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# Olefin epoxidation by a (salen)Mn(III) catalyst covalently grafted on glass beads<sup>†</sup>

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The asymmetric epoxidation of unfunctionalized prochiral olefins catalyzed by chiral (salen)Mn(III) complexes is an important viable route to obtain chiral epoxides. Recently we proposed a monolayer of (salen)Mn(III) molecules on functionalized flat silica substrates as an active heterogeneous catalyst for enantioselective epoxidation of 6-cyano-2,2-dimethylchromene with huge turnover values. In the present study we synthesized a monolayer of modified (salen)Mn(III) molecules on previously functionalized glass bead substrates in order to increase the active surface area. The catalyst activity of this system was tested with different olefins and in some cases we observed enantioselectivity higher than in solution. The system was reused up to seven times with no variation in performance.

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# Introduction

Recently, we reported on a robust prototype (salen)Mn( $\mathfrak{m}$ )-based monolayer,<sup>1</sup> covalently bound to flat quartz substrates,<sup>2</sup> which resulted in a good chiral catalyst for asymmetric olefin epoxidation with huge turnover values.<sup>3</sup> Moreover, we also reported experimental photoelectron evidence of the formation of the surface-confined O=Mn<sup>V</sup>(salen) oxene active species.<sup>1</sup>

Olefin epoxidation reactions are of much importance since the obtained chiral epoxides contain two new stereocentres and can be easily transformed into a large variety of compounds active in many other technological fields.<sup>4-14</sup>

Homogeneous (salen)Mn(III) complexes are well suited to this purpose and high enantioselectivity in the asymmetric epoxidation of unfunctionalised olefins has been reported.<sup>15</sup>

In this context, much effort has been dedicated to heterogenize the Jacobsen catalyst throughout anchoring chiral (salen)Mn(III) complexes onto solid surfaces in order to enhance their stability, activity, selectivity, recovery and recycle.<sup>15–20</sup> However, the separation and recycling of the expensive chiral catalyst represents the main drawback of this procedure.<sup>10,22–24</sup> Very recently, Zhang and Wang reported on the asymmetric epoxidation of *cis/trans*- $\beta$ -methylstyrene using two Mn(salen) catalysts immobilized inside nanopores and the rigidity of the substrate–Mn complex linkage was found to be a key factor affecting catalytic performance.<sup>25</sup> In fact, they concluded that for immobilised Mn(salen) catalysts, a rigid linkage connecting active centres to the support is essential to obtain activity and enantioselectivity as high as those obtained in homogeneous systems. It emerges that the immobilisation strategy plays a fundamental role in this field.<sup>26</sup>

As part of our on-going study in this field we now developed a new (salen)Mn(m)-based monolayer that was grafted on the surface of some glass beads and tested its activity towards four selected alkenes (6-cyano-2,2-dimethylchromene, *cis*- $\beta$ -ethylstyrene, 1,2-dihydronaphthalene and indene). We found that the total conversion of alkenes occurred in short times. Enantiomeric excess values were similar or better than those obtained in homogeneous media and up to 90%, thus demonstrating the efficiency of the new (salen)Mn(m)based monolayer grafted on glass beads for asymmetric epoxidation.

## **Experimental details**

The detailed synthesis of the catalysts (Scheme 1) used in this work has been reported in the ESI.† NMR experiments were carried out at 27 °C on a Varian UNITY Inova 500 MHz spectrometer (<sup>1</sup>H at 499.88 MHz, <sup>13</sup>C NMR at 125.7 MHz) equipped with a pulsed field gradient module (*Z* axis) and a tuneable 5 mm Varian inverse detection probe (ID-PFG). <sup>1</sup>H NMR (Fig. S1–S4†) peak assignments follow from



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 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: Synthesis procedures,  $^1\mathrm{H}$  and  $^{13}\mathrm{C}$  NMR, APT, gCOSY, results of the epoxidation reactions using catalyst 5 in solution and AFM of glass beads (Fig. S1–S7, Table S1) are reported in the supporting information. See DOI: 10.1039/c4cy00831f

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Scheme 1 Synthetic pathway for the protected 5 and the unprotected 1. Reagents and conditions: (a) formaldehyde (aq. 37%), HCl, 90 °C, 90%; (b) *N*-hexanol-phthalimide, K<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>CN, 70 °C, 18 h, 40%; (c) (1*R*,2*R*)-1,2-diphenylethylenediamine, 3,5-di-*tert*-butylsalicylaldehyde hydrochloride, Et<sub>3</sub>N, EtOH, 80%; (d) Mn(AcO)<sub>3</sub>·2H<sub>2</sub>O, r.t., 24 h, 97%; (e) hydrazine monohydrate, EtOH, 60 °C, 10 min., 80%.

