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Porphyrin-Functionalized Dendrimers: Synthesis and Application as Recyclable Photocatalysts in a Nanofiltration Membrane Reactor

Suhas A. Chavan,[a] Wouter Maes,[b] Lieven E. M. Gevers,[a] Joos Wahlen,[a] Ivo F. J. Vankelecom,[a] Pierre A. Jacobs,[a] Wim Dehaen,[b] and Dirk E. De Vos*[a]

Abstract: The convergent synthesis of a series of porphyrin-functionalized pyrimidine dendrimers has been accomplished by a procedure involving the nucleophilic aromatic substitution (NAS) as a key reaction step. The resulting dendritic porphyrin catalysts show high activity in the light-induced generation of singlet oxygen ($^1O_2$) from ground-state oxygen. These materials are synthetically useful photosensitizers for the oxidation of various olefinic compounds to the corresponding allylic hydroperoxides. Catalytic activities and regio- and stereoselectivities of the dendritic photosensitizers are comparable to those observed for mononuclear porphyrin catalysts. Recycling of the dendrimer-enlarged homogeneous photocatalysts was possible by solvent-resistant nanofiltration (SRNF) by using an oxidatively stable membrane consisting of a polysiloxane polymer and ultrastable Y zeolite as inorganic filler. Moreover, this membrane technology provides a safe way to isolate the hydroperoxide products under very mild conditions. The membrane showed high retention for the macromolecular catalysts, even in chlorinated solvents, but some oxidative degradation of the porphyrin units of the dendrimer was observed over multiple catalytic runs.

Keywords: dendrimers · nanofiltration · nucleophilic aromatic substitution · oxidation · oxygen

Introduction

Homogeneous catalysts, which are present in the same phase as the reactants and products, may offer a number of advantages over their heterogeneous counterparts. For example, since the catalyst usually is a dissolved metal complex, all active sites are easily accessible, resulting in high catalytic activities. Furthermore, it is often possible to tune the selectivity of the catalyst via a proper ligand design. Despite these advantages, many homogeneous catalytic systems cannot be commercialized because of the difficulties associated with catalyst separation, recovery, and recycling.[1]

In recent years, a new concept has been proposed that combines the advantages of homogeneous and heterogeneous catalysis.[2] In this process, homogeneous catalysts are anchored to a soluble support, and the separation is carried out by a filtration technique. In order to obtain a high retention of the catalyst by ultra- or nanofiltration membranes, the homogeneous catalysts are anchored to soluble supports such as polymers[3] or dendrimers.[4] Dendrimers are large tree-like molecules with a persistent globular shape, which makes them very suitable for nanofiltration. Moreover, since the catalyst loading of dendrimers can be determined exactly, a direct comparison with unsupported mononuclear catalysts is possible. This is less straightforward for the less well-defined polymeric systems.

To date, the majority of applications of dendritic catalysts concerns hydroformylation, hydrogenation, C–C coupling reactions, polymerizations and related reactions in non-oxidizing atmospheres.[5] With a few exceptions,[6] oxidation processes are virtually absent from this spectrum, mainly because of the susceptibility of several previously used dendrimers to oxidative degradation. Clearly, there is a need for new, oxidatively stable dendritic macromolecules. Such well-defined materials could be very useful for the immobilization of oxidation catalysts.

Herein we report the synthesis and characterization of oxidatively stable pyrimidine dendrimers functionalized with porphyrin end groups. These dendritic catalysts are applied

[a] Dr. S. A. Chavan, L. E. M. Gevers, Dr. J. Wahlen, Prof. Dr. I. F. J. Vankelecom, Prof. Dr. P. A. Jacobs, Prof. Dr. D. E. De Vos
Centre for Surface Chemistry and Catalysis
Katholieke Universiteit Leuven, Kasteelpark Arenberg 23
3001 Leuven (Belgium)
Fax: (+32) 16-321-998
E-mail: dirk.devos@agr.kuleuven.ac.be

[b] Dr. W. Maes, Prof. Dr. W. Dehaen
Laboratory of Organic Synthesis
Katholieke Universiteit Leuven, Celestijnenlaan 200F
3001 Leuven (Belgium)

in the light-induced generation of singlet oxygen ($^1O_2$) from ground-state oxygen. Recycling of the dendrimer-enlarged homogeneous photosensitizers is investigated using nanofiltration techniques.

Results and Discussion

Dendrimer synthesis: Porphyrins have been incorporated in the framework of dendrimers by several research groups.[7–10] In most cases, they have been used as central building blocks.[8] On the other hand, reports on the attachment of porphyrins to the periphery of a dendritic backbone are relatively scarce.[9]

Recently, we got interested in the synthesis of dendrimers through a nucleophilic aromatic substitution (NAS) approach that utilizes the substitution of heteroarylhalogenides with phenolates to construct dendrimers in a convergent way.[11,12] This approach allows the incorporation of heterocyclic building blocks in the dendrimer framework. These heterocyclic dendrimers are promising materials for applications that require a more rigid structure or a larger resistance towards the applied conditions, for example, in catalytic oxidation. Following this strategy, dendrimers consisting of 1,3,4-oxadiazoles,[11a] 1,3,5-triazines,[11b] 1,2,4-triazoles[11c] and pyrimidines[12] have been prepared. Currently, the pyrimidine system seems to present an optimum within this route, combining an intermediate reactivity and a good structural stability. For the construction of a homogeneous dendritic photocatalyst, we considered the introduction of a suitable porphyrin ligand at the periphery of these oxidatively robust pyrimidine dendrons.

Synthesis of porphyrin-functionalized pyrimidine dendrimers: In order to obtain a homogeneous catalyst, it is essential to synthesize a porphyrin dendrimer displaying high solubility in organic solvents. By introducing bulky groups on the periphery of the dendrimer, solubility can be increased. Earlier synthetic work on porphyrins provided us with the phenolic porphyrin **1** (Figure 1).[13] The phenol moiety enables coupling to the pyrimidine monomer and the *tert*-butyl terminal groups ensure high solubility. AB_3-porphyrin **1** was synthesized by a mixed Rothemund condensation of *p*-hydroxybenzaldehyde and 3,5-bis(*tert*-butyl)benzaldehyde. Since the latter aldehyde is not commercially available it was first prepared starting from toluene.[14] The aldehydes were mixed with pyrrole under Lindsey conditions and column chromatographic purification afforded AB_3-porphyrin **1** (16%) and A_4-porphyrin **2** (12%) (Figure 1). Tetrakis-3,5-bis(*tert*-butyl)phenyl porphyrin **2** was obtained in a substantial amount and was used as G_0 model compound in the catalytic experiments.

