Photosensitized oxidation of alkenes with dendrimers as microreactors: controllable selectivity between energy and electron transfer pathway†

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Carboxylic acid terminated poly(aryl ether) dendrimers were used as microreactors to conduct the photooxidation of *trans*-stilbene and *trans*,*trans*-1,4-diphenyl-1,3-butadiene (DPB) sensitized by 9,10-dicyanoanthracene (DCA) in aqueous media. The photooxidation pathways can be successfully controlled by encapsulating the substrate and sensitizer molecules in the same or different sets of dendrimers. The singlet oxygen can transfer from one dendrimer to another. After the photoreaction, products could be more easily extracted from a dendrimer than from a micelle or a vesicle, and the dendrimer can be simply recovered by neutralization of the solution and reused.

Introduction

The dye-sensitized photooxidation of alkenes has been extensively investigated because of its importance in synthetic chemistry.[1] Foote and co-workers[2] have demonstrated two types of dye-sensitized photooxidation reactions involving molecular oxygen, a "Type I" electron transfer mechanism *via* superoxide radical anion ($O_2^{\bullet -}$) and a "Type II" energy transfer mechanism *via* singlet oxygen ($^1O_2$), which yield different oxidation products. In most cases, two types of photooxidation occur simultaneously without selectivity. To improve the selectivity in photosensitized oxidation of alkenes, various attempts have been made. Among these studies, the restriction of reactants in an organized or a constrained media, such as zeolites,[3] vesicles,[4] cyclodextrin,[5] and so on,[6] has been realized to be an effective way to control the reaction pathway.

In addition to these attempts to control the selectivity of photoreactions, amphiphilic dendrimers which contain analogous microenvironments to micelles, have been attracting more attention.[7] Fréchet's group[7a] designed a series of dendrimers with a benzophenonyl core and applied them to the photoinduced oxidation reaction of cyclopentadiene. Ramamurthy and co-workers[7b,c] synthesized several new poly(alkyl aryl ether) dendrimers with hydroxyl or carboxyl groups at the peripheries and applied them as microreactors to conduct several photoreactions. Their studies demonstrated that these dendrimers can act as "unimolecular micelles"[8] and offer much better constrainment than traditional micelles.

In the present work, we investigated photooxidations of *trans*-stilbene and *trans*,*trans*-1,4-diphenyl-1,3-butadiene (DPB) sensitized by 9,10-dicyanoanthracene (DCA) using carboxylic acid terminated poly(aryl ether) dendrimers as microreactors. The photochemical studies indicate that the photooxidations could be effectively controlled by locating substrate and sensitizer in one or separate sets of dendrimer molecules. In addition, these water soluble dendrimers can be easily recovered and reused, which makes them promising microreactors for photoreactions.

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Results and discussion

The carboxylic acid terminated poly(aryl ether) dendrimers (G*n*, n = 1–4) were synthesized up to the fourth generation by Fréchet's method as shown in Fig. 1.[9] The purity of dendrimers is above 95% according to their ^{1}H NMR spectra (^{1}H NMR spectra are given in the ESI†). All four generation dendrimers are soluble in aqueous solution (pH > 9). The photosensitized oxidations with dendrimers as microreactors were carried out by two procedures. In procedure I, the sensitizer DCA and alkenes were combined and well incorporated with one set of dendrimer solution by sonication. In procedure II, the sensitizer DCA was sonicated into one set of dendrimer solution while the alkenes were dissolved into the other set of dendrimer solution. The two sets of dendrimer solutions were then mixed together and the final mixture was not sonicated but stirred in the dark at room temperature for 24 h. Dialysis was performed in both procedures to remove the sensitizer and the alkenes which were located outside of the dendrimers. In order to get the same number of cavities among different generations of dendrimers, the concentrations of the dendrimers used in the photooxidation were set to 8.0, 4.0, 2.0, and 1.0 mM for G1–G4, respectively. Dynamic Light Scattering (DLS) studies were performed on aqueous solutions of dendrimers to confirm that these dendritic molecules do not aggregate at these concentrations, in agreement with the earlier study by Klaikherd *et al.*[10] The solutions for irradiation were bubbled with continuous oxygen and exposed to light with λ > 400 nm. After irradiation, the products were extracted by CH_2Cl_2 and analysed by gas chromatography.

