Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supplementary Information:

Synthesis of the Catalysts:

Metal Free Catalysts:

ODAN:

1,5-Diaminonaphtalene (500 mg, 3.16 mmol) and $(NH_4)_2S_2O_8$ (500 mg, 2.19 mmol) are dispersed in EtOH (50 mL). The dispersion is stirred for 24h at room temperature to obtain oligomers of 1,5-Diaminonaphtalene. The mixture is heated to 80 °C in order to completely evaporate the solvent and drive the polymerization of the oligomers. When dry the resulting grey powder is heated in the tube furnace to 1000 °C at a heating rate of 20 °C/min for 2h. The resulting black powder is refluxed for 8h in 0.5M H_2SO_4 to remove any metal impurities. After filtering and drying in the oven at 60 °C over night, the catalyst **ODAN** (143 mg) is ready to use.

Catalyst D0:

1,2-Diaminobenzene (500 mg, 4.63 mmol) and $(NH_4)_2S_2O_8$ (500 mg, 2.19 mmol) are dispersed in EtOH (50 mL). The dispersion is stirred for 24h at room temperature to obtain oligomers of 1,2-Diaminobenzene. The mixture is heated to 80 °C in order to completely evaporate the solvent and drive the polymerization of the oligomers. When dry the resulting yellow residue is heated in the tube furnace to 1000 °C at a heating rate of 20 °C/min for 2h. The resulting black solid is ground and refluxed for 8h in 0.5M H_2SO_4 to remove any metal impurities. After filtering and drying in the oven at 60 °C over night, the catalyst **D0** (198 mg) is ready to use.

Catalyst P0:

2,6-Diaminopyridine (500 mg, 4.58 mmol) and $(NH_4)_2S_2O_8$(500 mg, 2.19 mmol) are dispersed in EtOH (50 mL). The dispersion is stirred for 24h at room temperature to obtain oligomers of 2,6-Diaminopyridine. The mixture is heated to 80 °C in order to completely evaporate the solvent and drive the polymerization of the oligomers. When dry the resulting greenish residue is heated in the tube furnace to 1000 °C at a heating rate of 20 °C/min for 2h. The resulting black solid is ground and refluxed for 8h in 0.5M H_2SO_4 to remove any metal impurities. After filtering and drying in the oven at 60 °C over night, the catalyst **P0** (132 mg) is ready to use

Catalyst S0:

2,2'-Dithioaniline (500 mg, 2.01 mmol) and $(NH_4)_2S_2O_8$ (500 mg, 2.19 mmol) are dispersed in EtOH (50 mL). The dispersion is stirred for 24h at room temperature to obtain oligomers of 2,2'-Dithioaniline. The mixture is heated to 80 °C in order to completely evaporate the solvent and drive the polymerization of the oligomers. When dry the resulting yellow residue is heated in the tube furnace to 1000 °C at a heating rate of 20 °C/min for 2h. The resulting black solid is ground and refluxed for 8h in 0.5M H_2SO_4 to remove residual metal. After filtering and drying in the oven at 60 °C over night, the catalyst **S0** (134 mg) is ready to use.

<u>Metal containing catalysts:</u>

Fe-ODAN-14%:

1,5-Diaminonaphtalene (350 mg, 2.20 mmol) and $FeCl_2$ (114 mg, 0.900 mmol) are dispersed in EtOH (50 mL). The dispersion is stirred for 24h at room temperature to obtain oligomers of 1,5-Diaminonaphtalene. The mixture is heated to 80 °C in order to completely evaporate the solvent and drive the polymerization of the oligomers. When dry the resulting dark violet residue is heated in the tube furnace to 1000 °C at a heating rate of 20 °C/min for 2h while supplying a constant stream of inert nitrogen gas. The resulting black powder is refluxed for 8h in 0.5M H_2SO_4 to remove residual metal. After filtering and drying in the oven at 60 °C over night, the catalyst **Fe-ODAN-14%** (192 mg) is ready to use.

Co-ODAN-16%:

1,5-Diaminonaphtalene (350 mg, 2.20 mmol) and $CoCl_2*4H_2O$ (214 mg, 0.900 mmol) are dispersed in EtOH (50 mL). The dispersion is stirred for 24h at room temperature to obtain oligomers of 1,5-Diaminonaphtalene. The mixture is heated to 80 °C in order to completely evaporate the solvent and drive the polymerization of the oligomers. When dry the resulting dark violet residue is heated in the tube furnace to 1000 °C at a heating rate of 20 °C/min for 2h while supplying a constant stream of inert nitrogen gas. The resulting black powder is refluxed for 8h in 0.5M H_2SO_4 to remove residual metal. After filtering and drying in the oven at 60 °C over night, the catalyst **Co-ODAN-16%** (113 mg) is ready to use.

Fe-ODAN-1%:

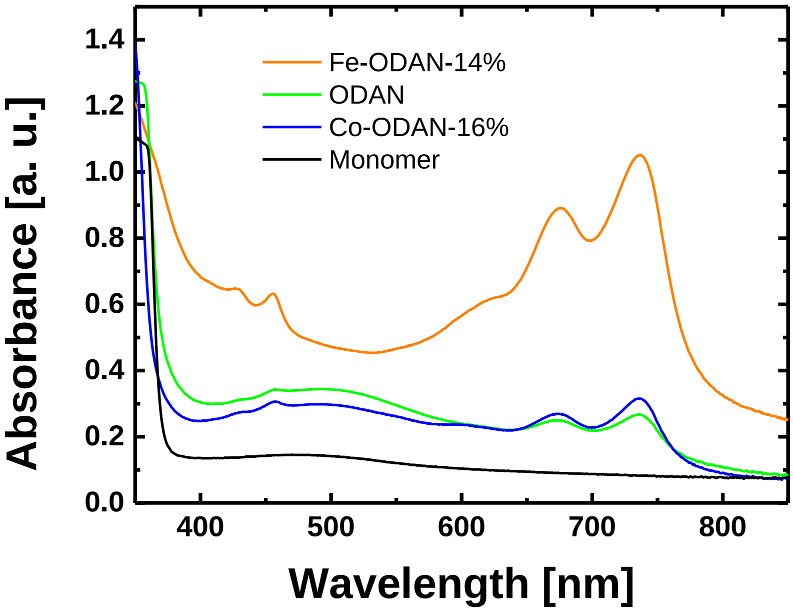
In a 250 mL round bottom flask, 1,5-Diaminonaphtalene (1 g, 6.32 mmol) is dissolved in Ethanol (220 mL). A solution of $FeCl_2$*$4H_2O$ (40 mg, 0.200 mmol) dissolved in ethanol (20 mL) is added to the solution. After 10 Minutes $NH_4S_2O_8$(1g, 4.38 mmol) is also added. The mixture is stirred for 24h. The solvent is removed under reduced pressure and the remaining black powder is subjected to heat treatment in the tube furnace to 950 °C at a heating rate of 20 °C/min for 2h while supplying a constant stream of inert nitrogen gas. The resulting black powder is refluxed for 8h in 0.5M H_2SO_4 to remove residual metal. After filtering and drying in the oven at 60 °C over night, the catalyst **Fe-ODAN-1%** (354 mg) is ready to use.