The propagation strategy was the same as for the preparation of the earlier reported heterocyclic dendrimers[11,12] and involved coupling of phenolic porphyrin **1** to the pyrimidine monomer **4** (4,6-dichloro-2-(4-methoxyphenyl)-pyrimidine) and subsequent deprotection of the obtained *p*-methoxyphenyl substituted first-generation dendron **5** with boron tribromide (Scheme 1). The obtained G_1-dendron **6** was again subjected to a nucleophilic aromatic substitution reaction on the monomer **4** to afford the second-generation dendron **7**. The reaction conditions required for NAS on the monomer **4** were the same as reported earlier.[12] Phenolic porphyrin **1** was activated with potassium carbonate and the mixture was stirred in refluxing acetonitrile for several days until negligible amounts of the mono-substituted dendron remained in the reaction mixture, as monitored by TLC analysis. The deprotection step was carried out at low temperature (−18 °C) in order to avoid destructive fragmentation of the dendron structure by cleavage of the internal diaryl ether moiety. The synthesized dendrons already possess high molecular weights in these early generations (G_1 = 2117, G_2 = 4388 Da), which should allow their easy recovery by nanofiltration techniques.

In order to obtain the final dendrimers, the synthesized dendrons were coupled to a polyfunctional core. For this purpose we considered the synthesis of a novel porphyrin core. Inspired by the success of the NAS reaction on pyrimi-

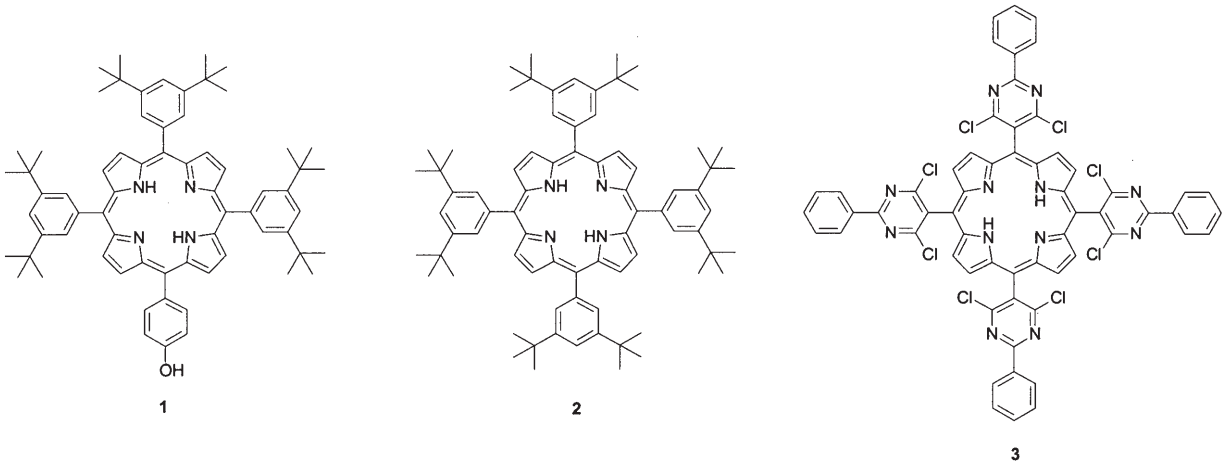
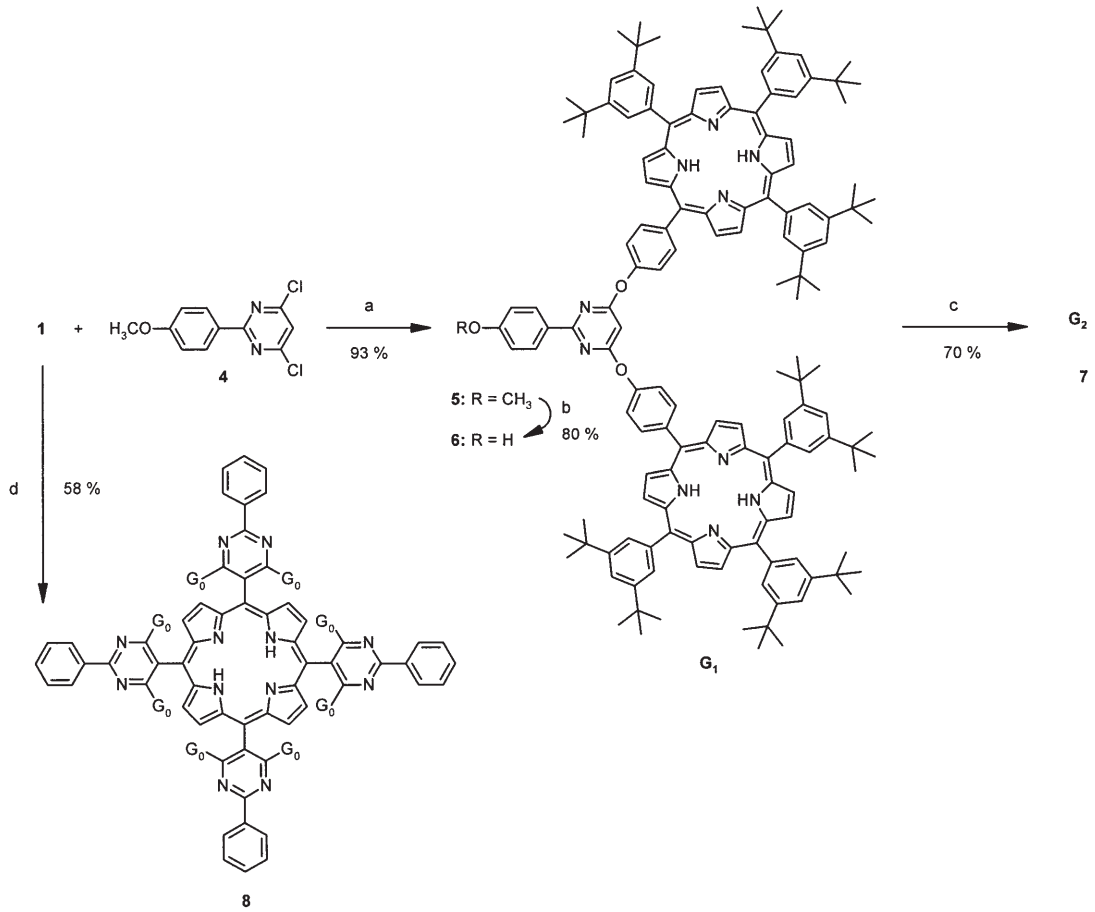


