Supplementary Material (ESI) for Chemical Communications


# An Achiral Manganese Salen Catalyst Encapsulated in a Peptidic Phosphonate Homochiral Solid for the Enantioselective Formation of Diols by Consecutive Epoxidation and Hydration Reactions

**Anat Milo and Ronny Neumann***

## Electronic Supporting Information

### Materials and Methods.

Starting materials were obtained from commercial suppliers and were used without further purification. Organic solvents were purchased in the purest form available (HPLC grade or better), anhydrous Dichloromethane (DCM) was used (Sigma-Aldrich), and THF was refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Syntheses and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. Freshly deionized 18.3 MΩcm water from a Millipore (Millipore Corp., Danvers, MA) water purification system was used for catalytic experiments.

The solution state NMR spectra were recorded at 20 °C on Bruker Avance spectrometers: $^{1}H$ at 250, 400 and 500 MHz, $^{13}C$ at 100 and 126 MHz, and $^{31}P\{^{1}H\}$ at 101 and 202 MHz. $^{1}H$, $^{13}C\{^{1}H\}$ NMR chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (δ scale). $^{1}H$ and $^{13}C\{^{1}H\}$ NMR chemical shifts were referenced to the residual signal of Chloroform-*d* and DMSO-*d*6 (7.24 and 2.50, 77.23 and 39.51 ppm respectively). Coupling constants (J) are reported in Hertz (Hz), and splitting patterns are designated as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet), *b* (broad). $^{31}P\{^{1}H\}$ NMR chemical shifts are reported in ppm downfield from an external 85% phosphoric acid standard in $D_2O$. The solid state CP-MAS - $^{31}P\{^{1}H\}$ NMR spectra were recorded at 20°C on Bruker "Avance" spectrometer using a 4mm triple resonance MAS probe at 202 MHz operated at MAS speed of 5925 Hz.

IR spectra were recorded on a Nicolet 6400 FT-IR spectrophotometer with the samples loaded into KBr pellets.

Matrix-assisted laser desorption/ionization (MALDI) mass-spectrometry was preformed on Bruker "Reflex III" reflector time-of-flight instrument with "Scout" multiprobe (384) inlet and gridless delayed extraction ion source. Electrospray ionization (ESI) mass-spectrometry was performed using a Micromass Platform instrument.

Elemental analyses were performed on FlashEA 1112 CHN Elemental Analyzer using Eager 300 software.

Thermo-gravimetric analysis (TGA) was carried out using a TA instruments Q-600 TGA from 40 to 1400°C with a temperature ramp rate of 10° $min^{-1}$.

Differential scanning calorimetry (DSC) was carried out using a TA Instruments Q-200 DSC from 40 to 255°C with a temperature ramp rate of 5° $min^{-1}$.

Transmission Electron Microscopy (TEM) and Energy Dispersive Spectrometry (EDS) studies were carried out with a FEI (Philips) CM-120 ST transmission electron microscope, operating at 120 kV. Samples were prepared by

dispersing the particles at the same concentration of THF:water used in the catalytic experiments (1:1) by ultrasonic treatment and then depositing them onto a holey carbon film supported on a copper grid. The samples were stable under electron beam radiation. EDS analysis was carried out using an EDAX instrument (Phoenix) equipped with a Si(Li) retractable detector with a super ultra thin window.

CryoTEM images were obtained on a FEI (Philips) T12 - Tecnai transmission electron microscope, operating at 120 kV. Samples were maintained under cryogenic temperature with a Gatan 626DH cryo holder. Images were rendered using a TVIPS F224HD bottom-mounted CCD camera. The samples were prepared by dispersing the particles in THF:water (1:1) by ultrasonic treatment, then depositing them onto a holey carbon film supported on a copper grid, and plunging them into liquid ethane with a CEVS plunger [Bellare, J. R.; Davis, H. T.; Scriven, L. E.; Talmon, Y. *J. Electron. Micr. Technol.* **1988**, *10*, *87*-111].

An ULTRA 55 FEG ZEISS Scanning Electron Microscope (SEM) with accelerating voltage of 0.1-30 kV was used to observe the morphology of the material. Imaging was achieved using a high efficiency in-lens SE detector as well as an EsB detector with filtering grid for the detection of energy and angle selective backscattered electrons. Samples were prepared by the same method described for TEM.

N2 Sorption experiments were carried out using Quantachrome NOVA 1000 high-speed sorption analyzer and data was analyzed using NOVAWin software. Materials were degassed for 14 h at 100 °C prior to the measurement.

X-ray powder diffraction patterns were measured in the 2θ as well as θ/2θ mode using a vertical θ/θ goniometer equipped with a rotating anode X-ray generator (Rigaku TTRAX III, 18 kW, Cu K). The sample was dispersed on a background-free silicon sample holder.

Solid-state UV-drift measurements were carried out on a Varian Cary-300 spectrometer mounted with a LabSphere Integrating sphere.

**Synthesis.**

*L−(+)-α-Phenylglycine N-carboxy anhydride (L-PhGly NCA).* *L*-PhGly NCA was prepared according to Katakai, R; Iizuka, Y. *J. Org. Chem.* **1985**, *50*, 715-716 using a modified procedure. *L*-PhGly (10 g, 66 mmol) and activated charcoal (160 mg) were pre-dried under vacuum over night. Dry THF (180 mL) was added, followed by the drop-wise addition of trichloromethyl chloroformate (6.5 mL, 10.66 g, 54 mmol). The reaction mixture was heated to 50°C and stirred until the amino acid dissolved (2-3 h). After cooling to room temperature, the reaction mixture was filtered through Celite 545, which was then washed with diethyl ether (400 mL), and the solvents were evaporated under reduced pressure. The residue was dissolved in the minimum amount of diethyl ether, and hexane (400 mL) was added to the solution leading to the immediate formation of pale yellow featherlike crystals. The crystals where separated by filtration, washed with hexane (200 mL), and dried under vacuum to afford *L*-PhGly NCA at 94% yield (10.9 g, 62 mmol), which was used directly in the next reaction.

