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Dendrimers as Photochemical Reaction Media. Photochemical Behavior of Unimolecular and Bimolecular Reactions in Water-Soluble Dendrimers

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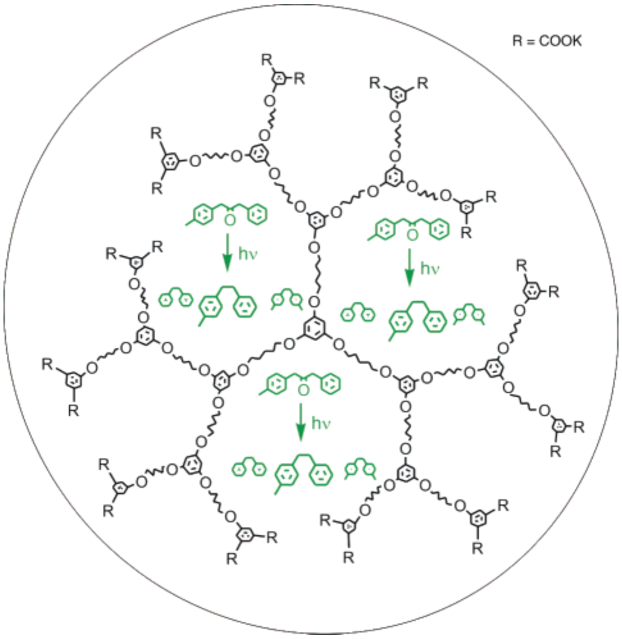

Synthesis and studies of poly(alkyl aryl ether) dendrimers, possessing carboxylic acid functionalities at their peripheries, are reported. 5-Bromopentyloxy methylisophthalate was utilized as the monomer to O-alkylate the phenolic hydroxyl groups of poly(alkyl aryl ether) dendrimers. Dendrimers of first, second, and third generations, possessing 6, 12, and 24 carboxylic acids, respectively, were thus prepared. These dendrimers were soluble in alkaline aqueous solutions, and the ensuing microenvironmental properties of the aqueous solutions were assessed by pyrene solubilization studies. Upon establishing the presence of nonpolar microenvironments within the dendritic structures, solubilizations of few organic substrates were conducted and their photochemical behaviors were assessed. Specifically, the photolysis of 1-phenyl-3-*p*-tolyl-propan-2-one and benzoin ethyl ether and photodimerization of acenaphthylene were conducted. These studies revealed that the product distribution and the "cage effect" were more distinct and efficient for the third generation dendrimer, than for the first and second generation dendrimers. The photochemical studies of carboxylic acid functionalized dendrimers were compared to that of hydroxyl group terminated poly(alkyl aryl ether) dendrimers.

Introduction

An outcome of the branches-upon-branches structural features present in dendrimers[1] is the evolution of defined inner cavities or microenvironments.[2] The presence of such inner cavities is more profound in the larger generation dendrimers than the lower generation dendrimers, due to spherical and globular shapes of the larger generation dendrimers. A number of studies have

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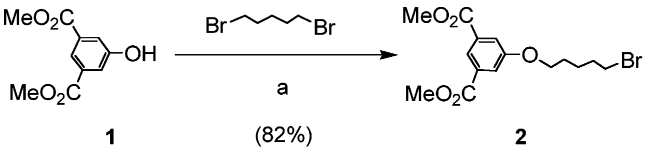
been conducted to encapsulate different types of organic molecules and metal ions inside the dendritic cavities.[2] Solubilization of water-insoluble organic substrates in aqueous solutions of dendrimers is an area of active interest.[3] The host ability of dendritic microenvironments forms a newer strategy to encapsulate guest molecules, and, in this respect, dendritic microenvironments might be considered analogous to well-known hosts, such as cyclodextrins[4] and micelles.[5,6] We have recently reported the synthesis of a series of phloroglucinol-based dendrimers, in which the phloroglucinol moiety acts as the core as well as the branch junctures and these branch junctures are linked with the aid of pentamethylene linkers.[7] Photochemical reactions of few water-insoluble substrates solubilized in aqueous phloroglucinol-based dendritic media showed the possibility of product selectivity in these novel reaction media. In few cases, such selectivities were comparable or better than in reaction media originating from traditional micelles.[8] In an effort to modify the peripheries of these phloroglucinol-based dendrimers with functional groups that would allow water solubility, carboxylic acid terminated dendrimers were synthesized. Upon synthesis, the encapsulation properties of these carboxylic acid modified dendrimers with photochemically active water-insoluble substrates were performed, in aqueous solutions. Synthesis and photochemical studies with the new carboxylic acid modified poly(alkyl aryl ether) dendrimers are reported herein.

