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Straightforward Synthesis of a Fluorous Tetraarylporphyrin: an Efficient and Recyclable Sensitizer for Photooxygenation Reactions

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Dedicated to Professor Guy Ourisson on the occasion of his 80th birthday.

Abstract: A fluorous tetraarylporphyrin has been prepared in a single reaction step starting from commercially available 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin [TPP(OH)$_4$]. The new compound was successfully employed as a sensitizer in photooxygenation reactions carried out under homogeneous conditions, showing activity comparable to the standard 5,10,15,20-tetraphenylporphyrin (TPP) sensitizer. Photooxygenation reactions were also investigated under fluorous biphasic conditions, yielding somewhat different product distributions. Because of its fluorous nature, the new porphyrin could be easily removed from the homogeneous mixture by liquid-liquid or solid phase extraction. In the case of fluorous biphasic reactions, the fluorous sensitizer could be recovered by simple phase separation and then reused, maintaining its efficiency at least upon five subsequent runs.

Keywords: cycloaddition; diastereoselectivity; photooxygenation; porphyrin; singlet oxygen

Introduction

Singlet oxygen ($^1O_2$) is an extremely reactive molecule which has found application in the synthesis of a number of organic compounds,[1] and also in medicine for the degradation of DNA in cancer cells.[2] This relatively short-lived reagent can be generated by the reaction of hydrogen peroxide with hypochlorite,[3] retro-Diels–Alder reaction of anthranyl endoperoxides,[4] decomposition of ozonides of phosphites,[5] electrodeless discharge in gaseous oxygen,[6] and photosensitization of ground-state triplet oxygen,[7] the most commonly used photosensitizer being methylene blue,[8] rose bengal,[9] and *meso*-tetraarylporphyrins.[10] The latter are capable of producing copious yields of singlet oxygen and both their stability under photooxygenation reaction conditions and their efficiency can be enhanced by introducing proper substituents at the phenyl rings.[11]

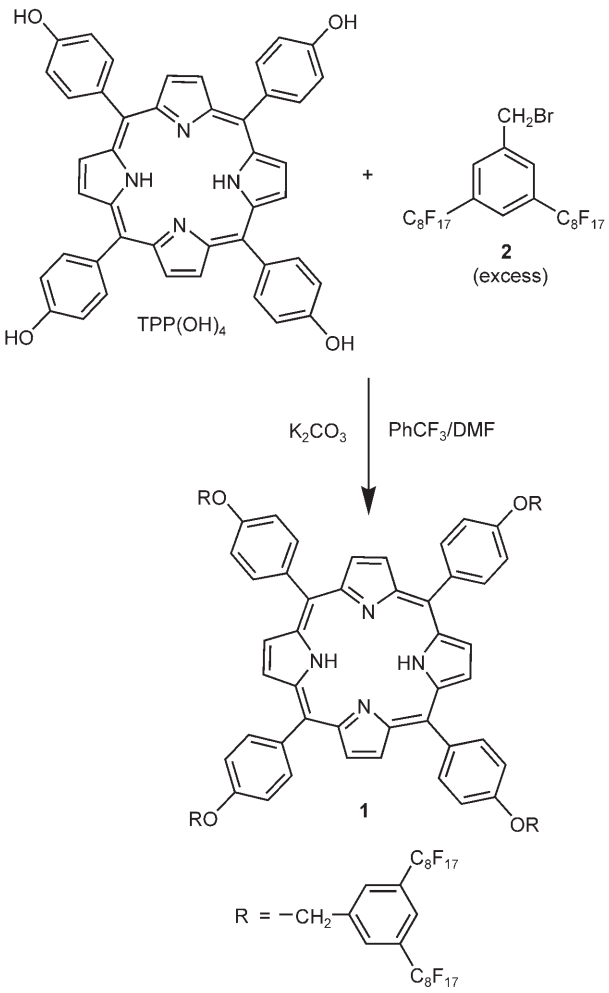
In contrast with other methods, dye-sensitized photooxygenations needs low energy irradiation and does not generate by-products in stoichiometric amounts. Nevertheless, the use of a sensitizer, even on a catalytic scale, does not set aside purification issues. Indeed, the dye and/or its decomposition derivatives can contaminate reaction products and need to be removed, usually with considerable effort. To solve this problem, immobilization of homogeneous dyes by means of insoluble organic or inorganic polymers has been widely investigated.[12] Early work focused on rose bengal,[13] and a polystyrene-supported version of this sensitizer has been commercialized for several years. More recently, alternative strategies have been disclosed, relying on the use of soluble dyes that can be easily separated and recovered because of their peculiar phase behavior. For instance, we have devised a highly active singlet oxygen generating system based on a poly(ethylene glycol)-supported tetraarylporphyrin.[14] This soluble dye precipitates out from homogeneous reaction mixtures upon addition of Et_2O and can be easily removed by simple filtration, thus allowing its recycling and greatly simplifying the isolation of the reaction products.

