JOC The Journal of Organic Chemistry

ARTICLE

pubs.acs.org/joc

Interfacial Regions Governing Internal Cavities of Dendrimers. Studies of Poly(alkyl aryl ether) Dendrimers Constituted with Linkers of Varying Alkyl Chain Length

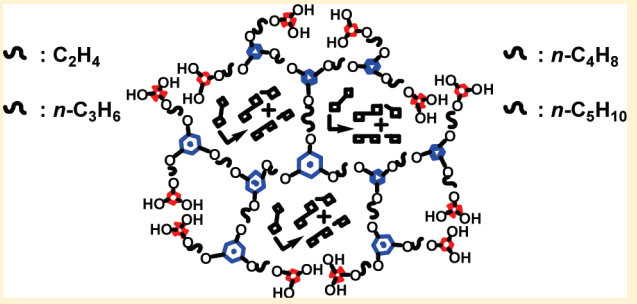
Baskar Natarajan,[†] Shipra Gupta,[‡] Vaidhyanathan Ramamurthy,*[,‡] and Narayanaswamy Jayaraman*[,†]

[†]Department of Organic Chemistry, Indian Institute of Science, Bangalore 560118, India

[‡]Department of Chemistry, University of Miami, Coral Gables, Florida 33124, United States

Supporting Information

ABSTRACT: This report deals with a study of the properties of internal cavities of dendritic macromolecules that are capable of encapsulating and mediating photoreactions of guest molecules. The internal cavity structures of dendrimers are determined by the interfacial regions between the aqueous exterior and hydrocarbon like interior constituted by the linkers that connect symmetrically sited branch points constituting the dendrimer and head groups that cap the dendrimers. Phloroglucinol-based poly(alkyl aryl ether) dendrimers constituted with a homologous series of alkyl linkers were undertaken for the current study. Twelve dendrimers within first, second, and third generations, having ethyl, *n*-propyl, *n*-butyl, and *n*-pentyl groups as the linkers and hydroxyl groups at peripheries in each generation, were synthesized. Encapsulation of pyrene and coumarins by aqueous basic solutions of dendrimers were monitored by UV−vis and fluorescence spectroscopies, which showed that a lower generation dendrimer with an optimal alkyl linker presented better encapsulation abilities than a higher generation dendrimer. Norrish type I photoreaction of dibenzyl ketone was carried out within the above series of dendrimers to probe their abilities to hold guests and reactive intermediate radical pairs within themselves. The extent of cage effect from the series of third generation dendrimers was observed to be higher with dendrimers having an *n*-pentyl group as the linker.

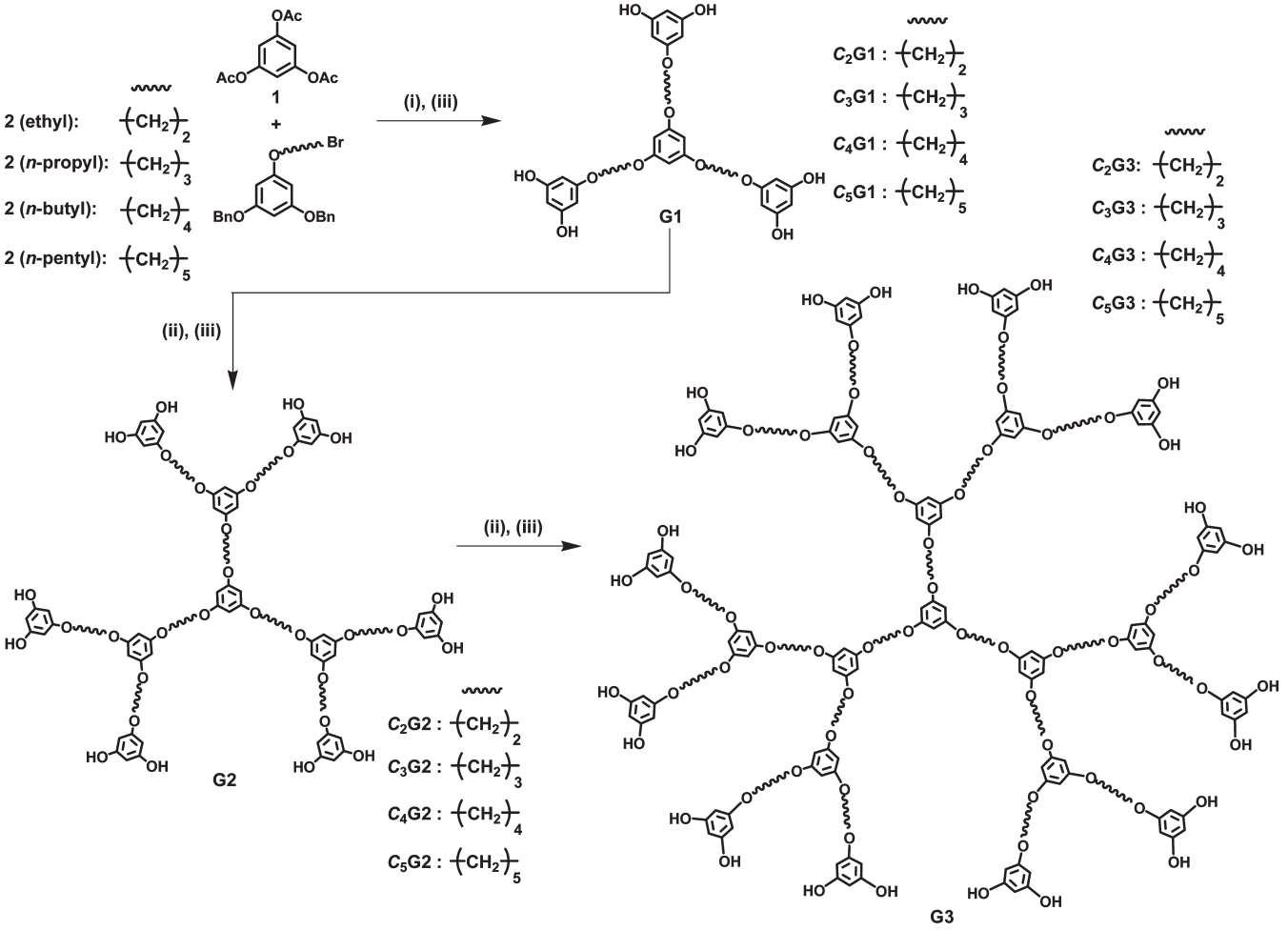


INTRODUCTION

Monodispersed macromolecules, namely, dendrimers, provide well-defined, inner cavities, resulting from branches-upon-branches structural feature.[1−6] The cavities provided by dendrimers could be visualized to be dynamic as it is not a cavity of fixed size as in the case of, for example, cyclodextrins. Because of fluctuations of the alkyl chain that constitutes the dendrimer, the cavity sizes and shapes are expected to change with time, similar to that in micelles, and hence we call the cavities provided by dendrimers "dynamic cavities". As a result of dense peripheries, higher generation dendrimers exhibit better-defined, dynamic inner cavities than lower generation ones. Exploring properties of the inner cavities of dendrimers is a continuing theme in diverse studies associated with dendritic macromolecules.[7,8] Polar exterior and nonpolar interior assisted by hydrophobic−hydrophilic balances control the microenvironment of the inner cavities of a dendritic structure.[9−18] With the presence of well-defined, dynamic inner cavities, more profoundly in the higher generations, dendrimers are similar to other container molecules,[19−23] wherein the interior, exterior, and the interface have been utilized for defined purposes. For example, the interior of dendritic structures, presenting dynamic inner cavities, are capable of encapsulating small molecules. Exterior peripheries of dendrimers offer enhanced binding affinities through co-operative effects to investigate multivalent interactions between ligands and receptors.[4] Interfacial regions provide a surface for manipulation of dynamic inner cavity structures and sizes. Linker moieties connecting the branch points define interface regions that separate the inner cavities from an aqueous exterior. Given that each branch point is arranged symmetrically about a core in a dendritic structure, the interfacial regions and the interior cavities are highly symmetrical and repetitive. Thus the dynamic inner cavities of dendrimers are micro- or nanocontainers capable of encapsulating guest molecules and controlling reactions occurring within them. Reactions in such restricted spaces, in general, are visualized in terms of a model based on "reaction cavity" a term used commonly to define a constrained microenvironment generated by container molecules, micelles, liposomes, cyclodextrins and related cavitands, zeolites, polymers and crystals.[24−28] In assessing the dynamic inner cavities suitable for photochemical reactions, it was demonstrated previously that phloroglucinol-based poly(alkyl aryl ether) dendrimers mediated such reactions at the microenvironments generated as a result of the polar exterior and relatively nonpolar interior in an aqueous