Results and Discussion

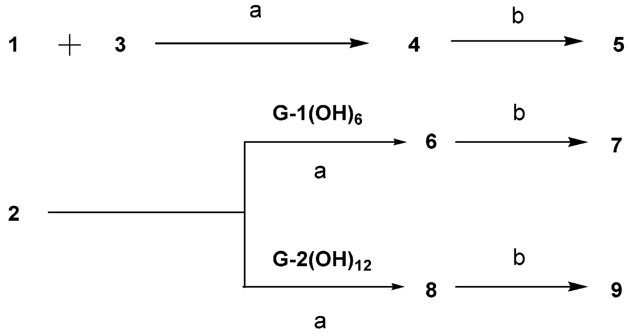
Synthesis. Syntheses of carboxylic acid functionalized dendrimers were performed by following protocols established previously for the synthesis of phloroglucinol-based poly(alkyl aryl ether) dendrimers. A divergent synthetic route was utilized accordingly to synthesize the carboxylic acid functionalized poly(alkyl aryl ether) dendrimers. 5-Bromopentyloxy methylisophthalate (**2**) was chosen to afford the carboxylic acid functionalities in the dendrimers. As the required monomer, diester **1** was functionalized with a bromopentyloxy linker, so as to afford the activated monomer **2** (Scheme 1). O-Alkylation of 1,3,5-tris-(5-bromopentyloxy)benzene (**3**) with **1** led to the isolation of G-1(CO_2Me)$_6$ (**4**), which upon hydrolysis afforded G-1(CO_2H)$_6$ (**5**) (Scheme 2). The monomer **2** was subjected to O-alkylation of hydroxy group terminated first (G-1(OH)$_6$) and second (G-2(OH)$_{12}$) dendrimers, containing 6 and 12 hydroxyl group,[7] respectively. The O-alkylation was performed in the presence of K_2CO_3 and **18-C-6**; in DMF and the corresponding methyl esters, **6** and **8** were obtained in good yields, respectively. Upon multiple O-alkylation of the preformed dendrimers, the methyl ester protecting groups were removed under basic conditions, so as to afford the second and third generation carboxylic acid terminated dendrimers, possessing 12 (G-2(CO_2H)$_{12}$) (**7**) and 24 (G-3(CO_2H)$_{24}$) (**9**) carboxylic acid groups, respectively, at their peripheries (Scheme 2). The methyl ester protected and free carboxylic acid containing dendrimers were characterized by IR, NMR spectroscopies, and elemental composition analysis, so as to establish their structural homogeneities. The molecular structures of the carboxylic acid terminated dendrimers **5**, **7**, and **9** are presented in Figure 1. Dendrimers **5**, **7**, and **9** were freely soluble in alkaline aqueous solutions pH > 9.

SCHEME 1[a]



[a] Reagents and conditions: (a) K_2CO_3, 2-butanone, 18-C-6 (cat.), 8 h.

SCHEME 2[a]



[a] Reagents and conditions: (a) K_2CO_3, 18-C-6 (cat.), 2-butanone or DMF, reflux, 12 h; (b) KOH, MeOH:THF:water (2:2:1), 15 h.

Pyrene as a Probe To Measure the Interior Hydrophobicity. Upon establishing the synthesis and water-soluble nature of the carboxylic acid terminated dendrimers, solubilization studies of pyrene in dendrimer solubilized aqueous solutions were conducted. Pyrene has a solubility in the range of 10^{-7} M in aqueous solutions and thus is practically insoluble in water. Thus, observing pyrene solubilization in aqueous solutions containing the host is an indirect reflection of the ability of the host to include an organic molecule. The encapsulation of the pyrene molecule can be followed by its fluorescence emission bands, typically the ratio of the I_1 and I_3 emission bands. The I_1/I_3 ratio is also a good measure of assessing the medium polarity.[9] Table 1 provides the

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(1) Many aspects of dendrimer chemistry are covered in: (a) *Top. Curr. Chem.* **1998**, *197*. (b) *Top. Curr. Chem.* **2000**, *210*. (c) *Top. Curr. Chem.* **2001**, *212*. (d) *Top. Curr. Chem.* **2002**, *217*.

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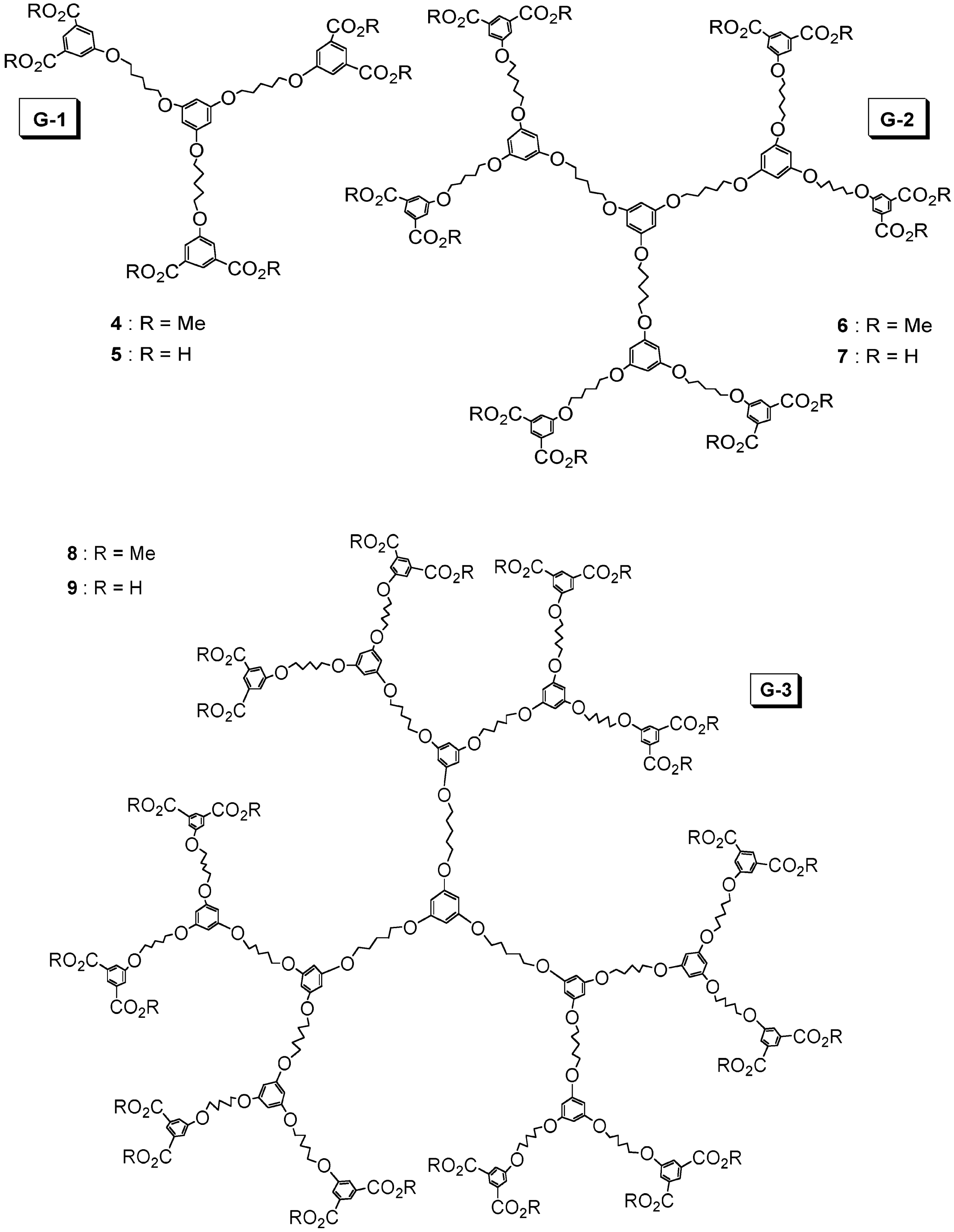


