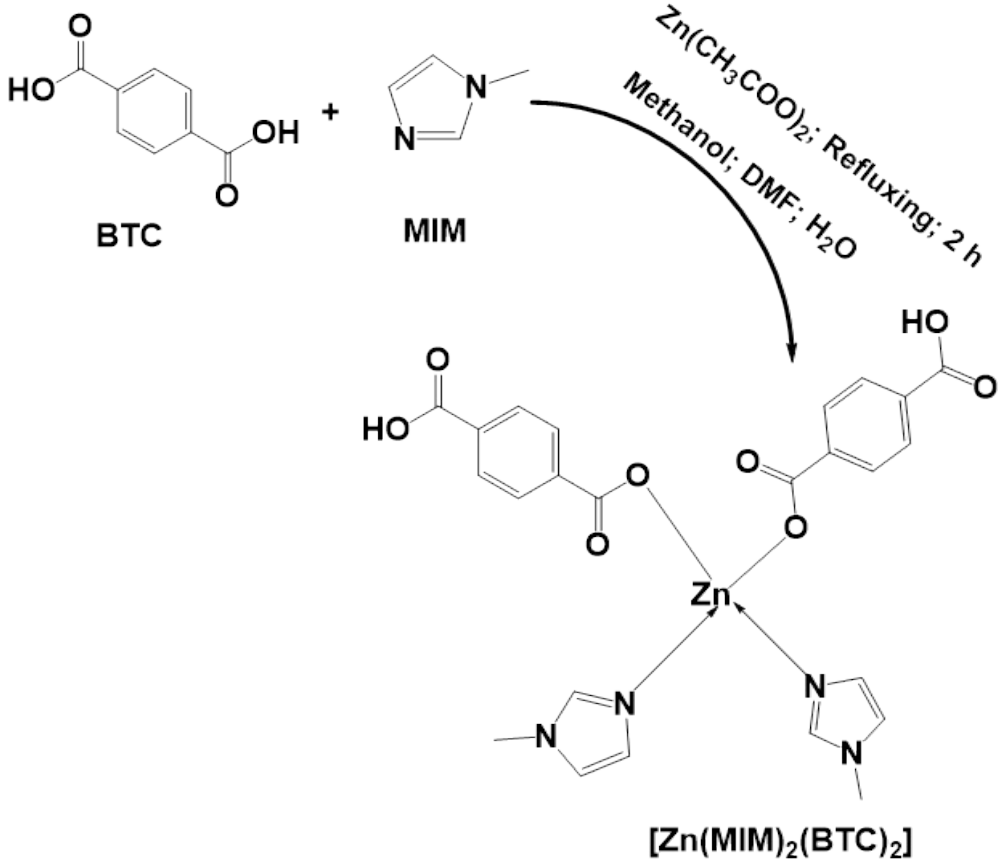
Synthesis and DFT studies of a new paddle-wheel hetero-ligand system Zn(II) coordination polymer as catalyst for degradation of microplastics

Vincent O. Adimula[a,b*], Halimat O. Adekeye[a], Funsho A. Oniye[a], Emmanuel O. Adeniyi[a], Samson O. Owalude[c], Eric Hosten[d], Adeniyi S. Ogunlaja[d], Oluwatobi S. Oluwafemi[b,e], Adedibu C. Tella[c,f]

[a]*Department of Industrial Chemistry, University of Ilorin, P.M.B.1515, Ilorin 240003, Nigeria*
[b]*Department of Chemical Sciences, University of Johannesburg, Doornfontein, 2028, Johannesburg, South Africa.*
[c]*Department of Chemistry, University of Ilorin, P.M.B.1515, Ilorin 240003, Nigeria*
[d]*Department of Chemistry, Nelson Mandela University, PO Box 77000, Port Elizabeth, 6031, South Africa*
[e]*Centre for Nanomaterials Science Research, Department of Chemical Sciences, University of Johannesburg, Johannesburg, South Africa.*
[f]*Department of Chemistry, University of South Africa, Pretoria, South Africa.*

*Corresponding Author: vincentadimula@gmail.com

Supplementary Data



Scheme S1 Reaction scheme for the design of $[Zn(MIM)_2(TPA)_2]$

Yield: 80%, melting pt.: >400 °C, elemental analysis (%): calc. (found) C, 51.27 (51.36); H, 3.72

(3.84); N, 10.32 (10.58); Co, 11.52 (11.65); Formula $C_{16}H_{16}N_4O_4Zn$; IR (KBr pellets (cm^{-1})): 420, 567, 1280, 1543.