*Preparation of tris(oligo-L-PhGly-2-aminoethyl)amine,* ***P1***. Dry THF (100 mL) was added to *L*-PhGly NCA (10.9 g, 62 mmol) under argon, followed by the rapid addition of tris(2-aminoethyl)amine (750 μL, 730 mg, 5 mmol) dissolved in THF (50 ml). The formation of a precipitate was immediate and the reaction mixture was stirred under argon overnight. The precipitate was separated by centrifuge at 6000 rpm, washed with diethyl ether, and dried under vacuum affording **2** at 98% Yield (calculated according to an average molecular weight of 1744 g/mol, 8.6 g, 4.9mmol). Anal. Calc. for $C_{102}H_{102}N_{16}O_{12}$: C, 70.25; H, 5.90; N, 12.85. Found: C, 68.53; H, 5.85; N, 12.49.

MALDI-TOF-MS. A distribution of peaks is observed with a repeating unit of 132 and the main peak at *m/z* = 1744, accounting for 12 repeating units in total as anticipated for the 12:1 *L*-PhGly NCA to tris(2-aminoethyl)amine used in the reaction. The peaks of M+Na adducts ions are predominant and can be seen at *m/z* = 1766.

IR (KBr, ν, $cm^{-1}$). 697.6, 731.5, 853.1, 918.4 (monosubstituted benzene CH bend and ring puckering); 1003.2, 1029.9, 1075.1, 1128.7, 1189.1, 1227.1 (aliphatic CH bend, NH bend and CN stretch); 1375.4 ($CH_2$ bend); 1453.9, 1496.8, 1585.6, 1602.3 (C=C aromatic stretch); 1509.1 (amide NH bend and CN stretch); 1647.9 (amide CO stretch); 2947.6 (aliphatic CH stretch); 3032.0, 3062.1 (aromatic ring stretch); 3300.4-3700 (amide NH and hydrogen bound OH stretch).

$^1$H NMR (500 MHz, DMSO-*d*6): δ = 2.29 (*b*, 6H, [$\dot{N}(CH_2)_3$]), 2.94 (*b*, 6H, [$\dot{N}(CH_2CH_2)_3$]), 4.59 (*m*, 2H, terminal [$NH_2$]), 5.45 (*b*, 3 H, [$(CH_2)_3NHCH(Ph)$], 5.76 (*b*, 6 H, [$CONHCH(Ph)$]), 7.20-7.50 (*b*, 60 H, [Ph]), 8.18 (*bd*, 3 H, [$(CH_2)_3NH_2^+CO^-$ C(Ph)]), 9.00 (*bd*, 9 H, [$C(Ph)NH_2^+CO^-$ C(Ph)]). The last two peaks are attributed to the zwitterionic character of the amide bonds. These peaks slightly shift at different pH values and seem to be split with a J constant of 110Hz, which is in the higher range of $^1J_{NH}$ coupling and thus could also suggest strong hydrogen bonding.

$^{13}$C{$^1$H} NMR (126 MHz, DMSO-*d*6): δ = 36.94 (*s*, [$\dot{N}(CH_2)_3$]), 52.77 (*s*, [$\dot{N}(CH_2)_3(CH_2)_3$]), 55.29-55.90 (*m*, [*C*H(Ph)]), 58.53 (*s*, [*C*H(Ph)$NH_2$]), 126.87-128.03 (*m*, [$CC_5H_5$]), 138.42 (*m*, [$CC_5H_5$]), 142.06 (*s*, [$CH(CC_5H_5)NH_2$]), 169.20 (*m*, [*C*OCH(Ph)]), 172.32 (*s*, [*C*OCH(Ph)$NH_2$]).

*Preparation of diethylphosphonoethanoyl chloride.* According to Teichert, A.; Jantos, K.; Harms, K.; Studer, A. *Org. Letters* **2004**, *6*, 3477–3480 (Diethoxyphosphoryl)acetic acid (1.4 ml, 1.7 g, 8.7 mmol) was added to neat thionyl chloride (5.95 g, 3.6 ml, 50 mmol). After stirring for 2 h at RT, the excess thionyl chloride and any gases formed were distilled under high vacuum to afford the corresponding acyl chloride (92%, 1.72 g, 8 mmol). The compound was used without further purification as a reagent in an amide coupling reaction.

$^1$H-NMR (250 MHz, $CDCl_3$): δ = 1.36 (*t*, $^3J_{HH}$ = 7.5, 6H, [$CH_3$]), 3.49 (*d*, $^2J_{PH}$ = 20, 2H, [$PCH_2$]), 4.21 (*qd*, $^3J_{HH}$ = 7.5, $^3J_{PH}$ = 1.5, 4H, [$POCH_2$]).

*Preparation of tris(diethylphosphonomethylcarbonyl-oligo-L-PhGly-2-aminoethyl)amine,* ***P2***. Dry DCM (50 mL) was added to **P1** (3.6 g) under argon, followed by the drop-wise addition of diethylphosphonoethanoyl chloride (1.72 g, 8 mmol) in DCM (10 mL). The reaction mixture was stirred under argon overnight, and the solvent was evaporated to give a mustard colored powder. The crude product was washed with 0.5 M NaOH and separated by centrifuge at 8000 rpm, followed by 3 washes with water until the pH value of supernatant was neutral, and then the solid was washed by diethyl ether. The fine yellow power obtained was dried under vacuum to give **P2** at 86% yield (3.8 g). Anal. Calc. for $C_{120}H_{135}N_{16}O_{24}P_3$: C, 63.26; H, 5.97; N, 9.84. Found: C, 63.08; H, 5.67; N, 9.97.