The phase behavior of a sensitizer can be also modified by introducing highly fluorinated domains in the molecule, thus enhancing its affinity for perfluoro-

carbons and related compounds and decreasing its solubility in organic solvents. Such a concept was demonstrated by DiMagno and co-workers,[15] who used a porphyrin bearing four perfluoroalkyl substituents in the *meso*-positions (a "fluorous" porphyrin) as a stable and highly active sensitizer in the fluorous biphasic (FB) photooxygenation of cyclohexene and allylic alcohols.[16] After completion of the reaction the two liquid layers were separated to give an organic phase containing the products and a recyclable fluorous phase containing the sensitizer. Despite its merits, this remains the only example of a fluorous singlet oxygen generating system reported so far. Further progress in this field has been thwarted by the shortage of practical, high-yielding synthetic routes towards fluorous porphyrins[17] and tetraarylporphyrins.[18] We here describe a simple and efficient preparation of a fluorous *meso*-tetraarylporphyrin starting from a commercially available porphyrin precursor. The new fluorous dye was successfully employed as a sensitizer in photooxygenation reactions, displaying very high activity, even after its facile recovery from the reaction mixture.

Results and Discussion

Only a few porphyrins with a high fluorine loading (F > 60%) endowed with high affinity for perfluorocarbons are known.[17,18] They were prepared without exception by cyclization of linear perfluoroalkylated building-blocks. According to our own experience, this strategy requires synthetically demanding starting materials, leading to the final products in low yields after extensive work-up and purification. Direct introduction of perfluoroalkyl side-chains (R_F) on the periphery of preformed porphyrins could help solve these problems, but currently only porphyrins with a fluorine loading that is possibly too low to be useful for FB applications are accessible through direct perfluoroalkylation.[19] We had previously shown that functionalization of reactive *meso*-aryl groups can be conveniently exploited for introducing up to four R_F on the periphery of tetraarylporphyrins. No special technique was required for the isolation and purification of the products, which had a fluorine loading of up to 45%, high enough to modify their solubility properties with respect to the parent compounds, but still too low for FB applications.[20] This seriously limited the potential of our approach, which was not further investigated. However, in the last few years many new perfluoroalkylating reagents have been disclosed,[21] and this will likely broaden the scope of our functionalization technique, as exemplified by the synthesis of the new fluorous sensitizer **1** (Scheme 1). *O*-Alkylation of the four *meso*-aryl groups of the commercially available 15,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin [$TPP(OH)_4$] was carried out in a mixture DMF/$PhCF_3$ using a modest excess of 3,5-bis(perfluorooctyl)benzyl bromide **2** as the alkylating agent.[22] The starting porphyrin was quantitatively converted into **1** and the excess of alkylating agent was readily eliminated from the crude product by repeated washing with $CHCl_3$. Pure fluorous tetraarylporphyrin **1** was thus recovered in 95% yield.

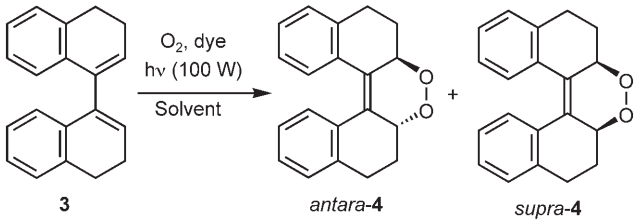


Scheme 1. Synthesis of porphyrin **1**.

Fluorine loading of **1** is slightly lower than 60%, but thanks to the presence of eight R_F ponytails the new porphyrin is highly fluorophilic, thus exhibiting selective solubility in perfluorocarbons. Partition coefficients of **1** ($P = [dye]_{Perfluorocarbon}/[dye]_{Organic\ Solvent}$) between perfluoro-1,3-dimethylcyclohexane (PFDMC) and organic solvents such as CCl_4, CH_3CN and toluene were constantly > 100, as determined by UV/Vis spectroscopy at 20 °C.[18b] It should be noted that **1** strongly absorbs in the UV/Vis and even traces of this compound can be easily detected in the organic phase.

A number of techniques complementary to the classic FB approach have been developed in the last

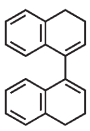
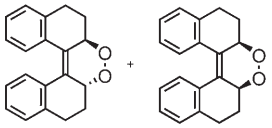
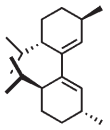
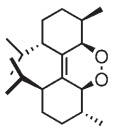
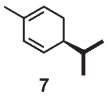
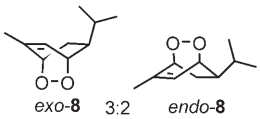
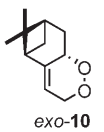
few years, providing new options for separating fluorous molecules from reaction mixtures.[23] In particular, selective retention of fluorous molecules on fluorous reverse phase silica gel (FRPSG) has found widespread application for quick separations of mixtures involving fluorous reagents and scavengers,[24] and it is now receiving increasing attention in catalysis.[25] Indeed, thanks to the energetically favorable interactions with the highly fluorinated silica surface, fluorous catalysts can be heterogenized by adsorption on FRPSG and then used as standard solid catalysts. In order to obtain a simple heterogeneous sensitizer this technique was first explored. FRPSG, prepared according to a literature procedure,[25a] was added to a stirred solution of porphyrin **1** in methyl *tert*-butyl ether (MTBE). Evaporation of the solvent afforded a red powder with a porphyrin loading of 1%. The efficiency of FRPSG-supported **1** as a sensitizer was then evaluated in the photooxygenation of bisdialine **3** (Scheme 2).[14,26] The solid catalyst was added to a solution of the model substrate in CCl_4 (molar ratio substrate/**1** = 350) and the mixture was irradiated with visible light (100 Watt) while oxygen was bubbled for 5 h. Very low conversion (less than 1%) of **3** into the expected *supra* and *antara* diastereomeric endoperoxides **4** was observed.



