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Hybrid materials based on imidazo[4,5-*b*]porphyrins for catalytic oxidation of sulfides

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Abstract. Heterogenized metalloporphyrin catalysts for oxidation reactions are extensively explored in view to improve chemical production. In this work, *meso*-tetraarylporphyrins were immobilized on hydrated mesoporous titanium dioxide ($S_{\text{BET}} = 705 \text{ m}^2 \text{ g}^{-1}$) through carboxylate or phosphonate anchoring groups separated from the macrocycle by the 2-arylimidazole linker fused across one of pyrrolic rings of the macrocycle. Structural characteristics of mesoporous hybrid materials thus obtained and the integrity of immobilized complexes were investigated by different physico-chemical methods. Finally, the catalytic efficiency of the most stable material **Mn(TMPIP)/TiO₂** with the phosphonate anchor was evaluated in the selective oxidation of sulfides to sulfoxides by oxygen in the presence of isobutyraldehyde. The heterogenized complex has shown excellent catalytic activity exhibiting a turnover (TON) of ~ 1100 in a single catalytic run of the sulfoxidation of thioanisole. The catalyst was successfully reused in seven consecutive catalytic cycles.

Keywords: metalloporphyrin, titania, heterogenized catalyst, oxidation.

1. Introduction

Oxidation reactions are key technological processes for converting petroleum-based feedstocks to useful chemicals of a high oxidation state such as alcohols, carbonyl

compounds, and epoxides and are also widely used in synthesis of pharmaceuticals, agrochemicals, and fine chemicals.^{1,2} Among all transformations of organic compounds, the oxidation reactions are especially challenging because they often have low selectivity and require stoichiometric amounts of toxic and hazardous oxidizing reagents such as oxometal oxidants or peracids.³ Thus, these processes are among the most dangerous and pollutant transformations in chemical productions. Development of reactions in which molecular oxygen is used as a terminal oxidant together with a reusable catalyst and a nontoxic solvent are extremely important from both economic and environmental reasons.⁴ It is not surprising that catalytic aerobic oxidation reactions performed with both non-metal and metal catalysts have been received great attention.^{5,6}

In nature, such processes are carried out in highly selective manner by mono- and dioxygenases under mild conditions.^{7,8} This stimulated investigations of biomimetic porphyrin catalysts pioneered by Gloves and co-workers who studied the oxidation of organic compounds by strong oxidants in the presence of iron(III) porphyrinates in the late seventy of the last century.⁹⁻¹¹ Later extensive studies on metalloporphyrin-catalysed oxidation have demonstrated that the catalytic efficiency of manganese(III), ruthenium(III) and cobalt(III) porphyrins can even exceed that of iron(III) complexes in part due to the high stability of these complexes.^{12-14 15,16} Another remarkable feature of metalloporphyrins is that these catalysts are efficient in different types of oxidation processes such as the epoxidation and hydration of alkenes, the hydroxylation of alkanes, the dehydrogenation of amines, and the oxidation of arenes, amines, sulfides, alcohols, and aldehydes and so forth.^{8,17} The reaction rate and selectivity can be controlled varying the nature of the central metal ion and substituents at the periphery of porphyrin macrocycle. The peripheral substituents also influence the catalyst stability and *meso*-tetraarylporphyrins bearing *ortho*-disubstituted aryl residues and electron deficient aryl groups exhibit a high efficiency in part due to their increased chemical stability.^{18,19} Lately, major interest in these reactions appeared when it was shown that metalloporphyrins can catalyse reactions with environment-friendly oxidants such as hydrogen peroxide or molecular oxygen which can be used in the presence of isobutyraldehyde (IBA) as a sacrificial reagent or in photooxidation processes.⁸

Unfortunately, the use of metalloporphyrins in practical organic synthesis is still limited because these catalysts are expensive and often have disappointingly low TON and TOF. It was recognized that heterogenization of homogeneous catalysts significantly increased their efficiency. In fact, solid catalysts based on metalloporphyrins commonly display a higher stability than their homogeneous counterparts because the deactivation of

metalloporphyrin catalysts mainly proceeds through the formation of catalytically inactive dimeric complexes. The catalyst dimerization can be decreased when porphyrin molecules are attached to a solid support in particular through covalent bonding.²⁰ Being heterogenized, the expensive metalloporphyrins can be recovered after reaction completing and reused in the next catalytic cycle. This simplifies the product isolation and could decrease the cost of industrial production. Thus, recent research was mainly focused on preparing efficient heterogenized porphyrin catalysts.²¹

Several different strategies were investigated for immobilization of porphyrin complexes onto inorganic and organic supports,^{22-24 25 26-28} including zeolites,^{29,30} clays,³¹⁻³⁴ silicas,³⁵⁻³⁸ polymers,^{20,39} metal-organic frameworks (MOF)^{21,40-43} and covalent organic frameworks (COF)⁴⁴. Metalloporphyrin catalysts were also grafted onto photoactive anatase and nanocrystalline anatase/hydrozincite composite material using triethoxysilane anchoring group⁴⁵ or electrostatic interactions,⁴⁶ respectively. Surprisingly, photocatalytic decomposition of porphyrins immobilized on these photoactive supports was slow and the materials thus obtained were stable enough to be used as reusable catalysts. Recently, the method for preparation of hybrid materials bearing two porphyrin complexes incorporated into charged layer supports was developed.^{46,47} Most of previously reported heterogenized complexes were efficient as catalysts and a synergetic action of support and transition metal catalysts was observed in some cases.^{42,43,47} It was also shown that immobilization of metalloporphyrin catalysts can switch the chemoselectivity of oxidation reactions.^{46,48}

Porous materials with high surface areas are widely explored in catalysis because they allow to increase catalyst loading and to diminish the influence of physical phenomenon of mass transfer on reaction rates. Different types of porous materials were investigated but all of them have serious drawbacks. Mesoporous silicas commonly display a low chemical stability. MOF and COF bearing catalytic centres in porphyrinic linkers are expensive because a high amount of metalloporphyrins is required for their preparation and drying procedures leading to porous crystalline networks are very troublesome and time-consuming. Microporous zeolites are also inconvenient as solid supports for porphyrins because the size of porphyrin molecules is close to that of most available zeolite Y supercage (~1.3 nm in diameter) and diffusion of organic compounds through zeolite lattice apertures is sterically hindered in these hybrid materials. There is thus a need in more efficient immobilization strategies for preparing porous catalysts based on metalloporphyrins.

In this work, we report grafting porphyrin complexes on the surface of hydrated mesoporous titanium(IV) oxide (TiO_2 , $S_{\text{BET}} = 650\text{--}705 \text{ m}^2 \text{ g}^{-1}$). This cheap and photocatalytically inactive support was recently prepared by us using a non-templating sol-gel process. Our grafting methodology is based on the use of imidazo[4,5-*b*]porphyrins as molecular precursors (Figure 1). This fused porphyrin–heterocycle compounds which were pioneered by Crossley and et al.⁴⁹ were widely studied but were not used for preparation of heterogenized catalysts.⁵⁰ The 2-aryl-imidazole residue is of interest as a linker in synthesis of functional materials because the introduction of different substituents in the aryl residue of this linker is straightforward.^{49,51} This long and rigid spacer provides a perpendicular orientation of the porphyrin ring with respect to the solid surface. The synthetic strategy based the introduction of the 2-arylimidazole residue fused across one pyrrolic ring of the macrocycle opens a way for covalent grafting *meso*-tetraarylporphyrins, in particular their derivatives with sterically hindered *o*-disubstituted aryl groups which are known to be most efficient catalysts for the oxidation reactions.⁵² In this work, this strategy was used for grafting porphyrin catalysts onto titanium dioxide through carboxylate or phosphonate anchoring group as shown in Figure 1. Structural characteristics of mesoporous hybrid materials thus obtained and the integrity of the immobilized molecules were studied by different physico-chemical techniques. Finally, the catalytic efficiency of the most stable material **Mn(TMPIP)/TiO₂** was evaluated in the selective oxidation of sulfides to sulfoxides by molecular oxygen in the presence of IBA. The **Mn(TMPIP)/TiO₂** material has shown an excellent catalytic activity and was successfully reused in seven catalytic cycles.

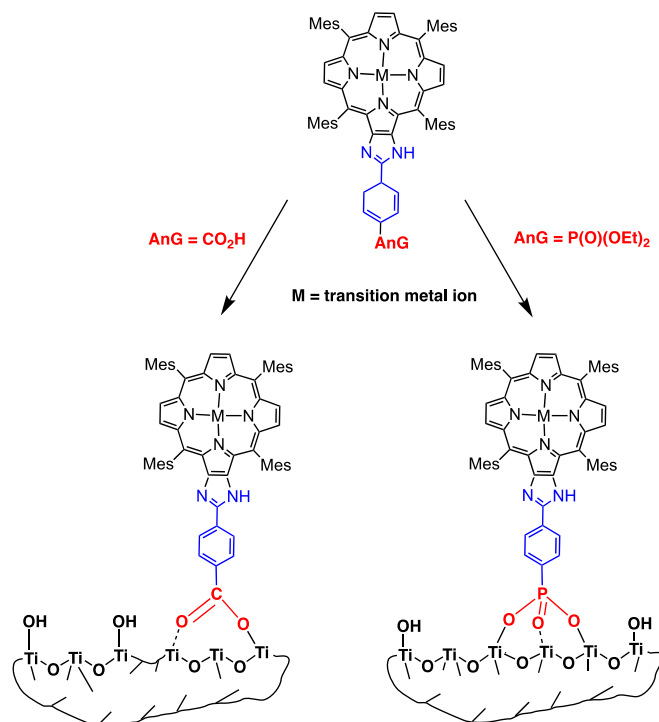
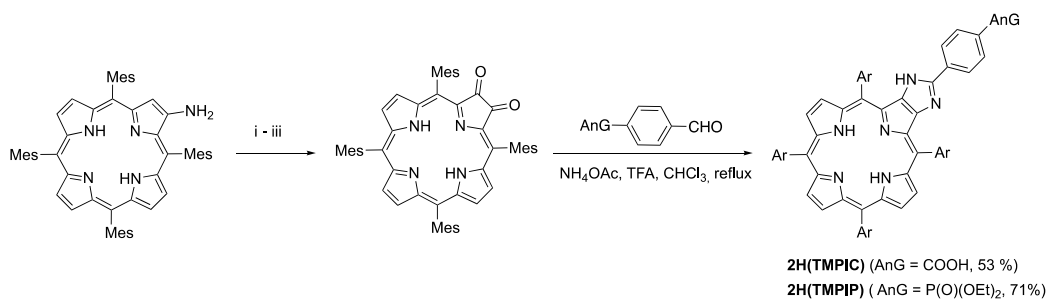


Figure 1. Strategies for immobilization of porphyrin catalysts on a hydrated titania support which were investigated in this work.