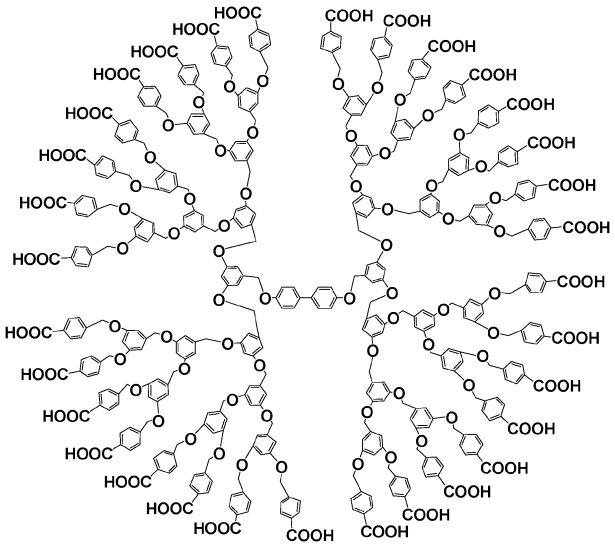
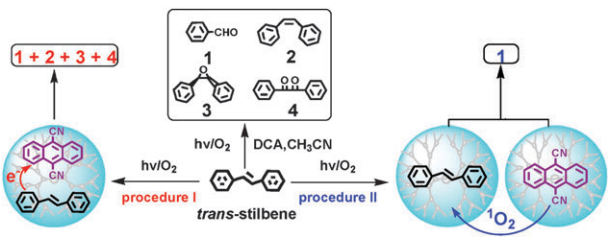


Fig. 1 Structure of G4 dendrimer.

Photosensitized oxidation of *trans*-stilbene

To determine the effects of dendrimers in controlling the reaction pathway, a comparison photooxidation of *trans*-stilbene in homogenous CH_3CN solution was performed, which produces benzaldehyde **1**, *cis*-stilbene **2**, *trans*-2,3-diphenyloxirane **3**, and benzil **4** without selectivity (Scheme 1). The distribution of products is presented in Table 1, which is in agreement with that reported by Foote *et al.*[2] Among the four products, **1** could be generated *via* either energy transfer pathway or electron transfer pathway, and the other three products are definitely derived *via* the electron transfer mechanism.[3b,4a] The product distribution of the DCA-photosensitized oxidation of *trans*-stilbene in the present of dendrimers significantly differs from that in homogeneous solution and obviously depends on the experimental procedures.

In procedure I, all products **1–4** could be detected. However, the yields of **2**, **3**, and **4** (34%, 34%, and 23%, respectively) in G1 dendrimer mediums were significantly higher than those in CH_3CN (8%, 7%, and 18%, respectively). This observation indicates that the present of the dendrimers makes the products from the electron transfer pathway dominate the photooxidation reaction. It's reasonable that, under this situation, *trans*-stilbene and DCA are both encapsulated within the same dendrimer molecules and *trans*-stilbene is close to the sensitizer DCA. Thus, the intersystem crossing from the singlet state to the triplet state of DCA is suppressed by the rapid electron transfer process between the excited DCA and *trans*-stilbene. As a consequence of the electron transfer process, the radical



Scheme 1

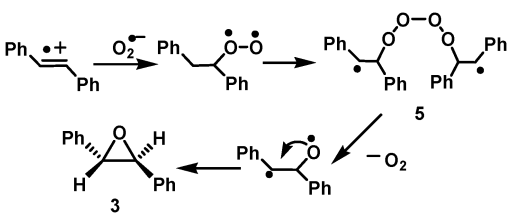
Table 1 Product distribution in DCA-sensitized photooxidation of *trans*-stilbene and DPB in CH_3CN and in dendrimer or vesicle aqueous solutions with different procedures

