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PAPER

Unsurpassed cage effect for the photolysis of dibenzyl ketones in water-soluble dendrimers†

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Amphiphilic water-soluble poly(alkyl aryl ether) dendrimers G*n* ($n = 1$–3) with charge-neutral tetraethylene glycol monomethyl ethers at their periphery were synthesized as microreactors to control the photochemical reactions of dibenzyl ketone derivatives in aqueous solutions. Photophysical studies demonstrated that G*n* can encapsulate organic molecules and provide a hydrophobic microenvironment. The product distribution of photolysis of dibenzyl ketone derivatives can be successfully controlled by encapsulating the substrates within dendrimers, and an unsurpassed cage effect of 1.00 is reached in high generation dendrimers, revealing that a thick and compact "shell" was formed at the periphery of the dendrimers. The cage effect is also significantly influenced by the substituent at the *para*-position of the guest molecules. The higher generation dendrimers exhibit a better confined microenvironment and the aggregates possess more compact cavities to "lock" the guests than the corresponding unimolecular dendrimers. After photolysis, the separation of products can be easily achieved by extracting from the dendrimer solutions and the dendrimers are simply recovered and reused.

Introduction

The selectivity of photoreactions continues to be one of the main topics in organic chemistry and the development of catalytic hosts capable of extraordinary efficiency and specificity in organic photochemical reactions has been attracting much interest toward this goal.[1] Different kinds of hosts have been synthesized and used as microreactors to conduct photoreactions of encapsulated guests. Among these, zeolites,[2,3] micelles,[4,5] vesicles,[6] cyclodextrins[7] and so on,[8,9] are commonly applied, and the photochemical reactions inside them proceed with enhanced rates or a special product selectivity, which is generally attributed to entropic effects.[10] Dendrimers as a new series of synthetic microreactors have been attracting more attention in photochemistry.[11–15]

Amphiphilic dendrimers with a hydrophilic exterior and a hydrophobic interior contain analogous microenvironments to micelles. The initial example of the use dendrimers as microreactors for photoreactions was reported by Fréchet's group.[11] They designed and synthesized a series of amphiphilic dendrimers with a benzophenonyl core as oxygen sensitizer, apolar interior and polar exterior, and applied them to the photoinduced oxidation of cyclopentadiene in O_2-saturated methanol. The experiment results showed that the higher generation dendrimers lead to faster reaction and higher conversion rate. The same dendrimers were also used for the photosensitized oxygenation of sulfides by Shiraishi's group, giving a similar conclusion.[12] Recently, we used carboxylic acid terminated poly(aryl ether) dendrimers as microreactors to conduct photooxidation of olefins in aqueous media, and demonstrated that the photooxidation pathways can be successfully controlled by encapsulating the substrate and sensitizer molecules in the same or different sets of dendrimers.[13] Ramamurthy and co-workers[14,15] synthesized several poly(alkyl aryl ether) dendrimers with hydroxyl or carboxyl groups at the peripheries and applied them as microreactors to conduct photoreactions. It has been demonstrated that these dendrimers can act as "unimolecular micelles" and offer much better constrainment than traditional micelles, although their hydrophobic pockets are not totally "leak-proof" for encapsulated guests.

The interest in "leak-proof" dendritic microreactors urges us to develop new dendritic systems with "tight and closed walls" keeping guests inside the hydrophobic cavities. In the present work, we synthesized a series of water-soluble poly(alkyl aryl ether) dendrimers (G*n*, $n = 1$–3) with a charge-neutral tetraethyleneglycol monomethyl ether as the hydrophilic group at the periphery (Fig. 1). Pyrene was used as a probe to evaluate the encapsulation and microenvironment properties of the dendrimers and the photolysis of dibenzyl ketone derivatives within G*n* was studied, affording an unsurpassed cage effect of 1.00 for high generation dendrimers. Based on these results, we established that the tangled tetraethyleneglycol monomethyl ether chains of dendrimers can provide a compact and thick shell, acting as a "wall" to prevent the escape of guest molecules. In addition, isolation of guests from

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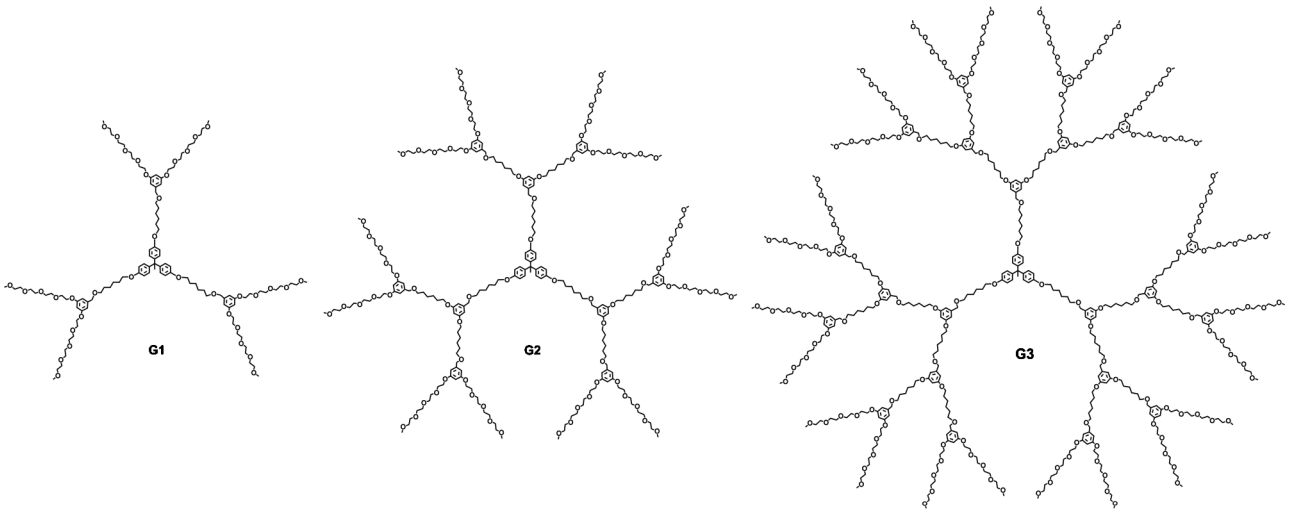


Fig. 1 Structures of the amphiphilic dendrimers of generation 1 to 3 (G1–G3).