Received: March 3, 2011
Published: April 13, 2011

Scheme 1[a]



[a] Reagents and conditions: (i) NaH, H_2O, DMF, 24 h; (ii) **2**, K_2CO_3, 18-crown-ether (catalytic), 2-butanone/DMF (2:1), 90 °C, 24−72 h; (iii) Pd/C (10%), H_2, THF, reflux, 12−15 h.

medium.[29,30] In order to assess how changes in the interface regions modify the structures of dynamic inner cavities, we undertook to study dendrimers with systematically changing linker lengths. With this objective, we report herein synthesis of a homologous series of poly(alkyl aryl ether) dendrimers, wherein the spacer lengths between the branch points were varied systematically. The reaction cavity properties inherent in these homologous series of dendrimers, from one to three generations, presenting 6−24 hydroxyl group functionalities at their peripheries, were investigated in an aqueous basic solution. Each generation presented a set of homologous series of dendrimers, with linker lengths varying from an ethyl to *n*-pentyl group. Microenvironments resulting from dynamic inner cavities of dendrimers were assessed with pyrene and coumarins as photophysical probes. Following this, photochemical reaction pertaining to the cleavage of dibenzyl ketone was used to study changing microenvironments in the case of third generation dendrimers with differing linker lengths. Details of synthesis and photochemical studies are reported below.

RESULTS AND DISCUSSION

Synthesis of Dendrimers. Synthesis of phloroglucinol-based poly(alkyl aryl ether) dendrimers with various alkyl spacer groups was performed by adopting the method established previously.[31] Required monomers with varying spacer length were synthesized by *O*-alkylation of di-*O*-benzyl phloroglucinol with excess dibromoalkanes, namely, 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, and 1,5-dibromopentane, in the presence of K_2CO_3 and 18-crown-ether (catalytic). First generation dendrimers with varying spacer lengths were synthesized by a 3-fold alkylation of phloroglucinol triacetate (**1**)[31] with monomer **2**, in the presence of NaH and water (Scheme 1). Subsequent removal of benzyl groups (Pd/C, H_2) led to hydroxyl group terminated first generation dendrimers, C_2**G1**, C_3**G1**, C_4**G1**, and C_5**G1**. Synthesis of second generation dendrimers, C_n**G2**, was performed through 6-fold alkylation of C_n**G1** dendrimers with monomer **2**, in the presence of K_2CO_3 and 18-crown-ether (catalytic) in 2-butanone/DMF (2:1). Deprotection of benzyl groups afforded hydroxyl group terminated second generation dendrimers C_n**G2** in good yields. Repeating the sequence of reactions with C_n**G2** dendrimers, 12-fold *O*-alkylation followed by deprotection afforded third generation dendrimers C_n**G3** in a moderate yield, even when the reaction was conducted for a longer period. The benzyl-protected dendrimers were colorless gums, whereas hydroxyl group terminated dendrimers were white foamy solids. Further, benzyl-protected dendrimers

dx.doi.org/10.1021/jo200464g |*J. Org. Chem.* 2011, 76, 4018–4026

Table 1. Solubilization of Pyrene and Its Relative I_3/I_1 Fluorescence Band Intensity in Aqueous Basic Solutions of Dendrimers

aq solution of dendrimer		solubilized pyrene (μM)	ΔG_{tr} (cal/mol)	I_3/I_1
G1	C_2	1.33	−709	0.52
	C_3	1.58	−812	0.56
	C_4	1.73	−866	0.56
	C_5	2.32	−1040	0.67
G2	C_2	2.80	−1151	0.53
	C_3	3.48	−1280	0.63
	C_4	4.40	−1418	0.64
	C_5	11.3	−1976	0.78
G3	C_2	5.71	−1572	0.61
	C_3	8.36	−1798	0.79
	C_4	17.9	−2248	0.75
	C_5	33.2	−2614	0.84

were soluble in many organic solvents, whereas hydroxyl group terminated dendrimers were soluble in EtOAc, THF, MeOH, DMF, and DMSO and insoluble in PhMe, Et_2O, and CH_2Cl_2. Characterizations of dendrimers C_nG1-C_nG3 were performed by ^1H and ^{13}C NMR spectroscopies. The generation growth, and monodispersities of dendrimers were also confirmed by ESI-MS or MALDI-TOF mass spectrometry and elemental composition analyses.

Assessing Dynamic Inner Cavities with Probes. Studies of the microenvironments attendant in each dendrimer in the series C_nG1-C_nG3 were assessed initially by identifying the extent of pyrene solubilization in aqueous basic solutions, which was prepared by addition of the required molar equivalents of NaOH. To assess solubilization, pyrene was admixed with an aqueous basic solution of dendrimers and stirred at 25 °C for 12 h in dark, after which the solution was filtered, and the extent of pyrene solubilization in each dendrimer was determined by UV−vis absorption spectroscopy (ε_{335} 50,730 mol^{-1} cm^{-1}).[32,33] The amount of pyrene solubilized in water (pH ∼10) was estimated to be 0.4 μM, whereas that in aqueous basic third generation C_2, C_3, C_4, and C_5 dendrimer solutions (100 μM) was found to be 5.7, 8.4, 17.9, and 33.2 μM, respectively. A similar pyrene solubilization trend was observed with second generation dendrimers, with varying alkyl linker lengths. Across three generations, first generation dendrimers C_nG1 showed the least pyrene solubilization. The solubility of pyrene in aqueous basic solutions of dendrimers was also adjudged by the free energy (ΔG_{tr}) of transfer associated with solubilization (Table 1). The free energy of transfer became favorable progressively as the dendrimer generations advanced and as the linker lengths progressed from ethyl to *n*-pentyl group. From the solubilization assessments, a relation of interfacial regions constituted by alkyl group versus generation number emerges. The most distinct observation is the higher solubilization of pyrene by C_5G2 compared with that by C_2G3 and C_3G3, i.e., although C_2G3 and C_3G3 are third generation dendrimers, they solubilize pyrene less than C_5G2, which is a second generation dendrimer with a pentamethylene linker between the branch points. Qualitatively, the number of aromatic rings and the number of hydroxyl groups remain uniform within a generation, leaving differences in the solubility profiles to remain with the alkyl chain length. Second generation dendrimers possess fewer alkyl spacers than third generation dendrimers. On the other hand, hydrophobicities generated at the interior voids of the dendritic structure are related to the alkyl chain length. Thus, C_5G2 appeared to provide higher hydrophobicity than C_2G3, even when the latter is a third generation dendrimer.

