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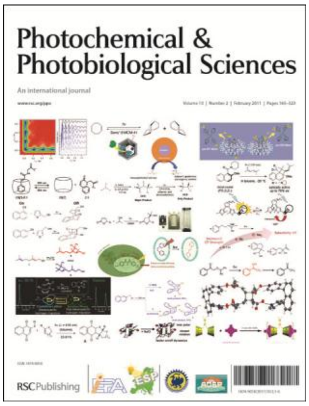

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PAPER

Sweet chiral porphyrins as singlet oxygen sensitizers for asymmetric Type II photooxygenation†

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Carbohydrate-decorated *meso*-tetraarylporphyrins **P-G** and **P-C** were synthesized *via* Lewis-acid catalyzed condensation of acetylated carbohydrate-substituted benzaldehydes and pyrrole. Their efficiency of singlet oxygen production was compared with the corresponding non-substituted porphyrin. The oxidation of the spin trap molecule TEMP (2,2,6,6-tetramethyl-4-piperidone) by singlet oxygen to TEMPO was measured by ESR spectroscopy, showing higher reaction rates for the sugar porphyrins. These results were corroborate by laser flash photolysis measurements that resulted in higher triplet lifetimes of glucosyl- and cellobiosyl porphyrins in comparison with tetrakis(4-hydroxyphenyl)porphyrin. Low ee was detected in the photooxygenation of ethyl tiglate.

Introduction

The lowest electronically excited singlet state of oxygen ($^1O_2$) is a versatile reagent in organic oxidation chemistry. This molecule can be generated by numerous methods, photochemical as well as thermal, and thus singlet oxygen chemistry is often not considered as a pure photochemical topic. In order to generate singlet oxygen in solution, energy transfer sensitization from triplet dye molecules is the most convenient method. Apparently, singlet oxygen is an electronically excited molecule and thus decays to its ground state by radiationless or radiative processes in competition with chemical reactions which makes the use of this oxygenation reagent often cumbersome because of the limited lifetime of $^1O_2$, especially in protic solvents.[1–3] Concerning the "atom economy" of photooxygenation, the process where both oxygen atoms are transferred into the substrate, 100% from molecular oxygen is an obvious advantage over all other oxidants, *e.g.* hydrogen peroxide.[4] The primary peroxidic products from this "Type II photooxygenation" can be reduced to numerous polyoxygenated derivatives, *e.g.* to epoxyalcohols from allylic hydroperoxides by means of titanium(IV)-catalysis.[5]

Taking into account the relatively low singlet oxygen lifetimes in protic and especially aqueous (biological or non-biological)[6] solution phase in the region of a few μs, as well as the high diffusion rate of singlet oxygen, two major problems for modern synthetic applications are apparent: (a) the reactivity problem of substrates with low nucleophilicity and low solubility in "typical" singlet oxygen solvents such as chlorinated or fluorinated hydrocarbons (where singlet oxygen lifetimes can reach the 100 ms time regime);[7] (b) the selectivity problem, especially non substrate-induced enantioselectivity of alkenes in singlet oxygen ene reactions. Two possible solutions are the use of non-traditional chiral reaction environments and the use of chiral singlet oxygen sensitizers.