1.0 Density Functional Theory (DFT) Studies

Density Functional Theory (DFT) cluster calculations were carried out to investigate the local electronic structure of the Zn-centered active-site model and its interaction with H_2O_2. These calculations do not attempt to model the full degradation mechanism of microplastics, which is a complex, multistep process involving radical chemistry, solvent effects, and polymer fragmentation. Instead, the DFT calculations provide a molecular-level insight about the catalyst-oxidant interaction. The following softwares, Avogadro (version 1.102.1), and ORCA 6.0 software were used to carry out the calculations with Perdew-Burke-Ernzerhof (PBE) exchange correlation functional,[26] a generalized gradient approximation known for its balance of accuracy and computational efficiency in describing transition metal complexes. The def2-SVP basis set was used, along with D3BJ dispersion correction to accurately account for non-covalent or dispersion (vanderWaals) interactions crucial for catalyst-substrate binding and TightSCF convergence setting was selected as a computationally efficient criterion to reduce numerical noise and enhance geometry optimization. The MESP (Molecular Electrostatic Potential) was generated from ORCA cube files (density + potential) and visualized in Avogadro. Single-point energies were computed in the gas phase and in implicit solvation model specifically Conductor-like Polarizable Continuum Model (CPCM) with the solvent parameters for water (CPCM (Water)) using the same geometry to estimate the bulk-solvent stabilization, while the implicit solvation energy was calculated using the formula: $\Delta E_{solv} = E(water) - E(gas)$; where ΔE_{solv} is the solvation energy of the system, E(water) is the absolute energy of the system in implicit water solvent, and E(gas) is the absolute energy of the system in gas-phase.

The quantum chemical descriptors (molecular electrostatic potential (MESP), lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) using the same functional and basis set to see the distribution of the electron densities in addition to the solvation energies were computed to provide a comprehensive knowledge of the behaviour of $[Zn(MIM)_2(TPA)_2]$ as a catalyst.[26] However, it is important to note that this DFT results are primarily qualitative in nature, and higher-level methods may be required for quantitative thermodynamics and kinetics calculations.

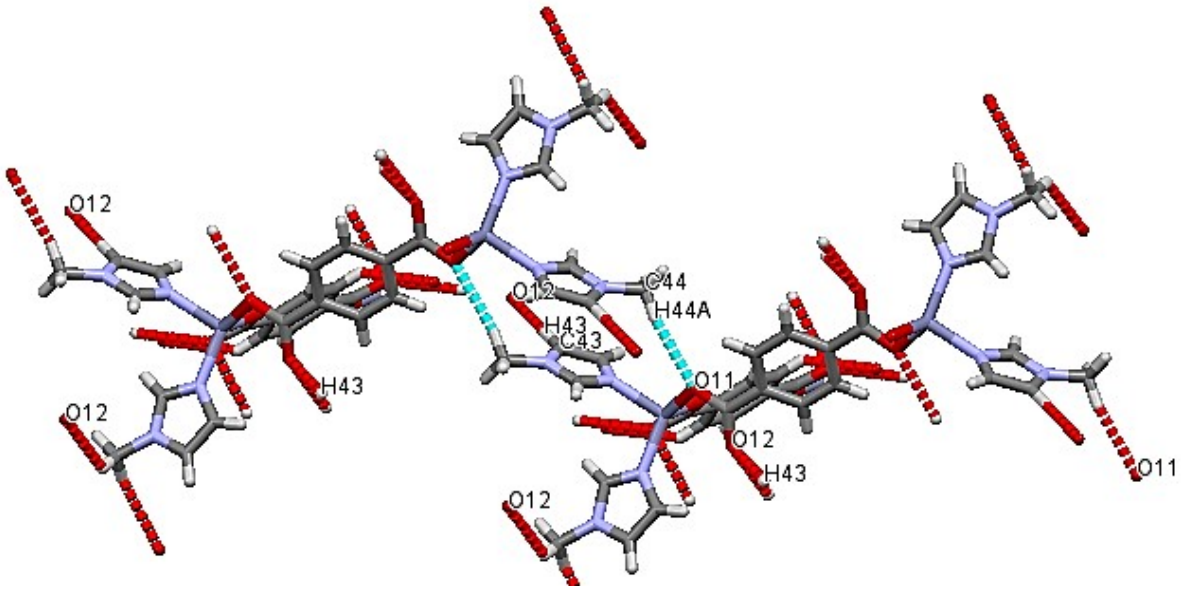


Fig. S1 Intermolecular hydrogen bonding interaction in the $[Zn(MIM)_2(TPA)_2]$.