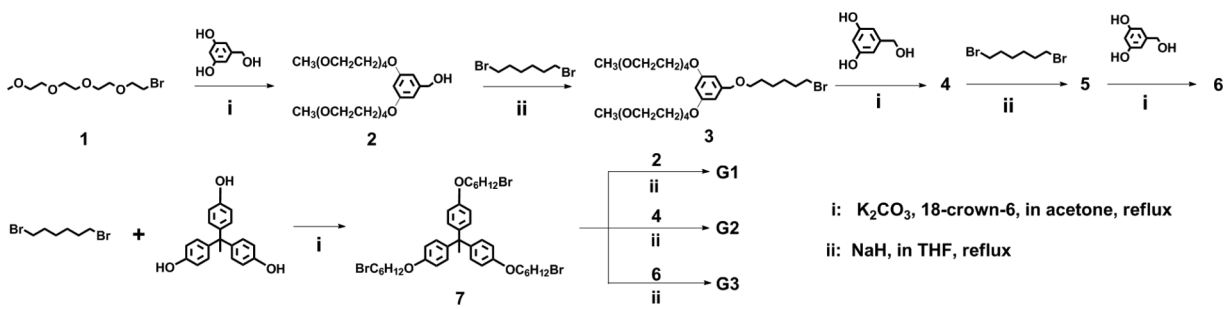
dendrimer solutions after the photolysis was easily realized by extracting with *n*-hexane and the dendrimers could be recovered and reused without loss of selectivity, which accords with the concept of "green chemistry".[16]

Results and discussion

Synthesis and aggregation behavior of dendrimers in aqueous solution

The dendrimers (G*n*, *n* = 1–3) are constituted with 1,1,1-tris(4-hydroxyphenyl)ethane, 3,5-dihydroxybenzyl alcohol, a hexamethylene chain and a tetraethylene glycol monomethyl ether, acting as the core, branching juncture, spacer and the hydrophilic periphery, respectively. The tetraethylene glycol monomethyl ether functionalized poly(alkyl aryl ether) dendritic benzyl alcohols (**2**, **4**, **6**, G*n*-OH, *n* = 1–3) were synthesized by an adapted convergent synthetic methodology[17] as shown in Scheme 1. Alkylation of 1,1,1-tris(4-hydroxyphenyl)ethane with 1,6-dibromohexane was first performed to afford the alkyl core (**7**). The poly(alkyl aryl ether) dendrimers (G*n*, *n* = 1–3) were obtained by coupling the alkyl core (**7**) with three pieces of G*n*-OH (*n* = 1–3). In this constitution, the first, second and third generation dendrimers possess 6, 12 and 24 tetraethylene glycol monomethyl ether groups at their peripheries, respectively. The details of the synthesis and characterization of the compounds are described in Experiment section. All the compounds have been purified by column chromatography and characterized by ^{1}H NMR, IR, and mass spectrometry (MALDI-TOF or ESI).

With tetraethylene glycol monomethyl ether chains at the periphery, all these dendrimers G*n* (*n* = 1–3) are soluble in water. Based on the fact that the amphiphilic dendrimers are capable of forming aggregates in water,[18] dynamic light scattering (DLS) experiments were carried out to illustrate the aggregation behavior of dendrimers G*n* (*n* = 1–3) in aqueous solution. During the DLS experiments the periphery group concentration of G*n* remains same to give a similar amount of hydrophobic moiety for different generations. No measurable formation of particle was observed for G*n* (*n* = 1–3) as the periphery group concentration below 9.6×10^{-4} M, suggesting that all these dendrimers afford unimolecular micelles at these experimental conditions. When the periphery group concentration reaches 9.6×10^{-3} M, particles with hydrodynamic radius (R_h) of 944, 1380, 817 nm and polydispersity of 0.45, 0.50, 0.40 were detected in G1, G2 and G3 aqueous solution, respectively, indicative of the formation of the G*n* assembly. The DLS experimental results of G*n* in aqueous solution at different concentrations are summarized in Table 1 and a figure for the DLS measurement on these dendrimers is provided in supplementary material (see supplementary material Figure S14). The formation of spherical aggregates was also observed by an optical microscope in G*n* aqueous solution. The size of the G2 aggregate is larger than those of G1 and G3. The proportion of



Scheme 1 Synthesis of water-soluble dendrimers.

Table 1 DLS data of G*n* in aqueous solution at different concentrations

Generation	Concentration (mM)	R_h (nm)	Polydispersity
Diluted			
G1	16×10^{-2}	Not found	—
G2	8.0×10^{-2}	Not found	—
G3	4.0×10^{-2}	Not found	—
Concentrated			
G1	1.6	944	0.45
G2	0.80	1380	0.50
G3	0.40	817	0.40

tetraethylene glycol groups in the dendritic architecture at a certain generation, which leads to the difference of hydrophilic–lipophilic balance, and the conformation of dendritic molecules might be the cause for the observed anomalous behavior of the G2 aggregate.

Encapsulation ability and interior micropolarity of dendrimers

Prior to utilizing the dendrimers as reaction media, understanding the encapsulation ability and interior micropolarity of the dendrimers is essential. Pyrene is used as one of the most common probes to detect the environment polarity, and is chosen as the probe to detect the interior of dendrimers as others and we did before.[14,18,19] Fig. 2 illustrates the UV-VIS absorption spectra of pyrene in water and aqueous solutions of G*n* dendrimers. The solubility of pyrene is very low in water, and is evidently enhanced in the presence of G*n* (n = 1–3) dendrimers. According to the UV-VIS data, the solubility of pyrene increases by a factor about 37, 65, and 91 times higher for G1, G2, and G3 dendrimers, respectively, indicative of an increase of the hydrophobic interior with increasing generation. The average numbers of pyrene molecules encapsulated within each dendrimer are estimated from the extinction coefficient, which are 0.8, 1.4 and 2.0 for G1, G2 and G3, respectively. These results indicate that dendrimers G*n* (n = 1–3) are capable of providing a hydrophobic microenvironment which sequesters lipophilic molecules within their interior cavities.

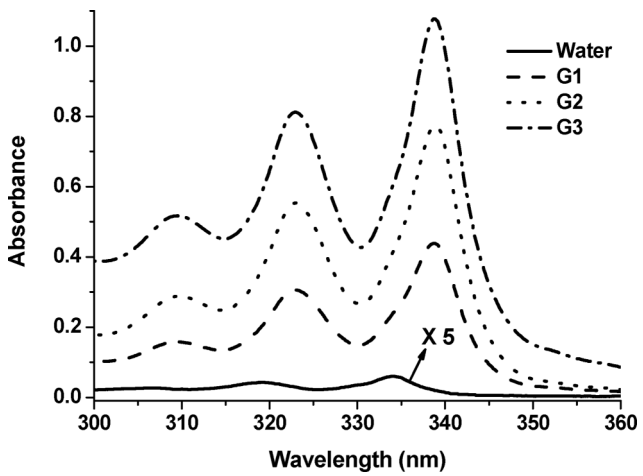


Fig. 2 Absorption spectra of pyrene in water and aqueous solutions of dendrimers ($c = 1.0 \times 10^{-5}$ M).

The ratio of the first and third emission bands of pyrene, I_1/I_3, is relatively larger in polar environments and smaller in less polar solvents, and this is usually utilized to characterize the polarity of the microenvironment.[20] The fluorescence spectra of pyrene were measured in water and aqueous solutions of the unimolecular/aggregated dendrimer G*n*, and several of them normalized to the first emission band are shown in Fig. 3. An obvious increase of the third emission band relative to the first one is observed in G*n* (n = 1–3) dendrimer aqueous solutions, whether in unimolecular or aggregate form, and the ratio I_1/I_3 *vs.* generation is plotted in the inset of Fig. 3. There is a steep decrease of I_1/I_3 between water and G1 aqueous solutions, demonstrating that the dendrimers G*n* (n = 1–3) are capable of encapsulating molecules and provide a hydrophobic microenvironment. The trend of the ratio I_1/I_3 with dendrimer generation in G*n* (n = 1–3) aqueous solution indicates that the higher generation dendrimer provides a more hydrophobic cavity. The smaller value of I_1/I_3 in aggregated G1 to G3 aqueous solution in comparison with that in the corresponding unimolecular dendrimer solution shows that the dendrimer aggregates can isolate the encapsulated molecules from the surrounding water better.