Scheme 2. Dye-sensitized photooxygenation of bisdialine **3**.

Since heterogeneization failed to give an efficient sensitizing system, we next investigated the photooxygenation of organic substrates under homogeneous conditions. Fortunately, porphyrin **1** proved to be slightly soluble in chlorinated solvents (e.g., $CHCl_3$, CCl_4), at such an extent to allow photooxygenations to occur at a reasonable rate. In fact, when a solution of bisdialine **3** (1.0×10^{-2} M) and **1** (2.3×10^{-5} M, molar ratio substrate/**1** = 435) in CCl_4 was irradiated with a 100 Watt lamp while bubbling oxygen, the substrate was completely consumed within 40 min (Table 1, entry 1). This is in good agreement with the

Table 1. Photooxygenation of unsaturated substrates under homogeneous conditions.[a]

Entry	Substrate	Sensitizer	Solvent	Watt	*t* [h]	Conv. [%]	Yield [%]	Product(s)
1		**1**	CCl_4	100	0.67	99	96	
2		TPP	CCl_4	100	0.50	99	96	
	3							*antara*-**4** 4:1 *supra*-**4**
3		**1**	CCl_4	500	15	36	31	
4		TPP	CCl_4	500	15	43	36	
	5							**6**
5		**1**	CCl_4	100	0.17	99	91	
6		TPP	CCl_4	100	0.17	99	86	
	7							*exo*-**8** 3:2 *endo*-**8**
7		**1**	CCl_4	200	0.75	99	90	
8		TPP	CCl_4	200	0.17	99	88	
	9							*exo*-**10**
9[b]		**1**	CH_2Cl_2	500	4	82	56	
10[b]		TPP	CH_2Cl_2	500	4	97	68	
	11							**12**

[a] [Substrate] = 1.0×10^{-2} M, [dye] = 2.3×10^{-5} M (S/dye = 435); oxygen supply = bubbling; conversion = TLC, GC or ^{1}H NMR; yields = isolated.

[b] Reaction performed in the presence of 1.0 equiv. of Ac_2O, 0.5 equivs. of pyridine and 0.02 equivs. of DMAP (see ref.[31]).

result obtained using a popular sensitizer such as 5,10,15,20-tetraphenylporphyrin (TPP) under the same experimental conditions (entry 2, molar ratio substrate/TPP = 435).[27] Porphyrin **1** proved to be an efficient sensitizer also when the photooxygenation of **3** was carried out in $CHCl_3$, but in that case protonation of the porphyrin by HCl from the solvent was observed. Indeed, the solution shifted from red to green as the reaction progressed. The original purple color of **1** could be restored by addition of solid $NaHCO_3$, but in order to prevent any possible degradation of the catalyst, CCl_4 was used in the following experiments. The outcome of the fluorous dye-sensitized photooxygenation of other unsaturated substrates is summarized in Table 1, together with results obtained using TPP as a sensitizer.

In detail, the photooxygenation of the poorly conjugated (+)-1,1-dimenthene **5**[28] promoted by the fluorous dye proceeded quite slowly, affording the expected endoperoxide **6** in 31% overall yield (86% with respect to the converted substrate) in 15 h (entry 3). Similarly, endoperoxide **6** was obtained in 36% overall yield (83.7% with respect to the converted substrate) when the reaction was run in the presence of TPP (entry 4). Slightly better results were previously obtained using a poly(ethylene glycol)-supported tetraarylporphyrin (yield of **6** = 42%, t = 15 h), but in that case a higher sensitizer loading (3 mol% vs. 0.23 mol% used here) and the addition of a proton scavenger were required.[14] Noticeably, the photooxygenation of (−)-α-phellandrene **7** promoted by **1** (entry 5) selectively produced a mixture of two diastereomeric endoperoxides (*exo*-**8** and *endo*-**8**) in a 3:2 ratio, free of ene-type by-products (e.g., peroxides or aromatics) commonly observed when the oxidation is carried out with other methods.[29] As expected on the basis of steric considerations, the photooxygenation of (−)-nopadiene **9**[30] (entry 7) afforded the *exo*-cycloadduct **10**, not yet described in the literature, as the sole product. Finally, cyclopentadiene dimer **11** (entry 9) was reacted in the presence of acetic anhydride and pyridine, according to the protocol established by Mihelich and Eickoff,[31] to give the corresponding α,β-unsaturated ketone **12**. This reaction required the use of CH_2Cl_2 as solvent, in fact, photooxygenation failed to furnish the desired product when run in the less polar CCl_4. For all these reactions, the product distributions were the same with the two porphyrin dyes, but differently from TPP, porphyrin **1** was easily removed from reaction products using specific fluorous separation techniques and eventually recycled. Results obtained in the case of the photooxidation of bisdialine **3** are summarized in Table 2.