In the last decade, the area of polymer-supported organic reactions and polymer-supported catalysts has impressively increased. Photooxygenation in solution using insoluble polymer-bound sensitizers facilitates the problem of dye recovery. A commercial polymer-bound sensitizer is the polystyrene-bound Rose Bengal developed by Schaap and Neckers,[8] followed by a series of immobilized sensitizers, *e.g.* the immobilized fullerene C_{60},[9] ionic porphyrins immobilized on cationically functionalized polystyrene,[10] tetrakis-(4-hydroxyphenyl)porphyrin supported to polyethylene glycol,[11] polystyrene-bound benzophenones,[12] immobilized pyrylium salts on Merrifield resins,[13] sensitizer-incorporated Nafion membranes,[14] or ion-exchange resins ionically bound to photosensitizers.[15] Other heterogeneous catalysts using clay,[16] silica,[17] and zeolites[18,19] as support materials were also recently developed. From the viewpoint of solution photochemistry, the use of non-polar solvents (especially chlorinated hydrocarbons) enhances dye oxidation and bleeding if long reaction times are needed, which decreases the singlet oxygen quantum yield and hence the reaction efficiency. On the other hand, photooxygenation reactions carried out in aqueous solutions are not favored due to low solubility of most organic substrates, the low singlet oxygen lifetime, and hydrophobic aggregations of nonpolar sensitizers (leading to self quenching) which as a consequence reduces the triplet lifetime.[20] We have recently reported a solution to circumvent some of the mentioned technical problems: under solvent-free reaction conditions, in which the substrates are embedded in a porphyrin-loaded polystyrene matrix, irradiation and product isolation accompanied by complete

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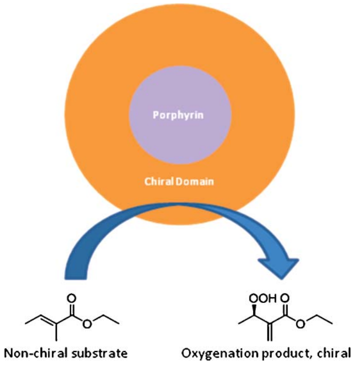
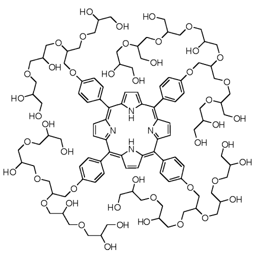
sensitizer separation by extraction with ethanol offers a shortcut to *green* photo-oxygenation reactions.[21]

In contrast to the high diastereoselectivity control of the singlet oxygen ene reaction with chiral allylic alcohols,[22] enantioselective reactions are still rare. Several attempts to control the enantioselectivity were reported. The use of cyclodextrins covalently bound to porphyrin sensitizers in the photooxygenation of linoleic acid resulted in low ee values (10–20%).[23,24] The photooxygenation of 2-methyl-4-phenyl-2-butene in NaY zeolite in presence of (+)-ephedrine as chiral inductor also resulted in 15% ee hydroperoxide formation.[25] Recently, Córdova *et al.* published a fundamental report on the amino acid-catalyzed asymmetric incorporation of molecular oxygen into the α position of a series of aldehydes and ketones.[26,27]

The idea behind the concept of triplet dye sensitization with singlet oxygenation in the vicinity of the sensitizer is depicted in Scheme 1: in order to compensate the fast diffusion of singlet oxygen from the area of the collision-induced energy transfer, a relatively unpolar large core-shell structure is necessary that allows substrate molecule binding as well as higher singlet oxygen lifetimes that in the polar protic solvent environments. In a first approach, the chiral modification of porphyrins by anionic polymerisation with glycidol led to remarkable changes of diastereoselectivity in the photooxygenation of allylic alcohol mesitylol (Scheme 2).[28]



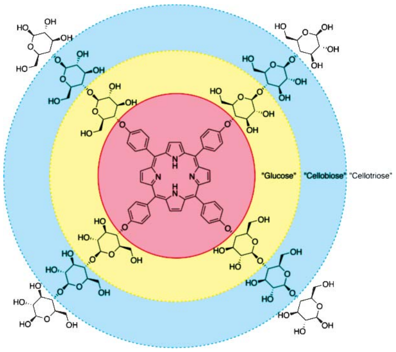
Scheme 1 Core-shell structured sensitizer concept.



Scheme 2 Core-shell structured polyglycerol porphyrin.[27]

Core-shell structured concepts of photooxygenations are based on a sensitizing core that produces the reactant singlet oxygen which diffuses into a chiral environment where asymmetric induction is expected to occur. Although this catalysis concept has been evaluated in few reactions already, mechanistic and photophysical properties of core-shell triplet sensitizers are still rare. For efficient (enantioselective) steering effects, photo-oxygenation in the chiral shell needs to be favoured in comparison with the achiral reaction medium. This might result from a situation where the singlet oxygen lifetime is considerably higher in the chiral shell than in the surrounding solvent.