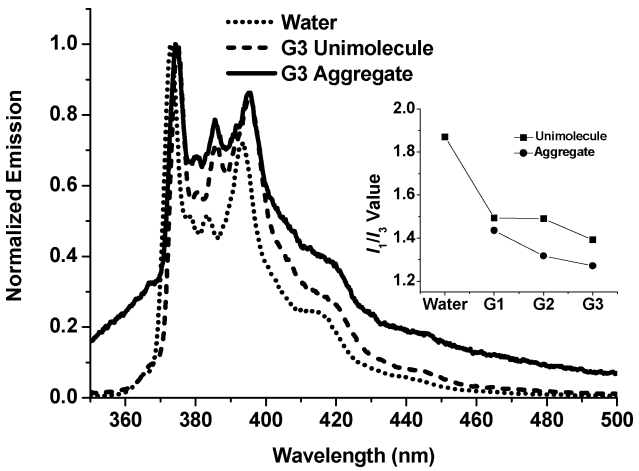


Fig. 3 Fluorescence spectra of pyrene in water and aqueous solution of G3 dendrimers ($c = 1.0 \times 10^{-5}$ M for unimolecular G3and 4.0×10^{-4} M for G3 aggregate). λ_{ex} = 335 nm. (*inset*: plot of the ratio of I_1/I_3 bands of pyrene *vs.* dendrimer generation).

Photolysis of dibenzyl ketone derivatives within dendritic microreactors

Since the initial discovery by Turro and co-workers that the product distribution resulting from photolysis of dibenzyl ketone could be controlled by micelles,[21] this reaction has been selected as the benchmark to assess the efficacy of a medium as the "cage". Therefore, this Norrish type I reaction was selected to evaluate the mobility of guests within the hydrophobic pockets of dendrimers in this work. Irradiation of dibenzyl ketone derivatives results in an α-cleavage followed by a decarbonylation to give the secondary radical pair.[3,22] These photolysis reactions are known to give a range of products, and the product distributions are sensitive to the surrounding reaction environment. In general, the three diaryl ethanes **AA**, **AB**, and **BB** resulting from the radical pair are formed in the ratio of 1 : 2 : 1 in homogenous solutions as shown in Scheme 2. When the secondary radical pair is held within a restrained medium and can not move freely, the only expected product is **AB**. The cage effect for this reaction can be calculated according to eqn (1).

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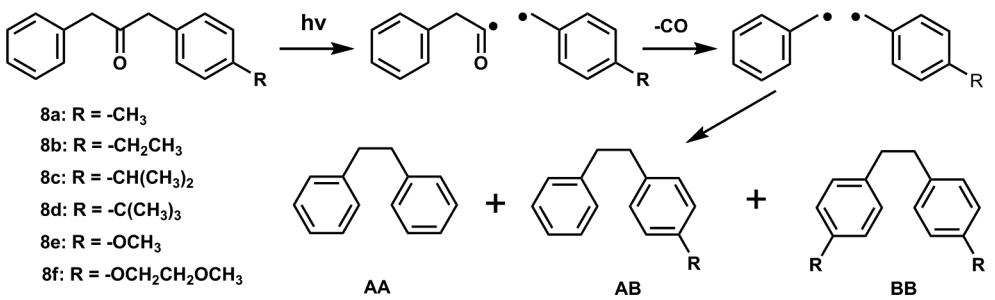


Scheme 2 Photolysis of dibenzyl ketones derivatives.

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

The Norrish I reaction of 1-phenyl-3-*p*-tolyl-propan-2-one (**8a**) has been widely used as the standard to estimate the cage effect of various media, and was first investigated in dilute aqueous solution of dendrimers G*n* (unimolecular dendrimers, $n = 1$–3). The substrate molecules were encapsulated in the inner cavities of dendrimers by sonicating for 10 min and then stirring the mixture of the substrate molecules ($c = 4 \times 10^{-5}$ M) and the G*n* ($n = 1$–3) aqueous solution for 24 h. Then dialyses were performed in G*n* ($n =$ 1–3) aqueous solutions to remove the unencapsulated substrate molecules. In order to get a similar amount of hydrophobic moiety for different generation dendrimers, the concentrations of dendrimers used in the photolysis were set to 0.16, 0.08 and 0.04 mM for the G1 to G3 unimolecular system, respectively. According to the ratio of the concentrations of guest and dendrimers, the average loading number per dendrimer is no more than one for the substrate molecule. The photolysis was performed in deaerated G*n* aqueous solutions by exposing them to $\lambda > 300$ nm light. After irradiation, the products were extracted with hexane or dichloromethane and analysed by gas chromatography. As a comparison, the photochemical behavior of **8a** in hexane was also investigated. Analysis of the product distribution gave the cage effects of photolysis in different media, which are summarized in Table 2.

As expected, irradiation of **8a** in hexane resulted in diaryl ethane products **AA**, **AB** and **BB** in a 1 : 2 : 1 ratio with a cage effect of zero. Photolysis of the substrate molecules encapsulated in G*n* ($n = 1$–3) dendrimers gave a distribution of products strikingly different from that in homogeneous solution. The cage effect for **8a** increased dramatically as the generations advanced, demonstrating a much more confined microenvironment provided by higher generation dendrimers. Excitingly, only **AB** product was obtained within G2 and G3 dendrimers, affording an ideal cage effect of 1.00. The photochemistry of **8a** in restrictive media such as traditional micelles and polymeric micelles has been extensively investigated by Ramamurthy *et al.*,[5,9] and the cage effects were never over 0.80. The cage effects obtained from our tetraethylene glycol monomethyl ether terminated dendrimers are also much higher than the corresponding carboxylic acid terminated or phenolic hydroxyl terminated poly(alkyl aryl ether) dendrimers, as listed in Table 2.[14,15] The impressive cage effect results for G2 and G3 indicate that the tetraethylene glycol monomethyl ether terminated dendrimers possess extremely confined hydrophobic cavities for the photolysis of **8a**. Their "leak-proof" character of G2 and G3 may be attributed to a thick and compact "shell" at their periphery resulting from intertwisting of tetraethylene glycol monomethyl ether chains, which prevents the reactants and radical pairs escaping from hosts into the outer aqueous phase within their lifetimes.