	trans-Stilbene				DPB					
Medium	**1**	**2**	**3**	**4**	**1**	**6**	**7**	**8**	**9**	**10**
CH_3CN	67	8	7	18	84	84	1	5	0	10
Procedure I										
G1	9	34	34	23	48	48	20	32	0	0
G2	10	41	2	47	26	26	0	74	0	0
G3	3	48	0	49	32	32	0	68	0	0
G4	3	52	0	45	73	73	0	27	0	0
Vesicles[a]	21	0	73	6	53	53	23	0	24	0
Procedure II										
G1	100	0	0	0	0	0	0	0	0	100
G2	100	0	0	0	0	0	0	0	0	100
G3	100	0	0	0	0	0	0	0	0	100
G4	100	0	0	0	0	0	0	0	0	100
Vesicles[a]	100	0	0	0	100	100	0	0	0	0

[a] From literature.[4]

ions ($DCA^{\bullet -}$ and *trans*-$stilbene^{\bullet +}$) are formed leading to the photooxidation products, **2**, **3**, **4** and a comparatively low yield of **1**. Notably, the yield of **1** shows a discontinuity from 10% to 3% on going from G2 to G3, which can be correlated to the onset of the transition from a leaking to a globular structure as the steric requirements of the dendritic branch increases. The globular shape dendrimer has a more confined interior, within which *trans*-stilbene and the sensitizer DCA locate much closer facilitating the electron transfer pathway. Product **3** is also produced *via* the electron transfer pathway, but it was only detected in G1 and G2 dendrimers in our experiments. As Eriksen and Foote reported,[11] the epoxide **3** is formed from a bulky intermediate **5** *via* the Bartlett mechanism (Scheme 2).[12] Therefore, the lack of epoxide product **3** in G3 and G4 dendrimers and the little formation in G2 dendrimer might be attributed to the fact that the interior of higher generation dendrimers is much more congested than that of lower ones, and there is inadequate space for the formation of **5**.

On the contrary, benzaldehyde **1** is the unique product of the photosensitized oxidation in procedure II (Table 1). Evidently, this product was produced *via* the energy transfer pathway. Based on calculations,[13] the inter-dendrimer distances are about 7, 8, 10 and 13 nm for G1 to G4 dendrimer solutions, respectively. The small and uncharged $^1O_2$ molecule has a relatively long lifetime allowing it to diffuse a long distance in nonviscous media. The average diffusion distance of the $^1O_2$ molecule in aqueous solution is estimated to be about 780 nm.[14] This diffusion distance is much longer than the inter-dendrimer distance estimated above, and $^1O_2$ generated in the DCA-containing dendrimers *via* energy transfer from the triplet DCA to the ground state O_2, is capable of diffusing into



Scheme 2

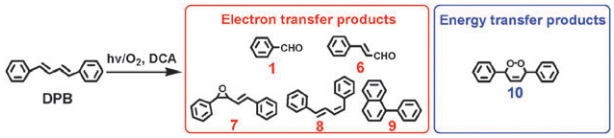
the *trans*-stilbene-containing dendrimers to react with olefin molecules and form an intermediate dioxetane, which decomposes to yield the product **1**. A quenching experiment was also performed to confirm the diffusion mechanism of singlet oxygen by employing a $^1O_2$ quencher, 9,10-diphenylanthracene (DPA), which can react specifically with $^1O_2$ forming a thermostable endoperoxide.[15] The quenching experiment was conducted in procedure II, while the sensitizer DCA and the $^1O_2$ quencher DPA were located in different sets of dendrimers. Upon irradiation of an oxygen saturated DCA-containing and DPA-containing dendrimer solution with $\lambda > 425$ nm light, an evident drop of the DPA absorbance at 375 nm was observed, indicative of the endoperoxide formation, a cycloaddition product of DPA and $^1O_2$. This gives the evidence that the $^1O_2$ can diffuse from one dendrimer to another and then initiate oxidation reactions. The isolation of *trans*-stilbene in one set of dendrimers from DCA in the other set of dendrimers suppresses the occurrence of electron transfer process between the substrate and the sensitizer. Hence, no electron transfer product *via* the electron transfer pathway should be expected to be produced. It is also worth emphasizing that there is no difference between the product distributions for G1 to G4 in procedure II conditions. This suggests that neither substrate nor sensitizer molecules could escape from dendrimers into the aqueous solution or the other set of dendrimers during the operation and irradiation processes, and the generation shows little effect on the product distribution of photooxidation in the procedure II experiments.