Physical Characterisation:

UV-Vis spectroscopy of precursor:

Precursor refers to the polymerised material before heat treatment.

The measurement was carried out on a Perkin Elmer Lambda 25 spectrometer. The ethanolic solutions of the polymers after the polymerisation process were diluted to correspond to a monomer concentration of 5 * 10^{-2} M.



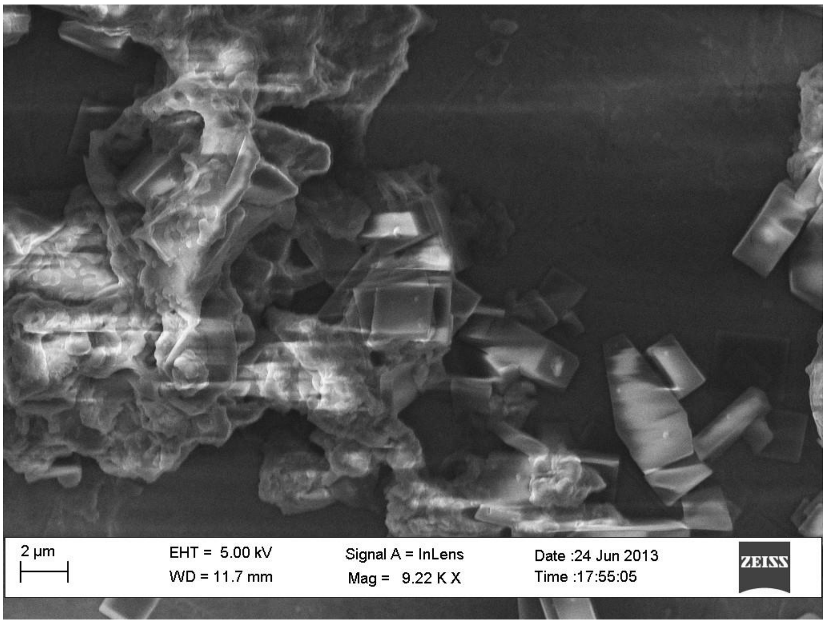
S 1: UV-Vis spectrum of the monomer and after polymerisation with $NH_4S_2O_8$ (ODAN), $FeCl_2$ (Fe-ODAN-14%), $CoCl_2$ (Co-ODAN-16%).

Mass Spectrometry of precursor:

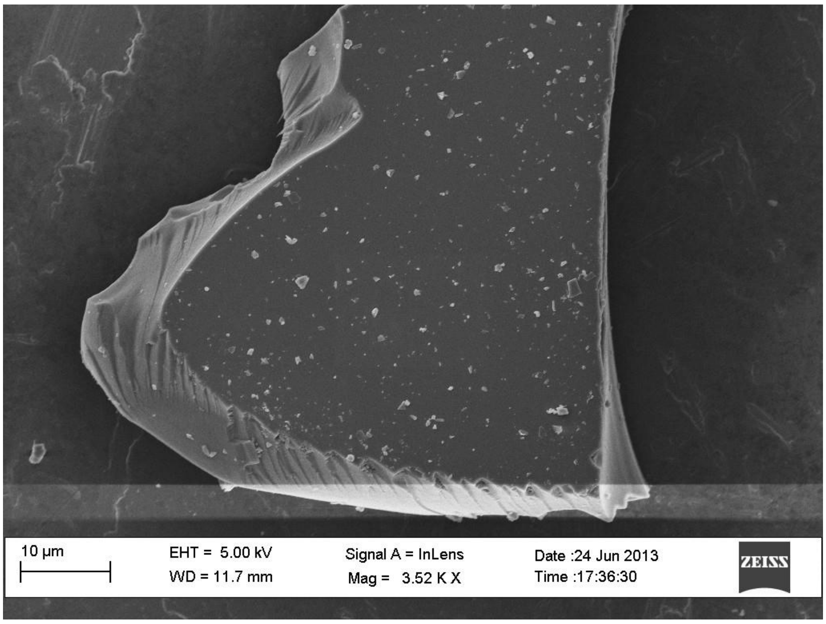
The spectra were recorded on a Micromass MALDI Micro Mx

MALDI-TOF spectra of the 1,5-Diaminonaphthalene based precursors where recorded to confirm a polymerisation. The spectra can be found in the Appendix of this document.

SEM of other metal free catalyst with coarse structure P0:



S 2: Scanning electron microscopy image of precursor to catalyst P0, showing large agglomerates unlike the nanospheres seen for the catalysts based on 1,5-Diaminonaphtalene.



S 3: Scanning electron microscopy image of catalyst P0 after grinding with mortar and pestel, showing a large graphitic structure unlike the higly porous structure seen for the catalysts based on 1,5-Diaminonaphtalene.

Conductivity Measurement:

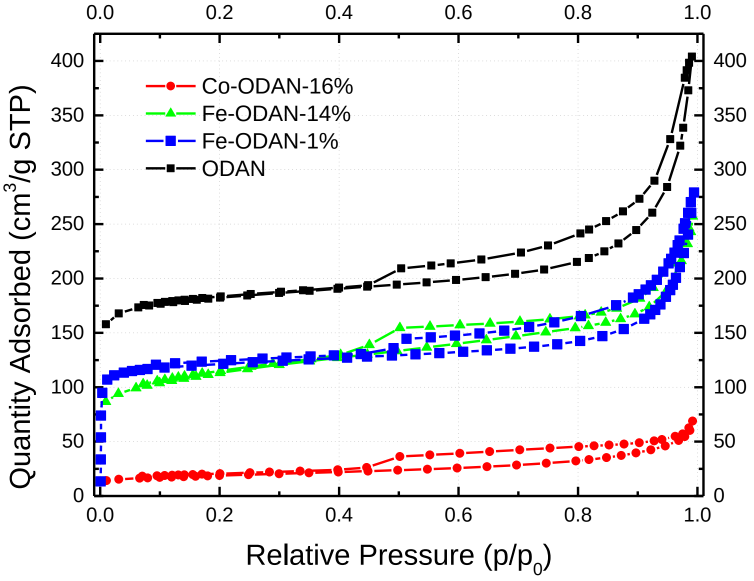
The conductivity was determined similar to a literature method.[1] The cell used for the measurement consists of a home-made acrylic die (inner diameter 2.0 mm, piston area $3.11*10^{-6}$ m^2) with 2 removable brass pistons on either side. The device is placed between a micrometre calliper (Mitutoyo Digimatic Micrometer 0-25mm), in order to compress the powder at a fixed pressure and measure the column height at the same time. The dc electrical resistance of the compressed powder was then measured via the four-point method with a HP 34401A high-performance digital multimeter. The height of the column was determined from the measured displacement of the brass pistons. In order to isolate the brass pistons against the calliper the end of those was covered with isolating PTFE tape. The force of the calliper compressing the powder was approximated to be 6N from Hooke's law **F = -kx** by measuring the displacement of a spring with known force constant, where **F** is the force, **k** the force constant in N/mm and **x** the distance of displacement in mm. The spring used was a Steel Alloy Compression Spring, 20mm x 4.63mm, k = 2N/mm from RS components. The pressure compressing the powder is therefore ~2 MPa. Although this is a rough estimation, it has been shown that at a pressure above 2 MPa the conductivity of carbon powders does not change significantly.[1] the conductivity has then been determined to be approximately $100 Sm^{-1}$.