Figure 1. Model compound **2** and dendrimer building blocks **1** and **3**.



Scheme 1. Synthesis of the porphyrin dendrons **5** and **7** and porphyrin dendrimer **8**. a) K_2CO_3, CH_3CN, reflux; b) BBr_3, CH_2Cl_2, $-18\,^{\circ}C$; c) **4**, K_2CO_3, CH_3CN/DMF, reflux; d) **3**, K_2CO_3, DMF, 70 °C.

dine monomer **4** and the earlier reported *meso*-dichloropyrimidinyl porphyrins,[15] octafunctional porphyrin core **3** was synthesized (Figure 1). Pyrrole and 4,6-dichloro-2-phenylpyrimidine-5-carbaldehyde[16] were mixed in equimolar amounts under Lindsey conditions and, after column chromatographic purification, the desired porphyrin was isolated in 20% yield. Characterization of this porphyrin suffered from its low solubility. However, the low solubility could be an advantage in the complete functionalization of the core since partially substituted species show a remarkably higher solubility.

Obviously, full substitution of the porphyrin core **3** might be limited due to steric effects. In order to check the feasibility of the eightfold substitution, porphyrin **3** was reacted with G_0-dendron **1**. After four days of reaction, substitution seemed to be complete and nonaporphyrin **8** was isolated in an acceptable yield (58%, Scheme 1). This nonaporphyrin dendrimer possesses a molecular weight of 8650 Dalton.

Characterization of the porphyrin-functionalized pyrimidine dendrimers: All compounds were fully characterized by using NMR spectroscopy (^1H and ^{13}C), electrospray ionization mass spectrometry (ESI-MS) and UV-visible spectroscopy. The ^1H NMR spectra of the various generation dendrons clearly show the signals corresponding to the different monomer layers and integration indicates which generation is involved. Since the detection range of the ESI mass spectrometer is limited to m/z 4000, the dendrons and dendrimers of high molecular weight were identified by their multiple charged ions. The UV-visible absorption spectra of the different porphyrin dendrimers show absorption peaks for the porphyrin moiety (intense Soret band at 420 nm and four Q bands in the range of 515–650 nm) and a broad absorption band centered around 290 nm due to the pyrimidine building block. The observed molar extinction coefficients are proportional to the number of porphyrin units.

The structure and purity of the octafunctional porphyrin core **3** could not be proven by NMR spectroscopy because of its very low solubility in organic solvents. The structure was, however, confirmed by mass spectrometry and UV-visible spectroscopy and, more importantly, by its reactivity to yield octafunctional phenoxy-substituted porphyrins in high yield. For example, eight-fold substitution with 4-*tert*-butylphenol resulted in a yield of 70% (experimental data not included).

The signals in the ^1H NMR spectrum of nonaporphyrin **8** were broadened and therefore the extent of substitution on the porphyrin core could not be unambiguously established

by integration. This broadening of the NMR peaks is caused by the restricted movement of the dendron branches. The structure was, however, confirmed by the ESI mass spectrum in which the multiple charged ions ($[M+H]^{4+}$ = 1390.0, $[M+H]^{3+}$ = 1853.3, $[M+H]^{2+}$ = 2778.9) ensured a complete substitution pattern. ^{13}C NMR data were not included for the nonaporphyrin because the abundance of some signals was too low.

Generation of singlet oxygen catalyzed by porphyrin-functionalized dendrimers: Porphyrins are well-known catalysts for the photosensitized generation of singlet oxygen ($^1O_2$) from ground-state oxygen ($^3O_2$).[17] The reaction occurs via light-induced excitation of a photosensitizer from its ground state (^1PS) to an excited singlet state ($^1PS^*$) [see Equations (1)–(3)]. Intersystem crossing yields the excited triplet state ($^3PS^*$). Triplet–singlet energy transfer from $^3PS^*$ to triplet oxygen results in the formation of excited singlet molecular oxygen.

$$\text{photoexcitation } {}^1PS + h\nu \rightarrow {}^1PS^* \quad (1)$$

$$\text{intersystem crossing } {}^1PS^* \rightarrow {}^3PS^* \quad (2)$$

$$\text{quenching of triplet state } {}^3PS^* + {}^3O_2 \rightarrow {}^1PS + {}^1O_2 \quad (3)$$

The singlet oxygen formed can react with an olefinic substrate S to yield the corresponding allylic hydroperoxide SO_2 [see Equations (4)–(7)].[18] Other decay pathways of the highly reactive singlet oxygen are physical quenching by the substrate, quenching by the solvent and phosphorescence. In solution, the non-radiative pathways predominate in the total deactivation process and the deactivation channel by phosphorescence can be neglected.

$$\text{chemical reaction } {}^1O_2 + S \rightarrow SO_2 \quad (4)$$

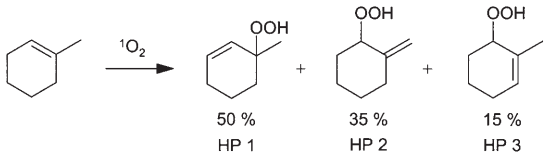
$$\text{physical quenching } {}^1O_2 + S \rightarrow {}^3O_2 + S \quad (5)$$

$$\text{quenching by solvent } {}^1O_2 + \text{solvent} \rightarrow {}^3O_2 + \text{solvent} \quad (6)$$

$$\text{phosphorescence } {}^1O_2 \rightarrow {}^3O_2 + h\nu \quad (7)$$

Photooxidation of 1-methyl-1-cyclohexene: With the porphyrin-functionalized dendrimers in hand, we first investigated the photooxidation of 1-methyl-1-cyclohexene. This olefin contains three different allylic hydrogen atoms and its reaction with singlet oxygen yields three allylic hydroperoxide products with a characteristic product distribution (Scheme 2).[19]