2. Results and Discussion

2.1. Synthesis of (2-arylimidazo[4,5-*b*])porphyrinato)manganese(III) chlorides and their characterization

meso-Tetramesityl-substituted imidazo[4,5-*b*]porphyrins were chosen for investigation in this work as their synthesis is reproducible and they can be obtained in a hundred-milligram scale using available laboratory equipment. The free base 2-arylimidazo[4,5-*b*]porphyrins **2H(TMPIC)** and **2H(TMPIP)** bearing carboxylate and phosphonate anchoring groups on the aryl substituent were prepared through the oxidation of corresponding β -aminoporphyrin to 2,3-dioxochlorin followed by the Debus–Radziszewski condensation of this dione with aromatic aldehydes (Scheme 1).⁵¹



Scheme 1. Synthesis of **2H(TMPIC)** and **2H(TMPIP)**. General conditions and reagents: (i) $\text{Cu}(\text{NO}_3)_2$, acetic anhydride, 40 °C, 30 min; (ii) $\text{H}_2\text{SO}_4+\text{TFA}$, CH_2Cl_2 , r.t., 2.5 h; (III) $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$, HCl , CH_2Cl_2 , r.t., 2.5 h.

Insertion of manganese ions was carried out using synthetic procedures developed for 5,10,15,20-tetraphenylporphyrin.⁵³ Free base porphyrins **2H(TMPIC)** and **2H(TMPIP)** were heated with an excess of manganese(II) chloride (5 equiv.) in DMF under air until a complete consumption of starting compound. Complexes **Mn(TMPIC)** and **Mn(TMPIP)** were isolated by column chromatography on silica gel and characterized by HRMS-ESI spectrometry, FTIR and UV–vis spectroscopies, with the last one being the most useful spectroscopic technique. The complexes display UV–vis spectra characteristic of manganese(III) porphyrins showing specific shapes compared to other porphyrin complexes due to strong metal–porphyrin π interactions.^{54,55} The mixing of metal and porphyrin orbitals leads to appearance of a number of charge-transfer bands which alter classical electron absorption spectra of the porphyrin complexes in which only π – π^* transitions of the macrocycle are observed. For example, in the spectrum of **Mn(TMPIP)** in CHCl_3 , several bands appear in the region of 300–450 nm with the maxima at 312, 382 and 402 nm (VI and Vs bands) and a sharp charge-transfer band is observed at 484 nm ($\log \varepsilon = 4.92$, V band) (see Supporting Information (SI), Figure S1). Moreover, less intensive bands appear at 576 nm (IV band) and 622 (III band) and 749 (II band). The successful insertion of manganese ion was also confirmed by observation of $[\text{M}+\text{H}]^+$, $[\text{M}-\text{Cl}]^+$ and $[\text{M}-\text{Cl}+\text{H}]^{2+}$ ion peaks with matching isotopic pattern as the most prominent peaks in the high resolution mass spectra of complexes **Mn(TMPIP)** and **Mn(TMPIC)** (see SI, Figures S2 and S3).

DFT calculations were employed to gain insight into electronic structures for the frontier orbitals of complexes **Mn(TMPIC)** and **Mn(TMPIP)** and (5,10,15,20-tetraphenylporphyrinato)manganese(III) chloride (**Mn(TPP)**). The computations were performed using B3LYP functional using 6-31G* basis set for all atoms including all-electron set for Mn. As shown in Figure 2, efficient mixing of metal and porphyrin orbitals is observed in HOMO and LUMO orbitals. In complexes **Mn(TMPIC)** and **Mn(TMPIP)**, the electronic

density of HOMO is also located on the fused imidazole fragment. In contrast, the 2-aryl residue is not involved in the HOMO and LUMO electronic states of both imidazoporphyrins. Thus, the introduction of any anchoring group does not significantly change the electronic structure of 2-arylimidazo[4,5-*b*]porphyrins and energies of frontier molecular orbitals. This appears to indicate that an electronic communication between the catalytic site and any solid support may be weak when 2-arylimidazole linker is used for preparing heterogenized catalysts.

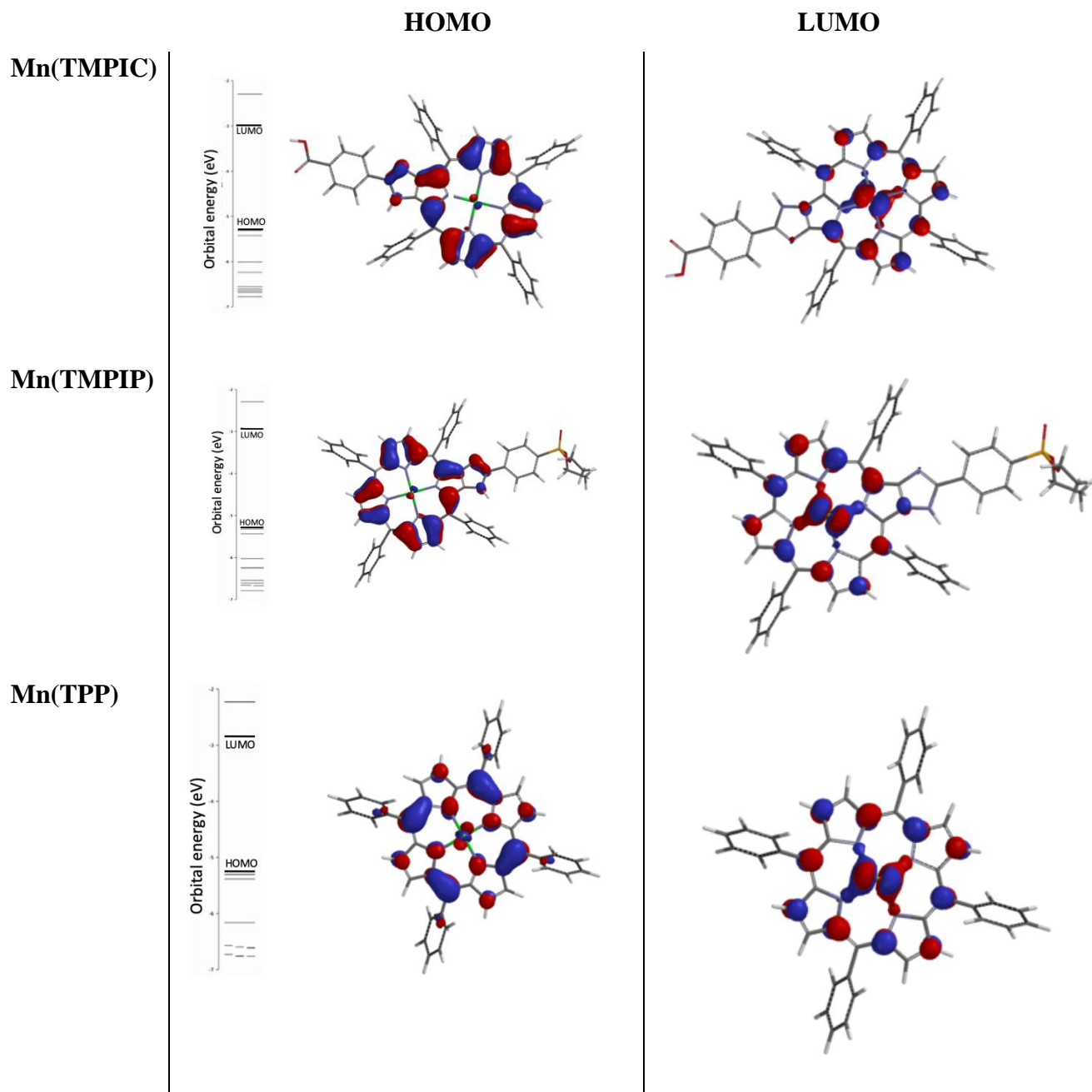


Figure 2. The isodensity plot of HOMO and LUMO orbitals for chromophores **Mn(TPP)**, **Mn(TMPIC)** and **Mn(TMPIP)** obtained from DFT calculations.