SEM, TEM, XRD and XPS sample preparation:

SEM samples were prepared by drop drying the samples from an aqueous suspension onto Alumina stubs. TEM samples were prepared by drop drying the samples from an aqueous suspension onto copper grids. XRD samples were prepared by drop drying the samples from a suspension of the materials in acetone onto single crystal silicon substrates. XPS samples were prepared by pressing the sample powder into an indium substrate.

SEM was carried out on a JSM5610LV SEM. TEM was carried out on a JEOL 2010 TEM. X-Ray powder diffraction (XRD) was carried out on a PANalytical MPD, with a Cu anode (K alpha=8048.0 eV). X-ray Photoelectron Spectroscopy (XPS) analyses were performed using a Kratos Analytical AXIS UltraDLD spectrometer. A monochromatic aluminium source (Al $K\alpha$ = 1486.6 eV) was used for excitation. The analyser was operated in constant pass energy of 40 eV using an analysis area of approximately 700 µm × 300 µm. Charge compensation was applied to minimise charging effects occurring during the analysis. The adventitious C1s (285.0 eV) binding energy (BE) was used as internal reference. Pressure was in the 10^{-10} mbar range during the experiments. Quantification and simulation of the experimental photopeaks were carried out using CasaXPS and XPSPEAK41 software. Quantification is performed using non-linear Shirley background subtraction.

Nitrogen Adsorption Analysis (BET):



S4: Nitrogen adsorption/desorption isotherms for catalysts ODAN, Fe-ODAN-1%, Fe-ODAN-14% and Co-ODAN-16%. An increase in surface area is observed towards the lower overall metal content.

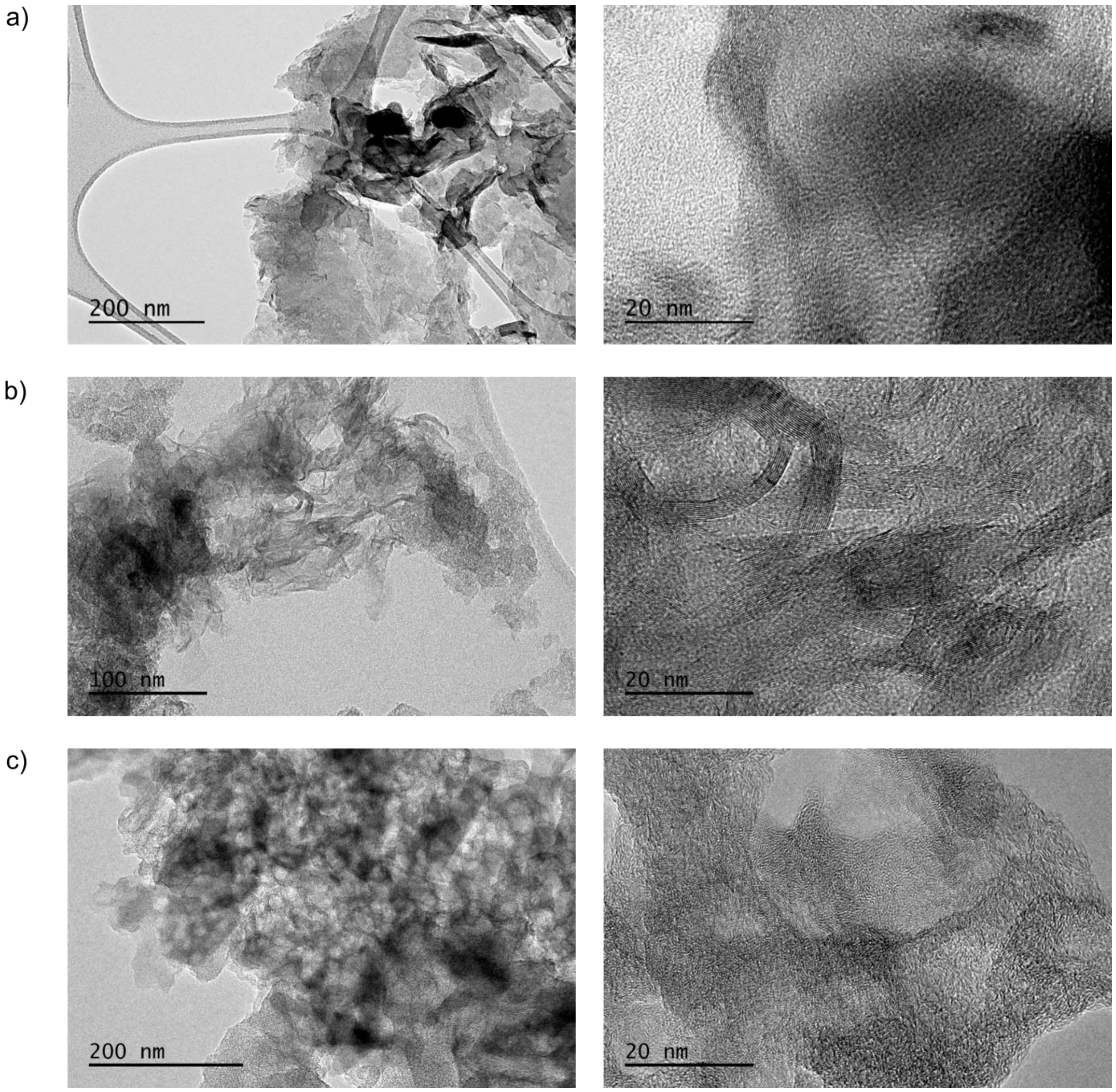
The instrument used was a Micromeritics TriStar 3000 surface area and porosity analyser. The adsorbent was N_2, the temperature was 77K. The best region for the linear fit was determined by the Rouquerol method.

The surface area was determined by the BET method. The molecular cross sectional area for nitrogen is 0.1620 nm^2.

