Fluorous Biphasic Catalytic Oxidation of Sulfides by Molecular Oxygen/2,2-Dimethylpropanal

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Dedicated to the memory of Professor Shigeru Oae

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The use of perfluoroalkyl-substituted cobalt complexes as catalysts for the oxidation of alkyl aryl sulfides with molecular oxygen/2,2-dimethypropanal has been studied in a fluorous organic biphasic system. The addition of very small amounts of a Co^{II}–tetraarylporphyrin (Co-**4**) led to increased substrate conversions (67–100%). Sulfoxide was generally obtained as the main product, together with variable quantities of sulfone (0–100%), depending on the nature of the substrate. A perfluoroalkyl-substituted Co^{II}–phthalocyanine (Co-**6**) proved to be less efficient with regard to substrate conversion (40–78%), but afforded sulfoxides selectively. Although the mechanism has not been investigated in detail, the reaction probably proceeds through a free-radical oxidative process, initiated by the Co^{II} complexes. The attempts at recycling the catalysts through phase separation were partly ineffectual owing to their instability under the reaction conditions, which is more pronounced in the case of Co-**6**.

Introduction

The concept of Fluorous Biphasic (FB) catalysis is currently attracting considerable interest, in view of the potential advantages over classical homogeneous catalytic systems.[1] The easy separation and recycling of the perfluorinated organometallic complexes used in FB catalytic systems are perhaps the most appealing features of this technique. The peculiar physico-chemical properties of the perfluorocarbons used as reaction media also suggest new intriguing possibilities, e.g. in terms of unexpected selectivities due to the unique solvation environment.[2] In the past, we took advantage of the chemical inertness of perfluorocarbons and of their exceptionally high affinity for dioxygen in the FB catalytic oxidation of hydrocarbons.[3] Another important oxidative process ideally suited for FB modification is the conversion of sulfides to sulfoxides or sulfones. This reaction has been thoroughly investigated for many years and the use of several oxidizing agents combined with classic catalytic as well as enzymatic systems have been proposed.[4,5] For obvious reasons, those systems relying on the use of molecular oxygen or air would be most attractive, provided that acceptable reactivities and selectivities were obtained. The combination of perfluorinated solvents and catalysts has thus been explored by a few groups that briefly reported the aerobic oxidation of sulfides in FB catalytic systems, both in the absence[6] and in the presence[7] of a reducing agent such as a branched alkyl aldehyde. More recently, Bégué and his group discovered the beneficial role played by hexafluoro-2-propanol in the stoichiometric oxidation of sulfides to sulfoxides with aqueous 30% hydrogen peroxide.[8] High yields and complete selectivities for sulfoxides were obtained under mild reaction conditions. The use of solid $Mn(OAc)_3 \cdot 2H_2O$ as a catalyst for the oxidation of sulfides with dioxygen/2,2-dimethypropanal in perfluoro-2-butyltetrahydrofuran was also examined, but in this case no particular solvent effect was observed.[8a] The positive features expected from the combination of the FB approach with the use of oxygen as primary oxidant were possibly hidden by the heterogeneous nature of the catalyst. Our long-standing interest in the biomimetic oxidation of sulfides prompted us to investigate the use of the cobalt complexes of perfluoroalkylated tetradentate N-ligands (tetraarylporphyrins and phthalocyanines) as homogeneous FB catalysts for this reaction. We describe here the results obtained with two of these complexes, as well as a new effective approach to the synthesis of tetraarylporphyrin **4** (Scheme 1), previously prepared by a rather cumbersome procedure.[3a]

Results and Discussion

Synthesis of the Catalysts

Tetraarylporphyrins are versatile ligands able to complex almost all transition-metal cations. Such complexes have been used as catalysts for a variety of biomimetic oxidation reactions, including the selective conversion of sulfides into sulfoxides or sulfones.[9] Three years ago we achieved the