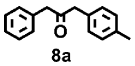
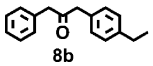
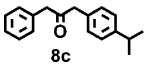
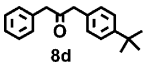
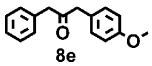
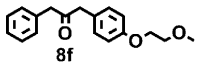
Table 2 Photolysis of **8a** in different media

Medium	Relative ratio			Cage effect
	AA	**AB**	**BB**	
Hexane	23	50	27	0.00
H_2O	21	53	26	0.06
unimolecular G1[a]	16	63	21	**0.26**
unimolecular G2[a]	0	100	0	**1.00**
unimolecular G3[a]	0	100	0	**1.00**
G1–$(OH)_6$[b]	15	54	28	0.11
G2–$(OH)_{12}$[b]	11	67	17	0.42
G3–$(OH)_{24}$[b]	4	80	6	0.77
G1–$(CO_2H)_6$[c]	16	32	10	0.09
G2–$(CO_2H)_{12}$[c]	18	44	10	0.18
G3–$(CO_2H)_{24}$[c]	10	61	10	0.50

[a] [G1] = 1.6×10^{-4} M, [G2] = 8.0×10^{-5} M, [G3] = 4.0×10^{-5} M. [b] From literature.[14] [c] From literature.[15]

Previous studies have demonstrated that dendrimers show different selectivity of encapsulating substrates with varied size and shape,[23] suggesting that smaller substrates are more conveniently encapsulated in the inner cavities of dendrimers than the bulky substrates. To further investigate the G*n* dendrimers as confined microreactors for conducting photoreactions of encapsulated guest molecules, a series of dibenzyl ketone derivatives with different size substituents (**8a**–**8d**) were selected as the substrates, and their structures are shown in Table 3. The photolysis of these compounds was conducted in aqueous solutions of unimolecular dendrimers G*n* ($n = 1$–3) and in hexane as a comparison. All the different substituted dibenzyl ketones exhibit the same cage effect of zero in homogeneous solution of hexane, but showed an obvious substituent effect on photoproduct distributions in dilute aqueous solutions of dendrimers G*n* ($n = 2$–3). As the size of the substituent of the dibenzyl ketones increases from methyl (**8a**) to *tert*-butyl (**8d**), the cage effect drops from 1.00 to 0.58 and 0.72 in G2 and G3, respectively. In consideration of the flexible backbone of dendrimers, the lower cage effects in G*n* ($n = 2$–3) can be explained by incomplete encapsulation of the bulky dibenzyl ketones. Although the hydrophobicity of the guest molecules increases significantly as the substituents change from methyl to *tert*-butyl, the size of the guest molecule plays a more important role for the observed cage effect than that of

Table 3 Photolysis of dibenzyl ketone derivatives in hexane and aqueous solutions of dendrimers

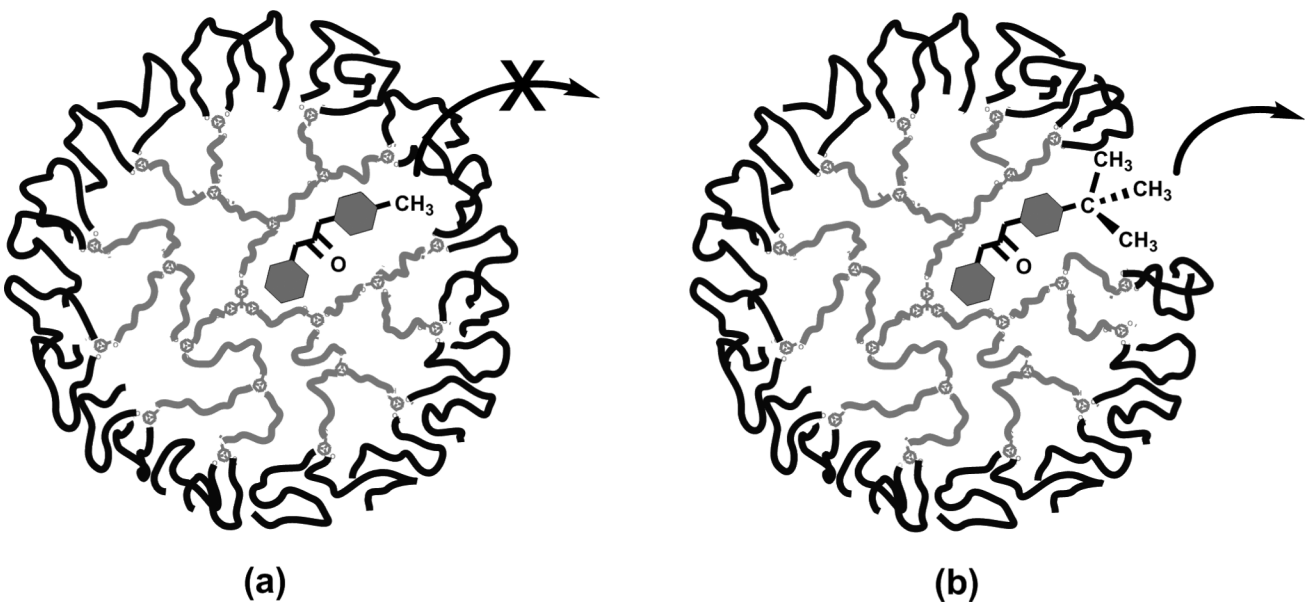
Medium	Cage effect of different guest molecule[a,b]					
	 8a	 8b	 8c	 8d	 8e	 8f
Hexane	0.00	0.00	0.00	0.00	0.00	0.00
Unimolecular[c]						
G1	0.26	0.26	0.28	0.28	0.88	0.46
G2	1.00	0.80	0.78	0.58	1.00	1.00
G3	1.00	1.00	0.95	0.72	1.00	1.00
Aggregate[d]						
G1	0.67	0.62	0.60	0.56	0.92	0.47
G2	1.00	0.96	0.84	0.60	1.00	1.00
G3	1.00	1.00	0.96	0.92	1.00	1.00

[a] [guest molecule] $\approx 4 \times 10^{-5}$ M for unimolecular G*n* and 4×10^{-4} M for G*n* aggregate. [b] Error range ~ 0.02. [c] [G1] = 1.6×10^{-4} M, [G2] = 8.0×10^{-5} M, [G3] = 4.0×10^{-5} M. [d] [G1] = 1.6×10^{-3} M, [G2] = 8.0×10^{-4} M, [G3] = 4.0×10^{-4} M.

the hydrophobicity of the guest. The steric hindrance of guests prevents dendrimers from forming a dense "shell", resulting in a leakage of the bulky substrates and the formation of radical pairs from host dendrimers. A visual expression of the substituent effect is illustrated in Scheme 3.

The photolysis of two alkyl ether substituted dibenzyl ketone substrates (**8e**, **8f**) in an aqueous solution of unimolecular dendrimers G*n* (n = 1–3) was also investigated. The methoxyl substituted dibenzyl ketone (**8e**) with a similar size to **8b** exhibits cage effects of 0.88 in G1 dendrimer and 1.00 in G*n* (n = 2,3), which are much higher than the ethyl substituted ketone (**8b**) in the corresponding conditions. Obviously, the higher cage effect comes from the substituent at the *para*-position of guest molecule, which interacts with the hydrophilic periphery ether chains of dendrimers, and consequently, the encapsulation of the guest molecule within dendrimers is stabilized and the cage effects are enhanced. The effect of substituents was further strengthened by the photolysis of **8f**, which has a relatively long ether substituent. Although the substituent possesses five atoms, the cage effects for **8f** can still reach to 1.00 in aqueous solution of unimolecular dendrimers G*n* (n = 2, 3), while the lower cage effect in G1 can be attributed to the incompatible sizes of host and guest molecules.