2D-COSY (Fig. S5<sup>†</sup>) experiments. Gas chromatographic analyses of the reaction mixtures were carried out on a gas chromatograph equipped with a flame ionization detector and that has programming capability.

ESI mass spectra (Fig. S6<sup>†</sup>) were acquired using ES-MS Thermo-Finnigan LCQ-DECA in MeOH (positive ion mode).

Glass beads of 3 mm diameter were first cleaned with "piranha" solution (conc  $H_2SO_4:35\%$   $H_2O_2$  70:30 v/v) at 90 °C for 60 min and then cooled to room temperature. The piranha solution is very dangerous and needs to be handled with caution! Glass beads were then rinsed (ten times) with double distilled water and kept in a solution containing  $H_2O$ ,  $H_2O_2$  (30%) and  $NH_3$  (28%) in a 5:1:1 volume ratio, respectively, at room temperature for 1 h.<sup>27-29</sup> Repeated washes with double distilled water, followed by drying under a vacuum, were carried out just prior to coupling agent (CA) deposition. All successive substrate treatments were performed in a glove box under a  $N_2$  atmosphere (1 ppm  $O_2$ , 1 ppm H<sub>2</sub>O). Freshly cleaned glass beads were immersed at room temperature for 20 min in an *n*-pentane (0.5:100 v/v)solution of trichloro[4-(chloromethyl)phenyl]silane to afford the siloxane-coated substrates.<sup>27-30</sup> These were washed (ten times) with *n*-pentane, sonicated in *n*-pentane for 10 min to remove any physisorbed CA, immersed in a freshly prepared  $9.5 \times 10^{-4}$  M toluene solution of (salen)Mn(III) (1) and kept at 90  $^{\circ}\mathrm{C}$  for 72 h while stirring. The (salen)Mn(III) monolayers on glass beads thus formed were cooled to room temperature and then sonicated (two times) for 10 min with toluene to remove any residual unreacted Mn complex.

X-ray photoelectron spectroscopy (XPS) spectra were obtained with a PHI 5600 Multi Technique System and the resolution, procedures for calibration, satellite subtraction and background removal were already reported.<sup>31,32</sup>

UV-vis measurements were carried out on a Jasco UV-vis V-650 spectrometer and the spectra were recorded with a 0.2 nm resolution at room temperature.

The glass bead surface morphology was studied by atomic force microscopy (AFM) in an instrument manufactured by NT-MDT. The noise level before and after each measurement was 0.01 nm. AFM characterisation was performed in highamplitude tapping mode (Fig. S7).<sup>+</sup>

#### Results and discussion

Scheme 1 shows the synthesis strategy for the Mn(m)-catalyst (1). 3-*tert*-Butyl-2-hydroxybenzaldehyde was chloromethylated in the 5-position by treatment with aqueous formaldehyde and hydrochloric acid to obtain 2. Then *N*-hexanol-phthalimide was linked to 2 under alkaline conditions leading to 3.

The asymmetric salen ligand 4 was obtained by the reaction of (1R,2R)-1,2-diphenylethylenediamine,3,5-di-*tert*butylsalicylaldehyde hydrochloride and aldehyde 3 in the presence of triethylamine.<sup>33</sup> The Mn-catalyst 5 was isolated by treatment of ligand 4 with manganese(m) acetate in ethanol. Finally, deprotection of the amino group in 5 by reaction with hydrazine monohydrate gave Mn catalyst 1. All of the details regarding the synthetic reactions have been reported in the ESI (Fig. S1–S6). At variance with the (salen)Mn(m) that we already used on flat quartz substrates,<sup>1</sup> this system is asymmetric since it has only one pendant amino group for surface grafting. This method should allow an increased molecular density on the substrate surface since this system has a higher degree of freedom upon grafting.

The (salen)Mn(III)-based monolayer Mn\_1\_MGB was synthesized by covalent grafting of 1 to glass beads that were previously silylated (Scheme 2).<sup>2</sup>

Silylation was performed under  $N_2$  with trichloro[4-(chloromethyl)phenyl]silane, a bi-functional coupling agent that binds both the substrate and the (salen)Mn(m).<sup>2</sup> The grafted molecules were found to be insoluble in toluene, MeCN, THF, and EtOH.

Fig. 1 shows the absorption spectra of a toluene solution of 1 (black line) at  $5.7 \times 10^{-6}$  M and of a representative Mn\_1\_MGB (red line).

The solution UV-vis spectrum shows two bands: the first centred at 296.4 with two weak bands at 286.2 and 306.4 nm and the second at 374.2 nm with a shoulder at 393.0 nm. These two bands are consistent with the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions of 1, respectively.<sup>1</sup> The Mn\_1\_MGB UV-vis spectrum closely resembles that of the solution with two features at 287.4 and 302.8 nm and another band at 366.1 nm with a shoulder at 388.6 nm. The calculated molecular surface coverage,  $d_{\text{surf}} = A\varepsilon^{-1}$  (number of molecules of 1 cm<sup>-2</sup> in Mn\_1\_MGB) is  $7.8 \times 10^{13}$  molecules cm<sup>-2</sup>.<sup>34</sup> This value is almost two times higher than that already reported for its



Scheme 2 Covalent grafting of 1 to silylated glass beads. Reagents and conditions: glass silylation: in a glove box under a N<sub>2</sub> atmosphere, 0.5:100 v/v trichloro[4-(chloromethyl)phenyl]silane/*n*-pentane, 25 °C, 25'; catalyst grafting: a  $9.5 \times 10^{-4}$  M toluene solution of (salen)Mn(III), 95 °C, 72 h.



Fig. 1 UV-vis spectra of a  $5.7 \times 10^{-6}$  M toluene solution (black line) of 1 and of a representative Mn\_1\_MGB (red line).

parent system with two pendant groups and confirms the objective of this new synthetic design.<sup>1</sup> The resulting footprint is 128 Å<sup>2</sup> per molecule.<sup>2</sup>

Fig. 2 shows the set-up of Mn\_1\_MGB on the sample holder for XPS measurements.

The glass beads were stacked with double-sided Scotch tape appropriate for XPS. A representative XPS of Mn\_1\_MGB in the Mn 2p energy region is reported in Fig. 3.

The two spin–orbit components appear at 641.8 and 653.7 eV and partially overlap with the high energy shake-up satellites typical of Mn(m) species.<sup>1,35</sup>

Fig. 4 shows the XPS of Mn\_1\_MGB in the N 1s binding energy region. On the basis of a localized bonding scheme, (salen)Mn(III) shows two imine and one amine nitrogens in the formula unit. The photoelectron spectrum of the grafted



Fig. 2 Set-up of Mn\_1\_MGB for XPS measurements.



Fig. 3 Mg K $\alpha$  excited XPS of Mn\_1\_MGB in the Mn 2p binding energy region.



Fig. 4 Mg K $\alpha$  excited XPS of Mn\_1\_MGB in the N 1s binding energy region.

complex shows a rather symmetric N 1s signal at 400.0 eV as a consequence of some electronic level reorganization of the imine functionalities upon Mn(III) complexation.<sup>1</sup>

On the basis of XPS atomic concentration analysis we estimated a surface coverage of  $5.7 \times 10^{13}$  and this value is rather close to that obtained from UV-vis measurements (*vide supra*).<sup>36–38</sup> Therefore we estimated the molecular size of 1 on the surface using MM+ calculation (HyperChem 7.5) and Fig. 5 shows the geometric arrangement.<sup>39</sup>

On the basis of these calculations the occupied area on the substrate is 134.7  $\text{\AA}^2$  per molecule. This value is strongly reminiscent of that obtained from UV-vis measurements and confirms the high density of **1** on the bead surfaces.

In order to test the activity of **Mn\_1\_MGB** as a catalyst in epoxidation reactions the following four alkenes, 6-cyano-2,2dimethylchromene, *cis*-β-ethylstyrene, 1,2-dihydronaphthalene



Fig. 5 MM+ optimization of the arrangement of 1.

and indene, have been selected. Table 1 lists the results obtained for the epoxidation of 6-cyano-2,2-dimethylchromene into 3,4-epoxy-6-cyano-2,2-dimethylchromene. Results indicate that the reaction time for total conversion decreases as the number of glass beads used in the reaction medium increases. Enantiomeric excess values (85–91%) are slightly higher than the corresponding ones (80%) obtained in solution (Table S1†). As expected, TON and TOF values are in the range of  $10^4$ – $10^5$  and  $10^2$ – $10^3$ , respectively. Table 1 shows that the addition of 4-phenylpyridine-*N*-oxide (PPNO) does not significantly influence the e.e. and conv. values. In order to check on the robustness of **Mn\_1\_MGB** the above epoxidation process was repeated 7 times for 24 h. After each cycle, **Mn\_1\_MGB** was

washed with water and dichloromethane and then reused for the next cycle. Fig. 6 shows that both enantiomeric excess values and %conversion remained almost unaltered thus confirming the high stability of the present heterogeneous catalyst.

Table 2 shows the epoxidation data obtained using cis- $\beta$ ethylstyrene. Reaction times are similar to those previously observed for 6-cyano-2,2-dimethylchromene, and also in this case the detected enantiomeric excess values are higher with respect to those observed in solution (Table S1).† However, an inversion of the *cis/trans* ratio was observed: in solution, catalyst 5 leads mainly to the *cis* isomer (*cis/trans* = 5), while **Mn\_1\_MGB** predominantly generates the *trans* isomer (90%).



Fig. 6 Variations in e.e. and conv. values after reusing 60 spheres (beads) in the epoxidation of 6-cyano-2,2-dimethylchromene for 24 h with Mn\_1\_MGB.

Number of glass bead catalyst	Reaction time/h	e.e. <sup>b</sup> %	Conv. <sup>b</sup> %	TON <sup>c</sup>	$\mathrm{TOF}^d$ $(\mathrm{h}^{-1})$
10	7	88	5	6202	886
	24	86	15	18606	775
	48	85	35	43 415	904
	72	87	55	68 2 2 4	948
	96	85	75	93 032	969
	130	86	100	124 043	982
30	7	89	12	5036	719
	24	88	25	10 4 9 2	437
	48	87	50	20984	437
	72	88	75	31 477	437
	96	87	100	41 969	437
60	7	87	30	6183	883
	24	89	45	9275	386
	48	87	77	15870	331
	72	85	100	20611	286
60 + PPNO	7	90	29	5977	854
	24	91	47	9687	404
	48	91	78	16076	335
	72	90	100	20611	286

Table 1 Results of the epoxidation of 6-cyano-2,2-dimethylchromene into 3,4-epoxy-6-cyano-2,2,-dimethylchromene using Mn\_1\_MGB<sup>a</sup>

<sup>*a*</sup> In all of these experiments 0.081 mmol of 6-cyano-2,2-dimethylchromene was dissolved in 1 mL of  $CH_2Cl_2$ ; NaClO was 0.81 mmol and the total volume of the reacting solutions buffered with 1 mL of 0.05 M Na<sub>2</sub>HPO<sub>4</sub> at pH = 11.2 was 3 mL. <sup>*b*</sup> Determined by GC with a dimethylpentyl-beta (DIMEPEBETA-086) chiral column (25 m × 0.25 mm ID, 0.25 µm film). <sup>*c*</sup> TON = mmol of the overall products/mmol of the catalyst. <sup>*d*</sup> TOF = TON/reaction time (h).

Table 2	Results of the epoxidation of	cis- $\beta$ -ethylstyrene at 2	25 °C using Mn_1_MGE
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Number of glass bead catalyst	Reaction time/h	e.e. <sup>b</sup> cis %	e.e. <sup>b</sup> trans %	Conv. <sup>b</sup> %	TON <sup>c</sup>	$\mathrm{TOF}^d$ (h <sup>-1</sup> )
10	7	80	89	17	20 958	2994
	24	80	90	29	35 556	1482
	48	83	89	56	69 275	1443
	72	84	90	73	91 095	1265
	96	84	91	100	124 043	1292
30	7	80	88	29	12 106	1729
	24	81	90	54	22798	950
	48	83	91	89	37 454	780
	72	84	88	100	41 969	583
60	7	72	88	40	8310	1187
	24	81	86	70	14 433	601
	48	85	88	94	19355	403
	72	85	87	100	20611	286
60 + PPNO	7	89	91	49	10 051	1436
	24	88	92	77	15 951	665
	48	88	91	93	19245	401
	72	89	91	100	20611	286

<sup>*a*</sup> In all of these experiments 0.081 mmol of *cis*-β-ethylstyrene was dissolved in 1 mL of CH<sub>2</sub>Cl<sub>2</sub>; NaClO was 0.81 mmol and the total volume of the reacting solutions buffered with 1 mL of 0.05 M Na<sub>2</sub>HPO<sub>4</sub> at pH = 11.2 was 3 mL. <sup>*b*</sup> Determined by GC with a DiAcTBuSiliBETA-ov-1701 chiral column (25 m × 0.25 mm ID, 0.25 µm film), [*trans*]/[*cis*] = 7. <sup>*c*</sup> TON = mmol of the overall products/mmol of the catalyst. <sup>*d*</sup> TOF = TON/reaction time (h).

Very recently Zhang and Wang reported that for immobilized Mn(salen) catalysts, a rigid linkage connecting active centres to the support is essential to obtain activity and enantioselectivity as high as that obtained in homogeneous systems.<sup>25</sup> In fact, the immobilised catalyst with a flexible linkage gave lower chemical selectivity, enantioselectivity and inverted *cis/trans* ratio compared to the homogeneous Jacobsen catalyst and to the immobilized catalyst with a rigid linkage. This is possible because of the rotation of the C-C bond in radical intermediates that affects the *cis/trans* ratio. In our case as well as in Zhang and Wang's case, the linkages are connected to the 6-position in the salen ligand, which is far from the Mn(m) atoms. Moreover, the only difference between the catalyst (5) we used for homogeneous solution reactions and the catalyst (1) anchored onto the glass beads (Mn\_1\_MGB) is the naphthylamide group that protects the amino group and this is unlikely to result in different chemical selectivities to epoxides, *cis/trans* ratio and e.e. values. Therefore, the inversion of the *cis/trans* ratio we observed from homogeneous to heterogeneous medium must be due to the rigid silane linker used to functionalize the glass bead surface for the successive grafting of 1.<sup>25</sup> Notably, we always observed a better e.e. value with Mn\_1\_MGB than in solution.

Similar epoxidation reactions have been performed with Mn\_1\_MGB using 1,2-dihydronaphthalene and indene and Tables 3 and 4 show relevant results, respectively.

Notably, reaction times for the total conversion of 1,2dihydronaphthalene and indene are shorter than those observed for *cis*- $\beta$ -ethylstyrene and 6-cyano-2,2-dimethylchromene.

Table 3	Results of the epoxidation	of 1,2-dihydronaphthalene	using Mn_1_MGB <sup>a</sup>

Number of glass bead catalyst	Reaction time/h	e.e. <sup>b</sup> %	Conv. <sup>b</sup> %	TON <sup>c</sup>	$\mathrm{TOF}^d$ $(\mathrm{h}^{-1})$
10	7	80	23	33 108	4730
	24	78	49	61 073	2545
	48	80	77	103718	2161
	72	80	100	124 043	1723
30	7	81	27	9640	1377
	24	80	55	20 664	861
	48	79	84	32 209	671
	72	80	100	41 969	583
60	7	79	31	6363	909
	24	81	84	17 293	721
	48	80	100	20611	429
60 + PPNO	7	80	38	7790	1113
	24	79	93	19222	801
	48	81	100	20.611	429

<sup>*a*</sup> In all of these experiments 0.081 mmol of 1,2-dihydronaphthalene was dissolved in 1 mL of  $CH_2Cl_2$ ; NaClO was 0.81 mmol and the total volume of the reacting solutions buffered with 1 mL of 0.05 M Na<sub>2</sub>HPO<sub>4</sub> at pH 11.2 was 3 mL. <sup>*b*</sup> Determined by GC with a dimethyl-pentyl-beta (DMePeBETACDX) chiral column (25 m × 0.25 mm ID, 0.25  $\mu$ m film). <sup>*c*</sup> TON = mmol of the overall products/mmol of the catalyst. <sup>*d*</sup> TOF = TON/reaction time (h).