In order to study the dependence of singlet oxygen generation on the shell size, singlet oxygen quantum yields of carbohydrate-substituted porphyrins were compared to those of a non-functionalized porphyrin in methanol solution. Several carbohydrate-containing shell structures were designed that could build up a series of spatially increasing structures for singlet oxygen diffusion (Scheme 3). The substitution of tetraphenylporphyrin derivatives with mono- and disaccharides leads to core-shell systems with similar properties as polyglycerol porphyrins, but with exactly defined stereogenic centres and molecular weights. Sugars are cheap and widely available from the chiral pool, exhibiting stereochemically defined hydroxy functions. Their incorporation as porphyrin substituents was described by Maillard and coworkers.[29,30] In order to compare shell sizes only and not configurational differences, glucose and cellobiose substituents were synthesized in this study. The TEMPO-formation was measured by ESR spectroscopy and compared for three core-shell systems of different shell sizes. Sensitizers used for this technique were glycosyl- and cellobiosyl-substituted porphyrins and the *meso*-tetrakis-(4-hydroxyphenyl)-porphyrin (**4HPP**).

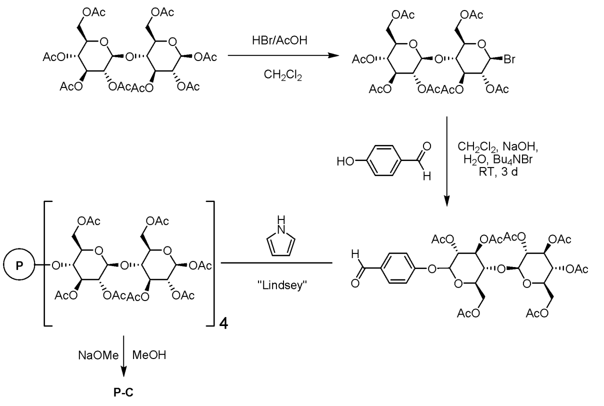


Scheme 3 Core-shell structured polyglycerol porphyrin.

The detection of singlet oxygen by the spin trap 2,2,6,6-tetramethyl-4-piperidone (TEMP) is a technique that uses ESR spectroscopy detecting the oxidized radical 2,2,6,6-tetramethyl-4-piperidone-*N*-oxyl (TEMPO).[32] Integrals of the triplet signal of TEMPO correlate to the amount of TEMP oxidized by singlet oxygen and are used in order to compare quantum yields of singlet oxygen generation by plotting the time-dependent TEMPO-formation.

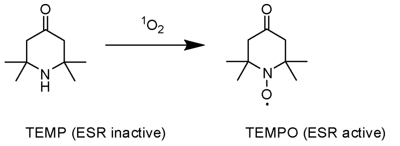
Results and discussion

The method reported by Maillard *et al.* yielded small amounts of glycosylated porphyrins. The linear synthesis started with bromination of per-acetylated sugars at the anomeric center under phase transfer conditions yielding the corresponding per-acetylated, carbohydrate-conjugated benzaldehydes in moderate yields of 30–75%. Their subsequent reaction with pyrrole and Lewis acid gave low to moderate yields of protected sugar porphyrins, catalyzed by the "Lindsey method" with Lewis acid boron trifluoride etherate. Deprotection of the acetylated sugar porphyrins was achieved with full conversion by addition of sodium methanolate to dry methanol solutions, giving highly polar porphyrins **P-G**[29,31] (glucose-substituted porphyrin) and **P-C** (cellobiose-substituted porphyrin) that are unsoluble in most organic solvents (Scheme 4). For comparison, the synthetic precursor, unfunctionalized **4HPP** was used.

