This article was downloaded by: [Universite Laval] On: 28 February 2013, At: 03:07 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

Synthesis, Characterization, and Thermogravimetric Studies of a Phosphorus-Containing Dendron Built from 1,5-Diaminonaphthalene at the Core

E. Dadapeer^a, B. Satheesh Krishna^a & C. Naga Raju^a

^a Department of Chemistry, Sri Venkateswara University, Tirupati, India

Version of record first published: 21 Feb 2013.

To cite this article: E. Dadapeer, B. Satheesh Krishna & C. Naga Raju (2013): Synthesis, Characterization, and Thermogravimetric Studies of a Phosphorus-Containing Dendron Built from 1,5-Diaminonaphthalene at the Core, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 43:9, 1219-1228

To link to this article: <u>http://dx.doi.org/10.1080/00397911.2011.628773</u>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <u>http://www.tandfonline.com/page/terms-and-conditions</u>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.



Synthetic Communications[®], 43: 1219–1228, 2013 Copyright © Taylor & Francis Group, LLC ISSN: 0039-7911 print/1532-2432 online DOI: 10.1080/00397911.2011.628773

SYNTHESIS, CHARACTERIZATION, AND THERMOGRAVIMETRIC STUDIES OF A PHOSPHORUS-CONTAINING DENDRON BUILT FROM 1,5-DIAMINONAPHTHALENE AT THE CORE

E. Dadapeer, B. Satheesh Krishna, and C. Naga Raju

Department of Chemistry, Sri Venkateswara University, Tirupati, India

GRAPHICAL ABSTRACT



Abstract A facile divergent synthesis of a phosphorus-containing dendron containing 1,5-diaminonaphthalene is described. The phosphorus-containing dendron, functionalized with a 1,5diaminonaphthalene unit at the core and phenolic OH groups grafted at the periphery, has been accomplished in a versatile, simple fashion, using Schiff's condensation and nucleophilic substitution reactions with POCl₃, 3-hydroxy-benzaldehyde, 4-hydroxy-benzaldehyde, and 3-amino-phenol iteratively. The structures of intermediate dendrons were characterized by infrared, NMR (¹H, ¹³C, and ³¹P), liquid chromatography–mass spectrometry, and C, H, N analysis. The structure of the final dendron (6) was confirmed by infrared, NMR (¹H, ¹³C, and ³¹P), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, and C, H, N analysis. The thermal stability and degradation of the resulting final dendron was checked by thermal gravitometric analysis/differential thermal analysis.

Keywords 1,5-Diaminonaphthalene; facile divergent synthesis; phosphorus-containing dendron; Schiff's condensation; TGA/DTA analysis

Received July 18, 2011.

Address correspondence to C. Naga Raju, Department of Chemistry, Sri Venkateswara University, Tirupati 517502, India. E-mail: rajuchamarthi10@gmail.com

INTRODUCTION

Dendrimers are highly branched monodispersed compounds having a three-dimensional structure of dendritic wedges (dendrons) that proceed from one center, called the core or focal point.^[1] These molecules have a variety of applications from biology to material science based on their size, topography, molecular weight, and properties.^[2] The dendritic molecules having one function located at the focal point and several other functions on the surface are called dendrons. Several dendrons can be associated with their core by reaction with a multifunctional core, depending on the function.^[3] The specially designed dendrimers can be obtained using dendrons.^[4] In phosphorus-containing dendrimers and dendrons, the element phosphorus characterizes each step of the synthesis.^[5] In the buildup of phosphorus-containing dendron, we use aldehyde, P-Cl, -NH₂, and -OH groups because they offer a wide range of possibilities for grafting other functions on the surface of the intermediate compounds.^[6] In the preparation of the dendrimer or dendron, the most reactive site is the core function and the -NH₂ group is preferred because it can form versatile a Schiff's base with an aldehyde. In a dendrimer or dendron the most reactive sites are the terminal groups. The dendrimers and dendrons generally constitute three components, namely an interior core, repeating branching units, and functional terminal groups attached to the outermost branching units. The dendritic architectures are sometimes found in the biological world, such as branches and roots of plants.^[7] These natural dendritic architectures are similar to the artificial dendrimers and dendrons.^[8] To understand the properties and applications imparted by dendrimers, it is highly desirable to study their structure by well-defined NMR,^[9] infrared (IR),^[10] matrix-assisted laser desorptionionization time-of-flight mass spectrometry (MALDI-TOF-MS)^[11] (for analyzing the high molecular weight), thermal analysis, and scanning electron microscopy. The presence of phosphorus in a dendrimer or in a dendron confers fascinating properties.^[12]

