Azo-functionalized dendrimers

Kap-Soo Cheon, Peter M. Kazmaier, Sam-Rok Keum, Kuk-Tae Park, and Erwin Buncel

Abstract: We report the synthesis of azo-functionalized Starburst polyamidoamine (PAMAM) dendrimers. The following three systems of azo-functionalized PAMAM dendrimers were prepared by different synthetic routes: (*i*) phenylazo derivatives; (*ii*) naphthalimide azo derivatives; and (*iii*) phthalimide azo derivatives. Model compounds in each system were synthesized for spectroscopic comparison. Confirmation of structure was achieved using a combination of NMR and IR spectroscopy to ascertain the functional sites (i.e., the azo and the cyclic imides), while mass spectrometry and UV–vis spectrophotometry were employed to ascertain the extent of functionalization. Substitution by the azo pendent groups increased the thermal stability of PAMAM dendrimers (TGA weight loss of the naphthalimide azo-functionalized PAMAM dendrimers up to 300 °C, ca. 5%).

Key words: dendrimers, azo compounds, hydrazones, tautomerism, hydrogen bonding.

Résumé : On a réalisé la synthèse de dendrimères polyamidoamine (PAMAM) Starburst fonctionnalisés à l'azote. Faisant appel à diverses voies de synthèse, on a préparé trois systèmes de dendrimères PAMAM fonctionnalisés à l'azote, soit des dérivés phénylazo, des dérivés naphtalimideazo et des dérivés phtalamideazo. On a préparé des composés modèles de chaque système pour comparaison spectroscopique. La confirmation de la structure a été réalisée par une combinaison de spectroscopies RMN et IR qui ont permis de confirmer la présence des sites fonctionnels (par exemple, la fonction azo et les imides cycliques) alors que la spectrométrie de masse et la spectrophotométrie UV–vis a permis de déterminer le degré de fonctionnalisation. La substitution par des groupes azo pendants augmente la stabilité thermique des dendrimères PAMAM (lors de l'analyse thermogravimétrique jusqu'à 300 °C, la perte de poids des dendrimères PAMAM fonctionnalisés à l'azote par le naphtalimide est d'environ 5 %).

Mots clés : dendrimères, composés azo, hydrazones, tautomérie, liaison hydrogène.

[Traduit par la Rédaction]

Introduction

Starburst dendrimers are a new class of highly ordered and branched cascade molecules that have received a great deal of attention (1). Recently, functionalization of dendrimers has shown promising new applications in diverse areas, including materials sciences and life sciences, where applications in medical diagnostics have been proposed (2).

Azo functionalities have been inserted onto dendrimers both as inside linkers and as modifiers of the periphery (3). The resulting molecules have been utilized for their photoswitchable properties and investigated for applications in optical data storage systems, holographic gratings, and drug delivery systems as host molecules (3*e*).

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The photoconductive properties of azo compounds were discovered by Rau (4) in 1969, and several years later, the first commercial bisazo pigments (Chlorodiane Blue) for photogenerating pigments in bilayer xerographic devices appeared (5). Azo-functionalized linear polymers have shown promise in the development of electrographic imaging applications, particularly for photoreceptors in xerographic systems (6).

Photoconductivity in organic pigments proceeds primarily by the following two mechanisms: a so-called extrinsic and an intrinsic mechanism (7). The extrinsic mechanism takes advantage of sensitization at the pigment surface; that is to say, a hole-transporting molecule, such as a triarylamine, donates an electron to the exciton generated in the pigment to effect charge separation and hole injection. Surface-functionalized dendrimers have, potentially, a tremendous advantage, since the chromophores are arranged in a thin layer around an inert and impervious core. Thus, if photogeneration takes place in an azo-functionalized dendrimer, the exciton is confined to the surface and is constantly exposed to the hole-transporting sensitizer, and so very rapid and highly efficient hole injection should take place for these systems. We therefore undertook to synthesize a surface-functionalized dendrimer with azo couplers, which are known to have excellent photoimaging properties.

We report the functionalization of ethylenediamine-based Starburst dendrimers using mono-azo moieties. The reac-

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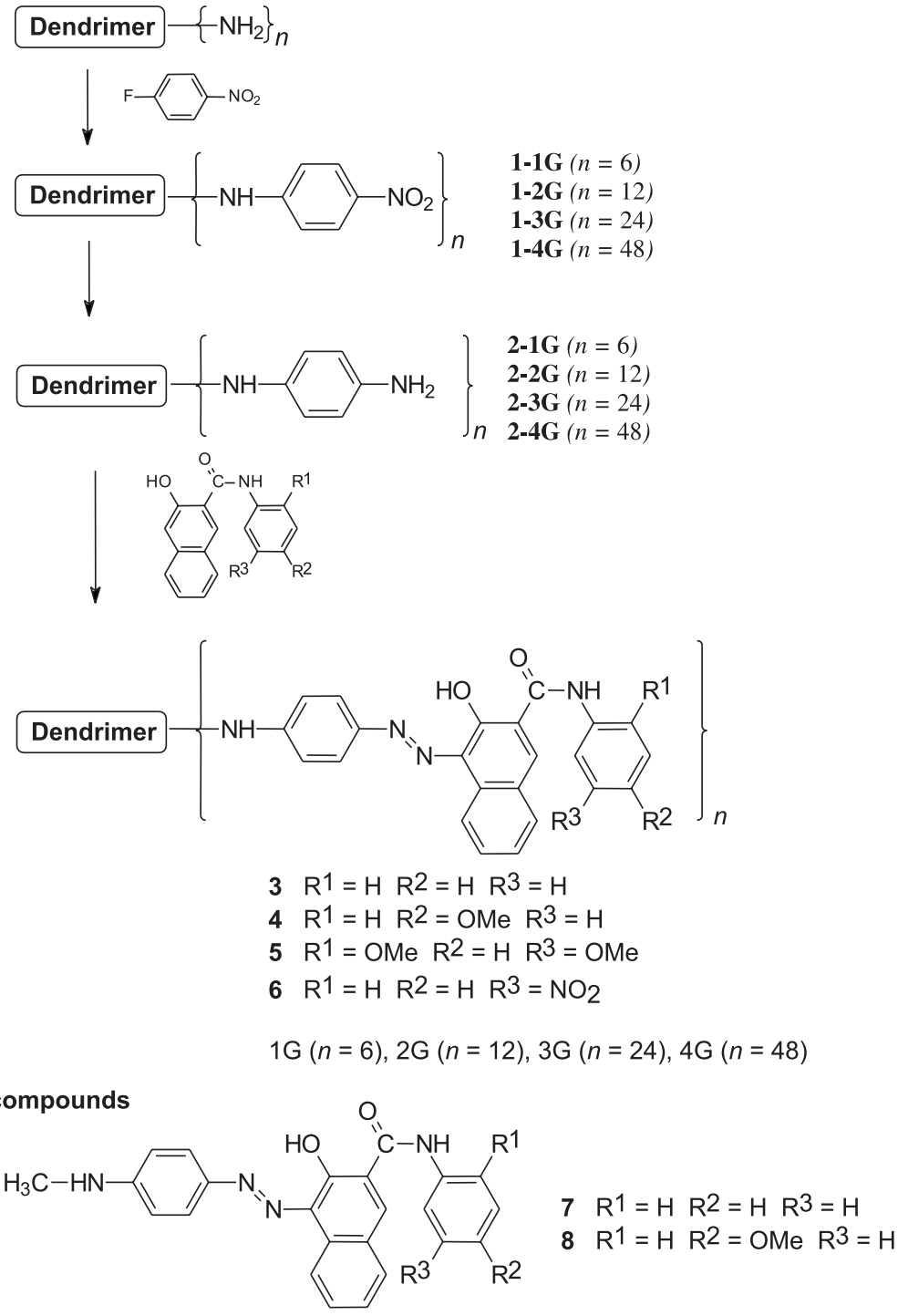
Scheme 1.

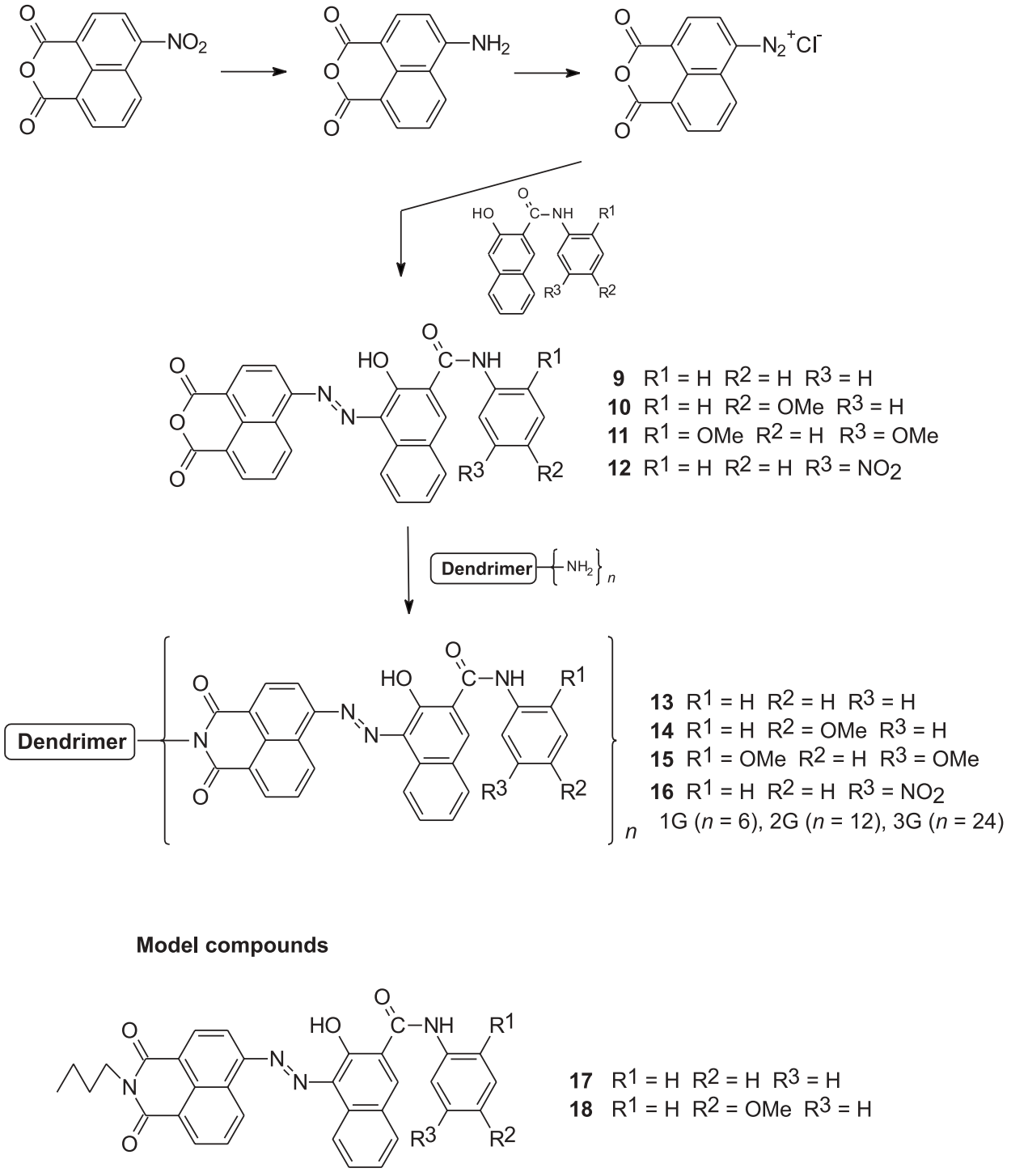


Model compounds

tions are shown in Schemes 1–3. A key feature of this chemistry is to select reaction conditions that take advantage of the water solubility of dendrimers and allow functionalization of the dendrimers under reaction conditions that do not lead to degradation of the dendrimer core. Polyamidoamine (PAMAM) dendrimers have been chosen for functionalization by azo dyes in this study because they are commercially available and have been well studied in terms of characterization and properties. The number of ending sites and molecular weights in each generation (G) of PAMAM dendrimers are as follows: 1st G (6 groups, 1043); 2nd G (12 groups, 2411); 3rd G (24 groups, 5147); 4th G (48 groups, 10 619). The present work encompasses up to the fourth generation of PAMAM dendrimers.