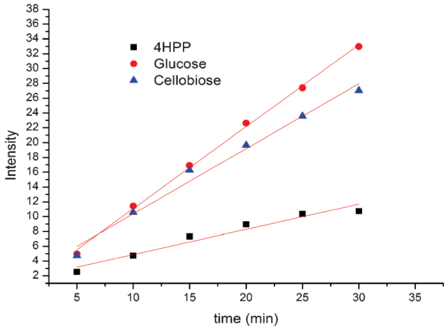


Scheme 4 Synthesis of the *meso*-tetraphenyl porphyrin **P-C**.

A methanol solution of TEMP was added to a methanol solution of the corresponding porphyrin and irradiated with a halogen lamp under exactly identical conditions. The intensity of the nitroxyl radical ESR signal that formed upon singlet oxygen formation (Scheme 5) was determined every five minutes and plotted against the time. There was no dye bleaching observable over the whole irradiation time. Scheme 6 shows that TEMPO (singlet oxygen) formation for 4-hydroxyphenylporphyrin (**4HPP**) in methanol is slower than for the sugar porphyrins, although the large sugar substituent cellobiose does not exhibit the highest values.



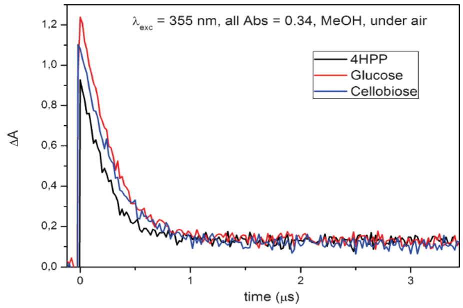
Scheme 5 Oxidation of 2,2,6,6-tetramethyl-4-piperidone (TEMP) to 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) by singlet oxygen.



Scheme 6 ESR measurements of TEMPO formation for **4HPP** and the porphyrins **P-G** (glucose) and **P-C** (cellobiose).

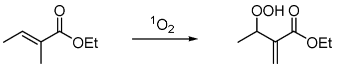
Spin trapping of TEMP is an indirect method and does not necessarily measure the quantum yields of singlet oxygen production of the porphyrin sensitizer. The observation of a more efficient TEMPO conversion still needs to be interpreted, as these results could either point at a higher lifetime of singlet oxygen in the sugar shells, leading to a higher effective concentration of reactive oxygen in the reaction with TEMP; a second possible mechanism would be the higher efficiency of sugar porphyrins reaching their excited triplet state compared to the non-substituted porphyrin. A higher concentration of triplet state porphyrin also leads to a higher concentration of singlet oxygen and thus a faster conversion. In order to differentiate between these two mechanisms, the triplet state formation of porphyrins was measured by laser flash photolysis.

The laser flash photolysis experiments (Scheme 7) under air showed the same tendencies as the spin trapping with TEMP. Sugar porphyrins exhibited a 10–20% higher triplet state formation upon 308 nm laser excitation than non-substituted 4-HPP. Although the sugar shell of glycoconjugated porphyrin has the smaller substituent, its triplet formation exceeded cellobiosyl porphyrin by 9%. The triplet lifetimes that were determined by LFP from first order exponential decay for the three sensitizers in this report were: 0.24, 0.28, and 0.30 µs for 4HPP, P-G, and P-C, respectively, and are in good agreement with the reference value of 0.32 µs for tetraphenylporphyrin.[33]



Scheme 7 Triplet decay from laser flash photolyses of **4HPP** and the porphyrins **P-G** (glucose) and **P-C** (cellobiose).

With these chiral carbohydrate-decorated porphyrins we performed preliminary photooxygenations experiments. The ene reaction of ethyl tiglate was used as the standard procedure and the enantiomeric excesses determined after reduction of the hydroperoxide by chiral HPLC (Scheme 8). The reactions were performed in polystyrene matrices,[21] with the porphyrins 4HPP, P-G, and P-C embedded (0.5 mol%). From the substrate conversion under identical reaction conditions, a profile of the sensitizer activity resulted that was in good agreement with the results of the TEMP oxidation P-G ~ P-C > 4HPP. At room temperature, we could not find any enantioselection, however, at −5 °C for the system P-G in polystyrene, 1% ee was determined. This result was also obtained in methanol/D_2O solution mixture at −10 °C. These experiments are currently followed with core-shell sensitizer systems with more extended carbohydrate shells.