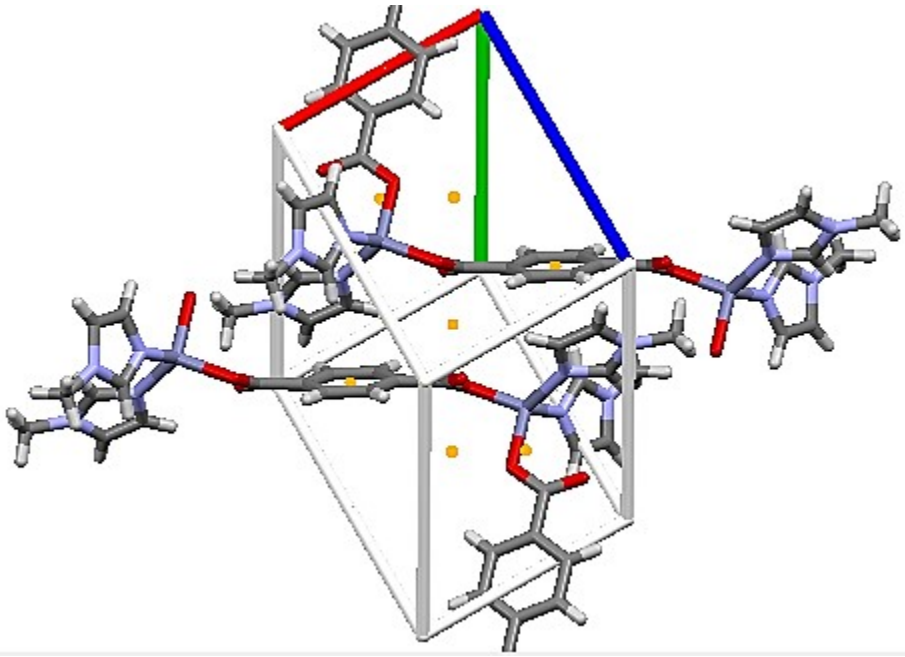


Fig. S2 $\pi\cdots\pi$ stacking view of $[Zn(MIM)_2(TPA)_2]$.