MALDI-TOF-MS. A Gaussian distribution of peaks is observed with a repeating unit of 132. We note here the peaks corresponding to **P2** with 12 *L*-PhGly units for qualitative analysis in accord with the main peak of the precursor **P1**. *m/z* = 2276 $[M+H]^+$, adducts *m/z*= 2298 $[M+Na]^+$, *m/z* = 2319 $[M+2Na]^+$, *m/z* = 2340 $[M+Na+K]^+$, *m/z* = 2364 $[M+2Na+K]^+$, *m/z* = 2385 $[M+3Na+K]^+$.

IR (KBr, ν, $cm^{-1}$). 698.0, 733.3, 858.9 (monosubstituted benzene CH bend and ring puckering); 976.2, 1028.4 (ester PO bend); 1046.0 (phosphonate PO stretch); 1061.9, 1129.4, 1190.2 (aliphatic CH bend, NH bend and CN stretch; some aliphatic features are hidden under new peaks); 1234.3 (phosphonate CP stretch); 1369.3, 1375.4 ($CH_3$ and $CH_2$ bend); 1453.9, 1496.8, 1585.6, 1602.3 (C=C aromatic stretch); 1511.7 (amide NH bend and CN stretch); 1647.9 (amide CO stretch); 2932.5, 2982.6 (aliphatic $CH_3$, $CH_2$ and CH stretch); 3032.9, 3062.1 (aromatic ring stretch); 3298.1 – 3700 (amide NH stretch and hydrogen bound OH from water).

$^1$H NMR (500 MHz, DMSO-*d*6): δ = 1.15 (*b*, 13 H, [$PO(OCH_2CH_3)_2$]), 2.29 (*b*, 6 H, [$N(CH_2)_3$]), 3.01-3.04 (*m*, 9 H, [$N(CH_2CH_2)_3$] and [$COCH_2PO$]), 3.97 (*m*, 9 H [$PO(OCH_2CH_3)_2$]), 4.59 (*m*, 1 H, ammonium [$HN(CH_2)_3$]), 5.43 (*b*, 3 H, [$(CH_2)_3NHCH(Ph)$], 5.76 (*b*, 6 H, [$CONHCH(Ph)$]), 7.15-7.43 (*b*, 60 H, [Ph]), 8.16 (*bd*, 2 H, [$(CH_2)_3NH_2^+CO^-C(Ph)$]), 9.01 (*bd*, 8 H, [$C(Ph)NH_2^+CO^-C(Ph)$]), 8.60 (*s*, 1H, [PO(OH)]), 8.68 (*m*, 1 H, [$NH_2^+CO^-CHPO$]).

$^{13}$C{$^1$H} NMR (126 MHz, DMSO-*d*6): δ = 16.15 (*s*, [$PO(OCH_2CH_3)$]), 33.60 (*s*, [$COCH_2PO$]), 34.63 (*s*, [$NH_2^+CO^-CHP$]), 36.93 (*s*, [$N(CH_2)_3$]), 52.83 (*s*, [$N(CH_2)_3(CH_2)_3$]), 55.76 (*m*, [$CH(Ph)$]), 57.89 (*s*, [$CH(Ph)NH_2$]), 61.64 (*s*, [$PO(OCH_2CH_3)_2$], 127.03-128.16 (*m*, [$CC_5H_5$]), 129.52 (*s*, [$CH(CC_5H_5)\ NH_2^+CO^-\ CHP$]), 138.42 (*m*, [$CC_5H_5$]), 140.92 (*s*, [$CH(CC_5H_5)NHCOCH_2P$]), 163.68 (*s*, [$NHCOCH_2P$]), 169.17 (*m*, [$COCH(Ph)$]), 171.63 (*s*, [$COCH(Ph)NHCOCH_2P$]).

$^{31}$P{$^1$H} NMR (202 MHz, DMSO-*d*6, 20°C) δ = 23.94 (*s*, [$PO(OCH_2CH_3)_2$]).

*Preparation of tris(phosphonomethylcarbonyl-oligo-L-Phe-gly-2-aminoethyl)anime, **P3***. **P2** was hydrolyzed mildly using a modified procedure explicitly introduced by Morris*, A. D.;* Cordi A. A. *Synth. Commun.* **1997**, *27*, 1259-1266 in order to avoid amide bond cleavage and racemization. The modifications introduced here are due to the polymeric nature of the reactant. Acetonitrile (150 mL) was added to **P2** (3.1 g), followed by the addition of bromotrimethylsilane (2.7 ml, 3.1g, 19.8 mmol) and heated to reflux for 1.5 h with a $CaCl_2$ guard tube. The orange suspension was cooled to room temperature, the solvent was evaporated, and water (80 ml) was added to the fine orange powder. The suspension was treated by vortex and sonic bath; the precipitate was separated by centrifuge at 9000 rpm, and washed with water twice and lyophilized over night. The crude product was washed with ether and dried over night to give **P3** as a dark yellow powder (98% yield, 3.0 g). Anal. Calc. for $C_{108}H_{111}N_{16}O_{24}P_3$: C, 61.48; H, 5.30; N, 10.62. Found: C, 60.74; H, 5.62; N, 10.19.

MALDI-TOF-MS. A Gaussian distribution of peaks with a repeating unit of 66 is observed. We note here the peaks corresponding to **P3** with 12 *L*-PhGly units for qualitative analysis in accord with the main peak of the precursor **P1**. *m/z* = 1055.6 $[M+H]^{2+}$, adducts *m/z* = 1066.7 $[M+Na]^{2+}$, *m/z* = 1077.8 $[M+2Na]^{2+}$, *m/z* = 1088.2 $[M+3Na]^{2+}$, *m/z* = 1092.7 $[M+Na+K]^{2+}$, *m/z* = 1103.8 $[M+2Na+K]^{2+}$.

