to O in CBA), 115.19 (*o*-ArC to O in CPA), 122.58 (*m*-ArC to O in CBA), 122.76 (*m*-ArC to O in CPA), 125.40 (*m*-ArC to –COO), 130.46, 130.57, 130.87, 131.02, 131.28 (ArC next and *ortho* to –COO), 147.01 (*p*-ArC to –O in CBA), 147.62 (*p*-ArC to O in CPA), 155.80 (*p*-ArC to –COOH), 155.88 (*p*-ArC to –COO–C), 161.39 (ArC next to O in CPA), 162.57 (ArC next to O in CBA), 165.54, 165.84 (Ar–COO–C), 166.21 (Ar–COOH).

Anal. Calc. for $C_{512}H_{468}N_{62}O_{93}$: C, 68.50; H, 5.25; N, 9.67. Found: C, 68.79; H, 5.13; N, 9.72%.

2.2.7. Dendrimers G1 and G2

G1 and G2 were obtained through the reaction of G-1-COOH and G-2-COOH with trimethanol propane, respectively. The synthesis procedure was similar to that of G-1-COOH. However, the reaction times were prolonged to 36 h and 72 h, obtaining 70% and 50% yields, respectively.

1H NMR (300 MHz, $CDCl_3$) for G1: δ = 0.99 (t, – CH_3 , 18H), 1.12 (t, – CH_3 (at core), 3H), 1.25 (s, – CH_2CH_3 (at core), 2H), 1.52 (m, – CH_2CH_3 , 12H), 1.81 (m, – $CH_2CH_2CH_3$, 12H), 4.05 (t, – $CH_2CH_2CH_2CH_3$, 12H), 4.48 (d, Ar–O– CH_2 –CH(O)– CH_2 –O, 6H), 4.59 (s, C– CH_2 –O, 6H), 4.84 (m, Ar–O– CH_2 –CH(O)– CH_2 –O, 6H), 5.86 (m, Ar–O– CH_2 –CH(O)– CH_2 –O, 3H), 6.99 (d, Ar–H, 12H, *ortho* to O in CPA moiety), 7.08 (d, Ar–H, 6H, *ortho* to O in CBA moiety), 7.90 (m, Ar–H, 36H, *ortho* to N), 8.17 (m, Ar–H, 18H, *ortho* to –COO).

^{13}C NMR (75 MHz, $CDCl_3$) for G1: δ = 7.82 (CH_3 – CH_2 –C–(CH_2 –O) $_3$), 13.94 (–OCH $_2CH_2CH_2$ – CH_3), 19.31 (–OCH $_2CH_2CH_2CH_3$), 24.01 (CH_3 – CH_2 –C–(CH_2 –O) $_3$), 31.29 (–OCH $_2CH_2CH_2CH_3$), 41.79 (CH_3 – CH_2 –C–(CH_2 –O) $_3$), 63.34 (–O– CH_2 –CH(O)– CH_2 –O), 66.67 (–O– CH_2 –CH(O)– CH_2 –O), 67.18 (CH_3 – CH_2 –C–(CH_2 –O) $_3$), 68.20 (–OCH $_2CH_2CH_2CH_3$), 70.52 (–O– CH_2 –CH(O)– CH_2 O), 114.89 (*o*-ArC to O in CBA), 115.14 (*o*-ArC to O in CPA), 122.56 (*m*-ArC to O in CBA), 122.66 (*m*-ArC to O in CPA), 125.37 (*m*-ArC to –COO), 130.43, 130.53, 130.72, 130.83, 130.99 (ArC next and *ortho* to –COO), 146.92 (*p*-ArC to –O in CBA), 147.53 (*p*-ArC to O in CPA), 155.64 (*p*-ArC to –COO in CPA), 155.80 (*p*-ArC to –COO in CBA), 161.39 (ArC next to O in CPA), 162.52 (ArC next to O in CBA), 165.48, 165.78 (ArCOO in CBA), 165.93 (ArCOO in CPA).

Anal. Calc. for $C_{156}H_{152}N_{18}O_{27}$: C, 69.11; H, 5.65; N, 9.30. Found: C, 69.52; H, 5.68; N, 9.23%.

1H NMR (300 MHz, $CDCl_3$) for G2: δ = 0.99 (– CH_3 , 36H), 1.12 (– CH_3 (at core), 3H), 1.26 (– CH_2CH_3 (at core), 2H), 1.51 (– CH_2CH_3 , 24H), 1.81 (– $CH_2CH_2CH_3$, 24H), 4.05 (– $CH_2CH_2CH_2CH_3$, 24H), 4.49 (Ar–O– CH_2 –CH(O)– CH_2 –O, 18H), 4.58 (C– CH_2 –O, 6H), 4.84 (Ar–O– CH_2 –CH(O)– CH_2 –O, 18H), 5.85 (Ar–O– CH_2 –CH(O)– CH_2 –O, 9H), 6.99 (Ar–H, 24H, *ortho* to O in CPA moiety), 7.08 (Ar–H, 18H, *ortho* to O in CBA moiety), 7.91 (Ar–H, 84H, *ortho* to N), 8.17 (Ar–H, 42H, *ortho* to –COO).

