Electronic Supplementary Information

Surface-Confined O=Mn^{V}(salen) Oxene Catalyst and High Turnover Values in Asymmetric Epoxidation of Unfunctionalized Olefins

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All chemicals were reagent grade, some of them packed under nitrogen, and were used throughout the present syntheses without further purification. (*1R,2R*)-(+)-1,2-diphenylethylenediamine, 2,3-dihydroxy benzaldheyde, 2-*tert*-buthyl phenol and phtalic anhydride were commercially available reagent-grade materials (Aldrich). *N*-12-bromododecylphtalimmide was synthesised as previously reported.[S1]

Synthesis of aldehyde 2

2.2 mL of 2-*tert*-butyl-phenol (14 mmol) were dissolved in 600 mL of dry chloroform under nitrogen. The solution was cooled at 0°C. Then, 5 mL (55 mmol) of Cl_2CHOCH_3 and 55 mL (55 mmol) of a 1 M solution of $SnCl_4$ in CH_2Cl_2 were added. The mixture was stirred at 0°C under nitrogen for 1 h. Then, 500 mL of brine was added while stirring. The organic phase was extracted (3 times) with chloroform, dried over $MgSO_4$ and separated by flash chromatography (hexane:EtOAc 98:2) to give the pure compound **2** (yield = 35%). ^{1}H NMR (500MHz, $CDCl_3$) δ 11.7 (s, 1H), 9.9 (s, 1H), 7.5 (d, J = 7.5 Hz, 1H), 7.4 (d, J = 7 Hz, 1H), 1.4 (s, 9H). ESI/MS: *m/z* = 178.2 $[M+H]^+$. Anal. Calcd. for C, 74.13; H, 7.92; O, 17.95. Found: C, 74.11; H, 7.89.

Synthesis of aldehyde 3

170 mg (5.9 mmol) of *p*-formaldehyde, 95 mg (0.28 mmol) of TBABr (tetrabutylammonium bromide) and 40 mL of conc. HCl were added to 500 mg (2.8 mmol) of the aldehyde **2**. The mixture was stirred at room temperature 3 days. The organic phase was extracted with diethyl ether (3 times), neutralized with a solution of Na_2CO_3 30%, dried over $MgSO_4$ and concentrated in vacuo, thus giving the pure compound **3** as a yellow solid (yield = 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.8 (s, 1H), 9.9 (s, 1H), 7.5 ppm (d, J = 8 Hz, 1H), 7.4 (d, J = 8 Hz, 1H), 4.5 (s, 2H), 1.5 (s, 9H). ESI/MS *m/z* = 226.1 $[M+H]^+$. Anal. Calcd. for C, 63.58; H, 6.67; Cl, 15.64; O, 14.12. Found: C, 63.53; H, 6.61; Cl, 15.62.

Synthesis of the hexanol phtalimide 4

1.00 g (6.9 mmol) of pthalic anhydride and 792 mg (6,8 mmol) of 6-amino-1-hexanol were poured in a vessel. The reaction was carried out in a microwave apparatus in dry conditions: power 80 Watt, temperature 160°C, time 5 min. The pure compound **4** was obtained as dark brown solid (yield = 94%). ^{1}H NMR (500 MHz, $CDCl_3$) 7.9 (d, J = 9 Hz, 2H), 7.8 (d, J = 9 Hz, 2H), 3.70 (t, J = 7 Hz, 2H), 3.64 (t, J = 7 Hz, 2H), 1.7 (m, 2H), 1.6 (m, 2H), 1.4 ppm (m, 4H). ESI-MS m/z 437.2 $[M+H]^+$. Anal. Calcd. for C, 68.00; H, 6.93; N, 5.66; O, 19.41. Found: C, 67.97; H, 6.91; N, 5.63.

Synthesis of aldehyde 5

200 mg (0.9 mmol) of aldehyde **3**, 220 mg (0.9 mmol) of hexanol pthalimide **4**, 54 mg (0.9 mmol) of KOH, 286 mg (2.1 mmol) of K_2CO_3 and 30 mg (0.09 mmol) of TBABr were poured in a vessel. The reaction was carried out in a microwave apparatus in dry conditions: power 40 Watt, temperature 127°C, time 5 min. The crude product was extracted with CH_2Cl_2, dried over $MgSO_4$ and concentrated in vacuo. Compound **5** was purified by flash chromatography (hexane: EtOAc 98:2) (yield = 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.76 (s, 1H), 9.87 (s, 1H), 7.84 (m, 2H), 7.71 (m, 2H), 7.47 (d, J = 2 Hz, 1H), 7.38 (d, J = 2 Hz, 1H), 4.42 (s, 2H), 3.68 (t, J = 7 Hz, 2H), 3.48 (t, J = 7.5 Hz, 2H), 1.69 (m, 2H), 1.61 (m, 2H), 1.41 (s, 9H), 1.35-1.40 (m, 4H). ESI-MS *m/z* 438.2 $[M+H]^+$. Anal. Calcd. for C, 71.37; H, 7.14; N, 3.20; O, 18.28. Found: C, 71.32; H, 7.10; N, 3.18.