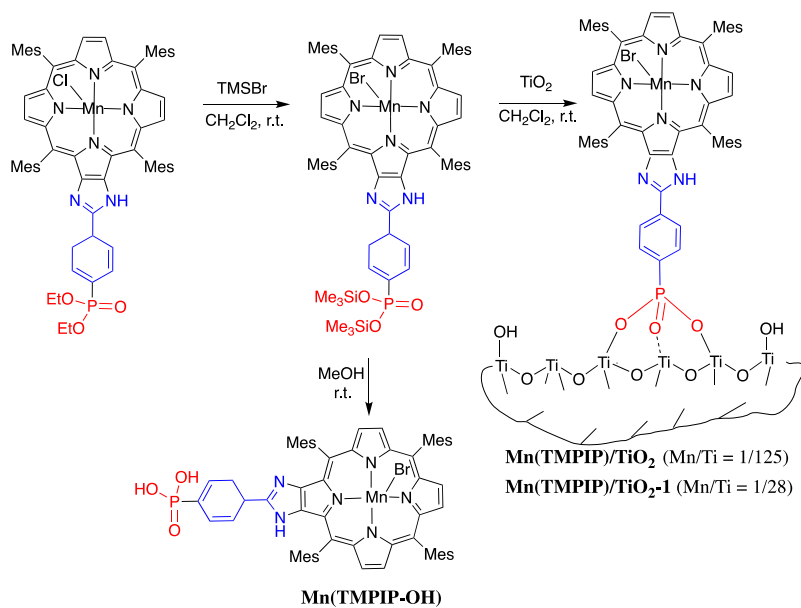
Complexes **Mn(TMPIC)** and **Mn(TMPIP)** were found to be soluble in methanol and chlorinated solvents such as chloroform and dichloromethane that is important for their use in material chemistry.

2.2 Immobilization of manganese(III) complexes **Mn(TMPIC)** and **Mn(TMPIP)** on TiO_2

Recent studies of hybrid organic-inorganic materials based on organophosphonates have revealed great interest of metal oxide and phosphonate networks for preparing functional materials in particular due to their thermal and chemical stability.⁵⁶⁻⁵⁹ Nevertheless, studies on TiO_2 -supported transition metal catalysts are limited⁶⁰⁻⁶⁷ probably because the synthesis of porous TiO_2 is challenging and time-consuming. On the other hand, immobilization of organic chromophore onto porous titania films was widely explored in view of production of clean energy from the sun in dye-sensitized solar cells.⁶⁸ Among different anchors, the carboxylate group was most commonly used and sometimes gave better results as compared to the phosphonate anchoring group. In this work, we compared efficiency of the carboxylate and phosphonate anchors for fabrication of heterogenized catalysts.

Mn(TMPIC) and **Mn(TMPIP)** were grafted onto the surface of hydrated amorphous titanium dioxide, which does not exhibit any photocatalytic activity by its own. Such cost-effective mesoporous TiO_2 ($S_{\text{BET}} = 650\text{--}705 \text{ m}^2 \text{ g}^{-1}$) is readily available by a template-free sol-gel method developed by us recently.⁶⁹

To prepare target materials from phosphonate-substituted complex **Mn(TMPIP)**, we employed a sol-gel process in organic solvents,^{70,71} since the immobilization of phosphonic acids in aqueous media probably occurs through monodentate P–O–Ti interactions and yields less-stable materials.⁶⁴ Dialkyl phosphoester **Mn(TMPIP)** was first transformed into more reactive bis(trimethylsilyl)phosphonate by reacting the complex with a large excess (30 equiv) of bromotrimethylsilane (TMSBr) in CH_2Cl_2 for 2 d at room temperature (Scheme 2). Evaporation of the reaction mixture to dryness gave the target compound in quantitative yield.



Scheme 2. Preparation of materials **Mn(TMPIP)/TiO₂** and **Mn(TMPIP)/TiO₂-1**.

Then this moisture-sensitive complex was engaged in the next step dissolving the solid in dry CH₂Cl₂ and adding this solution to a suspension of mesoporous titania in the same solvent at room temperature under Ar. The material was isolated by centrifugation after stirring for 2 d, washed and dried under reduced pressure. In these experiments, the Mn/Ti molar ratio was varied between 1:100 and 1:15 to prepare a solid with spatially separated catalytic sites (**Mn(TMPIP)/TiO₂**) and to get insight into maximal loading of catalytic sites on this support (**Mn(TMPIP)/TiO₂-1**).

The studies on the composition of hybrid materials thus obtained were started by EDX chemical analysis in STEM mode of solid **Mn(TMPIP)/TiO₂** because this technique is well suited for determination of the axial ligand in the heterogenized **Mn(TMPIP)**. It was previously demonstrated that the treatment of porphyrinatogallium(III) chlorides with TMSBr in toluene led to the exchange of axial chloride ligands by bromide ions.⁷² We hypothesized that this exchange reaction can also be observed under our experimental conditions. The EDX spectrum confirmed successful grafting Mn complex by the presence of all expected elements with only one exception being chlorine (Figures 3 and S4(see SI)). We also observed an EDX peak corresponding to bromine. This indicated that the ligand exchange reaction was observed during the activation of diethoxyphosphoryl group by TMSBr. Elemental mapping images shown in Figure 2 revealed homogeneous distribution of all elements in the studied samples.

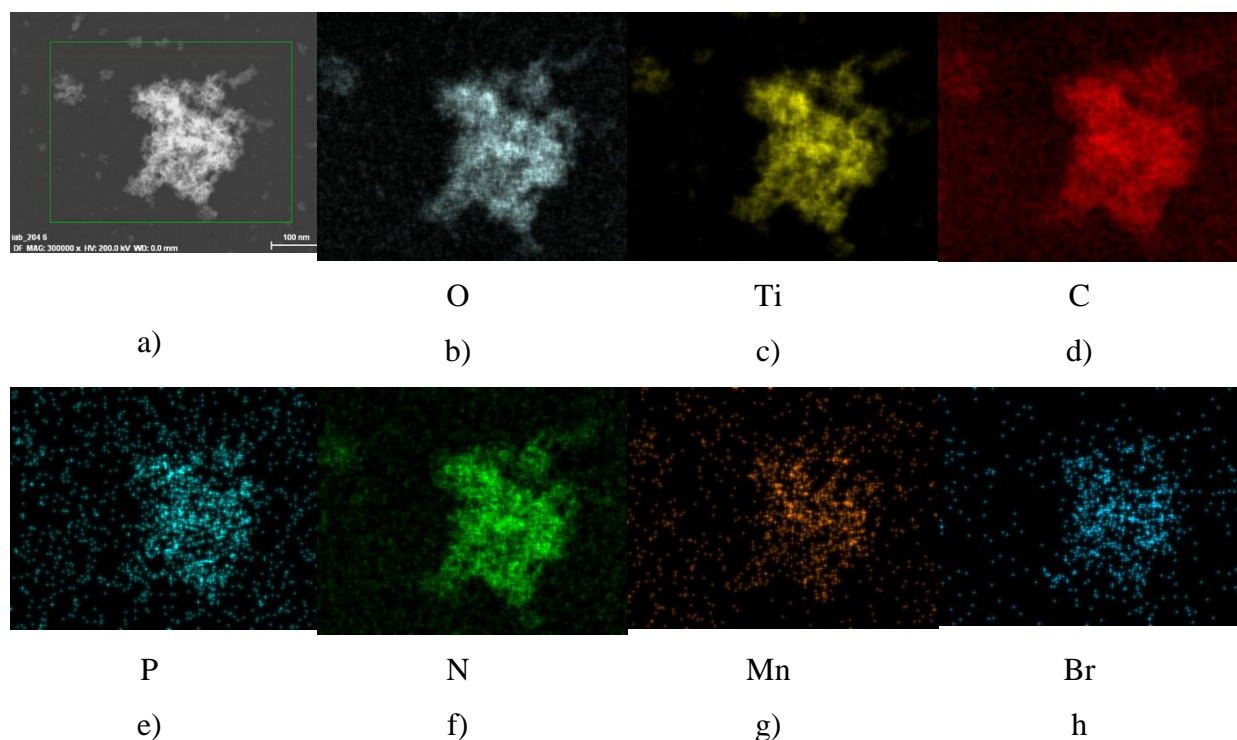
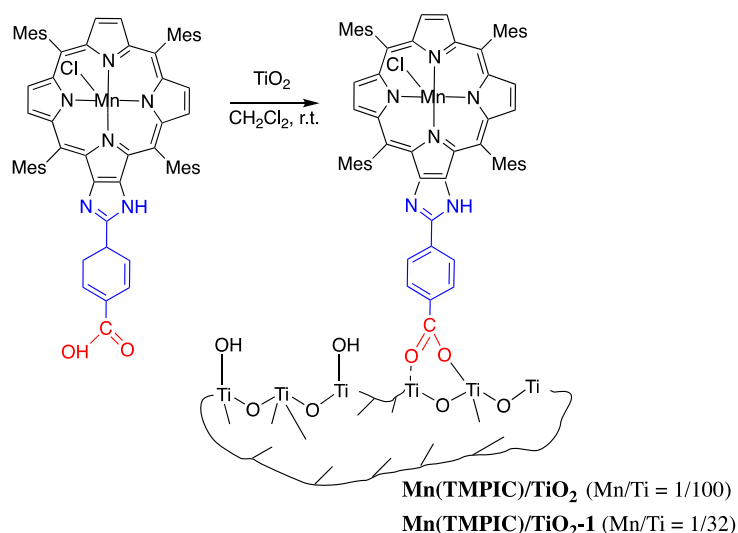


Figure 3. STEM image of Mn(TMPIP)/TiO_2 before the analysis (a) and EDS elemental mapping images of Mn(TMPIP)/TiO_2 (b-h): O (b), Ti (c), C (d), P (e), N (f), Mn (g), Br(h). Time of exposition to the electron beam was 1 h.