Since azo dyes and pigments containing the 2-naphthol-3-anilide moiety have shown high photoconductivity (low dark decay values; high photosensitivity) (8, 9), the derivatives of 2-naphthol-3-anilide were used as couplers for the synthesis of all azo-functionalized PAMAM dendrimers, as well as model compounds. The structure of the azo-modified gener-

Scheme 2.



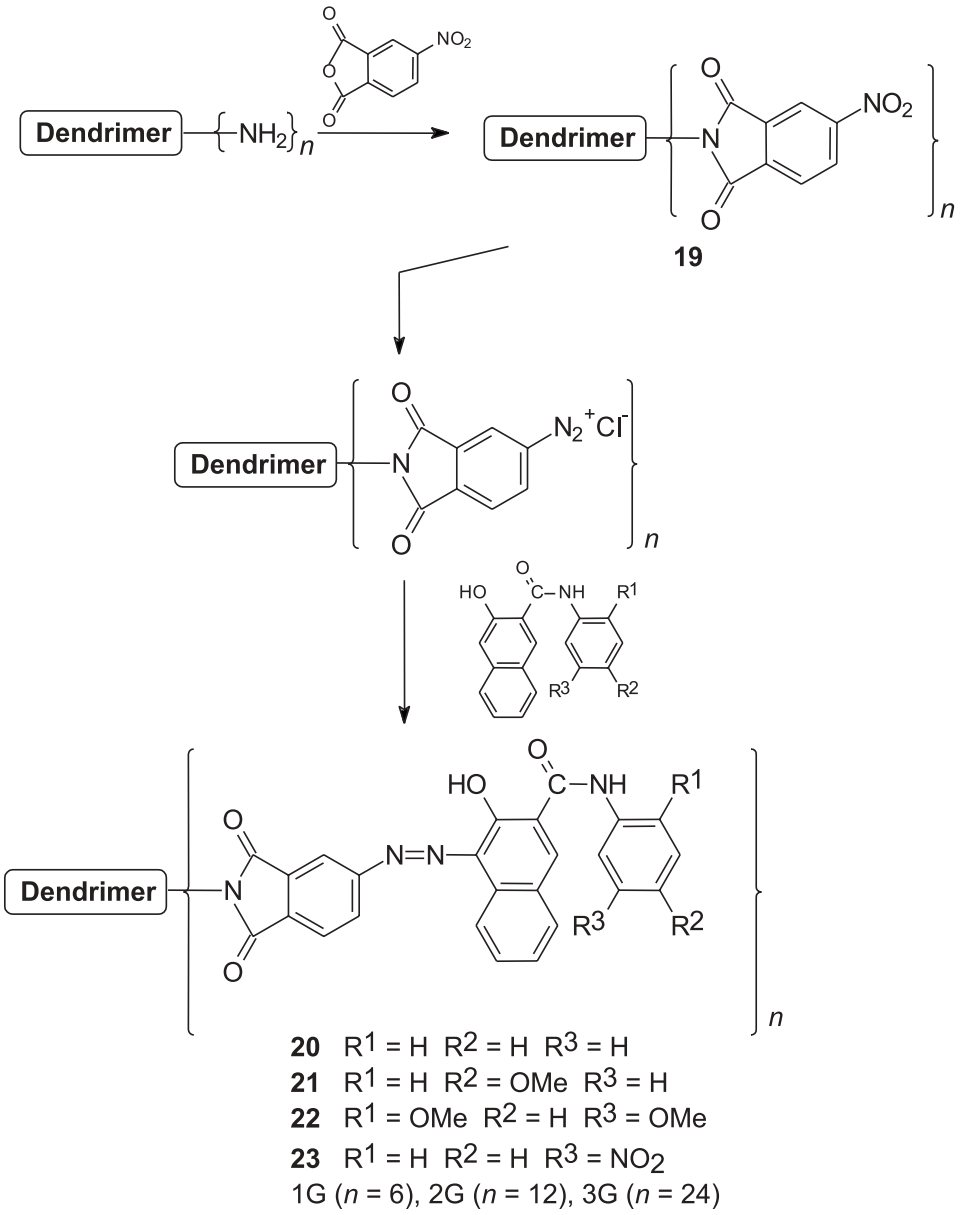
ation 1 of PAMAM dendrimers synthesized and characterized in this study is exemplified in Fig. 1 (see also Schemes 1–3). Hereafter, the symbol Dendrimer will be used for the generic structure of the PAMAM dendrimer.

Results and discussion

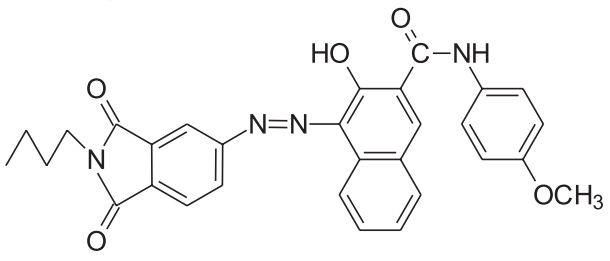
The following three systems of azo-functionalized polyamidoamine (PAMAM) dendrimers were examined in this study: (*i*) phenylazo derivatives (Scheme 1); (*ii*) naphthalimide azo derivatives (Scheme 2); (*iii*) phthalimide azo derivatives (Scheme 3). Note that, since the three systems contain the same 2-naphthol-3-anilide moiety, for simplicity the naming of the three systems excludes the 2-naphthol-3-anilide portion. Several model compounds for the three systems were prepared in order to validate the synthetic methods. Furthermore, the spectroscopic characteristics of the model compounds were useful for identifying structures of the azo-functionalized dendrimers.

Structural confirmation and the determination of the de-

Scheme 3.



Model compound



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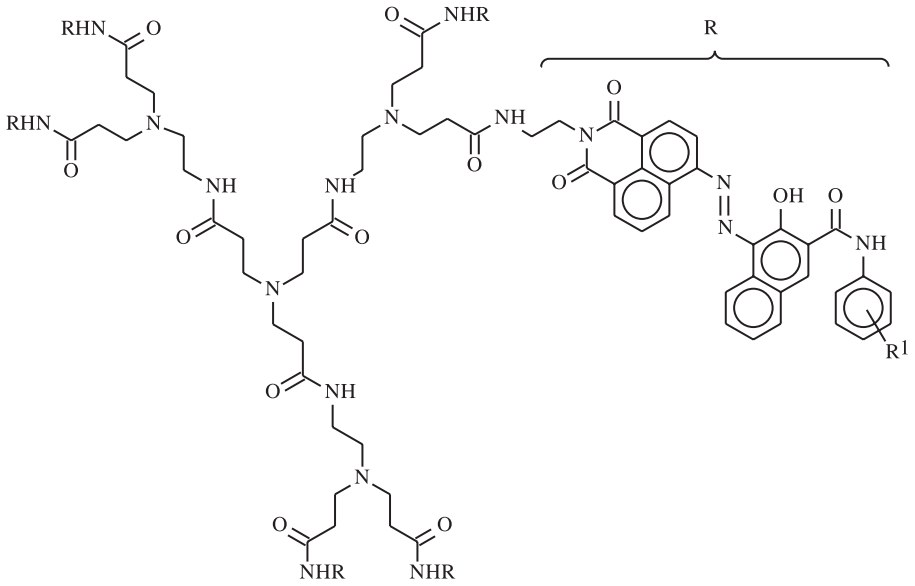
gree of functionalization were achieved using a combination of ^{1}H NMR, ^{13}C NMR, and IR spectroscopy to ascertain the site of azo coupling and the functional sites (i.e., the cyclic imides), while mass spectrometry and UV–vis spectrophotometry were employed to ascertain the extent of periphery substitution. UV–vis and ^{13}C NMR evidence revealed that the model compounds and dendrimers exist as equilibrium mixtures of azo and hydrazone tautomeric forms, with the

Fig. 1. Structure of naphthalimide azo-derivatized generation 1 PAMAM dendrimer.



R^1 = H (**13**), 4'-methoxy (**14**)
2', 5'-dimethoxy (**15**), 3'-nitro (**16**)

position of equilibrium being dependent on both structure and solvent medium.

Synthesis and characterization[2]

Phenylazo derivatives

The synthesis of phenylazo derivatives of polyamidoamine (PAMAM) dendrimers was achieved by the route shown in Scheme 1. Reactions of the various generations (from 1st G to 4th G) of PAMAM with *p*-fluoronitrobenzene provided the nitrophenyl moiety to the ending sites of the dendrimer. The structure of the nitrophenyl derivative **1** was identified by ^{1}H and ^{13}C NMR. Reduction of the pendent nitro group to the aromatic amine was accomplished by hydrogenation in the presence of Pd–C catalyst, giving almost quantitative yields of the amino compounds, **2**. ^{13}C NMR spectroscopy was used to verify complete reduction; the absence of a trace of carbon peaks corresponding to the nitro derivative indicated complete reduction. The resulting aminophenyl derivatives were used for formation of the diazonium salts, followed by the diazo-coupling reactions with 2-hydroxynaphthoic acid couplers, giving dendrimer compounds **3**–**6.** Model compounds **7** and **8** were synthesized by the same methods and fully characterized to facilitate the spectroscopic characterization of the resulting phenylazo derivatives of the dendrimer. The sites of azo coupling for the resulting azo-functionalized dendrimers were confirmed by ^{13}C NMR spectroscopy. The ^{13}C chemical shifts of the aromatic portion for the dendrimers are similar to those of the model compound **7**, which confirms the functionalization of the azo moiety at the surface of the dendrimer.

UV–vis spectroscopy was employed to determine the degree of functionalization. The molar extinction coefficient (ε) value at 384 nm of the nitrophenyl derivatives was taken as a measure of the degree of the functionalization by comparison with the corresponding ε value of *N*-methyl-4-nitroaniline (model compound). In other words, the ε value of the nitrophenyl derivative of the PAMAM dendrimer 1G, which has 6 reaction sites, should be 6 times that of the model compound if the reaction sites were fully functionalized. Adherence to the Beer–Lambert law was checked by measuring the absorbance *A* at different concentrations (from 1.04×10^{-5} to 1.51×10^{-4} mol L^{-1}) and plotting *A* vs. concentration. The degree of functionalization could be deduced from a comparison of the ε values of the dendrimer and the model compound, as summarized in Table 1.

According to the UV–vis results, the ending sites of the nitrophenyl-derivatized dendrimers **1**–**1G** to **1**–**4G** were not fully functionalized, i.e., the first generation of PAMAM, having 6 ending sites, was functionalized on 5 sites; for the 2nd G, 9 sites were functionalized; 17 sites and 30 sites were functionalized for the 3rd G and 4th G dendrimers, respectively. This lack of full functionalization with generation could be caused by reduced nucleophilicity of the ending amine moieties of the dendrimers with increasing generation because of crowdedness of the dendrimer surface.

Comparison of ε values between the azo-functionalized dendrimers **3** and the model compound **7** provided the de-

[2] Spectroscopic data of compounds synthesized are provided as supplementary material. Copies of material on deposit may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2.

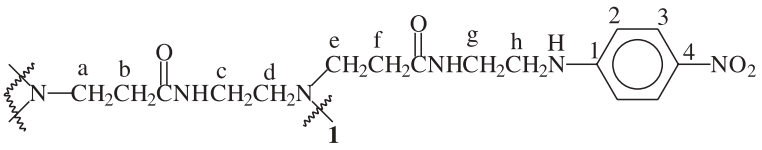
Table 1. Comparison of UV–vis data of *N*-methyl-4-nitroaniline (model compound) and nitrophenyl derivatives of PAMAM dendrimers.