Synthesis of the salen ligand 6

12.1 mg (0.057 mmol) of (*1R,2R*)-diphenylethylendiamine were added to a 20 mL solution of absolute ethanol containing 50 mg (0.114 mmol) of aldehyde **5**. The reaction proceeds until the almost disappearing of the starting reagent (checked by TLC analysis). Then, the solvent was removed under reduced pressure thus obtaining the pure salen ligand **6** (yield = 95%). ^{1}H

NMR (500 MHz, $CDCl_3$) δ 13.74 (s br. 2H), 8.34 (s, 2H), 7.82 (m, 4H), 7.70 (m, 4H), 7.16-7.21 (m, 12H), 6.96 (d, J = 2 Hz, 2H), 4.73 (s, 2H), 4.30 (s, 4H), 3.63 (t, J = 7 Hz, 4H), 3.37 (t, J = 7 Hz, 4H), 1.67 (m, 4H), 1.56 (m, 4H), 1.40 (s, 18H), 1.30-1.39 (m 8H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 168.39, 166.78, 159.78, 139.49, 137.16, 133.78, 132.13, 129.53, 128.25, 127.96, 127.43, 123.09, 118.16, 80.00, 72.67, 70.01, 37.97, 34.78, 29.30, 28.55, 26.72, 26.48, 25.83, 25.17. ESI-MS *m/z* 1051 $[M+H]^+$. Anal. Calcd. for C, 75.40; H, 7.09; N, 5.33; O, 12.17. Found: C, 75.35; H, 7.05; N, 5.30.

Synthesis of 1-Mn

The absolute ethanol solution of the given salen-ligand **6** was stirred overnight at room temperature with 1.5 equivalents of manganese(III) acetate. When the starting ligand was completely converted (checked by TLC analysis), the solvent was removed under reduced pressure. Then, 5 mL of CH_2Cl_2 were added to the remaining crude solid to dissolve the Mn complex. The residual precipitate (not reacted manganese(III) acetate) was removed and the CH_2Cl_2 solution was concentred in vacuo thus giving the corresponding catalyst with nearly quantitative yield. **1-Mn** catalyst was characterized by ESI-MS measurements: **1-Mn** *m/z* 1103 $[M]^+$.

Synthesis of the Mn_1 catalyst (de-protection)

40 equivalents of hydrazine monohydrate were added to the solution containing **1-Mn** catalyst in ethanol. The related mixture was stirred at reflux for 7 h. Then, the solvent was removed under reduced pressure and the given compound extracted by addition of chloroform with nearly quantitative yield. De-protected **Mn_1** catalyst was characterized by ESI-MS measurements: **Mn_1** *m/z* 843 $[M]^+$.

Synthesis of the uranyl complex of salen ligand 6

The absolute ethanol solution of the given salen-ligand **6** was stirred overnight at room temperature with 1.5 equivalents of uranyl(VI) acetate. When the starting ligand was completely converted (checked by TLC analysis), the solvent was removed under reduced pressure. Then, CH_2Cl_2 was added to the remaining crude solid to dissolve the UO_2 complex. The residual precipitate (not reacted uranyl acetate) was removed and the CH_2Cl_2 solution was concentred in vacuo thus giving the corresponding complex (yield = 10%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (s, 2H), 7.82 (m, 4H), 7.70 (m, 4H), 7.19-7.24 (m, 12H), 6.96 (d, *J* = 2 Hz, 2H), 4.90 (s, 2H), 4.52 (s, 4H), 3.83 (t, *J* = 7 Hz, 4H), 3.57 (t, *J* = 7 Hz, 4H), 1.77 (m, 4H), 1.66 (m, 4H), 1.40 (s, 18H), 1.30-1.39 (m 8H). ESI/MS: *m/z* = 1318.6 $[M+H]^+$.

Monolayer formation

Silica (quartz) substrates were cleaned in a "piranha" solution (98% H_2SO_4 : 30% H_2O_2 70 : 30 v/v) at 85 °C for 50 min and then left to cool to room temperature. ***Warning: the "piranha" solution is extremely dangerous and needs to be used with particular care. Its preparation has to be done within the hood, by immersion of the piranha-containing beaker in cold water. The operator needs to wear a safety coat, gloves and protect eyes with glasses***. Substrates were then repeatedly rinsed with double distilled water and kept in a H_2O : 30% H_2O_2 : NH_3 5 : 1 : 1 v/v/v mixture at room temperature for 1 h. Then, they were washed again with double distilled water, dried under vacuum and transferred in a glove box under a N_2 atmosphere where they were dipped, at room temperature, for 25 min, in a 0.3 : 100 v/v *n*-pentane solution of the chemisorptive reagent, trichloro[4-(chloromethyl)phenyl]silane (siloxane), to afford a coupling agent (CA) monolayer. The siloxane-coated substrates were washed with copious amounts of *n*-pentane, heated up to 130°C for 3 min to complete the CA grafting, sonicated in acetone for 3 min to remove any eventual remaining physisorbed CA, immersed into a 4.4×10^{-4} M toluene solution of the (salen)Mn(III) and kept at 90 °C for 80 h while stirring. The formed (salen)Mn(III) monolayer (**Mn_1-SAM**) was cooled to room

temperature and sonicated with CH_3CN, toluene and THF to remove any residual unreacted (salen)Mn(III). The monolayer surface morphology was studied by atomic force microscopy (AFM) in tapping mode using an instrument manufactured by the NT-MTD. The monolayer surface was homogeneous and flat. No IR measurements can be performed on quartz substrates since in the 2500-400 cm^{-1} range quartz absorbs the 100% of the IR radiation and Raman spectra on monolayers are uninformative.

Epoxidation reactions

Epoxidation reactions of 6-ciano-2,2-dimethyl-chromene were performed to test the behaviour of the **Mn_1** catalyst and the related SAM. The 6-ciano-2,2-dimethyl-chromene was chosen as a model substrate and its epoxide is of potential value as a pharmaceutical intermediate. In all these experiments, performed at room temperature, 0.17 mmol of the alkene were dissolved in 4 mL of CH_2Cl_2 and mixed with 4 mL of a Na_2HPO_4,= 0.05 M buffer solution at pH = 11.2 containing also 1.6 mmol of NaOCl. For heterogenized reactions, the Mn-SAM catalyst having a 2x1 cm size was suspended with nylon wires in the stirred reaction mixtures. The catalyst was $8.5x10^{-3}$ and 2.6×10^{-7} mmol for homogeneous and heterogenized epoxidations, respectively.