In order to assess polarities of microenvironments generated at the dendritic interior cavities, fluorescence spectra of pyrene in aqueous basic solutions of dendrimer were recorded (Figure 1). The ratio of vibrational band intensities I_3/I_1 of pyrene fluorescence is known to depend on the microenvironment polarity.[34,35] Pyrene solubilized aqueous basic dendrimer solutions (200 μM) were prepared, and the I_3/I_1 values arising from pyrene fluorescence were measured (Table 1). A higher I_3/I_1 value indicates a hydrophobic environment and *vice versa*. It was found that across the dendrimer generations (**G1**−**G3**) with uniform spacer lengths, I_3/I_1 increased with increasing generations. On the other hand, within a dendrimer generation with various spacer units, I_3/I_1 was found to increase progressively from ethyl to *n*-pentyl spacer. The third generation C_5, C_4, and C_3 spacered dendrimers exhibited higher hydrophobic interior (I_3/I_1 = 0.84, 0.75, 0.79, respectively), whereas third generation C_2 spacered dendrimer showed lower microenvironment polarity (I_3/I_1 = 0.61). Among second generation dendrimers, I_3/I_1 for C_5 spacered dendrimer was 0.78, which was ∼1.2−1.5 times higher than propyl (C_3) and ethyl (C_2) spacered dendrimers. In the case of first generation dendrimers, there was no increment in the I_3/I_1 values, which reflected the absence of a hydrophobic interior arising from this series of dendrimers, except for the C_5G1 dendrimer (I_3/I_1 = 0.67). A broad excimer emission of pyrene was detected for the first generation dendrimers (Figure 2), which weakened further for the second generation dendrimers. Third generation dendrimers did not exhibit detectable excimer emission. Excimer emission results from the association of an excited state pyrene molecule with ground state molecule. This also could result from ground state aggregation of pyrene molecules. Aggregation is more likely in a hydrophilic environment and the appearance of an excimer in **G1** but not in **G3** dendrimer is in agreement with the micropolarity reported by pyrene molecules. The higher the polarity (**G1** dendrimer; lower I_3/I_1), the higher are the chances of aggregation, and excimer emission is more probable. The local concentration of pyrene is likely to be more in **G1** than in the **G3** dendrimer, which could also be the cause for excimer emission in the **G1** dendrimer. Further, as observed in the solubilization experiments, C_5G2 showed higher microenvironmental polarity than C_2G3 and to an extent C_3G3, thereby indicating that the role of the alkyl chain constituting the interfacial region is as important as a higher generation of the dendrimer.

Assessing Dynamic Inner Cavity with Coumarins as Probes. Subsequent to pyrene solubilization experiments, microenvironments of the dendrimers were assessed with coumarin dyes, comprising coumarin 480 (C480), coumarin 1 (C1) and coumarin 153 (C153) (Figure 3). Coumarins belong to a family of laser dyes whose fluorescence quantum yield and lifetime increase with the decrease in solvent polarity.[36] These probes are used extensively in various supramolecular assemblies.[37,38] Fluorescence spectra of C1, C480 (20 μM), and C153 (40 μM) in water and in aqueous basic solutions containing dendrimers (300−800 μM) (pH ∼10) were recorded. In a titration experiment, aqueous basic dendrimer solution was added to aqueous coumarin solutions, until no further spectral change was observed. Table 2 shows λ_{em} of C480, C1, and C153 after

dx.doi.org/10.1021/jo200464g |*J. Org. Chem.* 2011, 76, 4018–4026

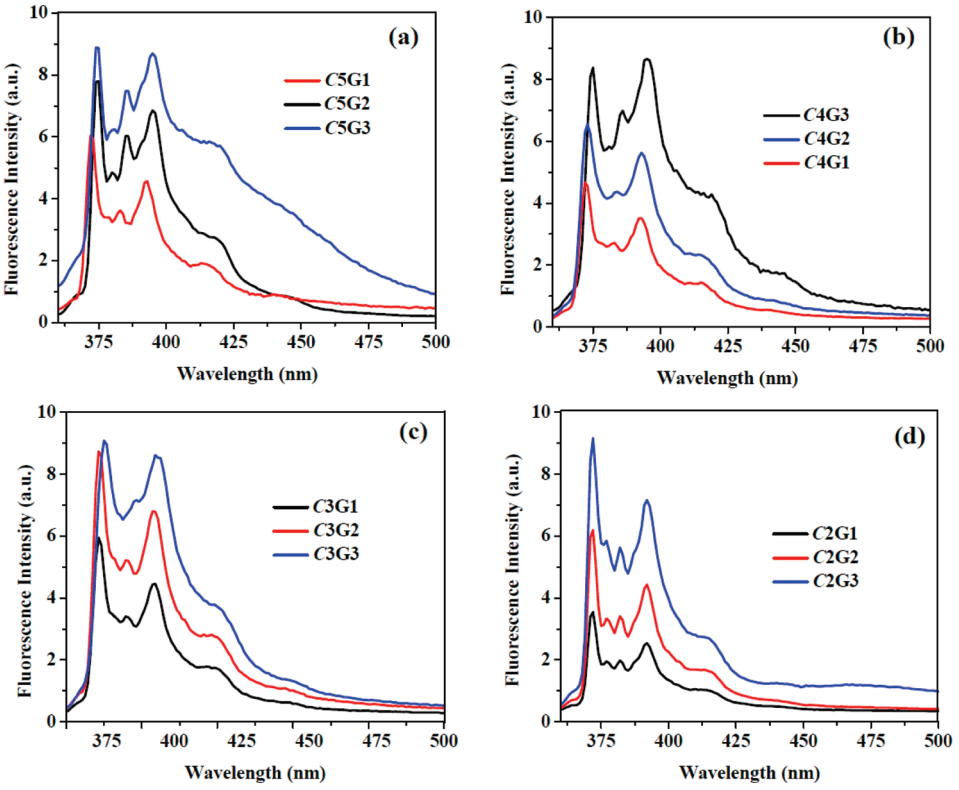


Figure 1. Emission spectra of pyrene in the presence of dendrimers. [pyrene] = 0.01 mM and [dendrimer] = 0.2 mM in aq NaOH (0.1 M), excitation wavelength = 335 nm.

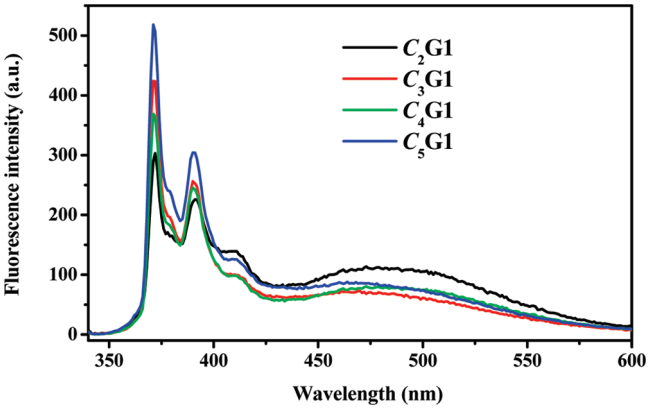


Figure 2. Emission spectra of pyrene in the presence of first generation dendrimers C_2**G1**−C_5**G1** in aq alkaline medium (0.2 mM), λ_{ex} = 335 nm.