The DLS experiments have demonstrated that the amphiphilic dendrimers G*n* (n = 1–3) can form aggregates at high concentration in aqueous solutions, and the photochemical behavior of **8a**–**8f** in dendrimer aggregates was examined. The concentrations of dendrimers used in the aggregated system were set to 1.6, 0.8 and 0.4 mM for G1 to G3, respectively, and the concentration of substrate molecules was about 4×10^{-4} M. According to the average diameter of dendrimer aggregate, every aggregate contains at least several hundreds of dendrimer molecules, indicating that each aggregate was occupied by several substrate molecules. The results of the photolysis were also summarized in Table 3. Apparently,



Scheme 3 Representations of substituent effect: (a) **8a** and (b) **8b** in G3 dendrimer.

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the cage effects are generally higher in the aggregates than those in corresponding unimolecular dendrimer unless it already reaches 1.00, revealing that the aggregates possess more compact cavities to "lock" guests than the corresponding unimolecular dendrimers. The guest molecules are kept isolated by each cavity of aggregates, which makes the radical pairs formed in the cavity facilitate the recombination within their lifetime.

Conclusion

The amphiphilic water-soluble poly(alkyl aryl ether) dendrimers (G*n*, *n* = 1–3) with tetraethyleneglycol monomethyl ether as the terminal groups can act as microreactors to control the photochemical reaction of dibenzyl ketone derivatives, and an unsurpassed cage effect of 1.00 is reached in high generation dendrimers, which is much better than that of hydroxyl or carboxyl group terminated dendrimers. The cage effect is also significantly influenced by the substituent of the guest molecule. The higher generation dendrimers exhibit better confined microenvironments, and the aggregates possess more restricted cavities than the corresponding unimolecular dendrimers. It is worth noting that the products of photoreactions can be easily extracted from the dendrimer solution and the dendrimer is readily recovered and reused, which makes dendrimers a better choice of photochemical microreactors.

Experimental section

Materials

All reagents were purchased from Acros, Alfa Aesar, or Aldrich and used without further purification unless otherwise noted. Milli-Q water was used in aqueous experiments. Dichloromethane (CH_2Cl_2) was distilled from CaH_2.

Instruments

^{1}H NMR (400 MHz) spectra were obtained from a Bruker Avance Π-400 spectrometer. IR spectra were recorded on a Varian Excalibur 3100 spectrometer. MALDI-TOF mass spectra were carried out on a Bruker Microflex spectrometer. ESI mass spectra were recorded on a Waters LCT Premier XE spectrometer. Dynamic Light Scattering measurements were performed on a Malvern Zetasizer 3000HS. Absorption and emission spectra were run on a Shimadzu UV-1601PC spectrometer and a Hitachi F-4500 spectrometer, respectively. Gas chromatography (GC) experiments were carried out on a BeiFen 3420 gas chromatograph fitted with 3% OV-17 column and FID detector. GC-MS experiments were run on a Waters GCT Premier GC mass spectrometer with a J&W DB-5MS column.

Absorption spectra of pyrene

An excess of pyrene was added to water or an aqueous solution of the dendrimer ($c = 1 \times 10^{-5}$ M), and stirred at room temperature for 24 h. Then the solution was filtered through a filter paper (medium porosity) to remove any floating particles. The absorption spectra of these solutions were recorded using quartz cells.

Fluorescence spectra of pyrene

A pyrene stock solution was made in dichloromethane. The required amount of this solution was transferred into a vial, and the dichloromethane was evaporated. Then the necessary amount of water or dendrimer solution was added to make the concentration of pyrene 1×10^{-6} M, and the solution was stirred at room temperature for 24 h. Fluorescence spectra were obtained by exciting the pyrene solution at 335 nm.

Inclusion of reactants within dendrimers

The procedures adopted for all substrates were similar and one of them is described below. A certain amount of substrate was added to a glass reactor and a known amount of dendrimer in aqueous solution was added to the reactor. After sonication for 10 min, the solution was stirred for 24 h in the dark. At the same time dialysis was performed to remove the substrate molecules located outside of the dendrimers in solution.

Photolysis and product analysis in aqueous dendrimer solution

The samples were purged with nitrogen for 30 min prior to use, and nitrogen was bubbled through the solution during the photolysis. A 500 W medium-high pressure Hg lamp was employed as the light source, and the glass reactor was able to cut off the light with the wavelength below 300 nm. Irradiation for 30 min resulted in ~80% conversion in all cases. After photolysis, reactants and products were extracted from aqueous solution using *n*-hexane or CH_2Cl_2 and the organic layer was dried over anhydrous $MgSO_4$, concentrated, and analyzed by gas chromatography. All the photoreaction products were analyzed and characterized by GC-MS.

Synthesis of dendrimers

Bromide (1). To a stirred solution of the tetraethylene glycol monomethyl ether (6.8 g, 32.8 mmol) in tetrahydrofuran (100 mL) was added carbon tetrabromide (13.6 g, 41.0 mmol) followed by the portionwise addition of triphenylphosphine (10.7 g, 41.0 mmol). The reaction mixture was stirred at room temperature for 30 min, filtered, evaporated to dryness, and partitioned between water and dichloromethane. The aqueous layer was then extracted with dichloromethane (2 × 100 mL), and the combined extracts were dried with Na_2SO_4 and evaporated to dryness. The crude product was purified by column chromatography, eluting with a 2 : 1 mixture of hexane and dichloromethane. After evaporation of the solvents, the bromide (**1**) was obtained as a colorless oil (8.0 g, 90.0% yield).

G1–OH (2). To a stirred solution of bromide (**1**) (7.9 g, 29.2 mmol) and 3,5-dihydroxybenzyl alcohol (1.9 g, 13.3 mmol) in acetone (200 mL) were added potassium carbonate (9.2 g, 66.5 mmol) and 18-crown-6 (0.70 g, 2.7 mmol). The reaction mixture was heated at reflux under nitrogen for 18 h, filtered, evaporated to dryness, and partitioned between water and dichloromethane. The aqueous layer was then extracted with dichloromethane (2 × 100 mL), and the combined extracts were dried (Na_2SO_4) and evaporated to dryness. The crude material was then purified by column chromatography, eluting with a 50 : 1 mixture of dichloromethane and methanol to give the G1–OH

(2) as a colorless oil (6.6 g, 95.4% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.51 (s, *o*-Ar, 2 H), 6.37 (s, *p*-Ar, 1 H), 4.56 (s, Ar**CH$_2$**OH, 2 H), 4.07 (t, J = 4.7 Hz, OCH$_2$**CH$_2$**OAr, 4 H), 3.80 (t, J = 4.7 Hz, O**CH$_2$**CH$_2$OAr, 4 H), 3.70–3.50 (m, O**CH$_2$CH$_2$**O, 24 H), 3.34 (s, **CH$_3$**O, 6 H). IR (KBr pellet) ν_{max}: 3442, 2925, 2875, 1597, 1450, 1353, 1294, 1171, 1107 cm^{-1}. MALDI-TOF MS: calcd. m/z 520.3, found [M + Na]$^+$: 543.2.

