Site-Isolated Porphyrin Catalysts in Imprinted Polymers

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Abstract: A *meso*-tetraaryl ruthenium porphyrin complex having four polymerizable vinylbenzoxy groups (**2**) has been synthesized by reaction of pyrrole with 4-(vinylbenzoxy)benzaldehyde and subsequent metalation with [Ru₃(CO)₁₂]. The porphyrin complex was immobilized by copolymerization with ethylene glycol dimethacrylate. The resulting polymer **P2** was found to catalyze the oxidation of alcohols and alkanes with 2,6-dichloropyridine *N*-oxide without activation by mineral acids. Under similar conditions, the homogeneous catalyst **2** was completely inefficient. By using diphenylamino-methane and 1-aminoadamantane as coordinatively bound templates during the polymerization procedure, the molecularly imprinted polymers **P3** and **P4** have been synthesized. Compared with the polymer **P2**, the imprinted catalysts displayed a significantly increased activity with rate enhancements of up to a factor of 16.

Keywords: heterogeneous catalysis · molecular imprinting · oxidation · porphyrin complexes · ruthenium

Introduction

Starting with the pioneering work of Hirobe et al.,[1] ruthenium–porphyrin catalysts in conjunction with 2,6-disubstituted pyridine *N*-oxides as the oxidant have been widely used for oxygen-transfer reactions.[2] Recent developments include the utilization of dendritic ruthenium porphyrins,[3] the extension to asymmetric reactions using chiral porphyrin complexes,[4] the investigation of new substrates such as alkanes[5] or amides,[6] and the utilization of alternative oxidation agents such as N_2O[7] or O_2.[8] Generally, Ru–carbonyl complexes of the formula [Ru(por)(CO)] (por = *meso*-tetra-(aryl)porphyrin) are used as catalyst precursors. They are easily accessible from [Ru₃(CO)₁₂] and the free-base porphyrin. Alternatively, dichloro or dioxo complexes of the formula [Ru(X)₂(por)] (X = O, Cl) have been employed.[2]

Immobilized ruthenium–porphyrin catalysts have been synthesized by encapsulation in mesoporous molecular sieves[9] or sol–gel silica,[10] by electropolymerization of complexes with fluorene groups,[11] and by covalent attachment to Merrifield resins.[12] Good catalytic activity was observed for these systems although problems with leaching were encountered in some cases.[9b,10] We have recently reported a supported Ru–porphyrin catalyst, which was obtained by copolymerization of [Ru{*meso*-tetra(styryl)porphyrin}(CO)] with an excess of ethylene glycol dimethacrylate (EGDMA).[13] The resulting mesoporous, highly cross-linked polymer was found to efficiently catalyze the epoxidation of olefins as well as the oxidation of alkanes and secondary alcohols. Herein, we describe the synthesis of a new EGDMA copolymer **P2**, which is based on the ruthenium complex **2** having four polymerizable 4-vinylbenzoxy groups (Scheme 1). For the oxidation of secondary alcohols and alkanes with 2,6-dichloropyridine *N*-oxide (Cl₂pyNO), this polymeric catalyst was found to be by far superior to the homogeneous counterpart. Furthermore, the activity of the supported catalyst could be increased significantly by using the technique of molecular imprinting.[14,15]

Results and Discussion

In order to obtain the metallomonomer **2**, we first synthesized the free-base porphyrin **1** by reaction of pyrrole with 4-(vinylbenzoxy)benzaldehyde in propionic acid under reflux (Scheme 1).[16] After cooling, the product precipitated as a purple, microcrystalline material in a 12% yield. Compared to other procedures for the preparation of porphyrin ligands with polymerizable acrylate[17,18] or styrene[13] side chains, this new method has the advantage that the required aldehyde can be easily synthesized from commercially available starting materials.[19] The porphyrin is then obtained in