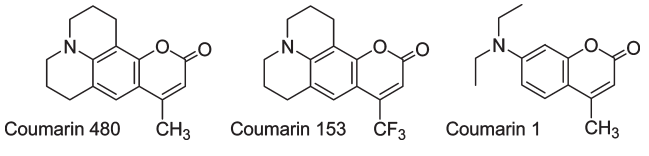


Figure 3. Molecular structures of coumarins used for solubilization studies.

the addition of C_n**G1**−C_n**G3** dendrimers. As an example, the emission spectra of C153 recorded in C_5**G1**, C_5**G2**, and C_5**G3** are shown in Figure 4. A blue shift in λ_{em} was observed in general, upon addition of a dendrimer to coumarin, which indicated a decrease in the polarity of the microenvironment possessing the probe.[39,40] It was observed that across the dendritic generations **G1**−**G3** with uniform spacer lengths, blue shift increased with increasing dendrimer generations. In the case of C480, blue shifts for C_5**G3** and C_5**G2** dendrimers were observed to be 15 and 8 nm, respectively, whereas C_5**G1** did not exhibit a shift in λ_{em}. Similarly, for C153, blue shifts for C_5**G3** and C_5**G2** dendrimers were observed to be 36 and 26 nm, respectively, and there was no shift with the C_5**G1** dendrimer. In the case of C1 dye, addition of C_5**G3** and C_5**G2** dendrimers afforded a blue shift of 18 and 14 nm, respectively, with no shift in the case of C_5**G1** dendrimer. Negligible blue shift in the emission spectra of probes on addition of **G1** dendrimers was in accordance with the results obtained for pyrene as probe.

On the other hand, within a dendrimer generation with various spacer units, blue shift was found to be higher for C_5, C_4 spacers, when compared to C_3 and C_2 spacer dendrimers. For example, for C480, within the third generation dendrimers, blue shift was 15 nm for C_5**G3**, whereas the shift was 10 nm for C_2**G3** dendrimer. Similarly, for C153, a blue shift of 36 nm was observed for C_5**G3**, whereas that for C_2**G3** was 22 nm (Figure 4). The same trend was observed in case of C1 dye. As observed with pyrene probe, the above results indicated that across the generations, third generation dendrimers possess more hydrophobic environments, whereas within a generation, there was a continuous decrease in hydrophobicity of the environment with systematic decrease in the spacer length.

Analysis of results with three different coumarins also revealed that the blue shift was higher in case of C153 (36 nm), in comparison to C1 and C480 (18 and 15 nm, respectively), presumably due to the nonpolar nature of C153,[41] having a CF_3

dx.doi.org/10.1021/jo200464g |*J. Org. Chem.* 2011, 76, 4018–4026

Table 2. Blue Shifts in Emission λ_{max} and E_T 30 Values of Coumarins in Various Dendrimer Solutions

	coumarin 480[a,b]			coumarin 1[a,c]			coumarin 153[d]		
aq dendrimer solution	emission (λ_{max}) (nm)	blue shift (nm)	E_T value (kcal/mol)	emission (λ_{max}) (nm)	blue shift (nm)	E_T value (kcal/mol)	emission (λ_{max}) (nm)	blue shift (nm)	E_T value (kcal/mol)
C_2G1	487	0	63.1	470	0	63.1	550	0	63.1
C_3G1	487	0	63.1	470	0	63.1	550	0	63.1
C_4G1	487	0	63.1	470	0	63.1	550	0	63.1
C_5G1	487	0	63.1	470	0	63.1	550	0	63.1
C_2G2	487	0	63.1	466	4	53.0	548	2	51.7
C_3G2	483	4	60.3	462	8	51.8	534	16	48.1
C_4G2	479	8	58.5	459	11	50.8	530	20	47.1
C_5G2	479	8	58.5	456	14	49.9	524	26	45.5
C_2G3	477	10	57.7	456	14	49.9	528	22	46.6
C_3G3	475	12	57.0	456	14	49.9	524	26	45.5
C_4G3	472	15	55.4	454	16	49.2	524	26	45.5
C_5G3	472	15	55.4	452	18	48.5	514	36	43.0

[a] [C_nG1] = 0.4 mM in 0.1 M aq NaOH; [C_nG2] and [C_nG3] = 0.3 mM in 0.1 M aq NaOH. [b] [C480] = 0.02 mM; λ_{em} for C480 in water = 487 nm. [c] [C1] = 0.02 mM; λ_{em} for C1 in water = 470 nm. [d] [C_nG1] = 0.8 mM in 0.1 M aq NaOH; [C_nG2] and [C_nG3] = 0.6 mM in 0.1 M aq NaOH; [C153] = 0.04 mM; λ_{em} for C153 in water = 550 nm.

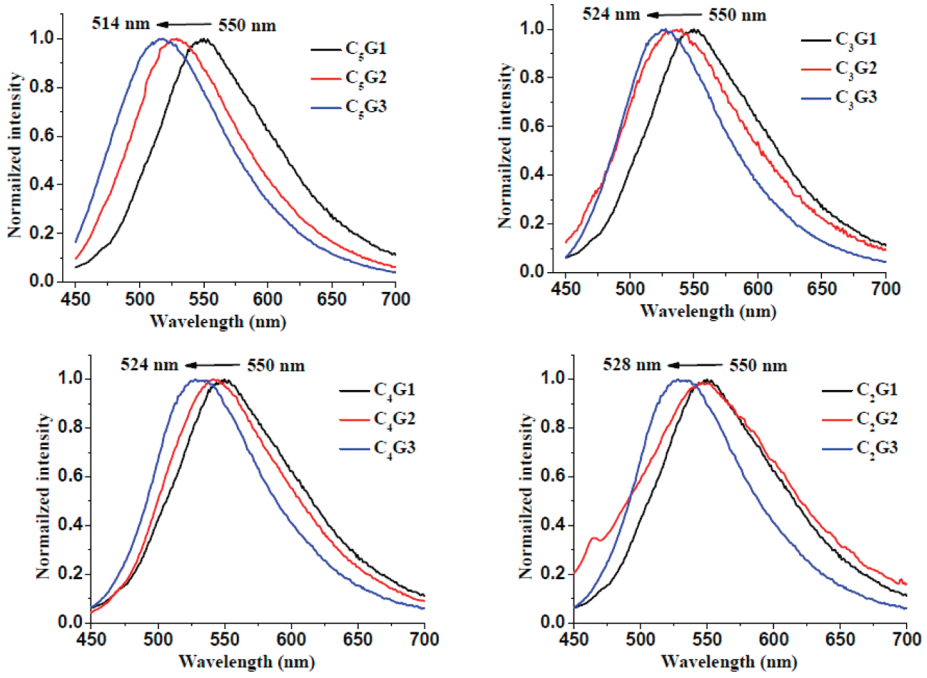


Figure 4. Emission spectra of coumarin 153 in the presence of various generation dendrimers (C_nG1–C_nG3, n = 2, 3, 4, 5) [C_nG1] = 0.8 mM in 0.1 M aq NaOH; [C_nG2] and [C_nG3] = 0.6 mM in 0.1 M aq NaOH; [C153] = 0.04 mM; λ_{ex} = 400 nm and λ_{em} for C153 in water = 550 nm.

group and the attendant higher affinity of this dye to occupy hydrophobic sites within dendritic interior.

Apart from the magnitude of blue shifts, the polarity of the microenvironments located inside the dendrimers was also judged on an E_T 30 scale for all the three coumarins. Usually the more hydrophobic the environment, the lesser is the E_T 30 value.[42] The E_T 30 values obtained in all the cases corresponded to the observed magnitude of the blue shifts. For example, across generations, for C480, E_T 30 value for C_5G3 was 55.4 kcal/mol (methanol-like), whereas for C_5G1, the value was 63.1 kcal/mol (water-like). Similarly, within a generation, with varying spacers, E_T 30 value for C_5G3 was 55.4 kcal/mol (methanol-like), whereas that for C_2G3 was 57.7 kcal/mol (glycerol-like). The above assessment of microenvironments at dendritic interiors using coumarins reiterated previous observations that alkyl chain length connecting the branch junctures of dendritic structure is an important criterion, in addition to dendrimer generations. As observed with pyrene, experiments with coumarins also showed higher microenvironmental polarity for second generation C_5G2 dendrimer than third generation C_2G3 and C_3G3 dendrimers.