^{13}C NMR (75 MHz, CDCl_3) for G2: $\delta = 7.82$ ($\text{CH}_3\text{-CH}_2\text{-C-(CH}_2\text{-O)}_3$), 13.93 ($-\text{OCH}_2\text{CH}_2\text{-CH}_2\text{CH}_3$), 19.31 ($-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 24.01 ($\text{CH}_3\text{-CH}_2\text{-C-(CH}_2\text{-O)}_3$), 31.31 ($-\text{OCH}_2\text{CH}_2\text{-CH}_2\text{CH}_3$), 41.79 ($\text{CH}_3\text{-CH}_2\text{-C-(CH}_2\text{-O)}_3$), 63.34 ($-\text{O-CH}_2\text{-CH(O)-CH}_2\text{-O}$), 66.67 ($-\text{O-CH}_2\text{-CH(O)-CH}_2\text{-O}$), 67.18 ($\text{CH}_3\text{-CH}_2\text{-C-(CH}_2\text{-O)}_3$), 68.24 ($-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 70.52 ($-\text{O-CH}_2\text{-CH(O)-CH}_2\text{-O}$), 114.92 (*o*-ArC to O in CBA), 115.14 (*o*-ArC to O in CPA), 122.56 (*m*-ArC to O in CBA), 122.66 (*m*-ArC to O in CPA), 125.32 (*m*-ArC to $-\text{COO}$), 130.43, 130.53, 130.72, 130.82, 130.97 (ArC next and *ortho* to $-\text{COO}$), 146.97 (*p*-ArC to $-\text{O}$ in CBA), 147.53 (*p*-ArC to O in CPA), 155.62, 155.80 (*p*-ArC to $-\text{COO}$), 161.39 (ArC next to O in CPA), 162.49 (ArC next to O in CBA), 165.48, 165.77, 165.91 (ArCOO).

Anal. Calc. for $\text{C}_{354}\text{H}_{332}\text{N}_{42}\text{O}_{63}$: C, 68.77; H, 5.41; N, 9.52. Found: C, 68.37; H, 5.44; N, 9.47%.

2.3. Nujol Mull technique sample preparation in FTIR analysis

The appropriate amount of dendrimer was mixed with one drop of nujol and mulled in a mortar. Then the mixture was smeared on a KBr disc for FTIR measurement.

2.4. MALDI-TOF mass spectrometry analysis

Dendron (1 μL) or dendrimer solutions (10^{-3} M) in THF was mixed with 50 μL of 2,5-dihydroxybenzoic (2,5-DHB) (10 g L^{-1}) in THF as a matrix solution. 10 μL of NaI solution (5 g L^{-1} in THF) were added for inducing cationization in some measurements. Then 1 μL of the mixed solution was deposited onto the sample stage and allowed to dry in air.

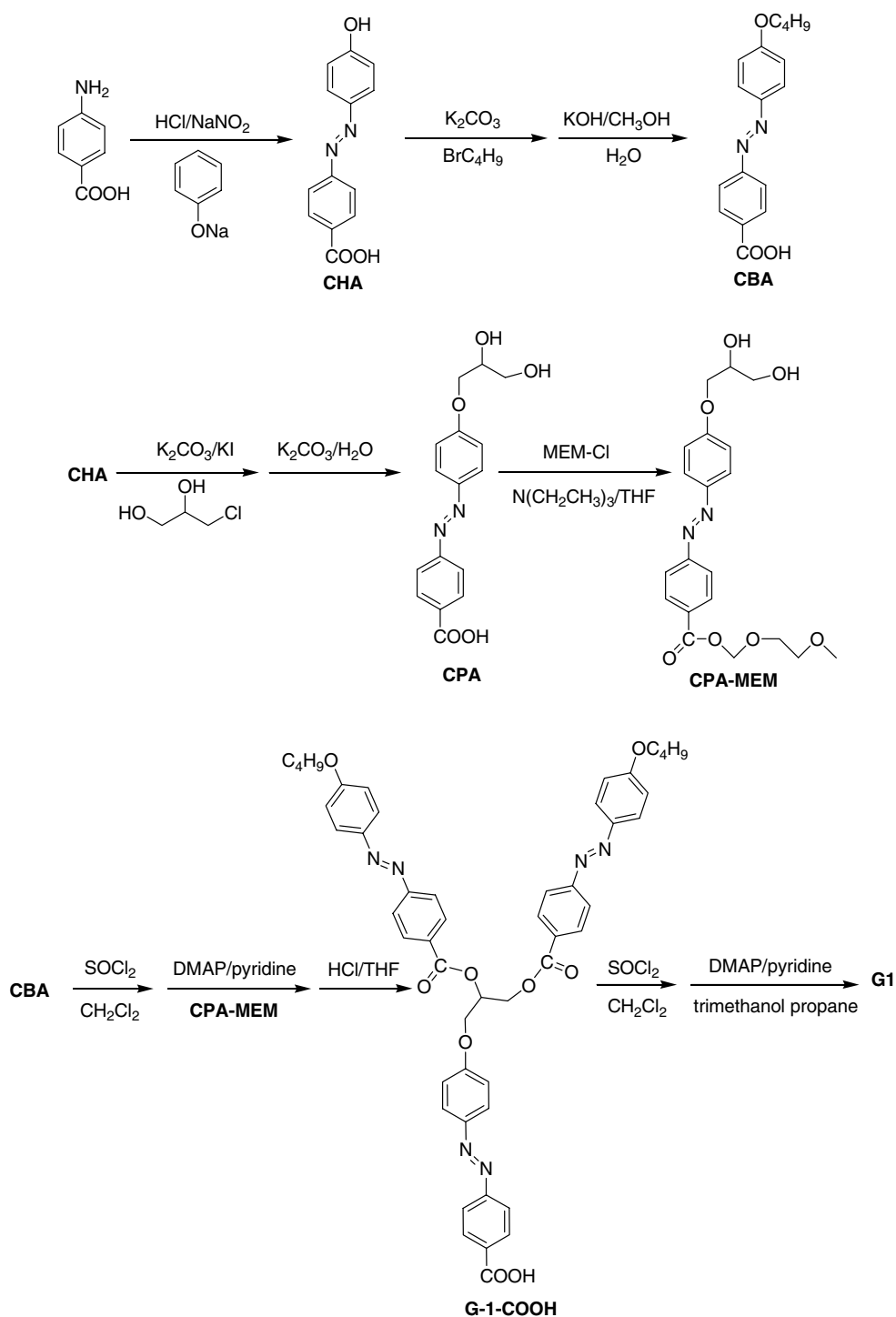
3. Results and discussion

3.1. Synthesis of azobenzene constructed dendrons and dendrimers

The convergent synthetic routes for dendron G-1-COOH, as well dendrimer G1 are outlined in Scheme 1. The chemical structures of azobenzene constructed dendron G-4-COOH and dendrimer G2 are shown in Scheme 2. The designed AB_2 monomer 4-carboxy-4'-(1,2-propanediolether)-azobenzene (CPA) is used as a dendritic branch for