Scheme 8 Singlet oxygen ene reaction with ethyltiglate.

Experimental

Materials

Chemicals were purchased from Sigma Aldrich and used without further purification. Solvents for ESR and laser measurements were of HPLC grade and purchased from the Sigma Aldrich company.

Porphyrin syntheses

General procedure for the synthesis of sugar-substituted benzaldehydes. A solution of 4-hydroxybenzaldehyde (42 mmol, 1.5 eq.) in 50 ml of methylene chloride was stirred at room temperature with 70 ml of a 5% aqueous solution of sodium hydroxide and tetrabutylammonium bromide (7 mmol, 0.25 eq). A solution of the acyl-protected α-D-carbohydrate bromide (28 mmol, 1.0 eq.) in 20 ml of methylene chloride was subsequently added. The solution was stirred for 3 days. After separation, the organic phase was washed twice with 5% aqueous sodium hydroxide solution and water, then dried over sodium sulfate. The solvent was evaporated after filtration, yielding slightly yellowish solids.

General procedure for the synthesis of protected sugar-substituted porphyrins. 2.2 mg of pyrrole (1.0 eq.) and 2.2 mmol of the acyl-protected α-D-carbohydrate benzaldehyde (1.0 eq.) in 45 ml of methylene chloride were added to 200 ml of a mixture of methylene chloride containing 0.75% ethanol; the solution was purged with argon for 10 min. A 0.5 M boron trifluoride-etherate solution (100 µl) in 2 ml of methylene chloride was added. The mixture was stirred at room temperature for 16 h, subsequently 0.4 g of *p*-chloranil (1.63 mmol, 0.74 eq.) was added and the mixture was refluxed for 1 h. The solvent was evaporated and the resulting black oil was purified by flash column chromatography.

General procedure for the deprotection of acetylated sugar-substituted porphyrins. The protected porphyrin (0.045 mmol) was solved in 10 ml of dry methanol and 100 µl of a solution of sodium methanolate in dry methanol (0.1 N) was added. The mixture was stirred for 2 h at room temperature, then the solvent was evaporated and the product was purified by Sephadex LH20 column chromatography.

4-(2,3,4,6-Tetraacetyl-β-D-glucopyranosyl)benzaldehyde: ^{1}H-NMR: (300 MHz, $CDCl_3$), δ (ppm) = 9.93 (s, 1H, CHO), 7.84 (d, 2H, *o*-phenyl, $J = 8$ Hz), 7.10 (d, 2H, *m*-phenyl, $J = 8$ Hz), 5.26 (m, 5H, "ose"), 4.21 (m, 2H, "ose"), 2.05 (s, 12H, $COOCH_3$).

5,10,15,20-Tetrakis[4-(2,3,4,6-tetracetyl-β-D-glucosyl)phenyl]-porphyrin:[29] ^{1}H-NMR: (300 MHz, $CDCl_3$), δ (ppm) = 8.83 (s, 1H, pyrr.), 8.10 (d, 2H, *o*-phenyl, $J = 8$ Hz), 7.35 (d, 2H, *m*-phenyl, $J = 8$ Hz), 5.45 (m, 12H, C-1′, C-2′, C-3′, "ose"), 5.29 (m, 4H, C-4′, "ose"), 4.40 (m, 8H, C-6′, "ose"), 4.03 (m, 4H, C-5′, "ose"), 2.20 (s, 12H, acetyl), 2.12–1.98 (m, 36H, $COOCH_3$), −2.84 (s, 2H, NH).