The empirical formulas of materials thus obtained were derived from the content of six elements (C, H, N, Ti, Mn, P) (see SI, Tables S1). The Ti/Mn ratio in the materials Mn(TMPIP)/TiO_2 and $\text{Mn(TMPIP)/TiO}_2\text{-1}$ was found to be of 1:125 and 1:28, respectively. Thus, the content of heterogenized Mn(TMPIP) was lower than expected values in both cases despite the fact that coloured filtrates were obtained only during synthesis of $\text{Mn(TMPIP)/TiO}_2\text{-1}$. To prove quantitative immobilization of Mn(TMPIP) onto the solid Mn(TMPIP)/TiO_2 , the combined organic and aqueous filtrates obtained during washing the solid were evaporated and dried under reduced pressure. The residue thus obtained was dissolved in methanol and analyzed by UV–vis spectroscopy to check the presence of starting complex Mn(TMPIP) and corresponding phosphonic acid Mn(TMPIP-OH) . These two compounds are the only porphyrin products which can be present in solution if grafting was incomplete. To perform qualitative analysis, complex Mn(TMPIP-OH) was prepared as shown in Scheme 2. Base on the results of this UV–vis study, we safely concluded that more than 98% of complex Mn(TMPIP) was immobilized on a titania support. In contrast, the filtrates were intensively coloured when Mn(TMPIP) and titania were reacted in a 1:15 molar ratio and the experimental content of Mn in the

target solid was about twice lower than it was expected. This likely indicates that maximal catalyst loading (~1:30) was achieved under these experimental conditions.

To enable the immobilization of **Mn(TMPIC)**, the complex was dissolved in dry CH_2Cl_2 and this solution was added to mesoporous titania suspended in the same solvent and stirred for 2 d at room temperature (Scheme 3).



Scheme 2. Preparation of materials **Mn(TMPIC)/TiO₂** and **Mn(TMPIC)/TiO₂-1**.

The Mn/Ti molar ratio was also varied between 1:100 and 1:15 for comparative reasons. The empirical formulas of **Mn(TMPIC)/TiO₂** and **Mn(TMPIC)/TiO₂-1** thus obtained were derived from the content of five elements (C, H, N, Ti, Mn) and were very similar to those of materials based on **Mn(TMPIP)** (Table S1). Quantitative immobilization was observed when complex and inorganic support were reacted in the ratio of 1:100 and maximal catalyst loading was about 1:32.

The intact structure of the heterogenized complexes **Mn(TMPIP)** and **Mn(TMPIC)** was confirmed by UV–vis diffuse reflectance and FTIR spectroscopies. In brief, the spectral signatures of both manganese complexes before and after immobilization on TiO_2 were remarkably similar except characteristic vibration bands of carboxylic and phosphonic anchors. Kubelka-Munk transformed UV–vis diffuse reflectance spectra of the studied solids show a strong and broad absorption feature in the high energy region (< 300 nm). This band was attributed to the TiO_2 phase. The spectral shape of materials in the 350–750 nm region resembles closely to those observed for **Mn(TMPIC)** and **Mn(TMPIP)** complexes, confirming that the metalloporphyrin residue keeps their integrity after immobilization (Figure 4).

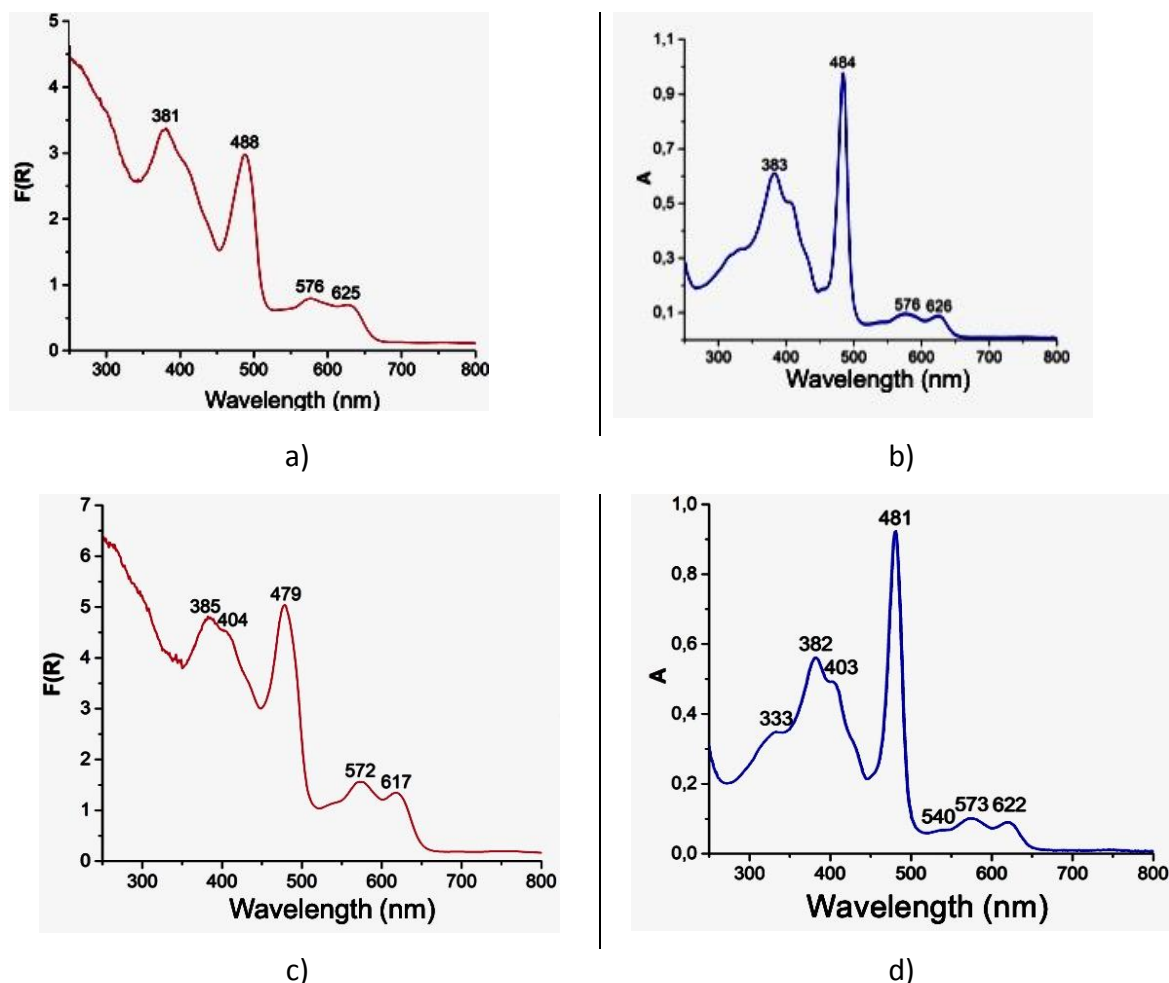


Figure 4. Kubelka-Munk transformed diffusion reflectance spectra of **Mn(TMPIP)/TiO₂-1** (a) and **Mn(TMPIC)/TiO₂-1** (c). UV-vis spectra of **Mn(TMPIP)** (b) and **Mn(TMPIC)** (d) in chloroform.

In the FTIR spectra (see SI, Figures S5 and S6), vibration bands assigned to the porphyrin macrocycle ($720\text{--}850$ and $1000\text{--}1200\text{ cm}^{-1}$) and aryl residues ($1350\text{--}1610\text{ cm}^{-1}$) are all much weaker as compared to the Ti–OH and O–H stretching modes ($3500\text{--}3700\text{ cm}^{-1}$) even in the spectra of **Mn(TMPIP)/TiO₂-1** and **Mn(TMPIC)/TiO₂-1** materials with high Mn/Ti ratios. Notably, the shape of **Mn(TMPIP)/TiO₂-1** spectrum in the region of $850\text{--}1260\text{ cm}^{-1}$ where characteristic bands associated with vibrations of the phosphonate substituent is observed, is significantly different from those of diethoxyphosphoryl-substituted complex **Mn(TMPIP)** and phosphonic acid **Mn(TMPIP-OH)**. Valence vibration bands of P=O residue (1250 and 1277 cm^{-1}) of the diethoxyphosphoryl group and of P–O–H of phosphonic acid (916 cm^{-1}) are absent. This likely reveals the formation of metal–O–P bonds whose stretching vibrations are overlapped with those of the porphyrin macrocycle giving a rather strong band at 1003 cm^{-1} . In the spectrum of **Mn(TMPIC)/TiO₂-1**, stretching vibrations of

carboxylic acid group (1719 cm^{-1} for **Mn(TMPIC)**) were not observed pointing out the involvement of this anchoring group in the interaction with the titania support.

The morphology of **Mn(TMPIP)/TiO₂** was studied by SEM and compared to that of the bare TiO₂ (Figure 5). The latter is composed of strongly aggregated nanoparticles of similar shape and narrow grain-size distribution. Incorporation of **Mn(TMPIP)** does not have any influence on the cauliflower-like morphology of the solid. The mesoporous nanospheroids with a diameter ranging from 5 to 20 nm, are irregularly distributed in the space and separated by large holes of hundreds of nanometers, thus providing a good accessibility to the bound complexes of catalytic sites. This morphology is therefore perfectly suited for application in catalysis.

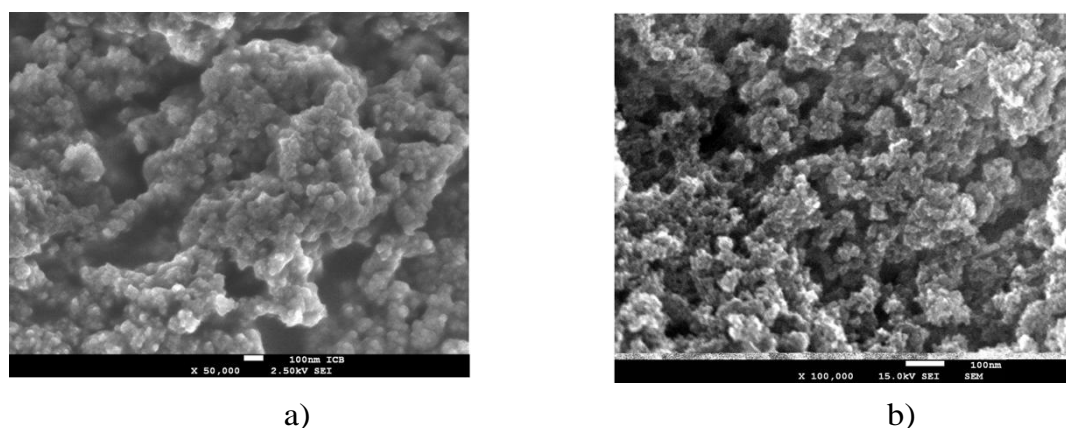


Figure 5. SEM microphotographs of (a) bare hydrated TiO₂, and (b) **Mn(TMPIP)/TiO₂**.