4 : R = Me
5 : R = H

6 : R = Me
7 : R = H

8 : R = Me
9 : R = H

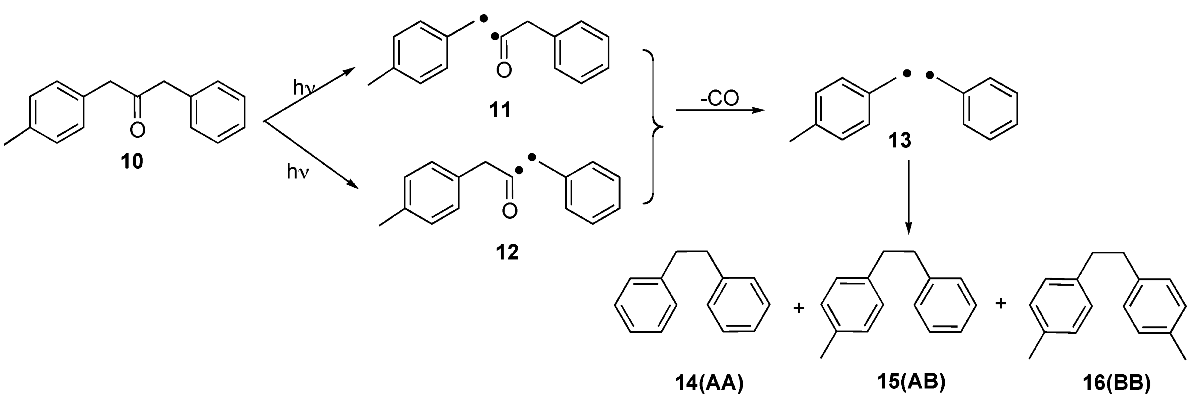
FIGURE 1. Structures of the carboxylic acid terminated first (**G-1**), second (**G-2**), and third (**G-3**) generation dendrimers.

TABLE 1. Ratio of I_1/I_3 Bands of Pyrene in Acid Dendrimer and Water

[pyrene] M	[host] M	phenolic dendrimers	I_1/I_3 ratio	acid dendrimers	I_1/I_3 ratio
1×10^{-4}	2×10^{-4}	G-3(OH)$_{24}$	1.18	G-3(CO$_2$H)$_{24}$	1.23
1×10^{-4}	2×10^{-4}	G-2(OH)$_{12}$	1.30	G-2(CO$_2$H)$_{12}$	1.47
1×10^{-4}	2×10^{-4}	G-1(OH)$_6$	1.48	G-1(CO$_2$H)$_6$	1.60
1×10^{-4}		water (pH > 9)	1.70	water (pH > 9)	1.70

ratios of I_1 to I_3 bands of pyrene upon its solubilization in aqueous solutions containing the carboxylic acid terminated dendrimers. A comparison of the I_1/I_3 ratio across the carboxylic acid terminated dendrimers showed an increasingly hydrophobic microenvironment being encountered by the pyrene molecule as the dendrimer

SCHEME 3



generation advanced. The peripheral hydrophilic region, constituted with carboxylic acid functionality and the relatively hydrophobic inner pentamethylene linker regions, should afford an increasing nonpolar microenvironment at the interior of the dendritic structure. Results of similar studies performed for the corresponding hydroxyl group terminated dendrimers,[8] reported previously, are also included in Table 1. Comparison of I_1/I_3 values obtained from these dendrimers reveals that the phenolic dendrimers are more hydrophobic than the carboxylic acid dendrimers.

Photochemistry of Organic Guests Included within the Dendrimer Core. Upon identifying the solubilization properties of the dendrimers, their ability to function as photochemical reaction media was studied, particularly, with respect to the unimolecular and bimolecular photochemical reactions. Unimolecular reactions involving photoysis of 1-phenyl-3-*p*-tolyl-propan-2-one (4-methyl dibenzyl ketone) and photolysis of benzoin ethyl ether were undertaken. Bimolecular photoreaction using the dendrimers as the media was concerned with the photodimerization of acenaphthylene. Results of these reactions are discussed individually below. In all of the cases studied, an analysis of the results involving the carboxylic acid terminated dendrimers is compared with that of the hydroxyl group terminated dendrimers.