Photolysis of 1-Phenyl-3-*p*-tolyl-propane-2-one Included within the C_nG3 Dendrimers. Studies with polarity probes

dx.doi.org/10.1021/jo200464g |J. Org. Chem. 2011, 76, 4018–4026

Scheme 2. Photolysis of Dibenzylketone inside Aqueous Basic Solutions of Dendrimers

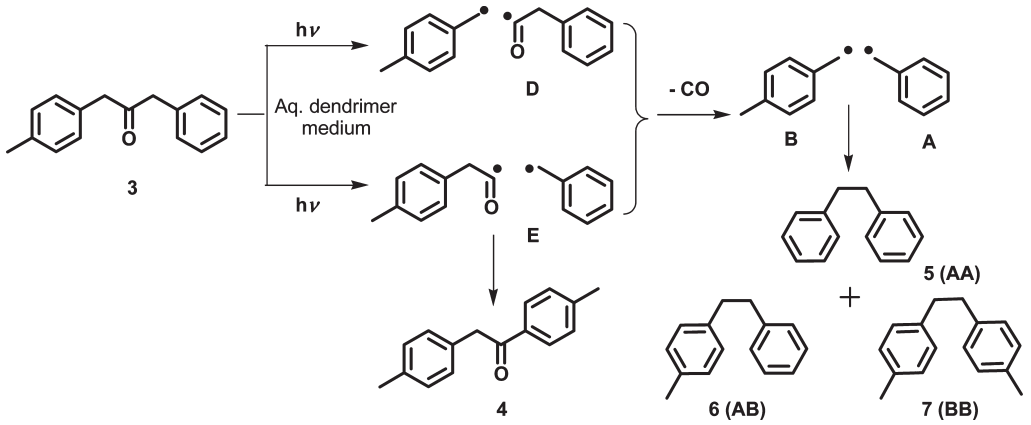


Table 3. Photolysis of 1-Phenyl-3-*p*-tolyl-propan-2-one in Aqueous Basic Dendrimer Solutions[a,b]

medium	AA	AB	BB	4	cage effect
hexane	21	51	29		0.05
C_2G3	30	46	24		
C_3G3	10	77	13		0.54
C_4G3	9	81	10		0.62
C_5G3		69		31	1.0

[a] [C_nG3] = 1.0 mM in 0.01 M aq NaOH. [b] Cage effect = (**AB** − **BB** − **AA**)/(**AA** + **AB** + **BB**)

pyrene and coumarins showed pronounced hydrophobic interiors, especially with third generation dendrimers. An effort was thus undertaken to verify the ability of third generation dendrimers to act as reaction media. In this instance, abilities of poly(alkyl aryl ether) dendrimers to mediate various photochemical reactions were assessed previously.[29,30] In continuation, it was deemed necessary to probe the mobility of guest molecules in the hydrophobic environments of dendrimers with varying interfacial regions resulting from different spacer groups within a dendrimer generation. The series within third generation dendrimers, constituted with C_2-C_5 alkyl chain length, was chosen, in order to conduct photolysis of dibenzyl ketone (Scheme 2).[43]

Irradiation of 1-phenyl-3-*p*-tolyl-propane-2-one **3** in hexane solution resulted in an α-cleavage, yielding the primary radical pairs **D** and **E**, followed by decarbonylation, to afford a secondary radical pair **A** and **B**. In hexane solution, no product from the radical pairs **D** and **E** was detected. Three diaryl ethanes **5** (**AA**), **6** (**AB**) and **7** (**BB**), resulting from the radical pairs **A** and **B**, were formed in the ratio 1:2:1. In restricted environments, the rearrangement product **4** is formed from the radical pair **E**.[44] When the radical pairs **A** and **B** were held within a cage with little translational mobility, the only product expected was **6** (**AB**).[45−48] The cage effect (**AB** − **AA** − **BB**)/(**AA** + **AB** + **BB**) and the yield of rearrangement product **4** provide information concerning the "leakiness" of the reaction cavity with respect to radical pairs **D**, **E**, **A**, and **B**.

The results of photolysis of 1-phenyl-3-p-tolyl-propane-2-one **3** in hexane and in aqueous basic third generation dendrimers with various spacer groups are summarized in Table 3. It was observed that in case of **C_5G3** dendrimer the cage effect was 1.0 with the formation of rearrangement product **4** in 31% yield. As the spacer length decreased to **C_4G3**, the cage effect also decreased to 0.62. The cage effect for **C_3G3** was observed to be 0.54, whereas negligible cage effect was observed in the case of **C_2G3** dendrimer. These results indicated that the third generation dendrimers with the pentamethylene linker possessed higher hydrophobicity, as concluded from the above solubilization and photophysical studies. As the spacer length decreased, the hydrophobicity also decreased.

CONCLUSION

The study presented herein attempts to assess interfacial regions constituting the dynamic inner cavities of dendrimers. For this purpose, phloroglucinol-based poly(alkyl aryl ether) dendrimers were synthesized with varying alkyl spacers up to three generations. Each generation of dendrimer possessed linkers varying between ethyl and *n*-pentyl alkyl spacers connecting the branch points, thereby changing the sizes of the dynamic inner cavities of dendrimers. Upon synthesis, solubilities of pyrene in aqueous basic solutions were assessed first, followed by a series of studies to identify the microenvironmental properties arising from dendritic interiors. Fluorescence studies of encapsulated dye molecules, namely, pyrene and coumarins, showed that dendrimers containing longer alkyl chain length exhibited significant hydrophobic microenvironments compared with dendrimers with shorter alkyl chain length, within each dendrimer generation. The role of alkyl chain in endowing higher hydrophobicity could be observed for a lower generation dendrimer with longer alkyl chain compared with a higher generation dendrimer with shorter alkyl chain. A photoreaction pertaining to photocleavage of dibenzyl ketone at the interior of third generation dendrimer series showed that dendrimer with longer alkyl chain afforded higher rigidities to reactive intermediates, thereby reducing the "leakiness" of intermediates to bulk environment and facilitating product formation with high selectivities.

EXPERIMENTAL SECTION

General Procedure for Alkylation Reaction. A mixture of dendritic phenol (1 molar equiv), monomer **2** (1.2 molar equiv per OH group), K_2CO_3 (1.2 molar equiv per OH group), and 18-crown-ether (catalytic) in 2-butanone/DMF (2:1 v/v) was refluxed for 24−72 h. Solvents were then removed in vacuo, and the resulting residue was dissolved in EtOAc, washed with water, dried (Na_2SO_4), concentrated, and purified (SiO_2) to afford benzyl-protected poly(alkyl aryl ether) dendrimers, as gums.

dx.doi.org/10.1021/jo200464g |*J. Org. Chem.* 2011, 76, 4018–4026

General Procedure for Debenzylation Reaction. A mixture of benzyl-protected dendrimer and Pd−C (10%) in THF was refluxed in the presence of H_2 (g) for 24 h. The reaction mixture was filtered through Celite, concentrated, and purified (SiO_2) to afford hydroxyl group-terminated poly(alkyl aryl ether) dendrimers, as white foams.

C_2G1. A mixture of **1** (0.45 g, 1.78 mmol), **2** (ethyl spacer) (3.0 g, 7.15 mmol), and NaH (60% in mineral oil, 0.6 g) in DMF (30 mL) was stirred at 0 °C for 15 min, followed by addition of aq DMF (2%) (6 mL), over a period of 2 h. The reaction mixture was stirred for 24 h at rt, solvents were removed in vacuo, and the resulting residue dissolved in EtOAc, washed with water, dried (Na_2SO_4), concentrated, and purified (SiO_2, PhMe/EtOAc = 98:2) to afford benzyl-protected dendrimer ***C_2G1*** (1.45 g, 72%), as a white gum.