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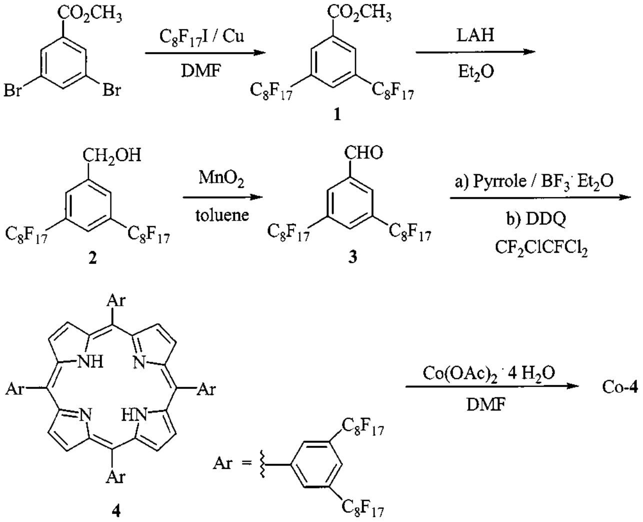


Scheme 1

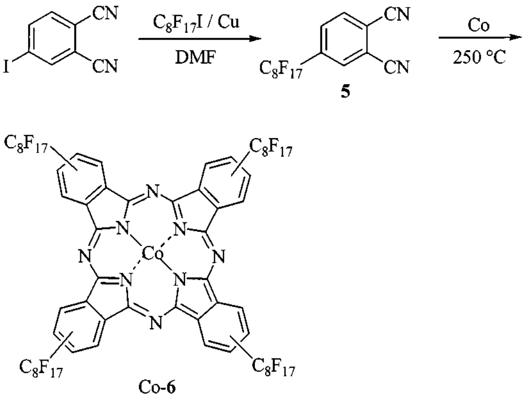
synthesis of the highly fluorinated ligand **4** and of the corresponding Co^{II} complex which are both selectively soluble in perfluorocarbons.[3a] Unfortunately, the preparation of **4** was complicated by the number of low-yielding synthetic steps required, and the scope of this approach was therefore considerably restricted.

The absence of **4** (or Co-**4**) in the organic phase of various FB systems was checked taking advantage of the characteristic, intense UV/Vis absorption shown by porphyrins and their metal complexes (Soret band, $\lambda = 400-425$ nm, ε in the order of 10^4-10^5 $dm^3\ mol^{-1}\ cm^{-1}$). Phthalocyanines also strongly absorb in the UV/Vis region, so traces of these compounds can be easily detected in solution.

As repeatedly highlighted by Curran and co-workers, partly fluorinated solvents such as α,α,α-trifluorotoluene can have a beneficial influence on the course of reactions involving highly fluorinated reagents.[10] It was thus decided to undertake the synthesis of **4** through Lewis acid catalyzed condensation of pyrrole and 3,5-bis(*n*-perfluorooctyl)benzaldehyde (**3**), using a partly fluorinated solvent as the reaction medium (Scheme 1). Aldehyde **3** was readily prepared by the copper-catalyzed coupling reaction of methyl 3,5-dibromobenzoate with $C_8F_{17}I$ (92% yield), followed by reduction of the perfluoroalkylated ester **1** to benzyl alcohol **2** (90% yield) and selective oxidation (73% yield), according to a procedure that we developed for a related salicylaldehyde.[3d]

Preliminary tests run in common organic solvents showed that condensation of aldehyde **3** and pyrrole fails to give porphyrin **4** under a variety of conditions. The replacement of CH_2Cl_2 with $CFCl_2CFCl_2$ allowed for the reaction to proceed as desired, under conditions otherwise similar to those used by Lindsey and co-workers in the synthesis of a number of tetraarylporphyrins.[11] Porphyrin **4** was obtained in 23% yield after purification by column chromatography on silica gel with $CFCl_2CFCl_2$ as the eluent. The cobalt complex of **4** was then prepared as previously described.[3a]

Transition-metal complexes of phthalocyanines are an important group of macrocyclic compounds endowed with properties close to those of metalloporphyrins.[12] A perfluorocarbon-soluble Co^{II}–phthalocyanine obtained through direct free-radical perfluoroalkylation of Co^{II}–phthalocyanine with $C_8F_{17}I$ was found to catalyze the aerobic FB oxidation of hydrocarbons and sulfides in the absence of a reducing agent.[6] In this case, however, conversions were low and the precise structure of the ligand (i.e. the number and the location of the perfluoroalkyl substituents on the macrocycle) was not reported. An alternative synthetic pathway leading to the better-defined perfluorocarbon-soluble Co^{II}–phthalocyanine **6** is reported in Scheme 2.[13] Complex Co-**6** was easily obtained when 1,2-dicyano-4-(*n*-perfluorooctyl)benzene (**5**) was heated with finely divided cobalt metal in a tightly closed vessel, according to a classical procedure for the synthesis of metallophthalocyanines (Scheme 2).[14] The presence of a single C_8F_{17} substituent on each of the four benzene rings of the phthalocyanine is ensured by the choice of the perfluoroalkylated precursor. We did not try to determine the substitution pattern of Co-**6** and the fluorinated chains are therefore shown at random positions.