N₂ adsorption–desorption isotherms of all four hybrid materials were recorded at 77 K and the results of these analyses were summarized in Table S2 (see SI). Upon the derivatization of TiO₂, no change in the shape of the isotherms was observed, whereas a marked decrease in the BET surface area and volume of pores for all samples was noted, which was consistent with the presence of grafted complexes in the mesopores. It's worthy to note, that materials **Mn(TMPIP)/TiO₂-1** and **Mn(TMPIC)/TiO₂-1** with high porphyrin loading display smaller BET surface areas and pore volumes as compared to their counterparts **Mn(TMPIP)/TiO₂** and **Mn(TMPIP)/TiO₂** charged less in porphyrin complexes. These data agree well with the hypothesis that both complexes are located not only at the outside titania surface but also in its mesopores.

Powder X-ray diffraction measurements confirmed that the pristine mesoporous titania and all samples of functionalized materials prepared in this work are non-crystalline solids.

The materials with high catalysts loading **Mn(TMPIP)/TiO₂-1** and **Mn(TMPLIC)/TiO₂-1** were chosen for comparative studies of their stability in different organic solvents and in aqueous media with variable pH. A suspension of the solid in toluene, chlorinated (CH₂Cl₂, CHCl₃), polar (CH₃CN, DMF) and protic (MeOH, EtOH) solvents was centrifugated after 1 week and solutions thus obtained were analyzed visually or using a laboratory spectrophotometer. Only material **Mn(TMPIP)/TiO₂-1** with the phosphonate anchor was stable in all these solvents which are commonly used in organic synthesis. **Mn(TMPLIC)/TiO₂-1** was rapidly washed off in protic solvents (> 50%) and also in acetonitrile (~ 10%).

Stability of **Mn(TMPIP)/TiO₂-1** was also explored in aqueous media in all pH range. The leaching of the complex was observed only in basic solutions (pH >9). We also found that **Mn(TMPIP)/TiO₂-1** was stable in the presence of triethylamine in CHCl₃ and DMF. This is important for organic synthesis because tertiary amines are common reagents in catalytic and photocatalytic transformations.

The most stable heterogenized complex with spatially separated catalytic sites (**Mn(TMPIP)/TiO₂**) was next studied as a catalyst in oxidation reactions.

2.3. Catalytic reactions

To get insight into the catalytic properties of **Mn(TMPIP)/TiO₂**, we studied its catalytic efficiency and reusability in the oxidation reactions using molecular oxygen as a terminal oxidant and isobutyraldehyde (IBA) as a sacrificial reagent (Mukaiyama conditions⁷³) because these mild oxidation conditions are suitable for transformations of different compounds such as alkanes, alkenes, aldehydes, cyclic ketones, sulfides and alcohols.^{74,75} Metalloporphyrins are known as active catalysts for these reactions under homogeneous conditions.^{12,16,74,76-78} In our work, the oxidation of sulfide to sulfoxide was chosen as a model reaction. The selective sulfoxidation attracts considerable interest due to its relevance to biochemistry, warfare agents disposal, environmental consequences of fuel desulfurization and in organic synthesis.⁷⁹⁻⁸⁶ The overoxidation of sulfides to sulfones and the cleavage of S–C and (S)C–H bonds are commonly observed as side reactions⁸⁷⁻⁸⁹ and thus selective methods for transformation of different sulfides are in high demand in particular in asymmetric synthesis of ligands and in the development of pharmaceuticals involving selective late-stage oxygenation.^{84,86,90-92}

In the preliminary experiments the oxidation of thioanisole with molecular oxygen (1 atm) was performed in the presence of 0.09 mol% of TiO₂-supported complex **Mn(TMPIP)**

and 6 equivalents of IBA in toluene at 80 °C and monitored by GC-MS (Table 1). Starting sulfide was consumed in less than 30 min but the overoxidation of sulfoxide to methyl phenyl sulfone (42%) was observed as a side reaction (entry 1). To diminish the overoxidation, the temperature was decreased to 40 °C (entry 2). Under these conditions, the reaction proceeded slowly but sulfone was obtained in similar yield (37%). Comparing the amount of sulfone in the reaction mixture before and after complete consumption of sulfide in the reaction performed at 30 °C (entry 3), we concluded that the overoxidation was slow until the starting sulfide was present in the reaction mixture but was significantly accelerated after the sulfide consumption. The results obtained at 20 °C confirmed this hypothesis but the control of the overoxidation was difficult even under these mild conditions because the reaction was too rapid (entry 4). Thus, the amount of IBA was decreased up to 3 equivalents. The rate of oxidation was decreased and methyl phenyl sulfoxide was the main product (96%) when 76% of starting sulfide was consumed (entry 5). However, when this reaction was prolonged for additional 2 h, only 10% of starting sulfide was reacted probably due to a complete consumption of IBA. The oxidation at 50 °C gave also only sulfoxide when 52% of sulfide was reacted (entry 6) but 6% of starting compound was still observed after 8 hours of reacting. Finally, adjusting amount of IBA to reach a complete conversion and an appropriate reaction rate, the sulfoxide was obtained in about quantitative yield (entry 7).

Table 1. Oxidation of thioanisole by molecular oxygen in the presence of **Mn(TMPIP)/TiO₂** and IBA¹.

Entry	IBA (equiv.)	Temperature (°C)	Time (h)	Conversion ² (%)	Selectivity ² (%)	
					Sulfoxide	Sulfone
1	6	80	0.5	100	58	42
2	6	40	2	100	63	37
3	6	30	2.5	92	99	1
			3	100	53	47
4	6	20	2	85	100	0
			2.5	100	82	12
5	3	80	1.5	76	96	4
			3.5	86	86	14
6	3	50	1.5	52	100	0
			8	94	95	5
7	5	20	3	100	98	2
8 ³	5	20	3	0		

9	0	20	3	0
10 ⁴	5	20	3	0
11 ⁵	5	20	3	0

¹ Reaction conditions: 2.5 mmol of thioanisole, molecular oxygen (1 atm), IBA, 0.09 mol% of heterogenized complex (calculations were based on the data of ICP analysis of **Mn(TMPIP)/TiO₂**), toluene (10 mL) were stirred at given temperature. ² Conversion and selectivity were determined by GC-MS analysis of reaction mixtures. Naphthalene was used as an internal standard. ³ The reaction was performed without transition metal catalyst. ⁴ The experiment was performed in Ar (1 atm). ⁵ The reaction was carried out in the presence of 0.009 mol % of the heterogenized complex.

It's noteworthy that the oxidation did not proceed at all in the absence of **Mn(TMPIP)/TiO₂**, IBA or oxygen under these conditions (entries 7–9). Our attempts to decrease catalyst loading in ten times (entry 10) and used non-functionalized TiO₂ as a catalyst failed.

Thus, as low as 0.09 mol% of TiO₂-supported **Mn(TMPIP)** were required for the selective sulfoxidation of thioanisole with molecular oxygen in the presence of 5 equivalent of IBA (TON = ~1100, TOF = ~ 370) in a single catalytic run of the sulfoxidation of thioanisole. The overoxidation of sulfide to sulfone in the presence of this catalyst proceeds even at room temperature but sulfoxides can be obtained in about quantitative yield controlling amount of IBA, temperature and time of reacting.

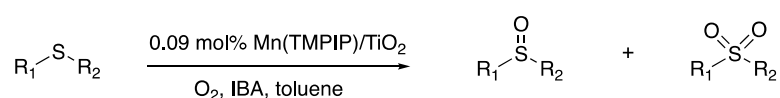
To determine whether the catalyst leaching was observed under reaction conditions and show that the non-supported manganese catalyst did not catalyze this reaction, a “hot filtration test” was performed (see SI, Figure S7). A half of solution was filtered when 50% of starting sulfide was consumed and both reactions were continued under identical conditions. In the filtered solution, the oxidation was also observed but was much slower than in the suspension. To prove the absence of catalyst leaching, we determined the content of manganese containing compounds in the residue obtained after evaporation of the homogeneous reaction mixture using ICP-OES technique. The manganese content was found to be less than 5 ppm. Based on these data, we assumed that the oxidation reaction observed in the filtrated solution proceeds without participation of transition metal catalysts. This can be the sluggish autoxidation of sulfides in the presence of O₂ and IBA as reported previously.^{93,94}

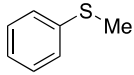
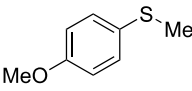
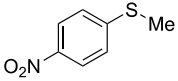
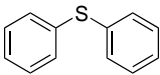
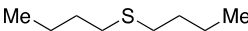
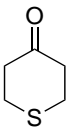
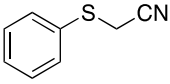
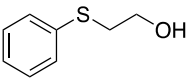
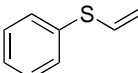
Encouraged by these results, we investigated the scope of substrates for this reaction. To our surprise, various sulfides can be selectively oxidized to sulfoxides under ambient conditions controlling amount of IBA introduced in the reaction (Table 2). The rate of oxidation of aryl methyl sulfides is dependent on the nature of substituents on the phenyl ring. Electron rich derivatives are more reactive as compared to compounds with electron deficient aryl group. Nevertheless, all target products were obtained in almost quantitative yield. The

oxidation of more sterically hindered diphenyl sulfide which is known to be resistant to oxidation by O₂ under photocatalytical conditions⁹⁵ requires a slightly higher amount (3.3 equivalents) of IBA and 6 h of reacting under otherwise identical conditions to give the target product in 92% yield.