Fluorous solid phase extraction (F-SPE)[24,32] was first investigated. After completion of the reaction the organic solution containing *antara*- and *supra*-**4** and the fluorous dye was loaded onto a home-made FRPSG cartridge (**1**/FRSG = 1:100 w/w). The organic products with little affinity for the fluorophilic silica surface were eluted at once, whereas **1** was retained on the top of the cartridge from where it was subsequently removed by a simple solvent switch to PFDMC. The fluorous solution containing **1** was evaporated and the recovered dye was successfully reused in a second run, but suddenly lost its sensitizing ability in the following runs (Table 2, entries 1–4). The high fluorophilicity of **1** allowed us to compare F-SPE to another quick fluorous work-up method, namely liquid-liquid extraction of the reaction mixture with a perfluorocarbon (F-LLE). The purification of the products from the sensitizer was thus achieved by adding a small amount of PFDMC to the organic solution (PFDMC/CCl_4 = 1:5 v/v). The resulting biphasic mixture was stirred for a few minutes, then the red fluorous layer on the bottom of the reactor and the upper pale yellow organic solution containing the products were separated. The fluorous layer was evaporated in situ and a fresh solution of bisdialine **3** in CCl_4 was added. The efficiency of the recovered dye was maintained completely in three subsequent runs, after which catalytic activity decreased (Table 2, entries 5–8).

Table 2. Recycling of **1**: photooxygenation of bisdialine under homogeneous conditions.[a]

Entry	Run	Method[b]	Conversion [%]	Isolated Yield [%]
1	1	F-SPE	99	94
2	2		99	95
3	3		43	40
4	4		33	30
5	1	F-LLE	99	97
6	2		99	94
7	3		99	95
8	4		79	74

[a] Solvent = CCl_4; reaction time = 40 min; [substrate] = 1.0×10^{-2} M, [**1**] = 2.3×10^{-5} M (S/**1** = 435); oxygen supply = bubbling; conversion = TLC and ^{1}H NMR.
[b] F-SPE = fluorous solid phase extraction; F-LLE = fluorous liquid-liquid extraction.

The quick and reliable separation of porphyrin **1** from organic products could be also achieved by operating photooxygenations under classic FB conditions. Early experiments (Table 3) were performed in the liquid-liquid biphasic system PFDMC/CH_3CN (1:1 v/v) with bisdialine **3** as substrate and a molar ratio substrate/**1** = 100. The reactions barely proceeded when a stream of oxygen was bubbled through the FB system during the irradiation (entry 1). Indeed, the quite volatile perfluorocarbon (bp 102 °C) was stripped out leaving the dye as a suspended powder in the CH_3CN solution. For this reason the experimental set-up was modified according to the photooxygenation procedure described by DiMagno and co-workers,[17b] who

Table 3. Photooxygenation of bisdialine **3** under homogeneous and FB conditions.[a]

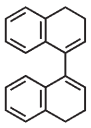
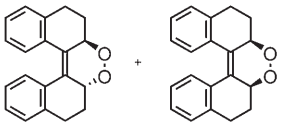
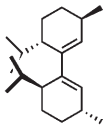
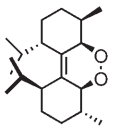
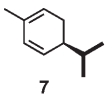
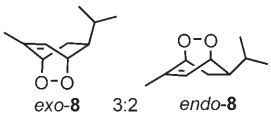
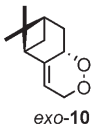
Entry	Solvent System	Sensitizer	Oxygen Supply	*t* [h]	Conversion [%]	Isolated yield [%]
1	CH_3CN/PFDMC	**1**	bubbling	0.5	<1	-
2	CH_3CN/PFDMC	**1**	diffusion	18	88	76
3	$PhCF_3$	**1**	diffusion	4	99	92
4	$PhCF_3$	**1**	bubbling	2	99	94
5	CH_2Cl_2	TPP	diffusion	4	93	88
6	CH_2Cl_2	TPP	bubbling	1	99	96

[a] S/dye = 100 in all experiments. For reaction details, see Experimental Section. Conversions were determined by ^{1}H NMR or GC of the crude reaction mixtures.

avoided bubbling and allowed molecular oxygen to diffuse into a vigorously stirred FB system. This resort prevented a massive loss of PFDMC, but oxidation of **3** still proceeded quite slowly (88% conversion after 18 h, entry 2), possibly due to singlet oxygen quenching by collision during its migration from the fluorous phase, where it is generated, to the organic solvent, where the addition to the substrate takes place. Our hypothesis was supported by the results of experiments carried out under homogeneous conditions in α,α,α-trifluorotoluene ($PhCF_3$), an amphiphilic fluorinated solvent able to dissolve both fluorous and organic compounds. In that case, the photooxygenation of **3** with oxygen diffusion required only 4 h to go to completion (entry 3). Complete conversion of **3** was even faster when oxygen was bubbled in the $PhCF_3$ solution containing the substrate and the fluorous sensitizer (entry 4). These results are in good agreement with those obtained using TPP under similar experimental conditions (entries 5 and 6).