5,10,15,20-Tetrakis(4-β-D-glucosylphenyl)porphyrin (**P-G**):[29] ^{1}H-NMR: (300 MHz, $CDCl_3$), δ (ppm) = 9.01 (s, 8H, pyrr), 8.25 (d, 8H, *ortho*, $J = 8$ Hz), 7.78 (d, 8H, *meta*, $J = 8$ Hz), 7.94 broad (4H, OH "ose"), 7.48 broad (4H, OH "ose"), 6.87 broad (4H, OH "ose"), 6.00 (d, 4H, C1 "ose", $J = 8$ Hz), 4.78–4.52 (m, 8H, C6 "ose"), 4.50 (m, 4H, C2 "ose", 4H, C3 "ose", 4H, C4 "ose"), 4.31 (m, 4H, C6 "ose"), −2.39 (s, 2H, NH).

4-(2,3,4,6-2′,3′,6′-Heptaacetyl-β-D-cellobiosyl)benzaldehyde: ^{1}H-NMR: (300 MHz, $CDCl_3$), δ (ppm) = 9.89 (s, 1H, CHO), 7.83 (d, 2H, *o*-phenyl, $J = 8$ Hz), 7. 06 (d, 2H, *m*-phenyl, $J = 8$ Hz), 5. 65 (d, 1H, "ose"), 5.40–4.97 (m, 7H "ose"), 4.58–3.78 (m, 7H, "ose"), 2.13–1.93 (m, 21H, $COOCH_3$).

5,10,15,20-Tetrakis[4-(2,3,4,6-2′,3′,6′-heptaacety-D-cellobiosyl)-phenyl]porphyrin: ^{1}H-NMR: (300 MHz, $CDCl_3$), δ (ppm) = 8.84 (s, 8H, pyrr), 8.13 (d, 8H, *ortho*, $J = 8$ Hz), 7.37 (d, 8H, *meta*, $J = 8$ Hz), 5.41 (m, 4H, C1 "ose", $J = 8$ Hz), 5.23–5.09 (m, 8H, C6 "ose"), 4.68–4.41 (m, 4H, C2 "ose"), 4.30–4.24 (m, 4H, C3 "ose"), 4.13–4.09 (4H, C4 "ose"), 3.75 (m, 4H, C6 "ose"), 2.21–2.00 (m, 21H, $COOCH_3$), −2.83 (s, 2H, NH).

5,10,15,20-Tetrakis(D-cellobiosyl-phenyl)porphyrine (**P-C**): ^{1}H-NMR: (300 MHz, pyridine-d_6), δ (ppm) = 9.01 (s, 8H, pyrr), 8.25 (d, 8H, *ortho*, $J = 8$ Hz), 7.78 (d, 8H, *meta*, $J = 8$ Hz), 7.94 broad (4H, OH "ose"), 7.48 broad (4H, OH "ose"), 6.87 broad (4H, OH "ose"), 6.00 (m, 4H, C1 "ose", $J = 8$ Hz), 4.78–4.52 (m, 8H, C6 "ose"), 4.50 (m, 4H, C2 "ose", 4H, C3 "ose", 4H, C4 "ose"), 4.31 (m, 4H, C6 "ose"), 2.39 (s, 2H, NH).

Spin trapping experiments

Spin trapping measurements were performed on a Bruker EMX 10/12 ESR spectrometer. 10 mM methanol solutions of TEMP were adjusted to an absorption of 0.3 at 300 nm with the corresponding porphyrins and irradiated with a halogen lamp in a flat cell under exactly identical conditions. The integral of the triplet ESR signal that formed upon singlet oxygen formation was recorded every five minutes and plotted against the time. No dye bleaching was observed over the whole irradiation time.

Laser flash photolysis

Methanol stock solutions of three sugar porphyrins were adjusted to an absorption of 0.34 in a standard cuvette. Samples were measured with a 308 nm laser setup and the relative absorption was plotted against time. Two series of measurement were performed, first under standard photooxidation conditions (saturated with air), then under argon atmosphere in order to avoid potential interference by molecular oxygen.

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