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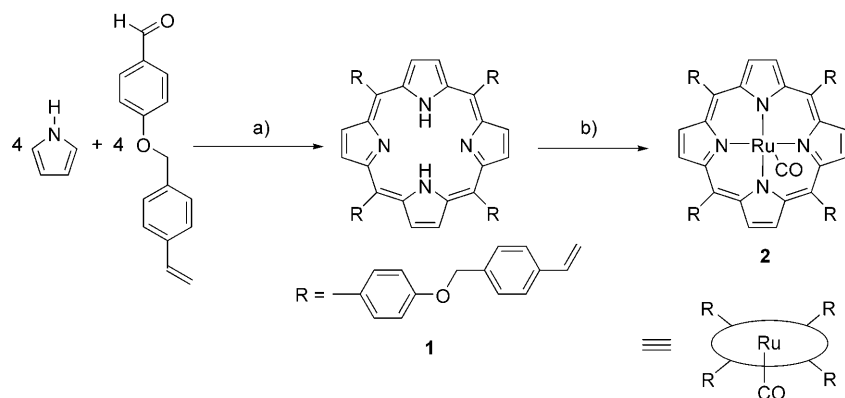
Scheme 1. Synthesis of the tetraarylporphyrin **1** and its {Ru(CO)} complex **2**: a) 142 °C, $CH_3CH_2CO_2H$; b) 111 °C, $[Ru_3(CO)_{12}]$, styrene, toluene.

of the metallomonomer **2**. As the oxidant, Cl_2pyNO was employed. The results are summarized in Table 1.

For all alcohols that were investigated, good to excellent conversions to the corresponding ketones were observed after 6 h. Even for the least reactive substrate, indanol, a quantitative conversion was determined after 24 h. It is important to note that for the homogeneous oxidation of alcohols and alkanes with [Ru(por)(CO)] cata-

a one-step procedure with no chromatographic purification steps being required.

Following a standard procedure,[20] the free-base porphyrin **1** was metalated by reaction with $[Ru_3(CO)_{12}]$ to give complex **2** in a 70 % yield. An excess of styrene was added as a "hydrogen scavenger" because previous results had shown that reduction of the vinyl groups can occur during the reaction with $[Ru_3(CO)_{12}]$.[13] The infrared spectrum of complex **2** showed a characteristic carbonyl band at $\nu_{CO} = 1929$ cm^{-1}. Compared with the free ligand **1**, a hypsochromic shift of 7.3 nm was found for the Soret band of **2**.

Complex **2** was subsequently copolymerized with EGDMA (**2**/EGDMA = 1:400) in the presence of chloroform as the porogen (Scheme 2). To initiate the reaction, 2,2′-azobis(isobutyronitrile) (AIBN) was employed. After 24 h, a dark-red polymer (**P2**) was obtained, which was
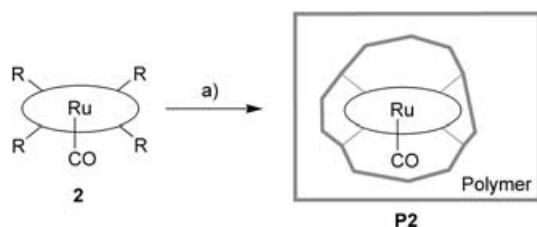
Scheme 2. Synthesis of the polymeric catalyst **P2**: a) 65 °C, CHCl$_3$, EGDMA, AIBN.

Table 1. Catalytic oxidation of secondary alcohols with the polymeric catalyst **P2**.[a]

| Substrate	Product	Conversion [%]
		>99
		91
		91
		80 (99)[b]
		89
		96
		82

[a] The reactions were performed in benzene at 55 °C with a substrate/Cl_2pyNO/catalyst molar ratio of 200:250:1. The conversion was determined after 6 h by gas chromatography. [b] Conversion after 24 h.

ground in a mortar. The nearly colorless washing solutions indicated a quantitative incorporation of the metallomonomer **2** in the polymeric EGDMA matrix. A BET surface area of 409 m^{2}g^{-1} and an average pore size of 54 Å was determined for **P2**.[21] These data suggested that the Ru complexes in the interior of the polymeric particles are accessible for catalytic transformations.