As shown in Table 4 (entry 1), the FB photooxygenation of **3** could be performed under continuous

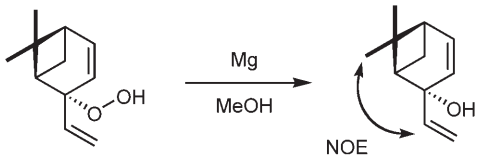
Table 4. Photooxygenation of unsaturated substrates promoted by **1** under CH_3CN/FC5312 FB conditions.[a]

Entry	Substrate	Watt	*t* [h]	Conv. [%]	Yield [%]	Product(s)
1	 **3**	100	2.50	87	78	 *antara*-**4** 3:2 *supra*-**4**
2	 **5**	500	15	62	60	 **6**
3	 **7**	100	0.17	99	59	 *exo*-**8** 3:2 *endo*-**8**
4	 **9**	200	0.75	99	41[b]	 *exo*-**10**
5[c]	 **11**	500	4	70	48	 **12**

[a] [Substrate] = 5.8×10^{-2} M (in 4 mL of CH_3CN), [**1**] = 1.14×10^{-3} M (in 2 mL of FC5312); (S/**1** = 100), oxygen supply = bubbling; conversion = TLC, GC or ^{1}H NMR; yields = isolated.
[b] Peroxide *exo*-**13** (Scheme 3) was also formed in similar yield.
[c] Reaction performed in the presence of 1 equivs. of Ac_2O, 0.5 equivs. of pyridine and 0.02 equivs. of DMAP (see ref.[31]).

oxygen supply by replacing PFDMC with a less volatile perfluorocarbon such as FC-5312 (mainly perfluorotripentylamine, boiling range = 201–221 °C). The reaction proceeded slower than under homogeneous conditions (Table 1, entries 1 and 2), possibly because of the poor solubility of **3** in CH_3CN. Nevertheless, a mixture of or *supra* and *antara* diastereomeric endoperoxides **4** was obtained in a reasonable 78% overall isolated yield (90% with respect to the converted substrate). Besides the two major products, small, but not negligible, amounts of polar materials were formed, which were not detected in the homogeneous reaction. Diastereoselectivity of the FB reaction also proved to be slightly lower (*antara/supra* ratio = 3:2 *vs.* 4:1 under homogeneous conditions).

On the contrary, the sluggish photooxygenation of (+)-1,1-dimenthene **5** (entry 2) afforded an acceptable conversion (62%) into the expected endoperoxide **6**, with negligible traces of by-products. (−)-Phellandrene **7** (entry 3) afforded a crude mixture in which large amounts of phenols and peroxides were formed, by an ene-type cycloaddition route. The expected endoperoxides *exo*- and *endo*-**8** were obtained in a 3:2 diastereomeric ratio, unchanged with respect to the homogeneous reaction. (−)-Nopadiene **9** (entry 4) was converted into the endoperoxide *exo*-**10** with high diastereoselectivity, but the reaction crude showed the presence of a comparable amount of a compound that was tentatively assessed as the peroxide *exo*-**13** (Scheme 3), arising from an ene-type cycloaddition of



exo-**13** *exo*-**14**

Scheme 3. Reduction of peroxide *exo*-**13** and NOE observed in alcohol *exo*-**14**.

singlet oxygen on the less hindered face of the allylic system of the molecule. This hypothesis was confirmed by comparison of the vinyl signals of the crude [$\delta = 6.54$ (dd $J = 8.7$ and 6.2 Hz), 5.93 (dd $J = 17.6$ and 11.0 Hz), 5.67 (dd $J = 8.7$ and 2.6 Hz), 5.43 (dd $J = 17.6$ and 1.0 Hz), 5.41 (dd $J = 11.0$ and 1.0 Hz)] with the downfield resonances of alcohol *exo*-**14** (see Experimental Section), that was isolated in 28% yield after reduction of the crude with magnesium turnings in methanol.[33] The stereochemistry of alcohol *exo*-**14** was confirmed by NOESY correlation between the upfield methyl (0.92 ppm) and the hydrogen of the vinyl group (5.35 ppm) (Scheme 3). Dicyclopentadiene **11** (entry 5) reacted smoothly in the biphasic system, to afford ketone **12** in 48% overall yield.

In all these experiments, the organic layer containing the products was separated by simple decantation from the fluorous layer containing **1**. Recycling of the latter was investigated in the case of the photooxygenation of (−)-nopadiene **9**. The activity of the fluorous layer was maintained over five subsequent runs, with no detectable loss of activity and selectivity for the major product *exo*-**10** (Table 5). It is noteworthy to observe that the activity of the dye was maintained for an appreciable number of runs, despite the presence in the reaction mixture of a relevant amount of peroxide *exo*-**13**, that is a possible inhibitor of the porphyrin.[15]

Table 5. Recycling of **1**: photooxygenation of (−)-nopadiene **9** under CH_3CN/FC5312 FB conditions.[a]

Run	Conversion [%]	Isolated Yield [%]
1	99	41
2[b]	99	39
3[b]	99	41
4[b]	99	36
5[b]	99	42

[a] Reaction time = 45 min; [substrate] = 5.8×10^{-2} M (in 4 mL of CH_3CN), [**1**] = 1.14×10^{-3} M (in 2 mL of FC5312); (S/**1** = 100); oxygen supply = bubbling; conversion = GC.

[b] The fluorous phase recovered from the preceding run was used.