A mixture of the above intermediate (1.3 g, 1.16 mmol) and Pd/C (10%) (0.3 g) in THF (30 mL) was refluxed for 24 h and treated as described in the general procedure to afford ***C_2G1*** (0.6 g, 87%), as a foam. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 4.12 (br, 6 H), 4.21 (br, 6 H), 5.81 (s, 6 H), 5.83 (s, 3 H), 6.19 (s, 3 H), 9.20 (s, 6 H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 65.9, 66.4, 93.1, 94.0, 95.7, 159.0, 160.1, 160.2; ESI-MS m/z calcd for $C_{30}H_{30}O_{12}$ $[M + Na]^+$ 605.1635, found 605.1635. Anal. Calcd for $C_{30}H_{30}O_{12}$: C, 61.85; H, 5.19. Found: C, 61.43; H, 6.13.

C_3G1. A mixture of **1** (0.5 g, 2.0 mmol), **2** (*n*-propyl spacer) (3.4 g, 7.9 mmol), and NaH (60% in mineral oil, 0.65 g) in DMF (35 mL) was stirred at 0 °C for 15 min, followed by addition of aq DMF (2%) (6 mL), over a period of 2 h. The reaction mixture stirred for 12 h at rt, solvents were removed in vacuo, and the resulting residue was dissolved in EtOAc, washed with water, dried (Na_2SO_4), concentrated, and purified (SiO_2, PhMe/EtOAc = 98:2), to afford benzyl-protected dendrimer ***C_3G1*** (1.8 g, 76%), as a white gum.

A mixture of the above intermediate (1.5 g, 1.3 mmol) and Pd/C (10%) (0.3 g) in THF (35 mL) was refluxed for 24 h and treated as described in the general procedure to afford ***C_3G1*** (0.75 g, 91%), as a foam. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.01 (m, J = 6.2 Hz, 6 H), 3.90 (m, J = 6.2 Hz, 6 H), 3.97 (m, 6 H), 5.73 (s, 6 H), 5.75 (s, 3 H), 6.05 (s, 3 H), 9.10 (s, 6 H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 28.6, 63.7, 64.2, 93.1, 93.8, 95.5, 159.0, 160.3, 160.4. ESI-MS m/z calcd for $C_{33}H_{36}O_{12}$ $[M + Na]^+$ 647.2104, found 647.2106. Anal. Calcd for $C_{33}H_{36}O_{12}$: C, 63.45; H, 5.81. Found: C, 63.60; H, 6.89.

C_4G1. A mixture of **1** (0.83 g, 3.3 mmol), **2** (*n*-butyl spacer) (5.8 g, 13.2 mmol) and NaH (60% in mineral oil, 1.1 g, 26.3 mmol) in DMF (50 mL) was stirred at 0 °C for 15 min, followed by addition of aq DMF (2%) (6 mL), over a period of 2 h. The reaction mixture stirred for 12 h at rt, solvents were removed in vacuo, and the resulting residue was dissolved in EtOAc, washed with water, dried (Na_2SO_4), concentrated, and purified (SiO_2, PhMe/EtOAc = 98:2), to afford benzyl-protected dendrimer ***C_4G1*** (2.8 g, 71%), as a white gum.

A mixture of the above intermediate (2.5 g, 2.01 mmol) and Pd/C (10%) in THF (50 mL) was refluxed for 24 h and treated as described in the general procedure to afford ***C_4G1*** (1.15 g, 87%), as a foam. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.78 (br, 12 H), 3.86 (br, 6 H), 3.94 (br, 6 H), 5.77 (s, 6 H), 5.80 (s, 3 H), 6.06 (s, 3 H), 9.13 (s, 6 H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 25.4, 66.7, 67.1, 93.1, 93.7, 95.4, 158.9, 160.4. ESI-MS m/z calcd for $C_{36}H_{42}O_{12}$ $[M + Na]^+$ 689.2574, found 689.2578. Anal. Calcd for $C_{36}H_{42}O_{12}$: C, 64.85; H, 6.35. Found: C, 63.75; H, 6.03.

C_2G2. A mixture of ***C_2G1*** (1.41 g, 2.42 mmol), **2** (ethyl spacer) (7.5 g, 18.2 mmol), K_2CO_3 (3.0 g, 21.8 mmol), and 18-crown-ether (catalytic) in 2-butanone (40 mL) and DMF (20 mL) was stirred at 90 °C for 30 h and treated as described in the general procedure to afford benzyl-protected dendrimer ***C_2G2*** (5.0 g, 79%), as a colorless gum.

A mixture of above intermediate (4.0 g, 1.55 mmol) and Pd/C (10%) (1.0 g) in THF (50 mL) was refluxed for 24 h and treated as described in the general procedure to afford ***C_2G2*** (1.9 g, 81%), as a foam. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 4.12 (br, 12 H), 4.21 (br, 24 H), 5.81 (s, 12 H), 5.83 (s, 6 H), 6.20 (s, 12 H), 9.19 (s, 12 H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 65.9, 66.4, 93.1, 94.0, 95.7, 159.0, 160.1, 160.2. ESI-MS m/z calcd for $C_{78}H_{78}O_{30}$ $[M + Na]^+$ 1517.4476, found 1517.4468. Anal. Calcd for $C_{78}H_{78}O_{30}$: C, 62.65; H, 5.26. Found: C, 62.55; H, 6.43.

C_3G2. A mixture of ***C_3G1*** (1.15 g, 1.84 mmol), **2** (*n*-propyl spacer) (5.9 g, 13.8 mmol), K_2CO_3 (2.3 g, 16.5 mmol), and 18-crown-ether (catalytic) in 2-butanone (45 mL) and DMF (15 mL) was stirred at 90 °C for 30 h and treated as described in the general procedure to afford benzyl-protected dendrimer ***C_3G2*** (3.6 g, 73%), as a colorless gum.

A mixture of the above intermediate (3.5 g, 1.3 mmol) and Pd/C (10%) in THF (50 mL) was refluxed for 24 h and treated as described in the general procedure to afford ***C_3G2*** (1.8 g, 85%), as a white foam. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.05 (m, J = 6.0 Hz, 18 H), 3.94 (t, J = 6.0 Hz, 12 H), 4.02 (m, 24 H), 5.78 (s, 12 H), 5.80 (s, 6 H), 6.10 (s, 12 H), 9.15 (s, 12 H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 28.6, 63.7, 64.2, 93.1, 93.8, 95.5, 159.0, 160.2, 160.3. MALDI-TOF-MS m/z calcd for $C_{87}H_{96}O_{30}$ $[M + H]^+$ 1622.68, found 1622.50. Anal. Calcd for $C_{87}H_{96}O_{30}$: C, 64.44; H, 5.97. Found: C, 63.63; H, 5.13.

C_4G2. A mixture of ***C_4G1*** (1.2 g, 1.8 mmol), **2** (*n*-butyl spacer) (6.0 g, 13.5 mmol), K_2CO_3 (2.3 g, 16.2 mmol), and 18-crown-ether (catalytic) in 2-butanone (45 mL) and DMF (15 mL) was stirred at 90 °C for 30 h and treated as described in the general procedure to afford benzyl-protected dendrimer ***C_4G2*** (3.7 g, 73%), as a colorless gum.

A mixture of the above intermediate (3.5 g, 1.24 mmol) and Pd/C (10%) in THF (50 mL) was refluxed for 24 h and treated as described in the general procedure to afford ***C_4G2*** (1.75 g, 81%), as a foam. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.77 (br, 36 H), 3.85 (br, 12 H), 3.93 (br, 24 H), 5.77 (s, 12 H), 5.80 (s, 6 H), 6.06 (s, 12 H), 9.13 (s, 12 H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 25.5, 66.7, 67.1, 93.1, 93.7, 95.7, 158.9, 160.4. MALDI-TOF-MS m/z calcd for $C_{96}H_{114}O_{30}$ $[M + H]^+$ 1748.74, found 1748.43. Anal. Calcd for $C_{96}H_{114}O_{30}$: C, 65.97; H, 6.57. Found: C, 65.26; H, 5.85.