G1–Br (3). To a stirred solution of G1–OH (2) (3.8 g, 7.3 mmol) and 1,6-dibromohexane (14.2 g, 58.4 mmol) in THF (200 mL) was added sodium hydride (1.75 g, 73.0 mmol). The reaction mixture was heated at reflux under nitrogen for 24 h, filtered, evaporated to dryness, and partitioned between water and dichloromethane. The aqueous layer was then extracted with dichloromethane (2 × 100 mL), and the combined extracts were dried (Na_2SO_4) and evaporated to dryness. The crude material was then purified by column chromatography, eluting with a 50 : 1 mixture of dichloromethane and methanol to give the G1–Br (3) as a colorless oil (4.2 g, 84.4% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.49 (s, *o*-Ar, 2 H), 6.40 (s, *p*-Ar, 1 H), 4.41 (s, Ar**CH$_2$**OCH$_2$, 2 H), 4.09 (t, J = 4.8 Hz, OCH$_2$**CH$_2$**OAr, 4 H), 3.84 (t, J = 4.8 Hz, O**CH$_2$**CH$_2$OAr, 4 H), 3.73–3.53 (m, O**CH$_2$CH$_2$**O, 24 H), 3.45–3.39 (m, ArCH$_2$O**CH$_2$**CH$_2$ and CH$_2$**CH$_2$**Br, 4 H), 3.37 (s, **CH$_3$**O, 6 H), 1.86 (quintet, J = 7.0 Hz, CH$_2$**CH$_2$**CH$_2$Br, 2 H), 1.61 (quintet, J = 7.4 Hz, CH$_2$OCH$_2$**CH$_2$**CH$_2$, 2 H), 1.45 (m, CH$_2$CH$_2$**(CH$_2$)$_2$**CH$_2$CH$_2$, 4 H). IR (KBr pellet) ν_{max}: 2930, 2869, 1596, 1450, 1353, 1294, 1171, 1110 cm^{-1}. MALDI-TOF MS: calcd. m/z 682.3, found [M + Na]$^+$: 705.2 and [M + K]$^+$: 721.2.

G2–OH (4). This compound was prepared from 1.0 equiv of 3,5-dihydroxybenzyl alcohol and 2.2 equiv of the G1–Br (**3**), according to the general procedure for Gn–OH with potassium carbonate and 18-crown-6 in acetone. The crude product was purified by column chromatography, eluting with a 40 : 1 mixture of dichloromethane and methanol, to give the G2–OH (**4**) as a colorless oil (78.1% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.49 (s, *o*-Ar, 6 H), 6.40 (s, *p*-Ar, 2 H), 6.35 (s, *p*-Ar, 1 H), 4.60 (d, J = 6.0 Hz, Ar**CH$_2$**OH, 2 H), 4.41 (s, Ar**CH$_2$**OCH$_2$, 4 H), 4.09 (t, J = 4.8 Hz, OCH$_2$**CH$_2$**OAr, 8 H), 3.93 (t, J = 6.5 Hz, CH$_2$CH$_2$**CH$_2$**OAr, 4 H), 3.82 (t, J = 4.8 Hz, O**CH$_2$**CH$_2$OAr, 8 H), 3.72–3.53 (m, O**CH$_2$CH$_2$**O, 48 H), 3.44 (t, J = 6.5 Hz, ArCH$_2$O**CH$_2$**CH$_2$, 4 H), 3.37 (s, **CH$_3$**O, 12 H), 1.76 (quintet, J = 7.0 Hz, CH$_2$**CH$_2$**CH$_2$OAr, 4 H), 1.63 (quintet, J = 7.4 Hz, CH$_2$OCH$_2$**CH$_2$**CH$_2$, 4 H), 1.45 (m, CH$_2$CH$_2$**(CH$_2$)$_2$**CH$_2$CH$_2$, 8 H). IR (KBr pellet) ν_{max}: 3449, 2925, 2856, 1597, 1451, 1353, 1294, 1168, 1108 cm^{-1}. MALDI-TOF MS: calcd. m/z 1344.8, found [M + Na]$^+$: 1367.5.

G2–Br (5). This compound was prepared from the G2–OH (**4**) according to the general procedure for Gn–Br with sodium hydride in tetrahydrofuran. The crude product was purified by column chromatography eluting with a 50 : 1 mixture of dichloromethane and methanol to give the G2–Br (**5**) as a colorless oil (91.2% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.50 (s, *o*-Ar, 4 H), 6.46 (s, *o*-Ar, 2 H), 6.40 (s, *p*-Ar, 2 H), 6.35 (s, *p*-Ar, 1 H), 4.41 (s, Ar**CH$_2$**OCH$_2$, 6 H), 4.09 (t, J = 4.8 Hz, OCH$_2$**CH$_2$**OAr, 8 H), 3.92 (t, J = 6.5 Hz, CH$_2$CH$_2$**CH$_2$**OAr, 4 H), 3.83 (t, J = 4.8 Hz, O**CH$_2$**CH$_2$OAr, 8 H), 3.73–3.53 (m, O**CH$_2$CH$_2$**O, 48 H), 3.46–3.40 (m, ArCH$_2$O**CH$_2$**CH$_2$ and CH$_2$**CH$_2$**Br, 6 H), 3.37 (s, **CH$_3$**O, 12 H), 1.86 (quintet, J = 7.1 Hz, CH$_2$**CH$_2$**CH$_2$Br, 2 H), 1.77 (quintet, J = 7.0 Hz, CH$_2$**CH$_2$**CH$_2$OAr, 4 H), 1.63 (m, CH$_2$OCH$_2$**CH$_2$**CH$_2$, 6 H), 1.45 (m, CH$_2$CH$_2$**(CH$_2$)$_2$**CH$_2$CH$_2$, 12 H). IR (KBr pellet) ν_{max}: 2925, 2857, 1596, 1450, 1353, 1294, 1168, 1107 cm^{-1}. MALDI-TOF MS: calcd. m/z 1506.8, found [M + Na]$^+$: 1529.6.