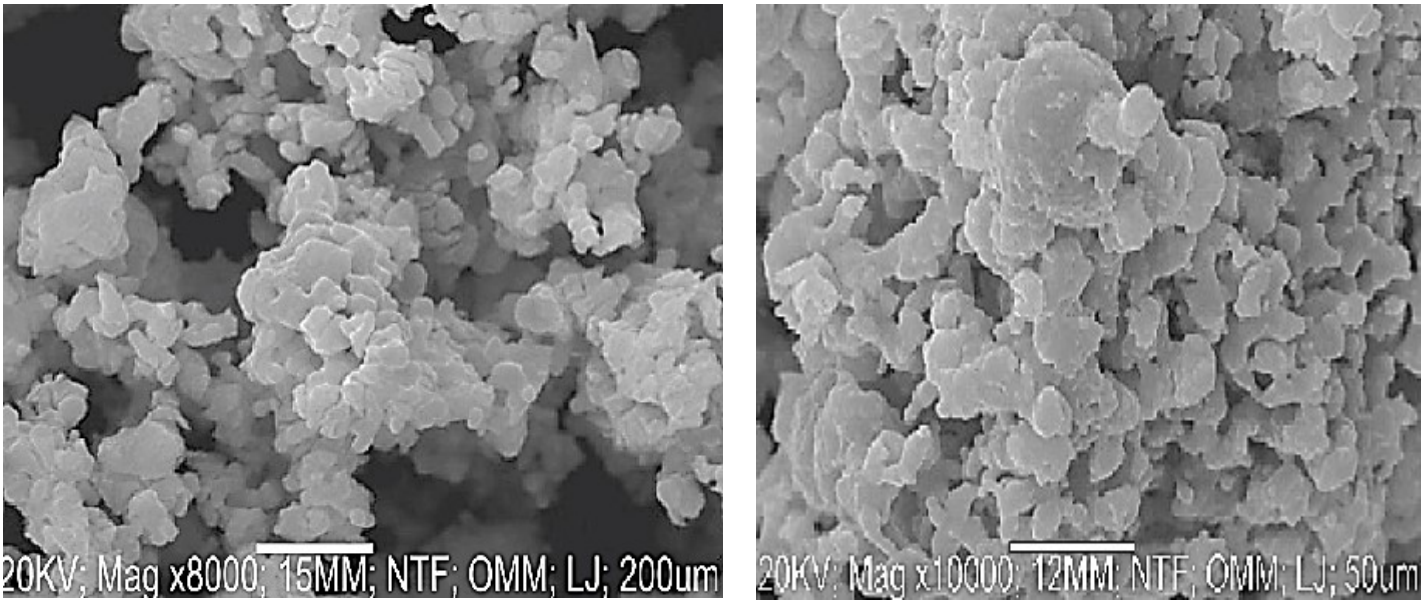


Fig. S3 SEM images of the $[Zn(MIM)_2(TPA)_2]$ at different magnifications

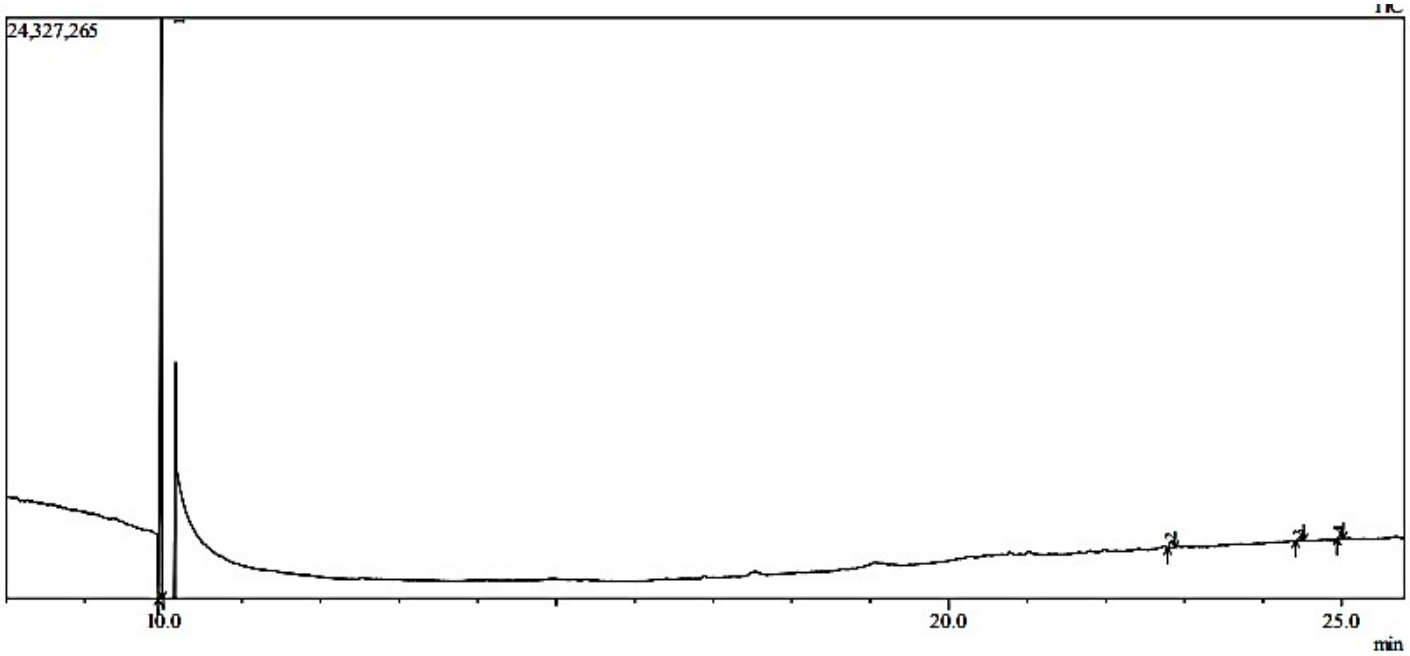
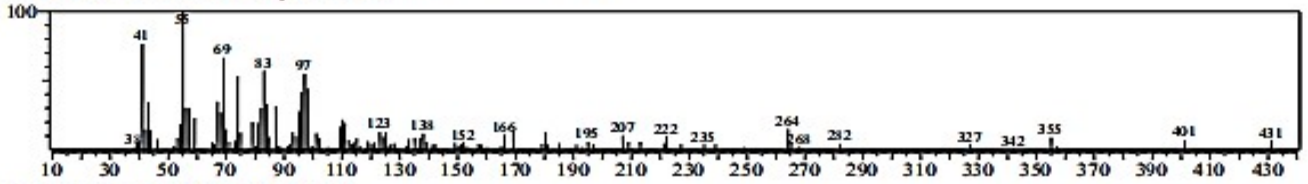
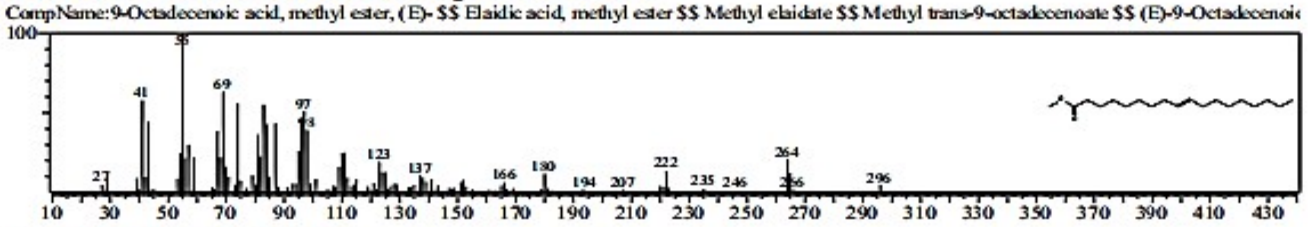