Photolysis of 1-Phenyl-3-*p*-tolyl-propan-2-one. 1-Phenyl-3-*p*-tolyl-propan-2-one (**10**) upon photolysis undergoes α-cleavage leading to primary radical pairs (**11** and **12**) as shown in Scheme 3.[10,11] In hexane solution, diaryl ethane products **14** (**AA**), **15** (**AB**), and **16** (**BB**) were formed, through the secondary radical (**13**) in a 1:2:1 ratio. The cage effect for this reaction was calculated according to the equation:

$$\text{cage effect} = \frac{\mathbf{AB} - (\mathbf{AA} + \mathbf{BB})}{(\mathbf{AB} + \mathbf{AA} + \mathbf{BB})} \qquad (1)$$

Analysis of the product distribution, arising from the involvement of the dendrimers, revealed that the cage effect increased progressively as the generations advanced (Table 2). A cage effect of 0.5 was thus obtained for the third generation dendrimer, and this value was also higher, when compared to the dendrimer generations 1 and 2. Although cage effect in G-3 acid dendrimer is greater as compared to isotropic solution, the cage effect is still less when compared to the corresponding G-3 phenolic dendrimer (see footnote c in Table 2). Cage effect results suggest that the G-3 phenolic dendrimer is more confining (less open) than the G-3 acid dendrimer, the results of which are consistent with the pyrene polarity studies.

TABLE 2. Photolysis of 4-Methyl Dibenzyl Ketone in Water-Soluble Hosts

medium	host:guest	relative ratio AA	BB	AB	cage effect
hexane		1.4	1.0	2.4	0.00
aq KOH		1.6	1.0	2.8	0.04
G-1(CO_2H)$_6$	6:1	1.6	1.0	3.2	0.09
G-2(CO_2H)$_{12}$	2:1	1.8	1.0	4.4	0.18
G-3(CO_2H)$_{24}$	1:1	1.0	1.0	6.1	0.50

[a] [**10**] = 2.9 × 10^{-4} M; [G-1(CO_2H)$_6$] = 1.8 × 10^{-3} M; [G-2(CO_2H)$_{12}$] = 6 × 10^{-4} M; [G-3(CO_2H)$_{24}$] = 3 × 10^{-4} M. pH = 10−11.4. [b] Irradiation time G-1 = 12 h, G-2 = 20 h, G-3 = 48 h to achieve 30% conversion to photoproducts. [c] Cage effect in corresponding phenolic dendrimers G-1, G-2, and G-3 are 0.11, 0.42, and 0.77, respectively.

Photolysis of Benzoin Ethyl Ether. The second guest that we have investigated to ascertain the confinement provided by the acid dendrimers is benzoin ethyl ether (**17**). This substrate upon photolysis can lead to products arising from either cleavage (Norrish type I) or hydrogen abstraction (Norrish type II).[12] Type I products formed from triplet radical pair **19** are pinacol ether (**22**), benzil (**23**), and the rearrangement products (*ortho* isomer (**24**) and *para* isomer (**25**)) (Scheme 4).[13] Type II products formed from radical pair **18** include deoxybenzoin (**20**) and oxetanol (**21**).

In an organic solvent like hexane and in aqueous solution (pH = 7.0), type I products **22** and **23** were formed in greater amounts (97% yield), while in basic aqueous solution type II product deoxy benzoin (**20**) was the major product (Table 3). Reasons for the enhanced

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SCHEME 4

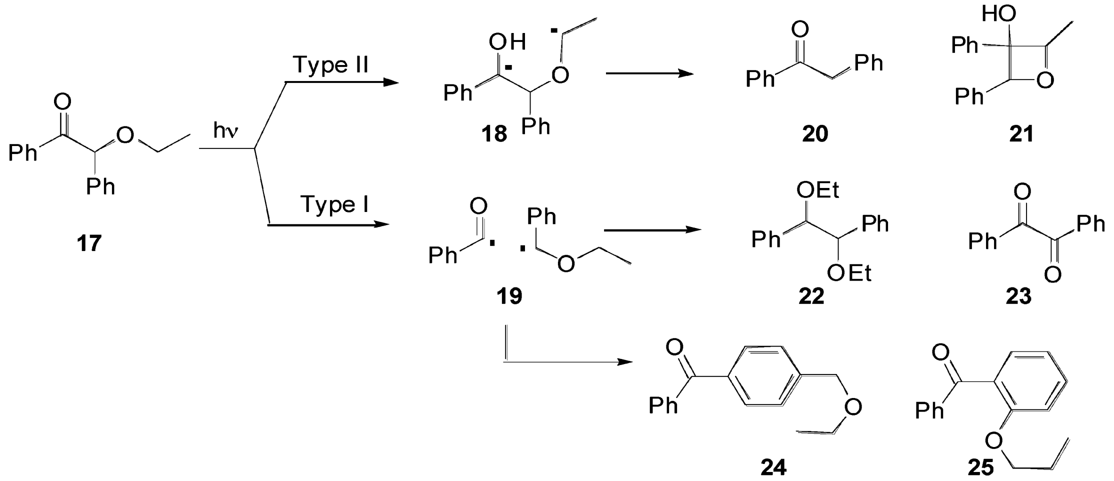


TABLE 3. Photolysis of Benzoin Ethyl Ether in Water-Soluble Hosts[a]

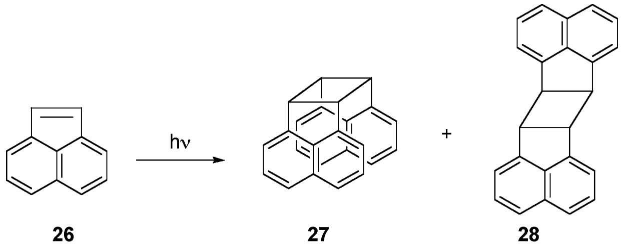
medium	**20**	**21**	**22**	**23**
hexane		4	54	40
water	10	5	82	3[d]
KOH[b]	70	3	23	4
G-1$(CO_2H)_6$	80	3	13	4
G-2$(CO_2H)_{12}$	88	5	2	5
G-3$(CO_2H)_{24}$	95	2	2	1
G-3$(OH)_{24}$[c]	21	57	1	