The product distribution of this photosensitized oxidation in vesicles reported earlier by Tung *et al.*[4] was also listed in Table 1. The product **3** was in a high yield and no isomerization product **2** was detected in vesicles, which is remarkably different from those in dendrimers. This demonstrates that vesicles can provide a relatively larger cavity to accommodate the bulky intermediate of **5** for the production of **3**, and a more restrictive microenvironment to bar the isomerization of *trans*-stilbene than dendrimers.

Photosensitized oxidation of DPB

Furthermore, another substrate alkene DPB was investigated. Under the same experimental conditions, irradiation of an oxygen saturated DPB solution in CH_3CN gave benzaldehyde **1**, cinnamaldehyde **6**, epoxide **7**, isomerized product **8**, and endoperoxide **10** (Scheme 3). The product distribution is consistent with that reported in the literature[3b,4,16] except that 1-phenylnaphthalene **9** is replaced by a photoisomerization product of DPB **8**. Among these products, **10** is a product of 1,4-cycloaddition of $^1O_2$ to DPB and the other products are presumably all derived *via* the electron transfer pathway.[3b,4a,b] As observed in the case of *trans*-stilbene, the product distribution of the DCA photosensitized oxidation of DPB in dendrimer aqueous solutions is significantly different from that in homogeneous solution, and it is remarkably dependent on the experimental procedures.

In procedure I, the electron transfer products are dominant as expected, because of the proximity of the alkene molecule to the sensitizer. **1** and **6** are most likely derived from an intermediate dioxetane, a cycloaddition product of DPB



Scheme 3

radical cation and $O_2^{\bullet -}$. Epoxide **7** was only detected in G1 dendrimer, which can also be attributed to the lack of enough room to accommodate the large intermediate[11,12] in higher generation dendrimers. The isomerized product **8** is probably formed directly from the DPB radical cation by bond rotation and electron back-transfer. As shown in Table 1, there is a precipitous drop in the proportion of product **8** from G3 to G4 (68% to 27%), which illuminates well that the higher generation dendrimer is more restrictive. As the DPB radical cation is encapsulated in dendrimers, the confined environment slows down the bond rotation, which restrains the yield of **8**. So, itcan be inferred that there is a great disparity in the microenvironment of dendrimers between G3 and G4 and the latter has a more constrained inner cavity.

In procedure II, the sensitizer DCA and the substrate DPB are located in different sets of dendrimers and separated apart from each other. Irradiation of the oxygen-saturated sample resulted exclusively in the energy transfer product **10**, 1,4-cycloaddition product of $^1O_2$ to DPB (Table 1). Considering the sample had been stored in the dark at room temperature for 24 h during the dialysis process, the unique energy transfer product **10** from the photosensitized oxidation reveals that the inter-dendrimer exchange between substrate and sensitizer did not occur. The electron transfer pathway is restrained by the isolation of the sensitizer from the substrate.

In comparison with results reported by Tung *et al.*,[4] the products obtained in vesicles (Table 1) were different from those in dendrimers. The high yield of epoxide **7** and the lack of isomer **8** in vesicles from procedure I can also be ascribed to larger inner cavities and more constrained microenvironments as in the *trans*-stilbene case. The photosensitized oxidation in vesicles from procedure II produced **1** and **6** quantitatively, which were thought derived from a dioxetane intermediate, a 1,2-cycloaddition product through the energy transfer pathway. The preferential formation of the products of 1,2-cycloaddition over those of 1,4-cycloaddition in vesicles is proposed in terms of a greater difficulty in achieving the necessary geometry for 1,4-cycloaddition in a vesicle medium. This observation further strengthens the idea that vesicles have more confined microenvironments than dendrimers.

The recovery and reuse of these dendrimers were also checked. The dendrimers can be simply recovered by neutralization of the solution and collection with filtration or centrifugation. The photosensitized oxidation experiments within recovered-dendrimers showed similar results to fresh ones, indicating the advantages of the recovery and reuse properties of dendrimers.