Linear and cyclic dialkyl sulfides were found to be less reactive than aryl sulfides and were oxidized in the presence of 6–9 equivalents of IBA. The oxidation of cyclic derivative seems to be less selective because sulfoxide and sulfone were obtained in 92:8 ratio when only 92% of sulfide was consumed.

Table 2. Oxidation of sulfides by molecular oxygen in the presence of **Mn(TMPIP)/TiO₂** and IBA¹.



Entry	Sulfide	IBA (equiv.)	Time (h)	Conversion ² (%)	Selectivity ² (%)	
					Sulfoxide	Sulfone
1		5	2.5	100	98	2
2		5	2	100	98	2
3		5	7	100	97	3
4		3.3	6	100	92	8
5		6	4	94	98	2
6		9	2.5	92	92	8
7		3	3	99	94	6
8		10	4	98	97	3
9		7	4	98	89	11

¹ Reaction conditions: 2.5 mmol of thioanisole, IBA, 0.09 mol% of heterogenized complex (calculations were based on the data of ICP analysis of **Mn(TMPIP)/TiO₂**), toluene (10mL) were stirred at given temperature under molecular oxygen (1 atm). ² Conversion and selectivity were determined by GC-MS analysis of reaction mixtures. Naphthalene was used as an internal standard.

Finally, we explored the sulfoxidation of compounds bearing additional oxidizable sites such as vinyl, hydroxyl and cyano substituents (entries 7–9). To our great satisfaction, all target sulfoxides were obtained in high yield and the overoxidation of sulfoxide was only observed as a side reaction. Despite the reactions were optimized only briefly, even in the case of most problematic phenyl vinyl sulfide, the sulfoxide : sulfone ratio was 89 : 11 when 90% of starting compound were consumed.

The mechanistic pathways of the oxidation by O₂–IBA reagent system were debated in the literature.^{12,96-100} Several active species with and without transition metal atoms were identified. The relative efficacy by which a sulfide molecule is oxidized by one versus the other pathways appears to be dependent on the nature of transition metal catalyst, solvent and temperature. Despite mechanistic studies of porphyrin catalysts are very limited, high-valent metalloporphyrin–oxo intermediates were considered as main active oxygen-containing intermediates.^{99,101-103} Our data do not contradict this hypothesis because the oxidation is more rapid in the presence of Mn(III) complex as it was shown in the “hot filtration test”. However, other less active oxygen-containing intermediate species can also contribute in the formation of the target product. Detail mechanistic studies of this reaction are beyond the scope of these work.

Catalyst recovery and refining were straightforward. After completion of the reaction, the catalyst was isolated by centrifugation, washed with toluene and introduced in the next cycle. Seven consecutive oxidation reactions of thioanisole were carried out giving the target sulfoxides in comparable yields (94–98 %) (Figure 6 and Table S3 (see SI)). The reaction time was different in these experiments but the changes were non-systematic. We assume that this reaction parameter is highly dependent on the efficiency of stirring heterogeneous reaction mixtures and is useless as a criterion of the catalyst activity. The content of resting manganese derivatives in the crude products was found to be less than 5 ppm by using the ICP-OES analysis (Table S3 (see SI)). The integrity of the **Mn(TMPIP)/TiO₂** catalyst was also confirmed studying the solid recovered after the last catalytic cycle by diffuse reflectance spectroscopy. As shown in Figure S8 (see SI), the solid exhibits the absorption features which are characteristic for **Mn(TMPIP)** in CHCl₃ solution and **Mn(TMPIP)/TiO₂** material. Small bathochromic shift of spectral band positions was observed for several bands in the spectrum of the recovered solid. This likely indicates a difference in the adsorbed solvent molecules in the starting and reused catalysts or the chemical modification of the TiO₂ surface (the esterification by isobutyric acid, for instance) during the oxidation reaction. Nevertheless,

based on these spectral data, we can safely conclude that heterogenized porphyrin macrocycles are not decomposed after seven consecutive oxidation cycles.

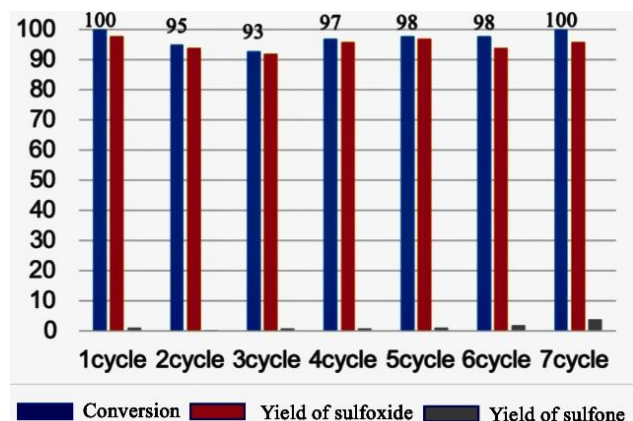


Figure 6. Recycling of Mn(TMPIP)/TiO_2 in the oxidation of thioanisole by O_2 in the presence of IBA.

When oxidation of thioanisole was performed under homogeneous conditions replacing Mn(TMPIP)/TiO_2 by its soluble counterpart Mn(TMPIP) or commercially available (*meso*-tetramesitylporphyrinato)manganese(III) chloride (Mn(TM)) only starting thioanisole was observed in the reaction mixture after 24 h of reacting. When Mn(TMPIP) loading was increased up to 0.5 mol%, only 15% of thioanisole was converted to sulfoxide after 24 h. Thus, immobilization of Mn(TMPIP) on hydrated titania significantly increases its catalytic efficiency allowing to perform the sulfoxidation under ambient conditions. The reason of the synergetic effect is unclear at this point of investigation. We cannot exclude that the adsorption of sulfoxide on a large surface of inorganic support accelerates the oxidation reaction but most probably peroxide intermediates formed on the surface of hydrated TiO_2 ¹⁰⁴ are also participated in the oxidation.

Comparing Mn(TMPIP)/TiO_2 with porphyrin catalysts reported previously, we can conclude that this material is situated among the best catalysts known for the sulfoxidation reaction. Indeed, the oxidation of sulfides by sodium periodate in the presence of Mn(III) porphyrins grafted on polystyrene¹⁰⁵ or silica¹⁰⁶ led to a mixture of sulfoxides and sulfones. When Mn(III) porphyrins were grafted on graphene oxide and used as catalysts for the sulfoxidation by hydrogen peroxide-urea adduct, about 2 mol% of catalysts were required and the reactions were less selective in particular when aromatic sulfides were used as substrates.¹⁰⁷ Fe(III) porphyrins grafted on activated multi-walled carbon nanotubes were efficient in ethanol when tetra-*n*-butylammonium peroxomonosulfate was used as an oxidant but some of the studied reactions were difficult to control.¹⁰⁸ Several heterogenized porphyrin catalysts were also reported for oxidation of sulfides to sulfoxides under Mukaiyama

conditions. Manganese(III) complex with 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphyrin immobilized in montmorillonite gave the selective transformation only when the reaction was conducted at 50–80 °C.³³ Only COP based on Fe(III) porphyrin has shown catalytic activity similar to that of **Mn(TMPIP)/TiO₂**.⁴⁴ However, this immobilization procedure requires a large amount of complex and yields hybrid material in which the number of catalytic sites cannot be optimized.

It's also worth noting that porphyrin catalysts bearing phosphonate anchors were successfully immobilized onto zinc phosphonate network¹⁰⁹ and onto zirconium phosphonate films materials¹¹⁰. We developed a synthetic approach to porous heterogenized porphyrin catalysts.

3. Materials and Methods.

3.1. General

Unless otherwise noted, all chemicals and starting materials were obtained commercially from Acros or Aldrich-Sigma Co. and used without further purification. (5,10,15,20-tetramesitylporphyrinato)manganese(III) chloride (**Mn(TMP)**) was provided by PorphyChem. 2-Nitro-5,10,15,20-tetramesitylporphyrin was prepared according to the literature protocol.¹¹¹ [5,10,15,20-tetramesityl-2-(4-carboxyphenyl)-1*H*-imidazo[4,5-*b*]porphyrin (**2H(TMPIIC)**) and [5,10,15,20-tetramesityl-2-[4-(diethoxyphosphoryl)phenyl]-1*H*-imidazo[4,5-*b*]porphyrin (**2H(TMPIP)**) were synthesized according to a procedure developed by us previously.^{51,112} Mesoporous hydrated titanium(IV) oxide was prepared using a surfactant-free sol-gel procedure reported by us previously.¹¹³ The content of Ti in the solid thus obtained was determined by ICP-OES analysis. Preparative column chromatography was carried out using silica gel 60 (40–63 μm) from Merck Co. CH₂Cl₂ was distilled over CaH₂.

UV–vis absorption spectra were collected with an Agilent Cary 60 using Suprasil 300 cuvettes (Hellma, *l* = 1 cm). Diffuse reflectance spectra of materials were acquired on a Cary 5000 (Agilent) UV–vis–NIR spectrophotometer outfitted with a praying MantisTM accessory (Harrick). The baselineTM was recorded with a Spectralon[®] pellet. Corrected reflectance data (*R*) were converted to *f*(*R*) values using the Kubelka–Munk function expressed as $f(R) = (1 - R^2)/2R$.

FTIR spectra were registered either on a Nicolet iS 5 or a Bruker Vector 22 spectrophotometer. A micro-ATR accessory (Pike) was used in order to obtain FTIR spectra of polycrystalline solid complexes.