[a] G-1$(CO_2H)_6$ = 2.5 × 10^{-3} M, G-2$(CO_2H)_{12}$ = 8.4 × 10^{-4} M, G-3$(CO_2H)_{24}$ = 7.8 × 10^{-4} M, [benzoin ethyl ether] = 4.16 × 10^{-4} M. [b] pH ≈ 11. [c] In addition to the tabulated products [**20**–**23**], rearrangement products **24** and **25** were also formed in 8% and 14% yields, respectively. pH ≈ 10. [d] % yield of benzil is less because benzoyl triplet radical reacts to give benzaldehyde in aqueous solution. Benzaldehyde being volatile and soluble in water, % yield was not reported.

yield of **20** under basic conditions are yet to be understood. When benzoin ethyl ether encapsulated G-3 acid dendrimer was irradiated, deoxy benzoin is formed in 95% yield, while cage escape type I products **22** and **23** were formed only in trace amounts (Table 3). Because deoxybenzoin is formed in considerable amount in basic aqueous solution even in the absence of dendrimer, now the question arises whether the reaction is taking place within the hydrophobic pockets of the dendrimer or in basic aqueous solution. The absence of cage escape products **22** and **23** suggests that the photoreaction is probably taking place within the dendrimer. Despite the increased yield of Type II products (with respect to Type I) in both phenolic and carboxylic acid dendrimers, differences in product distribution between them are noteworthy. While in carboxylic acid dendrimers the main Type II product was deoxybenzoin, in phenolic dendrimer both oxetanol and deoxybenzoin were obtained. Further, in phenolic dendrimer rearrangement products **24** and **25** were obtained in an overall yield of 22% (G-3). These differences suggest the headgroup has a role in dictating the interior character of the dendrimers. Because of the complication by the basic medium, clear-cut conclusions concerning the origin of Type II products in carboxylic acid dendrimers could not be made.

Photodimerization of Acenaphthylene. With unimolecular reactions, we have shown that phenolic dendrimers are much more confining than the acid dendrimers. In continuation of this comparative studies, we have carried out a bimolecular reaction, photodimerization of acenaphthylene both in phenolic and carboxylic group terminated dendrimers. Acenaphthylene (**26**) on photolysis undergoes dimerization to form syn- and anti-dimers (Scheme 5).[14]

SCHEME 5



Dimerization can occur from both singlet and triplet states.[9] Syn- and anti-dimer ratios vary with the nature of the excited state, the concentration of acenaphthylene, and the polarity of the solvent. In a highly concentrated solution and from the S_1 state (short-lived excited state), acenaphthylene molecules being present in close proximity form the syn-dimer (**27**), whereas in dilute solution and from the T_1 state (long-lived), dimerization results in both syn- and anti (**28**)-dimers. Experimental results obtained with pyrene, 1-phenyl-3-*p*-tolyl-propan-2-one, and benzoin ethyl ether in acid and phenolic dendrimers made us conclude that acid dendrimers that are more open and less hydrophobic would be more effective in solubilizing organic guest molecules than phenolic dendrimers. Solubility studies (Table 4) conducted with acenaphthylene support our conclusion. Acenaphthylene that is poorly soluble in water (<2.2 × 10^{-5} M) becomes more soluble in the presence of phenolic and acid dendrimers. As expected acenaphthylene is more soluble in the presence of phenolic dendrimer (175 × 10^{-5} M, G-3) than in the presence of acid dendrimer (92 × 10^{-5} M, G-3). Such an enhanced local concentration would be expected to lead to more efficient photodimerization. Consistent with this, acenaphthylene photodimerization was found to be faster within dendritic media as com-

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TABLE 4. Solubility Studies of Acenaphthylene (26) in G2 Dendrimer

amount of dendrimer in 5 mL of soln	concn of dendrimer	amount of acenaphthylene solubilized	concn of acenaphthylene solubilized
		0.017 mg	0.22×10^{-4} M
G2(OH)$_{12}$	8×10^{-4} M	0.70 mg	9.2×10^{-4} M
G3(OH)$_{24}$	3.8×10^{-4} M	1.33 mg	17.5×10^{-4} M
G2(COOH)$_{12}$	9×10^{-4} M	0.57 mg	7.5×10^{-4} M
G3(COOH)$_{24}$	4.1×10^{-4} M	0.70 mg	9.2×10^{-4} M

TABLE 5. The Photodimerization of Acenaphthylene (26) in Water-Soluble Hosts

medium	host:guest	average **27**:**28**	medium	host:guest	average **27**:**28**
G-1(OH)$_{24}$	2:1[a]	71:29	G-3(CO$_2$H)$_{24}$	9:1[b]	68:32
G-2(OH)$_{24}$	1:1[a]	75:25	G-3(CO$_2$H)$_{24}$	1:1[b]	59:41
G-3(OH)$_{24}$	1:2[a]	80:20	G-3(CO$_2$H)$_{24}$	1:1[b]	43:57

[a] G-1(OH)$_{24}$ = 14×10^{-4} M, G-2(OH)$_{24}$ = 8×10^{-4} M, G-3(OH)$_{24}$ = 3.8×10^{-4} M. [b] G-1(CO$_2$H)$_6$ = 22.6×10^{-4} M, G-2(CO$_2$H)$_{12}$ = 9.04×10^{-4} M G-3(CO$_2$H)$_{24}$ = 4.11×10^{-4} M.

pared to that in an organic solvent. For example, for the same amount of acenaphthylene and irradiation time, the yield of dimer within phenolic dendrimer was 40−50%, while in methanol it was less than 5%.