In view of many potential applications for dendrimers,^[13] in this article, we report the facile iterative divergent synthesis of phosphorus-containing dendrons, built from 1,5-diaminonaphthalene at the core and phenolic OH groups at the periphery. The characterization, scanning electron microscopic, and thermogravimetric properties of the phosphorus dendron are also studied.

RESULTS AND DISCUSSION

Scheme 1 shows the synthetic strategy for assembling a facile phosphorusdendron framework. 1,5-Diaminonaphthalene was used in the preparation of dendron based on its solubility and commercial availability, previously naphthalene was used in the preparation of a dendrimer.^[14]

Compound 1 was synthesized by a Schiff's condensation reaction of 1 molar equivalent of 1,5-diaminonaphthalene with 2 equivalents of 3-hydroxy-benzaldehyde with stirring for 4 h in refluxing dry EtOH. In the second step, compound 1 was treated with 2 equivalents of POCl₃ in dry tetrahydrofuran (THF) in the presence of triethylamine at 5 to 40 °C with stirring for 4 h to form compound 2. After filtration, compound 2 was reacted with 4 equivalents of 3-hydroxy-benzaldehyde in dry THF in presence of triethylamine at 40–45 °C with stirring for 5 h to obtain



Scheme 1. Synthesis of dendron 6.

compound 3. Compound 3 was treated with 4 equivalents of 3-amino phenol with stirring for 6 h in refluxing dry EtOH to afford compound 4. In the next step, compound 4 was then reacted with 4 equivalents of $POCl_3$ in dry THF in the presence of triethylamine at 5 to 50 °C with stirring for 6 h to form compound 5. After filtration, compound 5 was treated with 8 equivalents of hydroquinone in dry THF in the presence of triethylamine at 10 to $50\,^{\circ}$ C with stirring for 6 h to get compound 6. As the size of the dendron increases, the reaction is sluggish and the yield is poor. To improve the yield of 6 the temperature is maintained at 45-50 °C and stirring for a longer period. The synthesis of the dendron 6 was accomplished by adopting a facile iterative divergent method as shown in Scheme 1. The overall yield of the final dendrimer 6 was 55%. All the intermediate compounds 1, 2, 3, 4 and 5 were characterized by IR, NMR (¹H, ¹³C and ³¹P), liquid chromatography-mass spectrometry (LC-MS) data, and C, H, N analysis. The data are given in the experimental section. The synthetic and analytical data of the dendron 6 are is also presented in the experimental section. The dendron 6 exhibited absorption bands for -OH, P=O, and CH=N in the regions 3381, 1233, 1240 and 1627, and 1643 cm⁻¹ respectively. P-O-C_(aromatic) gave two absorptions in the regions 933 and $1160 \, \text{cm}^{-1}$.^[15] In the ¹H NMR spectra (400 MHz) of **6**, the aromatic protons gave multiplets in the region δ 6.63–7.57, the -OH protons resonated at δ 10.41 as singlets, and the imine CH protons (CH=N) gave two singlets at δ 8.09 and 8.35, indicating two different environments. ¹³C NMR spectrum was recorded for compound **6** and the data are given in the experimental section. The aromatic carbons resonated in the region 108.7–160.5 ppm. Two -<u>CH</u>=N carbon signals were observed at δ 157.6 and 158.3 (see Fig. 1 for notation for 13 C). The compound **6** showed two 31 P NMR signals,



Figure 1. Notation for ¹³C NMR of dendron 6.

indicating two different types of phosphorus atoms. The intermediate compounds **2**, **3**, **4**, and **5** gave phosphorus-31 resonance signals at δ –30.45, –32.09, –28.54 and –22.48, and –31.88 respectively.^[16] The mass spectral properties of the dendron **6** was studied by MALDI-TOF mass spectrometry. The mass obtained from the MALDI measurements corresponds closely to the calculated value. The molecular decomposition of the dendron **6** was investigated by both thermogravimetric analysis (TGA) and differential thermal analysis (DTA).