MALDI-TOF mass-spectra were obtained on a Bruker Ultraflex II LRF 2000 mass-spectrometer in positive ion mode with the dithranol matrix. Accurate mass measurements (HRMS-ESI) were performed with a Thermo Scientific Orbitrap Elite high-field Orbitrap hybrid mass spectrometer. The samples were dissolved in methanol/chloroform (1:1, v/v) solvent mixture and analyzed in positive mode. Microanalyses (CHN) were performed on a Thermo Electron Flash EA 1112 analyser. Mn, P, and Ti contents were measured by inductively coupled plasma optical emission spectrometry (ICP-OES DUO) on an ICAP 7400 instrument from Thermo Scientific. The samples were mineralized using standard procedures.

Field-emission scanning electron microscopy (FESEM) was realized using a JEOL JSM 7600F instrument located in the ARCEN analysis centre of the University of Bourgogne (Dijon). Images were made using GentleBeam-High SEM mode. Transmission electron microscopy (TEM) analyses were conducted using a JEOL JEM-2100F microscope operating at 200 kV and located in the ARCEN analysis centre of the University of Bourgogne (Dijon). EDX spectrometry in STEM and TEM mode was used for chemical mapping and qualitative elemental analysis using a Bruker XFlash Detector 5030 spectrometer fitted on the JEM-2100F microscope.

Nitrogen adsorption-desorption isotherms were measured with a BELSORP max analyzer (BEL Japan, INC.) at 77 K with samples degassed for 6 h at 80 °C under reduced pressure (10^{-5} torr). Specific surface areas (S_{BET}) were calculated according to the Brunauer–Emmett–Teller (BET) method. Field-emission scanning electron microscopy (FESEM) images were collected with a Carl Zeiss Ultra Plus instrument.

Powder X-ray diffraction experiments were performed with an Empyrean diffractometer from the PANalytical company in the range $3^\circ < 2\theta < 50^\circ$, using a copper anticathode X-ray tube ($\text{Cu K}\alpha_1 = 1.54060 \text{ \AA}$ and $\text{Cu K}\alpha_2 = 1.54443 \text{ \AA}$) and a X'Celerator detector outfitted with an anti-scattering slit of 5 mm. The uncrushed samples were placed between two Mylar sheets and the analysis was carried out in transmission mode using a focusing X-ray mirror equipped with fixed divergent and anti-scattering slits (aperture 0.5°) and 0.02 rad Soller slits.

All elemental analyses except SEM and EDX analyses were performed at the "Pôle Chimie Moléculaire", the technological platform for chemical analysis and molecular synthesis (<http://www.wpcm.fr>) of the Institut de Chimie Moléculaire de l'Université de Bourgogne and WelienceTM, a private subsidiary of the Université de Bourgogne.

3.2. Synthesis of manganese(III) complexes **Mn(TMPIC)**, **Mn(TMPIP)** and **Mn(TMPIP-OH)**

General procedure. To a solution of free base porphyrin (0.1 mmol) in dimethylformamide (13 mL) manganese dichloride (63 mg, 0.5 mmol, 5 equiv.) was added at 150 °C. The reaction mixture was stirred at this temperature and monitored by TCL. After complete consumption of starting porphyrin (4 h), the reaction mixture was cooled to room temperature and evaporated under reduced pressure. The residue thus obtained was dissolved in dichloromethane (30 mL) and the solution was washed with water (3 x 20 mL), dried over MgSO₄ and evaporated under reduced pressure. The residue thus obtained was chromatographed on silica gel using CH₂Cl₂/MeOH as eluent.

[5,10,15,20-tetramesityl-2-(4-carboxyphenyl)-1H-imidazo[4,5-

*b]porphyrinato]manganese(III) chloride (**Mn(TMPIC)**). The complex was prepared according to the general procedure from **2H(TMPIC)** (120 mg, 0.127 mmol) and isolated as a green solid using CH₂Cl₂/MeOH (95:5 v/v) as an eluent. Yield 92% (116 mg); mp >320 °C, decomp.. UV–Vis (CHCl₃, λ_{max}, nm (log(ε (cm⁻¹M⁻¹)))): 333 (4.60), 382 (4.80), 403 (4.75), 481 (5.00), 540 (sh), 573 (4.09), 622 (4.04), 748 (3.04). FTIR (neat, v, cm⁻¹): 3410 (w, NH), 2913 (m), 2849 (m), 1719 (m, C=O), 1610 (m), 1437 (w), 1378 (w), 1331 (w), 1250 (w), 1225 (w), 1195 (m), 1003 (s), 862 (w), 851 (w), 833 (m), 802 (m), 721 (m). HRMS-ESI: *m/z* [M-Cl]⁺ calcd for C₆₄H₅₆MnN₆O₂: 995.38398; found: 995.38814.*

[5,10,15,20-tetramesityl-2-[4-(diethoxyphosphoryl)phenyl]-1H-imidazo[4,5-

*b]porphyrinato]manganese(III) chloride (**Mn(TMPIP)**). The complex was prepared according to the general procedure from **2H(TMPIP)** (554 mg, 0.535 mmol) and isolated as a green solid using CH₂Cl₂/MeOH (95:5 v/v) as eluent. Yield 60% (330 mg); mp >320 °C, decomp.. UV–Vis (CHCl₃, λ_{max}, nm (log(ε (cm⁻¹M⁻¹)))): 327 (4.46), 383 (4.72), 407 (4.65), 484 (4.92), 576 (3.93), 626 (3.89), 749 (2.92). FTIR (neat, v, cm⁻¹): 3385 (w, NH), 2916 (w), 2854 (w), 1609 (w), 1475 (w), 1437 (w), 1410 (w), 1377 (w), 1333 (w), 1248 (m, P=O), 1227 (m, P=O), 1196 (m), 1130 (m), 1051 (m), 1016 (s, P–O–C), 1003 (s), 953 (m), 851 (w), 833 (m), 800 (s), 762 (w), 719 (m), 665 (w). HRMS-ESI: *m/z* [M-Cl+H]²⁺ calcd for C₆₇H₆₆MnN₆O₃P: 544.21518; found: 554.21526; [M-Cl]⁺ calcd for C₆₇H₆₅MnN₆O₃P: 1087.42308; found: 1087.42690; [M+H]⁺ calcd for C₆₇H₆₆ClMnN₆O₃P: 1123.39976; found: 1123.39579.*

[5,10,15,20-tetramesityl-2-[4-(dihydroxyphosphoryl)phenyl]-1H-imidazo[4,5-

*b]porphyrinato]manganese(III) bromide (**Mn(TMPIP-OH)**).*

A dry Schlenk tube was charged with diethyl phosphonate ester **Mn(TMPIP)** (15 mg, 0.0134 mmol) and dry CH₂Cl₂ (5 mL) under argon. Then, TMSBr (53 mL, 0.4 mmol, 30 equiv.) was added *via* a syringe and the resulting mixture was stirred for 3 d at r. t. and monitored by MALDI-TOF mass spectrometry. After complete consumption of ethyl phosphoesters, methanol (2 mL) was added to the reaction mixture and stirring was continued for 30 min. Evaporation of volatiles under reduced pressure afforded the target phosphonic acid as dark green solid. Yield: 90% (14 mg); mp >350 °C, decomp.. UV-Vis (CHCl₃, λ_{max}, nm (log(ε (cm⁻¹M⁻¹))): 303 (4.40), 385 (4.78), 419 (4.73), 452 (4.53), 491 (4.81), 587 (3.90), 633 (3.92), 760 (2.86). FTIR (neat, ν, cm⁻¹): 2918 (m), 2853 (m), 1609 (w), 1437 (m), 1408 (w), 1379 (w), 1335 (w), 1196 (m), 1134 (w), 1003 (s), 916 (m, P-OH), 851 (w), 831 (s), 802 (s), 719 (s), 663 (w). HRMS-ESI: *m/z* [M-Br]⁺ calcd for C₆₃H₅₇MnN₆O₃P: 1031.36048; found: 1031.36328; [M-HBr+Na]⁺ calcd for C₆₃H₅₆MnN₆NaO₃P: 1053.34242; found: 1053.34345.

3.3. Synthesis of heterogenized catalysts

Grafting complex Mn(TMPIC). A dry Schlenk tube was charged with carboxylic acid **Mn(TMPIC)** (18 mg, 0.018 mmol) and dry CH₂Cl₂ (50 mL) under argon. Then mesoporous hydrated TiO₂ (18 mmol, 100 equiv.) was added under an argon stream. The suspension was stirred for 2 d at r. t. The solid was collected by centrifugation, thoroughly washed with THF (2 x 20 mL), water (15 mL), MeOH (3 x 15 mL), and ether (2 x 15 mL). The material was finally dried for 24 h at 80 °C under reduced pressure (2 mmHg). Yield: 165 mg.

The solid **Mn(TMPIC)/TiO₂-1** with a high content of **Mn(TMPIC)** (**Mn(TMPIC)**:TiO₂ ratio was 1:15) was prepared according to this procedure.

Grafting complex Mn(TMPIP). A dry Schlenk tube was charged with diethyl phosphonate ester **Mn(TMPIP)** (360 mg, 0.32 mmol) and dry CH₂Cl₂ (50 mL) under argon. Then, TMSBr (30 equiv.) was added *via* a syringe and the resulting mixture was stirred for 48 h at r. t.. The reaction was monitored by MALDI-TOF mass spectrometry to ensure a complete conversion has occurred before evaporation of volatiles under reduced pressure. Then, 50 mL of dry CH₂Cl₂ were introduced into the Schlenk tube with a syringe, followed by the addition of mesoporous hydrated TiO₂ (32 mmol, of 100 equiv.) under an argon stream. The suspension was stirred for 2 d at r. t. The solid was collected by centrifugation, thoroughly washed with THF (2 x 20 mL), water (15 mL), MeOH (3 x 15 mL), and ether (2 x 15 mL). The material was dried for 24 h at 80 °C under reduced pressure (2 mmHg). Yield: 3050 mg.