IR (KBr, ν, $cm^{-1}$). 697.9, 732.0, 849.3, 916.3 (monosubstituted benzene CH bend and ring puckering); 1030.6 (phosphonic acid PO bend); 1072.7 (phosphonic acid PO stretch); 1003.9, 1138.1, 1159.2, 1188.5 (aliphatic CH

bend, NH bend and CN stretch; some aliphatic features are hidden under new peaks); 1223.5 (phosphonic acid CP stretch); 1375.8 ($CH_2$ bend); 1454.6, 1497.3, 1586.0, 1603.6 (C=C aromatic stretch); 1518.5 (amide NH bend and CN stretch); 1651.5 (amide CO stretch); 2630-2670 (phosphonic acid OH stretch); 2949.2 (aliphatic CH stretch); 3034.6, 3062.3 (aromatic ring stretch); 3300.9, 3395.0–3700 (amide NH stretch and hydrogen bound OH from water and phosphonic acid).

$^1$H NMR (500MHz, DMSO-d6): δ = 2.36 (*b*, 6 H, [$^{\cdot}$N($CH_2$)$_3$]), 2.76 (*b*, 6 H, [$^{\cdot}$N($CH_2C\mathit{H}_2$)$_3$]), 3.03, 3.18 (*b*, 3-6H, [COC$\mathit{H}_2$PO] and [N$\mathit{H}_2^+$CO$^-$C$\mathit{H}$PO]), 5.15, 5.38, 5.76 (*b*, 12 H, N$\mathit{H}$CH(Ph)]), 7.16-7.40 (*b*, 60 H, [Ph]), 8.66-9.26 (*bm*, 15 H, [PO(OH)$_2$], [N$\mathit{H}_2^+$CO$^-$C(Ph)], [N$\mathit{H}_2^+$CO$^-$CHPO]).

$^{13}$C{$^1$H} NMR (126MHz, DMSO-d6): δ = 36.57 (*b*, [CO$\mathit{C}$H$_2$PO] and [$^{\cdot}$N($CH_2$)$_3$]), 37.76 (*s*, [NH$_2^+$CO$^-$ $\mathit{C}$HP]), 52.39 (*s*, [$^{\cdot}$N($CH_2$)$_3$($\mathit{C}$H$_2$)$_3$]), 55.78 (*m*, [$\mathit{C}$H(Ph)]), 126.82-128.85 (*m*, [C$\mathit{C}_5$H$_5$]), 134.02 (*s*, [CH($\mathit{C}$C$_5$H$_5$)NHCOCH$_2$P]), 138.38 (*m*, [$\mathit{C}$C$_5$H$_5$]), 165.59, 166.85 (*s*, [NH$\mathit{C}$OCH$_2$P]), 168.93 (*m*, [$\mathit{C}$OCH(Ph)]), 171.97 (*s*, [$\mathit{C}$OCH(Ph)NHCOCH$_2$P]).

$^{31}$P{$^1$H} NMR (202MHz, DMSO-d6, 20°C): δ = 19.68 (*b*, [PO(OH)$_2$]), traces 2.33 (*m*, [PO(O)$_2$]$^-$).

*Preparation of $H_2$-Salen.* $H_2$-Salen and Mn-salen were prepared by a modified procedure from Yang, J. Y. Bachmann, J. Nocera, D. G. *J. Org. Chem.* **2006**, *71*, 8706. Salicylic acid (3.34 mL, 3.0 g, 0.05 mol) and ethylenediamine (10.45 mL, 15.05 g, 0.1 mol) were heated to reflux in EtOH (150 ml) for 1 h, and the reaction mixture was left at -20°C overnight. Bright-yellow needle-shaped crystals formed that were filtered and washed with cold EtOH and dried over night under reduced pressure to afford $H_2$-Salen at a 99.6% yield (13.36 g, 0.0498 mol).

$^1$H NMR (400 MHz, DMSO-*d*6): δ = 3.91 (*s*, 2H, [NCH$_2$]), 6.87 (*dd* overlapping *ddd*, $^3J_{HH}$ = 8, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1.5, 4H, [C$\mathit{H}$CCHN] & [C$\mathit{H}$COH]), 7.30 (*ddd*, $^3J_{HH}$ = 8, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1.5, 2H, [C$\mathit{H}$CHCOH]), 7.39 (*dd*, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1.5, 2H, [C$\mathit{H}$CHCCHN]), 8.55 (*s*, 2H, [CHN]), 13.27 (*s*, [OH]).

$^{13}$C{$^1$H} NMR (100MHz, DMSO-d6): δ = 58.51 ([NCH$_2$]), 116.24 ([$\mathit{C}$HCOH]), 118.24 ([$\mathit{C}$HCHCCHN]), 118.43 ([(C$_5$H$_5$O)$\mathit{C}$]), 131.37 ([$\mathit{C}$HCCHN]), 132.04 ([$\mathit{C}$HCHCOH]), 160.40([COH]), 166.57([CHN]).

*Preparation of Mn-Salen.* Manganese(II) acetate tetrahydrate (0.35 g, 1.42 mmol) and $H_2$-Salen (0.25 g, 0.93 mmol) were added to 20 mL of ethanol, and the mixture was refluxed for 2 h. Upon cooling, 5 mL of an aqueous saturated sodium chloride solution was added, and the mixture was extracted with 2 × 50 mL of dichloromethane. The combined organic portions were then washed with 50 mL of water and dried over $MgSO_4$. The solvent was removed by rotary evaporation and dried under reduced pressure to afford a golden brown powder at 98% yield (0.32 g, 0.91 mmol). ESI-MS. *m/z* = 356.25.