the first time. The 4-carboxy-4'-(*n*-butylether)-azobenzene (CBA) is chosen as the peripheral monomer in order to improve solubility of the dendrons and the dendrimers. The carboxyl group of CPA is protected using MEM-Cl to avoid the possible exchange reactions. With the monomers CBA and CPA-MEM, dendrons were synthesized via an AB_2 -type stepwise growing procedure. The carboxyl group of CBA was converted to acyl chloride using SOCl_2 and then reacted with the hydroxyl groups of CPA-MEM. The MEM group was subsequently removed and we got the first generation dendron G-1-COOH. The second to fourth generation dendrons could be obtained via a similar procedure. Linking the carboxyl group of G-1-COOH or G-2-COOH with the hydroxyl group of trimethanol propane gave the first and second generation dendrimers. However, we failed to prepare higher generation dendrons and dendrimers due to the much lower yields under different reaction conditions. All azobenzene constructed dendrons and dendrimers were obtained as orange red solids, showing good solubility in aprotic solvents, such as CHCl_3 and THF.

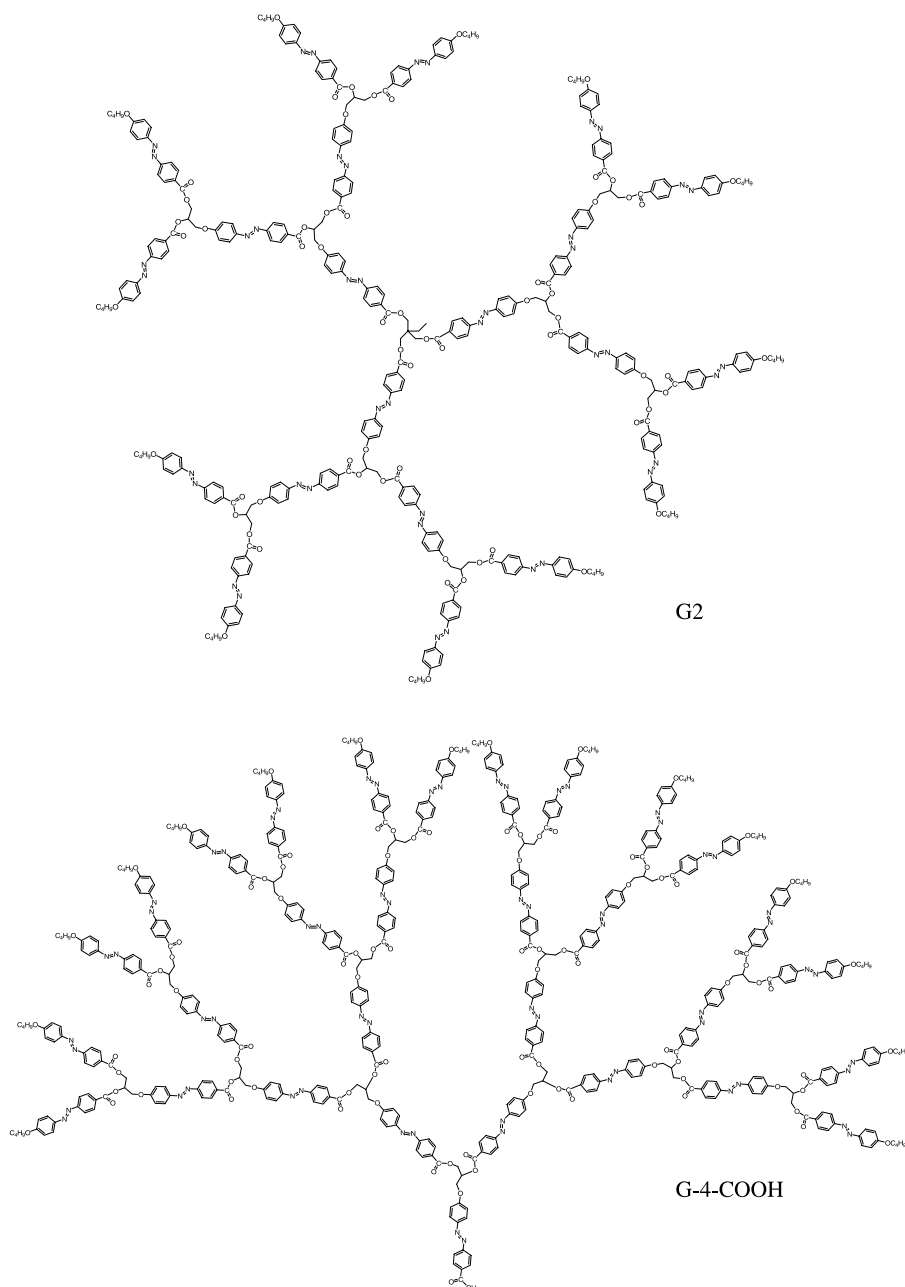
The ^1H NMR spectroscopy was utilized for monitoring the reaction process. ^1H NMR spectra of CPA and CBA are shown in Fig. 1. The resonances at 3.40–4.20 ppm related to $-\text{CH}_2$ and $-\text{CH}$ of CPA (Fig. 1a), and 4.10 ppm related to the methylene protons adjacent to the oxygen atom in CBA (Fig. 1b) that appeared in the spectra, indicate the formation of AB_2 monomer and peripheral monomer. ^1H NMR spectra of G-1-COO-MEM, G-1-COOH, and G1 are shown in Fig. 2. As inferred from the spectra (Fig. 2a and b), when the hydroxyl groups in CPA moiety are reacted, the resonances related to $-\text{CH}_2$ and $-\text{CH}$ of CPA moiety arise in the region from ~ 3.48 to ~ 4.52 , ~ 3.85 to ~ 5.86 , ~ 4.02 and ~ 4.15 to ~ 4.85 ppm (two separate dd peaks combined), respectively. No original resonances for CPA (Fig. 1a) could be observed indicating that all hydroxyl groups in CPA moieties are consumed. Furthermore, the relative integration area ratio of $-\text{CH}_2$ of CPA moiety (~ 4.52 ppm) versus $-\text{CH}_2$ of CBA moiety (~ 4.10 ppm) is a useful diagnostic tool for characterizing the generation progression of a dendron. The ratio of 1:2 for G-1-COOH, 3:4 for G-2-COOH, 7:8 for G-3-COOH, and 15:16 for G-4-COOH are obtained, increasing with the generation of dendron growing, as shown in Fig. 3. This method was also applied for character-



Scheme 1. Synthetic routes for dendron G-1-COOH and dendrimer G1.

izing the formed dendrimers. The resonance related to $-CH_2$ of trimethanol propane moiety appears at around 4.58 ppm as the adjacent hydroxyl group

was reacted, as shown in Fig. 2c. Its integration area ratio versus that at around 5.84 ppm related to the protons at the focal point can be used to



Scheme 2. Chemical structures of dendrimer G2 and dendron G-4-COOH.

determine the formation of dendrimers. Fig. 4 shows the ^1H NMR spectra of G1 and G2 with the ratios of about 3:6 and 9:6, respectively.

The FTIR spectra of dendron G-1-COOH, trimethanol propane, and G1 are shown in Fig. 5. In order to eliminate the influence of absorption from water in KBr, all the spectra were obtained using Nujol Mull technique instead of KBr-pressed-disk

method. The peaks at around 1682 cm^{-1} and 1719 cm^{-1} are assigned to the absorption of benzoic acid and benzoic ester carbonyl ($\text{C}=\text{O}$) stretch, respectively. The wide band appeared over 3000 cm^{-1} belongs to the hydroxyl group of trimethanol propane. It can be seen that the absorption occurred at 1682 cm^{-1} and over 3440 cm^{-1} disappeared completely for the dendrimer G1, giv-

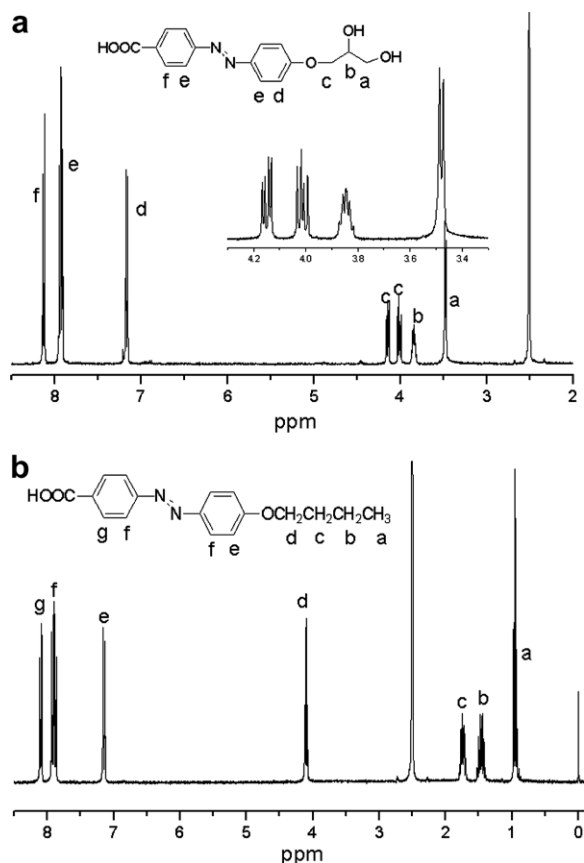


Fig. 1. ^1H NMR spectra of (a) CPA and (b) CBA.

ing the evidence that all hydroxyl and carboxyl groups are consumed.

The molecular structures of dendrons and dendrimers were corroborated by GPC and MALDI-TOF-MS measurements (Table 1). As shown in Fig. 6, all the GPC traces show narrow peaks, indicating that the products possess monodispersed molecular weights. However, the characterization by GPC is generally of limited value since the dendrimers themselves are less polydisperse than the polymer standards used to calibrate the columns. Therefore, the utilization of MALDI-TOF-MS technique to confirm the structures of the dendrons and dendrimers are of particular importance. Because all the dendrons and dendrimers showed a strong π - π^* absorption band of azobenzene at 360 nm, the UV laser irradiation (337 nm) easily led to the decomposition of the molecules during testing. The fragment and adduct ions were observed for all the samples with DHB as the matrix. As alkali ion cationization is known to reduce fragmentation, the alkali metal salt (NaI)