C_2G3. A mixture of ***C_2G2*** (1.1 g, 0.75 mmol), **2** (ethyl spacer) (4.5 g, 10.8 mmol), K_2CO_3 (1.8 g, 13.0 mmol), and 18-crown-ether (catalytic) in 2-butanone (30 mL) and DMF (20 mL) was stirred at 90 °C for 48 h and treated as described in the general procedure to afford benzyl-protected dendrimer ***C_2G3*** (2.7 g, 65%), as a colorless gum.

A mixture of the above intermediate (2.5 g, 0.45 mmol) and Pd/C (10%) in THF (50 mL) was refluxed for 24 h and treated as described in the general procedure to afford ***C_2G3*** (1.1 g, 73%), as a foam. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 4.10 (br, 24 H), 4.20 (br, 60 H), 5.80 (s, 24 H), 5.82 (s, 12 H), 6.20 (s, 30 H), 9.19 (s, 24 H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 65.9, 66.4, 93.1, 94.0, 95.7, 159.0, 160.0, 160.2. MALDI-TOF-MS m/z calcd for $C_{174}H_{174}O_{66}$ $[M]^+$ 3321.03, found 3321.82. Anal. Calcd for $C_{174}H_{174}O_{66}$: C, 62.92; H, 5.28. Found: C, 62.28; H, 6.31.

C_3G3. A mixture of ***C_3G2*** (1.15 g, 0.73 mmol), **2** (*n*-propyl spacer) (4.7 g, 11.0 mmol), K_2CO_3 (1.8 g, 13.0 mmol), and 18-crown-ether (catalytic) in 2-butanone (35 mL) and DMF (25 mL) was stirred at 90 °C for 48 h and treated as described in the general procedure to afford benzyl-protected dendrimer ***C_3G3*** (2.9 g, 68%), as a colorless gum.

A mixture of the above intermediate (2.7 g, 0.46 mmol) and Pd/C (10%) in THF (50 mL) was refluxed for 24 h and treated as described in the general procedure to afford ***C_3G3*** (1.2 g, 71%), as a foam. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.04 (m, J = 6.0 Hz, 42 H), 3.93 (t, J = 6.0 Hz, 24 H), 4.00 (br, 60 H), 5.78 (s, 24 H), 5.81 (s, 12 H), 6.10 (s, 30 H), 9.14 (s, 24 H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 28.6, 63.7, 64.2, 93.1, 93.8, 95.5, 159.0, 160.3, 160.4. MALDI-TOF-MS m/z calcd for $C_{195}H_{216}O_{66}$ $[M + H]^+$ 3616.36, found 3616.93. Anal. Calcd for $C_{195}H_{216}O_{66}$: C, 64.77; H, 6.02. Found: C, 64.67; H, 5.29.

C_4G3. A mixture of ***C_4G2*** (0.76 g, 0.43 mmol), **2** (*n*-butyl spacer) (2.9 g, 6.5 mmol), K_2CO_3 (1.1 g, 7.8 mmol), and 18-crown-ether (catalytic) in 2-butanone (35 mL) and DMF (15 mL) was stirred at 90 °C for 48 h and treated as described in the general procedure to afford benzyl-protected dendrimer ***C_4G3*** (1.65 g, 63%), as a colorless gum.

A mixture of the above intermediate (1.6 g, 0.26 mmol) and Pd/C (10%) in THF (50 mL) was refluxed for 24 h and treated as described in the general procedure to afford **C_4G3** (0.68 g, 67%), as a foam. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.76 (br, 84 H), 3.84 (br, 24 H), 3.98 (br, 60 H), 5.77 (s, 24 H), 5.80 (s, 12 H), 6.05 (s, 30 H), 9.13 (s, 24 H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 25.4, 66.6, 67.1, 93.1, 93.6, 95.4, 158.9, 160.4. MALDI-TOF-MS m/z calcd for $C_{216}H_{258}O_{66}$ $[M + H]^+$ 3910.69, found 3911.08. Anal. Calcd for $C_{216}H_{258}O_{66}$: C, 66.35; H, 6.65. Found: C, 65.26; H, 5.85.

Encapsulation of Pyrene in Dendritic Interior. A solution of dendrimer (2 μmol) and pyrene (5 mg) in THF (1 mL) was prepared, and the solvent was removed in vacuo. The resulting residue was added with aq NaOH (1.1 molar equiv per hydroxyl group) solution (10 mL) (pH ~10), the mixture was stirred for 12 h in the dark, filtered (0.45 μ), and extracted with PhMe (4 × 5 mL), and the organic portion was evaporated in vacuo. The resulting residue was dissolved in EtOH (3 mL), and the amount of pyrene was determined by UV−vis spectroscopy (ε_{335} 50,734 mol^{-1} cm^{-1}).[32,33] The free energy transfer (ΔG_{tr})[49] of pyrene solubilization was calculated from equation $\Delta G_{tr} = -RT \ln(C_s/C_w)$, where C_s and C_w were the solubilities of pyrene in aqueous basic solution of dendrimer and in water (pH ~9.5), respectively.

Fluorescence Measurements. Fluorescence spectra were recorded at room temperature on an steady-state fluorimeter. The concentrations of the probes were [C1] and [C480] = 0.02 mM, and [C153] = 0.04 mM in water. The excitation wavelength for C480 and C1 was 375 nm, and for C153 it was 400 nm. A stock solution of the dendrimer (10 mM) was prepared in aq NaOH (100 mM). These dendrimer solutions were added step-by-step to an aq solution of coumarins. Each consecutive step was 1 mol equiv to the probe concentration. The dendrimer solution was added until no further change in the spectra could be observed. The concentration of pyrene was 0.01 mM, and the excitation wavelength was 335 nm. The required amount of pyrene was taken in a test tube, 3 mL of 0.2 mM dendrimer solution was added to it, and the mixture was stirred for 24 h. The solutions were filtered, nitrogen was purged for 30 min, and the fluorescence spectra were recorded at room temperature.

Photolysis of Substrate−Dendrimer Complex. 1-Phenyl-3-*p*-tolyl-propane-2-one (**3**) was synthesized as described in the literature.[50] A solution of substrate **3** in $CHCl_3$ (4×10^{-4} M) was taken in a test tube, solvents were removed carefully, the residue was added to an aqueous basic solution of dendrimer (1×10^{-3} M) (2−5 mL), and the mixture was stirred in dark for 12 h, while continuously purging with N_2. The mixture was filtered through an Acrodisc filter, and the filtrate in a Pyrex tube was irradiated with a 450 W medium-pressure Hg lamp, while purging with N_2. Irradiation for 12 h resulted in 30% conversion for substrate **3**. Absorption by the dendrimer might have been responsible for the low conversion.

Extraction of Photoproducts and Reactants from Dendrimer. After photolysis, the solution was acidified with aq HCl (10%), extracted with EtOAc/acetonitrile (7:3) solvent mixture, dried (Na_2SO_4), concentrated, and analyzed on a gas chromatograph, fitted with an HP-5 column.

Characterization of Photoproducts. Peaks in the GC traces were identified by co-injecting with authentic samples that were prepared by solution irradiation. Photoproducts **5** (**AA**) and **7** (**BB**) were commercially available. Photoproduct **6** (**AB**) was identified on the basis of the GC−MS fragmentation pattern. Mass spectral data m/z (relative intensity): 196 (M^+, 17%), 105 (100%), 91 (12%), 77 (11%). Photoproduct **4** isolated from irradiation was characterized by ^{1}H NMR spectroscopy and GC mass spectrometry.[29,30]

■ ASSOCIATED CONTENT

Supporting Information. General experimental procedure, ^{1}H and ^{13}C NMR data and spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jayaraman@orgchem.iisc.ernet.in; vramamurthy@mail.as.miami.edu.