Photolysis of acenaphthylene (**26**) encapsulated within phenolic dendrimer solutions under nitrogen purging conditions yielded the syn- and anti-dimers in the ratio 2.5:1 (G-1), 3:1 (G-2), and 4:1 (G-3) (Table 5). In case of acid dendrimers, upon direct irradiation syn- and anti-dimers were formed in the ratio 2.1:1 (G-1), 1.4:1 (G-2), and 0.75:1 (G-3). On comparing the ratios of the dimers formed within acid and phenolic dendrimers, the percent of anti dimer (the triplet product) is formed in greater amount in acid dendrimers. This increase in triplet product (anti dimer) can be explained with the solubilization data provided in Table 4. G-3 acid dendrimer was able to encapsulate on an average only one acenaphthylene molecule per unit, whereas the phenolic G-3 dendrimer was able to encapsulate on an average two acenaphthylene molecules per unit. Due to this decrease in local concentration of acenaphthylene molecules within acid dendrimer, we believe that the triplet derived product anti dimer is formed in greater amounts.

Summary

Over the years, photoreactions have been examined in various media. These include organic crystals, host−guest assemblies in solid state and solution, micelles and liquid crystals, etc. Dendrimers add an additional dimension to these media. In this report, we have shown that dendrimers can effectively solubilize organic compounds, and also the dendritic cavities can be efficiently used for conducting photochemical reactions in aqueous solutions. The hydrophilic and hydrophobic balance available for the dendrimers in aqueous solutions determines the extent of solubilization of an organic substrate. Thus, a higher generation dendrimer, offering a better hydrophilic−hydrophobic balance along with defined inner cavities, would be more preferable as hosts than the lower generation dendrimers. Additional advantages of recovery and reuse of the dendritic media should entail these new media to be considered on par with other known reaction media. Utility of these new media in photochemical reactions is fully established in this report.

Experimental Section

5-Bromopentyloxy Methylisophthalate (2). A mixture of **1** (5 g, 0.02 mmol), 1,5-dibromopentane (22 g, 0.09 mmol), K$_2$CO$_3$ (4.0 g, 0.03 mmol), and 18-C-6 (cat.) in 2-butanone (60 mL) was refluxed for 8 h, and the solvents were removed in vacuo. The resulting residue was dissolved in CH$_2$Cl$_2$, washed with water, dried (Na$_2$SO$_4$), concentrated, and purified (SiO$_2$, PhMe/EtOAc = 98.5/1.5) to afford **2**, as a white solid (7 g, 82%). Mp: 41−43 °C. TLC: R_f = 0.54 (PhMe/EtOAc = 96:4). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 1.54−1.64 (m, 2H), 1.74−1.94 (m, 4H), 3.40 (t, J = 6.6 Hz, 2H), 3.88 (s, 6H), 4.00 (t, 2H, J = 6.3 Hz), 7.67 (s, 2H), 8.20 (s, 1H). ^{13}C NMR (75.5 MHz, CDCl$_3$) δ: 24.6, 28.1, 32.3, 33.4, 52.3, 68.0, 119.6, 122.7, 131.6, 158.9, 166.0. HR-MS m/z: 381.0314 ([M + Na]$^+$). FT-IR (neat): 1730. Anal. Calcd for C$_{15}$H$_{19}$O$_5$Br: C, 50.17; H, 5.33. Found: C, 50.37; H, 5.42.

G1-(COOMe)$_6$ (4). A mixture of **3**[7] (0.23 g, 0.39 mmol), **1** (0.31 g, 1.3 mmol), K$_2$CO$_3$ (0.18 g, 1.30 mmol), and 18-C-6 (cat.) in 2-butanone (20 mL) was refluxed for 12 h, and the solvents were removed in vacuo. The resulting residue was dissolved in CH$_2$Cl$_2$, washed with water, dried (Na$_2$SO$_4$), concentrated, and purified (SiO$_2$, PhCH$_3$/EtOAc = 92/8) to afford **4**, as a gummy solid (0.36 g, 94%). TLC: R_f = 0.54 (PhMe/EtOAc = 90:10). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 1.66−1.68 (m, 6H), 1.81−1.93 (m, 12H), 3.93−3.97 (m, 24H), 4.07 (t, J = 6.3 Hz, 6H), 6.08 (s, 3H), 7.74 (s, 6H), 8.26 (s, 3H). ^{13}C NMR (75.5 MHz, CDCl$_3$) δ: 22.6, 28.8, 28.9, 52.3, 67.6, 68.3, 93.7, 119.7, 122.8, 131.6, 159.0, 160.8, 166.1. EI-MS m/z: 962 ([M + H]$^+$), 984 ([M + Na]$^+$), 1000 ([M + K]$^+$). FT-IR (neat): 1729. Anal. Calcd for C$_{51}$H$_{60}$O$_{18}$: C, 63.74; H, 6.29. Found: C, 63.61; H, 6.39.

G1-(COOH)$_6$ (5). **4** (0.15 g, 0.16 mmol) was dissolved in MeOH:THF:H$_2$O (10 mL) (2:2:1) and KOH (0.11 g, 1.92 mmol). The solution was stirred for 15 h at room temperature; solvents were removed partly and acidified with aqueous HCl (10%) to pH 4. The white precipitate was filtered, washed with cold water, and dried to afford **5**, as a white solid (0.14 g, 95%). Mp: 140−150 °C (dec). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 1.56 (br, 6H), 1.75 (br, 12H), 3.90 (br, 6H), 4.07 (br, 6H), 6.03 (s, 3H), 7.62 (s, 6H), 8.04 (s, 3H). ^{13}C NMR (75.5 MHz, CDCl$_3$) δ: 22.1, 28.3, 28.4, 67.2, 67.9, 93.5, 118.9, 122.2, 132.4, 158.6, 160.4, 166.4. EI-MS m/z: 878 ([M + H]$^+$), 900 ([M + Na]$^+$), 916 ([M + K]$^+$). FT-IR (KBr): 1697, 3440. Anal. Calcd for C$_{45}$H$_{48}$O$_{18}$: C, 61.63; H, 5.52. Found: C, 61.22; H, 5.93.