The photooxidation of 1-methyl-1-cyclohexene (1 M) in $CHCl_3$ was performed under an oxygen atmosphere at 0 °C by using tetraphenylporphyrin (TPP), model compound **2**, the porphyrin-functionalized dendrons **5** and **7**, and dendrimer **8**. In all cases the same amount of porphyrin (0.1 μM) was used. The substrate-to-catalyst ratio was 10000 to 1. The results of the photooxidation after 1 and 3 h are shown in Table 1. The porphyrin catalysts show a high activity in the photosensitized production of singlet oxygen. After 3 h, a turnover number (TON, based on the number of porphyrin units) between 3000 and 5000 is reached for all catalysts. This implies that even for the large catalysts, all porphyrin units at the periphery of the dendritic support act as independent catalysts and remain well accessible to the reactants. For the dendritic catalysts, the catalytic activity and the regioselectivity in the photooxidation of 1-methyl-1-cyclohexene are very similar to those observed for model compound **2** and other known photosensitizers such as tetraphenylporphyrin.[19]



Scheme 2. Reaction of singlet oxygen with 1-methyl-1-cyclohexene.

Table 1. Photooxidation of 1-methyl-1-cyclohexene: comparison of tetraphenylporphyrin, model compound **2**, dendrons **5** and **7**, and dendrimer **8**.[a]

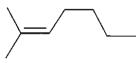
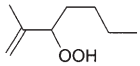
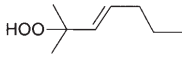
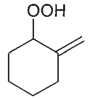
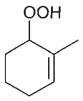
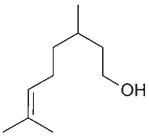
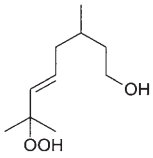
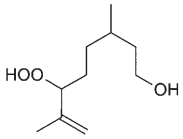
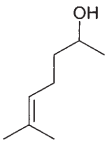
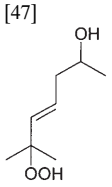
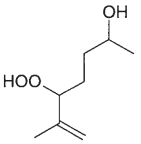
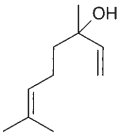
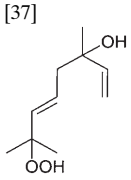
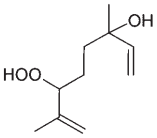
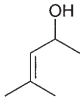
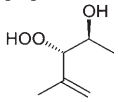
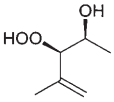
Catalyst	M_w[b] [Da]	t [h]	Conv. [%]	Sel.[c] [%]	HP 1 [%]	HP 2 [%]	HP 3 [%]	TON[d]
TPP[e]	614.8	1	16.3	78.9	37.2	45.5	17.3	1632
		3	32.4	89.9	44.6	42.3	13.0	3240
2	1063.6	1	16.4	92.1	36.6	46.3	17.1	1645
		3	36.0	92.3	43.2	41.6	15.2	3597
5	2116.9	1	17.5	94.4	35.8	48.6	15.6	1745
		3	34.1	91.0	42.7	44.4	12.9	3412
7	4388.0	1	24.2	92.2	37.4	45.1	17.5	2417
		3	48.8	94.5	43.6	42.2	14.2	4877
8	8649.9	1	16.8	94.6	32.6	50.0	17.4	1681
		3	30.0	87.8	40.9	43.6	15.5	3001

[a] Reaction conditions: 0.3 μmol porphyrin units, 3 mmol 1-methyl-1-cyclohexene, 3 mL $CHCl_3$, 0 °C, $h\nu$, O_2. [b] Molecular weight. [c] Overall selectivity towards allylic hydroperoxides. [d] Turnover number based on porphyrin units. [e] 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphyrin.

Photooxidation of olefinic compounds: Selected examples of the peroxidation of various olefinic compounds catalyzed by porphyrin-functionalized G_1-dendron **5** are shown in Table 2. It is evident from these data that the dendritic catalyst **5** is an active and selective photocatalyst. The reactions are all characterized by high conversions (> 90 %) and very high selectivities (> 99 %) towards the desired allylic hydroperoxides. High TONs of 10000 are observed after 8 h of reaction. The observed regio- and stereoselectivities of the products are identical to the known selectivity of singlet oxygen reactions.

Alkyl-substituted olefins react with $^1O_2$ via the so-called Schenck or ene reaction, and mixtures of regioisomeric allyl-

Table 2. Photooxidation of various olefins catalyzed by G_1-dendron **5**.[a]

Substrate	Product distribution [%]			Conv.[b] [%]
	 [53]	 [47]		100
	 [43]	 [8]	 [49]	100
	 [47]	 [53]		92
	 [37]	 [63]		100
	 [41]	 [59]		100
	 [94][c]	 [6][c]		92

[a] Reaction conditions: 0.15 μmol porphyrin units, 1.5 mmol substrate, 1.5 mL $CHCl_3$, 0 °C, 8 h, *hν*, O_2. [b] Selectivity to allylic hydroperoxides was higher than 95% in all cases. [c] Pair of enantiomers.

ic hydroperoxides with a unique product distribution are obtained.[20] This is illustrated by the oxidation of simple acyclic and cyclic trialkylsubstituted alkenes such as 2-methyl-2-heptene and 1-methyl-1-cyclohexene. Oxyfunctionalized olefins such as 6-methyl-5-hepten-2-ol and citronellol cleanly yielded the allylic hydroperoxide products, without oxidation of the secondary or primary alcohol function. Photooxidation of citronellol is the first step in the preparation of rose oxide, a well-known perfumery ingredient used in rose and geranium perfumes.[21] For linalool, a monoterpene containing an allylic alcohol functionality, oxidation occurred at the isolated, electron-rich 6,7-double bond. No peroxidation of the less electron-rich, allylic double bond was observed. The derived allylic alcohols can be used for the synthesis of 3,7-dimethyl-1,5,7-trien-3-ol, an important aroma compound found in black tea.[22]