*Preparation of **Mn-salen/TiP-PhGly**.* **P3** was dried thoroughly under reduced pressure at 60 °C in order to minimize the amount of adsorbed water molecules, as these would interfere with the non-hydrolytic condensation process. Ti(O*i*Pr)$_4$ (215 µl, 201.2 mg) in anhydrous DMSO (4 mL) was added drop-wise to a solution of **P3** (0.5 g,) and **Mn-salen** (10 mg, 0.028 mmol) in anhydrous DMSO (14 mL) and left under vigorous stirring under argon atmosphere in a sealed pressure tube (Ace glass) for 72h, during which a brownish gel like precipitate was formed. The gel was separated by centrifuge at 8000 rpm, washed with water and diethyl ether and dried under reduced

pressure to afford 0.3 g of fine yellow powder. Found: C, 44.66; H, 4.93; N, 7.05.

*Characterization of* ***Mn-salen/TiP-PhGly****.*

*Infrared* (KBr, ν, $cm^{-1}$). 500-700 (TiO vibrations), 698.2, 731.1 (monosubstituted benzene CH bend and ring puckering); 1029.3 (Titanium phosphonate PO bend); 1102.6 (Titanium phosphonate PO stretch); 1003.9, 1138.1, 1159.2, 1188.5 (aliphatic CH bend, NH bend and CN stretch; some aliphatic features are hidden under new peaks); 1223.5 (phosphonic acid CP stretch); 1399.1 ($CH_2$ bend); 1454.6, 1497.3, 1586.0, 1603.6 (C=C aromatic stretch); 1520.7(amide NH bend and CN stretch); 1652.3 (amide CO stretch); 2937.6 (aliphatic CH stretch); 3031.5, 3063.3 (aromatic ring stretch); 3298.5, 3395.2–3700 (amide NH stretch and hydrogen bound OH from water and phosphonic acid). Comparison of the FT-IR spectra reveals that most of the peaks remain unchanged thus indicating that the ligand is not modified to a great extent during the condensation reaction. Some discrepancies can be found in the shift and intensity of the broad bands between 3000 – 3500 $cm^{-1}$, which are attributed to inter- and intra-molecular stretching vibrations of hydrogen bound nitrogen and oxygen. These discrepancies stem from hydration and variations to the extent of hydrogen bonding as a consequence of structural changes. The most important differences between the materials are: The bands at 976, 1029 and 1046 $cm^{-1}$ in the spectrum of **P2,** 1031 and 1072 $cm^{-1}$ in **P3,** and 980, 1029, 1045 and 1103 $cm^{-1}$ in **Mn-salen/TiP-PhGly**, which are assigned to P-O···C, P-O···H and P-O···Ti bending and stretching vibration modes, respectively. The band at 1234 $cm^{-1}$ in the spectrum of **P2**, 1224 $cm^{-1}$ in **P3**, and 1223 $cm^{-1}$ in **Mn-salen/TiP-PhGly**, which are assigned to the C-P stretch; And finally the bands at 1369 $cm^{-1}$ in the spectrum of **P2**, 1376 $cm^{-1}$ in **P3**, and 1399 $cm^{-1}$ in **Mn-salen/TiP-PhGly**, which are assigned to $CH_2$ bends. The changes and shifts of bands around 1100 $cm^{-1}$ in the transition from **P3** to **Mn-salen/TiP-PhGly**, can be attributed to stretching vibrations of the β-keto phosphoryl (P=O). The excess of bands in **Mn-salen/TiP-PhGly** would suggest different connectivities of phosphorous to titanium via any number of its three oxygen atoms. Some of these types of connectivities have been found in crystal structures of clusters formed by non-hydrolytic condensation between M-OR and $P(=O)(-OH)_2$ functions, and was described by Mutin, P.H.; Mehring, M.; Guerrero, G.; Vioux, A. *Mat. Res. Soc. Symp. Proc.* **2000**, *628*, 241–246 as depicted in figure S1.

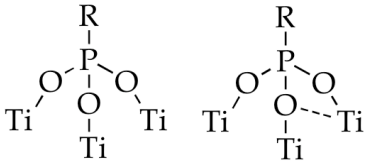


***Figure S1***. Connectivities of known titanium-phosphonates.

*NMR* The $^{31}P\{^{1}H\}$ MAS NMR of **Mn-salen/TiP-PhGly** gave 2 new minor peaks at -3.29, 12.5 and a major peak at 21.17 ppm which could also indicate 3 different forms of connectivity of P-O-Ti; via 1,2 or 3 of the phosphonate oxygen atoms.

*Adsorption.* In order to assess the porous nature of **Mn-salen/TiP-PhGly**, a sample of 60 mg was treated by mortar and pastel and vacuum degassed over night at 100 °C. A nitrogen gas sorption measurement at 77 K was carried out using a Quantachrome NOVA/1000 gas analyzer. The material shows a moderate specific surface area of 77 $m^2/g$ according to the Brunauer-Emmett-Teller (BET) gas adsorption method. This assessment is permitted as the value of C, which is related exponentially to the enthalpy of adsorption is neither below 20 nor above 100, and as