Scheme 2

The fluorine load of Co-**6** (F = 57.6%) is lower than that required to make other oxidation catalysts (e.g. Mn^{III}–tetraarylporphyrins or Mn^{III}–salen complexes) preferentially soluble in perfluorocarbons (F > 60%).[3] Nevertheless, Co-**6** easily dissolves in *n*-perfluorooctane, giving deep-blue solutions, whereas it is completely insoluble in other organic solvents such as acetone and alcohols, as estimated by visual tests. Diethyl ether is an exception, but the solubility of Co-**6** in this solvent is much lower than in perfluorooctane (1.3 $mg\ mL^{-1}$ versus > 15 $mg\ mL^{-1}$). The partition coefficient of Co-**6** in *n*-perfluorooctane/CH_2Cl_2 (1:1, v/v) is 25.6 at 20 °C, as indicated by a decrease in the intensity of the characteristic UV/Vis absorption band at 654 nm after stirring a solution of Co-**6** in *n*-perfluorooctane (2.86×10^{-4} M) with CH_2Cl_2 for 2 h. Taking only the solubility of Co-**6** in CH_2Cl_2 (which is just 0.04 $mg\ mL^{-1}$) into account, a partition coefficient higher than 366 would be expected. The marginal leaching of the complex into the organic phase of the FB system can thus be mainly ascribed to the low, but not negligible, mutual miscibility of the two solvents.[15]

The remarkably high fluorous affinity of Co-**6** for perfluorocarbons is probably related to its electroneutrality, which is in contrast with the cationic nature of Mn^{III}−tetraarylporphyrins and Mn^{III}−salen complexes. Indeed, the very low dielectric constants of perfluorocarbons diminishes the solubilization of charged complexes, even though being highly fluorinated. The present finding also confirms the tentative nature of all predictions of the solubility behaviour of a molecule in perfluorocarbons, when only the fluorine load is taken into account.[3d]

FB Oxidation of Sulfides

The catalytic oxidation of methyl *p*-tolyl sulfide (1 mmol) with molecular oxygen (1 atm) in the presence of 2,2-dimethylpropanal (3 mmol) was chosen as a model reaction in order to test the feasibility of the FB approach. Reactions catalyzed by Co-**4** or Co-**6** were carried out in the dark at 20 °C under O_2, with the catalyst dissolved in the fluorous phase and the substrate dissolved in CH_2Cl_2. 2,2-Dimethylpropanal was added in small portions to the vigorously stirred biphasic mixture until the aldehyde/starting sulfide molar ratio was equal to 3, and the reaction progress was followed by ^1H NMR spectroscopy of samples drawn from the organic layer. The porphyrin complex Co-**4** effectively catalyzes the oxidation of methyl *p*-tolyl sulfide and the reaction was complete in 4 h, even with a very high substrate/catalyst ratio (S/C = 1000, Table 1, Entry 1). This figure compares favourably with the substrate/catalyst ratio (S/C = 35) of a preceding example of liquid/liquid FB oxidation of sulfides with O_2/aldehyde,[7] and with the S/C = 20−60 commonly reported for similar homogeneous catalytic reactions.[9,16] The selectivity for sulfoxide was higher than that observed by Bégué and co-workers in the oxidation of ethyl phenyl sulfide catalyzed by solid $Mn(OAc)_3 \cdot 2H_2O$ in perfluoro-2-butyltetrahydrofuran,[8a] but partial formation of sulfone could not be avoided.