Conclusions

Fluorous *meso*-tetraarylporphyrin **1** has been conveniently prepared starting from a commercially available porphyrin precursor. This synthetic approach is simpler and more effective than those previously introduced. In addition, no particular work-up or purification procedure is required. The new compound was successfully employed as a sensitizer in photooxygenation reactions, exhibiting activity comparable to the standard 5,10,15,20-tetraphenylporphyrin (TPP) sensitizer when reactions were performed in a conventional solvent such as CCl_4 under homogeneous conditions. Replacement of the chlorinated solvent with the liquid-liquid biphasic system perfluorocarbon/CH_3CN led to a modest reduction of the sensitizer activity along with somewhat different product distributions. In both cases the fluorous sensitizer **1** offered the advantages usually associated with the use of polymer-supported sensitizers (simplified work-up procedures, quick recovery, recyclability) without some of their common limitations (lack of versatility, severe mass transfer limitations). When reactions were run under homogeneous conditions, the effective recycling of **1** throughout a higher number of reaction runs was mainly hampered by bleaching processes, as evidenced by the progressive disappearance of the char-

acteristic UV-Vis Soret band of the porphyrin. The introduction of sterically demanding substituents at the periphery of the macrocycle could further improve the photostability of the fluorous dye, as already shown in the case of homogeneous tetraarylporphyrins.[11a]

Experimental Section

General Remarks

High purity grade solvents and reagents were employed without further purification. Perfluoro-(1,3-dimethylcyclohexane) (Apollo Scientific Ltd., UK) was used as received. $TPP(OH)_4$, (−)-phellandrene **7** and cyclopentadiene dimer **11** were purchased from Sigma–Aldrich and used as received. 3,5-Bis(perfluorooctyl)benzyl bromide,[22] bisdialine **3**,[26] (+)-1,1-dimenthene **5**,[28] and (−)-nopadiene **9**[30] were prepared as described in the literature. Elemental analyses: Departmental Service of Microanalysis (University of Milano).

O-Alkylation of $TPP(OH)_4$ was monitored by TLC, photooxygenation reactions were followed by TLC, GC-MS and ^{1}H NMR. Photooxygenations were performed with halogen lamps ranging from 100 to 500 Watt positioned at 10 cm from the reaction vessels. Reactor type ***A*** for experiments with O_2 bubbling consists of a 20 cm long, 10 mm i.d. jacketed test tube, equipped with an 8 mm Teflon coated stirring bar and a rubber septum punctured with a syringe needle (O_2 outlet) and a 0.5 mm i.d. Teflon tubing (O_2 inlet). Reactor type ***B*** for experiments without O_2 bubbling consists in a 20 cm long, 2.2 cm i.d. jacketed test tube, equipped with a 20 mm Teflon coated stirring bar and three-way stopcock connected to oxygen supply and vacuum.

Photooxygenation products are known compounds, except for (1*R*,7*R*,9*R*)-(−)-10,10-dimethyl-5,6-dioxatricyclo-[7.1.1.0^{2,7}]undec-2-ene (*exo*-**10**) and (1*R*,2*S*,5*R*)-2-hydroperoxy-6,6-dimethyl-2-vinylbicyclo[3.1.1]hept-3-ene (*exo*-**13**), that was converted into the more stable (1*R*,2*S*,5*R*)-2-hydroxy-6,6-dimethyl-2-vinylbicyclo[3.1.1]hept-3-ene (*exo*-**14**), whose physical data are reported herein. ***Warning:*** as in any work involving peroxides we followed the standard precautions (e.g., the use of safety shields, to keep solutions cooled, to avoid contact with transition metals and to perform reactions on a minimal scale).

Fluorous Porphyrin 1

A flame-dried Schlenk tube was charged with $TPP(OH)_4$ (136 mg, 0.2 mmol), 3,5-bis(perfluorooctyl)benzyl bromide **2** (1.01 g, 1 mmol), K_2CO_3 (0.97 g, 7 mmol), $PhCF_3$ (10 mL) and DMF (2 mL). The mixture was stirred under nitrogen for 1 h at room temperature, then heated to 110 °C for 8 h and finally cooled to room temperature. The solvents were evaporated and the residue was treated with $PhCF_3$ (20 mL). Any undissolved material was filtered off and the liquid layer washed with H_2O, brine and dried over sodium sulfate. The solvent was evaporated to leave a sticky residue which was washed with cold $CHCl_3$ (5 × 1 mL) affording the title compound as a dark brown solid; yield: 0.83 g (95%); UV/Vis ($CFCl_2CF_2Cl$): λ_{max} (log ε) = 416 nm (5.53); ^{1}H NMR (300 MHz, $CFCl_2CF_2Cl$): $\delta = -2.68$ (br s, 2H), 5.49 (s, 8H), 7.39 (d, $J = 8.5$ Hz, 8H), 7.93 (s, 4H), 8.14 (s, 8H), 8.19 (d, $J = 8.5$ Hz, 8H), 8.87 (br s, 8H); anal. calcd. for $C_{136}H_{46}F_{136}N_4O_4$ (4383.63): C 37.26, H 1.06, N 1.28; found C 37.03, H 1.16, N 1.71.