To evaluate the catalytic properties of the polymer **P2**, we investigated the oxidation of secondary alcohols at 55 °C using 0.5 mol % Ru. The amount of polymer that was required was calculated based on a quantitative incorporation

lysts, it was reported that the addition of strong mineral acids such as HCl or HBr was crucial for the success of the reaction[4d,5e] unless a highly fluorinated[5c] or a sterically very encumbered porphyrin ligand[5a] was employed. In accordance with these observations, only a very low yield (<2 %) of ketones was obtained when complex **2** was used as a homogeneous catalyst instead of the polymer **P2** under otherwise identical conditions. It seems likely that a site-isolation effect is responsible for the significantly increased activity of the polymer **P2**. In fact, it has been reported that inactive dimeric μ-oxo–Ru^{IV} complexes may form rather

easily from the catalytically relevant [RuO(por)] and [Ru(O)$_2$(por)] species.[22, 23]

Next we were interested in whether we could improve the activity and selectivity of the immobilized catalyst by using the technique of molecular imprinting. The key step of molecular imprinting with a transition-metal catalyst is the utilization of a pseudosubstrate, which is coordinatively bound to the active site of the catalyst during the polymerization procedure.[15] After polymerization, the pseudosubstrate is selectively cleaved off, thereby generating an imprint ("substrate pocket") in direct proximity to the active site. So far, molecular imprinting studies with porphyrin metallomonomers have focused on ligand-recognition studies[18] and only recently a report about a molecularly imprinted hemin catalyst has been published.[24]

For [Ru(por)(CO)] complexes it was known that they form stable adducts with N-donor ligands.[2a, 25] We thus investigated whether primary amines could be used as pseudosubstrates. When one equivalent of aminodiphenylmethane was added to complex **2** in [D$_6$]acetone, the immediate formation of the new complex **3** was observed by ^{1}H NMR spectroscopy (Figure 1, Scheme 3). For the signal of the pyr-
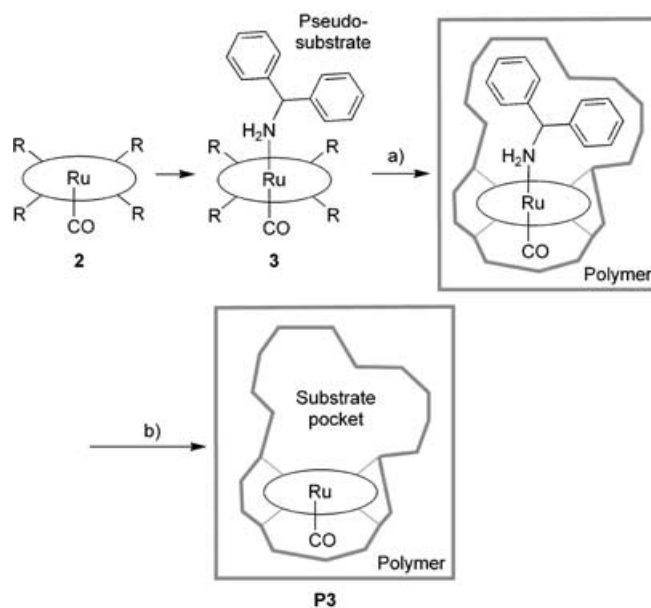
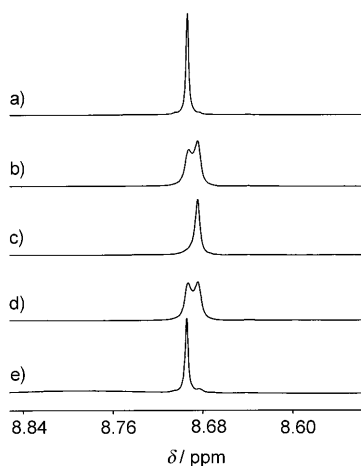Scheme 3. Synthesis of the imprinted polymer **P3**: a) 65 °C, CHCl$_3$, EGDMA, AIBN; b) CF$_3$CO$_2$H.