Compounds	λ_{max} ($\varepsilon \times 10^4$)[a]	No. of ending sites	No. of functionalized sites[b]
N-Methyl-4-nitroaniline	384 (1.65)	1	1
p-Nitrophenyl deriv. (**1**–**1G**)	384 (8.65)	6	5.2
p-Nitrophenyl deriv. (**1**–**2G**)	384 (14.69)	12	8.9
p-Nitrophenyl deriv. (**1**–**3G**)	384 (27.74)	24	16.8
p-Nitrophenyl deriv. (**1**–**4G**)	384 (49.52)	48	30.0

Note: deriv. = derivative.

[a]UV–vis data were obtained in EtOH.

[b]These values were deduced from the comparison of ε values between the nitrophenyl derivatives and *N*-methyl-4-nitroaniline.



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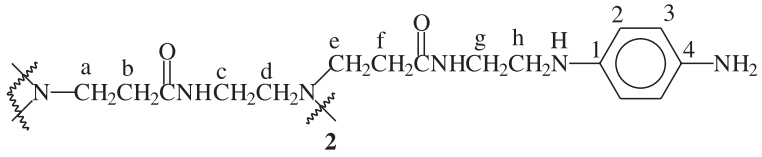

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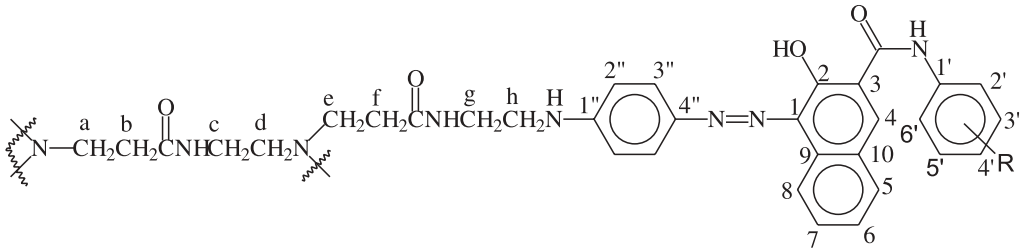
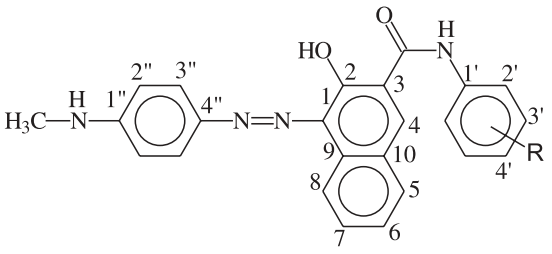


R = H (**3**), 4'-methoxy (**4**)
2', 5'-dimethoxy (**5**), 3'-nitro (**6**)



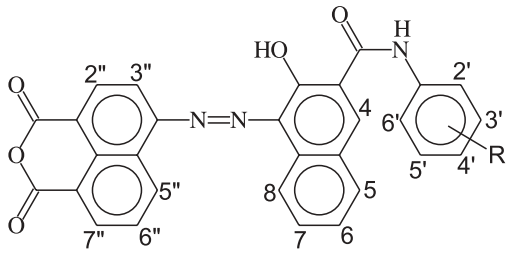
R = H (**7**),
4'-methoxy (**8**)

gree of functionalization summarized in Table 2. Though, in principle, the above method for evaluation of the number of azo pendent sites (i.e., loading) should be applicable, in the present system an uncertainty arises as a result of a solvent-dependent azo-hydrazone tautomerism, which is exhibited by both the model compounds and the dendrimers (vide infra) (10). In an attempt to circumvent this uncertainty, UV–vis measurements have been made in two solvents — toluene and 2,2,2-trifluoroethanol — these solvents having different polarities and H-bonding properties. The results presented in Table 2 show that there is fair agreement in the two sets of data, giving some credence to their validity. Both

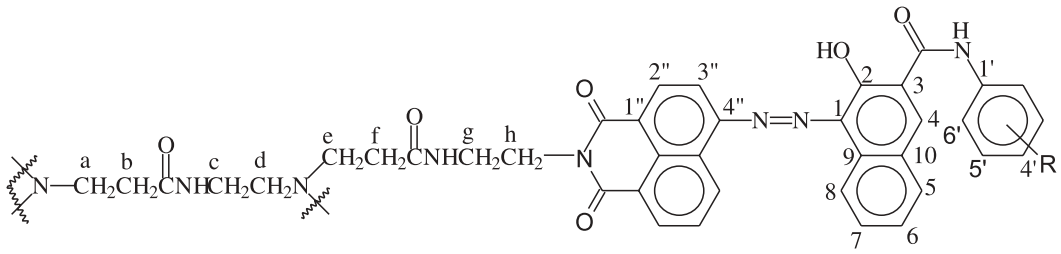
Table 2. Comparison of UV–vis data of model compound **7** with phenylazo derivatives of PAMAM dendrimers.

Compounds	No. of ending sites	*m/z* (ES) (calcd. MW)	TFE[a] λ_{max} ($\varepsilon\times10^4$)[b]	TFE[a] Calcd. No. azo pendent	Toluene λ_{max} ($\varepsilon\times10^4$)[b]	Toluene Calcd. No. azo pendent
Model (**7**)[c]	1	—	512 (1.42)	1	568 (1.50)	1
3–1G[c]	6	2979 (3237)	514 (7.23)	5.1	538 (6.96)	4.7
3–2G[d]	12	—	506 (10.4)	7.3	—	—
3–3G[d]	24	—	506 (21.0)	14.8	—	—
3–4G[d]	48	—	508 (31.5)	22.2	—	—

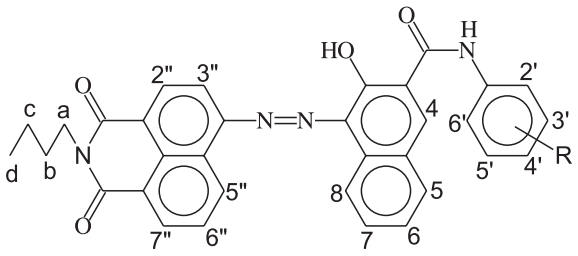
[a]2,2,2-Trifluoroethanol.
[b]These values were deduced from the comparison of ε values between dendrimers and the model compound.
[c]Stock solution was made in DMF.
[d]Stock solution was made in water.



R = H (**9**), 4'-methoxy (**10**)
2', 5'-dimethoxy (**11**), 3'-nitro (**12**)



R = H (**13**), 4'-methoxy (**14**)
2', 5'-dimethoxy (**15**), 3'-nitro (**16**)



R = H (**17**),
4'-methoxy (**18**)

sets show that there is incomplete functionalization. The number of azo pendent groups is similar to that for the *p*-nitrophenyl derivatives shown in Table 1, which indicates that the crucial step for this synthesis is the nucleophilic aromatic substitution reaction with *p*-fluoronitrobenzene.

The results of the degree of functionalization deduced from UV–vis data were comparable with those obtained from MS (ES) data. A series of multiply charged species (A_5–A_{10}) was recognized by the automated MS spectrometer. For example, in the case of dendrimer **3–1G**, multiply

Table 3. Comparison of UV–vis data of model compound **17** with naphthalimide azo derivatives of PAMAM dendrimers and MS (MALDI) data of dendrimers.

Compounds	No. of ending sites	*m/z* (MALDI) (calcd. MW)	Toluene		TFE	
			λ_{max} ($\varepsilon\times10^4$)	Calcd. No. azo pendent	λ_{max} ($\varepsilon\times10^4$)	Calcd. No. azo pendent
Model (**17**) [a]	1	—	536 (1.38)	1	530 (1.44)	1
(**13–1G**) [b]	6	3824 (3857)	518 (8.20)	5.9	504 (9.86)	6.8
(**14–1G**) [b]	6	3903 (4037)	528 (8.48)	6.1	502 (9.95)	6.9
(**15–1G**) [b]	6	4209 (4217)	512 (8.21)	6.0	498 (9.81)	6.8
(**16–1G**) [b]	6	4196 (4127)	512 (8.23)	6.0	502 (9.87)	6.9

[a]Stock solution was made in $CHCl_3$.
[b]Stock solution was made in DMSO.

charged peaks (A_8, A_7, etc.) yielded an average *m/z* 2978.53, which corresponds to the mass of a five-sites-functionalized dendrimer (Table 2). A series of multiply charged species originated from one species, while other series of multiply charged species were not found. Thus, the MS spectrum showed that dendrimer **3–1G** is the homogeneously five-sites-functionalized dendrimer by the azo moiety.

Naphthalimide azo derivatives

The synthetic method for the naphthalimide azo-functionalized dendrimers is described in Scheme 2. Initially, various azo dyes containing the naphthoic anhydride moiety were synthesized, using a standard diazo-coupling reaction. Then, the naphthoic anhydride moiety was attached to the ending sites of the dendrimers as the cyclic imides. The synthetic advantage of this method over the phenylazo system is that problems caused in purification of the modified PAMAM dendrimers formed in each step would be diminished, since attachment of the azo moiety to the dendrimer only occurred in the last step.

In the first step of the reaction sequence (Scheme 2), hydrogenation of the nitro group produced the amino compound, followed by a standard diazo coupling with the couplers to give the naphthoic anhydride azo compounds (**9–12**). These were coupled with PAMAM dendrimers by cyclic imide formation to give the azo-functionalized dendrimers (**13–16**). For the higher generations of PAMAM (2G and 3G), **9** was chosen for cyclic imide formation with the dendrimers. The model compounds (**17**, **18**) for this system were also synthesized. In the final step, *n*-$BuNH_2$ was used as the model compound for the PAMAM dendrimer, to determine the optimum reaction for the dendrimer synthesis and to compare its spectroscopic characteristics with those of the dendrimers. Two model compounds, **17** and **18**, were prepared.

The compounds **9–12** were fully characterized by NMR, IR, and CI mass spectroscopy. IR spectroscopy was specially useful for the characterization because the cyclic anhydride moiety shows two strong C=O stretching bands, resulting from asymmetrical and symmetrical C=O stretching modes; e.g., **9** (1773, 1734 cm^{-1}), **10** (1768, 1731 cm^{-1}), **11** (1771, 1734 cm^{-1}), and **12** (1773, 1736 cm^{-1}).

The model compounds (**17**, **18**) were first fully characterized. Formation of the cyclic imide linkage was indicated by the following: (*i*) ^1H NMR, the peak at 4.16 parts per million (ppm) being ascribed to the methylene protons attached to the cyclic imide nitrogen and (*ii*) IR C=O stretching bands for the naphthoic anhydrides, which shift to lower values because of the resonance effect of the imide linkage.

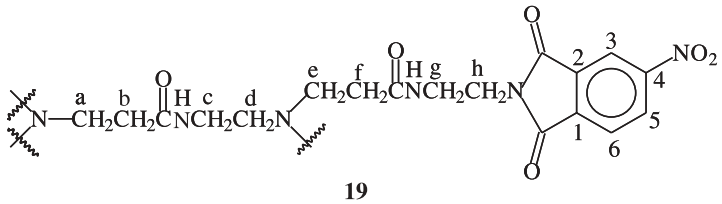
The naphthalimide azo-functionalized dendrimers (**13–16**) were insoluble in common organic solvents, making it difficult to obtain well-resolved ^1H and ^{13}C NMR spectra, even at a higher temperature and using a 10 mm NMR tube. Although complete NMR data of the dendrimers cannot be reported because of poor resolution of the spectra, peaks at 4.14 ppm and at ca. 6.9–8.6 ppm correspond to the characteristic methylene protons attached to the nitrogen of the cyclic imide and the protons of the azo moiety, respectively. Another characteristic for the dendrimers (**13–16**) is the shift of the C=O IR stretching frequencies to lower values, indicating formation of the cyclic imide linkage; e.g., 1658 and 1697 cm^{-1} for **13**, 1655 cm^{-1} for **14**, 1658 cm^{-1} for **15**, and 1696 and 1661 cm^{-1} for **16**.