TGA-DTA ANALYSIS

TGA-DTA measures both heat flow and weight changes in a material as a function of temperature in a controlled air atmosphere. An overlay of TGA-DTA plots for the test compound **6** up to $700 \,^{\circ}$ C in an air atmosphere is shown in Figs. 2 and 3. The decomposition of the final dendron **6** was followed by TGA.



Figure 3. DTA of dendron 6.

The compound is stable up to 90 °C. An initial decomposition starts in the range of 90–110 °C with a corresponding weight loss of approximately 3%. This is attributed to the loss of water molecules. Then the compound is stable up to 200 °C. Again the decomposition starts in the range 200–300 °C with a corresponding weight loss of approximately 43–44%. Then the compound is stable in the range of 300–450 °C, and immediately starts to decompose in between 450 and 550 °C with approximate weight loss of 18–20%. The total loss of the compound is around 65% of the total mass of the material. Similarly, DTA was also used on dendron **6** to detect the changes in the sample, either exothermic or endothermic. The DTA profile (Fig. 3) shows that the endotherm peak at 100 °C corresponds to the loss of water and exotherms at 250 and 490 °C correspond to the loss of most of the dendritic wedges of the dendron **6**.

EXPERIMENTAL

All the chemicals used were purchased from Sigma-Aldrich Chemical Company and used without further purification. All solvents (analytic reagent or extrapure grade) were dried by standard methods. Thin-layer chromatography (TLC) was performed on precoated plates with silica gel $60 F_{254}$ (Merk). Column chromatography was performed on silica gel (60–120 mesh), and ethyl acetate-hexane was used as eluent. IR spectra were recorded on JASCO Japan FT/IR-5300 spectrometer at the University of Hyderabad using KBr optics. ¹H and ¹³C NMR spectra were recorded on a Bruker A VIII 400 MHz NMR spectrometer at Laila Impex, Vizayawada (operating at 400 MHz for ¹H and 100 MHz for ¹³C NMR). Data were recorded in dimethylsulfoxide (DMSO-d₆) and chemical shifts were referenced to tetramethylsilane (TMS) (¹H and ¹³C). ³¹P NMR spectra were recorded on Bruker ACF Supercon 200 spectrometer operating at 81 MHz at the University of Hyderabad, Hyderabad. ³¹P NMR data were recorded in CDCl₃ and chemical shifts were referenced to 85% H₃PO₄. LC mass spectra of intermediate compounds 1, 2, 3, 4, and 5 were recorded on a LCMS-2010A Shimadzu spectrometer at the University of Hyderabad, Hyderabad. The MALDI mass spectrum of dendron 6 was recorded using an Applied Biosystems Voyager DE-PRO MALDI-TOF spectrometer. The sample was run using sinapic acid as the matrix with DMSO as the solvent in the dried-droplet preparation method, performed at the Indian Institute of Technology, Madras, Chennai. TGA-DTA measurement was taken using a TA instrument, Waterloo, USA, performed at Sri Krishnadevaraya University, Ananthapur, India. Elemental analyses were performed using a FLASH EA 1112 Thermo Finnigan instrument (France) at the University of Hyderabad, Hyderabad, India.

Synthesis of 1

A solution of 3-hydroxybenzaldehyde (0.01 mol, 1.22 g) in 20 mL of dry EtOH was added at room temperature to a stirred solution of 1,5-diaminonaphthalene (0.005 mol, 0.79 g) in 20 mL of dry EtOH. After stirring for 4 h at reflux temperature, formation of the compound 1 was ascertained by TLC analysis run in a 1:4 mixture of ethyl acetate and hexane, and the average R_f value observed was 0.75. The solvent was evaporated under reduced pressure to give the crude product. It was purified by

column chromatography. Yield: 85%. Anal. calcd. for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95; N, 7.65%. Found: C, 78.01; H, 4.89; N, 7.55%. IR (KBr, cm⁻¹): 3385 (Ar-OH), 1620 (CH=N); ¹H NMR (400 MHz, DMSO- d_6 , δ /ppm): 6.72–7.57 (14 H, m, Ar-H), 8.64 (2H, s, Ar-OH), 9.92 (2H, s, -CH=N); ¹³C (100 MHz, DMSO- d_6 , δ /ppm): 149.5 (C₀⁻¹), 116.6 (C₀⁻²), 127.5 (C₀⁻³), 125.6 (C₀⁻⁴), 130.2 (C₀⁻⁵/C₀⁻⁶), 157.0 (C₁⁻¹), 114.7 (C₁⁻²), 137.7 (C₁⁻³), 122.1 (C₁⁻⁴), 130.1 (C₁⁻⁵), 119.7 (C₁⁻⁶), 157.9 (CH=N). LC MS: m/z 367 (M + 1)⁺.

Synthesis of 2

A solution of POCl₃ (0.01 mol, 0.93 mL) in 20 mL of dry THF was added dropwise to a mixture of stirred solution of **1** and triethylamine (0.01 mol, 1.38 mL) in 25 mL of dry THF over a period of 20 min at -5 to 0 °C. After stirring for 5 h at 40–45 °C, formation of **2** was ascertained by TLC analysis run in a 1:4 mixture of ethyl acetate and hexane, and the average R_f value observed was 0.72. Triethylamine hydrochloride was removed by filtration. The solvent was evaporated under reduced pressure to give crude product. It was purified by column chromatography. Yield: 82%. Anal. calcd. for C₂₄H₁₆Cl₄N₂O₄P₂: C, 48.03; H, 2.69; N, 4.67. Found: C, 47.91; H, 2.53; N, 4.65. IR (KBr, cm⁻¹): 1221(P=O), 953, 1158 (P-O-C_{aromatic}), 1615 (CH=N). ¹H (400 MHz, DMSO-*d*₆, δ /ppm): 7.16–7.44 (14 H, m, Ar-H), 9.94 (2H, s, -CH=N). ¹³C (100 MHz, DMSO-*d*₆, δ /ppm): 150.1 (C₀¹), 116.8 (C₀²), 127.9 (C₀³), 126.6 (C₀⁴), 130.3 (C₀⁵/C₀⁶), 152.8 (C₁¹), 115.5 (C₁²), 138.1 (C₁³), 122.0 (C₁⁴), 131.1 (C₁⁵), 121.7 (C₁⁶), 158.2 (CH=N). ³¹P NMR (81 MHz, CDCl₃ δ /ppm): -30.45 ppm. LC MS: *m/z* 600 (M)⁺⁺.

Synthesis of 3

A solution of 3-hydroxy-benzaldehyde (0.02 mol, 2.44 g) in 25 mL of dry THF was added dropwise to a mixture of stirred solution of **2** and triethylamine (0.02 mol, 2.76 mL) in 25 mL of dry THF over a period of 20 min at 0 °C. After stirring for 5 h at 40–45 °C, formation of **3** was ascertained by TLC analysis run in a 3:7 mixture of ethyl acetate and hexane, and the average R_f value observed was 0.70. Triethylamine hydrochloride was removed by filtration. The solvent was evaporated under reduced pressure to get the crude product. It was purified by column chromatography. Yield: 75%. Anal. calcd. for $C_{52}H_{36}N_2O_{12}P_2$: C, 66.25; H, 3.85; N, 2.97. Found: C, 66.48; H, 3.82; N, 2.93. IR (KBr, cm⁻¹): 1690 (Ar-CHO), 1230 (P=O), 940, 1165 (P-O-C_{aromatic}), 1622 (CH=N). ¹H (400 MHz, DMSO- d_6 . δ /ppm): 7.02–7.57 (30 H, m, Ar-H), 8.62 (2H, s, –CH=N), 9.90 (4H, s, Ar-CHO). ¹³C (100 MHz, DMSO- d_6 . δ / ppm): 151.1 (C_0^{-1}), 115.7 (C_0^{-2}), 128.6 (C_0^{-3}), 127.6 (C_0^{-4}), 130.5 (C_0^{-5}/C_0^{-6}), 150.8 (C_1^{-1}), 115.8 (C_1^{-2}), 138.6 (C_1^{-3}), 121.5 (C_1^{-4}), 131.3 (C_1^{-5}), 121.9 (C_1^{-6}), 153.7 (C_2^{-1}), 113.5 (C_2^{-2}), 140.3 (C_2^{-3}), 124.0 (C_2^{-4}), 130.6 (C_2^{-5}), 126.4 (C_2^{-6}), 159.1 (CH=N),192.9 (Ar-CHO). ³¹P NMR (81 MHz, CDCl₃ δ /ppm): -32.09 ppm. LC MS: m/z 944 (M + 1)⁺.