Fig. S4 GCMS chromatogram of degradation products of micronized HDPE in the presence of the synthesized Zn-CP as catalyst.

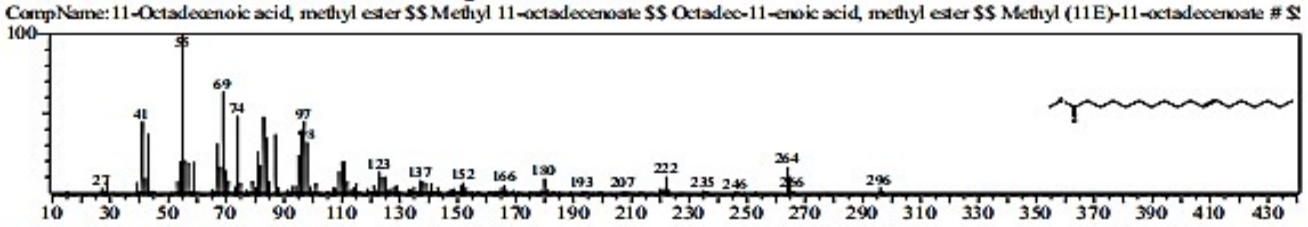
<< Target >>
Line#:2 R.Time:22.835(Scan#:2968) MassPeaks:139
RawMode:Averaged 22.830-22.840(2967-2969) BasePeak:55.10(18238)
BG Mode:Calc. from Peak Group 1 - Event 1



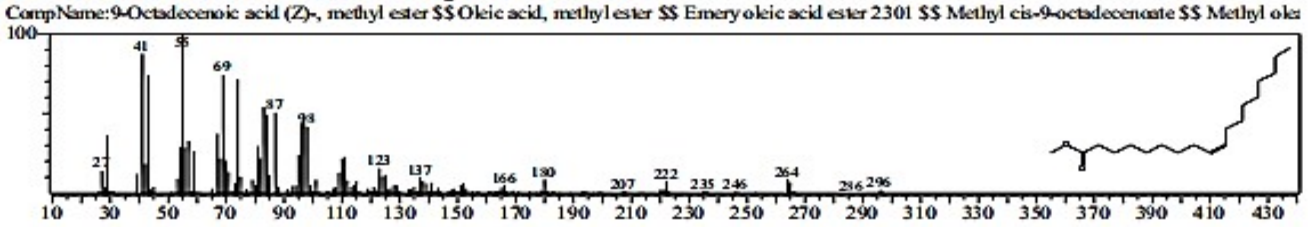
Hit#:1 Entry:25930 Library:NIST11s.lib
SI:89 Formula:C19H36O2 CAS:1937-62-8 MolWeight:296 RetIndex:2085
CompName:9-Octadecenoic acid, methyl ester, (E)- $$ Elaidic acid, methyl ester $$ Methyl elaidate $$ Methyl trans-9-octadecenoate $$ (E)-9-Octadecenoi



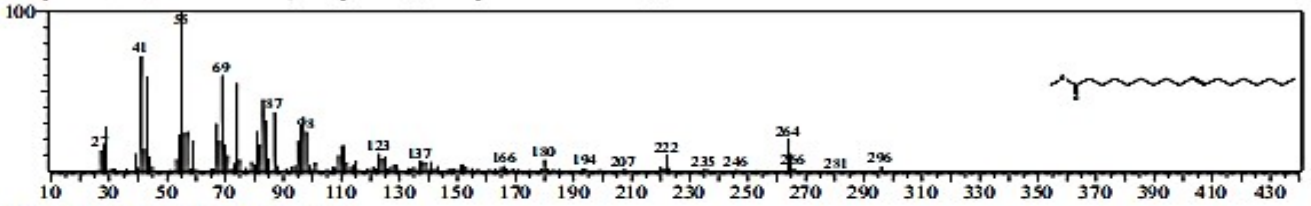
Hit#:2 Entry:25931 Library:NIST11s.lib
SI:88 Formula:C19H36O2 CAS:52380-33-3 MolWeight:296 RetIndex:2085
CompName:11-Octadecenoic acid, methyl ester $$ Methyl 11-octadecenoate $$ Octadec-11-enoic acid, methyl ester $$ Methyl (11E)-11-octadecenoate # $