Table 1. Catalytic oxidation of methyl *p*-tolyl sulfide with O_2/2,2-dimethylpropanal under fluorous two-phase conditions

Entry	Catalyst	Conversion (%)	Selectivity[a] Sulfoxide (%)	Sulfone (%)
1	Co-**4**	100	94	6
2[b]	Co-**4**	100	42	58
3[c]	Co-**4**	100	−	100
4	Co-**6**	40	100	−
5[d]	Co-**6**	11	97	3
6[e]	Co-**6**	27	100	−
7[f]	Co-**6**	6	100	−

[a] Reaction conditions: see Experimental Section; conversion and selectivity (yield/conversion) were determined by ^1H NMR spectroscopy. − [b] Reaction run with the fluorous layer recovered from Entry 1. − [c] Reaction run with the fluorous layer recovered from Entry 2. − [d] Reaction run with the fluorous layer recovered from Entry 4. − [e] Reaction run in the presence of 1 mol-% of 4-*tert*-butylcatechol. − [f] Reaction run in the presence of 5 mol-% of 4-*tert*-butylcatechol.

The phthalocyanine complex Co-**6** is less effective than Co-**4** at S/C = 1000, giving a substrate conversion of 40% in 4 h (Table 1, Entry 4). However, only sulfoxide was obtained, in agreement with the reported relationship between incomplete conversion and selectivity in solid/liquid FB systems.[8a] On this time scale, only small amounts of substrate were oxidized in FB blank experiments, as was also found by other authors investigating homogeneous reactions run in dichloroethane.[17]

Rather unexpectedly, catalyst recycling according to the well-established liquid/liquid FB protocol turned out to be unsuccessful. The fluorous phase, which was recovered by simply decanting from the organic solution containing the products, was added to a fresh CH_2Cl_2 solution of sulfide and treated with O_2/2,2-dimethypropanal. As shown in Table 1, in the case of Co-**6**, the substrate conversion decreased markedly without any significant variation in the selectivity when the fluorous layer was reused (Entry 5). Leaching of Co-**6** into the organic phase could not explain this drop of activity in view of the high partition coefficient of this complex in *n*-perfluorooctane/CH_2Cl_2. However, degradation of Co^{II}−phthalocyanines into several unidentified fragments was noticed in oxidation reactions proceeding under free-radical conditions.[18] When occurring in an FB system, a similar degradation would obviously prevent the recycling of the fluorous phase, as indeed we observed. The complete oxidation of methyl *p*-tolyl sulfide was still achieved in reactions catalyzed by Co-**4** (Entries 2 and 3), but the sulfone/sulfoxide ratio increased significantly after the first recycling of the fluorous phase, and only sulfone was obtained in the subsequent recycling. The change in selectivity was paralleled with the disappearance of the characteristic split UV/Vis absorption band of Co-**4** (λ_{max} = 405 and 427 nm) and by the emergence of a new band at 438 nm (assigned to [Co^{III}-**4**]$^+$)[19] that also disappeared after the third run. These observations indicated that the nature of the catalytic species involved in the oxidation reaction was no longer the same in the recycling steps. This was not found in the epoxidation of alkenes with O_2/aldehyde; in this case, the FB conditions enabled us to recycle Co-**4** as well as other fluorous complexes employed as catalysts for the reaction.[3]

A series of *para*-substituted methyl phenyl sulfides were oxidized in the presence of the two complexes under the FB conditions described above. Data shown in Table 2 confirmed that Co-**4** is a more active catalyst than Co-**6**, which in turn promotes the selective oxidation of most substrates to sulfoxides, with the remarkable exception of methyl *p*-nitrophenyl sulfide (Entry 8, Table 2).

The influence of *para* substituents on the selectivity of reactions catalyzed by Co-**4** was more evident, even though a definite trend could not be discerned. The formation of sulfone was enhanced by the strong electron-donating substituent $-OCH_3$ (Entry 9, Table 2), but the strong electron-withdrawing substituent $-NO_2$ behaved similarly (Entry 7, Table 2). Furthermore, the formation of sulfoxide was favoured by halogen substituents (Entries 3 and 5, Table 2) rather than by −H (Entry 1, Table 2) or $-CH_3$ (Entry 1, Table 1).