Parameters determined and corresponding BET Surface Area:

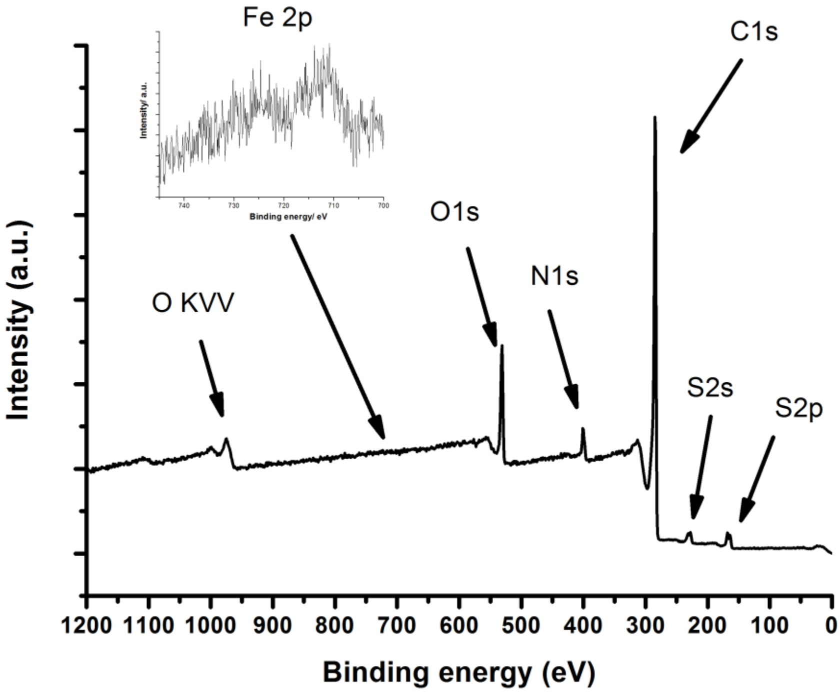
Sample	Slope [10^{-6} g/cm^3 STP]	y-intercept [10^{-6} g/cm^3 STP]	C	Qm [cm^3/g STP]	Correlation Coefficient	BET surface area [m]
Co-ODAN-16%	64343 ± 108	78 ± 7	826.31	15.52	0.99999	67.57 ± 0.11
Fe-ODAN-14%	10564 ± 21	11 ± 1	992	94.56	0.99999	411.6 ± 0.8
Fe-ODAN-1%	9096.0 ± 31	4 ± 1	2099	109.9	0.99998	478.3 ± 1.6
ODAN	6190.0 ± 47	0 ± 3	19606	161.5	0.99994	703.1 ± 5.4

TEM comparing Co-ODAN-16% , Fe-ODAN-14% and ODAN

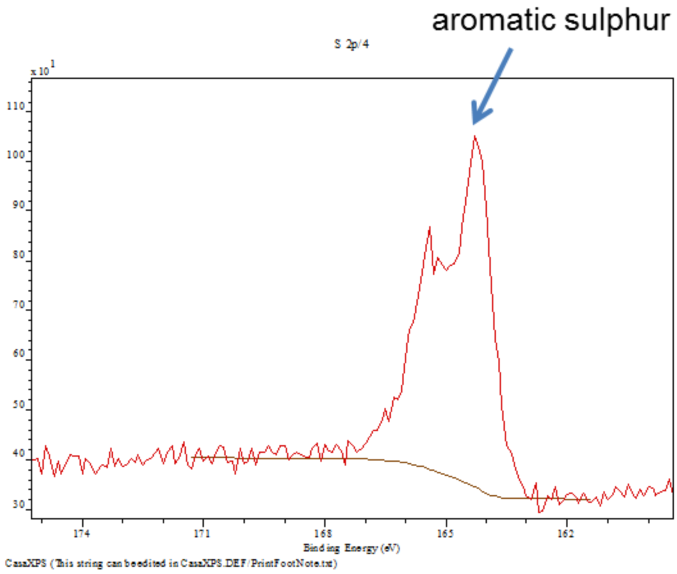


S 5: TEM low resolution (left) and high resolution (right) of a) Co-ODAN b) Fe-ODAN and c) ODAN

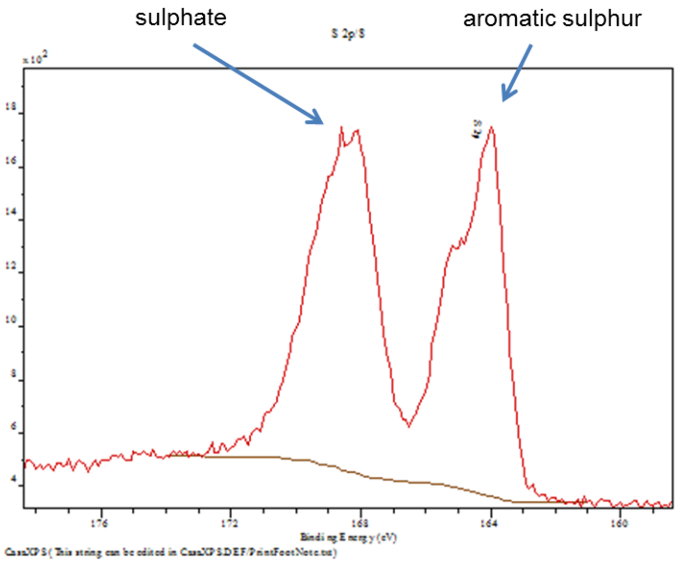
XPS of catalyst Fe-ODAN-1%:



S 6: XPS wide scan of catalyst Fe-ODAN-1% after acid leaching.



S 7: XPS S2p peak of a catalyst Fe-ODAN-1% without refluxing in 0.5M H_2SO_4 after heat treatment.



S8: XPS S2p peak of a catalyst Fe-ODAN-1% with treatment in 0.5 H_2SO_4 after heat treatment.

Neutron Activation Analysis (NAA):

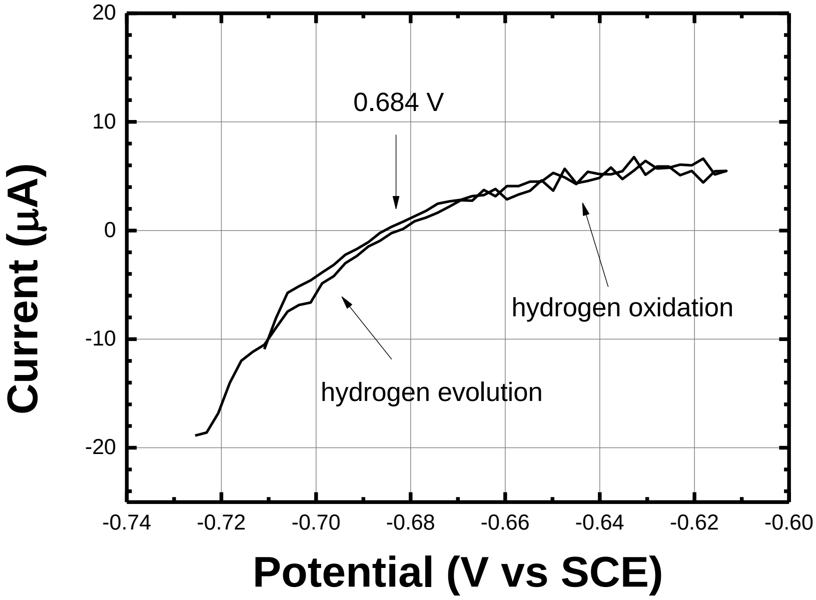
Metal	**ppm by weight**
Iron	10
Cobalt	7
Copper	2
Manganese	732
Tungsten	1

Platinum not detected; Manganese contamination possibly from the cleaning of glassware with permanganate.