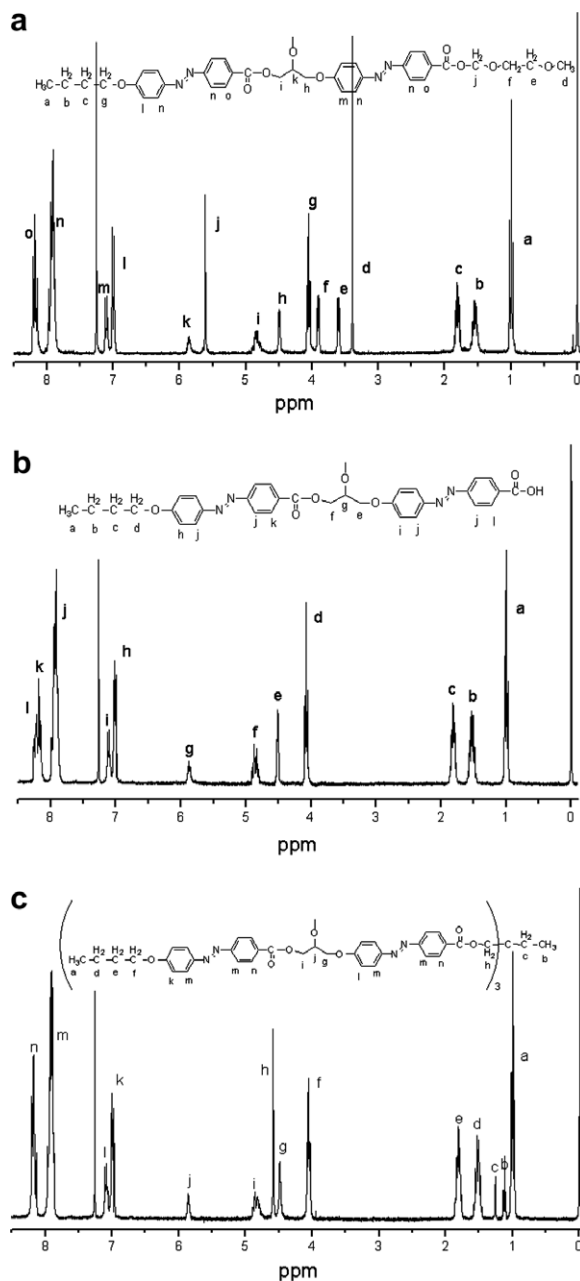


Fig. 2. ^1H NMR spectra of (a) G-1-COO-MEM; (b) G-1-COOH and (c) G1 in CDCl_3 .

was utilized. The MALDI-TOF mass spectra are given from Figs. 7–11. It has been seen from these spectra that the addition of NaI could dramatically reduce fragmentation. It is clear that these fragments, and of course these adducts, appear not to correspond to the existence of structural defects. The structural regularity of the dendrons and dendrimers have been confirmed by ^1H NMR spectra

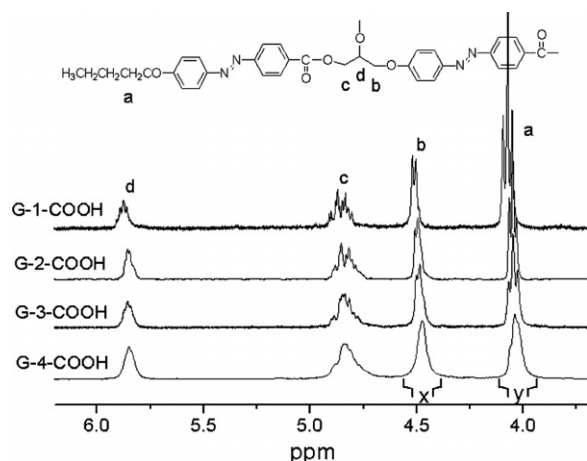


Fig. 3. ^1H NMR spectra of dendrons G-1-COOH to G-4-COOH. The values of $x:y$ are about 1:2, 3:4, 7:8 and 15:16 for G-1-COOH to G-4-COOH, respectively.

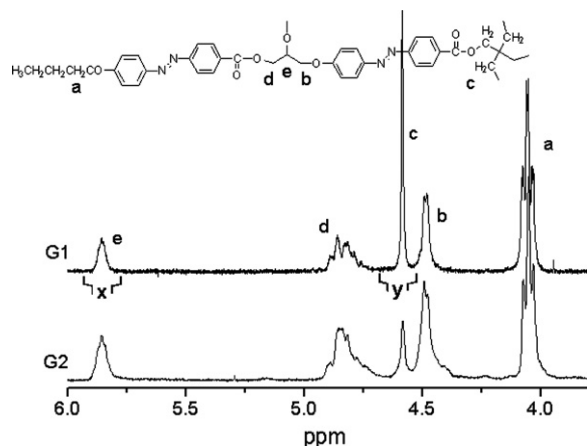


Fig. 4. ^1H NMR spectra of dendrimers G1 and G2. The values of $x:y$ are about 3:6 and 9:6 for G1 and G2, respectively.

and GPC measurements. Furthermore, the mainly appeared fragment ions ($m/z \sim 578$) could not be assigned while analyzing the reaction process. The conclusion can be drawn that the fragment ions

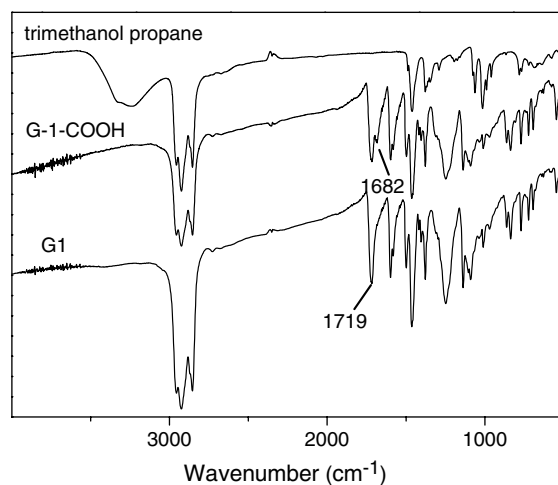


Fig. 5. FTIR spectra of trimethanol propane, G-1-COOH, and G1 using Nujol Mull technique.