The degree of functionalization was determined through comparison of the UV data of dendrimers **13–16** with that of model compound **17**, measured in two solvents to lessen the uncertainty in interpretation of the results because of azo-hydrazone tautomerism. The results (Table 3) showed that the endings of the G1 dendrimers are fully functionalized by the azo naphthalimide fragment. Note that UV data for the higher generations of the dendrimers (**13–2G**, **13–3G**) could not be obtained because of their insolubility.

The molecular weights of the first generation of the azo-modified dendrimers were determined by MALDI (matrix-assisted laser desorption ionization) MS, Table 3 (MALDI results for the higher generations of the dendrimers (2nd G and 3rd G) could not be obtained because of their insolubility). The mass data of the dendrimers **13–1G** to **16–1G** are reasonably close to calculated values for the six-sites functionalized by the azo naphthalimide fragment, which places some confidence in the capacity of the UV method to allow for estimation of the degree of functionalization of the dendrimers.

Phthalimide azo derivatives

The synthetic design toward phthalimide azo derivatives of the PAMAM dendrimers was initially similar to that of the naphthalimide system, as follows: preparation of azo compounds containing the phthalic anhydrides, followed by cyclic imide formation with PAMAM dendrimers. However, difficulty was encountered in formation of the cyclic imide linkage because of ring strain in the five-membered phthalimide ring, contrasting with the six-membered ring in the naphthalimide system. When more vigorous reaction



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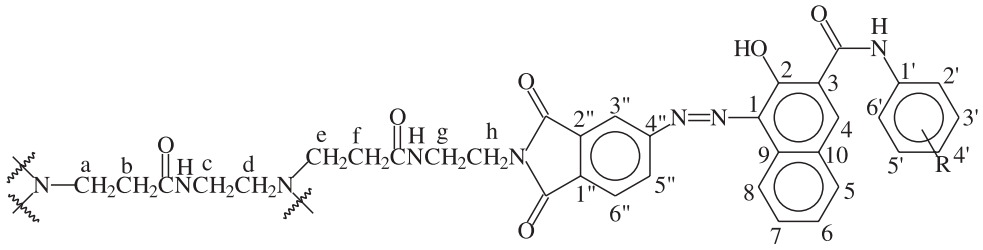
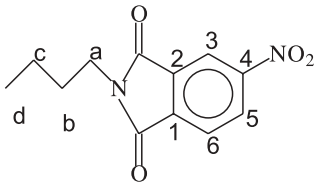


R = H (**20**), 4'-methoxy (**21**)
2',5'-dimethoxy (**22**), 3'-nitro (**23**)



24

conditions (i.e., high reaction temperature, 150–200 °C) were attempted (11), the azo chromophore was found to be unstable. Hence, an alternative synthetic strategy for this system was employed, as described in Scheme 3. The cyclic imide reaction between 4-nitrophthalic anhydride and the PAMAM dendrimers was first carried out at high temperature (130–150 °C), which was followed by catalytic hydrogenation to produce the corresponding amine derivatives and then diazo coupling with the couplers. For the synthesis of higher dendrimer generations (2nd G and 3rd G), naphthol AS-RL (**21** R^1 = H, R^2 = OMe, R^3 = H) was used as the coupler in the diazo coupling.

Formation of the cyclic imide linkage for dendrimer **19** was confirmed by ^{1}H and ^{13}C NMR, i.e., chemical shifts data for the CH_2 attached to the cyclic imide nitrogen (3.65 ppm in ^{1}H NMR and 36.57 ppm in ^{13}C NMR). The degree of functionalization in dendrimer **19** (G1, molecular weight 2093) was determined by MS (FAB+) ([M + 1]), which showed a peak at 2094, indicating full functionalization.

The model compound **25** was synthesized as an aid for structural verification of the phthalimide azo-functionalized dendrimers **20**–**23**. The ^{13}C NMR spectra (not shown) for the aromatic portion of **25** and of the dendrimer **21**–**1G** were compared. The similarity of the chemical shifts in the two ^{13}C NMR spectra provides confirmatory evidence for the structure of the dendrimer **21**. Another piece of information obtained from the ^{13}C NMR spectra (not shown) was that the peak corresponding to the CH_2 attached to the cyclic imide nitrogen appears at 36.82 ppm, in accord with the formation of the cyclic imide linkage. The cyclic imide linkage of the dendrimers (**20**–**23**) can be confirmed by the similar IR stretching frequency of the C=O group for the model and dendrimer compounds, e.g., 1770 and 1712 cm^{-1} for dendrimer **21** and 1769 and 1711 cm^{-1} for model compound **25**.

The UV data (measured in two solvents) of the phthalimide azo-functionalized dendrimers **20**–**23** are compared with that of the model compound **25** in Table 4. The results in 1,4-dioxane indicate that for 1G and 2G dendrimers, one site remains unfunctionalized, while for the 3G dendrimer, two sites are not functionalized by the phthalimide azo fragment. Note that the results in 2,2,2-trifluoroethanol (TFE) are slightly different from those in 1,4-dioxane, owing to an increase in the azo tautomer with dendrimer generations in TFE (10). Molecular weights of the dendrimers were also determined by MALDI MS and are summarized in Table 4. The MS data of the dendrimers (1G) are comparable to five-sites azo-functionalized dendrimers.

Thermal stability studies and xerographic properties

The thermal stability of the azo-functionalized dendrimers was evaluated by thermogravimetric analysis (TGA). The results of TGA weight-loss data obtained at 300 °C are summarized in Table 5. The TGA results of the azo-

Table 4. Comparison of UV–vis data of model compound (**25**) with phthalimide azo derivatives of PAMAM dendrimers and MS (MALDI) data of dendrimers.

Compounds	No. of ending sites	*m/z* (MALDI) (calcd. MW)	1,4-Dioxane λ_{max} ($\varepsilon\times10^4$)	1,4-Dioxane Calcd. No. azo pendent	TFE λ_{max} ($\varepsilon\times10^4$)	TFE Calcd. No. azo pendent
Model (**25**)[a]	1	—	500 (1.48)	1	498 (1.66)	1
(**20–1G**)[b]	6	3244 (3557)	498 (7.48)	5.1	486 (9.40)	5.7
(**21–1G**)[b]	6	3419 (3737)	498 (7.45)	5.0	486 (9.74)	5.9
(**22–1G**)[b]	6	3577 (3917)	498 (7.50)	5.1	486 (9.50)	5.7
(**23–1G**)[b]	6	3488 (3827)	498 (7.48)	5.1	490 (9.65)	5.8
(**21–2G**)[b]	12	—[c]	498 (15.8)	10.7	490 (19.5)	11.7
(**21–3G**)[b]	24	—[c]	498 (33.3)	22.5	488 (40.8)	24.6

[a]Stock solution was made in $CHCl_3$.
[b]Stock solution was made in DMSO.
[c]MALDI MS was attempted in order to obtain the molar mass of the higher generation of dendrimers, but this was not successful because of their insolubility.

Table 5. Summary of TGA (thermogravimetric analysis) weight-loss data of the azo-functionalized and non-functionalized dendrimers.

Compounds	TGA wt loss (%)[a]
PAMAM dendrimer	
1G	31.7
2G	28.7
3G	22.8
4G	22.1
Phenylazo derivatives	
Azo Na-AS deriv. (1G) **3**	17.7
Azo Na-RL deriv. (1G) **4**	8.3
Azo Na-BG deriv. (1G) **5**	22.6
Azo Na-BS deriv. (1G) **6**	20.5
Azo Na-AS deriv. (2G) **3–2G**	23.8
Azo Na-AS deriv. (3G) **3–3G**	23.9
Azo Na-AS deriv. (4G) **3–4G**	22.8
Naphthalimide azo derivatives	
Azo Na-AS deriv. (1G) **13**	4.6
Azo Na-RL deriv. (1G) **14**	5.6
Azo Na-BG deriv. (1G) **15**	6.1
Azo Na-BS deriv. (1G) **16**	6.0
Azo Na-AS deriv. (2G) **13–2G**	4.2
Azo Na-AS deriv. (3G) **13–3G**	4.0

[a]TGA wt loss data were obtained at 300 °C and with a heating rate of 20 °C/min under nitrogen.

functionalized dendrimers may be compared with those of the non-functionalized PAMAM dendrimers to investigate the effect of the azo moiety on thermal stability.

According to Table 5, the thermal stability of the azo-functionalized dendrimers shows no clear correlation with different substituents and with dendrimer generations. However, the azo-functionalized dendrimers are, in general, thermally more stable than the non-functionalized PAMAM dendrimers. The naphthalimide azo-functionalized dendrimers show especially good thermal stability (TGA wt loss ≈ 5% up to 300 °C). It can therefore be concluded that the thermal stability of the PAMAM dendrimers is increased through functionalization by the azo moiety.

Conclusions

In summary, three systems of the azo-functionalized PAMAM dendrimers were synthesized by different synthetic routes. The synthetic methods for the naphthalimide azo and the phthalimide azo systems were found to be more efficient than for the phenylazo system in terms of high yield, easy work-up, and high degree of functionalization. Significantly, formation of the six-membered cyclic imide in the naphthalimide azo system gave fully functionalized denderimers by the naphthalimide azo fragment. On the other hand, nucleophilic substitution involving *p*-fluoronitrobenzene and the dendrimeric amines employed for the phenylazo system revealed the limitation of the degree of functionalization with the higher dendrimer generations. ^1H and ^{13}C NMR and IR spectroscopy were employed to confirm structural identification of the dendrimers. Mass spectrometry (ES and MALDI) and UV–vis spectrophotometry (comparison of UV–vis data of the dendrimer compounds with those of the model compounds) were useful in the determination of the degree of functionalization. Thermogravimetric analysis showed that azo-functionalization increased the thermal stability of the PAMAM dendrimers.

Since one of the purposes of this study was to synthesize electronic materials that can show improved xerographic properties, and continuing with our investigations with dye and pigment molecules (e.g., azo (12), azoxy (13), spiropyran (14), and squaraine (15) dyes), the xerographic properties of the azo-modified dendrimers prepared will also be determined, via single-discharge measurements, surface potential vs. exposure (SPE) measurements, spectral sensitivity measurements, and xerographic cyclic stability measurements (16). The results of these studies will be reported in due course.

Experimental

Compounds synthesized were characterized by a combination of ^1H NMR, ^{13}C NMR, UV, IR, and mass spectroscopy and melting point and elemental analysis. ^1H and ^{13}C NMR spectra were obtained with a Bruker AM400 (^1H, 400.1 MHz; ^{13}C, 100.6 MHz) or Bruker AC - F 200 spectrometer (^1H, 200.1 MHz; ^{13}C, 50.3 MHz). Normally, $CDCl_3$

and DMSO-d_6 were used as the solvents and served as deuterium lock standards. Chemical shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ (δ ^1H = 7.24 ppm, δ ^{13}C = 77 ppm) and DMSO (δ ^1H = 2.50 ppm, δ ^{13}C = 49 ppm) in the solvents. Infrared spectra were obtained using a Bomen MB - 120 spectrophotometer with samples prepared as KBr disks. The low-resolution MS results were recorded with a Fison's VG Quattro (Triple-Quadrople MS–MS). Several techniques were used, as follows: chemical ionization (CI), fast atom bombardment (FAB), and electrospray (ES). MALDI (matrix-assisted laser desorption ionization) technique was used for dendrimer compounds. MALDI MS results were recorded with a Kompact MALDI III by Kratos Analytical, with sinapinic acid as the matrix. High-resolution MS analyses were performed at either the University of Ottawa (Ontario) or the Scripps Research Institute of California. UV–vis absorption spectra were obtained using a Hewlett-Packard HP8452A Diode Array spectrophotometer fitted with a thermostated cell compartment. Melting points were measured using a Thomas Hoover apparatus and are uncorrected. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, B.C.