Electrochemical Characterisation:

RHE Calibration:

Experiments performed in the Ringers solution, were measured against a saturated calomel electrode (SCE). It was calibrated with respect to reversible hydrogen electrode (RHE). The calibration was performed in the respective high purity hydrogen saturated electrolyte with a platinized Pt wire as the working electrode. CVs were run at a scan rate of 1 mV/s.



S 9: Cyclic Voltammetry of a platinized platinum wire in hydrogen saturated Ringers solution. Scan Rate 1 mV/s.

Ink preparation:

To prepare the electrode, 10 mg of sample was dispersed ultrasonically into 1.6 mL of ethanol, 0.4 mL of H_2O and 0.1 mL of 0.05% Nafion.

RDE measurements:

The respective amount of ink was drop coated onto the disk of the RDE tip which was mounted upside down onto the rotator. While drying the rotator was set to 700 rpm thus obtaining a uniform catalyst distribution across the electrode surface.

RRDE measurements:

The catalyst layer on the disk of the RRDE tip was prepared in the same way as done for the RDE experiments. The disk electrode was scanned cathodically at a rate of 1 or 5 mVs^{-1} and the ring potential was constant at 1.5 V vs RHE. The % peroxide yield was determined by the following equation:

$$\%\boldsymbol{HO_2^-} = \mathbf{200} * \frac{\boldsymbol{I_R/N}}{\boldsymbol{I_D} + \boldsymbol{I_R/N}}$$

where $\mathbf{I_D}$ is disk current, $\mathbf{I_R}$ is ring current and **N** is current collection efficiency of the Au ring. **N** is determined by the dimensions of the ring, the disk and gap between those two, to be 25.6% or 0.256.[2,3]

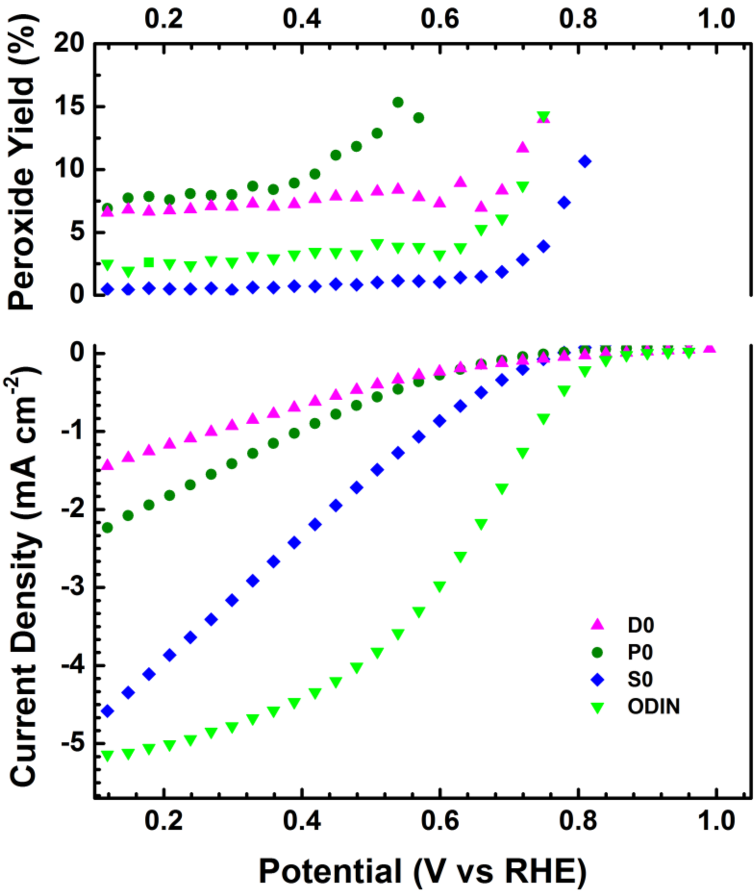
Tafel Plot:

The kinetic current density is calculated with the mass transport correction by the following equation:

$$\boldsymbol{j_k} = \frac{\boldsymbol{j} * \boldsymbol{j_L}}{(\boldsymbol{j_L} - \boldsymbol{j})}$$

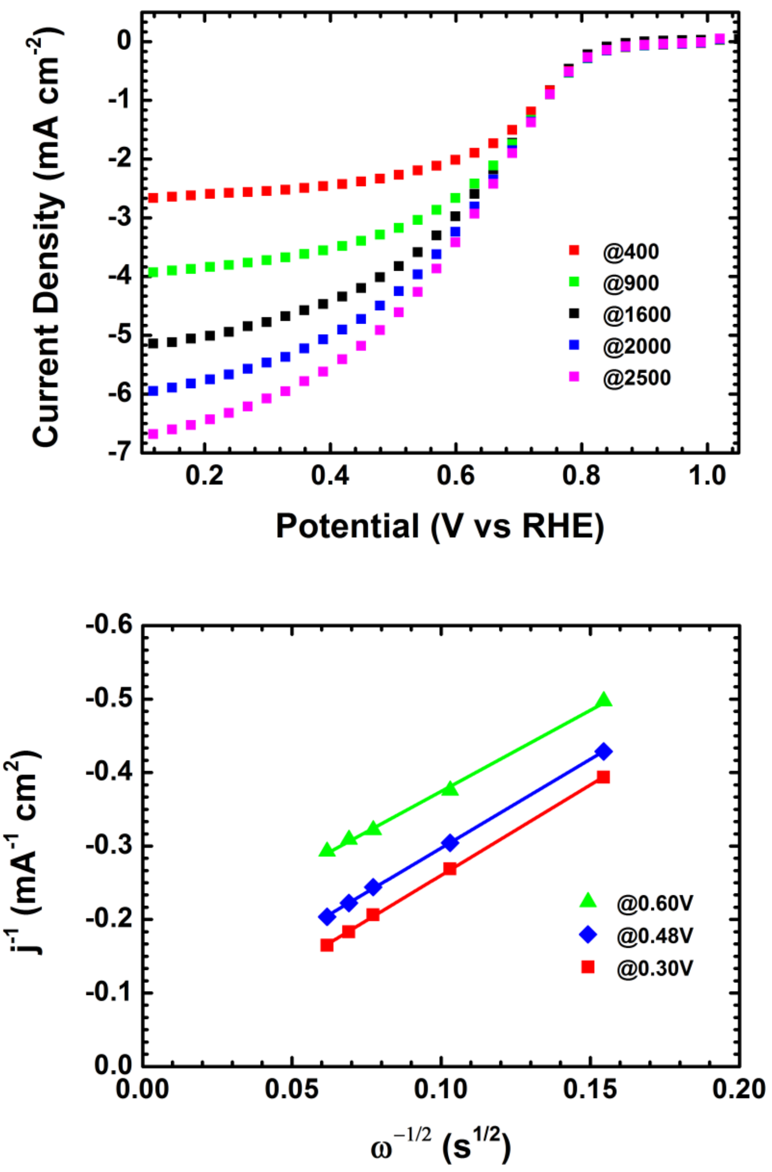
where $\boldsymbol{j_k}$ is the kinetic current density, $\boldsymbol{j}$ is the current density at the respective potential and $\boldsymbol{j_L}$ is the limiting current density.[2]