Table 2. Catalytic oxidation of *para*-substituted methyl phenyl sulfides with O_2/2,2-dimethylpropanal under fluorous two-phase conditions

Entry	Catalyst	Substrate	Conversion (%)[a]	Selectivity[a] Sulfoxide (%)	Sulfone (%)
1	Co-**4**	$PhSCH_3$	82	90	10
2	Co-**6**	$PhSCH_3$	68	100	–
3	Co-**4**	*p*-$ClPhSCH_3$	67	100	–
4	Co-**6**	*p*-$ClPhSCH_3$	58	100	–
5	Co-**4**	*p*-$FPhSCH_3$	100	95	5
6	Co-**6**	*p*-$FPhSCH_3$	49	100	–
7	Co-**4**	*p*-NO_2PhSCH_3	100	10	90
8	Co-**6**	*p*-NO_2PhSCH_3	100	15	85
9	Co-**4**	*p*-OCH_3PhSCH_3	100	–	100
10	Co-**6**	*p*-OCH_3PhSCH_3	59	100	–

[a] Reaction conditions: see Experimental Section; conversion and selectivity (yield/conversion) were determined by ^1H NMR spectroscopy.

These results are opposite to those obtained with biomimetic catalytic systems for which a heterolytic mechanism is now generally accepted. Indeed, microsomal cytochrome P-450 and metallotetraarylporphyrins promote the conversion of sulfides into sulfoxides with oxygen donors such as O_2/NADPH, PhIO and H_2O_2.[9c,20,21] In the presence of excess oxidizing agent, sulfoxides are subsequently converted into sulfones, and therefore mixtures of products are usually obtained. Electron-donating substituents increase the rate of oxidation of *para*-substituted methyl phenyl sulfoxides and an inverse linear relationship between the one-electron oxidation potential of the substrate and $\log(V_{max})$ has been found for microsomal cytochrome P-450 catalyzed oxidations with O_2/NADPH.[20b] The involvement of sulfur-centred radical cations, generated by the interaction of the substrate with a catalytic high-valent oxoiron species was first suggested,[20] but more recently convincing evidence for the direct oxygen transfer from a high-valent oxoiron–porphyrin radical cation to the neutral sulfide has been obtained.[9c,21]

The selectivity data presented here are better explained in terms of a homolytic mechanism in which the metal complexes simply speed up the formation of acyl and peroxyacyl radicals that are then responsible for the oxidation of the substrate.[22] This view is also supported by the inhibiting effect of the free-radical scavenger 4-*tert*-butylcatechol on the Co-**6** catalyzed oxidation of methyl *p*-tolyl sulfide (Table 1, Entries 6 and 7) and by the decrease in the stability of the catalyst relative to that observed in the epoxidation of alkenes with the same oxidizing system.[3] As found in the present work, metalloporphyrins and -phthalocyanines are prone to oxidative decomposition under free-radical conditions.[23,24] On the other hand, homolytic and heterolytic pathways coexist in the epoxidation of alkenes with O_2/aldehyde and the correct choice of reaction conditions can increase the relative importance of the latter.[25] For instance, the catalytic FB enantioselective epoxidation of indene with O_2/2,2-dimethylpropanal was achieved in the presence of Mn^{III}–salen complexes,[3d] thus pointing to the preponderance of a heterolytic reaction mechanism possibly involving (acylperoxo)metal complexes.[26]

Conclusions

The limited examples of catalytic aerobic oxidation of sulfides under fluorous biphasic conditions reported up to now indicate that this new methodology offers a viable access to sulfoxides and sulfones. We have started to explore the use of perfluoroalkylated metallotetraarylporphyrins and -phthalocyanines, and a first comparison can now be made with the other known FB catalysts. The cobalt(II) complex of porphyrin **4** gave good results in terms of selectivity for sulfoxide in comparison with solid $Mn(OAc)_3{\cdot}2H_2O$,[8a] being only slightly inferior to the nickel(II) complex of a perfluorinated 1,3-diketone reported by Knochel and co-workers.[7] Co-**4** was active at an S/C ratio of 1000, which is the highest value reported for a FB system. Although less active than Co-**4**, the phthalocyanine complex Co-**6** showed complete selectivity for sulfoxide, except in the oxidation of methyl 4-nitrophenyl sulfide. Despite the good chemoselectivity and efficiency observed, the two catalysts investigated here cannot withstand the free-radical conditions under which the FB oxidation of sulfides probably proceeds. Further modification of the peripheral structure of the perfluoroalkylated macrocycles is thus required to increase their robustness and to enhance the recoverability of the FB catalysts.