For the photooxidation of the allylic alcohol 4-methyl-3-penten-2-ol (mesitylol), very high selectivity towards the hydroperoxy homoallylic alcohols was observed. The high *threo*-diastereoselectivity is in accordance with data reported in literature for photooxidations in apolar solvents.[23] The photooxidation of mesitylol is the first step in the synthesis of 1,2,4-trioxanes. Some of these compounds show significant anti-Malaria activity against *Plasmodium falciparum*.[24]

Catalyst recycling by solvent-resistant nanofiltration (SRNF): Generally, the nanofiltration (NF) membrane that is used in the filtration step has to meet several key requirements. To assure long-term use, the membrane has to be stable under the reaction conditions. Furthermore, a suitable membrane should show complete retention for the catalyst and only a low retention for the formed products, the substrate and the solvent.

For application in photooxidation reactions in particular, a NF membrane should show high oxidative stability and should be stable in halogenated solvents such as chloroform ($CHCl_3$). The latter is important for singlet oxygen reactions since $^1O_2$ shows a very long lifetime in these solvents, which allows an efficient reaction with the olefinic substrate [Eqs. (4)–(7)]. Moreover, the diastereoselectivity of the oxidations is highest in this type of solvents.

Nanofiltration experiments were run in a batch operation mode; this allows to study essential parameters such as the long-term stability of the membrane and the retention of the catalyst. Batch operation implies a series of reaction and filtration steps. After the reaction, filtration is carried out to remove a part of the reaction solution and the original reactor volume is then restored by the addition of fresh reactant solution.

Nanofiltration of porphyrin-functionalized dendrimers: The commercial MPF-50 membrane has already been successfully used in the recovery of dendritic catalysts.[4] Preliminary experiments showed that this membrane is stable in $CHCl_3$. Nanofiltration tests were carried out in a dead-end membrane module at 20 °C by using a N_2 pressure of 30 bar as the driving force. Solutions of the porphyrin compounds in $CHCl_3$, isopropanol (IPA) or IPA/$CHCl_3$ mixtures were filtered over the MPF-50 membrane; feed, permeate and retentate solutions were collected and analyzed for the

amount of dendrimer using UV-visible spectroscopy (Soret band of the porphyrin units at 420 nm).

Table 3 shows that the MPF-50 membrane has low to very low rejection (5–50%) of the porphyrin catalysts. Moreover, it was necessary to add a substantial amount of isopropanol to $CHCl_3$ in order to obtain a reasonable solvent flux through the membrane.

Table 3. Retention of dendritic porphyrin catalysts by nanofiltration membranes.[a]

Membrane	Catalyst	M_W [Da]	Solvent	Rejection[b] [%]
MPF-50	**1**	1063.6	IPA/$CHCl_3$[c]	5
	5	2116.9	IPA/$CHCl_3$	40
	8	8649.9	IPA/$CHCl_3$	55
PDMS	**1**	1063.6	IPA	57
	5	2116.9	IPA	99
	7	4388.0	IPA	96
	8	8649.9	IPA	96
PDMS-USY-PAN	**5**	2116.9	$CHCl_3$	95

[a] 30 bar N_2 and 20°C. [b] Error ± 2% of the stated values. [c] IPA/$CHCl_3$ = 1/4, IPA = isopropanol.

These results prompted us to turn our attention to some laboratory-made NF membranes. First, a PDMS (polydimethylsiloxane) polymeric membrane was prepared. This membrane is stable in chlorinated solvents but due to extensive swelling in $CHCl_3$, the retention for the dendritic catalysts was low. In pure isopropanol, on the other hand, the PDMS membrane showed high retention for the dendritic catalysts **5**, **7** and **8** (Table 3). The rejection for compound **1** (M_W = 1063.6 Da), on the other hand, was only 50%.

To further increase the retention of the dendritic catalysts in $CHCl_3$ the PDMS membrane was modified via incorporation of ultrastable Y (USY) zeolite as inorganic filler.[25] This membrane showed a sufficient permeability for chloroform. By using the USY-modified PDMS membrane, a high retention of the G_1-dendron **5** (M_W = 2117 Da) was observed using pure $CHCl_3$ as the solvent (Table 3).

Recycling of porphyrin G_1-dendron 5 by solvent-resistant nanofiltration (SRNF): The preliminary NF experiments indicated that the USY-modified PDMS membrane shows high retention of porphyrin G_1-dendron **5** in pure chloroform as the solvent. The membrane was stable and showed sufficient permeability for $CHCl_3$. For recycling of **5**, a photooxidation reaction was first carried out using 1-methyl-1-cyclohexene (2 mmol) in $CHCl_3$ (2 mL) in the presence of G_1-dendron **5** (1 μmol porphyrin). At the end of the reaction, the mixture was diluted with $CHCl_3$ (5 mL) to allow filtration in a dead-end NF module (20°C, 30 bar N_2). The permeate was collected in a cooled flask (0°C) and was analyzed by UV-visible spectroscopy to determine the retention of the dendritic catalyst. At the end of the NF step, the retentate (2 mL) was collected, a new batch of 1-methyl-1-cyclohexene (2 mmol) was added and the mixture was transferred to the photooxidation cell where irradiation was continued. These photooxidation/nanofiltration steps were repeated several times. The conversion of 1-methyl-1-cyclohexene after each reaction step was determined by GC analysis and the leaching of G_1-catalyst **5** after the NF steps was analyzed by UV/Vis spectroscopy. Table 4 shows that the catalytic activity remains high after the first recycle (run 2). However, in the second and third recycle (runs 3 and 4), the conversion of 1-methyl-1-cyclohexene decreases significantly. The retention of the dendritic catalyst in the first two NF steps was determined to be around 95%.