the BET plot is linear in the region of analysis [Brunauer, S.; Emmett, P.H.; Teller E. *J. Am. Chem. Soc.* **1938**, *60*, 309–319]. The first step in the analysis of the nitrogen adsorption-desorption isotherm is the identification of the isotherm type – this would permit a tentative interpretation of the physisorption mechanism. The nitrogen adsorption-desorption isotherm of **Mn-salen/TiP-PhGly** corresponds to type II of the BDDT classification [Brunauer, S.; Deming, L.S.; Deming, W.S.; Teller, E. *J. Am. Chem. Soc.* **1940**, *62*, 1723–1732]. Conversely, this is not the form usually associated with titanium (IV) phosphonates, which give type IV isotherms with hysteresis due to mesoporous capillary condensation. In general the reversible type II isotherm is given by nonporous or macroporous solids and is the result of monolayer-multilayer adsorption. The monolayer capacity can usually be identified as the uptake at Point B provided that the knee is fairly sharp, which is not the case for **Mn-salen/TiP-PhGly**. Two problems arise when trying to define the isotherm of **Mn-salen/TiP-PhGly** as a reversible type II – the blunt knee at point B, and more importantly the hysteresis loop. The isotherm has a narrow hysteresis loop of what seems to be H3 type, characteristic of aggregates of plate-like particles, giving rise to slit-shaped pores. In most cases hysteresis loops occur in type IV isotherms, however, pseudo-type II isotherms exhibit hysteresis loops and are given by many materials containing slit-shaped pores or aggregates of platy particles [Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, T. *Pure Appl. Chem.* **1985**, *57*, 603—619; Rouquerol, J.; Avnir, D.; Fairbridge, C. W.; Everett, D. H.; Haynes, J. H.; Pernicone, N.; Ramsay, J. D. F.; Sing, K. S. W.; Unger, K. K. *Pure Appl. Chem.* **1994**, *66*, 1739–1758]. Such adsorbents give isotherms which are not completely reversible; the adsorption isotherm has the same overall shape as a normal Type II isotherm, but the desorption isotherm follows a different path, resulting in adsorption hysteresis, which in this compound is confined to the multilayer region at high relative pressures. Hysteresis appearing in the multilayer range of physisorption isotherms is usually associated with capillary condensation in mesopore structures. The analysis of the isotherm using the Dubinin-Astakhov (DA) method for micropores [Dubinin, M.M. *Progress in Surface and Membrane Science*, J.F. Danielli, M.D. Rosenberg and D.A. Cadenhead (Eds.), Academic Press, New York, 1975, 1–70] gives a pore size distribution with a maximum at 17.8 Å (Figure 2), which should represent intra-molecular pores formed inside organic-titanium-phosphonate species; the pore size is the approximate inner diameter of one cup shaped unit. Using the standard Barrett Joyner Halenda (BJH) method for pore size distribution [Barrett, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc.* **1951**, *73*, 373–380] gives approximately the same distance of 17.7 Å as well as a large distribution of pore sizes, notably mesopores at around 35 Å and 123 Å. In conclusion it would seem that this material has a large volume of micropores, as well as an array of differently sized and shaped meso- and macro-pores, leading to a pseudo-type II isotherm. Accordingly, the moderate specific surface area obtained by the BET plot may not account for the entire inner surface of **Mn-salen/TiP-PhGly**, as this model is based on the assumption of cylindrical pores.

*Powder X-ray diffraction.* Powder X-ray diffraction shows two broad amorphous peaks at d = 31.1 and 4.5 Å, which may be associated with the BET pore diameters. These broad peaks provide evidence of periodicity, albeit weak, alluding to a recurring size range stemming from the material's porous structure. The peak seen at d = 31 Å could be correlated to the BET meso pore size of 35 Å, which may subsist between the tripodal peptidic units and

the one at 4.5 could be 4d = 18, thus correlated to the micro pores seen in BET as well as to the width of one tripodal unit found by calculations (see Figure S3).

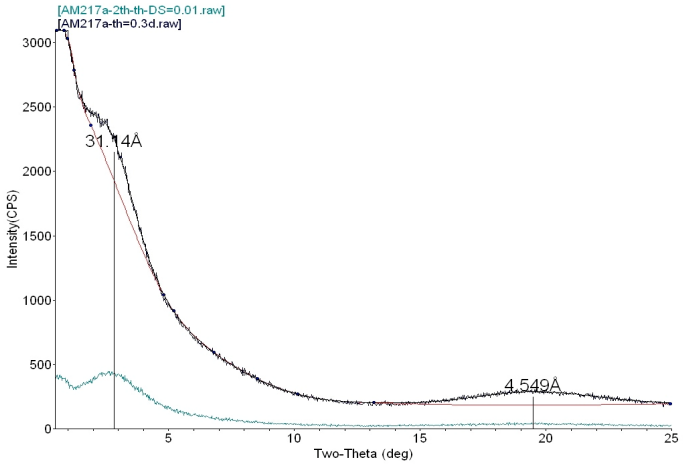


***Figure S2***. X-ray powder diffraction of **Mn-salen/TiP-PhGly**

Based on the results presented above a model was constructed, on which geometry optimization of the organic part was carried out using the semiempirical AM1 method [Pople, J.A.; Beveridge, D.L. *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, **1970**] to obtain the minimum energy conformation of **P3**, Figure S3. According to this model, the three chains of the tripod are coordinated via intra-molecular hydrogen bonding to form a U-shaped type cavity.