Synthesis of 4

A solution of 3-aminophenol (0.02 mol, 2.18 g) in 20 mL of dry EtOH was added to a stirred solution of 3 in 25 mL of dry EtOH at room temperature. After

stirring for 5 h at reflux temperature, formation of the compound **4** was ascertained by TLC analysis run in a 2:3 mixture of ethyl acetate and hexane, and the average R_f value observed was 0.65. The solvent was evaporated under reduced pressure to obtain the crude product. It was purified by column chromatography. Yield: 65%. Anal. calcd. for C₇₆H₅₆N₆O₁₂P₂: C, 69.83; H, 4.32; N, 6.43. Found: C, 69.88; H, 4.31; N, 6.39. IR (KBr, cm⁻¹): 3375 (Ar-OH), 1242 (P=O), 938, 1173 (P-O-C_{aromatic}), 1622, 1628 (CH=N). ¹H (400 MHz, DMSO-*d*₆. δ/ppm): 6.64–7.54 (46 H, m, Ar-H), 8.58, 8.63 (6H, s, -CH=N), 9.75 (4H, s, Ar-OH). ¹³C (100 MHz, DMSO-*d*₆, δ/ppm): 149.9 (C₀⁻¹), 115.0 (C₀⁻²), 127.1 (C₀⁻³), 128.1 (C₀⁻⁴), 129.8 (C₀⁻⁵/C₀⁻⁶), 151.2 (C₁⁻¹), 114.8 (C₁⁻²), 139.1 (C₁⁻³), 122.0 (C₁⁻⁴), 130.7 (C₁⁻⁵), 122.9 (C₁⁻⁶), 154.5 (C₂⁻¹), 114.1 (C₂⁻²), 141.1 (C₂⁻³), 125.1 (C₂⁻⁴), 130.9 (C₃⁻⁵), 127.3 (C₂⁻⁶), 160.5 (C₃⁻¹), 110.8 (C₃⁻²), 155.3 (C₃⁻³), 116.22 (C₃⁻⁴), 132.9 (C₃⁻⁵), 114.0 (C₃⁻⁶), 159.1, 160.8 (CH=N). ³¹P NMR (81 MHz, CDCl₃, δ/ ppm):-28.54 ppm. LC MS: *m/z* 1308 (M + 1)⁺.

Synthesis of 5

A solution of POCl₃ (0.02 mol, 1.86 mL) in 30 mL of dry THF was added dropwise to a stirred solution of 4 and triethylamine (0.02 mol, 2.76 mL mL) in 30 mL of dry THF, over a period of 20 min at -5 to 0 °C. After stirring for 5 h at 40-45 °C, formation of 5 was ascertained by TLC analysis run in a 7:3 mixture of ethyl acetate and hexane, and the average R_f value observed was 0.55. Triethylamine hydrochloride was removed by filtration. The solvent was evaporated under reduced pressure to get the crude product. It was purified by column chromatography. Yield: 58%. Anal. calcd. for C₇₆H₅₂N₆O₁₄P₆: C, 51.43; H, 2.95; N, 4.74. Found: C, 51.47; H, 2.91; N, 4.71. IR (KBr, cm⁻¹): 1228, 1242 (P=O), 933, 1160 (P-O-C_{aromatic}), 1618, 1635 (CH=N). ¹H (400 MHz, DMSO-*d*₆. δ/ppm): 7.09–7.41 (46 H, m, Ar-H), 8.91, 9.90 (6H, s, -CH=N). ¹³C (100 MHz, DMSO- d_6 , δ/ppm): 150.7 (C₀⁻¹), 116.1(C₀⁻²), 127.4 (C_0^{3}) , 128.6 (C_0^{4}) , 130.1 (C_0^{5}/C_0^{6}) , 152.2 (C_1^{-1}) , 115.2 (C_1^{-2}) , 140.2 (C_1^{-3}) , 121.8 (C_1^4), 129.8 (C_1^5), 123.4 (C_1^6), 155.1 (C_2^1), 115.9 (C_2^2), 142.5 (C_2^3), 126.0 (C_2^4) , 131.5 (C_2^5) , 126.9 (C_2^6) , 161.5 (C_3^1) , 109.7 (C_3^2) , 156.0 (C_3^3) , 116.5 (C_3^4) , 133.4(C₃⁵), 113.9 (C₃⁶), 160.9, 162.4 (CH=N). ³¹P NMR (81 MHz, CDCl₃, $\delta/$ ppm): -22.48, -31.88 ppm. LC MS: m/z 1776 (M+1)⁺.

Synthesis of 6

A solution of hydroquinone (0.04 mol, 4.40 g) in 35 mL of dry THF was added dropwise to a stirred solution of **5** and triethylamine (0.04 mol, 5.52 mL mL) in 35 mL of dry THF over a period of 20 min at -5 to 0 °C. After stirring for 5 h at 45–50 °C, formation of **6** was ascertained by TLC analysis run in a 4:1 mixture of ethyl acetate and hexane, and the average R_f value observed was 0.50. Triethylamine hydrochloride was removed by filtration. The solvent was evaporated under reduced pressure to get the crude product. It was purified by column chromatography. Yield: 55%. Anal. calcd. for $C_{124}H_{92}N_6O_{32}P_6$: C, 63.00; H, 3.92; N, 3.56. Found: C, 63.12; H, 3.90; N, 3.61. IR (KBr, cm⁻¹): 3381 (Ar-OH), 1233, 1240 (P=O), 925, 1172 (P-O- $C_{aromatic}$), 1627, 1643 (CH=N). ¹H (400 MHz, DMSO-*d*₆. δ /ppm): 6.63–7.57 (78 H, m, Ar-H), 8.09, 8.35 (6H, s, –CH=N), 10.41 (8H, s, Ar-OH). ¹³C (100 MHz, DMSO*d*₆. δ /ppm): 151.2 (C₀⁻¹), 115.9 (C₀⁻²), 128.2 (C₀⁻³), 129.2 (C₀⁻⁴), 131.1 (C₀⁻⁵/C₀⁻⁶), 151.8 (C₁¹), 115.6 (C₁²), 140.9 (C₁³), 121.9 (C₁⁴), 130.3 (C₁⁵), 122.6 (C₁⁶), 156.3 (C₂¹), 116.7 (C₂²), 143.1 (C₂³), 125.5 (C₂⁴), 130.7 (C₂⁵), 127.1 (C₂⁶), 160.5 (C₃¹), 108.7 (C₃²), 155.1 (C₃³), 117.1 (C₃⁴), 134.1 (C₃⁵), 114.6 (C₃⁶), 143.5 (C₄¹), 117.7 (C₄²/C₄⁶), 116.5 (C₄³/C₄⁵), 150.5 (C₄⁴), 157.6, 158.3 (CH=N). ³¹P NMR (81 MHz, CDCl₃, δ /ppm): – 41.44, –39.13 ppm. MALDI-TOF-MS: *m*/*z* 2364 (M)⁺ (calcd. 2363.9).