Table 4 Results of the epoxidation of indene using Mn\_1\_MGB<sup>4</sup>

Number of glass bead catalyst	Reaction time/h	e.e. <sup>b</sup> %	Conv. <sup>b</sup> %	TON <sup>c</sup>	$TOF^d$ (h <sup>-1</sup> )
10	7	80	28	34 657	4951
	24	78	72	89 302	3721
	48	80	100	124 043	2584
30	7	78	31	13 105	1872
	24	81	88	36 976	1541
	48	80	100	41 969	874
60	7	75	24	4852	693
	24	78	91	18758	782
	48	78	100	20 611	429
60 + PPNO	7	77	29	6067	867
	24	78	97	20 004	833

<sup>*a*</sup> In all of these experiments 0.081 mmol of indene was dissolved in 1 mL of  $CH_2Cl_2$ ; NaClO was 0.81 mmol and the total volume of the reacting solutions buffered with 1 mL of 0.05 M Na<sub>2</sub>HPO<sub>4</sub> at pH 11.2 was 3 mL. <sup>*b*</sup> Determined by GC with a dimethyl-pentyl-beta (DMePeBETACDX) chiral column (25 m × 0.25 mm ID, 0.25  $\mu$ m film). <sup>*c*</sup> TON = mmol of the overall products/mmol of the catalyst. <sup>*d*</sup> TOF = TON/reaction time (h).

In fact, the total conversion of 1,2-dihydronaphthalene was achieved in 72 h using 10 and 30 spheres and in 48 h using 60 spheres. Indene was completely converted to the respective epoxides in 48 h using 30 spheres. The observed different reaction times for the total conversion of the above alkenes can find a rationale on the basis of the different geometric structures of the substrates. Both indene and 1,2-dihydronaphthalene have planar structures, while cis-βethylstyrene and 6-cyano-2,2-dimethylchromene are slightly more bulky, due to the freedom in the  $\gamma$ -position in *cis*- $\beta$ ethylstyrene and the two methyl groups in 6-cyano-2,2dimethylchromene. Planar alkenes seem more suitable than bulky substrates to interact with the surface-confined Mn 1 MGB (Fig. 5). In these cases enantiomeric excess values are similar to our data obtained in solution (Table S1<sup>+</sup>) and similar to recently reported results.40-45

An interesting observation is the high present value of the turnover frequencies under heterogeneous conditions  $(1.24 \times 10^5 \text{ using 10 spheres})$  with respect to the solution (20) after total olefin transformation.<sup>20,21,41</sup> Obviously, the highest TON values have been observed for the lowest number of beads used in the reaction media (Tables 1–4). The TOF parameter<sup>41</sup> displays a similar trend on passing from homogeneous (10) to heterogeneous (4951 highest TOF for indene epoxidation after 7 h reaction) conditions. Evidently, these large TOF values (Tables 1–4) are due to the covalent nature of the active catalyst that precludes any leaching as measured in the reacting solution by inductively coupled plasma mass spectrometry.

The present increase in enantioselectivity from solution (80%, Table S1†) to heterogeneous (85–91%, Tables 1–2) catalysis observed for the first two alkenes may be consistent with the grafting geometry of this (salen)Mn(III) catalyst that is always appropriate for epoxidation reaction. We already noted that it is possible to assume that the O=Mn<sup>V</sup> group of O=Mn<sup>V</sup>(salen) points outside from the monolayer.<sup>1,25</sup> A similar conclusion has been arrived at by Milstein who reported improved TON values in catalytic reactions using molecular ordered Langmuir–Blodgett catalyst films.<sup>46</sup>

## Conclusions

A novel (salen)Mn(m) robust monolayer was covalently fabricated on glass bead substrates and resulted in an active catalyst for asymmetric epoxidation of four different alkenes. High enantioselectivity and high TON and TOF values have been observed. No observable leaching of the catalyst as well as no performance variation was noted after 7 reaction cycles.

According to the studies of  $Zhang^{25}$  and  $Tu^{47}$  the rigid silane group used to graft the present (salen)Mn(m) complex to the glass bead surface was advantageous to attain high activity and e.e. values. Our present study demonstrates the possibility to heterogenize the (salen)Mn(m) catalyst by improving the performance with respect to the solution reactions. In fact, we believe that some enantiomeric excess values are better than those obtained in homogeneous media because the (salen)Mn(m) catalyst, supported on the present glass beads, probably assumes the most appropriate conformation to promote efficient enantioselective oxygen transfer towards some substrates.

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