<u>Oxygen Reduction Reaction of other metal free catalysts:</u>

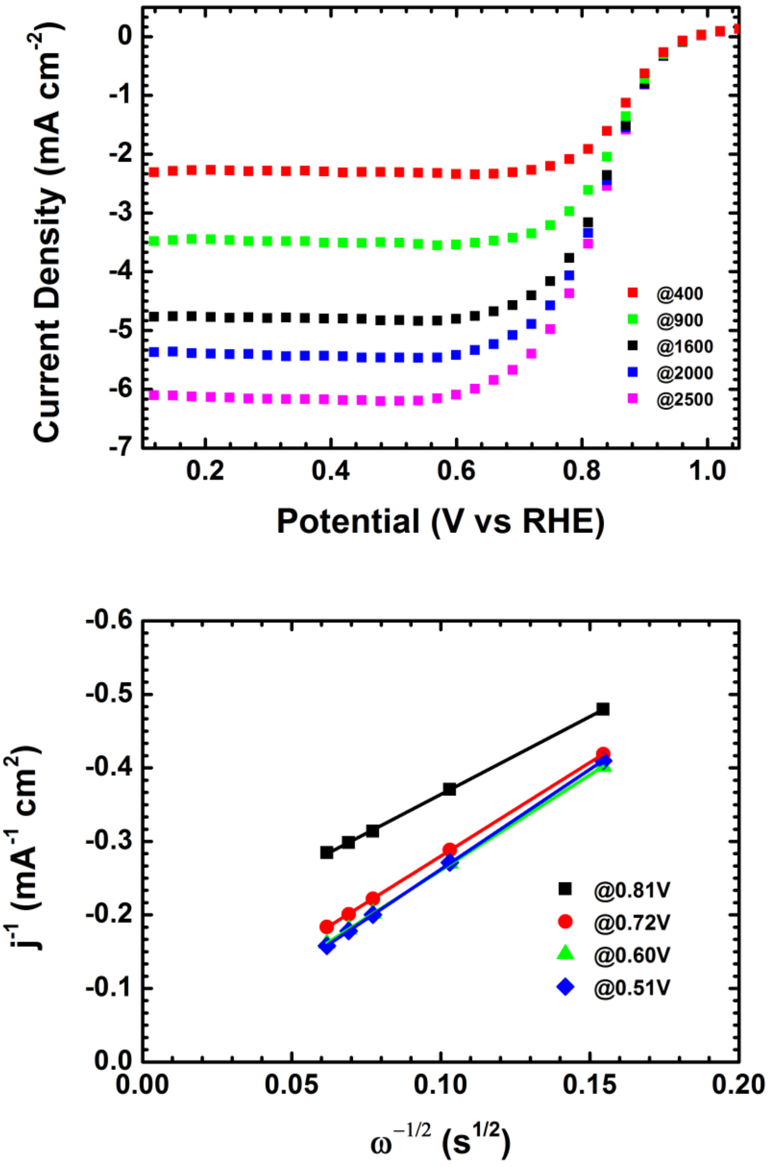


S 10: Steady-state RRDE measurement in 0.5M H_2SO_2. Rotating speed: 1600 rpm, 30s hold, 30 mV step potential, catalyst loading: 750 μg/cm^2, O2-saturated at 1 atm. (bottom) ORR activity. (top) Peroxide yield.

Koutecky Levich Analysis of ODAN catalyst:



S 11: (top) Steady-state RDE measurement in 0.5M H_2SO_2 at different rotating rates in rpm, 30s hold, 30 mV step potential, catalyst loading: 750 μg/cm^2 , O2-saturated at 1 atm. (bottom) Koutecky-Levich plot at different potentials.



S 12: (top) Steady-state RDE measurement in 0.1M NaOH at different rotating rates in rpm, 30s hold, 30 mV step potential, catalyst loading: 750 μg/cm^2 , O2-saturated at 1 atm. (bottom) Koutecky-Levich plot at different potentials.

The electron transfer number $\boldsymbol{n}$ can be calculated from the Koutecky-Levich equation:

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_K}$$

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6} \qquad j_k = nFkC_0$$

where $\boldsymbol{j}$ is the measured current density, $\boldsymbol{j_K}$ and $\boldsymbol{j_L}$ are the kinetic- and diffusion-limiting current densities, $\boldsymbol{\omega}$ is the angular velocity, $\boldsymbol{n}$ is transferred electron number, $\boldsymbol{F}$ is the Faraday constant, $\boldsymbol{C_0}$ is the bulk concentration of O_2, $\boldsymbol{D_0}$ is the diffusion coefficient of O_2 in the electrolyte, $\boldsymbol{\nu}$ is the kinematic viscosity of the electrolyte, and $\boldsymbol{k}$ is the electron-transfer rate constant.[3]

Potential (V vs RHE)	**Slope (mA^{-1} cm^2 $s^{-1/2}$)**
0.60	-2.21 ± 0.06
0.48	-2.42 ± 0.02
0.30	-2.46 ± 0.02

Table 1: Slopes of the Koutecky-Levich plot for the catalyst ODAN in 0.5M H_2SO_4

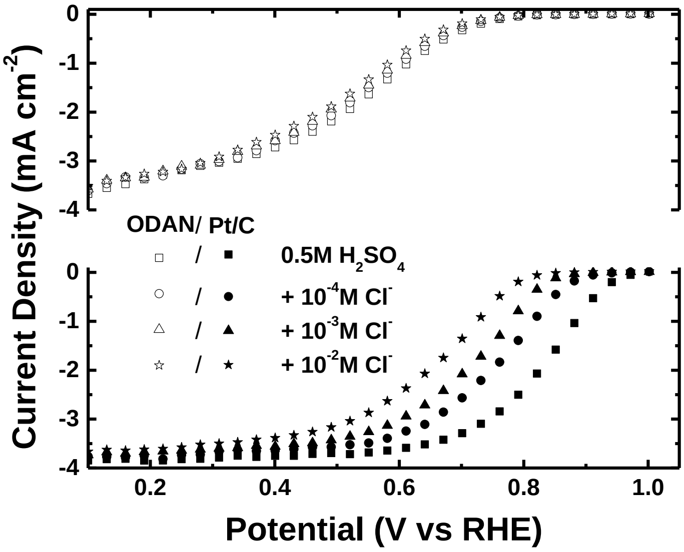
Potential (V vs RHE)	**Slope (mA^{-1} cm^2 $s^{-1/2}$)**
0.81	-2.12 ± 0.02
0.72	-2.55 ± 0.01
0.60	-2.60 ± 0.01
0.51	-2.72 ± 0.01