came out because of degradation during MALDI analysis. There are two main factors which may influence the fragmentation of the molecules in our system: the molecular weight and the polarity of the molecules. With increasing the molecular weight, the possibility of fragmentation increased. It is more difficult for the higher generation dendrons and dendrimers to give quasi-molecular ion signals. Moreover, the polarity of the molecules will influence the orientation of azobenzene moieties. The increase in the polarity will drive the azobenzene moieties orientated in a more ordered way, which will enhance the non-covalent aromatic-aromatic interaction (as can be seen from the results of thermal properties discussed below) and make it more difficult to give clear quasi-molecular ion signals. From the results of the MALDI-TOF mass spectra, it can be found that the dendrons give more fragments than the dendrimers. The polarity of G-1-COOH is much stronger than other dendrons and even the addition of NaI could not efficiently suppress fragmentation (Fig. 7). With the generation

Table 1
Molecular weights of synthesized azobenzene dendrimers

Compound	G-1-COOH	G-2-COOH	G-3-COOH	G-4-COOH	G1	G2
M_w^a	2094	4172	7889	15,415	5182	11,028
M_w/M_n	1.01	1.01	1.01	1.03	1.01	1.02
m/z^b	899.6	2055.2	4367.8	—	2733.3	6181.3
m/z (calcd)	899.0	2056.2	4370.6	8977.6	2733.0	6182.7

^a Measured by GPC (polystyrene standards).

^b Measured by MALDI-TOF mass spectroscopy.

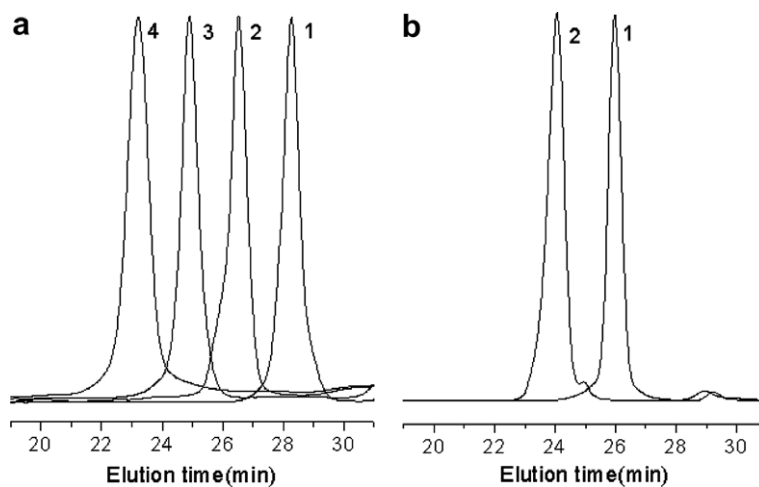


Fig. 6. GPC traces of (a) dendrons G-1-COOH to G-4-COOH (traces 1–4) and (b) dendrimers G1 (trace 1) and G2 (trace 2).

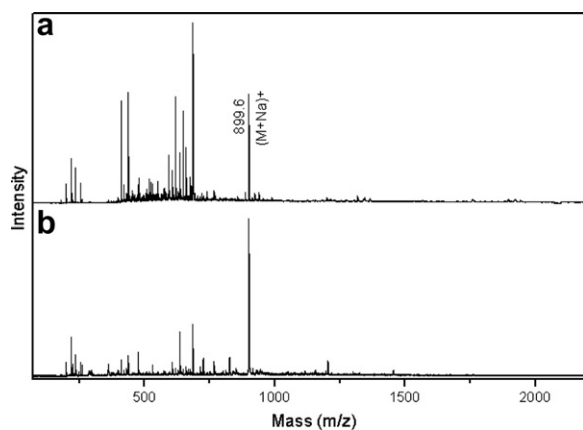


Fig. 7. MALDI-TOF mass spectra of G-1-COOH in the absence (a) or presence (b) of NaI (DHB matrix).

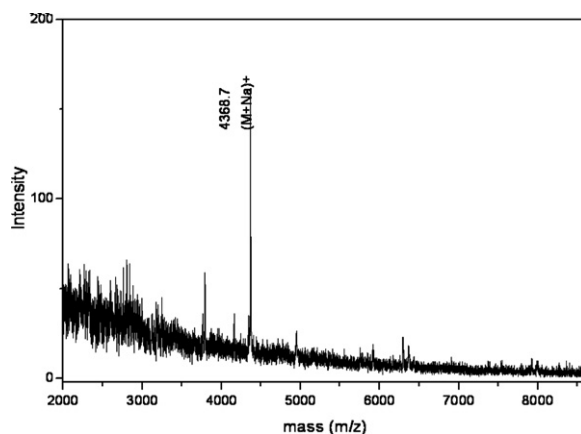


Fig. 9. MALDI-TOF mass spectrum of G-3-COOH.

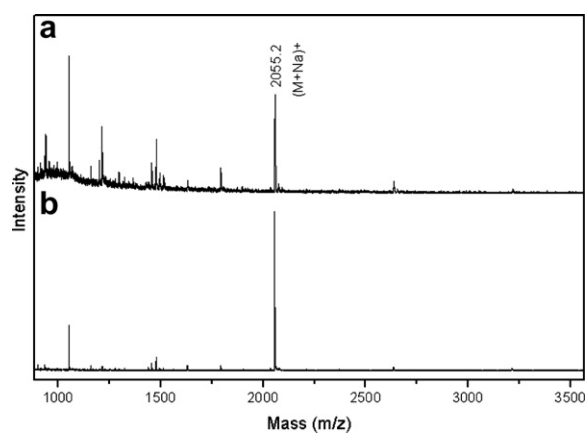


Fig. 8. MALDI-TOF mass spectra of G-2-COOH in the absence (a) or presence (b) of NaI (DHB matrix).