G2-(COOMe)$_{12}$ (6). A mixture of **G-1(OH)$_6$**[7] (60 mg, 0.085 mmol), **2** (0.27 g, 0.76 mmol), K$_2$CO$_3$ (0.11 g, 0.76 mmol), and 18-C-6 (cat.) in DMF (20 mL) was refluxed for 30 h, and the solvents were removed in vacuo. The resulting residue was dissolved in CH$_2$Cl$_2$, washed with water, dried (Na$_2$SO$_4$), concentrated, and purified (SiO$_2$, PhCH$_3$/EtOAc = 88/12) to afford **6**, as a gummy solid (0.17 g, 84%). TLC: R_f = 0.38 (PhMe/

EtOAc = 85:15). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 1.65−1.70 (m, 18H), 1.83−1.90 (m, 36H), 3.92 (br, 60H), 4.07 (t, J = 6.3 Hz, 12H), 6.01 (s, 12H), 7.70 (s, 12H), 8.21 (s, 6H). ^{13}C NMR (75.5 MHz, CDCl$_3$) δ: 22.7, 28.8, 28.9, 29.0, 52.4, 67.6, 67.7, 68.3, 93.8, 119.8, 122.8, 131.7, 159.1, 160.8, 166.2. MALDI-TOF MS m/z: 2400 ([M + Na]$^+$), 2417 ([M + K]$^+$). FT-IR (neat): 1730.80, 1719.23. Anal. Calcd for $C_{129}H_{156}O_{42}$: C, 65.14; H, 6.61. Found: C, 64.81; H, 6.91.

G2-(COOH)$_{12}$ (7). **6** (0.35 g, 0.148 mmol) was dissolved in MeOH:THF:H$_2$O (10 mL) (2:2:1) and KOH (0.19 g, 3.55 mmol). The solution was stirred for 15 h at room temperature; solvents were removed partly and acidified with aqueous HCl (10%) solution to pH 4. The white precipitate was filtered, washed with cold water, and dried to afford **7**, as a white solid (0.27 g, 83%). Mp: 140−150 °C (dec). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 1.49−1.58 (br, 18H), 1.68−1.80 (br, 36H), 3.90 (t, 6.3 Hz, 24H), 4.00 (t, 6.3 Hz, 12H), 6.02 (s, 12H), 7.60 (s, 12H), 8.04 (s, 6H). ^{13}C NMR (75.5 MHz, CDCl$_3$) δ: 24.8, 31.0, 70.0, 70.64, 96.3, 121.5, 135.2, 161.5, 163.2, 169.1. FT-IR (KBr): 1702, 1697, 3440. Anal. Calcd for $C_{117}H_{132}O_{42}$: C, 63.57; H, 6.01. Found: C, 63.51; H, 6.33.

G3-(COOMe)$_{24}$ (8). A mixture of **G-2(OH)$_{12}$**[7] (36 mg, 0.019 mmol), **2** (0.13 g, 0.35 mmol), K$_2$CO$_3$ (48 mg, 0.35 mmol), and 18-C-6 (cat.) in DMF (20 mL) was refluxed for 35 h, and the solvents were removed in vacuo. The resulting residue was dissolved in CH$_2$Cl$_2$, washed with water, dried (Na$_2$SO$_4$), concentrated, and purified (SiO$_2$, PhCH$_3$/EtOAc = 86/14) to afford **8**, as a gummy solid (58 mg, 58%). TLC R_f 0.44 (PhCH$_3$/EtOAc = 83:17). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 1.63−1.69 (m, 42H), 1.80−1.90 (m, 84H), 3.86−4.01 (br, 132H), 4.05 (t, J = 6.3 Hz, 24H), 6.06 (s, 30H), 7.73 (s, 24H), 8.25 (s, 12H). ^{13}C NMR (75.5 MHz, CDCl$_3$) δ: 22.1, 28.3, 28.4, 67.2, 67.9, 93.5, 118.9, 122.2, 132.4, 158.6, 160.4, 166.4. FT-IR (neat): 1725. Anal. Calcd for $C_{285}H_{348}O_{90}$: C, 65.66; H, 6.73. Found: C, 65.22; H, 7.21.

G3-(COOH)$_{24}$ (9). **8** (72 mg, 0.014 mmol) was dissolved in MeOH:THF:H$_2$O (10 mL) (2:2:1) and KOH (37 mg, 0.66 mmol). The solution was stirred for 15 h at room temperature; solvents were removed partly and acidified with HCl (10%) solution to pH 4. The white precipitate was filtered, washed with cold water, and dried to afford **9** as a white solid (63 mg, 95%). Mp: 140−150 °C (dec). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 1.51−1.68 (br, 126H), 3.86 (br, 60H), 4.04 (br, 24H), 6.01 (s, 30H), 7.60 (s, 24H), 8.04 (s, 12H). ^{13}C NMR (75.5 MHz, CDCl$_3$) δ: 22.2, 28.3, 28.4, 67.3, 68.0, 93.6, 119.0, 122.2, 132.6, 158.8, 160.5, 166.5. FT-IR (KBr): 1726.94, 1721.16, 3437.49. Anal. Calcd for $C_{261}H_{300}O_{90}$: C, 64.03; H, 6.20. Found: C, 64.06; H, 6.71.