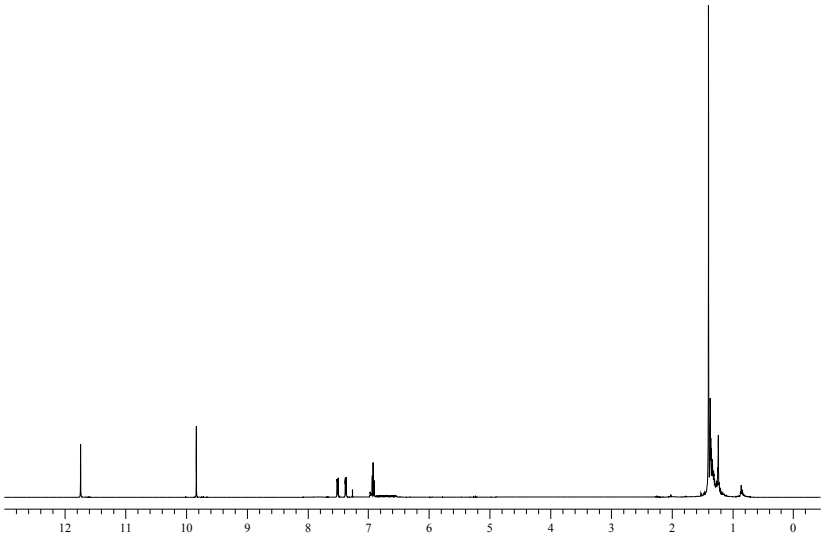

Figure S1. ^{1}H NMR spectra of aldehyde **2** in $CDCl_3$

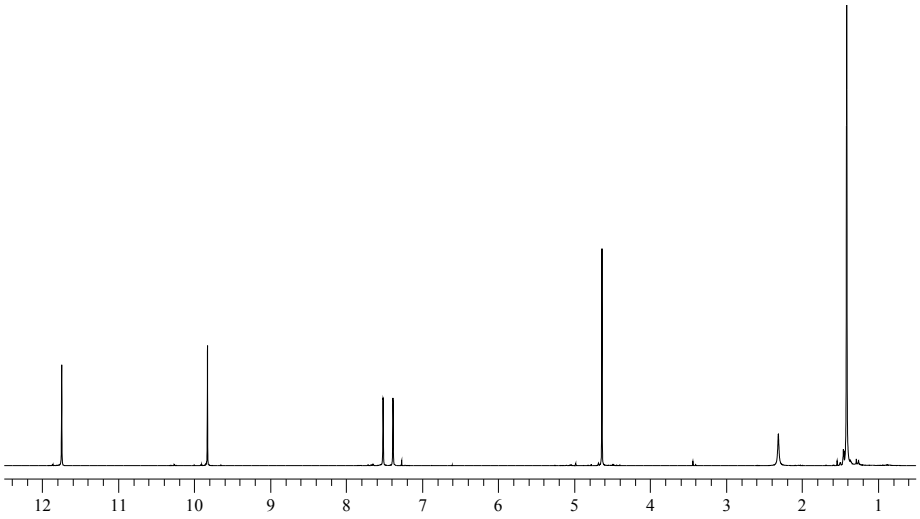

Figure S2. ^{1}H NMR spectra of aldehyde **3**

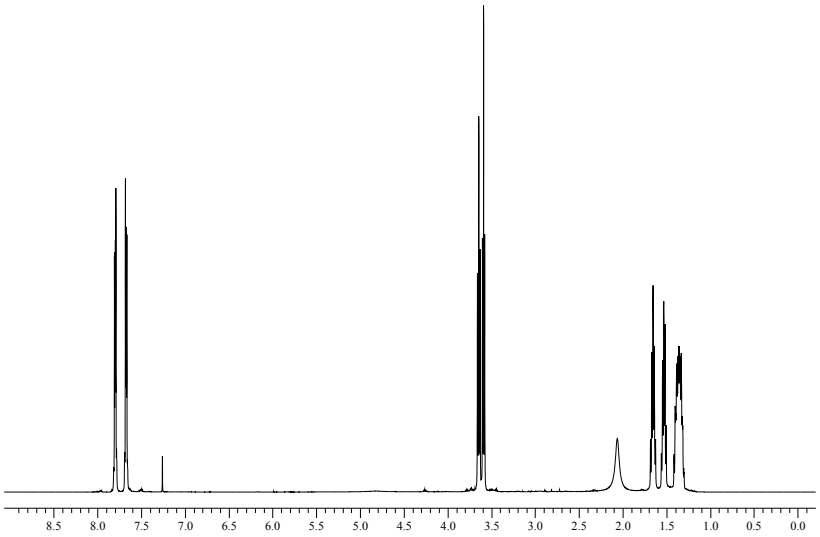

Figure S3. ^{1}H NMR of hexanol phtalimide **4** in $CDCl_3$

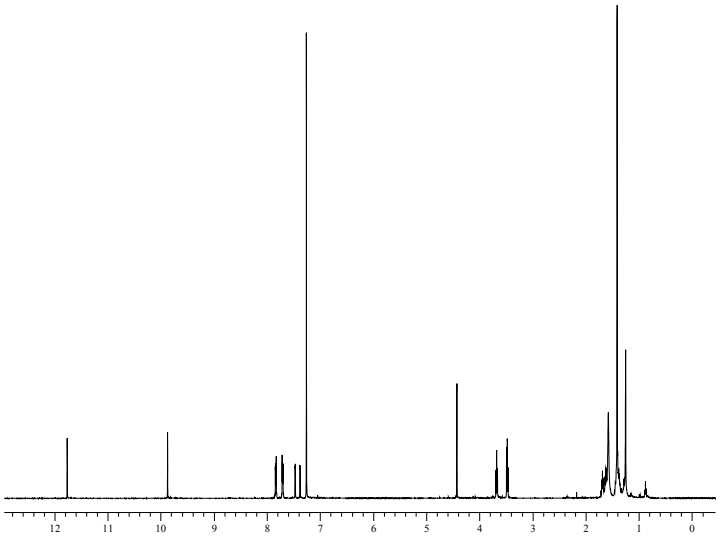

Figure S4. ^{1}H NMR of aldehyde **5** in $CDCl_3$

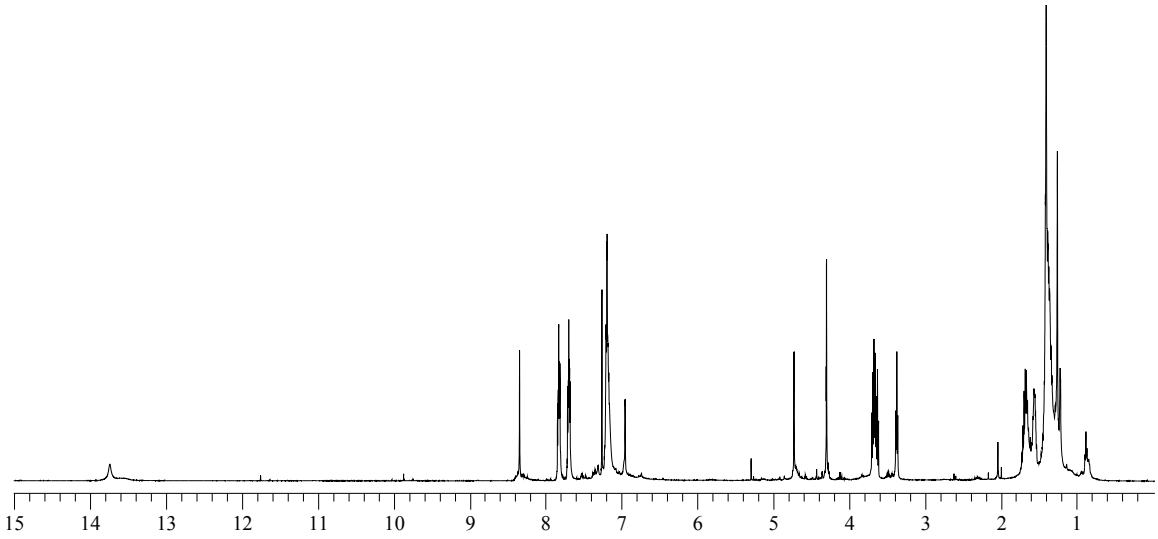

Figure S5. ^{1}H NMR of salen ligand **6** in $CDCl_3$

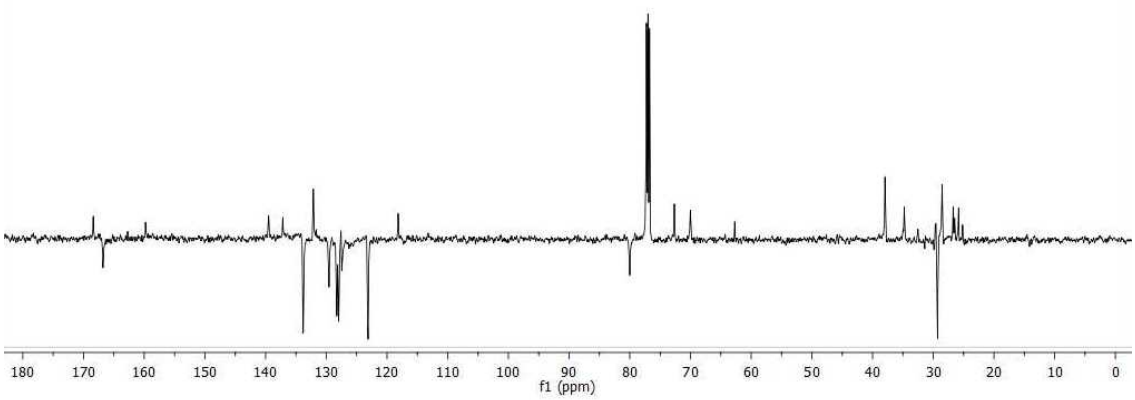

Figure S6. APT of salen ligand **6** in $CDCl_3$

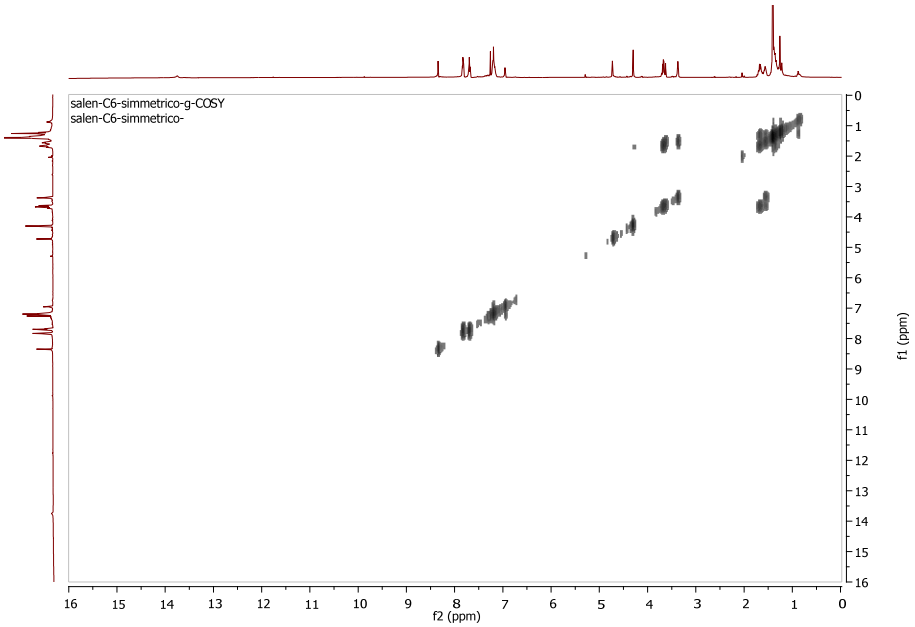