CONCLUSION

Facile iterative divergent synthesis of a novel phosphorus dendron 6 was accomplished. The Schiff's base (imine) formation reactions were performed in dry ethanol and substitution reactions were performed in dry THF in presence of triethylamine. The thermal stability and changes in weight in relation to change in temperature and the heat of the dendron 6 were established by TGA-DTA analysis.

ACKNOWLEDGMENT

The authors thank Human Resource Development Group, Council of Scientific and Industrial Research, New Delhi, India, for sanctioning a major research project [No. 01(2309)/09/EMR-II].

REFERENCES

- 1. Frechet, J. M. J.; Tomalia, D. A. *Dendrimers and Other Dendritic Polymers*; Wiley: New York, 2002.
- Newkome, G. R.; Moorefield, C. N.; Vogtle, F. Dendrimers and Dendrons: Concepts, Synthesis, Applications; VCH: Weinheim, 2001.
- Zimmerman, S. C.; Zeng, F.; Reichert, D. E. C.; Kolotuchin, S. V. Self-assembling dendrimers. *Science* 1996, 271, 1095–1098.
- Maraval, V.; Laurent, R.; Donnadieu, B.; Mauzac, M.; Caminade, A. M.; Majoral, J. P. Rapid synthesis of phosphorus-containing dendrimers with controlled molecular architectures: First example of surface-block, layer-block, and segment-block dendrimers issued from the same dendron. J. Am. Chem. Soc. 2000, 122, 2499–2511.
- 5. Majoral, J. P.; Caminade, A. M.; Maraval, V. The specific contribution of phosphorus in dendrimer chemistry. *Chem. Commun.* 2002, 2929–2942.
- Furer, V. L.; Vandyukova, I. I.; Vandyukov, A. E.; Majoral, J. P.; Caminade, A. M.; Kovalenko, V. I. FTIR and FT-Raman spectra and DFT vibrational analysis of phosphorus-containing dendrons. *Spectrochim. Acta Part A*, 2008, *71*, 1110–1118.
- Leclaire, J.; Gagiral, R.; Fery-Forgues, S.; Coppel, Y.; Donnadieu, B.; Caminade, A. M.; Majoral, J. P. Octa-substituted metal-free phthalocyanine as core of phosphorus dendrimers: A probe for the properties of the internal structure. J. Am. Chem. Soc. 2005, 127, 15762–15770.
- Caminade, A. M.; Majoral, J. P. Water-soluble phosphorus-containing dendrimers. *Prog. Polym. Sci.* 2005, 30, 491–505.
- Caminade, A. M.; Laurent, R.; Majoral, J. P. Characterization of dendrimers. Adv. Drug Deliv. Rev. 2005, 57, 2130–2146.
- Davis, A. P.; Ma, G.; Allen, H. C. Surface vibrational sum frequency and Raman studies of PAMAM G0, G1 and acylated PAMAM G0 dendrimers. *Anal. Chim. Acta* 2003, 496, 117–131.

- Bahr, U.; Deppe, A.; Karas, M.; Hillenkamp, F.; Giessman, U. Mass spectrometry of synthetic polymers by UV-matrix-assisted laser desorption/ionization. *Anal. Chem.* 1992, 64, 2866–2869.
- 12. Caminade, A. M.; Majoral, J. P. Nanomaterials based on phosphorus dendrimers. *Account Chem. Res.* 2004, *37*, 341–348.
- 13. Svenson, S.; Tomalia, D. A.Dendrimers in biomedical applications—Reflections on the field. *Adv. Drug. Deliv. Rev.* 2005, *57*, 2106–2129.
- Vogtle, F.; Gorka, M.; Hesse, R.; Ceroni, P.; Maestri, M.; Balzani, V. Photochemical and photophysical properties of poly(propylene amine) dendrimers with peripheral naphthalene and azobenzene groups. *Photochem. Photobiol. Sci.* 2002, *1*, 45–51.
- 15. Thomas, L. C. Interpretation of Infrared Spectra of Organophosphorus Compounds; Heydon and Sons: London, 1974.
- 16. Quin, L. D.; Verkade, J. G. *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; VCH Publishers Inc.: New York, 1994.