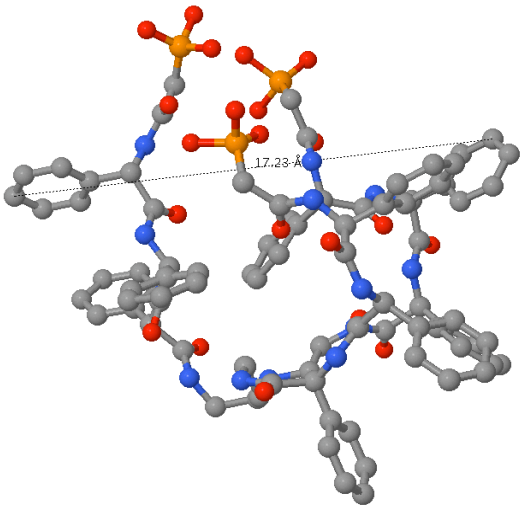


***Figure S3.*** AM1 geometry optimisation of L-PheGly-Phosphonic acid ligand.

Derived from similarly formed phosphonate crystal structures, a cross-linked polymer could be surmised to contain tripod arms linked via ten titanium atoms between each two phosphorus atoms, and organized in a titanium phosphonate octahedral coordination sphere. Based on literature precedence, lamellae of titanium phosphonate layers may be expected to form [Clearfield, A. *Prog. Inorg. Chem.* **1998**, *47*, 371–510; Clearfield, A. *Curr. Opin. Sol. State Mater. Sci.* **1996**, *1*, 268–278]. This model was constructed in order to get a general idea about the possible connectivities and micropores in **TiP-PhGly**, and cannot be an exact representation of the structure of the material since only an average of nine L-PheGly groups, three on each arm, was considered.

*Thermal gravimetric analysis (TGA)*. The results are presented in Figure S4. The weight loss up to 215 °C is probably due to loss of DMSO that was used in the preparation of **Mn-salen/TiP-PhGly**. The two following weight losses (55.76%) are attributed to the organic oligopeptide and salen ligand portion of **Mn-salen/TiP-PhGly**. Elemental analysis carried out separately gave a total of 56.64% for CNH (see above). The TGA showed 33% inorganic content that was not consumed even at 1400°C thus corroborating the EDX assessments of 30-40% Ti-O content throughout the material.

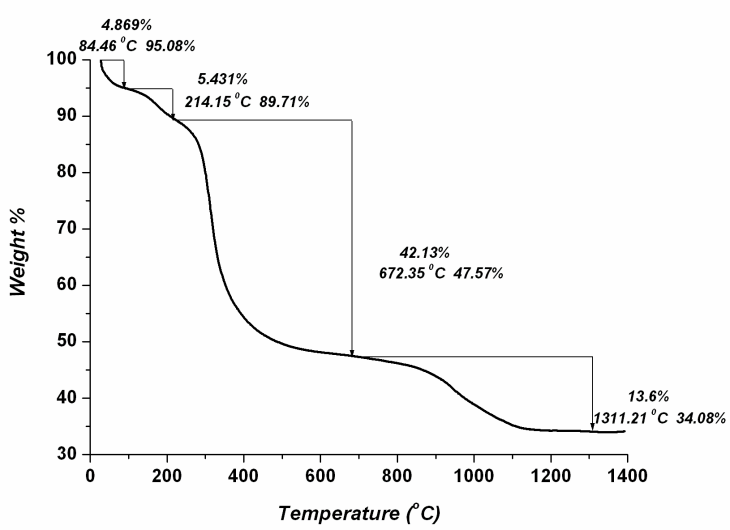


***Figure S4.*** Thermal gravimetric analysis (TGA) curve of **Mn-salen/TiP-PhGly**.

*UV-Vis Spectroscopy*. UV−vis measurements were carried out at room temperature on a Varian Cary-300 Bio UV−vis spectrometer. Solid-state measurements were carried out mounting a Labsphere Integrating Sphere on the spectrometer employing the diffuse reflectance mode. The solid samples were analyzed against a Labsphere Spectralon reflectance standard. The solid state absorption spectra were calculated from reflection spectra by the Kubelka-Munk function: $F(R) = k / s = (1-R)^2 / 2R$ (where $k$ is the absorption coefficient, s is the scattering coefficient which is considered wavelength independent in the present approximation due to large particle size, and $R$ is the reflectance) [Kubelka, P.; Munk, F. *Z Tech Physik,* **1931**, 12, 593–601]. However, it must be noted that the propagation of light through such inhomogeneous media differs significantly from the propagation of light in a homogeneous material, since the light is scattered on its path. Therefore, an approximate description of the solid-state absorbance can be obtained, allowing only for qualitative comparison with solution-state absorbance measurements.

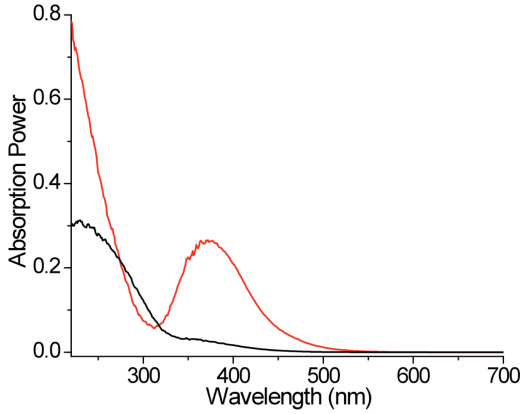

***Figure S5***. The solid state absorption spectra of **Mn-salen/TiP-PhGly** (red) and **TiP-PhGly** (black), calculated from reflection spectra by the Kubelka-Munk function.

*Electron Microscopy*. The morphology of the material was examined using SEM, TEM, and cryo-TEM measurements, disclosing an amorphous seemingly porosive network containing ordered areas, Figure S6. The high-energy backscattered electrons emitted within a few nanometers from the surface in SEM Figure S6A, reveal a presence of lighter feather-like species of higher atomic number moieties or differently oriented fragments, which could be attributed to encapsulated areas of the polymer (Manganese being the heaviest atom used). EDX measurements revealed Mn evenly distributed throughout the material at a 1:9 atomic ratio with phosphorus, and amorphous areas containing an average 5:1 ratio of titanium to phosphorus.