G3–OH (6). This compound was prepared from 1.0 equiv of 3,5-dihydroxybenzyl alcohol and 2.2 equiv of the G2–Br (**5**), according to the general procedure for Gn–OH with potassium carbonate and 18-crown-6 in acetone. The crude product was purified by column chromatography, eluting with a 35 : 1 mixture of dichloromethane and methanol, to give the G3–OH (6) as a colorless oil (75.5% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.49 (s, *o*-Ar, 8 H), 6.46 (s, *o*-Ar, 6 H), 6.40 (s, *p*-Ar, 4 H), 6.35 (s, *p*-Ar, 3 H), 4.60 (d, J = 6.0 Hz, Ar**CH$_2$**OH, 2 H), 4.41 (s, Ar**CH$_2$**OCH$_2$, 12 H), 4.09 (t, J = 4.8 Hz, OCH$_2$**CH$_2$**OAr, 16 H), 3.92 (t, J = 6.5 Hz, CH$_2$CH$_2$**CH$_2$**OAr, 12 H), 3.83 (t, J = 4.8 Hz, O**CH$_2$**CH$_2$OAr, 16 H), 3.73–3.53 (m, O**CH$_2$CH$_2$**O, 96 H), 3.44 (m, ArCH$_2$O**CH$_2$**CH$_2$, 12 H), 3.37 (s, **CH$_3$**O, 24 H), 1.75 (quintet, J = 7.0 Hz, CH$_2$**CH$_2$**CH$_2$OAr, 12 H), 1.63 (quintet, J = 7.4 Hz, CH$_2$OCH$_2$**CH$_2$**CH$_2$, 12 H), 1.45 (m, CH$_2$CH$_2$**(CH$_2$)$_2$**CH$_2$CH$_2$, 24 H). IR (KBr pellet) ν_{max}: 3443, 2926, 2857, 1596, 1450, 1354, 1293, 1168, 1108 cm^{-1}. MALDI-TOF MS: calcd. m/z 2993.8, found [M + K]$^+$: 3032.0.

Core (7). To a stirred solution of 1,6-dibromohexane (6.5 g, 26.4 mmol), potassium carbonate (1.7 g, 12.4 mmol) and 18-crown-6 (0.17 g, 0.66 mmol) in acetone (100 mL) was added 1,1,1-tris(4-hydroxyphenyl)ethane (1.0 g, 3.3 mmol). The reaction mixture was heated at reflux under nitrogen for 18 h, filtered, evaporated to dryness, and partitioned between water and dichloromethane. The aqueous layer was then extracted with dichloromethane (2 × 100 mL), and the combined extracts were dried (Na_2SO_4) and evaporated to dryness. The crude material was then purified by column chromatography, eluting with a 15 : 1 mixture of hexane and ethyl acetate to give the core (**7**) as a colorless oil (2.2 g, 82.1% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.98 (d, J = 6.9 Hz, *m*-Ar, 6 H), 6.77 (d, J = 6.9 Hz, *p*-Ar, 6 H), 3.93 (t, J = 6.6 Hz, CH$_2$**CH$_2$**O, 6 H), 3.42 (t, J = 6.6 Hz, CH$_2$**CH$_2$**Br, 6 H), 2.10 (s, **CH$_3$**C, 3 H), 1.89 (quintet, J = 7.0 Hz, CH$_2$**CH$_2$**CH$_2$Br, 6 H), 1.78 (quintet, J = 6.7 Hz, CH$_2$**CH$_2$**CH$_2$OAr, 6 H), 1.50 (m, CH$_2$CH$_2$**(CH$_2$)$_2$**CH$_2$CH$_2$, 12 H). IR (KBr pellet) ν_{max}: 2937, 2860, 1608, 1508, 1473, 1291, 1248, 1181, 1119 cm^{-1}. MALDI-TOF MS: calcd. m/z 794.1, found [M + Na]$^+$: 817.2.

G1. To a stirred solution of core (**7**) (0.76 g, 0.96 mmol) and G1–OH (3) (1.65 g, 3.2 mmol) in THF (20 mL) was added sodium hydride (0.76 g, 32 mmol). The reaction mixture was heated at reflux under nitrogen for 48 h, filtered, evaporated to dryness, and partitioned between water and dichloromethane. The aqueous layer was then extracted with dichloromethane (2 × 20 mL), and the combined extracts were dried (Na_2SO_4) and evaporated to dryness. The crude material was then purified by column chromatography, eluting with a 40 : 1 mixture of dichloromethane and methanol to give the G1 as a colorless oil (1.5 g, 74.0% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.97 (d, J = 8.8 Hz, *m*-Ar, 6 H), 6.76 (d, J = 8.8 Hz, *p*-Ar, 6 H), 6.50 (s, *o*-Ar, 6 H), 6.40 (s, *p*-Ar, 3 H), 4.41 (s, Ar**CH$_2$**OCH$_2$, 6 H), 4.09 (t, J = 4.7 Hz, OCH$_2$**CH$_2$**OAr, 12 H), 3.91 (t, J = 6.4 Hz, CH$_2$CH$_2$**CH$_2$**OAr, 6 H), 3.84 (t, J = 4.7 Hz, O**CH$_2$**CH$_2$OAr, 12 H), 3.73–3.53 (m, O**CH$_2$CH$_2$**O, 72 H), 3.44 (t, J = 6.6 Hz, ArCH$_2$O**CH$_2$**CH$_2$, 6 H), 3.37 (s, **CH$_3$**O, 18 H), 2.09 (s, **CH$_3$**C, 3 H),1.77 (quintet,

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J = 7.0 Hz, $CH_2\mathbf{CH_2}CH_2OAr$, 6 H), 1.63 (quintet, J = 7.4 Hz, $CH_2OCH_2\mathbf{CH_2}CH_2$, 6 H), 1.45 (m, $CH_2CH_2\mathbf{(CH_2)_2}CH_2CH_2$, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.8, 156.9, 141.5, 140.9, 129.4, 113.4, 106.0, 100.6, 72.6, 71.8, 70.7, 70.5, 70.4, 70.2, 69.6, 67.6, 67.3, 58.9, 29.6, 29.2, 29.0, 26.0. IR (KBr pellet) ν_{max}: 2932, 2869, 1596, 1508, 1450, 1353, 1294, 1248, 1176, 1110 cm^{-1}. MALDI-TOF MS: calcd. m/z 2113.2, found [M + Na]$^+$: 2136.4 and [M + K]$^+$: 2152.4. UV-vis (in H_2O) $\lambda_{max}(\varepsilon)$: 280 nm ($4.48 \times 10^3$ M^{-1} cm^{-1}).