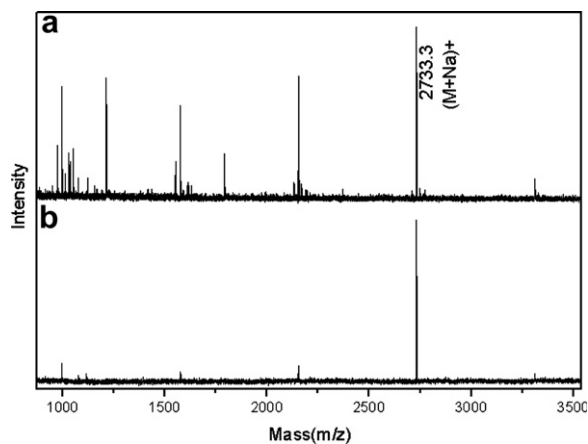


Fig. 10. MALDI-TOF mass spectra of G1 in the absence (a) or presence (b) of NaI (DHB matrix).

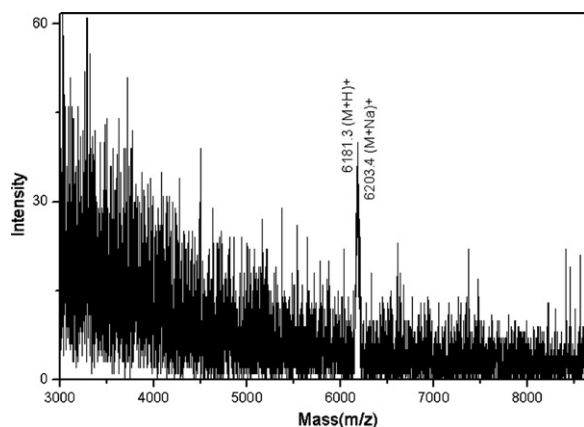


Fig. 11. MALDI-TOF mass spectrum of G2.

of the dendron increased, the polarity decreased and thus G-2-COOH gave rather neat signals (Fig. 8). For G-3-COOH, although its polarity further decreases, the larger molecular weight resulted in the much lower peak intensity, and even no quasi-molecular ion signals could be observed without the NaI addition (Fig. 9). Furthermore, we failed to detect any signals within the appropriate mass range for G-4-COOH. For dendrimer G1 (Fig. 10), due to the global shape and absence of carboxyl groups, the polarity of the molecule further decreased and the fragmentation were suppressed compared with the dendrons. The signal of dendrimer G2 with higher molecular weight was also successfully detected although the resolution was not very satisfactory due to the weak peak intensity (Fig. 11).

3.2. Thermal properties

The phase transition behaviors of the dendrons and dendrimers were studied using DSC, and the DSC curves are given in Fig. 12. All the dendrons show an inconspicuous endothermic peak right after the glass transition temperature (T_g). Their associated enthalpies decrease with the increase of the generation of dendron. However, the dendrimers are totally amorphous, displaying only T_g s. During the cooling scan, only an exothermic transition at T_g was observed and no exothermic peak corresponding to the endothermic peak was found for all the dendrons. Moreover, the observation on a polarizing microscope equipped with a hot stage shows no liquid crystal textures. Therefore, the inconspicuous endothermic peak appeared dur-

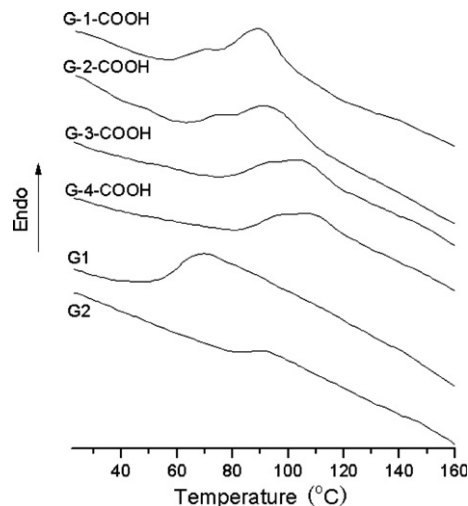


Fig. 12. DSC heating curves (second scan) for the dendrons and the dendrimers.

ing the heating scan for the dendrons could be due to partial crystallization of the dendrons. The existence of carboxyl group increases the polarity of the dendrons, which will drive the azobenzene moieties orientated in a more ordered way. Therefore, the non-covalent aromatic–aromatic interaction is enhanced and caused the partial crystallization. However, the branched architecture of the dendrons weakened this effect and the gradual crystallization process could not be observed during the cooling scan in DSC experiments. With the generation of dendrons increases, the polarity decreases, more azobenzene groups are trapped “in” the molecular structure. It is hard for higher generation dendrons to form the ordered structures and associated enthalpy decreases. Furthermore, for the dendrimers which have no carboxyl groups, even no such endothermic peaks could be observed.

3.3. Light-responsive properties

The samples were irradiated at 360 nm in CHCl_3 to induce the *trans*–*cis* isomerization. Fig. 13 shows the UV–Vis spectral changes of G-4-COOH (0.01 mg/ml in CHCl_3) upon irradiation at around 360 nm for different times. It can be seen that the UV-irradiation results in the decrease in the π – π^* absorption band of *trans*-azobenzene moiety which peaked at 360 nm with concomitant increases of the π – π^* and n – π^* bands of the *cis* isomer at around 290 and 460 nm, respectively. Moreover, the photostationary state is attained within

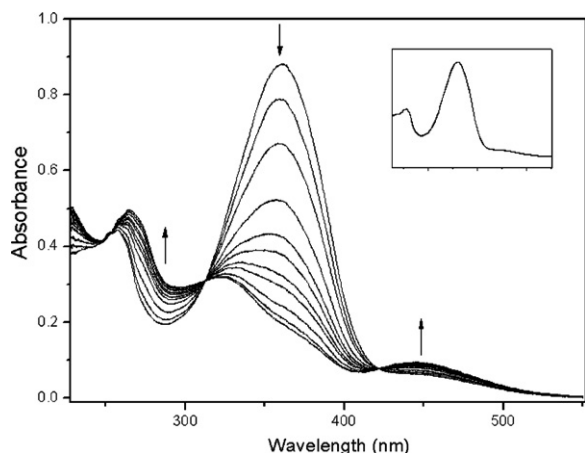


Fig. 13. UV-Vis spectra of G-4-COOH (0.01 mg/ml in CHCl_3) under irradiation (360 nm; irradiation time: 0 s, 10 s, 20 s, 40 s, 80 s, 120 s, 160 s, 240 s, 320 s, 400 s, and 600 s). Inset: UV-Vis spectra of G-4-COOH after 450 nm light irradiation.