Conclusions

Carboxyl-terminated dendrimers can act as microreactors to control the pathways of the photosensitized oxidation reaction

of *trans*-stilbene or DPB by locating the substrate and sensitizer molecules in the same or different sets of dendrimers, and the $^1O_2$ can transfer from one dendrimer to another. The higher generation dendrimers show a better control effect. After the photoreaction, products could be more easily extracted from a dendrimer than from a micelle or a vesicle, and the dendrimer can be simply recovered by neutralization of the solution and reused, which accords with the concept of "green chemistry".[17] Dendrimers have a relatively small inner cavity and less confined medium than vesicles, which gives dendrimer a special selectivity in photooxidation products.

Experimental section

Materials and instruments

The carboxylic acid terminated poly(aryl ether) dendrimers were synthesized up to the fourth generation following Fréchet's method. (as shown in ESI† Fig. S1) 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. Gas chromatography (GC) experiments were carried out on a BeiFen 3420 gas chromatography 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. Dynamic Light Scattering measurements were performed on a Malvern Zetasizer 3000HS.

Inclusion of reactants within dendrimers

The procedures adopted for the inclusion of reactants within dendrimers using two different methods are described as follows.

Procedure I. A certain amount of DCA (1×10^{-4} M) and alkene (1×10^{-4} M) were added to a glass reactor and a known amount of dendrimers in 5 mL aqueous KOH solutions (8×10^{-3}, 4×10^{-3}, 2×10^{-3} and 1×10^{-3} M for G1 to G4, respectively) were added to the reactor. After sonicating for 4 h, the solution was filtered to remove any floating particles and stirred for 24 h in the dark. At the same time dialysis was performed to remove the sensitizer and substrate molecules located outside of the dendrimers in solution.

Procedure II. A certain amount of DCA (1×10^{-4} M) and alkene/DPA (1×10^{-4} M) were added to two reactors, respectively. Two 2.5 mL aqueous KOH solutions with a known amount of dendrimers (8×10^{-3}, 4×10^{-3}, 2×10^{-3} and 1×10^{-3} M for G1 to G4, respectively) were added to these two reactors, respectively. After sonicating for 4 h, the solutions were filtered to remove any floating particles and mixed together. Then the final mixture was stirred with dialysis for 24 h in the dark to remove the sensitizer and substrate molecules unencapsulated into dendrimers.

After dialysis, the concentrations of olefins and sensitizers in dendrimer aqueous solutions were examined by UV-Vis absorption spectroscopy. The concentrations of substrates were *ca.* 20 μM, corresponding to 0.0025, 0.005, 0.01 and 0.02 molecule per dendrimer for G1 to G4, respectively.

Photooxidation and product analysis in dendrimer aqueous solutions

The samples were purged with oxygen for 30 min prior to use, and oxygen was bubbled through the solution during the photolysis. A 500 W medium-high pressure Hg lamp was employed as the light source, and a glass filter was used to cut off the light with the wavelength below 400 nm. The irradiation time is 8 h for procedure I or II. After irradiation, the basic aqueous solution was acidified with 10% dilute HCl to neutral. Reactant and products were extracted from the aqueous solution by using CH_2Cl_2 and the organic layer was dried over anhydrous $MgSO_4$, concentrated, analyzed by gas chromatography. All the photooxidation products derived from *trans*-stilbene and DPB were analyzed by GC-MS and identified by comparing with the commercially available samples.

Photooxidation and product analysis in acetonitrile solutions

Alkene (1 mg, 1×10^{-3} M) and 5 mL solution of DCA in acetonitrile (1×10^{-4} M) were mixed in a glass reactor. The mixture solution was purged with oxygen for 30 min prior to use, and oxygen was bubbled through the solution during the photolysis. A 500 W medium-high pressure Hg lamp was employed as the light source, and a glass filter was used to cut off light with a wavelength below 400 nm, which ensured the absence of direct excitation of the alkene substrates. After 2 h irradiation, the solution was concentrated and analyzed by GC.

Acknowledgements

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