G2. This compound was prepared from 1.0 equiv of core (**7**) and 3.3 equiv of G2–OH (**4**), according to the general procedure for G*n* with NaH in THF. The crude product was purified by column chromatography, eluting with a 30 : 1 mixture of dichloromethane and methanol, to give the G2 as a colorless oil (41.3% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.96 (d, J = 8.8 Hz, *m*-Ar, 6 H), 6.75 (d, J = 8.8 Hz, *p*-Ar, 6 H), 6.50 (s, *o*-Ar, 12 H), 6.46 (s, *o*-Ar, 6 H), 6.40 (s, *p*-Ar, 6 H), 6.35 (s, *p*-Ar, 3 H), 4.41 (s, $Ar\mathbf{CH_2}OCH_2$, 18 H), 4.09 (t, J = 4.8 Hz, $OCH_2\mathbf{CH_2}OAr$, 24 H), 3.92 (t, J = 6.5 Hz, $CH_2CH_2\mathbf{CH_2}OAr$, 18 H), 3.83 (t, J = 4.8 Hz, $O\mathbf{CH_2}CH_2OAr$, 24 H), 3.73–3.53 (m, $O\mathbf{CH_2CH_2}O$, 144 H), 3.44 (m, $ArCH_2O\mathbf{CH_2}CH_2$, 18 H), 3.37 (s, $\mathbf{CH_3}O$, 36 H), 2.09 (s, $\mathbf{CH_3}C$, 3 H), 1.77 (quintet, J = 7.0 Hz, $CH_2\mathbf{CH_2}CH_2OAr$, 18 H), 1.63 (m, $CH_2OCH_2\mathbf{CH_2}CH_2$, 18 H), 1.44 (m, $CH_2CH_2\mathbf{(CH_2)_2}CH_2CH_2$, 36 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.3, 159.9, 157.0, 141.6, 141.0, 129.5, 113.5, 106.1, 105.7, 100.7, 100.3, 72.8, 71.9, 70.7, 70.5, 70.4, 70.3, 69.6, 67.8, 67.7, 67.4, 58.9, 50.4 29.6, 29.2, 25.9. IR (KBr pellet) ν_{max}: 2927, 2863, 1596, 1508, 1453, 1353, 1293, 1248, 1168, 1110 cm^{-1}. MALDI-TOF MS: calcd. m/z 4589.7, found [M + Na]$^+$: 4612.1. UV-vis (in H_2O) $\lambda_{max}(\varepsilon)$: 280 nm ($9.32 \times 10^3$ M^{-1} cm^{-1}).

G3. This compound was prepared from 1.0 equiv of core (**7**) and 3.3 equiv of G3–OH (**6**), according to the general procedure for G*n* with NaH in THF. The crude product was purified by column chromatography, eluting with a 20 : 1 mixture of dichloromethane and methanol, to give G3 as a colorless oil (25.2% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.96 (d, J = 8.8 Hz, *m*-Ar, 6 H), 6.75 (d, J = 8.8 Hz, *p*-Ar, 6 H), 6.50 (s, *o*-Ar, 24 H), 6.46 (s, *o*-Ar, 18 H), 6.40 (s, *p*-Ar, 12 H), 6.35 (s, *p*-Ar, 9 H), 4.41 (s, $Ar\mathbf{CH_2}OCH_2$, 42 H), 4.09 (t, J = 4.8 Hz, $OCH_2\mathbf{CH_2}OAr$, 48 H), 3.92 (t, J = 6.5 Hz, $CH_2CH_2\mathbf{CH_2}OAr$, 42 H), 3.83 (t, J = 4.8 Hz, $O\mathbf{CH_2}CH_2OAr$, 48 H), 3.72–3.53 (m, $O\mathbf{CH_2CH_2}O$, 288 H), 3.44 (m, $ArCH_2O\mathbf{CH_2}CH_2$, 42 H), 3.37 (s, $\mathbf{CH_3}O$, 72 H), 2.09 (s, $\mathbf{CH_3}C$, 3 H), 1.76 (quintet, J = 7.0 Hz, $CH_2\mathbf{CH_2}CH_2OAr$, 42 H), 1.64 (m, $CH_2OCH_2\mathbf{CH_2}CH_2$, 42 H), 1.44 (m, $CH_2CH_2\mathbf{(CH_2)_2}CH_2CH_2$, 84 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.4, 160.1, 160.0, 159.8, 157.1, 141.6, 141.1, 132.3, 129.6, 113.6, 108.1, 108.0, 107.7, 106.6, 106.2, 105.8, 100.8, 100.5, 72.9, 72.0, 70.8, 70.7, 70.5, 70.4, 69.7, 69.6, 67.8, 67.5, 67.4, 59.1, 29.8, 29.3, 26.1, 25.9. IR (KBr pellet) ν_{max}: 2934, 2868, 1596, 1508, 1451, 1353, 1294, 1248, 1168, 1108 cm^{-1}. MALDI-TOF MS: calcd. m/z 9533.7, found [M + Na]$^+$: 9557.0. UV-vis (in H_2O) $\lambda_{max}(\varepsilon)$: 280 nm ($1.99 \times 10^4$ M^{-1} cm^{-1}).

General procedure for the synthesis of ketones

Sodium (2 equiv) was added to absolute alcohol and heated to reflux. A mixture of 4-alkylphenylacetonitrile (1 equiv) and ethyl phenylacetate (1.25 equiv) was added drop-wise. After heating at reflux for 3 h, the reaction was quenched with cold water. The aqueous layer was washed with three portions of ether and acidified with 10% aqueous hydrochloric acid. The product was extracted with ether. The combined organic layer was washed with aqueous sodium bicarbonate solution, followed by water, dried over anhydrous sodium sulfate and concentrated. To a 60% sulfuric acid solution, the above obtained product was added and stirred at 60–65 °C for 12–15 h. The reaction was cooled to room temperature and diluted with ice-cold water. It was extracted with three portions of ether and the combined organic layer was washed with aqueous sodium bicarbonate solution, dried and concentrated. Column chromatography (silica gel, hexane/ethyl acetate) was performed to obtain the pure ketones (30–40% yield, >99% purity by GC).

8a:^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.31 (m, 3 H), 7.15 (d, J = 7.8 Hz, 4 H), 7.07 (d, J = 7.9 Hz, 2 H), 3.72 (s, 2 H), 3.69 (s, 2 H), 2.38 (s, 3 H).

8b:^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.31 (m, 3 H), 7.16 (d, J = 7.8 Hz, 4 H), 7.07 (d, J = 7.9 Hz, 2 H), 3.72 (s, 2 H), 3.69 (s, 2 H), 2.64 (q, J = 7.6 Hz, 2 H), 1.23 (t, J = 7.6 Hz, 3 H).

8c:^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.31 (m, 3 H), 7.17 (m, 4 H), 7.08 (d, J = 8.0 Hz, 2 H), 3.72 (s, 2 H), 3.69 (s, 2 H), 2.89 (quintet, J = 6.9 Hz, 1 H), 1.24 (d, J = 6.9 Hz, 6 H).

8d:^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.33 (m, 5 H), 7.15 (d, J = 7.0 Hz, 2 H), 7.09 (d, J = 8.2 Hz, 2 H), 3.72 (s, 2 H), 3.69 (s, 2 H), 1.31 (s, 9 H).

8e:^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.32 (m, 3 H), 7.15 (d, J = 6.8 Hz, 2 H), 7.07 (d, J = 8.6 Hz, 2 H), 6.85 (d, J = 8.6 Hz, 2 H), 3.80 (s, 3 H), 3.71 (s, 2 H), 3.66 (s, 2 H).

8f:^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.32 (m, 3 H), 7.14 (d, J = 6.9 Hz, 2 H), 7.05 (d, J = 8.6 Hz, 2 H), 6.88 (d, J = 8.6 Hz, 2 H), 4.11 (t, J = 4.8 Hz, 2 H), 3.75 (t, J = 4.8 Hz, 2 H), 3.70 (s, 2 H), 3.65 (s, 2 H), 3.45 (s, 3 H).

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