Figure 1. Part of the ^{1}H NMR spectrum (400 MHz, [D$_6$]acetone) highlighting the signals of the pyrrole-CH groups of a) complex **2**, b) complex **2**+(0.5 equiv of H$_2$NCHPh$_2$), c) complex **2**+(1 equiv of H$_2$NCHPh$_2$), d) complex **2**+(1 equiv of H$_2$NCHPh$_2$)+(0.5 equiv CF$_3$COOH), and e) complex **2**+(1 equiv of H$_2$NCHPh$_2$)+(excess of CF$_3$COOH).

role-CH proton, for example, a shift towards higher field was observed during the progressive addition of amine to the ruthenium–porphyrin complex. The complexation of the amine could be cleanly reversed by addition of trifluoroacetic acid (Figure 1). These results suggested that aminodiphenylmethane could indeed be employed to create a substrate pocket next to the ruthenium center.

The imprinted polymer **P3** was synthesized as outlined in Scheme 3. Addition of one equivalent of aminodiphenylmethane to complex **2** gave the adduct **3**, which was copolymerized with EGDMA using chloroform as the porogen. The reaction conditions (initiator, temperature, EGDMA

ratio) were the same as those used for **P2** in order to allow for a direct evaluation of the imprinting effect. The pseudosubstrate was cleaved off by washing the polymer with a solution of CF$_3$CO$_2$H in acetone. As the decomplexation step was fast and quantitative for complex **3** in homogeneous solution, it was expected that the CF$_3$CO$_2$H treatment would also be effective for the polymer **P3**. This was indirectly confirmed by results of the catalysis experiments as outlined below.

First, the oxidation of diphenylmethane was investigated, a substrate which displays a strong structural similarity to the pseudosubstrate. For both polymeric catalysts, the time course of the reaction was examined by removing samples from the reaction mixture, which were analyzed by gas chromatography. The imprinted catalyst **P3** was found to be significantly more active than the nonimprinted polymer **P2**: the initial rate, calculated from the conversion of diphenylmethane after 6 h, was 6.4 times higher for polymer **P3** than for polymer **P2** (Figure 2). For both reactions, the main oxidation product was benzophenone with small amounts of diphenylmethanol being present, in particular at the beginning of the reaction. This points to the fact that the reaction proceeds in two steps and that the alcohol oxidation is considerably faster than the alkane oxidation. A slight induction period was evident from the time course of the reactions. This was not unexpected as the {Ru(CO)} complexes are catalyst precursors from which the catalytically active Ru=O species are generated by decarbonylation.[2]

When 2 equivalents of diphenylaminomethane were added to the reaction mixture, the rates dropped to zero indicating that the amine acts as a catalyst poison. Accordingly, only very low conversions were observed when the imprinted polymer **P3** was not washed with trifluoroacetic acid
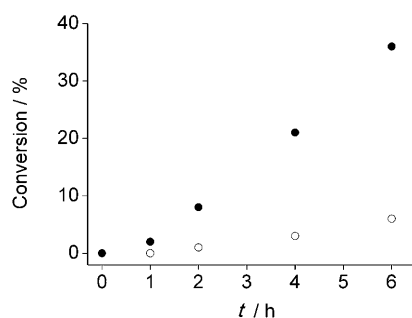
Figure 2. Oxidation of diphenylmethane by Cl$_2$pyNO with the nonimprinted catalyst **P2** (○) or with the imprinted catalyst **P3** (●). The reactions were performed in benzene at 35°C with a substrate/Cl$_2$pyNO/catalyst molar ratio of 100:250:1. The data points represent averaged values from two independent experiments, the errors are less than 1%.

prior to being used as a catalyst. These results clearly excluded the possibility that residual pseudosubstrate in the polymer **P3** was responsible for the increased activity. In order to verify that the difference in activity between **P2** and **P3** was not due to the washing step with trifluoroacetic acid, polymer **P2** was likewise treated with CF$_3$CO$_2$H/acetone. This treatment, however, had no effect on the catalytic activity of **P2** as evidenced by control experiments with a second batch of **P2**, which was exclusively washed with acetone.

