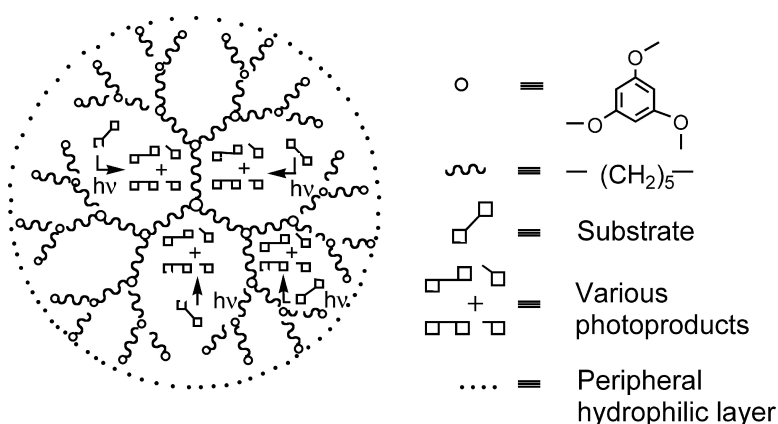Article

Water-Soluble Dendrimers as Photochemical Reaction Media: Chemical Behavior of Singlet and Triplet Radical Pairs Inside Dendritic Reaction Cavities

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Water-Soluble Dendrimers as Photochemical Reaction Media: Chemical Behavior of Singlet and Triplet Radical Pairs Inside Dendritic Reaction Cavities

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Abstract: Water-soluble poly(alkyl aryl ether) dendrimers have been explored for their use as hosts of organic substrates in aqueous media. Prototypical photoreactions, namely, photo-Fries reaction of (a) 1-naphthyl benzoate and (b) 1-naphthyl phenyl ester and α-cleavage reaction of (a) dibenzyl ketones and (b) benzoin alkyl ethers, have been examined. We find that a dendritic microenvironment not only restricts the mobility of radical intermediates but also rigidly encapsulates the substrate, intermediates, and products from "leaking" to the bulk environment. Comparative studies of the same photoreactions in micellar media demonstrate that dendritic media offer much better constrainment than the micelles.

Introduction

A branches-upon-branches architectural motif remains to be the most appealing structural feature of dendritic macromolecules. Ever since the prominence of dendrimers in the literature[1] over a decade ago, the structural features and the associated molecular and supramolecular properties have attracted a wide spectrum of investigations in a number of chemical, biological, and materials related studies involving dendritic macromolecules.[2] A densely packed periphery and well-defined cavities of different sizes at the interior result in the so-called "*exo-*" and "*endo-*" receptor properties in dendrimers, and the benefits of *exo-* and *endo-* receptor properties have been explored in a number of studies.[3] The evolution of microenvironments upon advancing the generation number of a homologous series of dendrimers is a characteristic feature of dendritic architecture. Particularly, the creation of microenvironments is more profound in those dendrimers that contain a polar exterior and nonpolar interior. Analogous to such microenvironments in regular micelles,[4] the presence of distinct microenvironments in

these dendrimers endow them the term "static, unimolecular micelles".[5]

Clearly, the possibilities of encapsulation of organic molecules open up avenues to exploit the dendritic microenvironment in varied studies. We envisaged that such a microenvironment could be utilized as reaction media, in a manner comparable to well-known hosts such as cyclodextrins and micelles.[6] We herein conceptualize this idea by invoking photochemically induced reactions of organic molecules encapsulated by dendrimers. Specifically, we describe encapsulation of water-insoluble organic guest molecules in aqueous dendrimer medium, derived from poly(alkyl aryl ether) dendrimers, and the photochemical reactions of these guest molecules inside the dendritic microenvironments. Based on photoreactions of four organic molecules and the photophysics of pyrene, we establish that poly(alkyl aryl ether) dendrimers provide hydrophobic reaction cavities similar to that of micelles but constrain the mobility of guest molecules more than the ones provided by micelles. Given the current emphasis on "green chemistry", use of water as the medium and light as the reagent is most appealing.[7] We utilize in this study dendrimers as vehicles to solubilize organic

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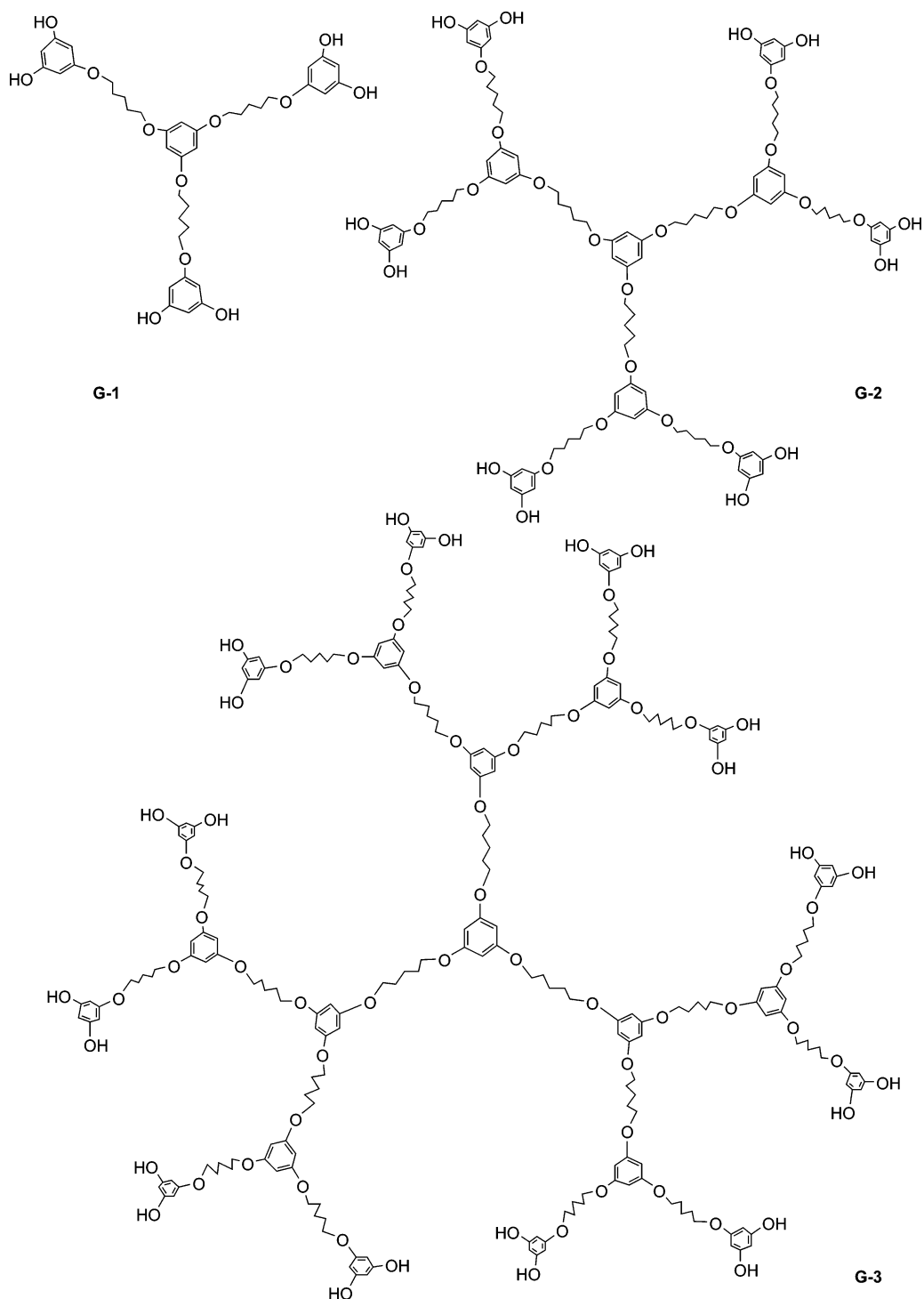
Figure 1. Structures of the dendrimers used in this study.

molecules in water and as restrictive reaction media to control photoproduct distribution.
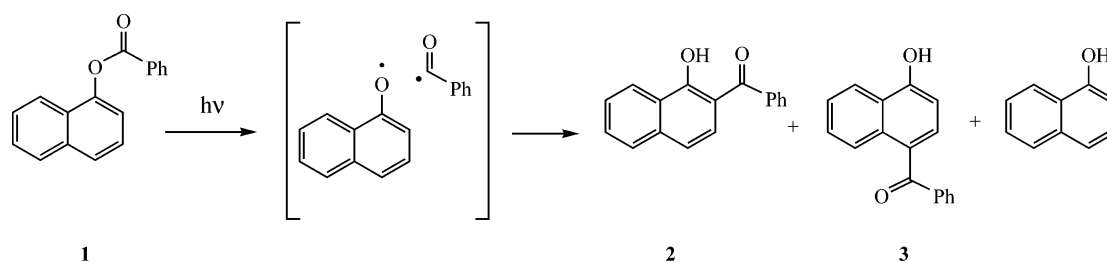
Results and Discussion

The dendrimers of choice to test them as reaction media are the poly(alkyl aryl ether) dendrimers reported recently (Figure 1).[8] These dendrimers are constituted with phloroglucinol, acting as the core and branching component, and a pentamethylene chain, which acts as the linker component. In this constitution,

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the first, second, and third generation dendrimers possess, respectively, 6, 12, and 24 phenolic hydroxyl groups at their peripheries. These dendrimers are soluble in water in their phenoxide form at a pH above 9. Prior to utilizing the dendrimers as reaction media, knowledge of hydrophilic−hydrophobic balance and the micropolarity arising due to hydrophilic exterior and the relatively hydrophobic interior is essential. To probe the micropolarity of the interior of dendrimers, we have employed pyrene as the probe.[9] Pyrene is soluble in water only to the extent of 1×10^{-6} M. The fluorescence spectrum shown in Figure 2 reveals that even under

Scheme 1

Table 1. Ratio of I_1/I_3 Bands of Pyrene[a] in Dendrimers and Water

[host], M	I_1/I_3	I_1/I_3 for solvents[b]
2×10^{-4} (G₃ dendrimer)	1.18	1.18 (ethanol)
2×10^{-4} (G₂ dendrimer)	1.30	1.35 (methanol)
2×10^{-4} (G₁ dendrimer)	1.48	1.50 (dioxane)
water pH > 9	1.70	1.87 (water)

[a] [Pyrene] = 1×10^{-5} M. [b] Literature values.

such low concentrations probably pyrene exists as aggregates in water (note the presence of emission in the region 430−500 nm due to a ground-state dimer). As reported earlier, the solubility of pyrene in aqueous solution, as determined by UV− vis spectroscopy, increases by a factor of 5, 8, and 24 for the first, second, and third generation dendrimers (100 μM each), respectively.[8] Emission spectra displayed in Figure 2 show the
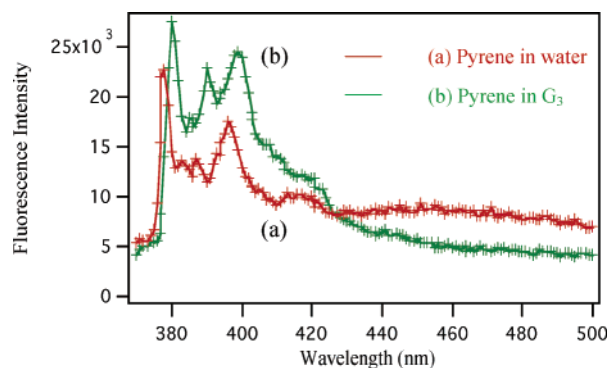

Figure 2. Fluorescence spectrum of pyrene in (red) water (pH 9.5) and (green) aqueous solution of G₃ dendrimer (200 μM, pH 9.5).

absence of a ground-state dimer of pyrene when G₃ dendrimers (2×10^{-4} M) were added to the aqueous basic solution. The absence of the ground-state dimer was also confirmed for aqueous solutions containing G₁ and G₂ dendrimers. The absence of emission due to a ground-state dimer and excimer in dendrimer media suggests that pyrene molecules are kept isolated by the latter, and within the excited-state lifetime, pyrene in the excited singlet state is unable to interact with another pyrene molecule present in the ground state.

It is well established that the ratio of the intensities of the vibrational peaks 1 and 3 (I_1 to I_3) in the fluorescence spectrum of pyrene is an excellent measure of the polarity of its immediate environment.[9] I_1/I_3 values measured from the fluorescence spectra of pyrene in aqueous dendritic media are presented in Table 1. A comparison of the I_1/I_3 of dendrimers vs I_1/I_3 of common solvents indicates that pyrene experiences an increasingly nonpolar environment as the dendrimer generation ad-

vances from first to third. For example, while the polarity experienced by pyrene in aqueous solution of G₁ (pH ~9) is similar to that of dioxane, that in aqueous solution of G₃ (pH ~9) is similar to that of ethanol. This effect is most likely due to an increase in the number of hydrophobic cavities as the dendrimer generation advance and to the better ability of cavities derived from higher generations to encapsulate the probe molecule. PAMAM dendrimers are also known to exhibit a similar property.[10]

Results presented above clearly suggest that the poly(alkyl aryl ether) dendrimers, especially the G₃, contain hydrophobic pockets (in water) in which one could conduct chemical reactions. To explore this possibility, we have carried out four photochemical reactions, namely, photo-Fries reaction of 1-naphthyl benzoate and 1-naphthyl phenylacyl ester and α-cleavage reaction of dibenzyl ketones and benzoin alkyl ethers. In these four reactions, a single molecule is photochemically cleaved into two pieces (radical pair), and dependent on the mobility of the two reactive species, the composition of the final products varies. As discussed below, the final products obtained within the hydrophobic pockets of poly(alkyl aryl ether) dendrimers are much more selective than those in common organic solvents.

The first reaction examined is the photo-Fries reaction of 1-naphthyl benzoate (**1**) (Scheme 1).[11,12] This molecule upon irradiation in hexane gives 2-benzoyl 1-naphthol (**2**) and 4-benzoyl 1-naphthol (**3**) in the ratio 3:1 (Table 2). However, in basic aqueous medium (pH ~9), this molecule undergoes hydrolysis to yield naphthol and benzoic acid (dark reaction). When an aqueous solution of G₃ dendrimer (2×10^{-4} M) was added to the aqueous solution (pH ~9; 5 mL) containing 4×10^{-4} M of 1-naphthyl benzoate, no hydrolysis occurred even after 12 h. This suggested that the G₃ dendrimer protects the reactant from water and OH⁻ ions by encapsulating it within its hydrophobic pockets. However, addition of an aqueous solution of G₁ dendrimer (2.3×10^{-3} M) had led to the thermal hydrolysis process (Table 2). These observations are consistent with the hydrophobicity information provided by the probe pyrene (G₁ is less hydrophobic than G₃). Irradiation of 1-naphthyl benzoate included in an aqueous solution of G₃ resulted in the same two products as in hexane, but the ratio was much different (19:1 as opposed to 3:1 in hexane; Table 2). Similar higher selectivity in favor of 2-benzoyl 1-naphthol was observed
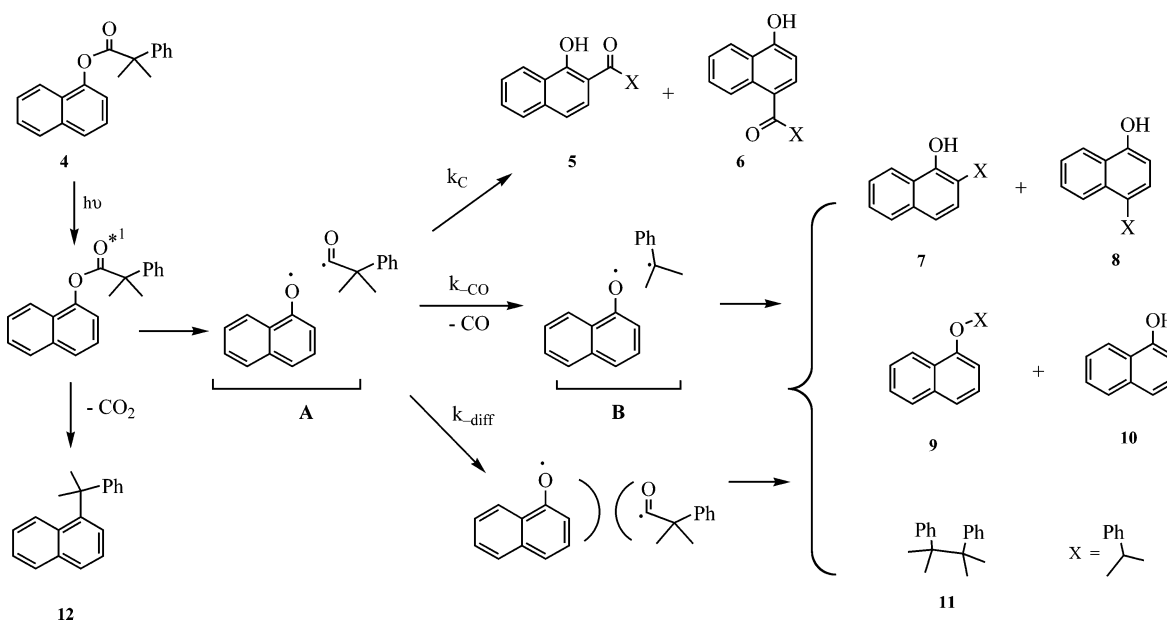
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Scheme 2

Table 2. Product Distribution upon Irradiation of Naphthyl Benzoate[a,b,c]

medium	2[c]	3[c]	naphthol	benzil	benzoic acid
hexane	62	24	10	4	
aq NaOH[d]	1		62		37
G3	95	5			
G2	93	7			
G1	9		64		27
G1[d]			65		25
NaDCh	99	1			
NaCh	85	15			
SDS	83	17			

[a] $[G_1] = 22.5 \times 10^{-4}$ M, $[G_2] = 8 \times 10^{-4}$ M, $[G_3] = 2 \times 10^{-4}$ M, [**1**] $= 4.0 \times 10^{-4}$ M. [b] Mean occupancy numbers: NaDCh, NaCh $= 0.2-0.25$ (15–17 monomers per aggregate); SDS $= 0.7-1.0$ (70 monomers per micelle). [c] For structures, see Scheme 1. [d] Product distribution resulting from dark (thermal) reaction of **1**.

Table 3. Product Distribution upon Photolysis of Dimethyl Naphthyl Phenyl Acetate in Various Media[a,b,c]

medium	5	6	7	8	9	10	11[c]	12
hexane	35	17	4	21		8	8	6
aq NaOH[d]						43		
aq NaOH[e]	27	3				69		
G3	96	4						
G2	93	7						
G1[e]	49	9				39		3
NaDCh	92			2		4	2	1
NaCh	80	10	2	1		5		2
SDS	83	13		1		2		2

[a] $[G_1] = 22.5 \times 10^{-4}$ M, $[G_2] = 8 \times 10^{-4}$ M, $[G_3] = 2 \times 10^{-4}$ M, [**4**] $= 3.42 \times 10^{-4}$ M. [b] Mean occupancy numbers: NaDCh, NaCh $= 0.17-0.23$; SDS $= 0.42-0.67$. [c] For structures, see Scheme 2. [d] Product distribution resulting from dark (thermal) reaction. [e] Product distribution resulting from thermal reaction and photoreaction.
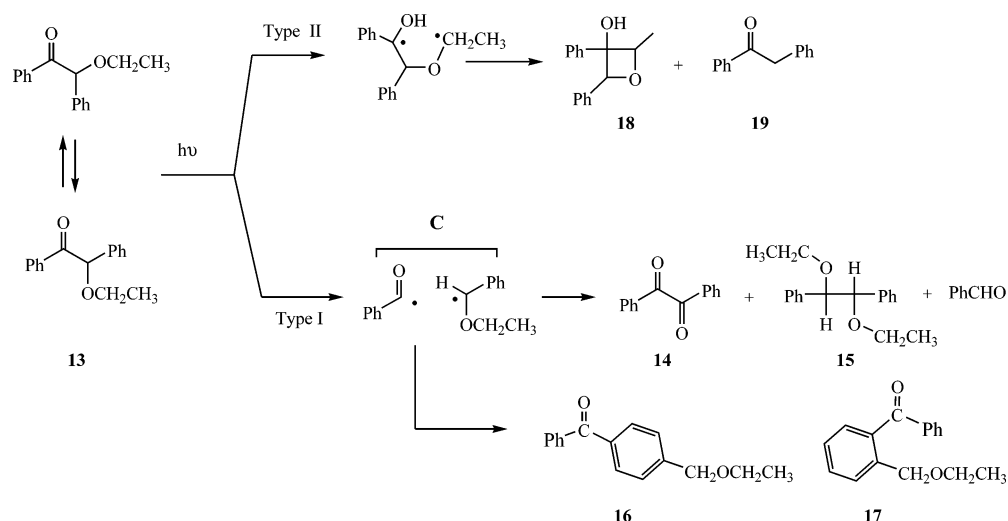
when an aqueous solution of G_2 (8×10^{-4} M) was used as the host. The higher selectivity observed with G_2 and G_3 as hosts suggests that the singlet radical pair, naphthoxyl and benzoyl, formed upon cleavage of 1-naphthyl benzoate has much less mobility within the hydrophobic pockets of dendrimers than in hexane. The short lifetime of the singlet radical pair and probable high microviscosity of the hydrophobic pockets of the dendrimers probably do not allow migration of benzoyl radical from the 1 to 4 position of the naphthoxyl radical.

The second photoreaction we investigated was the cleavage reaction of 1-naphthyl phenylacyl ester **4** (Scheme 2).[13] Photolysis of 1-naphthyl phenylacyl ester **4** in hexane resulted in a mixture of seven products, yields of which are presented in Table 3. Similar to 1-naphthyl benzoate discussed above, 1-naphthyl phenylacyl ester **4** underwent thermal hydrolysis in basic aqueous medium (pH ~9; 3.4×10^{-4} M). This thermal reaction once again was prevented by addition of aqueous

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solutions of G_2 and G_3 dendrimers to the above solution. Most interestingly, when the irradiation of 1-naphthyl phenylacyl ester **4** in basic aqueous solution containing 8×10^{-4} M G_2 or 2×10^{-4} M G_3 was conducted, only two products were obtained (Table 3). Of the two products (2- and 4- isomers), 2-phenylacyl 1-naphthol **5** predominated the product mixture. The selectivity obtained in the presence of dendrimers is dramatic, going from seven products in hexane solution to essentially a single product, 2-phenylacyl 1-naphthol **5**, in the presence of dendrimers. The above product selectivity could be understood based on the mechanism provided in Scheme 2. Homolytic cleavage of the ester occurs from their excited singlet state to yield geminate singlet radical pair **A**. It is followed by in-cage recombination (giving rearranged products **5** and **6**) or cage escape. Decarbonylation of phenylacyl radical within the cage results in the radical pair **B** and outside the cage leads to naphthoxyl and benzyl free radicals. Reaction of these radicals either within or outside the cage leads to products **7**–**10**. Diaryl ethane **11** is the result of coupling of the two dimethyl benzyl radicals outside the cage.

Absence of products **7**–**11** implies that the primary radical pair **A** does not give the radical pair **B**. This suggests that the recombination of the naphthoxyl and phenylacyl radicals within

Scheme 3

Type II

Type I

C

13   **18**   **19**   **14**   **15**   + PhCHO   **16**   **17**

a dendrimer must be rapid compared to their escape from a dendrimer and decarbonylation of the phenylacyl radical. The rate of decarbonylation of 1,1′-dimethyl 2-phenylacyl radical in solution has been estimated to be 1.5×10^8 s^{-1}.[14] Therefore, the rate of recombination of the radical pair **A** must be faster than the above rate. Further, the hydrophobic pockets of G_2 and G_3 dendrimers must not be "leaky" in the time scale of 6×10^{-9} s. Selective formation of 2-phenylacyl 1-naphthol (**5**) from 1-naphthyl phenylacyl ester **4** is consistent with the behavior of 1-naphthyl benzoate **1** discussed above and suggests that the reaction cavity of a dendrimer restricts the mobility of the radical pair **A**.

To address the question whether the hydrophobic pockets of G_2 and G_3 dendrimers in water can restrict the mobility of guest molecules (and reactive intermediates) even on a longer time scale, we have explored the photochemistry of benzoin ethyl ether (**13**)[15] and 1-phenyl-3-*para*-tolyl-propane-2-one (**20**).[16] These two systems cleave from the triplet state to yield triplet radical pairs. Under such conditions, coupling of the radical pair can occur only if it can cross to the singlet radical pair or separate to become free radicals. Results presented below on these two systems suggest that reaction cavities of dendrimers are "leak-proof" even on a microsecond time scale.

Benzoin ethyl ether (**13**) upon irradiation in solution yields products of Norrish type I and type II processes from the triplet state (Scheme 3; Table 4).[14] Generally, in isotropic solvent media, products of the Norrish type I process predominate the product mixture. In solution, α-cleavage leads to benzoyl and α-alkoxybenzyl triplet radical pair **C** (Scheme 3) which generally escapes the cage to yield benzil (**14**) and pinacol ether **15**. Minor amounts (<10%) of Norrish–Yang cyclization product **18** and deoxy benzoin (**19**) via γ-hydrogen abstraction are also formed (Scheme 3). In solution, the rearrangement products, *para*-benzoylbenzyl ethyl ether (**16**) and *ortho*-benzoylbenzyl ethyl ether (**17**), through coupling of the benzoyl and α-alkoxy-benzyl radical pair **C** are not obtained. Product distributions in

Table 4. Product Distribution on Photolysis of Benzoin Ethyl Ether[a,b,c]

medium	14	15	16	17	18	19[c]
hexane	40	56			4	
methanol	13	78			6	2
benzene	32	63			5	
water	3	82			5	10
aq NaOH		31			4	65
G_3[a]		1	8	14	57	21
G_3[d]		7	8	15	30	41
G_2		4	6	16	29	44
G_1			5	4	41	50
NaDCh	1	55	2		17	25
NaCh		66	2		20	12
SDS	7	39	1		41	12

[a] $[G_1] = 14 \times 10^{-4}$ M, $[G_2] = 11 \times 10^{-4}$ M, $[G_3] = 4.8 \times 10^{-4}$ M, $[13] = 2.9 \times 10^{-4}$ M. [b] Mean occupancy numbers: NaCh, NaDCh = ~0.2; SDS = ~0.6. [c] For structures, see Scheme 3. [d] $[G_3] = 2.4 \times 10^{-4}$ M.

neutral and basic aqueous media (pH ~9) provided in Table 4 clearly indicate that the Norrish type I process is predominant in these media, and this process does not yield the product of in-cage reaction, **16** and **17**. Irradiation of benzoin ethyl ether (3×10^{-4} M) in basic aqueous solution (pH ~9) containing G_1 (14×10^{-4} M), G_2 (11×10^{-4} M), and G_3 (4.8×10^{-4} M) dendrimers resulted in a product mixture different from that in neutral or basic aqueous media (Table 4). Several observations with respect to its photobehavior in dendrimer media are noteworthy from the results presented in Table 4: (a) Products of the Norrish type II process which were almost insignificant (<10%) in organic solvents became the major product (~70%) in dendrimer media. (b) The rearrangement products **16** and **17**, the ones not obtained in solution, are formed in significant amounts (~20%) in the presence of G_2 and G_3 dendrimers. (c) Pinacol ether **15**, the resultant of an out of cage reaction, a major product in organic solvents, is formed in negligible amounts (<2%) in the presence of dendrimers.

Formation of *para*-benzoylbenzyl ethyl ether and *ortho*-benzoylbenzyl ethyl ether in significant amounts (~20%) in the presence of dendrimers indicates that α-cleavage reaction does take place in this media. Absence of pinacol ethers under high concentrations of dendrimers suggests that the only reaction open to the benzoyl and α-alkoxybenzyl radical pair is the recombination to yield the reactant benzoin ethyl ether and the rearranged benzoylbenzyl ethyl ethers **16** and **17**. Formation of

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Scheme 4
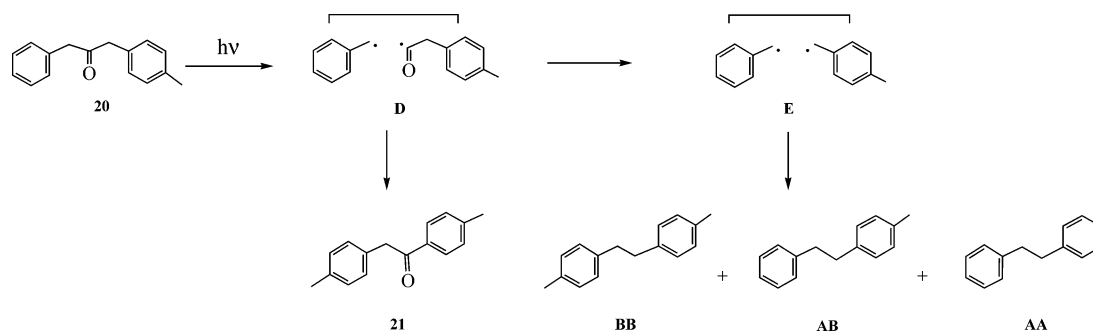
Norrish type II products in major amounts in the presence of dendrimer, we believe, is facilitated by the suppression of Norrish type I products due to recombination of the benzoyl and α-alkoxybenzyl radicals to yield the reactant benzoin alkyl ether. It is quite likely that at the hydrophobic–hydrophilic interface of a dendrimer–water, benzoin ethyl ether adopts a conformation that is suited for γ-hydrogen abstraction.[17] Further work is underway to probe this possibility.

The last reaction we have investigated in the context of probing the mobility of guests within the hydrophobic pockets of dendrimers is the Norrish type I reaction of 1-phenyl-3-*para*-tolyl-propane-2-one (**20**) (Scheme 4).[15] Irradiation of 1-phenyl-3-*para*-tolyl-propane-2-one in hexane solution results in α-cleavage (yielding the primary radical pair **D**) to be followed by decarbonylation (to give the secondary radical pair **E**). In hexane solution, no product from the radical pair **D** has been detected. The three diaryl ethanes **AA**, **AB**, and **BB** resulting from the radical pair **E** are formed in the ratio of 1:2:1 (Scheme 4). In restricted environments, the rearrangement product **21** is formed from the radical pair **D** (Scheme 4).[18] When the radical pair **E** is held within a cage (with a little translational mobility), the only product expected is **AB**.[19] The cage effect (**AB** − **AA** − **BB**)/(**AA** + **AB** + **BB**) and the yield of the rearrangement product **21** provide information concerning the "leakiness" of the reaction cavity with respect to the radical pairs **D** and **E**.

Results of photolysis of 1-phenyl-3-*para*-tolyl-propane-2-one in various media are summarized in Table 5. Clearly, in the presence of dendrimers, **AB** is formed in much larger amounts than in hexane. Observation of higher cage effect (>0.4) in the presence of dendrimers than that in hexane or water (<0.05) indicates that the reaction cavity in dendrimers is much more restrictive than that in isotropic solution. The fact that the cage effects are less than one in G_3 and G_2 dendrimers suggests that either the hydrophobic pockets of dendrimers are not totally "leak-proof" with respect to the radical pair **E** or each dendrimer molecule is multiply occupied. The key experiment of controlling the occupancy number by increasing the dendrimer concentration could not be carried out owing to absorption problems. At high concentrations (8×10^{-4} M) of the dendrimer, the presence of a phenyl chromophore on the

Table 5. Photolysis of 1-Phenyl-3-*p*-tolyl-propan-2-one[a,b,c]

medium	AA	AB	BB	cage effect[d]	21[c]
hexane	21	51	29	0.05	
aq NaOH	21	53	26	0.06	
G_3[e]	4	80	6	0.77	10
G_3[a]	9	69	16	0.46	5
G_2	11	67	17	0.42	5
G_1	15	54	28	0.11	3
NaDCh	14	60	21	0.24	6
NaCh	17	54	21	0.18	8
SDS	12	71	17	0.42	3

[a] $[G_1] = 30 \times 10^{-4}$ M, $[G_2] = 8 \times 10^{-4}$ M, $[G_3] = 2 \times 10^{-4}$ M, $[20] = (2.67-3.42) \times 10^{-4}$ M. [b] Mean occupancy numbers: NaCh, NaDCh = ∼ 0.11–0.14; SDS = 0.32–0.37. [c] For structures, see Scheme 4. [d] Cage effect = (**AB** − **AA** − **BB**)/(**AA** + **AB** + **BB**). [e] $[G_3] = 9 \times 10^{-4}$ M.

backbone of the dendrimer prevented absorption by the reactant 1-phenyl-3-*para*-tolyl-propane-2-one. In the limited concentration region investigated (2 to 9×10^{-4}), the cage effect increased from 0.46 to 0.77. In the absence of further study, we cannot be certain whether the observed change is due to multiple occupancy at lower concentration of the dendrimer or due to some amount of reaction taking place in water. A similar observation with respect to cage escape was made during irradiation of benzoin ethyl ether **13** included in G_3 (Scheme 3 and Table 4). For example, the yield of pinacol ether **15** decreased from 7% to 1% when the G_3 concentration increased from 2.4×10^{-4} to 4.8×10^{-4}M. Based on the behavior of the radicals from benzoin ethyl ether, we believe that the radical pair **E** from 1-phenyl-3-*para*-tolyl-propane-2-one may also prefer to stay within the hydrophobic pockets of the dendrimer. One should note that the escape rate would also depend on the hydrophobicity of the guest molecule (or the guest reactive intermediate). Further work is needed to resolve this issue.
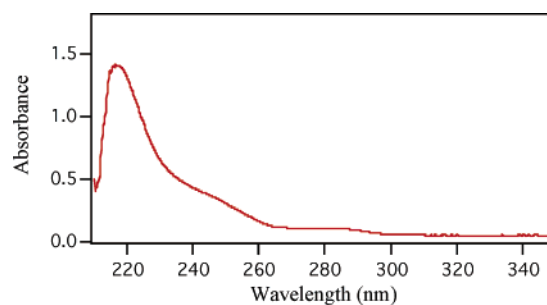
As indicated in the Introduction section, dendrimers are often considered to be "static unimolecular micelles". Given this feature, in the context of reaction media, we were interested in comparing the reaction cavity provided by dendrimers to that by sodium dodecyl sulfate (SDS), sodium cholate (NaCh), and sodium deoxycholate (NaDCh) micelles.[20] Product distributions

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for all four reactions discussed above obtained in micellar media above critical micelle concentration are included in Tables 2−5. Clearly the photoreaction is much less selective within conventional micelles than in dendrimers. Irradiation of 1-naphthyl benzoate in SDS and NaCh micelles gave both 2-benzoyl 1-naphthol (**2**) and 4-benzoyl 1-naphthol (**3**) in the ratio 4:1, a slight improvement from that in hexane (Table 2). However, within NaDCh micelles, 2-benzoyl 1-naphthol was selectively obtained. Analogous behavior was observed with 1-naphthyl phenylacyl ester **4** (Table 3). Within SDS and NaCh micelles, a mixture of 2-phenylacyl 1-naphthol **5** and 4-phenylacyl 1-naphthol **6** was obtained, whereas, within NaDCh micelles, 2-phenylacyl 1-naphthol alone was obtained. The higher selectivity observed in NaDCh micelles is consistent with the established higher rigidity of NaDCh micelles in relation to NaCh micelles.[20b−k] Photobehavior of benzoin ethyl ether in all three micelles (occupancy number, i.e., number of molecules per micelle: in SDS, 0.6; in bile salts micelles, 0.2) are different from that in dendrimers (Table 4). Most importantly, in all three micelles, the pinacol ether **15**, a product of cage escape, is formed in significant amounts (>25%). On the other hand, when dendrimer was used as the medium, no pinacol ether was formed at a higher dendrimer-to-reactant ratio. This suggests that dendrimers are much less "leaky" than a conventional micelle. Photochemistry of 1-phenyl-3-*para*-tolyl-propane-2-one within SDS micelles has been extensively investigated.[21] The cage effect (∼0.4) that we recorded in the SDS micelle is close to the literature value. Both NaCh and NaDCh micelles provided a lesser cage effect (∼0.20; Table 5). Clearly the cage effects observed in dendrimers are much higher than those in NaCh and NaDCh micelles.

As presented above, in the context of "green chemistry", the dendrimers are better media than micelles to perform product-selective photochemistry.[22] The presence of small amounts (10^{-4} M) of dendrimers can dissolve a large amount of organic molecules in water (pH ∼9). Based on four reactions listed in this report, we conclude that dendrimers provide a better hydrophobic environment than micelles and the reaction cavities of dendrimers incarcerate the reactants and the intermediates for a much longer time than a conventional micelle. Further, dendrimers have a higher capacity to solubilize organic compounds than micelles. Following photolysis, products could be more easily extracted from a dendrimer than from a micelle, the dendrimer itself can be precipitated and reused by making the medium neutral. The selectivity in photoproducts obtained and convenience of their use make dendrimers better media than conventional micelles to perform selective photoreactions. However, one should note the dendrimers described in this study absorb between 220 and 320 nm (Figure 3), and this could restrict their use with molecules absorbing only in this region. We are currently exploring the use of water-soluble dendrimers and other organic hosts as media for photoreactions.

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Figure 3. Absorption spectrum of dendrimer G_3 (see Figure 1 for structure of the dendrimer).

Experimental Section

Materials: Poly(alkyl aryl ether) dendrimers used for the study were synthesized and characterized following the literature procedure.[8] Sodium dodecyl sulfate (99%), sodium cholate (98%), and sodium deoxycholate (98%) procured from Sigma-Aldrich were used without further purification. Naphthyl benzoate (**1**) and 1-naphthyl phenylacyl ester **4** were prepared following literature procedures.[13g] Benzoin ethyl ether (**13**) obtained from Sigma-Aldrich was recrystallized twice from hexane. Substrate **20** was synthesized as described in the literature.[23]

Inclusion of Reactants within Dendrimers and Photolysis: The procedure adopted for all substrates were similar and one of them is described below. Substrate **1** (0.5 mg, 4×10^{-4} M) was added to a stirred solution of a known amount of dendrimer in 5 mL of aqueous NaOH ([G_1] = 22.5×10^{-4} M, [G_2] = 8×10^{-4} M, [G_3] = 2×10^{-4} M) . After the solution was stirred for 12 h, it 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 a 450 W medium-pressure Hg lamp. Irradiation for 2 h resulted in ∼30% conversion in the case of **1**, **4**, and **13**. In case of substrate **20**, the sample in aqueous G_1 solution was irradiated for 4 h, the sample in aqueous G_2 solution, for 7 h, and the sample in aqueous G_3 solution, for 12 h, to obtain 30% conversion. Absorption by the dendrimer was responsible for the low conversion.

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 an ethyl acetate and acetonitrile (7:3) solvent mixture, dried over anhydrous Na_2SO_4, concentrated, and analyzed on an HP-5890 series II gas chromatograph fitted with an SE-30 or HP-5 column. A known amount of internal standard was added before analysis for mass balance studies. For substrates **1**, **4**, and **20**, dodecane was used as the internal standard, and for substrate **13**, benzophenone was used as the internal standard.

Characterization of Photoproducts: Peaks in the GC traces were identified by coinjecting with authentic samples which were prepared by solution irradiation. Spectral data of photoproducts from **1** and **4** prepared by solution irradiation were compared with literature reports.[13] Among the photoproducts from **13**, benzaldehyde, **14**, and **19** were identified by comparison with the commercially available samples (Aldrich). Photoproducts **15** and **18** isolated from solution irradiation and **16** and **17** isolated from dendrimer irradiation were characterized by ^{1}H NMR and GC−MS.

^{1}H NMR of **15** (400 MHz, CDCl₃): δ 0.94 (t, 6 H), δ 2.83−3.65 (m, 4 H), δ 4.30 (s, 2 H), δ 7.09−7.58 (m, 10 H). 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 **16** (400 MHz, CDCl₃): δ 1.2 (t, 3 H), δ 3.51 (q, 2 H), δ 4.57 (s, 2 H), δ 7.40−7.80 (m, 9 H). Mass spectral data *m/z* (relative

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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 **17** (400 MHz, CDCl$_3$): δ 1.0 (t, 3 H), δ 3.38 (q, 2 H), δ 4.58 (s, 2 H), δ 7.30–7.80 (m, 9 H). 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 **18** (400 MHz, CDCl$_3$): δ 1.4 (d, 3 H), δ 5.2 (q, 1 H), δ 5.95 (s, 1 H), δ 7.20–7.80 (m, 10 H). 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).

In the case of **20**, the photoproducts **AA** and **BB** were commercially available (Aldrich and Lancaster). Photoproduct **AB** 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).

Rp **21** was identified by isolating the compound from photolysis of dendrimer samples.

^{1}H NMR of **21** (400 MHz, CDCl$_3$): δ 2.3 (s, 3 H), δ 2.4 (s, 3 H), δ 4.19 (s, 2 H), δ 7.09–7.24 (m, 6 H), δ 7.87–7.88 (m, 6 H). Mass spectral data *m/z* (relative intensity): 224 (M$^+$, 6), 119 (100), 105 (6), 91 (22), 77 (4), 65 (9).

Inclusion of Substrates within Micelles and Photolysis: Stock solutions of known concentration (3–5 mM) of the reactants **1**, **4**, **13**, and **20** in CH$_2$Cl$_2$–hexane were prepared. A volume of solutions corresponding to 0.5–1.0 mg of the substrates was pipetted into a test tube. The solution was purged with air to remove the solvent, and a thin film of the substrate was obtained. Weighed amounts of the surfactants (100–200 mg) were added to this followed by 5 mL of deionized water (in the case of SDS) or 5 mL of 0.2 M aq. NaCl (in the case of bile salts). After the solutions were stirred for 3 h, they were filtered through a Whatmann filter paper, and the filtrate was taken in a test tube, purged with dry N$_2$ for 15 min, and irradiated in a Pyrex test tube (40 min for **1** and **4**, 10 min for **13**, and 20 min for **20**). The conversions were maintained under 30%.

Extraction of Photoproducts and Starting Material: After irradiation, the solutions were diluted with deionized water to a surfactant concentration well below their critical micelle concentration. The photoproducts were extracted by using an organic solvent. In the case of SDS, the extracting solvent was a 10% ether–hexane mixture, and the separatory funnel was shaken carefully to avoid the formation of emulsion. The extraction procedure was repeated at least thrice. Ethyl acetate was used for extraction in the case of bile salt micelles. The

organic layers were washed several times with water and dried over anhydrous MgSO$_4$. The filtered solution was concentrated and analyzed on an HP-5890 series II gas chromatograph fitted with an SE-30 or HP-5 column.

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

Substrate **1**. Column: HP-5. Temperature program: initial temp, 100 °C; initial time, 1 min; rate, 5 °C/min; final temp, 220 °C; final time, 10 min. Retention times: 1-naphthol, 10.7 min; benzil, 16.8 min; benzoic acid, 6.8 min; ortho rearrangement product, 26.6 min; para rearrangement product, 33.8 min.

Substrate **4**. Column: HP-5. Temperature program: initial temp, 100 °C; initial time, 1 min; rate, 5 °C; final temp, 270 °C; final time, 10 min. Retention times: **10**, 10.7 min; **11**, 16.6 min; **12**, 21.8 min; **7**, 25.4 min; **4**, 27.0 min; **8**, 27.4 min; **5**, 28.4 min; **6**, 31.7 min.

Substrate **13**. 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: **19**, 25.5 min; **15**, 26.1 min; **14**, 28.6 min; **13**, 30.0 min; **17**, 32.3 min; **18**, 34.3 min; **16**, 43.4 min.

Substrate **20**. 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; **20**, 22.3 min; **21**, 24.3 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. The emission spectrum was recorded by excitation at 335 nm. The excitation spectrum was recorded at the 385 nm emission wavelength. To the aqueous solution of pyrene, dendrimer solution was added 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.