For UV–vis spectrophotometric studies, the solvents DMSO and EtOH were purified by distillation from calcium hydride and magnesium, respectively (17). Other organic solvents used in this study were the following: *N*,*N*-dimethylformamide (DMF), 2,2,2-trifluoroethanol (TFE), acetonitrile, toluene, chloroform, 1,4-dioxane, acetone, methanol, and hexane. These solvents were of spectroscopic grade and were purified, when necessary, according to literature procedures (17).

Stock solutions (0.1–1 mmol) of the dendrimer compounds were prepared by accurately weighing 1–10 mg and dissolving these in 1–5 mL of DMF or DMSO in volumetric flasks, which were wrapped in aluminum foil so as to prevent possible photochemical processes. Stock solutions (1–10 mmol) of the model compounds were prepared in $CHCl_3$ or DMF and were stored in the refrigerator. All UV–vis spectra in this study were obtained by injecting 20–50 µL of the stock solution into a 10 mm cell containing 2.5 mL of the solvent, followed by shaking the cell a few times and allowing a few seconds to pass to allow any air bubbles entrapped on mixing to escape, before taking the spectrum.

Compounds were purified by a combination of several techniques, as follows: thin layer and column chromatography, recrystallization, sonication, and ultrafiltration. Thin layer chromatography (TLC) was performed using silica gel 60 F_{254} plates (BDH) in various eluting solvent systems. Silica gel 60 (BDH, 230–400 mesh) was used for column chromatography. An Amicon ultrafiltration cell model 8400 was used for purification of high generations of the dendrimers. A Branson model 2200 sonication bath was used in all experiments requiring sonication.

The couplers (naphthol AS-RL, naphthol AS-BG, and naphthol AS-BS) for the diazo coupling reactions were supplied by Xerox Research Centre of Canada (XRCC). Various generations of polyamidoamine (PAMAM) dendrimers (1–4 G) were purchased from Michigan Molecular Institute, while the other starting materials were obtained from Aldrich Chemical Company.

Preparation of dye compounds

Phenylazo derivatives of the PAMAM dendrimers

*p-Nitrophenyl derivative of PAMAM dendrimer (**1**)*

The first generation polyamidoamine dendrimer (0.50 g, 0.48 mmol) was dissolved in 10 mL absolute ethanol, and to this was added 4-fluoronitrobenzene (0.41 g, 2.9 mmol), and the reaction mixture was refluxed for about 12 h. The solvent was removed in a rotary evaporator; the yellow oil was dissolved in 50 mL water, and the aqueous solution was washed four times with 50 mL portions of chloroform to remove any unreacted 4-fluoronitrobenzene. Removal of the water in a rotary evaporator gave 0.60 g of product (71% yield) as a yellow oil.

The synthetic method for the *p*-nitrophenylation of the 2nd, 3rd, and 4th generation (G) of PAMAM followed closely the above. The yields obtained were as follows: 2nd G (81%), 3rd G (85%), and 4th G (85%). The NMR characteristics of the *p*-nitrophenyl derivative of the PAMAM dendrimer 1G (**1**) are as follows:

1: ^1H NMR (DMSO-d_6) δ: 8.16 (outer amide NH, s), 7.96 (H_3, d), 7.86 (inner amide NH, s), 6.65 (H_2, d), 3.89 (NH, s), 3.08 (H_g, H_c, t), 2.79 (H_h, t), 2.63 (H_d, t), 2.42 (H_e, H_a, t), 2.20 (H_f, H_b, t). ^{13}C NMR (DMSO-d_6) δ: 171.88 (C=O-outer), 171.46 (C=O-inner), 154.46 (C_1), 135.70 (C_4), 126.22 (C_3), 110.75 (C_2), 52.11 (C_d), 49.59 (C_e, C_a), 41.87 (C_g), 37.71 (C_h), 36.90 (C_c), 33.23 (C_b, C_f).

*p-Aminophenyl derivative of polyamidoamine dendrimer (**2**)*

To a solution of dendrimer **1** (0.65 g, 0.37 mmol) in 150 mL of a 1:1 (volume fraction) mixture of water–ethanol in a glass Parr shaker bottle was added palladium on charcoal (100 mg of 5% Pd–C). The reaction mixture was pressurized to 45 psi (1 psi = 6.894 kPa) of hydrogen, and the Parr hydrogenation apparatus was shaken at room temperature for about 12 h. The reaction mixture was then filtered to remove the Pd–C, and the solvent was removed in vacuo to give the products **2–1G** (89% yield), **2–2G** (83%), **2–3G** (81%), and **2–4G** (34%).

2: ^1H NMR (DMSO-d_6) δ: 8.01 (outer amide NH, s), 7.83 (inner amide NH, s), 6.39 (H_2, H_3, m), 3.82 (NH_2, NH, s), 3.17 (H_g, H_c, t), 2.95 (H_h, t), 2.65 (H_d, t), 2.42 (H_e, H_a, t), 2.20 (H_f, H_b, t). ^{13}C NMR (DMSO-d_6) δ: 171.61 (C=O-outer), 171.19 (C=O-inner), 139.97 (C_4), 139.12 (C_1), 115.53 (C_2), 113.67 (C_3), 52.14 (C_d), 49.65 (C_e, C_a), 43.89 (C_g), 36.90 (C_h), 35.95 (C_c), 33.30 (C_b, C_f).

Phenylazo derivatives of PAMAM dendrimers

To a solution of the *p*-aminophenyl polyamidoamine dendrimer derivative **2–1G** (0.58 g, 0.37 mmol) in aqueous hydrochloric acid (0.64 mL concd HCl and 2 mL water) cooled below 2 °C in ice-water was added, slowly with stirring, a solution of sodium nitrite (0.15 g, 2.20 mmol) in 2 mL water. The resulting diazonium salt solution was coupled with various couplers (naphthol AS, naphthol AS-BG, naphthol AS-RL, and naphthol AS-BS). The diazo-coupling reaction with naphthol AS as the coupler is described below.

To the solution of the diazonium salt solution was added, slowly with stirring, naphthol AS (0.58 g, 2.2 mmol) in 6 mL *N*,*N*-dimethylformamide (DMF) and 1.8 mL 10%

aqueous sodium hydroxide solution, keeping the temperature below 2 °C, which gave a purplish-red precipitate. After all the diazonium salt solution had been added, the reaction mixture was allowed to stand in an ice bath for 1 h with stirring. The resulting precipitate was filtered and washed with cold water several times to remove residual DMF. The unreacted naphthol AS in the crude product was removed by soxhlet extraction with acetonitrile to give 0.48 g of pure product (39% yield, mp 216–218 °C).

The diazo-coupling reaction with other couplers (naphthol AS-RL, naphthol AS-BG, and naphthol AS-BS) was carried out by same method as above. Naphthol AS-RL azo derivative (**4**; 10% yield, mp > 250 °C); naphthol AS-BG azo derivative (**5**; 10% yield, mp 182–184 °C); naphthol AS-BS azo derivative (**6**; 14% yield, mp 188–190 °C). The diazo coupling reaction between higher generations of the aminophenyl derivative of the dendrimer (2G, 3G, and 4G) and naphthol AS was carried out by same method as above. 2G (20% yield, mp 178–180 °C); 3G (12% yield, mp 207–209 °C); 4G (14% yield, mp 211–213 °C). The characteristics of the phenylazo derivatives of the PAMAM dendrimers are as follows:

3–6

*R = H, **3–1G***: IR (KBr disk) (cm^{-1}): 3189, 2922, 2853, 1736, 1662, 1660, 1539, 1444, 1264, 1174, 1017, 808, 752, 692, 515. ^1H NMR (DMSO-d_6) δ: 12.4 (OH, s), 11.3 (amide NH, s), 8.6 ($H_{4,8}$, bs), 8.2 (H_5, amide NH, bs), 7.8 ($H_{3''}$, $H_{2'}$, H_7, inner amide NH, bt), 7.4 (H_6, $H_{3'}$, bt), 7.1 ($H_{4'}$, dd), 6.6 ($H_{2''}$, d), 3.8 (NH, bs), 3.2 (H_g, H_c, bs), 2.9 (H_h, bs), 2.7 (H_d, bs), 2.4 (H_e, H_a, bs), 2.1 (H_f, H_b, bs). ^{13}C NMR (DMSO-d_6) δ: 171.6 (C=O-outer), 170.9 (C=O-inner), 162.0 (C=O-phenyl), 161.5 (C_2), 150.4 ($C_{1''}$), 138.9 (C_4), 138.3 ($C_{1'}$), 138.1 ($C_{4''}$), 133.9 (C_1), 133.6 (C_{10}), 129.5 (C_5), 129.5 (C_7), 128.4 ($C_{3'}$), 125.5 (C_3, C_9), 124.6 (C_6), 123.3 ($C_{4'}$), 121.5 ($C_{3''}$), 120.3 (C_8), 119.7 ($C_{2''}$), 112.4 ($C_{2''}$), 52.0 (C_d), 49.5 (C_e), 49.3 (C_a), 43.4 (C_g), 42.3 (C_h), 36.8 (C_c), 33.2 (C_b, C_f). MS *m/z* (ES) calcd. for $C_{161}H_{167}N_{36}O_{19}$: 3234.4; found: 2978.5.

*Azo naphthol AS derivative of the PAMAM dendrimer -2G (**3–2G**)*: IR (KBr disk) (cm^{-1}): 3246, 2928, 1655, 1597, 1549, 1445, 1384, 1199.

*Azo naphthol AS derivative of the PAMAM dendrimer -3G (**3–3G**)*: IR (KBr disk) (cm^{-1}): 3253, 2927, 1654, 1596, 1550, 1384, 1199, 1147.

*Azo naphthol AS derivative of the PAMAM dendrimer -4G (**3–4G**)*: IR (KBr disk) (cm^{-1}): 3270, 2935, 1658, 1596, 1550, 1447, 1384, 1199.

*R = 4′-methoxy, **4–1G***: IR (KBr disk) (cm^{-1}): 3332, 3077, 2963, 1666, 1604, 1547, 1512, 1262, 1069, 806, 696, 462. ^1H NMR (DMSO-d_6) δ: 12.5 (OH, s), 11.4 (amide NH, s), 8.6 (H_4, H_8, bs), 8.3 (H_5, bs), 8.2 (outer amide NH, s), 7.9 ($H_{3''}$, bs), 7.8 ($H_{2'}$, H_7, bt), 7.2 (H_6, bt), 7.1 ($H_{3'}$, d), 6.7 ($H_{2''}$, d), 4.2 (NH, bs), 3.6 (OCH_3, s), 3.2 (H_g, H_c, bs), 2.9 (H_h, bs), 2.6 (H_d, H_e, H_a, bs), 2.2 (H_f, H_b, bs).