The rate enhancement due to molecular imprinting was found to depend strongly on the reaction temperature and the nature of the substrate. When the oxidation of diphenylmethane was performed at 55°C, the difference between the rates of reactions with the catalysts **P2** and **P3** was only a factor of 4.3. When the temperature was lowered to 20°C, on the other hand, the difference increased to a factor of 16.3 (Figure 3). A similar temperature dependence has been
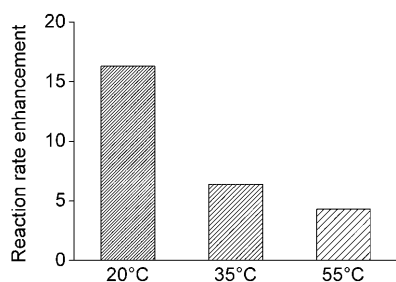

Figure 3. Rate enhancements for the oxidation of diphenylmethane with the imprinted catalyst **P3** when compared to the nonimprinted catalyst **P2** at three different temperatures. The reactions were performed in benzene with a substrate/Cl$_2$pyNO/catalyst molar ratio of 100:250:1. The rate enhancements were calculated from the conversions after 6 h.

reported for the binding affinities of some molecularly imprinted polymers;[26] this was attributed to the increased flexibility of the polymer backbone at higher temperatures, which reduces the structural integrity of the imprinting site,

and an analogous explanation can be put forward in the present case.

Similarly, the nature of the substrate has a pronounced effect on the relative reaction rates. This is evident when the results for the oxidation of diphenylmethanol, diphenylmethane, and anthracene are compared (Figure 4). All three
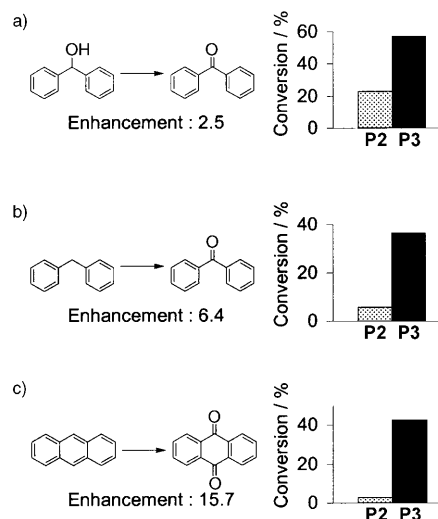

Figure 4. Conversions and rate enhancements for the oxidation of three different substrates with the imprinted catalyst **P3** compared with the nonimprinted catalyst **P2**. The reactions were performed in benzene at 35°C with a substrate/Cl$_2$pyNO/catalyst molar ratio of a) 1000:1250:1, values after 1 h, b) 200:500:1, values after 6 h, and c) 100:500:1, values after 6 h.

substrates have a size and shape which is related to that of the pseudosubstrate diphenylaminomethane. For diphenylmethanol, however, a rate enhancement due to imprinting of a factor of 2.5 was observed, whereas factors of 6.4 and 15.7 for the oxidation of diphenylmethane and anthracene, respectively, were determined. This difference can be explained by the fact that the oxidation of diphenylmethane and anthracene requires two- or multiple oxidation steps, respectively. As the imprinting effect will manifest itself in each step, higher rate enhancements are indeed expected for diphenylmethane and in particular for anthracene.

To further probe the selectivity of the polymeric catalysts, we performed competition experiments with equimolar amounts of two substrates, which undergo the same oxidation step (alcohol→ketone), but which differ in terms of their size and shape. Previous results with imprinted ruthenium catalysts for transfer hydrogenations had shown that molecular imprinting may result in an increased selectivity for the substrate, the structure of which most closely resembles that of the pseudosubstrate.[27] For the imprinted catalyst **P3**, however, the rate enhancements relative to **P2** were similar for all alcohol pairs tested. A moderate substrate selectivity was found when the imprinted polymer **P4** was employed. **P4** was generated by using 1-aminoadamantane instead of aminodiphenylmethane as the pseudosubstrate. In competi-

tion experiments with the substrate pair 2-adamantanol/2-octanol and the catalyst **P2**, the two substrates were oxidized with the same rates but in reactions with the imprinted catalyst **P4**, a clear preference for adamantanol was observed (Figure 5). The selectivity, as calculated from the rel-
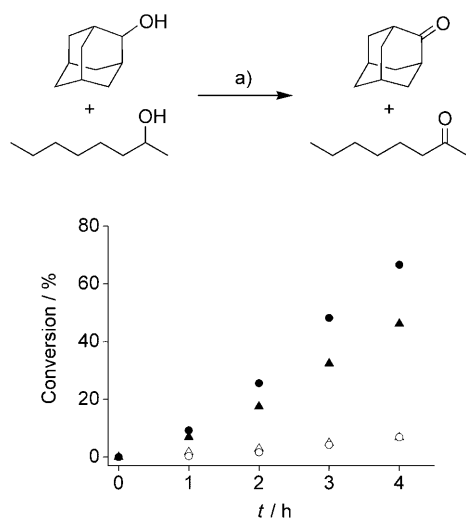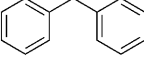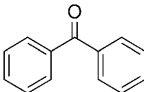
Figure 5. Oxidation of 2-adamantanol (circles) and 2-octanol (triangles) by Cl₂pyNo catalyzed with the nonimprinted catalyst **P2** (open symbols) or the imprinted catalyst **P4** (closed symbols). Reaction conditions: a) benzene, RT, 2-adamantanol/2-octanol/Cl₂pyNO/catalyst (molar ratio 100:100:250:1), and 1 mol% **P2** or **P4**. The data points represent averaged values from two independent experiments, the errors are less than 1%.

ative conversion after 4 h,[28] was found to be 1.0 for **P2** and 1.4 for **P4**.

The results indicated that the imprinting procedure had a strong effect on the catalytic activity of the porphyrin-containing polymers (in particular for substrates which undergo multiple consecutive oxidation steps) but only a small effect on the selectivity within the same class of substrates. This might be due to the fact that the pseudosubstrate was attached to the metallomonomer by a single coordinative bond. Consequently, the pseudosubstrate had a high conformational flexibility during the imprinting procedure, 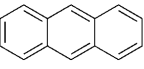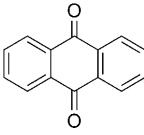which resulted in large but structurally ill-defined substrate pockets. This is in agreement with studies of Spivak et al. which highlight the importance of multipoint interactions during the formation of the molecularly imprinted polymer.[29]

Despite the moderate selectivity, the imprinted polymers show clear advantages in terms of catalytic performance. This was further substantiated by oxidation reactions with simple hydrocarbon substrates. Using only 1 mol% of the imprinted polymer **P3** and no activating mineral acid, good conversions were observed for most substrates investigated (Table 2). For the nonimprinted polymer **P2**, on the other hand, only one substrate—tetralon—displayed a conversion of more than 50% under similar conditions. As found for the oxidation of alcohols, negligible conversions of less than 2% were obtained in reactions with the homogeneous catalyst **2**.

Table 2. Catalytic oxidation of alkanes with the nonimprinted catalyst **P2** and the imprinted catalyst **P3**.[a]

Substrate	Product	Conv. [%] **P2**	Conv. [%] **P3**
		48	>99
		13	62
		76	98
		49	96
		6	38
		12	87

[a] The reactions were performed in benzene at 55°C with a substrate/Cl₂pyNO/catalyst molar ratio of 100:250:1 (100:500:1 for anthracene). The conversion (conv.) was determined after 24 h by gas chromatography.

Conclusion

A ruthenium–porphyrin complex has been incorporated into a mesoporous, highly cross-linked polymer by copolymerization with a large excess of EGDMA. Due to site isolation of the complexes within the rigid polymeric matrix it was possible to use the polymer as an efficient catalyst for the oxidation of alcohols and alkanes. This is in sharp contrast to the corresponding homogeneous catalyst, which was completely ineffective for these reactions. The utilization of an EGDMA polymer as the solid support allowed manipulation of the microenvironment of the catalyst by using the technique of molecular imprinting. It was thus possible to increase the activity of the catalyst by more than one order of magnitude by carrying out the polymerization in the presence of aminodiphenylmethane as a template. This increase in activity is significant given the fact that the imprinted and the nonimprinted polymer contain the same amount of ruthenium complexes with an identical first coordination sphere. Highly cross-linked organic polymers therefore represent ideal supports for immobilized Ru–porphyrin catalysts: they not only prevent intermolecular deactivation reactions but also allow manipulation of the microenvironment of the catalyst in a controlled fashion. It is conceivable that future research along these lines may lead to porphyrin catalysts with an even more defined substrate pocket. This could be achieved by using secondary interactions (e.g., hy-

drogen bonding) between the pseudosubstrate and the polymeric matrix. Attempts in this direction are currently being pursued in our laboratory.

Experimental Section

General: All complexes were synthesized under an inert atmosphere of dinitrogen using standard Schlenk techniques. The solvents (analytical grade purity) were degassed and stored under a dinitrogen atmosphere. 4-(Vinylbenzoxy)benzaldehyde was synthesized according to the literature.[19] Ethylene glycol dimethacrylate (EGDMA) was purchased from Aldrich. It was washed with NaOH (1 M) and saturated NaCl solution and dried with Na_2SO_4. After filtration, the monomer was distilled under reduced pressure. AIBN was purchased from Fluka and was re-crystallized from methanol before use. 2,6-Dichloropyridine N-oxide was purchased from Aldrich. Polymerizations were performed in a glovebox containing less than 1 ppm of oxygen and water. The ^{1}H and ^{13}C spectra were recorded on a Brucker Advance DPX 400 instrument using the residual protonated solvents as internal standards. The spectra were recorded at room temperature. The GC analyses were performed with a Varian 3800 gas chromatograph using a CP-Sil 8 CB column (30 m). The BET measurements were carried out by Quantachrome GmbH, Odelzhausen, on a Quantachrome Autosorb-3 instrument. Prior to the measurements, the samples were dried under vacuum at 100 °C for 2 h.

Synthesis of porphyrin 1: To propionic acid (100 mL) at reflux (b.p. 142 °C), pyrrole (1.9 mL, 27.3 mmol) and 4-(vinylbenzoxy)benzaldehyde (6.5 g, 27.3 mmol) were added and stirred for 30 min at reflux. After cooling, the violet precipitate was filtered off and washed with methanol (200 mL) and pentane (50 mL) and dried under vacuum. Yield: 920 mg (12 %); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = -2.77$ (s, 2H; NH), 5.31 (d, $^3J =$ 11 Hz, 4H; CH=CH$_2$), 5.35 (s, 8H, OCH$_2$), 5.83 (d, $^3J = 18$ Hz, 4H; CH=CH$_2$), 6.80 (dd, $^3J = 11$, $^3J = 18$ Hz, 4H; CH=CH$_2$), 7.35 (d, $^3J = 8$ Hz, 8H; RC$_6$H$_4$R′), 7.59 (m, 16H; RC$_6$H$_4$R′), 8.12 (d, $^3J = 8$ Hz, 8H; RC$_6$H$_4$R′), 8.86 ppm (s, 8H; pyrrole-H); ^{13}C NMR: not determined due to low solubility; UV/Vis (CHCl$_3$): λ_{max} (ε in cm^{2}mol^{-1}) = 423 (457000), 519 (35000), 551 (28000), 592 (21000), 650 nm (20000); MS (FAB$^+$) m/z: 1143.3 [M]$^+$; elemental analysis calcd (%) for C$_{80}$H$_{62}$N$_4$O$_4$ (1143.39): C 84.04, H 5.47, N 4.90; found: C 84.04, H 5.56, N 4.82.