UV-visible spectroscopic investigation of the catalyst solution after the fourth run revealed that only 10% of the original catalyst was still present in the reaction mixture.

A photodegradation experiment was carried out in the absence of 1-methyl-1-cyclohexene to account for the contribution of photodegradation to the total catalyst loss (degradation and leaching). A solution of G_1-dendron **5** in $CHCl_3$ was irradiated for 20 h at 0°C under an oxygen atmosphere. According to UV/Vis spectroscopy, only 25% of **5** remained in solution. The observed decrease in activity is therefore ascribed to the susceptibility of the porphyrin units to oxidative degradation and only to a lesser extent to leaching of the catalyst through the NF membrane.

Table 4. Reuse of G_1-dendron **5** in the photooxidation of 1-methyl-1-cyclohexene.[a]

Run	Conversion [%]	Selectivity [%]	HP 1 [%]	HP 2 [%]	HP 3 [%]	TON[b]
1	97.4	98.3	47.8	39.7	12.4	1948
2	96.0	91.1	46.3	41.3	12.4	1920
3	77.5	95.9	47.0	39.7	13.2	1550
4	63.6	97.2	44.2	41.4	14.4	1272

[a] Reaction conditions: 1 μmol porphyrin units, 2 mmol 1-methyl-1-cyclohexene, 2 mL $CHCl_3$, 0°C, *hν*, O_2, 5 h. [b] Turnover number based on porphyrin units.

Therefore, our current research efforts are directed towards the functionalization of the pyrimidine dendrimers with more oxidatively robust porphyrins (e.g. more sterically hindered or halogenated derivatives). On the other hand, the synthesis of porphyrin dendrimers with the porphyrin unit in the core and bulky groups at the periphery of the dendrimer might yield more stable photocatalysts.

Conclusion

In conclusion, porphyrin-functionalized pyrimidine dendrimers are active catalysts for the light-induced generation of singlet oxygen from ground-state oxygen. Although the dendritic pyrimidine supports showed high oxidative stability, the peripheral porphyrin units were prone to photodegradation. Recycling of these dendrimers was possible by nanofil-

tration technology. A PDMS membrane modified with zeolite USY particles showed high retention for the dendrimers and a high stability in $CHCl_3$ under oxidizing conditions. Moreover, the nanofiltration technique allows the separation of the hydroperoxide products from the catalyst under very mild conditions. From a safety viewpoint, this is an important issue since the most commonly used separation mode, distillation, often requires elevated temperatures, which may induce the explosive decomposition of the hydroperoxides.

Experimental Section

General methods: Solvents and starting materials were of reagent grade and were used without further purification. DMF was dried on molecular sieves 4 Å. A MPF-50 nanofiltration membrane (Koch Membrane Systems, Wilmington, MA, USA) with a molecular weight cut-off (MWCO) of 700 Dalton was used for the nanofiltration experiments. PDMS (RTV 615A + B) and adhesion promotor (SS 4155) were purchased from General Electric (USA). Component A is a pre-polymer containing vinyl groups. Component B contains hydrosilyl groups and acts as cross-linker. USY zeolite (CBV-780) with a Si/Al ratio of 20 and a crystal size between 0.4–0.8 μm was supplied by PQ Corporation. The zeolite was dried at 110 °C prior to use.

NMR spectra were acquired on a Bruker Avance 300 or a Bruker AMX 400 spectrometer and chemical shifts (δ) are reported in parts per million referenced to internal residual solvent protons (^{1}H) or the carbon signal of deuterated solvents (^{13}C). Mass spectrometry data were obtained with a Micromass Quattro II apparatus (electrospray ionization (ESI), solvent mixture: MeOH/CH_2Cl_2 + NH_4OAc). UV-visible spectra were recorded on a Perkin-Elmer Lambda 20 spectrometer. For GC analysis, a Hewlett Packard 5890 gas chromatograph equipped with a 0.32 mm i.d. by 50 m WCOT fused silica column coated with a Chrompack CP-Sil 5 CB stationary phase (1.2 μm d_f) was used. The instrument was equipped with a flame ionization detector and coupled to a HP 3396 integrator. Quantification of the reaction products was done by taking into account appropriate response factors. GC-MS analysis was performed on a Fisons GC 8000 Series gas chromatograph equipped with a 0.32 mm i.d. by 60 m WCOT fused silica column coated with a Varian CP-Sil 5 CB Low bleed/MS stationary phase (0.25 μm d_f). This GC was coupled to a Fisons MD 800 mass spectrometer.

Dendrimer synthesis

Preparation of porphyrin core 3: A solution of 4,6-dichloro-2-phenylpyrimidine-5-carbaldehyde (0.500 g, 1.976 mmol) and pyrrole (139 μL, 1.976 mmol) in CH_2Cl_2 (500 mL) was purged with Ar for 30 min, after which $BF_3{\cdot}OEt_2$ (200 μL, 1.62 mmol) was added and the solution was stirred at room temperature, under Ar and in the dark. After 2 h, *p*-chloranil (0.486 g, 1.976 mmol) was added and the mixture was heated at reflux for 1 h. The solvent was evaporated and the product was purified by column chromatography (silica gel, petroleum ether/CH_2Cl_2 1:1) to yield the octafunctionalized porphyrin core **3** (121 mg, 20 %). MS (ESI): *m*/*z*: 1203.0 $[M+H]^+$; IR (KBr): ν_{max} = 3425.2, 2980.3, 2337.3, 1724.1, 1591.6, 1554.9, 1420.5, 1370.0, 1293.3, 1240.5, 1110.0, 1060.7, 1025.9, 801.5, 759.3 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 281.3 (4.841), 291.8 (4.861), 424.8 (5.374), 517.4 (4.120), 546.9 (3.362), 593.0 (3.634), 655.0 nm (3.093).