(1*R*,7*R*,9*R*)-(−)-10,10-Dimethyl-5,6-dioxatricyclo-[7.1.1.0^{2,7}]undec-2-ene (*exo*-10)

Colorless oil; $[\alpha]_D^{22}$: −88 (*c* 1.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.00$ (s, 3H), 1.06 (d, $J = 9.4$ Hz, 1H), 1.32 (s, 3H), 1.52–1.62 (m, 1H), 2.07–2.14 (m, 1H), 2.36–2.48 (m, 1H), 2.63–2.70 (m, 2H), 4.48 (ddd, $J = 15.8$, 3.1 and 1.8 Hz, 1H), 4.91 (ddd, $J = 15.8$, 3.1 and 2.6 Hz, 1H), 5.38–5.43 (m, 1H), 5.39–5.43 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 23.8, 27.0, 30.2, 37.1, 39.7, 41.6, 50.5, 71.4, 75.0, 114.1, 143.8; IR (film): $\nu = 2921$, 2875, 1468, 1057, 1024 cm^{-1}; anal. calcd. for $C_{11}H_{16}O_2$ (180.24): C 73.30, H 8.95; found: C 73.33, H 8.93.

(1*R*,2*S*,5*R*)-(−)-2-Hydroxy-6,6-dimethyl-2-vinyl bicyclo[3.1.1]hept-3-ene (*exo*-14)

Colorless oil; $[\alpha]_D^{22}$: −10 (*c* 0.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDC1_3$): $\delta = 6.40$ (dd, $J = 8.3$ and 5.0 Hz, 1H), 6.07 (dd, $J =$ 17.4 and 10.8 Hz, 1H), 5.64 (dd, $J = 8.3$ and 2.2 Hz, 1H), 5.35 (dd, $J = 17.4$ and 1.2 Hz, 1H), 5.20 (dd, $J = 10.8$ and 1.2 Hz, 1H), 2.53–2.45 (m, 1H), 2.29–2.19 (m, 2H), 1.65 (d, $J = 9.3$ Hz, 1H), 1.38 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 142.2$, 139.4, 127.4, 114.6, 75.6, 52.2, 47.4, 42.8, 33.2, 27.4, 24.3; IR (film): $\nu = 3402$, 2978, 2937, 2870, 991 cm^{-1}; anal. calcd. for $C_{11}H_{16}O$ (180.24): C 80.44, H 9.82; found: C 80.46, H 9.84%.

FRPSG-Supported Fluorous Porphyrin

Fluorous reverse phase silica-gel (FRPSG, 1 g) prepared according to a literature procedure[25a] was added to a solution of **1** (10 mg, 22.8×10^{-4} mmol) in MTBE (30 mL). The mixture was maintained under vigorous stirring for 15 min at room temperature, then the solvent was removed under vacuum affording a dark red colored powder, which was extracted with CCl_4 for 3 h in a Sohxlet apparatus. The porphyrin was completely retained by the solid support, as shown by the absence of the characteristic UV-Vis Soret band of **1** ($\lambda = 416$ nm) in the UV-Vis spectrum of the liquid phase.

Photooxygenation of Bisdialine 3 with FRPSG-Supported Fluorous Porphyrin

A reactor (type ***A***, see General Remarks) was charged with a solution of **3** (20 mg, 8.0×10^{-2} mmol) in CCl_4 (10 mL) and FRPSG-supported porphyrin (100 mg, 2.3×10^{-4} mmol of **1**). The mixture was vigorously stirred while oxygen was bubbled (10 mL min^{-1}). The solution was irradiated with a 100 Watt halogen lamp for 5 h and the organic layer was analyzed by TLC and ^{1}H NMR.

General Procedure for Photooxygenations under Homogeneous Conditions (Table 1)

A reactor (type ***A***) was charged with **1** (1.0 mg, 2.3×10^{-4} mmol), CCl_4 (10 mL) and the mixture was vigorously stirred until the dye was dissolved. The diene (10.0×10^{-2} mmol) was added and oxygen was bubbled (10 mL min^{-1}) while the stirred solution was irradiated with an halogen lamp (power reported in Table 1) until the diene disappeared (TLC, GC or ^{1}H NMR analysis). The dye was removed either by F-SPE or by F-LLE. The decolored organic solution was concentrated and the products were recovered by flash chromatography over silica gel (*antara*- and *supra*-**4**: CH_2Cl_2/hexanes 2:8; **6**: CH_2Cl_2/hexanes 4:6; *exo*- and *endo*-**8**: CH_2Cl_2/hexanes 4:6; *exo*-**10**: CH_2Cl_2/hexanes 1:1; **12**: Et_2O/hexanes 3:7).

Recycling of Porphyrin 1 by F-SPE (Table 2)

A reactor (type ***A***) was charged with a solution of **3** (26 mg, 10.0×10^{-2} mmol) in CCl_4 (10 mL) and **1** (1.0 mg, 2.3×10^{-4} mmol), The mixture was vigorously stirred until the dye was dissolved. Oxygen was bubbled (10 mL min^{-1}) and the stirred solution was irradiated with a 100 Watt halogen lamp for 40 min. The solution was filtered through a cotton-plugged Pasteur pipette packed with FRPSG (100 mg). A pale yellow solution containing the product was eluted at first, while the top of the silica bed became dark red. The home-made FRPSG cartridge was then eluted with PFDMC (2.5 mL) into the reactor vessel. PFDMC was removed with a stream of nitrogen and the reaction was repeated with a fresh solution of bisdialine **3** in CCl_4.