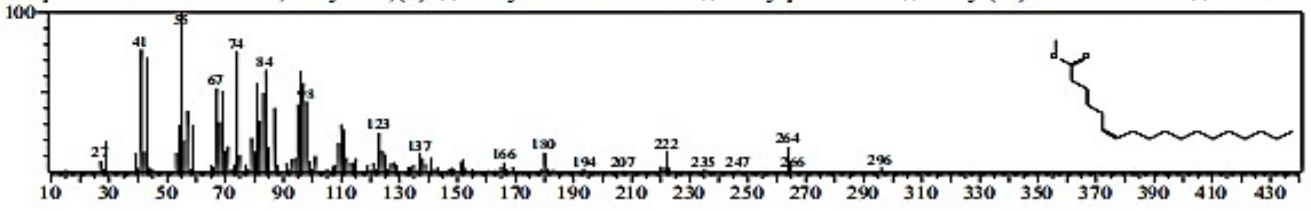
Hit#:3 Entry:25927 Library:NIST11s.lib
SI:88 Formula:C19H36O2 CAS:112-62-9 MolWeight:296 RetIndex:2085
CompName:9-Octadecenoic acid (Z)-, methyl ester $$ Oleic acid, methyl ester $$ Emery oleic acid ester 2301 $$ Methyl cis-9-octadecenoate $$ Methyl ole



Hit#:4 Entry:115408 Library:NIST11.lib
SI:88 Formula:C19H36O2 CAS:13481-95-3 MolWeight:296 RetIndex:2085
CompName:10-Octadecenoic acid, methyl ester $$ Methyl 10-octadecenoate $$



Hit#:5 Entry:115413 Library:NIST11.lib
SI:88 Formula:C19H36O2 CAS:2777-58-4 MolWeight:296 RetIndex:2085
CompName:6-Octadecenoic acid, methyl ester, (Z)- $$ Methyl cis-6-octadecenoate $$ Methyl petroselinate $$ Methyl (6Z)-6-octadecenoate #$$ cis-6-Octa