Preparation of G_1-dendron 5 ($R = CH_3$): Peripheral porphyrin **1** (53.4 mg, 55.2 μmol) and pyrimidine monomer **4** (6.2 mg, 24.3 μmol) were dissolved in CH_3CN (5 mL). K_2CO_3 (24.8 mg, 179.4 μmol) was added and the mixture was heated at reflux for 3 d. The mixture was evaporated to dryness and the residue was dissolved in CH_2Cl_2 (25 mL), washed with water (3 × 25 mL) and the organic phase was dried over $MgSO_4$. After purification by column chromatography (silica gel, petroleum ether/EtOAc 9:1), G_1-dendron **5** was obtained (48 mg, 93 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.00 (m, 8H), 8.93 (s, 8H), 8.49 (d, ^3J = 8.7 Hz, 2H), 8.38 (d, ^3J = 8.4 Hz, 4H), 8.13 (d, ^4J = 1.5 Hz, 8H), 8.10 (d, ^4J = 1.5 Hz, 4H), 7.83 (t, ^4J = 1.5 Hz, 4H), 7.82 (t, ^4J = 1.5 Hz, 2H), 7.72 (d, ^3J = 8.4 Hz, 4H), 7.06 (d, ^3J = 8.7 Hz, 2H), 6.67 (s, 1H), 3.86 (s, 3H), 1.56 (s, 72H), 1.54 (s, 36H), −2.61 ppm (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.2, 164.3, 162.5, 152.9, 148.8, 148.7, 141.4, 141.3, 139.9, 135.5, 131.4, 130.5, 129.8, 129.7, 129.6, 121.7, 121.5, 121.1, 120.0, 118.6, 114.0, 89.5, 55.4, 35.1, 31.8 ppm; MS (ESI): *m*/*z*: 1058.8 $[M+H]^{2+}$, 2117.4 $[M+H]^+$; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 294.9 (4.669), 423.2 (5.907), 517.4 (4.479), 552.9 (4.231), 592.0m (3.977), 647.7 nm (3.949).

Preparation of G_1-dendron 6 ($R = H$): An excess of BBr_3 (1 M in CH_2Cl_2, 120 μL) was added at −78 °C to a solution of the protected G_1-dendron **5** (50 mg, 23.6 μmol) in CH_2Cl_2 (10 mL), under dry conditions and then the mixture was placed in a freezer (−18 °C) for 3 d. Ice water (25 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried over $MgSO_4$ and evaporated in vacuum. The product was purified by column chromatography (silica gel, petroleum ether/EtOAc 9:1) and was obtained as a dark purple solid (40 mg, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.97 (m, 8H), 8.92 (s, 8H), 8.44 (d, ^3J = 8.6 Hz, 2H), 8.37 (d, ^3J = 8.4 Hz, 4H), 8.12 (d, ^4J = 1.8 Hz, 8H), 8.09 (d, ^4J = 1.8 Hz, 4H), 7.82 (t, ^4J = 1.8 Hz, 4H), 7.80 (t, ^4J = 1.8 Hz, 2H), 7.71 (d, ^3J = 8.4 Hz, 4H), 6.96 (d, ^3J = 8.6 Hz, 2H), 6.66 (s, 1H), 1.55 (s, 72H), 1.53 (s, 36H), −2.62 ppm (br s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.2, 164.3, 158.7, 152.9, 148.8, 148.7, 141.4, 141.3, 139.9, 135.5, 131.3 (br), 130.7, 129.9, 129.7, 121.7, 121.5, 121.1, 120.0, 118.5, 115.5, 89.5, 35.1, 35.0, 31.8 ppm; MS (ESI): *m*/*z*: 1052.2 $[M+H]^{2+}$, 2103.5 $[M+H]^+$.

Preparation of G_2-dendron 7 ($R = CH_3$): G_1-dendron **6** (29 mg, 13.9 μmol) and pyrimidine monomer **4** (1.1 mg, 4.31 μmol) were dissolved in CH_3CN/DMF (5+5 mL). K_2CO_3 (3.3 mg, 23.7 μmol) was added and the mixture was heated at reflux for 4 d. The mixture was evaporated to dryness and the residue was dissolved in CH_2Cl_2 (25 mL), washed with water (3 × 25 mL) and the organic phase was dried over $MgSO_4$. After purification by column chromatography (silica gel, petroleum ether/EtOAc 9:1), G_2-dendron **7** was obtained (13 mg, 70 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.95 (m, 32H), 8.67 (d, ^3J = 8.8 Hz, 4H), 8.39 (d, ^3J = 8.8 Hz, 8H), 8.08 (m, 26H), 7.75 (m, 20H), 7.44 (d, ^3J = 8.8 Hz, 4H), 6.77 (d, ^3J = 8.8 Hz, 2H), 6.71 (s, 2H), 6.27 (s, 1H), 3.56 (s, 3H), 1.52 (s, 72H), 1.50 (s, 144H), −2.66 ppm (br s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.3, 171.3, 164.1, 162.1, 155.5, 152.7, 148.7, 148.6, 141.2, 141.1, 140.1, 135.7, 133.9, 132.0–130.0, 130.9, 130.2, 129.9, 129.7, 129.0, 128.8, 121.8, 121.7, 121.5, 121.0, 119.8, 118.3, 113.6, 90.0, 89.4, 55.1, 35.0, 31.7 ppm; MS (ESI): *m*/*z*: 879.2 $[M+H]^{5+}$, 1098.3 $[M+H]^{4+}$, 1462.9 $[M+H]^{3+}$, 2194.4 $[M+H]^{2+}$; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 286.9 (5.134), 421.0 (6.308), 517.2 (4.914), 552.9 (4.673), 592.4 (4.376), 647.2 nm (4.376).