Experimental Section

General Remarks: Solvents were purified by standard methods and dried if necessary, except perfluorooctane, which was used as received. 2,2-Dimethypropanal was distilled prior to use and all the other commercially available reagents were used as received. Complex Co-**4** was prepared as described in ref.[3a] – TLC was carried out on silica gel 60 F_{254}. – Column chromatography (CC) was carried out on silica gel SI 60, mesh size 0.040–0.063 mm (Merck, Darmstadt, Germany) or neutral alumina 90 Activity I, mesh size 0.063–0.200 mm (Merck, Darmstadt, Germany). – Melting points (uncorrected) were determined with a Büchi SMP-20 capillary melting-point apparatus. – UV/Vis spectra were measured using a Lambda 6 Perkin–Elmer spectrometer. – ^1H NMR (300 MHz), ^{13}C NMR (75.4 MHz) and ^{19}F NMR (282 MHz) spectra were recorded with a Bruker XL 300 spectrometer with tetramethylsilane ($\delta = 0$), $CDCl_3$ ($\delta = 77$) and $CFCl_3$ ($\delta = 0$) as internal standard respectively, unless otherwise indicated. − Elemental analyses: Redox S.n.C. (Cologno Monzese, Italy) and Departmental Service of Microanalysis (University of Milano).

Perfluoroalkyl Ester 1: Activated copper bronze (1.90 g, 30 mmol)[27] was added to a solution of methyl 3,5-dibromobenzoate (1.47 g, 5 mmol) in DMF (10 mL). The stirred suspension was heated at 130 °C and purged with N_2. *n*-Perfluorooctyl iodide (3.96 mL, 15 mmol) was added dropwise to the stirred suspension over 15 min and the reaction mixture was stirred overnight at 130 °C. After cooling to room temp., the mixture was diluted with H_2O (20 mL) and Et_2O (50 mL) and filtered through a Celite plug. The solid residue was washed with Et_2O (3×30 mL). The aqueous phase was extracted with Et_2O (20 mL). The combined ether layers were washed with brine (30 mL) and dried with Na_2SO_4. The solvent was evaporated affording crude **1** (4.82 g, 99%) as a pale yellow solid (m.p. 59−61 °C) sufficiently pure for further reactions. Crystallization from MeOH gave pure **1** (4.47 g, 92%) as a white solid (m.p. 63−64 °C). − ^1H NMR ($CDCl_3$): $\delta = 4.00$ (s, 3 H), 7.97 (br. s, 1 H), 8.48 (br. s, 2 H). − ^{13}C NMR ($CDCl_3$) $\delta = 53.1$, 105−120 (m, C_8F_{17}), 129.4 (t, $J_{C-F} = 6$ Hz), 130.7 (t, $J_{C-F} = 24$ Hz), 131.5 (t, $J_{C-F} = 6$ Hz), 132.2, 164.3. − ^{19}F NMR ($CDCl_3$): $\delta = -81.4$ (t, $J = 10$ Hz, 3 F), −111.7 (t, $J = 14$ Hz, 2 F), −121.7 (br. s, 2 F), −122.4 (br. s, 6 F), −123.3 (br. s, 2 F), −126.7 (br. s, 2 F). − $C_{24}H_6F_{34}O_2$ (972.11): calcd. C 29.65, H 0.62; found C 29.62, H 0.66.

Benzyl Alcohol 2: A solution of crude ester **1** (4.86 g, 5 mmol) in dry Et_2O (70 mL) was added to a suspension of $LiAlH_4$ (0.26 g, 7.5 mmol) in dry Et_2O (10 mL). This mixture was stirred at room temp. under N_2 for 8 h, before EtOAc (1 mL) was added. After 15 min, H_2SO_4 (10%, 1 mL) was carefully dropped into the stirred mixture, which was stirred for a further 20 min. The upper organic phase was removed and the aqueous phase was extracted with Et_2O (3×20 mL). The combined ether layers were washed with brine (30 mL) and dried with Na_2SO_4. Evaporation of the solvent afforded a pale yellow solid (m.p. 96−98 °C) that was recrystallized from hexane to give pure **2** (4.25 g, 90%) as a white solid (m.p. 101−102 °C). − ^1H NMR ($CDCl_3$): $\delta = 1.92$ (br. s, 1 H), 4.88 (s, 2 H), 7.74 (br. s, 1 H), 7.84 (br. s, 2 H). − ^{13}C NMR ($CDCl_3$): $\delta = 64.1$, 105−120 (m, C_8F_{17}), 124.9 (t, $J_{C-F} = 6$ Hz), 128.7 (t, $J_{C-F} = 6$ Hz), 130.8 (t, $J_{C-F} = 23$ Hz), 143.5. − ^{19}F NMR ($CDCl_3$): $\delta = -81.3$ (t, $J = 10$ Hz, 3 F), −111.1 (t, $J = 13$ Hz, 2 F), −121.7 (br. s, 2 F), −122.4 (br. s, 6 F), −123.3 (br. s, 2 F), −126.7 (br. s, 2 F). − $C_{23}H_6F_{34}O$ (944.10): calcd. C 29.26, H 0.64; found C 29.31, H 0.65.