Synthesis of complex 2: A mixture of toluene (150 mL), porphyrin **1** (400 mg, 0.35 mmol), [Ru$_3$(CO)$_{12}$] (293 mg, 0.46 mmol), and styrene (4.0 mL, 42.3 mmol) was protected from light and heated to reflux for 48 h. The solvent was evaporated and the product was washed with hexane and then purified by column chromatography (SiO$_2$; first CHCl$_3$ then CHCl$_3$/THF 99:1). The product was dissolved in a minimal amount of chloroform and precipitated in hexane. Removal of the solvent and drying in vacuum yielded the product. Yield: 330 mg (70 %); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 5.32$ (br, 12H; OCH$_2$ and CH=CH$_2$), 5.83 (d, $^3J = 18$ Hz, 4H; CH=CH$_2$), 6.80 (dd, $^3J = 11$, $^3J = 18$ Hz, 4H; CH=CH$_2$), 7.31 (m, 8H; RC$_6$H$_4$R′), 7.59 (m, 16H; RC$_6$H$_4$R′), 8.12 (m, 8H; RC$_6$H$_4$R′), 8.86 ppm (s, 8H; pyrrole-H); ^{13}C NMR (400 MHz, CDCl$_3$): $\delta = 70.17$, 113.07, 113.10, 114.17, 121.51, 126.47, 127.94, 131.73, 134.72, 135.25, 135.30, 136.47, 137.47, 144.38, 158.06, 181.75 ppm (CO); IR: $\tilde{\nu}_{CO} =$ 1929 cm^{-1}; UV/Vis (CHCl$_3$): λ_{max} (ε in cm^{2}mol^{-1}) = 415 (229000), 531 (31000), 565 nm (17000); MS (FAB$^+$) m/z: 1270.3 [M−THF]$^+$; elemental analysis calcd (%) for C$_{81}$H$_{60}$N$_4$O$_5$Ru·THF (1342.56): C 76.04, H 5.11, N 4.17; found: C 76.55, H 4.66, N 4.02.

Synthesis of the polymer P2: EDGMA (2.7 mL, 14.32 mmol) was added to a solution of complex **2** (48 mg, 35.8 µmol) and AIBN (60 mg, 366 µmol) in CHCl$_3$ (2.7 mL) in a 6 mL screw-cap vial. The vial was closed and heated for 24 h at 65 °C. The resulting polymer was ground, treated 3 times with a solution of trifluoroacetic acid in acetone (40 mL, 0.02 M), washed with acetone (3×40 mL), and dried under vacuum. Yield: 2.7 g (95 %). BET surface area: 409 m^{2}g^{-1}; average pore size: 54 Å.

Synthesis of the polymer P3: EDGMA (1.8 mL, 9.55 mmol) was added to a solution of complex **2** (32 mg, 23.8 µmol), the template aminodiphenylmethane (4.36 mg, 23.8 µmol), and AIBN (40 mg, 244 µmol) in CHCl$_3$

(1.8 mL) in a 6 mL screw-cap vial. The vial was closed and heated for 24 h at 65 °C. The resulting polymer was ground, treated 3 times with a solution of trifluoroacetic acid in acetone (20 mL, 0.02 M), washed with acetone (3×20 mL), and dried under vacuum. Yield: 1.9 g (> 98 %). BET surface area: 357 m^{2}g^{-1}; average pore size: 58 Å.

Synthesis of the polymer P4: The synthesis was performed analogous to that of **P3** but using 1-aminoadamantane instead of aminodiphenylmethane.

Catalytic oxidation of alcohols: A suspension/solution of polymer **P2**/complex **2** (20.0 mg/0.33 mg, 0.248 µmol Ru) and Cl$_2$pyNO (10.2 mg, 62 µmol) in benzene (1.0 mL) was stirred for 5 min. The reaction was then started by addition of the substrate (49.6 µmol) and the Schlenk tube was placed immediately in an oil bath regulated at 55 °C. Samples (50 µL) were removed at regular intervals, filtered (or quenched with pyridine for the homogenous catalysis), and analyzed by GC.

Catalytic oxidation of alkanes: The reactions were performed as described for the oxidation of alcohols but 2.5 equivalents of Cl$_2$pyNO (with respect to the substrate) were added (20.3 mg, 124 µmol).

Acknowledgements

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