Preparation of nonaporphyrin 8: Octafunctional porphyrin **3** (5.3 mg, 4.41 μmol) and AB_3-porphyrin **1** (51.2 mg, 52.9 μmol) were dissolved in DMF (5 mL). K_2CO_3 (47 mg, 337 μmol) was added and the mixture was heated at 70 °C for 96 h. The mixture was evaporated to dryness and the residue was dissolved in CH_2Cl_2 (25 mL), washed with water (3 × 25 mL) and the organic phase was dried over $MgSO_4$. After purification by column chromatography (silica gel, petroleum ether/CH_2Cl_2 1:1), nonaporphyrin **8** was obtained (22 mg, 58 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.05 (s, 8H), 9.04–8.78 (m, 72H), 8.33 (d, ^3J = 8.4 Hz, 16H), 8.02 (d, ^4J = 1.5 Hz, 16H), 7.93 (d, ^4J = 1.5 Hz, 32H), 7.91 (d, ^3J = 8.4 Hz, 16H), 7.75 (s, 8H), 7.70 (t, ^3J = 7.0 Hz, 8H), 7.59 (t, ^3J = 7.0 Hz, 4H), 7.48 (s, 16H), 1.48 (s, 288H), 1.43 (s, 144H), −1.40 (br s, 2H), −2.73 ppm (br s, 16H); MS (ESI): *m*/*z*: 1442.4 $[M+H]^{6+}$, 1730.3 $[M+H]^{5+}$, 2162.8 $[M+H]^{4+}$; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 420.7 (6.484), 518.2 (5.053), 552.1 (4.952), 592.1 (4.628), 647.9 nm (4.464).

Membrane synthesis

Supports: A polyacrylonitrile (PAN) support was synthesized starting from a solution of 10 wt % PAN (Scientific Polymer Products, New York, USA, product number 134) in dimethylsulfoxide. The polymer solution was cast on a polypropylene–polyethylene (PP-PE) film (FO 2471, Viledon). The PAN/PP-PE support was immersed in deionized water.

The polyimide (PI, Matrimid 5218, Huntsman) support was synthesized starting from a 15 wt % PI solution in *N*-methylpyrrolidone/tetrahydrofuran 3:1 containing 2 wt % water. The polymer solution was coated on a

PP-PE film and immersed in deionized water. Prior to further use, the water was exchanged with isopropanol.

PDMS membrane: Thin-film composite PDMS membranes were prepared as follows. A 10 wt % PDMS solution (RTV 615A and B, pre-polymer and cross-linker in a 10:1 ratio) in hexane was pre-polymerized for 0.5 h at 60 °C, followed by cooling for 0.5 h to room temperature. A PAN/polyester support was impregnated with distilled water and fixed on a glass plate with the smallest pores directed to the top. The water was used to fill the pores and to prevent intrusion of the polymer solution into the support layer. The excess water was wiped off with a humid tissue. Before casting the solution on the support, the glass plate was tilted over an angle of 60° to allow the polymer solution to flow down over the support. After 5 min, the glass plate was turned upside down and the coating procedure was repeated. Three coatings were applied. After evaporation of the solvent, the membrane was placed in a vacuum oven at 100 °C to complete the cross-linking and to evaporate all traces of solvent.

USY-modified PDMS membrane:[25] The USY-modified PDMS membrane was synthesized as follows. First, USY zeolite (6 g, CBV-780, dried overnight at 110 °C) was dispersed in hexane (80 g). After 1 h ultrasonic treatment, cross-linker (1.9 g, RTV 615B) was added to the zeolite dispersion and this mixture was stirred for 2 h at 40 °C. Finally, pre-polymer (12.1 g, RTV 615A) was added and the mixture was stirred for another hour at 60 °C. The PAN/polyester support was fixed on a glass plate, saturated with water and treated with the adhesion promoter (SS 4155), before being tilted over an angle of 60°. The polymer solution was then poured over the PAN/polyester support. After evaporation of hexane, cross-linking was completed in an oven at 100 °C.

Retention measurements

Nanofiltration experiments were carried out in a 60 mL stainless-steel dead-end filtration cell with a membrane surface area of 12.5 cm^2 (Figure 2). The filtrations were performed at 20 °C and the cell was pressurized to 30 bar with N_2. Permeate samples were collected in small flasks and were analyzed using UV-visible spectroscopy.

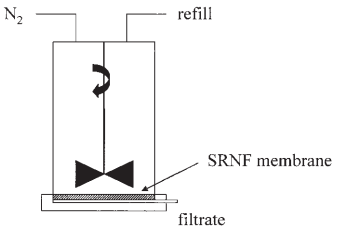


Figure 2. Dead-end nanofiltration module.

The rejection of the membranes for the different dendrimers was characterized by the rejection coefficient R which is a measure for the ability of the membrane to retain a certain solute. R is defined as: $R\,(\%) = 100\times(1-c_p/c_f)$, with c_f and c_p the concentration of the solute in the feed (f) and the permeate (p), respectively.

Catalytic experiments

CAUTION: Hydroperoxides are potentially explosive and should be handled with care!

Standard activity test: For all dendrimers and dendrons, a standard activity test was carried out by using 1-methyl-1-cyclohexene as a typical olefin substrate. Therefore, a 5 mL cylindrical flask was charged with 1-methyl-1-cyclohexene (3 mmol), $CHCl_3$ (3 mL) and an amount of dendrimer corresponding to 0.3 μmol porphyrin units. The solution was stirred under an oxygen atmosphere at 0 °C. The reaction mixture was irradiated with a Schott KL-1500 fiberoptics cold light source. Samples were withdrawn for GC analysis after 60, 180, 480 and 1440 min. Prior to GC analysis, the initially formed hydroperoxide products were reduced to the corresponding alcohols by using excess trimethylphosphine, $(CH_3)_3P$ (1 M), in tetrahydrofuran. This reduction step is fast and quantitative. GC analysis indicated that the three allylic alcohols of 1-methyl-1-cyclohexene were the sole products, and unless stated otherwise, other probable by-products, such as other hydroperoxide isomers, were not formed.

Photooxidation of various olefins catalyzed by G_1-dendron 5: The general procedure for the peroxidation of olefinic compounds was as follows. A 5 mL cylindrical flask was charged with the appropriate olefin (1.5 mmol), $CHCl_3$ (1.5 mL) and an amount of G_1-dendron **5** corresponding to 0.15 μmol porphyrin units. The solution was stirred under an oxygen atmosphere at 0 °C. The reaction mixture was irradiated with a Schott KL-1500 fiberoptics cold light source. The reaction progress was followed by GC analysis of the crude reaction mixture after reduction with excess $(CH_3)_3P$.

Products were identified by GC-MS, ^1H and ^{13}C NMR, and by comparison of their GC retention times with those of authentic allylic hydroperoxides or allylic alcohols prepared by photochemical oxidation in the presence of *meso*-tetraphenylporphyrin as photosensitizer.

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