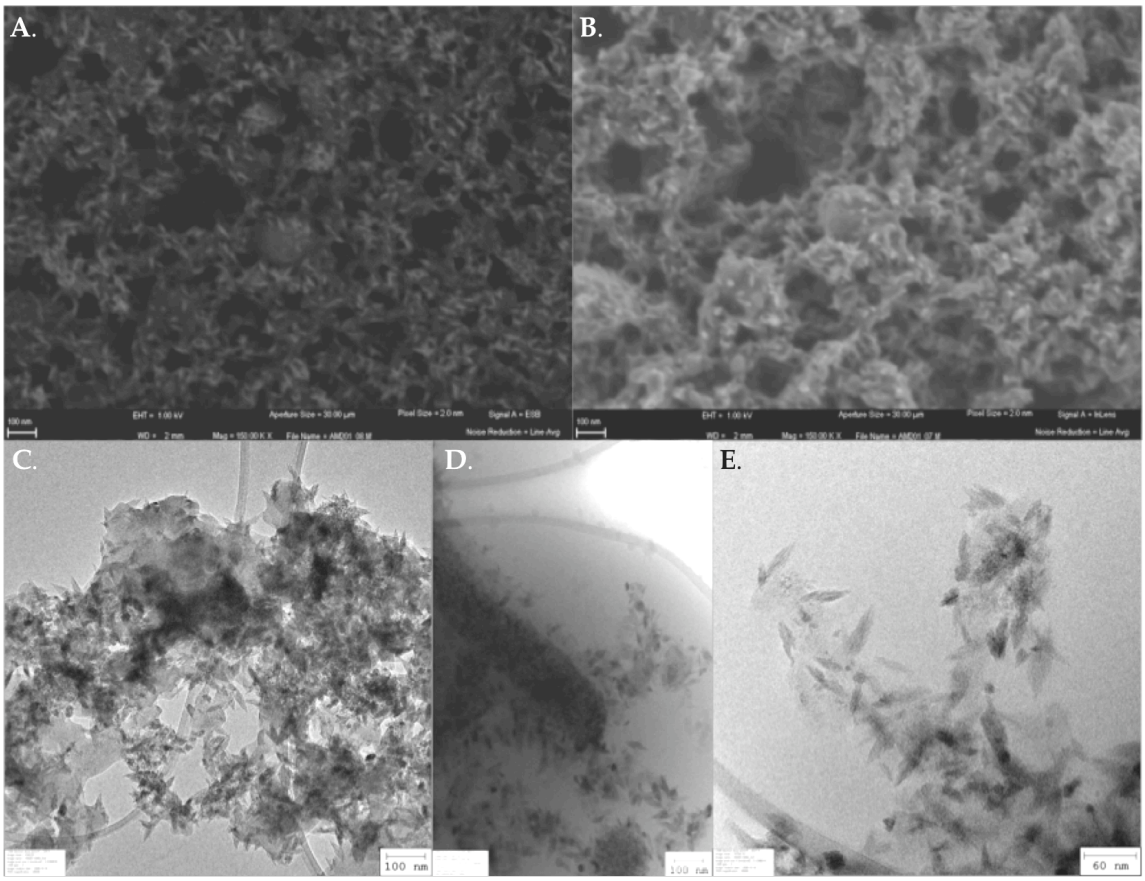


***Figure S6.*** Electron micrographs. A- Backscattered electron SEM image. B-The same segment in figure A imaged using a SEM secondary electron in-lens detector. C-E. Cryo-TEM images. Scale bars: A-D. 100 nm, E. 60 nm.

*Catalytic Experiments:*

10 μl of substituted styrene was added to 10 mg of **P3**, to these 500 μL of dry THF was added, and the suspension was treated by sonic bath for 5 minutes. The suspension was cooled to 3°C and 500 μL of deionized water containing 2 equivalents of NaOCl as oxidant, and buffered to pH 11.3 (for 1 mL: 0.036 g $Na_2HPO_4$), were added under vigorous stirring. The suspension was stirred for 48h after which the organic phase was separated by centrifuge, added to isopropyl alcohol and dried over $Na_2SO_4$. The products were then studied by GC, GCMS and

HPLC analysis. The reactions were repeated at least three times and results were averaged. In addition, the separation of the catalyst from the reaction phase is straightforward and is done by micro-centrifuge. According to UV and GC-MS analysis of the reaction mixture leaching of the encapsulated Mn-Salen complex was negligible. In all reactions the corresponding benzacetaldehyde β-chlorination as well as dichloride and chlorohydrin are formed as byproducts.

*Conditions for chiral HPLC separations:*

Styrene oxide: Diacel Chiralpak IC, 97:3 (Heptane:Isopropanol), 1.2 mL/min, 220 nm. 4.9 min and 5.5 min.

Styrene diol: Diacel Chiralpak IC, 90:10 (Heptane:Isopropanol), 1.2 mL/min, 220 nm. 8.5 min and 9.3 min.

α-methyl styrene oxide: Diacel Chiralpak IC, 97:3 (Heptane:Isopropanol), 1.2 mL/min, 220 nm. 4.5 min and 5.0 min.

α-methyl styrene diol: Diacel Chiralpak IC, 97:3 (Heptane:Isopropanol), 1.2 mL/min, 220 nm. 15 min and 25 min.

4-methyl styrene oxide: Diacel Chiralpak AD-H, 100 (Heptane), 1.0 mL/min, 220 nm. 17 min and 19 min.

4-methyl styrene diol: Diacel Chiralpak IC, 95:5 (Heptane:Isopropanol), 1.2 mL/min, 220 nm. 22 min and 32 min.

4-methyl α-methyl styrene oxide: Diacel Chiralpak IC, 97:3 (Heptane:Isopropanol), 1.2 mL/min, 220 nm. 4.7 min and 5.2 min.

4-methyl α-methyl styrene diol: Diacel Chiralpak IC, 97:3 (Heptane:Isopropanol), 1.2 mL/min, 220 nm. 14 min and 16 min.