Table 2: Slopes of the Koutecky-Levich plot for the catalyst ODAN in 0.1M NaOH

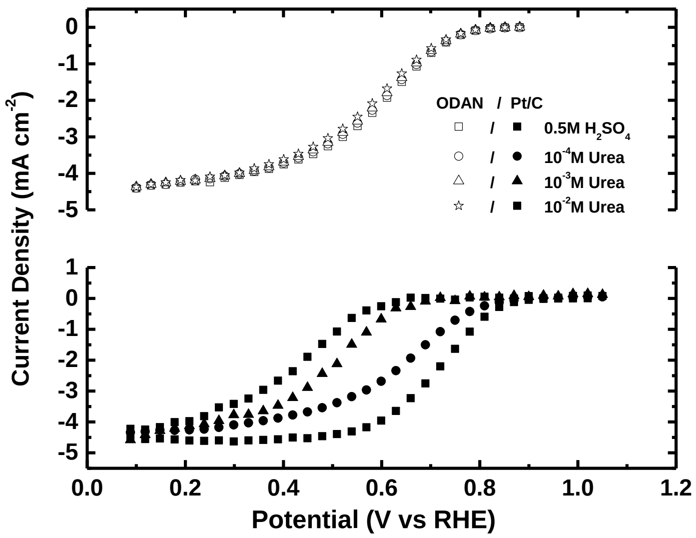
Assuming for 0.5M H_2SO_4 that $\boldsymbol{D_0}$ = 1.8*10^{-5}cm^2 s^{-1},$\boldsymbol{C_0}$ = 1.13*10^{-6}mol cm^{-3}and ν = 0.01 cm^2 s^{-1} (from Ref. 4) an electron transfer number ***n*** of 4.1 is calculated at 0.3 V versus RHE

Assuming for 0.1M NaOH that $\boldsymbol{D_0}$ = 1.9*10^{-5} cm^2 s^{-1}, $\boldsymbol{C_0}$ = 1.10*10^{-6}mol cm^{-3}and ν = 0.01 cm^2 s^{-1}(from Ref. 5) an electron transfer number ***n*** of 3.6 is calculated at 0.51 V versus RHE

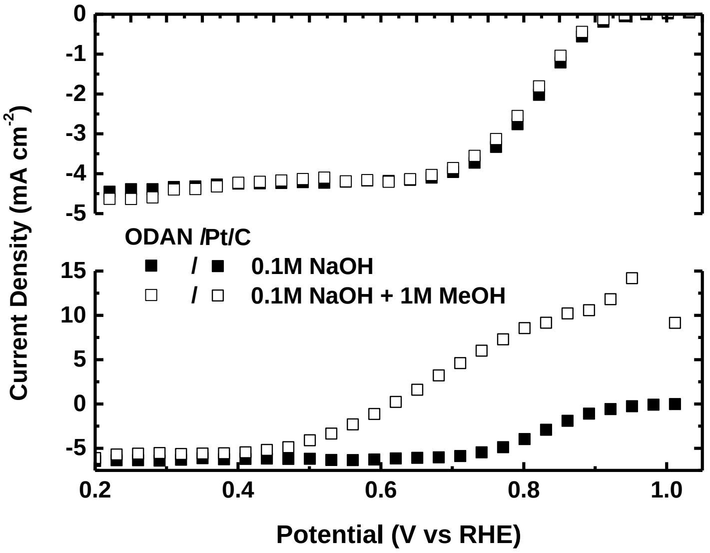
Poisoning Experiments:



S 13: Rotating Disc Electrode (RDE) measurements of ODAN (top) and Pt/C (bottom) with the subsequet addition of chloride ions.

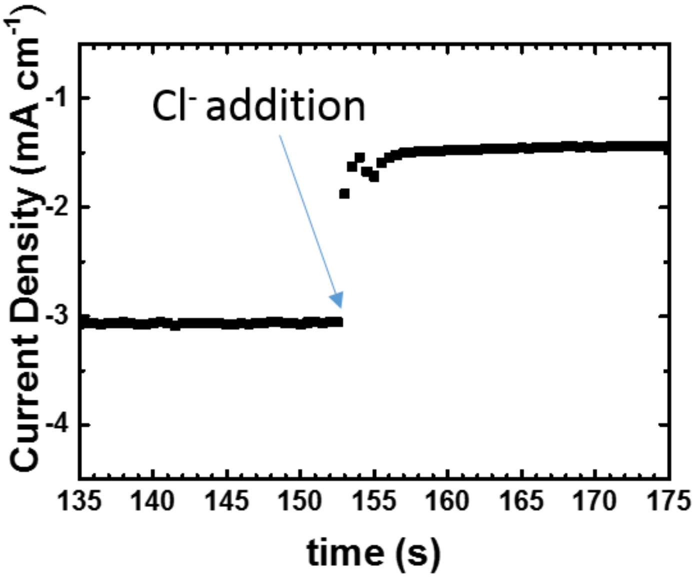


S 14: Rotating Disc Electrode (RDE) measurements of ODAN (top) and Pt/C (bottom) with the subsequet addition of urea.



S 15: : Rotating Disc Electrode (RDE) measurements of ODAN (top) and Pt/C (bottom) without and with addition of 1M MeOH.

Transient of Chloride contamination:



S 16: : Chronoamperometric measurement at 0.81V versus RHE for a Rotating Disk Electrode at 1600 rpm, with 60 µg cm^{-1} Pt/C. Before and after the addition of Chloride to reach a concentration of 10^{-4}M.