Figure S7. gCOSY of salen ligand **6** in $CDCl_3$

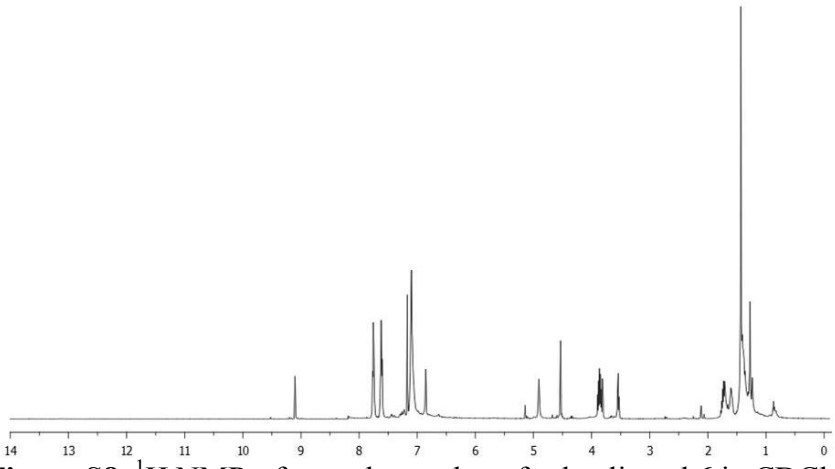

Figure S8. ^1H NMR of uranyl complex of salen ligand **6** in $CDCl_3$

Figure S9 shows the XPS spectrum for the **Mn_1-SAM** in the N 1s binding energy region. Simulation of the experimental profile reveals two components at 398.8 and 400.2 eV having a 1:1 intensity ratio. The peak at lower binding energy is consistent with ionization of the imine nitrogens and that at higher binding energy refers to two equivalent amine groups that bind the functionalized substrate. This observation indicates that both $–NH_2$ groups are involved in the surface grafting.

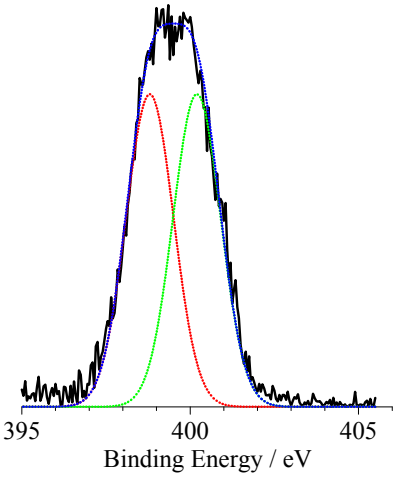

Figure S9. Al Kα excited **Mn_1-SAM** in the N 1s energy region. Solid black line refers to the experimental profiles; dashed red and green lines refer to the 398.8 and 400.2 eV Gaussian components, respectively. The dashed blue line superimposed to the experimental profile refer to the sum of the Gaussians.

References

S1. Pappalardo, S.; Villari, V.; Slovak, S.; Cohen, Y.; Gattuso, G.; Notti, A.; Pappalardo, A.; Pisagatti, I.; Parisi, M. F. *Chem. Eur. J.* **2007**, *13*, 8164-8173.