Benzaldehyde 3: MnO_2 (4.87 g, 56 mmol) was added to a solution of alcohol **2** (2.63 g, 5 mmol) in boiling toluene (100 mL). The stirred mixture was heated at reflux for 12 h in a Dean−Stark apparatus. The solid was filtered off, washed with Et_2O (100 mL) and the combined liquid phase was concentrated under reduced pressure. The solid residue was purified by column chromatography (silica gel, light petroleum ether/Et_2O, 95:5), affording pure **3** (2.22 g, 73%) as a colourless solid (m.p. 75−76 °C). − ^1H NMR ($CDCl_3$): $\delta = 8.05$ (br. s, 1 H), 8.32 (br. s, 2 H), 10.15 (s, 1 H). − ^{13}C NMR ($CDCl_3$): $\delta = 105-118$ (m, C_8F_{17}), 130.8 (t, $J_{C-F} = 6$ Hz), 131.6 (t, $J_{C-F} = 6$ Hz), 132.0 (t, $J_{C-F} = 24$ Hz), 137.7, 189.2. − ^{19}F NMR ($CDCl_3$): $\delta = -81.4$ (t, $J = 10$ Hz, 3 F), −111.6 (t, $J = 14$ Hz, 2 F), −121.5 (br. s, 2 F), −122.3 (br. s, 6 F), −123.2 (br. s, 2 F), −126.6 (br. s, 2 F). − $C_{23}H_4F_{34}O$ (942.08): calcd. C 29.32, H 0.43; found C 29.30, H 0.46.

Tetraarylporphyrin 4: A solution of aldehyde **3** (0.94 g, 1 mmol), pyrrole (0.07 g, 1 mmol) and $BF_3{\cdot}Et_2O$ (0.04 g, 0.3 mmol) in $CF_2ClCFCl_2$ (100 mL), was stirred at room temp. for 7 h. After addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 0.19 g, 0.75 mmol), the reaction mixture was stirred for 2 h. Et_3N (0.5 mL) was then added, and the solvent evaporated. The residue was washed with MeOH (20 mL), CH_2Cl_2 (20 mL) and hexane (20 mL) and purified by column chromatography (silica gel, $CF_2ClCFCl_2$) affording the title compound **4** as a dark purple solid (0.11 g, 20%) which is insoluble in organic solvents. − ^1H NMR ($CF_2ClCFCl_2$, ext. ref. [D_6]benzene): $\delta = -2.85$ (s, 2 H), 8.36 (s, 4 H), 8.72 (s, 8 H), 8.77 (s, 8 H). − UV/Vis ($CF_2ClCFCl_2$): $\lambda_{max} = 413$ nm ($\varepsilon = 7.2 \times 10^4$ dm^3 mol^{-1} cm^{-1}). − MS (FAB^+) for $C_{108}H_{22}F_{136}N_4$; *m/z* (%): 3959 (100). − $C_{108}H_{22}F_{136}N_4$ (3958.58): calcd. C 32.76, H 0.56, N 1.41; found C 32.80, H 0.59, N 1.36.