*R = 2′, 5′-dimethoxy, **5–1G***: IR (KBr disk) (cm^{-1}): 3323, 2964, 1657, 1603, 1539, 1449, 1263, 1069, 865, 808, 755, 700, 469. ^1H NMR (DMSO-d_6) δ: 12.4 (OH, s), 11.4 (amide NH, s), 8.5 ($H_{4,8}$, bs), 8.2 (H_5, bs), 8.1 (outer amide NH, s), 8.0 ($H_{6'}$, bs), 7.9 (inner amide NH), 7.8 ($H_{3''}$, bs), 7.7 (H_7, bt), 7.4 (H_6, bt), 7.2 ($H_{3'}$, d), 7.1 ($H_{4'}$, d), 6.9 ($H_{2''}$, bs), 4.1 (NH, bs), 3.8 (OCH_3, bs), 3.2 (H_g, H_c, bs), 3.0 (H_h, bs), 2.6 (H_d, bs), 2.4 (H_e, H_a, bs), 2.2 (H_f, H_b, bs). ^{13}C NMR (DMSO-d_6) δ: 172.0 (C=O-outer), 171.4 (C=O-inner), 162.0 (C=O-phenyl), 161.5 (C_2), 153.0 ($C_{5'}$), 148.8 ($C_{1''}$), 142.8 ($C_{2''}$), 139.7 ($C_{4''}$), 138.3 (C_4), 134.5 (C_1), 131.0 (C_5), 130.5 (C_7), 130.0 (C_{10}), 128.7 ($C_{1'}$), 125.7 (C_6), 125.6 (C_3), 125.6 (C_9), 122.4 ($C_{3''}$), 120.8 (C_8), 113.9 ($C_{2''}$), 11.4 ($C_{3'}$), 107.2 ($C_{4'}$), 106.9 ($C_{6'}$), 56.3 (OCH_3 at $C_{2'}$), 55.0 (OCH_3 at $C_{5'}$), 50.3 (C_d), 49.4 (C_a, C_e), 44.2 (C_g), 44.0 (C_h), 37.0 (C_c), 32.9 (C_b, C_f).

*R = 3′-nitro, **6–1G***: IR (KBr disk) (cm^{-1}): 3309, 2944, 1656, 1604, 1535, 1262, 1072, 806, 738, 464. ^1H NMR (DMSO-d_6) δ: 12.4 (OH, s), 11.4 (amide NH, s), 8.5 ($H_{4,8}$, broad s), 8.2 (H_5, broad s), 8.1 (outer amide NH, s), 8.0 ($H_{6'}$, bs), 7.9 (inner amide NH), 7.8 ($H_{3''}$, bs), 7.7 (H_7, bt), 7.4 (H_6, bt), 7.2 ($H_{3'}$, d), 7.1 ($H_{4'}$, d), 6.9 ($H_{2''}$, bs), 4.1 (NH, bs), 3.8 (OCH_3, bs), 3.2 (H_g, H_c, bs), 3.0 (H_h, bs), 2.6 (H_d, bs), 2.4 (H_e, H_a, bs), 2.2 (H_f, H_b, bs).

Model phenylazo derivatives of PAMAM dendrimers

The model compounds **7** and **8** were synthesized by the same method as that used for the dendrimer. **7** (29% yield, mp 224 to 225 °C); **8** (32% yield, mp 214 to 215 °C). The characteristics of the model compounds (**7** and **8**) are as follows:

7, 8

*R = H (**7**)*: IR (KBr disk) (cm^{-1}): 3343, 2922, 2853, 1736, 1662, 1660, 1539, 1444, 1264, 1174, 1017, 808, 752, 692, 515. ^1H NMR (DMSO-d_6) δ: 12.48 (OH, s, 1H), 11.30 (amide NH, s, 1H), 8.60 (H_4, d, 1H), 8.60 (H_8, d, 1H), 7.98 (H_5, d, 1H), 7.82 ($H_{3''}$, d, 2H), 7.80 ($H_{2'}$, d, 2H), 7.67 (H_7, t, 1H), 7.46 (H_6, t, 1H), 7.39 ($H_{3'}$ dd, 2H), 7.13 ($H_{4'}$, dd, 1H), 6.80 (NH, d, 1H), 6.73 ($H_{2''}$, d, 2H), 2.99 (CH_3, s, 3H). ^{13}C NMR (DMSO-d_6) δ: 162.7 (C=O), 161.8 (C_2), 152.0 ($C_{1''}$), 138.7 ($C_{1'}$), 138.4 (C_4), 134.3 ($C_{4''}$), 133.6 (C_{10}), 129.9 (C_7), 129.9 (C_5), 128.9 ($C_{3'}$), 128.6 (C_9), 125.9 (C_1), 125.9 (C_3), 125.0 (C_6), 123.7 ($C_{4'}$), 122.4 ($C_{3''}$), 120.8 (C_8), 119.8 ($C_{2'}$), 112.3 ($C_{2''}$), 29.14 (CH_3). MS *m/z* (ES+): 397. 3 ([M + 1]). MS *m/z* (high-resolution EI) calcd. for $C_{24}H_{20}N_4O_3$: 396.1586; found: 396.1598. Anal. calcd. for $C_{24}H_{20}N_4$ (MW 396.16): C 72.73, H 5.05, N 14.14; found: C 72.21, H 4.98, N 14.08.

*R = 4′-methoxy (**8**)*: IR (KBr disk) (cm^{-1}): 3340, 3021, 2879, 1735, 1660, 1658, 1540, 1450, 1258, 1170, 1015, 809, 690. ^1H NMR (DMSO-d_6) δ: 12.48 (OH, s, 1H), 11.12 (amide NH, s, 1H), 8.57 (H_8, d, 1H), 8.56 (H_4, s, 1H), 7.95 (H_5,d, 1H), 7.80 ($H_{3''}$, d, 2H), 7.70 ($H_{2'}$, d, 2H), 7.66 (H_7, t, 1H), 7.45 (H_6, t, 1H), 6.95 ($H_{3'}$, d, 2H), 6.78 (NH, d, 1H), 6.72 ($H_{2''}$, d, 2H), 3.76 (OCH_3, s, 3H), 2.80 (CH_3, d, 3H). ^{13}C NMR (DMSO-d_6) δ: 162.2 (C=O), 161.9 (C_2), 155.5 ($C_{4'}$), 152.0 ($C_{1''}$), 138.3 (C_4), 134.2 ($C_{4''}$), 133.5 (C_{10}), 131.8 ($C_{1'}$), 129.7 (C_5), 129.7 (C_7), 128.5 (C_9), 125.9 (C_1), 125.9 (C_3), 124.9(C_6), 122.3 ($C_{3''}$), 121.3 ($C_{2'}$), 120.7 (C_8), 114.0 ($C_{3'}$), 112.2 ($C_{2''}$), 55.1 (OCH_3), 29.4 (CH_3). MS *m/z* (CI+): 426.9 ([M + 1]). MS *m/z* (high-resolution EI) calcd. for $C_{25}H_{22}N_4$: 426.1692; found: 426.1673. Anal. calcd. for $C_{25}H_{22}N_4O_3$ (MW 426.17): C 70.40, H 5.20, N 13.14; found: C 69.86, H, 5.30, N 13.10.

Naphthalimide azo derivatives of the PAMAM dendrimers

4-Amino 1,8-naphthoic anhydride

This compound is commercially available but, because of its high cost, was instead synthesized in 97% yield by the hydrogenation (Pd–C catalyst) of 4-nitro 1,8-naphthoic anhydride.

Azo naphthoic anhydrides (9–12)

To a solution of 4-amino-1,8-naphthoic anhydride (0.82 g, 3.85 mmol) in 100 mL DMF and 10 mL water, cooled to 2 °C, was added concd. HCl (1.60 mL, 10.9 mmol), and to the cooled reaction mixture was added, slowly with stirring, a solution of sodium nitrite (0.37 g, 3.85 mmol) in 6 mL water. The resulting diazonium salt solution was coupled with various couplers (naphthol AS, naphthol AS-RL, naphthol AS-BG, and naphthol AS-BS). **9** (58% yield, mp > 250 °C); **10** (64% yield, mp > 250 °C); **11** (66% yield, mp > 250 °C); **12** (77% yield, mp > 250 °C).

The characteristics of the azo naphthoic anhydrides (**9**–**12**) are as follows:

9–12

*R = H (**9**)*: IR (KBr disk) (cm^{-1}): 3133, 1773, 1734, 1675, 1596, 1308, 1154, 1011, 817, 757, 693, 541. ^1H NMR (DMSO-d_6) δ: 13.39 (O-H, s, 1H), 9.27 (H_5, d, 1H), 9.20 ($H_{5''}$, d, 1H), 8.70 (H_4, s, 1H), 8.53 ($H_{7''}$, d, 1H), 8.49 ($H_{2''}$, d, 1H), 8.07 ($H_{3''}$, d, 1H), 7.96 ($H_{6''}$, t, 1H), 7.80 ($H_{2'}$, $H_{6'}$, d, 1H), 7.80 (H_8, d, 2H), 7.62 (H_6, t, 1H), 7.40 ($H_{3'}$, $H_{5'}$, t, 2H), 7.28 ($H_{4'}$, d, 1H), 7.10 (H_7, t, 1H). MS *m/z* (CI+): 488.4 ([M + 1]). MS *m/z* (high-resolution FAB+) calcd. for $C_{29}H_{18}N_3O_5$: 488.1246; found: 488.1256.

*R = 4′-methoxy (**10**)*: IR (KBr disk) (cm^{-1}): 3022, 1768, 1731, 1670, 1573, 1194, 1019, 757, 530. ^1H NMR (DMSO-d_6) δ: 13.54 (O-H, s, 1H), 9.40 (H_5, d, 1H), 9.36 ($H_{5''}$,d, 1H), 8.62 (H_4, s, 1H), 8.54 ($H_{7''}$, d, 1H), 8.49 ($H_{2''}$, d, 1H), 8.02 ($H_{3''}$, d, 1H), 7.94 ($H_{6''}$, t, 1H), 7.76 (H_8, d, 1H), 7.72 ($H_{2'}$, $H_{6'}$, d, 2H), 7.58 (H_6, t, 1H), 7.25 (H_7, t, 1H), 6.96 ($H_{3',5'}$, d, 2H), 3.79 (CH_3, s, 3H). MS *m/z* (CI+): 518.3 ([M + 1]). MS *m/z* (high-resolution EI) calcd. for $C_{30}H_{19}N_3O_6$: 517.1274; found: 517.1174.

*R = 2′, 5′-dimethoxy (**11**)*: IR (KBr disk) (cm^{-1}): 3214, 2929, 1771, 1734, 1671, 1570, 1153, 1017, 760, 701. ^1H NMR (DMSO-d_6) δ: 13.54 (O-H, s, 1H), 9.40 (H_5, d, 1H), 9.36 ($H_{5''}$, d, 1H), 8.63 (H_4, s, 1H), 8.54 ($H_{7''}$, d, 1H), 8.49 ($H_{2''}$, d, 1H), 8.30 ($H_{6'}$, d, 1H), 8.02 ($H_{3''}$, d, 1H), 7.94 ($H_{6''}$, t, 1H), 7.76 (H_8, d, 1H), 7.58 (H_6, t, 1H), 7.25 (H_7, t, 1H), 7.00 ($H_{3'}$, d, 1H), 3.92 (OCH_3 at $C_{2'}$, s, 3H), 3.73 (OCH_3 at $C_{5'}$, s, 3H). MS *m/z* (CI+): 548.3 ([M + 1]). MS *m/z* (high-resolution FAB+) calcd. for $C_{31}H_{22}N_3O_7$: 548.1458; found: 548.1446.

*R = 3′-nitro (**12**)*: IR (KBr disk) (cm^{-1}): 3120, 1773, 1736, 1678, 1593, 1013, 756. ^1H NMR (DMSO-d_6) δ: 13.50 (O-H, s, 1H), 9.40 (H_5, d, 1H), 9.20 ($H_{5''}$, d, 1H), 8.95 ($H_{2'}$, d, 2H), 8.63 (H_4, s, 1H), 8.54 ($H_{7''}$,d, 1H), 8.49 ($H_{2''}$, d, 1H), 8.02 ($H_{3''}$, d, 1H), 7.96 ($H_{6''}$, t, 1H), 7.95 ($H_{4'}$, d, 1H), 7.80 ($H_{6'}$, d, 1H), 7.76 (H_8, d, 1H), 7.68 ($H_{5'}$, t, 1H), 7.58 (H_6, t, 1H), 7.25 (H_7, t, 1H). MS *m/z* (CI+) calcd. for $C_{29}H_{17}N_4O_7$: 533.5; found: 534.5 ([M + 1]).