600 s at which almost all azobenzene moieties take a *cis* isomer. As the irradiated solution was then exposed to visible light at around 450 nm, the original state was recovered within 450 s. The similar results were obtained for other dendrons and dendrimers. The *trans*–*cis* isomerization of azobenzene moiety is fully reversible and, moreover, could be repeated many times without decomposition of the components.

The ^1H NMR analysis was also used for confirming the decomposition of dendritic molecules and determining the degree of *trans*–*cis* isomerization of azobenzene moieties. In order to explore the changes in the chemical shifts associated with *trans*–*cis* isomerization, the samples (0.5 mg/ml in CDCl_3) were UV irradiated for 30 min, 300 min and then kept in dark for 7 days at ambient temperature before testing. The results shown in Fig. 14 indicate that azobenzene moieties undergo a fully reversible *trans*–*cis* isomerization and no decomposition occurs in either the dendrons (Fig. 14a) or the dendrimers (Fig. 14b) upon a long time UV light irradiation. Moreover, the clear and separated change of resonances around 4.48 (marked with*) and 4.05 (marked with**) related to CPA and CBA can be used to determine the percentage of azobenzene group which takes *trans*–*cis* isomerization in CPA and CBA moieties in a given time (30 min). The changes in the integration areas at around 4.48 ppm and 4.05 ppm during the given irradiation time are listed in Table 2. Compared the data for dendrons with that for

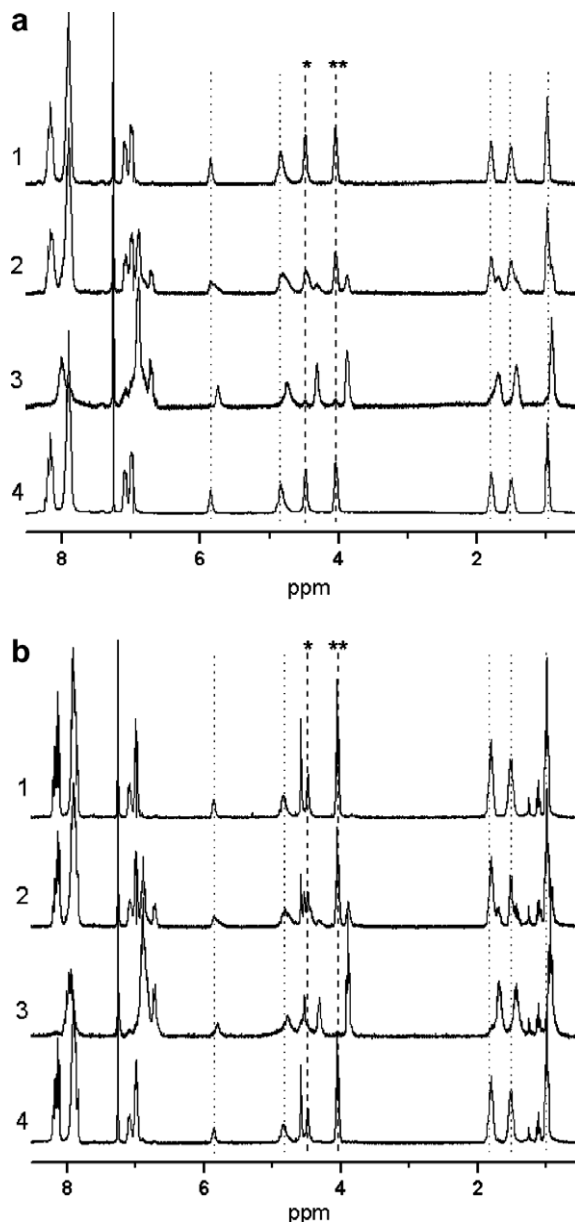


Fig. 14. ^1H NMR spectra of G-2-COOH (a) and G1 (b) in CDCl_3 : (1) initial; (2) after UV irradiation for 30 min and (3) for 300 min; (4) after thermal *cis*–*trans* isomerization for 7 days at ambient temperature in dark.

dendrimers, it was found that the possibility of isomerization of azobenzene in CPA moieties decreases if more CPA are located “in” the molecular structure. This can be interpreted that azobenzene moieties at the exterior absorb UV light more efficiently and those located inside are more difficult to take a *trans*–*cis* isomerization because of the steric hindrance.

Table 2

Percentage of azobenzene group taking *trans*–*cis* isomerization after 30 min irradiation

Sample	Percentage of <i>cis</i> -azo in the CPA moieties (%)	Percentage of <i>cis</i> -azo in the CBA moieties (%)	Total percentage of <i>cis</i> -azo (%)
G-1-COOH	29.4	31.7	30.9
G-2-COOH	27.6	29.6	28.7
G-3-COOH	24.4	29.9	27.3
G-4-COOH	22.8	29.1	26.0
G1	10.1	23.4	19.0
G2	13.43	20.9	17.7

4. Conclusion

The novel dendrimers with azobenzene moieties throughout their skeleton were successfully synthesized. The NMR, FTIR, GPC, and MALDI-TOF-MS analysis confirmed their regular molecular architecture. It will be of interest to investigate the self-assemble behavior of the polymers and the promising applications for the dendrimers as dendritic boxes in the subsequent works. The azobenzene constructed polymers also provide possibility for data storage and photodeformation applications.

Acknowledgements

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