The solid **Mn(TMPIP)/TiO₂-1** with a high content of **Mn(TMPIP)** (ratio of **Mn(TMPIP)**:TiO₂ was 1:15) was prepared according to this procedure.

3.3 Catalytic reactions.

General procedure. A 25 mL two-necked flask equipped with a magnetic stir bar and a back-flow condenser was charged with 0.09 mol% of heterogenized **Mn(TMPIP)** (calculations were based on the data of ICP-OES analysis of **Mn(TMPIP)/TiO₂**). The reaction vessel was evacuated and purged by oxygen 3 times. Subsequently, 2.5 mmol of sulfide, calculated amount of IBA (Tables 1 and 2), and 10 mL of toluene were added by syringe and the reaction mixture was stirred under oxygen (filled balloon) controlling the temperature (see Tables 1 and 2). The reaction was periodically monitored by GC-MS and quantitative analyses were performed using naphthalene as an internal standard. When the reaction was complete, the mixture was evaporated under reduced pressure at room temperature. The yield and purity of target product were determined by ¹H NMR comparing their spectral data with those reported previously in the literature and using tetradecane as an internal standard.

Methyl phenyl sulfoxide (Table 2, entry 1). ¹¹⁴ ¹H NMR (CDCl₃, 400 MHz): 2.72 (s, 3H, CH₃), 7.50–7.58 (m, 3H, Ar), 7.63–7.72 (m, 2H, Ar).

4-Methoxyphenyl methyl sulfoxide (Table 2, entry 2). ¹¹⁴ ¹H NMR (CDCl₃, 300 MHz): 2.70 (s, 3H, CH₃), 3.82 (s, 3H, OCH₃), 7.04–7.10 (m, 2H, Ar), 7.59–7.68 (m, 2H, Ar).

Methyl 4-nitrophenyl sulfoxide (Table 2, entry 3) ¹¹⁵. ¹H NMR (CDCl₃, 300 MHz): 2.81 (s, 3H, CH₃), 7.79–7.88 (m, 2H, Ar), 8.37–8.44 (m, 2H, Ar).

Diphenyl sulfoxide (Table 2, entry 4). ¹¹⁶ ¹H NMR (CDCl₃, 300 MHz): 7.29–7.43 (m, 6H, Ar), 7.56 (m, 4H, Ar).

Dibutyl sulfoxide (Table 2, entry 5). ¹¹⁴ 0.96 (t, *J* = 7.3 Hz, 3H, CH₃), 1.36–1.61 (m, 2H, CH₂), 1.65–1.83 (m, 2H, CH₂), 2.60–2.78 (m, 2H, CH₂).

Thian-4-one S-oxide (Table 2, entry 6). ¹¹⁷ ¹H NMR (CDCl₃, 300 MHz): 2.43–2.58 (m, 2H, CH₂), 2.78–2.95 (m, 2H, CH₂), 3.19–3.39 (m, 4H, 2CH₂).

(Phenylsulfinyl)acetonitrile (Table 2, entry 7). ¹¹⁸ ¹H NMR (CDCl₃, 300 MHz): 3.72 (s, 2H, CH₂), 7.49–7.75 (m, 5H, CH).

(2-Phenylsulfinyl)ethanol (Table 2, entry 8). ¹¹⁹ ¹H NMR (CDCl₃, 300 MHz): 3.07–3.13 (t, 2H, CH₂S), 3.72–3.77 (t, 2H, CH₂O), 7.19–7.28 (m, 3H, *p*-, *m*-CH), . 7.35 (d, *J* = 7 Hz, 2H, *o*-CH).

Phenyl vinyl sulfide (Table 2, entry 9). ¹²⁰ ¹H NMR (CDCl₃, 300 MHz): 5.88 (d, *J* = 9.7 Hz, 1H, CH₂), 6.18 (d, *J* = 16.4 Hz, 1H, CH₂), 6.65 (dd, *J* = 16.4, 9.7 Hz, 1H, CH), 7.44–7.77 (m, 5H, Ar).

Hot filtration test. General procedure. A 15 mL two-necked flask equipped with a magnetic stir bar was charged with 0.09 mol% of heterogenized **Mn(TMPIP)** (calculations were based on the data of ICP-OES analysis of **Mn(TMPIP)/TiO₂**). The reaction vessel was evacuated and purged by oxygen 3 times. Subsequently, 117 μL (1 mmol) of thioanisole, 456 μL (5 mmol) of IBA, and 4 mL of toluene were added by syringe and the reaction mixture was stirred at room temperature under oxygen (filled balloon) and periodically monitored by GC-MS. When a half of sulfide was consumed, a half of solution (2 mL) was withdrawn and filtered using membrane filter (0.22 μm). The second 15 mL two-necked flask equipped with a magnetic stir bar was evacuated and purged by oxygen 3 times. This reaction vessel was charged with the filtered solution obtained as described above and oxygen-filled balloon. Both reaction mixtures were stirred at room temperature and monitored by GS-MS. The results of GS-MS analyses are shown in Figure S7.

Catalyst recycling. A 25 mL two-necked flask equipped with a magnetic stir bar was charged with 0.09 mol% of heterogenized **Mn(TMPIP)** (calculations were based on the data of ICP-OES analysis of **Mn(TMPIP)/TiO₂**). The reaction vessel was evacuated and purged by oxygen 3 times. Subsequently, 293 μL (1 mmol) of thioanisole, 1.139 mL (5 mmol) of IBA, and 10 mL of toluene were added *via* a syringe and the reaction mixture was stirred at room temperature under oxygen (filled balloon) and monitored by GC-MS. After complete consumption of thioanisole, the reaction mixture was centrifugated and the catalyst was washed with toluene (3 x10 mL) and dried for 3 h at r. t.. The solid thus obtained was used as a catalyst in the next consecutive oxidation cycle. The filtrate was analysed by GC-MS using naphthalene as internal standard, evaporate under reduced pressure and analyzed by ICP-OES to determine the content of Mn. The results of these experiments are summarized in Table S3 and shown in Figure 6.

3.4. Computational details

The quantum calculations were carried out with Spartan'10 software (build 1.1.0, Wavefunction Inc.) running on a desktop computer with the Windows operating system. The structures were found by convergence to equilibrium geometry at an energy minimum with default values of gradient tolerance (4.5×10^{-4} hartree.bohr⁻¹) and distance tolerance (1.8×10^{-3} Å). The DFT calculations were performed at B3LYP level of theory with 6-31G* basis set.

The starting structures for calculation were prepared by minimization with semi-empirical PM6 method. The vibrational frequencies were calculated to prove the found structures to be minimal and showed no imaginary frequencies.

4. Conclusions

meso-Tetraarylporphyrins were immobilized on hydrated mesoporous titanium dioxide ($S_{\text{BET}} = 705 \text{ m}^2 \text{ g}^{-1}$) using carboxylate or phosphonate anchoring groups attached to 2-arylimidazole linker fused across one of pyrrolic rings of the macrocycle. Two types of hybrid materials with different loading of metalloporphyrins were prepared and characterized as both a bulk solids and at the molecular level by using different physicochemical methods including elemental analysis, UV–vis diffusion and infrared spectroscopies, SEM microphotography and nitrogen sorption isotherms. The morphology of these hybrid materials is similar to that of the pristine TiO_2 and is perfectly suited for application in catalysis. The mesoporous nanospheroids with a diameter ranging from 5 to 20 nm, are irregularly distributed in the space and separated by large holes of hundreds of nanometers, thus providing a good accessibility of catalytic sites. Homogeneous distribution of catalytic sites inside mesopores was proven by EDX analysis in STEM mode and studies of N_2 absorption isotherms. Quantitative immobilization of porphyrin catalysts can be achieved using both carboxylate and phosphonate anchors but only the later one gives hybrid materials which are stable in polar and protic solvents commonly used in organic synthesis.

Finally, catalytic properties of the most stable material **Mn(TMPIP)/TiO₂** with the phosphonate anchor were evaluated in the selective oxidation of sulfides to sulfoxides by molecular oxygen/IBA system. The heterogenized complex has shown excellent catalytic activity exhibiting a turnover (TON) of ~ 1100 in a single catalytic run of the sulfoxidation of thioanisole. TON can be increased to the value which appears be mainly limited by a patience of the experimenter by recycling the catalysts several times owing to exceptional stability of the solid. This catalyst allows for mild reaction conditions, a large scope of substrates, and excellent product yields in the reactions performed in toluene which is tolerated in industry.

Thus, we have developed a novel synthetic approach to the heterogenization of metalloporphyrins. This strategy has many potential benefits for sustainable chemistry technologies. Structural parameters of grafted metalloporphyrins can be fine-tuned by changing the nature of central metal ion and four aryl substituents attached to *meso*-positions of the porphyrin core that is important for optimization of their catalytic activity. The heterogenized catalysts thus prepared also benefit from rational design of the spacer which is

a long and rigid residue and provides a perpendicular orientation of the mean porphyrin plane with respect to a solid surface which is highly desirable for an easy accessibility of catalytic sites. The mesoporous titania is a cost-efficient, thermally and chemically stable support that decreases production costs. The least, but not the last, the quantity of the catalyst grafted onto TiO₂ surface can be easily controlled and adapted to the target catalytic reaction allowing for economic use of expensive porphyrin complexes. We believe that this immobilization strategy will be useful in catalysis because the scope of reactions catalysed by metalloporphyrins is constantly increased.

Supplementary Materials

The following supporting information can be downloaded at <https://www.mdpi.com/article/XXX>.

Author Contributions

Conceptualization, A.B.-L.; Methodology of porphyrin synthesis and DFT calculations, K.B.; Investigation, I.A.; TEM and SEM studies, R.C.; Writing, A.B.-L.; Project administration, K.B. and A.B.-L.; Funding acquisition, A.B.-L. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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