Naphthalimide azo derivatives of PAMAM dendrimers

The PAMAM 1G dendrimer (33.5 mg, 0.029 mmol) solution (8.8% in methanol) was evaporated to remove the methanol, and the residue was dissolved in 2 mL 1-methyl-2-pyrrolidinone (NMP). The resulting dendrimer solution was added to a solution of azo naphthol-AS naphthoic anhydride **9** (0.1 g, 0.21 mmol) and DABCO (39.4 mg, 0.35 mmol) in 5 mL, and the reaction mixture was stirred at 85 °C for 2 h. After cooling to room temperature, 200 mL of toluene was added, and the precipitate that formed was filtered, washed with toluene and petroleum ether, and dried at 80 °C for about 12 h. The crude product was sonicated in water for 10 min to remove protonated DABCO and unreacted PAMAM. After filtration, the solid was sonicated in acetone for 10 min to remove excess DABCO and unreacted azo starting compound. The solid obtained on filtration was checked by TLC using acetone as eluent; this showed the absence of starting materials and DABCO. The yields and mp are as follows: **13**–**1G** (81%, 242–244 °C); **13**–**2G** (68%, 234–236 °C); **13**–**3G** (69%, 241–243 °C); **14** (81%, >250 °C); **15** (50%, >250 °C); **16** (75%, 244–246 °C).

The characteristics of the azo naphthalimide deivatives of PAMAM dendrimers are as follows:

*Azo napthol AS derivative (1G), **13**–**1G***

IR (KBr disk) (cm^{-1}): 3376, 2892, 2361, 1941, 1697, 1658, 1589, 1546, 1011, 777, 755. ^1H NMR (DMSO-d_6) δ: 9.0–7.1 (aromatic protons, broad m), 4.2 (NH, s), 3.5 (H_g, H_c, bs), 2.9 (H_h, bs), 2.6 (H_d, bs), 2.4 (H_e, H_a, bs), 2.2 (H_f, H_b, bs). MS *m/z* (MALDI) calcd. for $C_{219}H_{183}N_{37}O_{33}$: 3858.4; found: 3824.3.

*Azo naphthol AS derivative (2G), **13**–**2G***

IR (KBr disk) (cm^{-1}): 3361, 2103, 1687, 1506, 1363, 1023, 777, 755.

*Azo naphthol AS derivative (3G), **13**–**3G***

IR (KBr disk) (cm^{-1}): 3440, 2880, 2115, 1934, 1698, 1662, 1542, 1492, 1359, 1009, 775, 754.

*Azo naphthol AS-RL derivative (1G), **14**–**1G***

IR (KBr disk) (cm^{-1}): 3059, 2925, 2832, 1655, 1566, 1511, 1441, 1403, 1354, 1239, 1024, 777, 752. ^1H NMR (DMSO-d_6) δ: 12.4 (OH, s), 11.3 (amide NH), 8.6–6.6 (aromatic protons, broad m), 4.1 (NH, s), 3.8 (OCH_3, s), 3.2 (H_g, H_c, bs), 2.9 (H_h, bs), 2.7 (H_d, bs), 2.4 (H_e, H_a, bs), 2.2 (H_f, H_b, bs). MS *m/z* (MALDI) calcd. for $C_{225}H_{195}N_{37}O_{39}$: 4038.4; found: 3902.9.

*Azo naphthol AS-BG derivative (1G), **15**–**1G***

IR (KBr disk) (cm^{-1}): 3241, 2933, 2832, 1658, 1584, 1373, 1227, 1043, 777, 756. ^1H NMR (DMSO-d_6) δ: 13.0 (OH, s), 11.2 (amide NH), 8.8–6.6 (aromatic protons, broad m), 4.0 (NH, s), 3.7 (OCH_3 at $C_{2'}$, $C_{5'}$, bs), 3.4 (H_g, H_c, bs), 3.0 (H_h, bs), 2.4 (H_d, H_e, H_a, bs), 2.2 (H_f, H_b, bs). MS *m/z* (MALDI) calcd. for $C_{231}H_{207}N_{37}O_{45}$: 4218.5; found: 4208.6.

*Azo naphthol AS-BS derivative (1G), **16**–**1G***

IR (KBr disk) (cm^{-1}): 3237, 2935, 2830, 1696, 1661, 1586, 1546, 1344, 1013, 777, 736. ^1H NMR (DMSO-d_6) δ: 12.4 (OH, s), 11.3 (amide NH), 8.6–6.6 (aromatic protons, broad m), 4.1 (NH, s), 3.2 (H_g, H_c, bs), 2.9 (H_h, bs), 2.7 (H_d,

bs), 2.4 (H_e, H_a, bs), 2.1 (H_f, H_b, bs). MS *m/z* (MALDI) calcd. for $C_{219}H_{177}N_{43}O_{45}$: 4128.3; found: 4196.3.

Model naphthalimide derivatives of PAMAM dendrimers

The reaction conditions for synthesis of the model compounds (**17**, **18**) were closely similar to those for the dendrimer compounds; *n*-$BuNH_2$ was used as a model amine for the PAMAM dendrimer. **17** (29% yield, mp > 250 °C); **18** (28% yield, mp > 250 °C).

The characteristics of the model naphthalimide derivatives of the PAMAM dendrimers (**17** and **18**) are as follows:

17, 18

R = H (17): IR (KBr disk) (cm^{-1}): 3215, 2933, 1697, 1659, 1588, 1547, 1353, 1008, 767, 750. ^{1}H NMR ($CDCl_3$) δ: 14.10 (O-H, s, 1H), 11.12 (amide NH, s, 1H), 8.93 (H_4, s, 1H), 8.66 ($H_{5''}$, d, 1H), 8.62 ($H_{2''}$, d, 1H), 8.44 ($H_{7''}$, d, 1H), 8.40 (H_5, d, 1H), 8.29 ($H_{3''}$, d, 1H), 7.93 ($H_{6''}$, t, 1H), 7.76 ($H_{2'}$, $H_{6'}$, d, 2H), 7.70 (H_8, d, 1H), 7.65 (H_6, t, 1H), 7.49 (H_7, t, 1H), 7.38 ($H_{3'}$, $H_{5'}$, t, 1H), 7.15 ($H_{4'}$, t, 1H), 4.16 (H_a, t, 2H), 1.71–1.36 (H_b, H_c, m, 4H), 0.99 (H_d, t, 3H). ^{13}C NMR ($CDCl_3$) δ: 179.53 (C_2), 163.18 (C=O amide), 162.65 (C=O at $C_{1''}$), 161.19 (C=O at $C_{8''}$), 150.57 (C_4), 141.84 ($C_{4''}$), 138.09 ($C_{1'}$), 134.50 (C_{10}), 133.11 ($C_{1''}$), 132.19 ($C_{2''}$), 131.73 (C_8), 131.70 ($C_{5''}$), 131.56 (C_6), 129.17 (C_9), 129.05 ($C_{3'}$), 128.24 (C_7), 127.74 ($C_{6''}$), 127.24 (C_3), 126.29 (C_1), 125.77 ($C_{7''}$), 124.60 ($C_{4'}$), 123.58 ($C_{8''}$), 122.53 (C_5), 121.57 ($C_{10''}$), 120.79 ($C_{2'}$), 119.88 ($C_{9''}$), 112.96 ($C_{3''}$), 40.39 (C_a), 30.24 (C_b), 20.42 (C_c), 13.84 (C_d). MS *m/z* (CI+): 543.4 ([M + 1]). MS *m/z* (high-resolution EI) calcd. for $C_{33}H_{26}N_4O_4$: 542.1954; found: 542.1969.

R = 4′-methoxy (18): IR (KBr disk) (cm^{-1}): 3038, 1694, 1655, 1592, 1308, 1008, 823, 760, 553. ^{1}H NMR ($CDCl_3$) δ: 14.06 (O-H, s, 1H), 11.01 (amide NH, s, 1H), 8.93 (H_4, s, 1H), 8.66 ($H_{5''}$, d, 1H), 8.62 ($H_{2''}$, d, 1H), 8.44 ($H_{7''}$, d, 1H), 8.40 (H_5, d, 1H), 8.30 ($H_{3''}$, d, 1H), 7.92 ($H_{6''}$, t, 1H), 7.68 (H_8, d, 1H), 7.65 ($H_{2'}$, $H_{6'}$, d, 2H), 7.61 (H_6, t, 1H), 7.50 (H_7, t, 1H), 6.90 ($H_{3'}$, $H_{5'}$, d, 2H), 4.16 (H_a, t, 2H), 3.82 (OCH_3, s, 3H), 1.71–1.36 (H_b, H_c, m, 4H), 0.98 (H_d, t, 3H). ^{13}C NMR ($CDCl_3$) δ: 179.81 (C_2), 164.91 (C=O amide), 164.68 (C=O at $C_{1''}$), 163.25 (C=O at $C_{8''}$), 157.79 ($C_{4'}$), 151.86 (C_4), 142.59 ($C_{4''}$), 134.60 (C_{10}), 133.42 ($C_{2''}$), 133.32 ($C_{1''}$), 133.06 (C_8), 132.80 ($C_{5''}$), 132.17 (C_6), 129.49 ($C_{1'}$), 129.23 (C_9), 128.80 (C_7), 128.04 ($C_{6''}$), 127.20 (C_3), 126.70 ($C_{7''}$), 124.57 (C_1), 124.14 ($C_{2'}$), 122.87 ($C_{8''}$), 122.79 (C_5), 121.42 ($C_{10''}$), 118.68 ($C_{9''}$), 114.70 ($C_{3'}$), 113.24 ($C_{3''}$), 55.75 (OCH_3), 41.11 (C_a), 30.08 (C_b), 20.29 (C_c), 13.66 (C_d). MS *m/z* (CI+): 573.3 ([M + 1]). MS *m/z* (high-resolution FAB+) calcd. for $C_{34}H_{29}N_4O_5$, 573.2138; found: 573.2126. Anal. calcd. for $C_{34}H_{28}N_4O_5$ (MW 573.21): C 71.33, H 4.90, N 9.79; found: C 70.77, H 4.88, N 9.49.

Phthalimide azo derivatives of the PAMAM dendrimers

Phthalimide azo derivatives of PAMAM dendrimers

Cyclic imide formation between the PAMAM dendrimer and 4-nitrophthalic anhydride was carried out as follows: To a solution of 4-nitrophthalic anhydride (1.25 g, 6.48 mmol) in 5 mL NMP was added a solution of PAMAM (0.97 g, 0.93 mmol) and DABCO (0.63 g, 5.55 mmol) dissolved in 5 mL NMP, and the reaction mixture was stirred at 130 °C for 40 min. After cooling to room temperature, 200 mL of toluene was added to give a white precipitate, which was washed with toluene and acetone several times to remove excess starting materials. Yield 78% (**19–1G**); 88% (**19–2G**); 90% (**19–3G**). The characteristics of compound **19** are as follows:

19

IR (KBr disk) (cm^{-1}): 3288, 3073, 2948, 1781, 1720. 1656, 1539, 1437, 1396, 1348, 1194, 1160, 1063, 720. ^{1}H NMR (DMSO-d_6) δ: 8.59 (H_5, dd), 8.47 (H_3, d), 8.10 (H_6, d), 8.02 (outer amide NH, s), 7.70 (inner amide NH, s), 3.65 (H_h, t), 3.30 (H_c, H_g, t), 2.61 (H_d, t), 2.36 (H_a, H_e, t), 2.29 (H_b, H_f, t). ^{13}C NMR (DMSO-d_6) δ: 171.63 (outer C=O), 171.02 (inner C=O), 166.31 (C=O at C_1), 166.03 (C=O at C_2), 151.31 (C_4), 136.38 (C_2), 133.11 (C_1), 129.47 (C_6), 124.46 (C_5), 117.68 (C_3), 52.01 (C_d), 48.47 (C_e, C_a), 44.38 (C_g), 36.57 (C_h), 32.94 (C_c), 30.09 (C_b, C_f). MS *m/z* (FAB^+) calcd. for $C_{93}H_{99}N_{25}O_{33}$: 2093.7; found: 2094.0 ([M + 1]).

The nitro compound (**19**) was reduced by hydrogenation in the presence of Pd–C catalyst to give the amino derivative used for the diazo coupling reaction with the couplers (naphthol AS, AS-RL, AS-BG, and AS-BS). The experimental procedure for the diazo coupling reaction followed standard reaction conditions and gave the following yields and mp: **20** (58%, 230–232 °C); **21** (63%, 218–220 °C); **21–2G** (31%, 218–221 °C); **21–3G** (38%, 225 to 226 °C); **22** (56%, 220–222 °C); **23** (55%, 231–233 °C).

The characteristics of azo phthalimide derivatives of PAMAM dendrimers are as follows:

20–23

R = H, 20–1G: IR (KBr disk) (cm^{-1}): 3248, 3054, 1770, 1712, 1667, 1545, 1443, 1380, 1259, 1200, 1158, 1012, 891, 817, 751, 539. ^{1}H NMR (DMSO-d_6) δ: 12.4 (OH,s), 11.3 (amide NH, s), 9.0 (H_4, bs), 8.4 (H_5, bs), 8.1 ($H_{3''}$, outer amide NH, bs), 7.9 ($H_{6''}$, inner amide NH, bs), 7.8 ($H_{2'}$, $H_{6'}$, $H_{5''}$, m), 7.7 (H_6, t), 7.6 (H_8, t), 7.4 ($H_{7,3',5'}$, m), 7.1 ($H_{4'}$, t), 3.8 (NH, bs), 3.4 (H_g, H_c, bs), 3.2 (H_h, bs), 2.8 (H_d, bs), 2.3 (H_f, H_b, H_e, H_a, bs). MS *m/z* (MALDI) calcd. for $C_{195}H_{171}N_{37}O_{33}$: 3558.3; found: 3243.9.

R = 4′-methoxy, 21–1G: IR (KBr disk) (cm^{-1}): 3245, 3053, 2791, 1770, 1713, 1667, 1532, 1390, 1246, 1022, 826, 747, 529. ^{1}H NMR (DMSO-d_6) δ: 12.8 (OH, s), 11.3 (amide NH, s), 8.9 (H_4, s), 8.6 (H_5, bs), 8.1 ($H_{3''}$, outer amide NH, bs), 7.9 ($H_{6''}$, inner amide NH, bs), 7.8 ($H_{5''}$, d), 7.7 ($H_{2'}$, d), 7.6 ($H_{6,8}$, bs), 7.3 (H_7, bt), 6.9 ($H_{3'}$, d), 3.8 (NH, s), 3.7 (OCH_3), 3.4 (H_g, H_c, bs), 3.1 (H_h, bs), 2.7 (H_d, bs), 2.4 ($H_{e,a}$, bs), 2.2 (H_f, H_b, bs). ^{13}C NMR (DMSO-d_6) δ: 177.14 (C_2), 169.64 (C=O outer), 167.34 (C=O at $C_{1''}$), 166.90 (C=O at $C_{2''}$), 166.57 (C=O inner), 160.42 (C=O at C_3), 155.51 ($C_{4'}$), 147.14 (C_4), 143.13 ($C_{4''}$), 133.81 ($C_{1'}$), 133.39 ($C_{2''}$), 131.99 (C_6), 131.22 (C_{10}), 131.09 (C_9), 130.58 (C_8), 129.82 ($C_{1''}$), 128.29 (C_7), 126.90 (C_3), 126.14 (C_1), 125.36 ($C_{6''}$), 122.20 (C_5), 121.11 ($C_{2'}$), 121.00 ($C_{5''}$), 113.77 ($C_{3'}$), 110.44 ($C_{3''}$), 54.96 (OCH_3), 52.59 (C_d), 51.59 (C_e, C_a), 37.03 (C_g), 36.82 (C_h), 34.41 (C_c), 30.13 (C_f), 30.02 (C_b). MS *m/z* (MALDI) calcd. for $C_{201}H_{183}N_{37}O_{39}$: 3738.3; found: 3419.4.

R = 4′-methoxy (2G), ***21–2G***: IR (KBr disk) (cm^{-1}): 3246, 3050, 2789, 1772, 1712, 1668, 1533, 1388, 1250, 1158, 1013, 834, 750, 540.

R = 4′-methoxy (3G), ***21–3G***: IR (KBr disk) (cm^{-1}): 3245, 3052, 2789, 1770, 1712, 1670, 1530, 1380, 1250, 1156, 1013, 880, 750, 541.

R = 2′,5′-dimethoxy, ***22–1G***: IR (KBr disk) (cm^{-1}): 3244, 3049, 2790, 1771, 1712, 1668, 1530, 1400, 1250, 1015, 880, 750, 538. ^{1}H NMR (DMSO-d_6) δ: 12.4 (OH, s), 11.3 (amide NH, s), 8.9 (H_4, s), 8.3 ($H_{6'}$, bs), 8.2 (H_5, outer amide NH, bs), 8.0 ($H_{3''}$, d), 7.9 ($H_{6''}$, inner amide NH, bs), 7.8 ($H_{5''}$, bs), 7.5 (H_6, bs), 7.4 ($H_{7,8}$, bs), 6.8 ($H_{3'}$, $_{4'}$ bs), 4.1 (NH, bs), 3.9 (OCH_3 at $C_{2'}$, s), 3.7 (OCH_3 at $C_{5'}$, s), 3.2 (H_g, H_c, bs), 2.9 (H_h, bs), 2.7 (H_d, bs), 2.4 (H_e, $_a$, bs), 2.2 (H_f, H_b, bs). ^{13}C NMR (DMSO-d_6) δ: 177.40 (C_2), 170.26 (C=O outer), 167.32 (C=O at $C_{1''}$), 166.94 (C=O at $C_{2''}$), 166.51 (C=O inner), 160.27 (C=O at C_3), 152.96 ($C_{5'}$), 147.46 (C_4), 142.80 ($C_{4''}$), 142.67 (C_4), 133.12 ($C_{2''}$), 132.29 ($C_{6''}$), 131.23 (C_6), 130.75 (C_8), 130.40 (C_{10}), 130.12 (C_9), 128.40 ($C_{1'}$), 128.25 ($C_{1''}$), 126.69 (C_7), 126.03 (C_3), 125.89 (C_1), 121.11 (C_5), 118.50 ($C_{5''}$), 117.98 ($C_{3''}$), 111.48 ($C_{3'}$), 107.59 ($C_{4'}$), 106.85 ($C_{6'}$), 56.39 (OCH_3 at $C_{5'}$), 55.17 (OCH_3 at $C_{2'}$), 51.67 (C_d), 49.17 (C_e, C_a), 37.02 (C_g), 36.81 (C_h), 34.40 (C_c), 30.13 (C_f), 30.01 (C_b). MS *m/z* (MALDI) calcd. for $C_{207}H_{195}N_{43}O_{45}$: 4002.3; found: 3577.4.

R = 3′-nitro, ***23–1G***: IR (KBr disk) (cm^{-1}): 3250, 3052, 1772, 1710, 1667, 1548, 1390, 1268, 1100, 1014, 890, 750, 540. ^{1}H NMR (DMSO-d_6) δ: 12.4 (OH, s), 11.3 (amide NH, s), 8.8–7.0 (aromatic protons, m), 3.8 (NH, bs), 3.2 (H_g, H_c, bs), 2.8 (H_h, bs), 2.7 (H_d, bs), 2.4 (H_e, $_a$, bs), 2.2 (H_f, H_b, bs). MS *m/z* (MALDI) calcd. for $C_{195}H_{165}N_{43}O_{45}$: 3828.2; found: 3488.2.

Model phthalimide derivatives of PAMAM dendrimers

The experimental procedure for the model azophthalimide derivatives of the PAMAM dendrimer was identical to that used for the dendrimers.

The cyclic imide reaction between 4-nitrophthalic anhydride and *n*-$BuNH_2$ was carried out according to literature procedure (18), to give **24** (81% yield). The NMR and IR characteristics of **24** are as follows:

24

IR (KBr disk) (cm^{-1}): 3111, 3055, 2948, 2870, 1771, 1702, 1623, 1536, 1439, 1402, 1347, 1069, 1051, 940, 866, 710, 603. ^{1}H NMR (DMSO-d_6) δ: 8.62 (H_5, dd, 1H), 8.48 (H_3, d, 1H), 8.11 (H_6, d, 1H), 3.61 (H_a, t, 2H), 1.62–1.26 (H_b, H_c, m, 4H), 0.90 (H_d, t, 3H). ^{13}C NMR (DMSO-d_6) δ: 166.30 (C=O at C_2), 166.03 (C=O at C_1), 151.30 (C_4), 136.31 (C_2), 133.04 (C_1), 129.48 (C_6), 124.40 (C_5), 117.69 (C_3), 37.66 (C_a), 29.80 (C_b), 19.43 (C_c), 13.43 (C_d).

Hydrogenation of the nitro compound **24** in the presence of Pd–C catalyst gave the amino compound (93% yield), which was used for the standard diazo coupling reaction with coupler (naphthol AS-RL), giving the model compound (**25**); 82% yield, mp 169 to 170 °C.

The characteristics of the model compound (**25**) are as follows:

IR (KBr disk) (cm^{-1}): 3246, 2940, 2867, 2863, 1769, 1711, 1672, 1608, 1544, 1499, 1445, 1382, 1245, 1199, 1158, 1010, 822, 748, 533. ^{1}H NMR ($CDCl_3$) δ: 14.94 (OH, s, 1H), 11.03 (amide NH, s, 1H), 8.84 (H_4, s, 1H), 8.31 (H_5, d, 1H), 8.02 ($H_{3''}$, d, 1H), 7.86 ($H_{6''}$, d, 1H), 7.75 ($H_{5''}$, dd, 1H), 7.63 ($H_{2'}$, d, 1H), 7.60 (H_6, t, 1H), 7.60 (H_8, d, 1H), 7.40 (H_7, t, 1H), 6.85 ($H_{3'}$, d, 1H), 3.79 (OCH_3, s, 3H), 3.69 (H_a, t, 2H), 1.68 (H_b, m, 2H), 1.40 (H_c, m, 2H), 0.97 (H_d, t, 3H). ^{13}C NMR ($CDCl_3$) δ: 178.42 (C_2), 167.22 (C=O at $C_{1''}$), 167.11 (C=O at $C_{2''}$), 159.83 (C=O at C_3), 155.82 ($C_{4'}$), 149.20 (C_4), 146.00 ($C_{4''}$), 134.06 ($C_{1'}$), 133.71 ($C_{2''}$), 131.48 (C_6), 131.17 (C_{10}), 130.82 (C_8), 130.52 (C_9), 128.31 ($C_{1''}$), 127.32 (C_7), 126.36 (C_3), 125.33 (C_1), 124.37 ($C_{6''}$), 121.92 (C_5), 121.04 ($C_{5''}$), 120.89 ($C_{2'}$), 113.60 ($C_{3'}$), 111.24 ($C_{3''}$), 55.15 (OCH_3), 37.86 (C_a), 30.53 (C_b), 20.05 (C_c), 13.59 (C_d). MS *m/z* (CI+): 523.3 ([M + 1]). MS *m/z* (high-resolution FAB+) calcd. for $C_{30}H_{27}O_5N_4$: 523.1981; found: 523.1970. Anal. calcd. for $C_{30}H_{26}N_4$ (MW 523.20): C 68.94, H 4.98, N 10.73; found: C 68.20, H 5.14, N 10.74.

Studies of thermal stability

Thermal analyses were performed under N_2 using a high-resolution TGA 2950 Thermogravimetric Analyzer at a heating rate of 20 °C/min.

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