Inclusion of Reactants within Dendrimers and Photolysis. The procedures adopted for all substrates were similar, and one of them is described below. To a stirred solution of a known amount of dendrimer in 5 mL of aqueous NaOH (G$_3$(CO$_2$H)$_{24}$) = 3 × 10^{-4} M) was added substrate **10** (2.9 × 10^{-4} M). Following stirring for 12 h, the solution was filtered through a Whatmann filter paper (medium porosity) to remove any floating particles. Filtrate was purged with nitrogen for 30 min and then irradiated in a Pyrex tube with 450 W medium-pressure Hg lamp. In case of substrate **10**, sample in aqueous G1 solution was irradiated for 12 h, samples in aqueous G2 solution for 28 h, and sample in aqueous G3 solution for 48 h to obtain 30% conversion. Absorption by the dendrimer was responsible for the low conversion. Two hours of irradiation resulted in ~30% conversion in the case of **17**. Substrate **26** was irradiated with a 380 nm filter for direct irradiation studies and with a 510 nm filter for triplet sensitization studies.

Extraction of Photoproducts and Reactants from Dendrimer Aqueous Solution. After photolysis, the basic aqueous solution was acidified with 10% dilute HCl. Reactants and products were extracted from aqueous solution using ethyl acetate and acetonitrile (7:3) solvent mixture, dried over anhydrous Na$_2$SO$_4$, concentrated, and analyzed on a HP-5890 series II gas chromatograph fitted with SE-30 or HP-5 column. A known amount of internal standard was added before analysis for mass balance studies. For substrate **10**, dodecane was used as the internal standard, and for substrate **17**, benzophenone was used as the internal standard.

Characterization of Photoproducts. Peaks in the GC traces were identified by co-injecting with authentic samples, which were prepared by solution irradiation. In the case of **10**, the photoproducts **AA** (**14**) and **BB** (**16**) were commercially available. Photoproduct **AB** (**15**) was identified based on the GC−MS fragmentation pattern.

Mass spectral data: m/z (relative intensity), 196 (M$^+$, 17), 105 (100), 91 (12), 77 (11).

Among the photoproducts from **17**, benzaldehyde, **23**, and **20** were identified by comparison with the commercially available samples (Aldrich). Photoproducts **22**, **24**, **25**, and **21** were isolated from solution irradiation and characterized by ^{1}H NMR and GC−MS.

^{1}H NMR of **22** (400 MHz, CDCl$_3$): δ 0.94 (t, 6H), δ 2.83−3.65 (m, 4H), δ 4.30 (s, 2H), δ 7.09−7.58 (m, 10H).

Mass spectral data: m/z (relative intensity): 165 (4), 152 (2), 136 (9), 135 (100), 107 (66), 79 (48), 77 (32), 51 (10).

^{1}H NMR of **24** (400 MHz, CDCl$_3$): δ 1.2 (t, 3H), δ 3.51 (q, 2H), δ 4.57 (s, 2H), δ 7.40−7.80 (m, 9H).

Mass spectral data: m/z (relative intensity), 240 (M$^+$, 18), 211 (18), 196 (34), 181 (5), 167 (49), 166 (100), 152 (10), 133 (21), 126 (14), 105 (77), 89 (24), 77 (50).

^{1}H NMR of **25** (400 MHz, CDCl$_3$): δ 1.0 (t, 3H), δ 3.38 (q, 2H), δ 4.58 (s, 2H), δ 7.30−7.80 (m, 9H).

Mass spectral data: m/z (relative intensity), 240 (M$^+$, 9), 211 (59), 194 (28), 181 (3), 165 (25), 152 (12), 133 (100), 105 (28), 77 (49), 51 (17).

^{1}H NMR of **21** (400 MHz, CDCl$_3$): δ 1.4 (d, 3H), δ 5.2 (q, 1H), δ 5.95 (s, 1H), δ 7.20−7.80 (m, 10H).

Mass spectral data: m/z (relative intensity), 196 (17), 167 (28), 152 (9), 134 (85), 133 (62), 118 (12), 105 (100), 91 (15), 77 (42).

Photoproducts **27** and **28** were isolated from solution irradiation and characterized by ^{1}H NMR and GC−MS.

^{1}H NMR of **27** (400 MHz, CDCl$_3$): δ 4.81 (s, 4H), 6.98−6.99 (d, 4H), 7.10−7.24 (m, 8H).

^{1}H NMR of **28** (400 MHz, CDCl$_3$): δ 4.07 (s, 4H), 7.49−7.51 (d, 4H), 7.56−7.60 (m, 4H), 7.71−7.73 (d, 4H).

The following conditions were used for GC analysis of the photoproducts. The temperatures of the injection and the detection ports were maintained at 225 and 250 °C.

Substrate **10**, column SE-30; temperature program, initial temp − 100 °C; initial time − 1 min; rate − 5 °C/min; final temp − 270 °C; final time − 10 min; retention times: **AA** − 14.3 min; **AB** − 17 min; **BB** − 19.3 min; **10** − 22.3 min; **13** − 24.3 min.

Substrate **17**, column SE-30; temperature program, initial temp − 70 °C; initial time − 1 min; rate − 5 °C/min; final temp − 175 °C; final time − 30 min; retention times: **20** − 25.5 min; **22** − 26.1 min; **23** − 28.6 min; **17** − 30.0 min; **25** − 32.3 min; **21** − 34.3 min; **24** − 43.4 min.

Substrate **26**, column SE-30; temperature program, initial temp − 70 °C; initial time − 1 min; rate − 10 °C/min; final temp − 270 °C; final time − 20 min; retention times: **26** − 12.3 min; **27** − 27 min; **28** − 33 min.

Fluorescence Measurements. Fluorescence spectra were recorded at room temperature on an Edinburgh FS900CDT steady-state fluorimeter. The concentration of pyrene aqueous solution used in the fluorescence measurement is 1 × 10^{-5} M. Emission spectrum was recorded by exciting at 335 nm. Excitation spectrum was recorded at 385 nm emission wavelength. To the aqueous solution of pyrene was added dendrimer solution such that the concentration of dendrimer was 2 × 10^{-4} M in solution. The solution was stirred for 3 h prior to recording the emission/excitation spectrum.

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