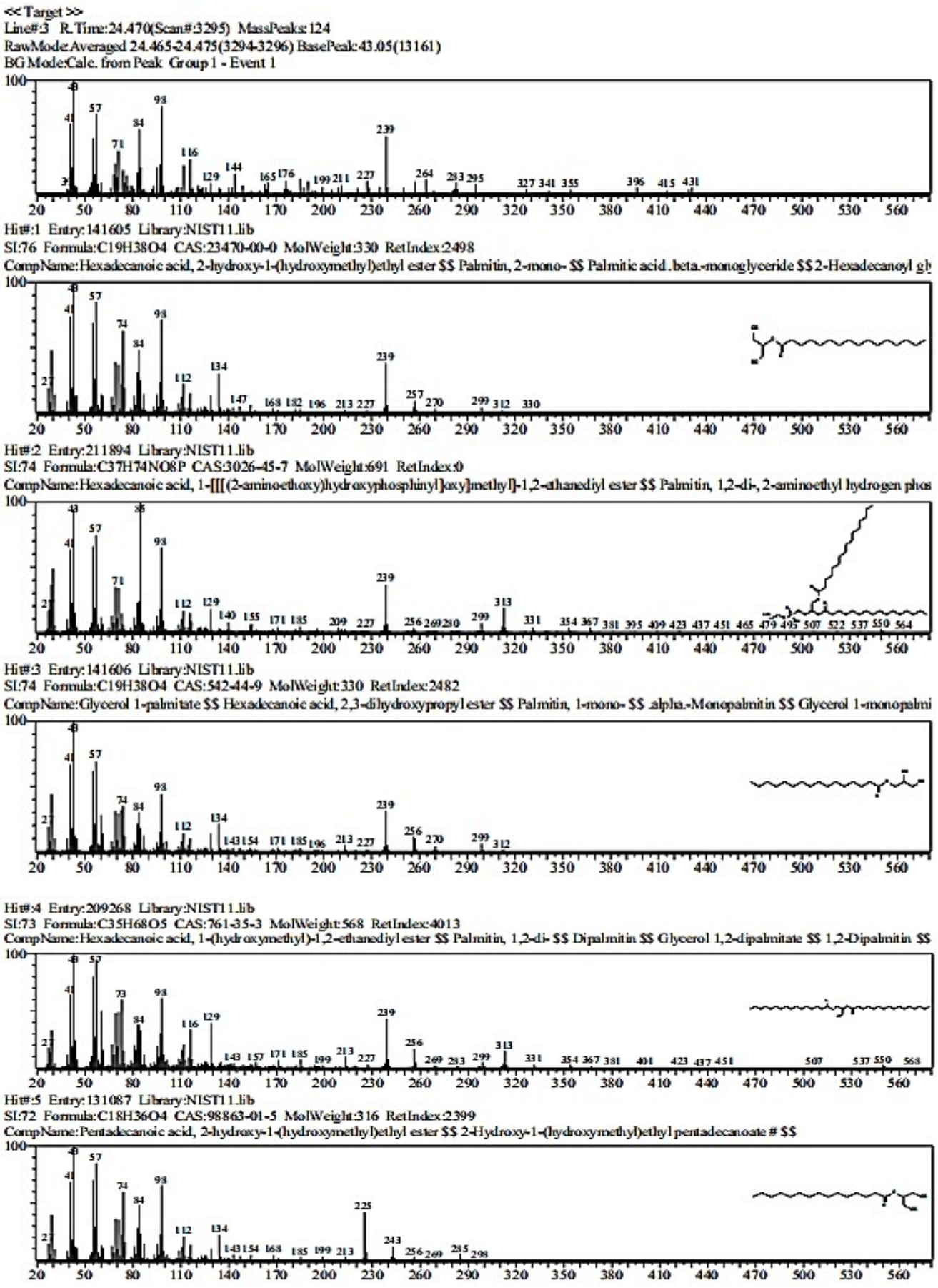


Fig. S5 Mass spectrum of the fragmentation products for the catalytic degradation of micronized HDPE in the presence of synthesized Zn-CP as catalyst.