(Perfluoroalkyl)phthalonitrile 5: Activated copper bronze (0.94 g, 15 mmol)[27] was added to a solution of 1,2-dicyano-4-iodobenzene (1.02 g, 4 mmol)[13] in dry DMSO (6 mL) in a Schlenk vessel. The stirred suspension was warmed to 110 °C and purged with N_2. *n*-Perfluorooctyl iodide (2.46 g, 4.5 mmol) was added dropwise to the stirred suspension over 10 min. After 3 h, the suspension was cooled to room temp., and H_2O (20 mL) and Et_2O (50 mL) were added. The solid was removed by filtration through a Celite plug and washed with Et_2O (3×15 mL). The aqueous phase was extracted with Et_2O (20 mL). The combined ether layers were washed with brine (30 mL) and dried with Na_2SO_4. The solvent was evaporated and the residue purified by column chromatography (light petroleum ether/Et_2O, 4:1), affording the title compound as a white solid (0.98 g, 45%). − M. p. 112−113 °C. − ^1H NMR ($CDCl_3$): $\delta = 7.95-7.99$ (m, 2 H), 8.01−8.03 (m, 1 H). − ^{13}C NMR ($CDCl_3$): $\delta = 105-120$ (m), 131.9 (t, $J = 6$ Hz), 132.4 (t, $J = 6$ Hz), 134.4, 134.7 (t, $J = 22$ Hz). − ^{19}F NMR ($CDCl_3$): $\delta = -81.2$ (t, $J = 10$ Hz, 3 F), −112.3 (t, $J = 14$ Hz, 2 F), −121.6 (br. s, 4 F), −122.3 (br. s, 4 F), −123.2 (br. s, 2 F), −126.6 (br. s, 2 F). − $C_{16}H_3F_{17}N_2$ (546.11): calcd. C 35.19, H 0.55, N 5.13; found C 35.23, H 0.60, N 5.13.

Co^{II} Complex of Phthalocyanine 6: 1,2-Dicyano-4-(*n*-perfluorooctyl)benzene (**5**) (2.18 g, 4 mmol) and finely divided cobalt metal (1.47 g, 2.5 mmol) were placed in a tightly closed, heavy-wall Pyrex tube and slowly heated to 180 °C. After 4 h, the dark, melted mixture was heated at 250 °C for 12 h. After cooling to room temp. the crude mixture was extracted with *n*-perfluorooctane (50 mL). The deep-blue solution was washed with toluene (3×20 mL) and CH_2Cl_2 (20 mL), and concentrated to dryness. The solid residue was warmed to 130 °C under vacuum, thus eliminating volatile byproducts. Co-**6** (0.27 g, 12%) was obtained as a blue solid. − UV/Vis ($CF_2ClCFCl_2$): $\lambda_{max} = 654$ nm ($\varepsilon = 4.0 \times 10^4$ dm^3 mol^{-1} cm^{-1}), 614 nm ($\varepsilon = 3.0 \times 10^4$ dm^3 mol^{-1} cm^{-1}), 318 nm ($\varepsilon = 4.7 \times 10^4$ dm^3 mol^{-1} cm^{-1}). − MS (FAB^+) for $C_{64}H_{22}F_{68}N_8$; *m/z* (%): 2244 (100). − $C_{64}H_{12}CoF_{68}N_8$ (2243.38): calcd. C 34.27, H 0.54, N 4.99; found C 34.44, H 0.81, N 4.75.

General Procedure for the Aerobic Epoxidation of Sulfides Under Fluorous Biphasic Conditions: Reactions were carried out in the dark in a 20-mL Schlenk vessel connected to a gas burette charged with O_2 (250 mL). The Schlenk vessel was placed in a thermoregulated bath maintained at 20 ± 0.2 °C and was then charged with: (i) a CH_2Cl_2 solution of the substrate (0.5 M, 2 mL); (ii) a solution of the catalyst in *n*-perfluorooctane (2.9×10^{-4} M, 3.5 mL). The two-phase mixture was magnetically stirred at 1300 ± 50 rpm in order to ensure optimum contact between the organic and the fluorous phase. 2,2-Dimethylpropanal (0.3 mL, 3 mmol) was added to the mixture over 20 min. After 4 h, the fluorous layer was recovered, washed with CH_2Cl_2 (2 × 1 mL) and reused in further runs. The combined CH_2Cl_2 layers were washed with aqueous $NaHCO_3$ (5%, 1 mL), brine (1 mL) and dried ($MgSO_4$). The solvent was evaporated under reduced pressure, affording a residue containing only the starting product plus sulfoxide and sulfone in variable amounts, as determined by ^1H NMR spectroscopy.

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