Recycling of Porphyrin 1 by F-LLE (Table 2)

Photooxygenation of **3** was carried out as described in the case of the F-SPE work-up procedure. When the reaction was over, PFDMC (2 mL) was added to the solution under vigorous stirring. After settling of a red fluorous phase, the supernatant was removed with a Pasteur pipette and the lower phase was washed with CCl_4 (2×1 mL). The organic layers were combined and evaporated under reduced pressure to give the product. PFDMC was removed from the reactor with a stream of nitrogen and the reaction was repeated with a fresh solution of bisdialine **3** in CCl_4.

Dye-Sensitized Photooxygenation of 3 under Various Conditions (Table 3)

a) FB conditions (oxygen bubbling): In a reactor (type ***A***) a solution of **3** (20 mg, 8.0×10^{-2} mmol) in CH_3CN (2 mL) and a solution of **1** (3.5 mg, 8.0×10^{-4} mmol) in PFDMC (2 mL) were placed. The vigorously stirred mixture was bubbled with oxygen and irradiated with a 100 Watt halogen lamp. The resultant fluorous solvent was completely removed after 30 min, leaving the porphyrin in the organic phase as a dark red powder.

b) FB conditions (oxygen diffusion): In a reactor (type ***B***, see General Remarks) a solution of **3** (20 mg, 8.0×10^{-2} mmol) in CH_3CN (2 mL) and a solution of **1** (3.5 mg, 8.0×10^{-4} mmol) in PFDMC (3 mL) were placed. The vessel was evacuated and purged three times with oxygen. The biphasic mixture was vigorously stirred and irradiated with a 100 Watt halogen lamp. The reaction was monitored by TLC and ^{1}H NMR analysis of the organic layer. The upper phase was separated and the colored fluorous phase was washed with CH_3CN (2×2 mL). The combined organic layers were concentrated and the products were recovered by flash chromatography over silica gel (eluant CH_2Cl_2/hexanes, 2:8).

c) Homogeneous conditions (oxygen bubbling): In a reactor (type ***A***) a solution containing **3** (20 mg, 8.0×10^{-2} mmol), **1** or TPP (8.0×10^{-4} mmol) in CH_2Cl_2 or $PhCF_3$ (6 mL) was vigorously stirred while oxygen was bubbled (10 mL min^{-1}). The solution was irradiated with a 100 Watt halogen lamp until the starting material had disappeared as shown by TLC and ^{1}H NMR analysis. The products were recovered by flash chromatography over silica gel (eluant CH_2Cl_2/hexanes, 2:8).

d) Homogeneous conditions (oxygen diffusion): A solution containing **3** (20 mg, 8.0×10^{-2} mmol), **1** or TPP (8.0×10^{-4} mmol) in CH_2Cl_2 or $PhCF_3$ (6 mL) was placed in a reactor (type ***B***). The vessel was evacuated and purged three times with oxygen. The solution was vigorously stirred and irradiated with a 100 Watt halogen lamp until starting material disappeared, as shown by TLC and ^{1}H NMR analysis. The products were recovered by flash chromatography over silica gel (eluant CH_2Cl_2/hexanes, 2:8).

General Procedure for Photooxygenations under FB Conditions (Table 4)

A reactor (type ***B***) was charged with a solution of **1** (10 mg, 2.3×10^{-3} mmol) in FC-5312 (2 mL) and a solution of diene (23.0×10^{-2} mmol) in CH_3CN (4 mL).[34] The liquid-liquid biphasic mixture, irradiated with a halogen lamp (power reported in Table 4), was vigorously stirred while oxygen was bubbled (10 mL min^{-1}). The reaction was followed by TLC, GC or ^{1}H NMR analysis of samples of the organic layer. After the time reported in Table 4 the reaction was stopped. The organic supernatant was separated and the dark red fluorous phase was washed with CH_3CN (2×2 mL), and eventually reused (see Table 5). The combined organic layers were concentrated and the products were recovered by flash chromatography over silica gel (*antara*- and *supra*-**4**: CH_2Cl_2/hexanes, 2:8; **6**: CH_2Cl_2/hexanes, 4:6; *exo*- and

endo-**8**: CH_2Cl_2/hexanes, 4:6; *exo*-**10**: CH_2Cl_2/hexanes, 1:1; **12**: Et_2O/hexanes, 3:7).

Recycling of Porphyrin 1 in Reactions under FB Conditions (Table 5)

A reactor (type ***B***) was charged with a solution of **1** (10 mg, 2.3×10^{-3} mmol) in FC-5312 (2 mL) and a solution of **9** (34 mg, 23.0×10^{-2} mmol) in CH_3CN (4 mL). The liquid-liquid biphasic mixture, irradiated with a halogen lamp (200 W), was vigorously stirred for 45 min while oxygen was bubbled (10 mL min^{-1}). Stirring was interrupted and the red fluorous phase was left to separate. The supernatant was removed with a Pasteur pipette and the lower phase was washed with CH_3CN (2×1 mL). The organic layers were combined and evaporated under reduced pressure to afford the product. A new solution of nopadiene **9** in CH_3CN was added and the cycle was repeated.

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