■ ACKNOWLEDGMENT

N.J. thanks Department of Science and Technology, New Delhi for a financial support. Council of Scientific and Industrial Research, New Delhi is acknowledged for a research fellowship to B.N. V.R. is grateful to the National Science Foundation, USA, for generous financial support (CHE-0848017).

■ REFERENCES

(1) Newkome, G. R.; Shreiner, C. *Chem. Rev.* **2010**, *110*, 6338–6442.
(2) Wurm, F.; Frey, H. *Prog. Polym. Sci.* **2011**, *36*, 1–52.
(3) Hourani, R.; Kakkar, A. *Macromol. Rapid Commun.* **2010**, *31*, 947–974.
(4) Astruc, D.; Boisselier, E.; Ornelas, C. *Chem. Rev.* **2010**, *110*, 1857–1959.
(5) Rosen, B. M.; Wilson, C. J.; Wilson, D. A.; Peterca, M.; Imam, M. R.; Percec, V. *Chem. Rev.* **2009**, *109*, 6275–6540.
(6) Carlmark, A.; Hawker, C.; Hult, A.; Malkoch, M. *Chem. Soc. Rev.* **2009**, *38*, 352–362.
(7) Smith, D. K.; Diederich, F. *Chem.—Eur. J.* **1998**, *4*, 1353–1361.
(8) Tomalia, D. A.; Fréchet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2719–2728.
(9) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Saunders, M. J.; Grossman, S. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1178–1180.
(10) Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1993**, *115*, 4375–4376.
(11) Habicher, T.; Diederich, F.; Gramlich, V. *Helv. Chim. Acta* **1999**, *82*, 1066–1095.
(12) Richter-Egger, D. L.; Landry, J. C.; Tesfai, A.; Tucker, S. A. *J. Phys. Chem. A* **2001**, *105*, 6826–6833.
(13) Morgan, M. T.; Immoos, C. E.; Degoricija, L. A.; Carnahan, M. A.; Lee, S. J.; Grinstaff, M. W. *Polym. Prepr.* **2002**, *43*, 1299.
(14) Chasse, T. L.; Sachdeva, R.; Li, Q.; Li, Z.; Petrie, R. J.; Gorman, C. B. *J. Am. Chem. Soc.* **2003**, *125*, 8250–8254.
(15) Ong, W.; Grindstaff, J.; Sobransingh, D.; Toba, R.; Quintela, J. M.; Peinador, C.; Kaifer, A. E. *J. Am. Chem. Soc.* **2005**, *127*, 3353–3361.
(16) Mchedlov-Petrossyan, N. O.; Bryleva, E. Y.; Vodolazkaya, N. A.; Dissanayake, A. A.; Ford, W. T. *Langmuir* **2008**, *24*, 5689–5699.
(17) Burakowska, E.; Quinn, J. R.; Zimmerman, S. C.; Haag, R. *J. Am. Chem. Soc.* **2009**, *131*, 10574–10580.
(18) Kannaiyan, D.; Imae, T. *Langmuir* **2009**, *25*, 5282–5285.
(19) Warmuth, R.; Yoon, J. *Acc. Chem. Res.* **2001**, *34*, 95–105.
(20) Sun, W.-Y.; Yoshizawa, M.; Kusukawa, T.; Fujita, M. *Curr. Opin. Chem. Biol.* **2002**, *6*, 757–764.
(21) Aulenta, F.; Hayes, W.; Rannard, S. *Eur. Polym. J.* **2003**, *39*, 741–1771.
(22) Rissanen, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 3652–3654.
(23) Pallavicini, P.; Diaz-Fernandez, Y. A.; Pasotti, L. *Coord. Chem. Rev.* **2009**, *253*, 2226–2240.
(24) Luty, T.; Eckhardt, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 2441–52.
(25) Ito, Y.; Yasui, S.; Yamauchi, J.; Ohba, S.; Kano, G. *J. Phys. Chem. A* **1998**, *102*, 5415–5420.
(26) Zimmerman, H. E.; Alabugin, I. V.; Smolenskaya, V. N. *Tetrahedron* **2000**, *56*, 6821–6831.
(27) Xu, J.; Weiss, R. G. *Org. Lett.* **2003**, *5*, 3077–3080.
(28) Kaliappan, R.; Ling, Y.; Kaifer, A. E.; Ramamurthy, V. *Langmuir* **2009**, *25*, 8982–8992.

(29) Kaanumalle, L. S.; Nithyanandhan, J.; Pattabiraman, M.; Jayaraman, N.; Ramamurthy, V. *J. Am. Chem. Soc.* **2004**, *126*, 8999–9006.
(30) Kaanumalle, L. S.; Ramesh, R.; Murthy Maddipatla, V. S. N.; Nithyanandhan, J.; Jayaraman, N.; Ramamurthy, V. *J. Org. Chem.* **2005**, *70*, 5062–5069.
(31) Nithyanandhan, J.; Jayaraman, N. *J. Org. Chem.* **2002**, *67*, 6282–6285.
(32) Clar, E. *J. Chem. Soc.* **1949**, 2013–2016.
(33) Friedel, R. A.; Orchin, M. *Ultraviolet Spectra of Aromatic Compounds*; John Wiley & Sons: New York, 1951; p 472.
(34) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039.
(35) Dong, D. C.; Winnik, M. A. *Can. J. Chem.* **1984**, *62*, 2560–2565.
(36) Nag, A.; Chakrabarty, T.; Bhattacharyya, K. *J. Phys. Chem.* **1990**, *94*, 4203.
(37) Porel, M.; Jayaraj, N.; Kaanumalle, L. S.; Maddipatla, M. V. S. N.; Parthasarthy, A.; Ramamurthy, V. *Langmuir* **2009**, *25*, 3473–3481.
(38) Das, D. K.; Das, A. K.; Mondal, T.; Mandal, A. K.; Bhattacharyya, K. *J. Phys. Chem. B* **2010**, *114*, 13159–13166.
(39) Wagner, B. D. *Molecules* **2009**, *14*, 210–237.
(40) Grant, C. D.; DeRitter, M. R.; Steege, K. E.; Fadeeva, T. A.; Castner, E. W., Jr. *Langmuir* **2005**, *21*, 1745–1752.
(41) Jones, G., II; Jackson, W. R.; Choi, C. Y.; Bergmark, W. R. *J. Phys. Chem.* **1985**, *89*, 294.
(42) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; Wiley-VCH: Weinheim, 2003.
(43) Lewis, F. D.; Lauterbach, R. T.; Heine, H.-G.; Hartmann, W.; Rudolph, H. *J. Am. Chem. Soc.* **1975**, *97*, 1519–1525.
(44) Frederick, B.; Johnston, L. J.; de Mayo, P.; Wong, S. K. *Can. J. Chem.* **1984**, *62*, 403–410.
(45) Turro, N. J. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 609–621.
(46) Gould, I. R.; Turro, N. J.; Zimmt, M. B. In *Adv. Phys. Org. Chem.*; Bethell, D., Ed.; Academic Press: London, 1984; Vol. 20, pp 1−53.
(47) Turro, N. J. *Chem. Commun.* **2002**, 2279–2292.
(48) Turro, N. J. *Acc. Chem. Res.* **2000**, *33*, 637–646.
(49) Balasubramanian, D.; Raman, B.; Sundari, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 74–77.
(50) *Organic Synthesis*; Rabjohn, N., Ed.; Wiley: New York, 1963; Vol. IV, p 176.