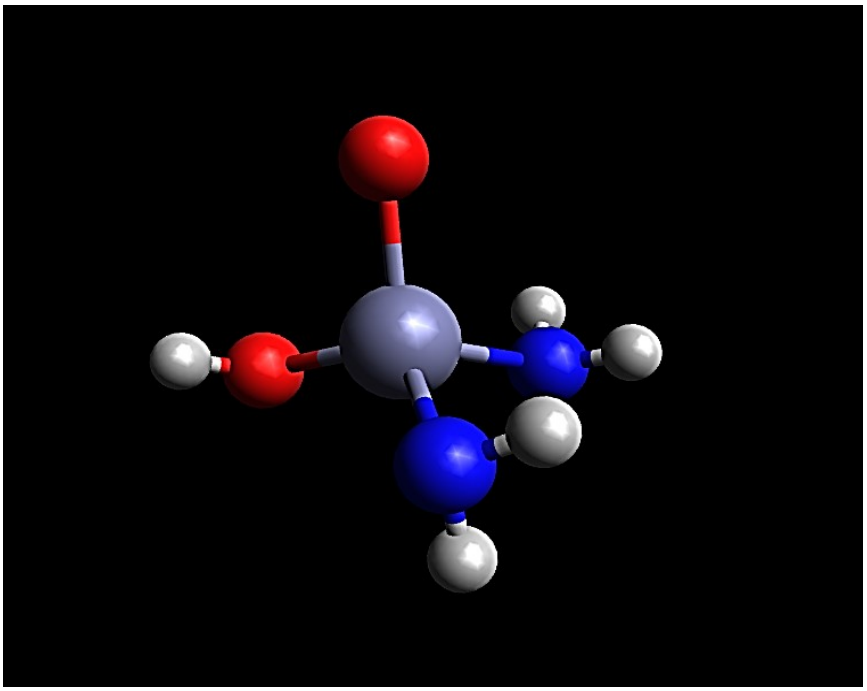


Fig. S6 Optimized structure of the Zn-CP active site

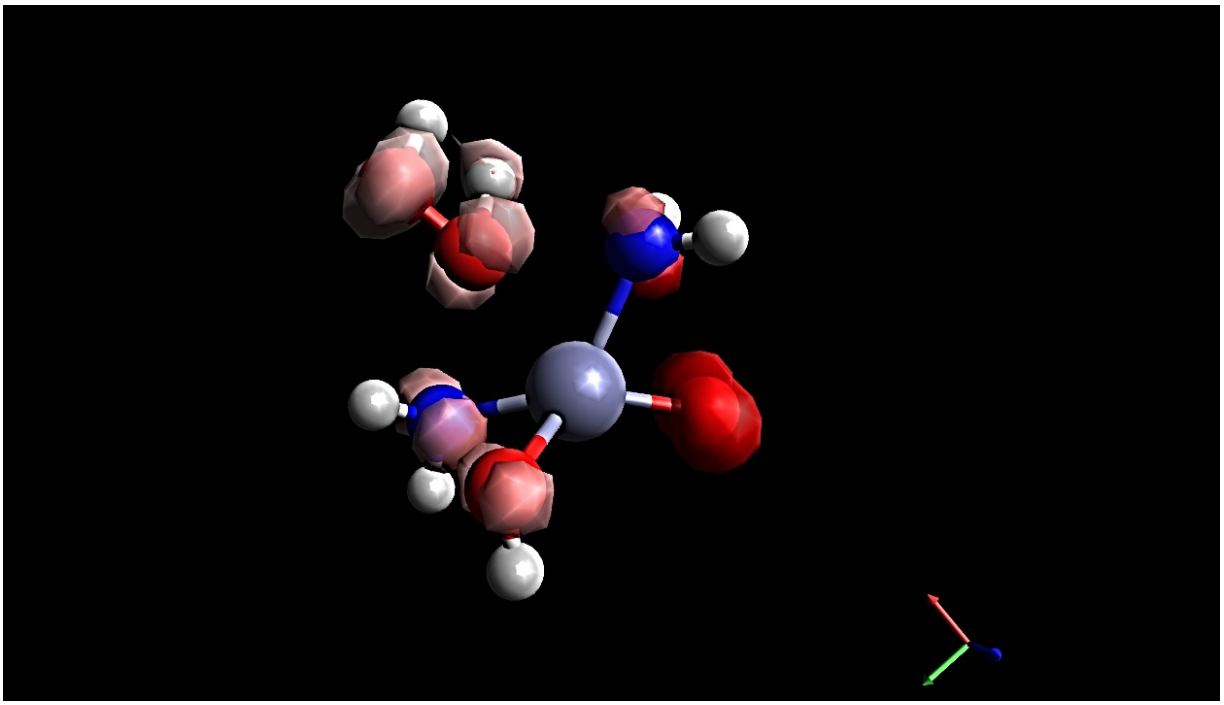


Fig. S7 the Zn–H_2O_2 Complex

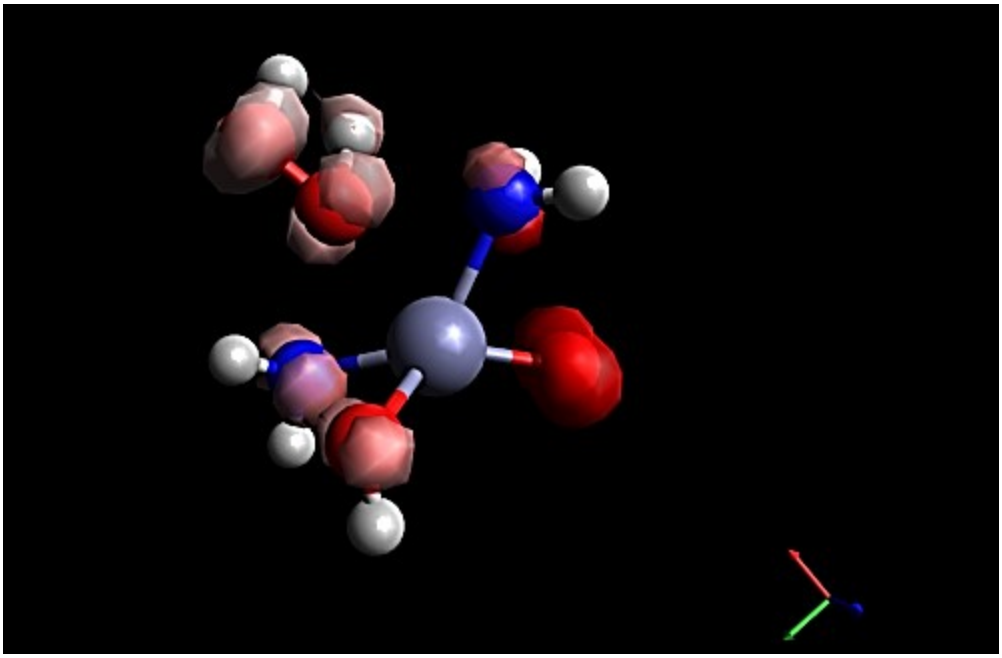


Fig. S8 MESP (Molecular Electrostatic Potential) map for the Zn-CP