References:

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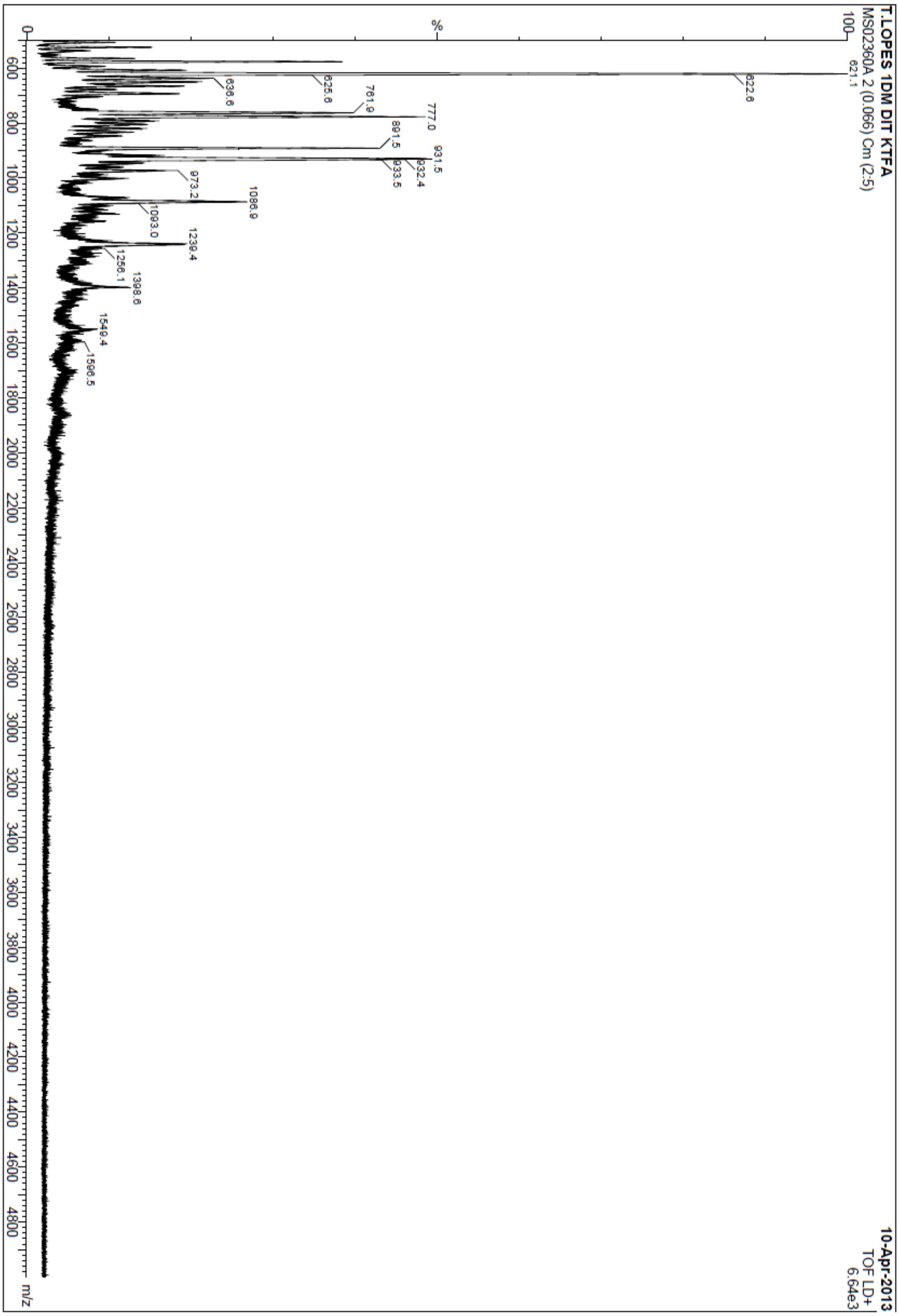
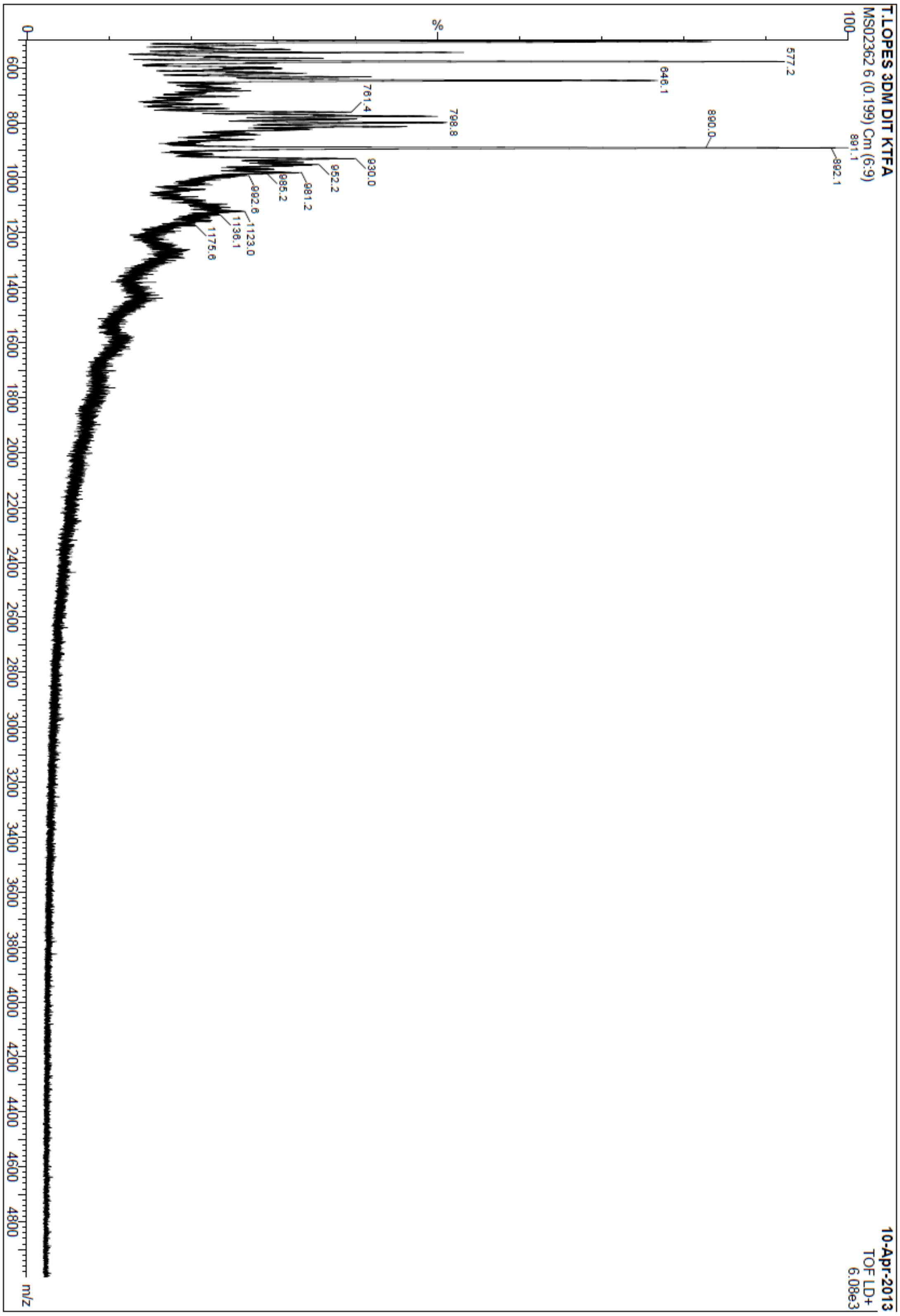
Appendix: Mass Spectra of precursors

ODAN precursor:



Fe-ODAN-14% precursor:



Co-ODAN-16% precursor: