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The First Alternating Mn^{II}-Mn^{III} 1D Chain: Structure, Magnetic Properties and Catalytic Oxidase Activities

Sayantan Ganguly,[a,b] Paramita Kar,[a,c] Maharudra Chakraborty,[a] Ashutosh Ghosh[a]*

[a]*Department of Chemistry, University College of Science, University of Calcutta, 92, A. P. C. Road, Kolkata-700 009, India; e-mail: ghosh_59@yahoo.com*

[b]*Department of Chemistry, Taki Government College, Taki, Hasnabad, West Bengal 743429, India*

[c]*Department of Chemistry, Bagnan College, Bagnan, Howrah, West Bengal 711303, India*

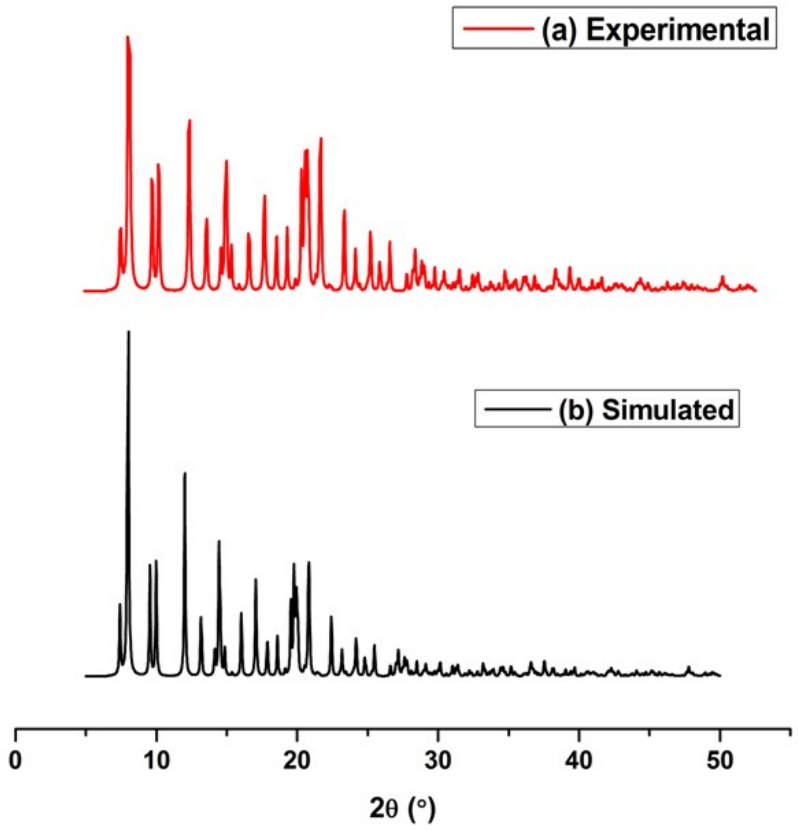

Fig. S1 Powder X-ray Diffraction Patterns of complex **1** (a) experimental (λ = 0.15418 nm) (b) simulated (calculated from the crystal structure of complex **1**)

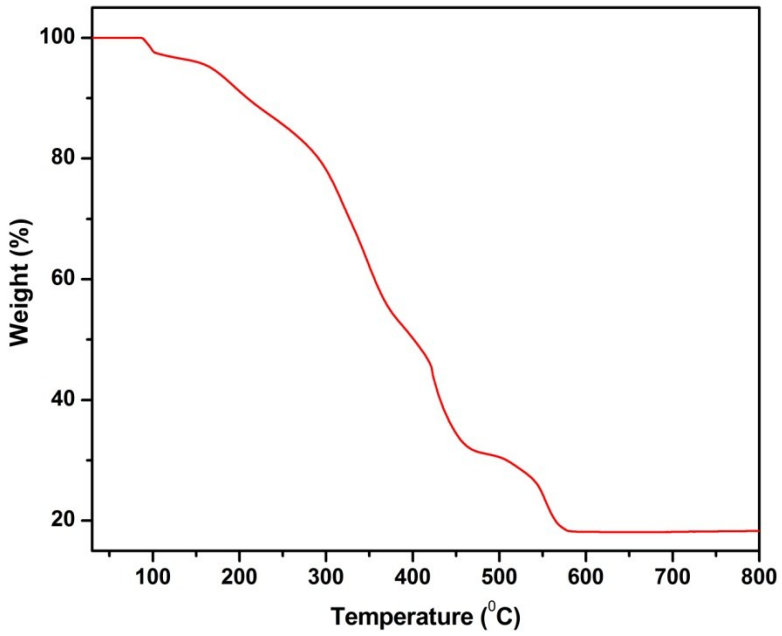

Fig. S2 Thermogram of complex **1**.

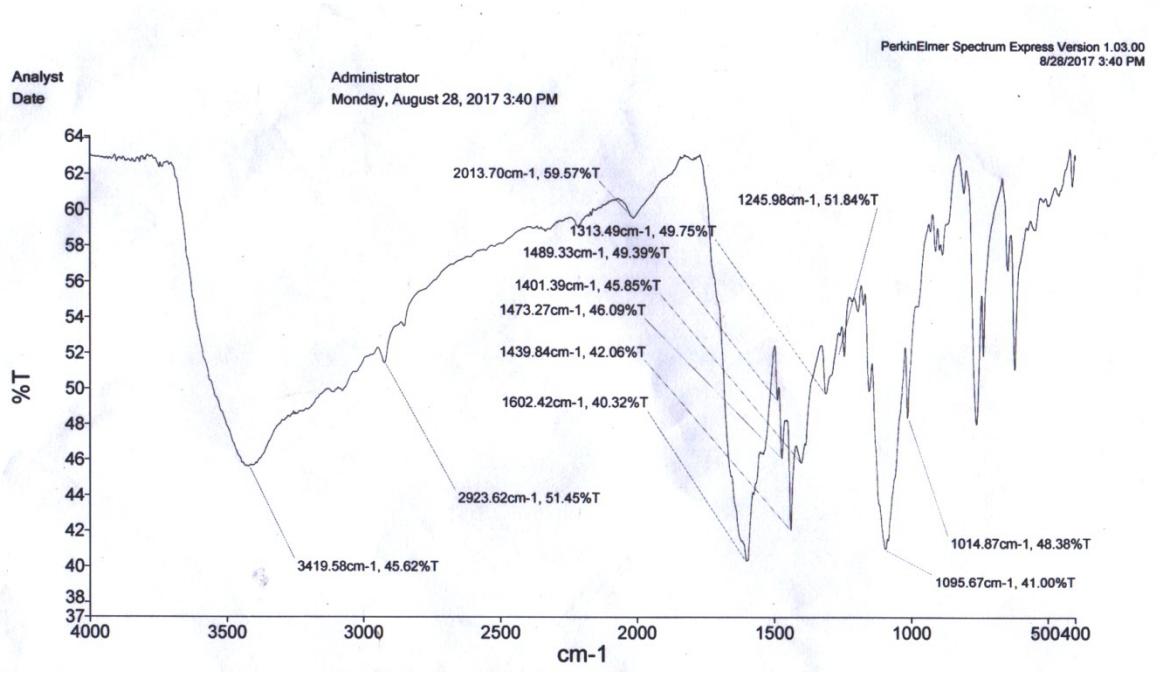

Fig. S3 Representative IR spectrum of complex **1**.

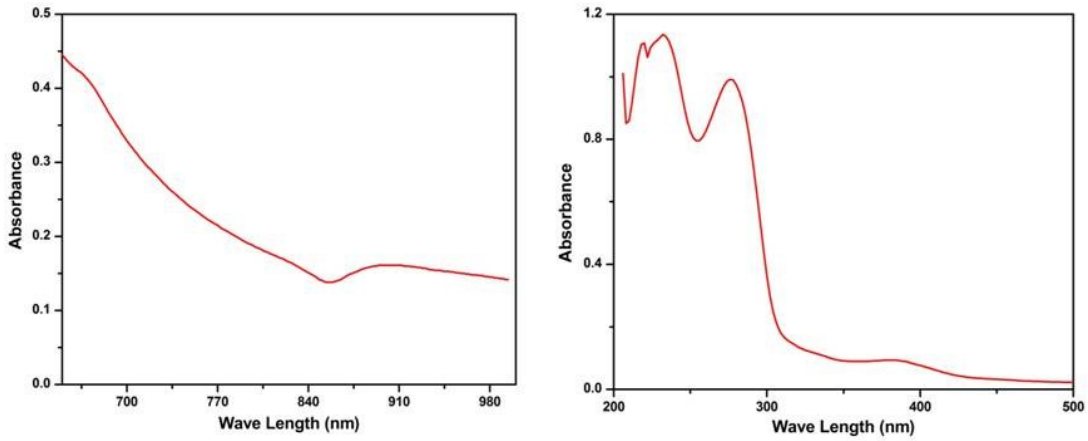

Fig. S4 Representative UV-Vis spectra of the complex 1 in Methanol solution (left) d-d transition and (right) charge transfer band.

Table S1 Representation of the d-d band and CT band in the complex **1**

Complex	**d-d band** (λ_{max}**(nm) (ε,M^{-1}cm^{-1}) in CH$_3$OH)**	**CT band** (λ_{max}**(nm) (ε,M^{-1}cm^{-1}) in CH$_3$OH)**
1	895 (152)	383(9530),276(99000),232(113000), 219(110600)

Table S2 Bond valence sum (BVS)[a] calculations for complex **1**.

Atom	**Mn^{II}**	**Mn^{III}**
Mn(1)	3.39	<u>3.21</u>
Mn(2)	<u>2.06</u>	1.96

[a] The underlined value is the one closest to the charge for which it was calculated. The oxidation state is the nearest whole number to the underlined value.

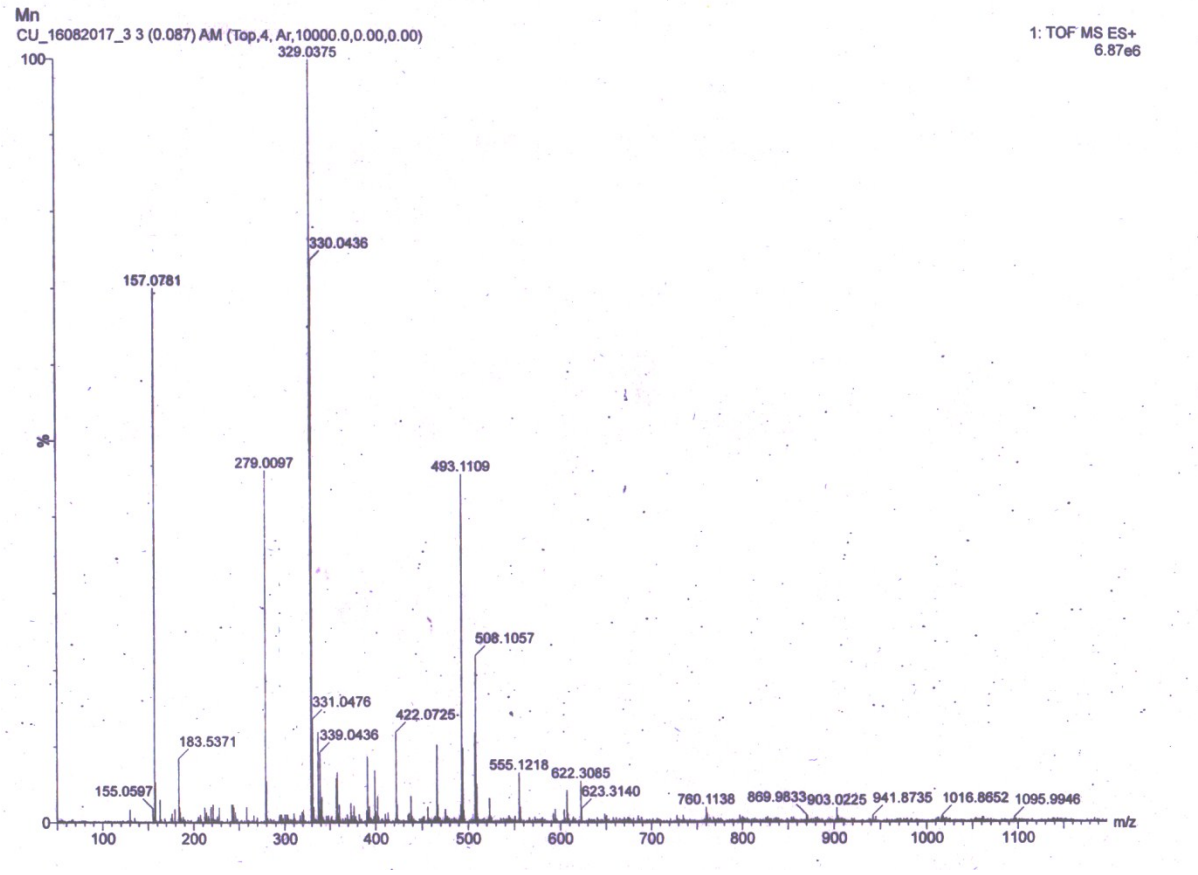

Fig. S5 Representative ESI mass spectrum of complex **1**.

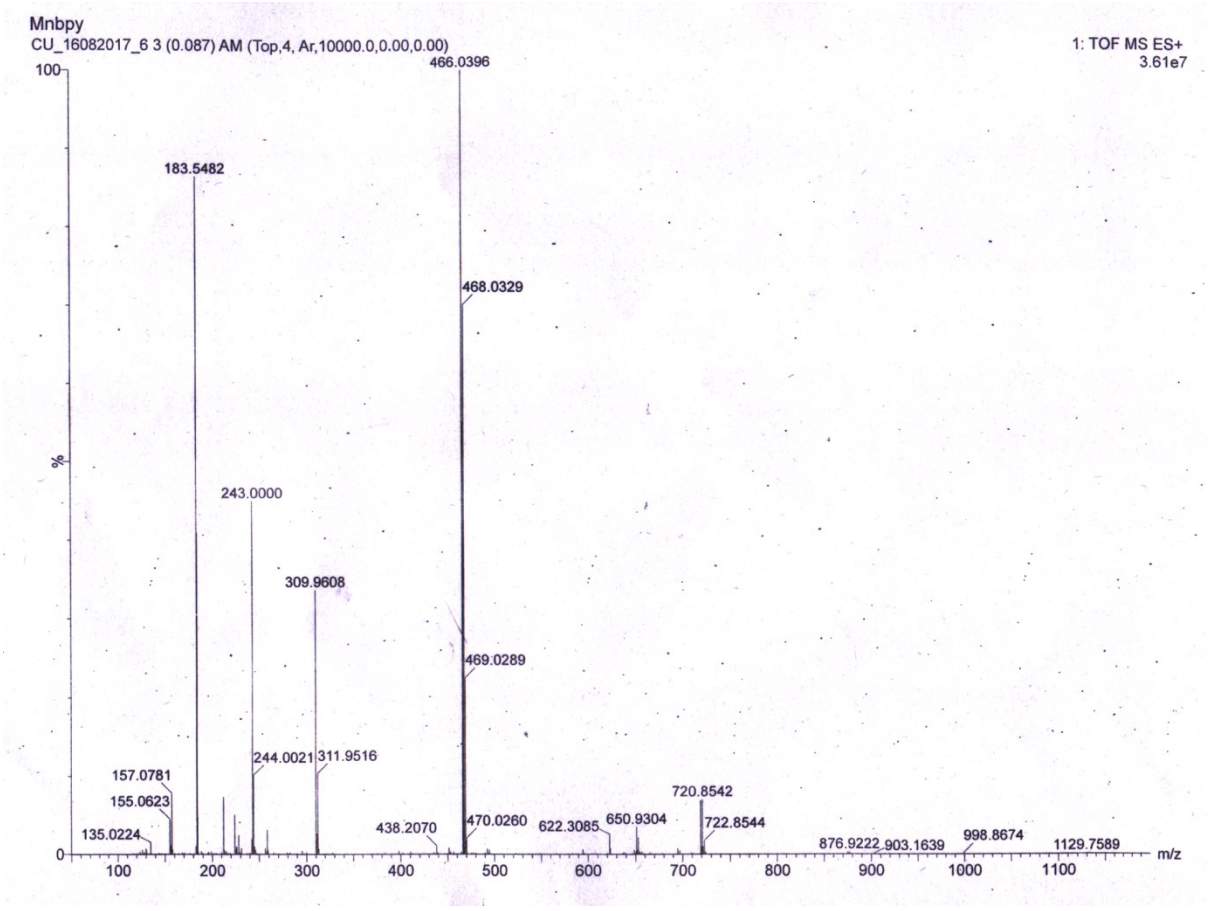

Fig. S6 Representative ESI mass spectrum of the complex $[Mn^{II}(bpy)_2(H_2O)(ClO_4)](ClO_4)$.

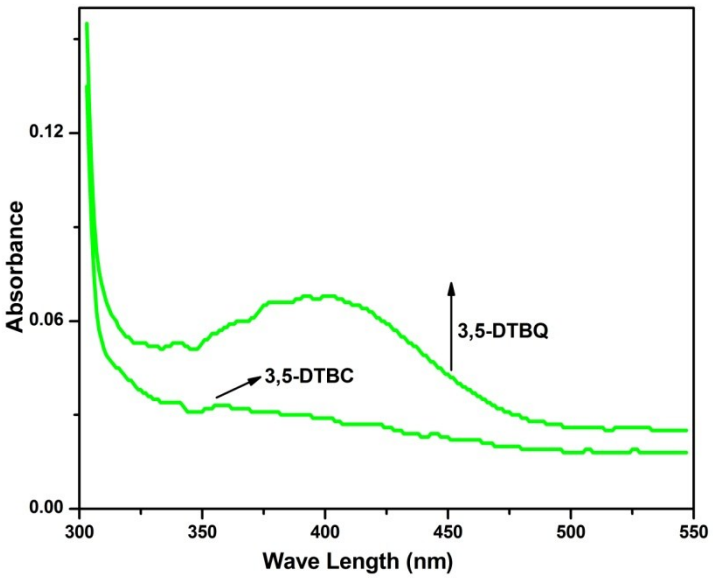

Fig. S7 Representative UV-Vis spectra of 3,5-DTBC (Blank).

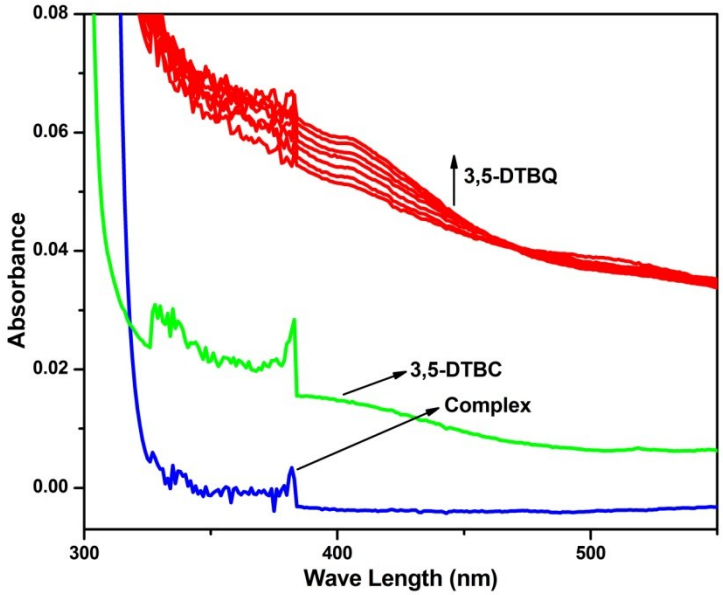

Fig. S8 Representative UV-Vis spectra of the complex $[Mn^{II}(bpy)_2(H_2O)(ClO_4)](ClO_4)$ with 3,5-DTBC.

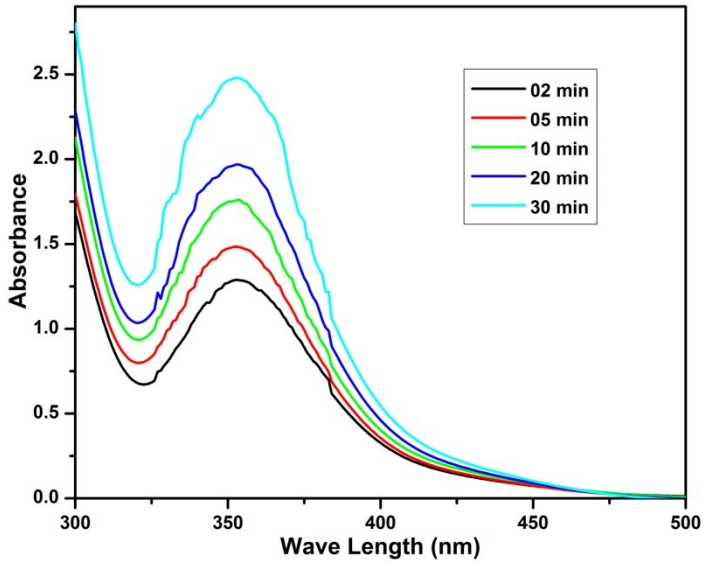

Fig. S9 Increase of the absorption band at around 353 nm during the estimation of H_2O_2 iodometrically. The spectra were recorded at different time interval

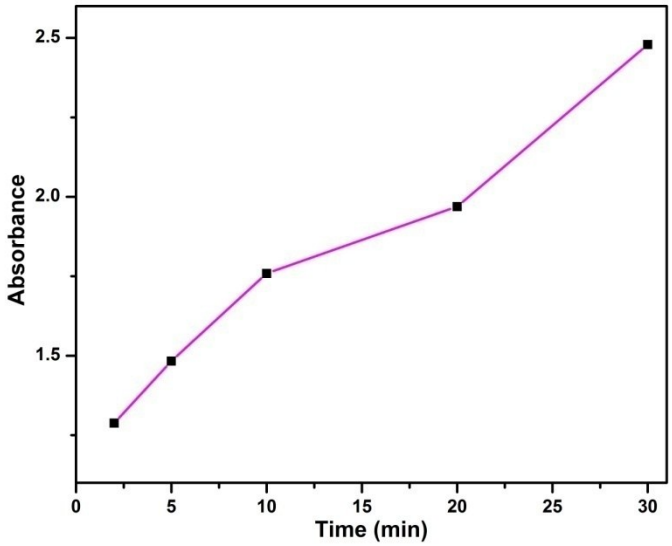

Fig. S10 Plot of absorption maxima at around 353 nm with different time (min)

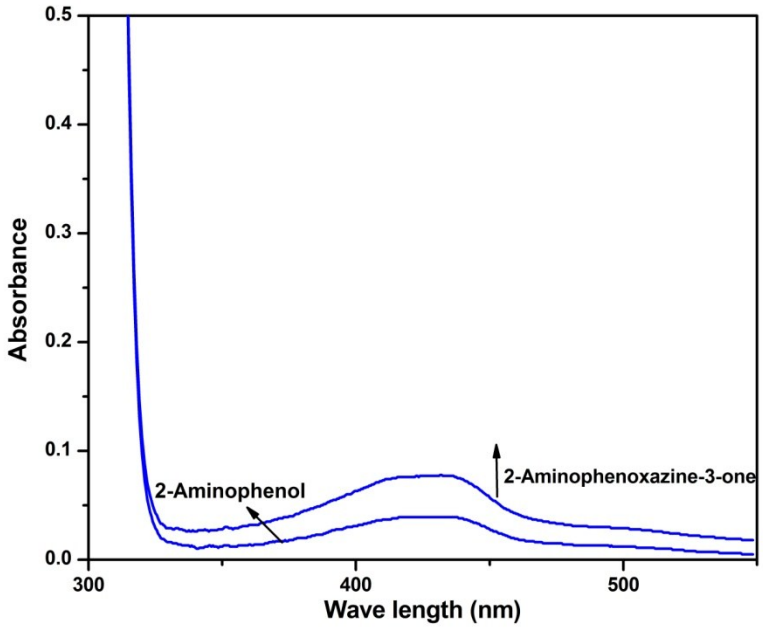

Fig. S11 Representative UV-Vis spectra of OAPH (Blank).

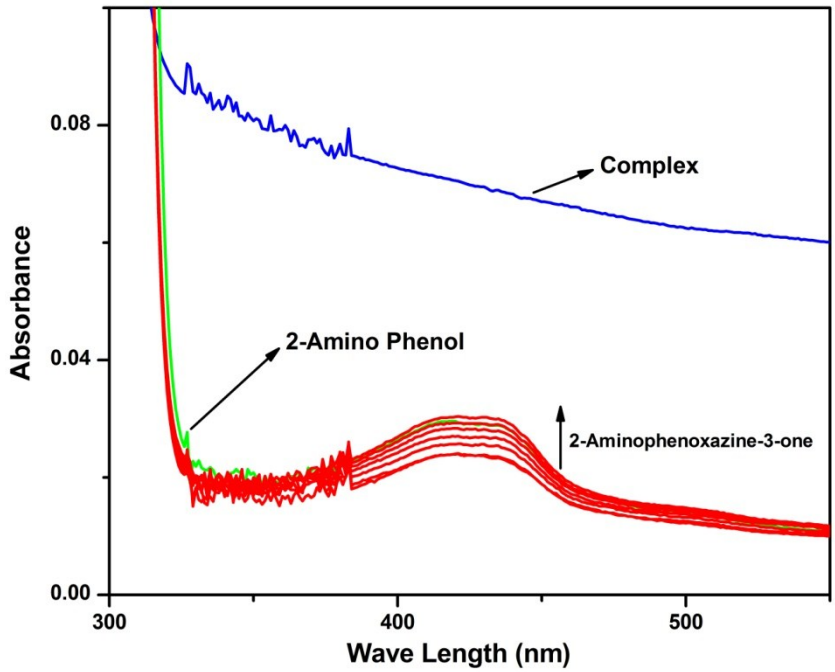

Fig. S12 Representative UV-Vis spectra of the complex $[Mn^{II}(bpy)_2(H_2O)(ClO_4)](ClO_4)$ with OAPH.

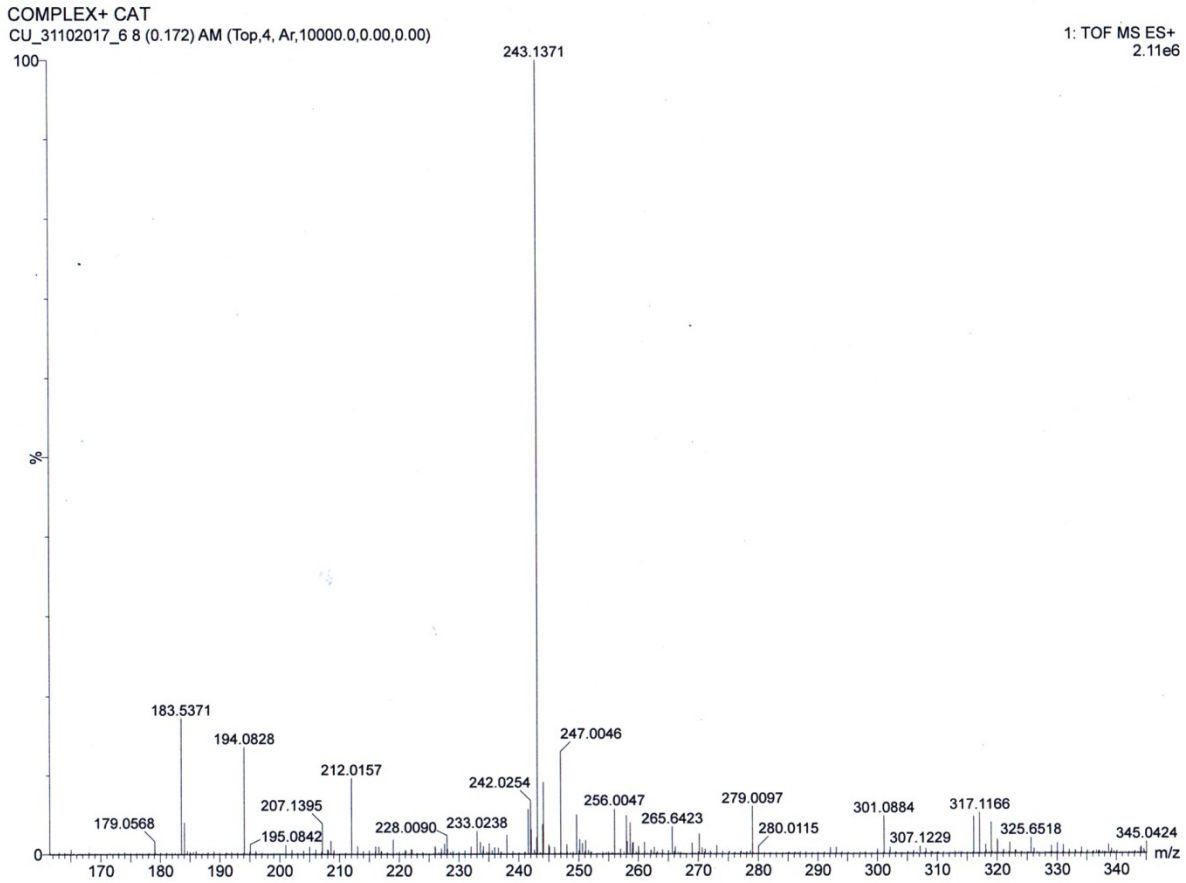

Fig. S13 Representative ESI mass spectrum of complex **1** with 3,5-DTBC.

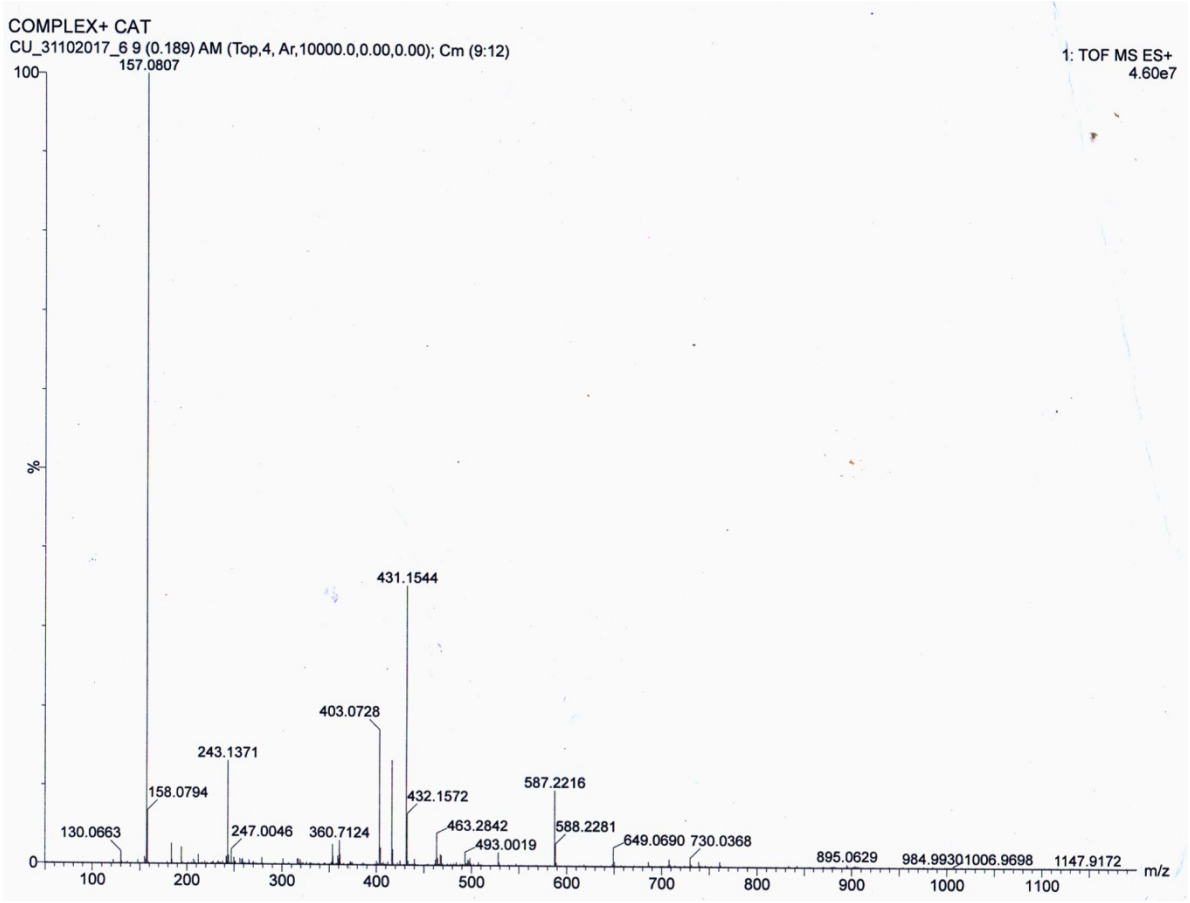

Fig. S14 Representative ESI mass spectrum of complex **1** with 3,5-DTBC.

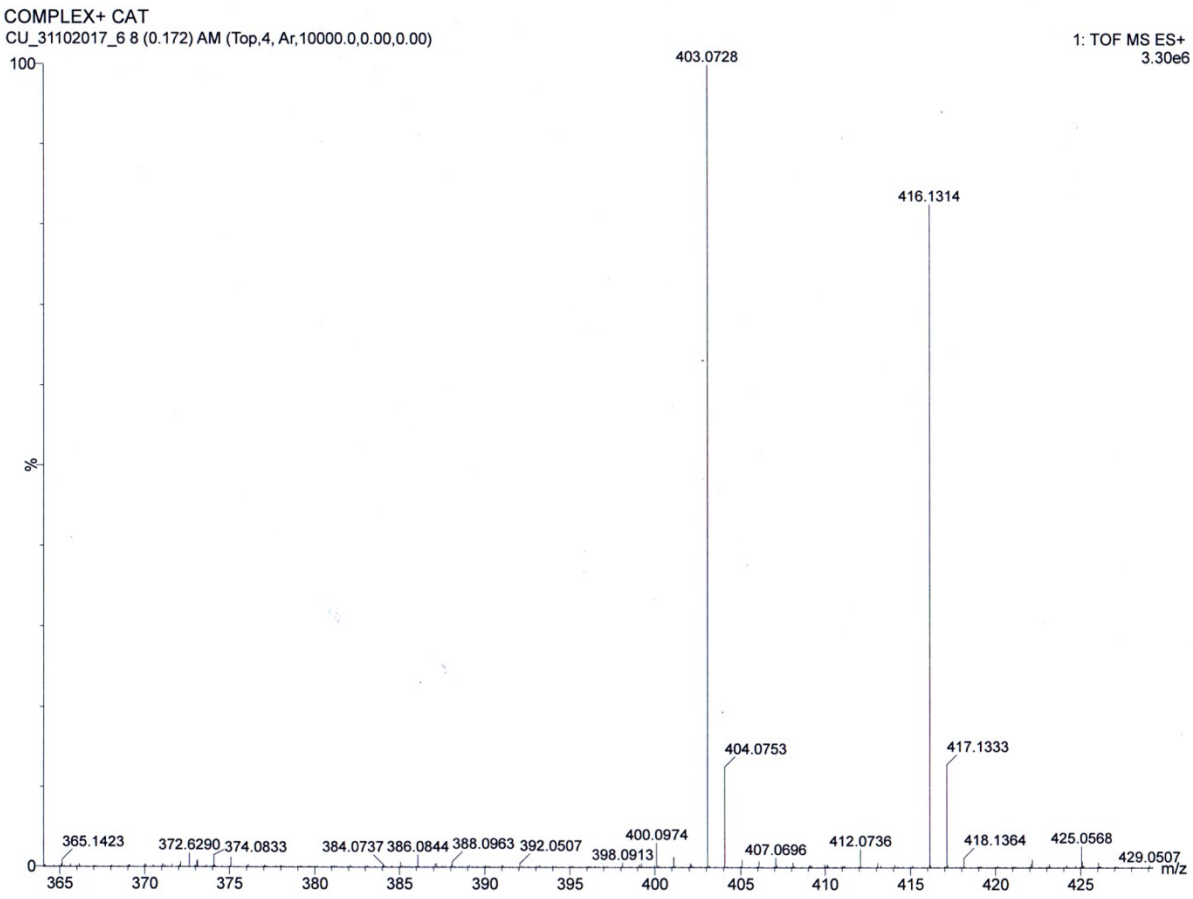

Fig. S15 Representative ESI mass spectrum of complex **1** with 3,5-DTBC.

Table S3 Kinetic parameters for the oxidation of 3,5-DTBC to 3,5-DTBQ catalyzed by different manganese complexes[b]

	Complexes	**k_{cat} (h^{-1}) in CH_3OH**	**k_{cat} (h^{-1}) in CH_3CN**	**k_{cat} (h^{-1}) in DMF**	**References**
Mn^{II} complexes	$[Mn^{II}(HL^1)(H_2O)_2(CH_3CN)](ClO_4)_2$	Not performed	Not performed	48.8	34a
	$[Mn^{II}(L^2)_2(OH_2)_2]$	598.0	Not performed	Not performed	34b
	$[Mn^{II}(HL^3)_2]\cdot 2ClO_4$	1038.0	Not performed	Not performed	33c
	$[Mn^{II}(HL^3)(N(CN)_2)$	871.2	Not performed	Not performed	33c
	$[Mn^{II}(HL^3)(SCN)_2]$	604.0	Not performed	Not performed	33c

	$[Mn^{II}(o\text{-}(NO_2)C_6H_4COO)_2(L^4)(H_2O)]_n$	Not performed	177	Not performed	9b
Mn^{III} complexes	$[4\text{-MePyH}][Mn^{III}(L^5)_2(4\text{-MePy})]$	Not performed	Not performed	19.5	34c
	$[4\text{-EtPyH}][Mn^{III}(L^5)_2(4\text{-EtPy})]$	Not performed	Not performed	25.9	34c
	$[Et_3NH][Mn^{III}(L^5)_2(4\text{-}CNPy)_2]\cdot H_2O$	Not performed	Not performed	36.0	34c
	$[Et_3NH][Mn^{III}(L^5)_2(3\text{-}CNPy)_2]\cdot 3\text{-}CNPy\cdot H_2O$	Not performed	Not performed	31.1	34c
	$[(4\text{-}OHpy)_2H][Mn^{III}(L^5)_2(MeOH)_2]$	Not performed	Not performed	40.5	34c
	$[Mn^{III}(HL^6)_2(CH_3OH)_2][Mn^{III}(HL^6)_2(N_3)_2]$	Not performed	292.4	Not performed	34d
	$[Mn^{III}L^7Cl\cdot 4H_2O]$	-	1790.0	-	34e
	$[Mn^{III}L^8Cl\cdot 4H_2O]$	2470.0	3600.0	-	34e
	$[Mn^{III}L^9Cl\cdot 4H_2O]$	3600.0	1080.0	-	34e
	$[Mn^{III}L^{10}Cl\cdot 4H_2O]$	7200.0	1800.0	-	34e
	$[Mn^{III}(L^{11})(OAc)(OCH_3)](PF_6)$	86.0	Not performed	Not performed	34f
	$[Mn^{III}(L^{12})(OAc)(OCH_3)](PF_6)$	101.0	Not performed	Not performed	34f
	$[Mn^{III}(L^{12})(Cl)_2](ClO_4)$	230.0	Not performed	Not performed	34f
	$[Mn^{III}(HL^{13})(Cl)_2].CH_3OH$	130.0	Not performed	Not performed	34f
	$[Mn^{III}_6(\mu_4\text{-}H_2L^{14})_2(\mu\text{-}HL^{15})_2(\mu_3\text{-}OH)_2(\mu_{1,3}\text{-}O_2CC_2H_5)_4](ClO_4)_2\cdot 2H_2O$	54.0	Not performed	Not performed	34g
Mn^{IV} complexes	$[Mn^{IV}(L^{16})_2](ClO_4)_2\cdot 0.88H_2O$	Not performed	136.0	Not performed	33e
	$[Mn^{IV}(HL^{16})_2(N_3)_2](ClO_4)_2\cdot 2H_2O$	Not	398.7	Not	33e

		performed		performed	
	$[\{Mn^{IV}(L^{17})(\mu\text{-}O)\}_2][ClO_4]_2.2CH_3CN.CH_3OH$	Not performed	8690.0	Not performed	34h
Mixed valence $Mn^{II/III}$ complexes	$[Mn^{III}_2\ Mn^{II}\ (\mu\text{-}H_2L^{18})_2(\mu_{1,3}\text{-}O_2CCH_3)_4(CH_3OH)_2](ClO_4)_2\cdot 4CH_3OH$	61.0	Not performed	Not performed	34g
	$[Mn^{III}_2\ Mn^{II}(O_2CMe)_4(L^{19})_2(H_2O)_2]\cdot 2H_2O$	Not performed	8220.0	Not performed	33g
	$[Mn^{III}_2\ Mn^{II}(O_2CCH_2Cl)_4(L^{19})_2(H_2O)_2]\cdot H_2O\cdot CH_3OH$	Not performed	9011.0	Not performed	33g
	$[Mn^{II}(L^{20})Cl][Mn^{III}(L^5)_2(H_2O)_2].4H_2O$	Not performed	Not performed	28.9	34i
	$[Mn^{III}Mn^{II}L^{21}(\mu\text{-}O_2CMe)(H_2O)_2](ClO_4)_2\cdot H_2O\cdot CH_3CN$	11.6	20.6	Not performed	34j
	$[Mn^{III}Mn^{II}L^{21}(\mu\text{-}O_2CPh)(CH_3OH)(ClO_4)](ClO_4)$	7.5	15.6	Not performed	34j
	$[\{Mn^{III}Mn^{II}L^{21}(\mu\text{-}O_2CEt)(EtOH)\}_2(\mu\text{-}O_2CEt)](ClO_4)_3$	44.6	64.7	Not performed	34j
	$[Mn^{III}_2Mn^{II}_4O_2(hmt)_4(OCOC_6H_5)_{10}]$	Not performed	2337.9	Not performed	34k
	$[Mn^{III}_2\ Mn^{II}_4\ O_2(pyz)_{0.61}/(MeOH)_{0.39}(o\text{-}(NO2)\text{-}C_6H_4COO)_{10}\cdot(H_2O)\cdot\{(CH_3)_2CO\}_2]\cdot(CH_3)_2CO$	Not performed	432.0	Not performed	9b
	$[Mn^{III}_2\ Mn^{II}_4O_2\ (pyz)_{0.28}/(MeCN)_{3.72}(o\text{-}(NO_2)C_6H_4COO)_{10}\cdot\ (H_2O)]$	Not performed	426.0	Not performed	9b
Mixed valence $Mn^{II/III}$	$[Mn^{III}_2Mn^{II}_4O_2(pyz)_2(C_6H_5CH_2COO)_{10}]_n$	Not performed	2547.0	Not performed	9c
	Complex **1**	126.9	Not	Not	Prese

coordination polymer			performed	performed	nt Study

[b] Where L^1 = 1,3-Bis(6′-methyl-2-pyridylimino)isoindoline, L^2 = 3-methoxy-4-hydroxy-benzaldehyde, HL^3 = 4-tert-butyl-2,6-bis-[(2-pyridin-2-yl-ethylimino)-methyl]-phenol, L^4 = Pyrazine, H_2L^5 = tetrabromo catechol, H_2L^6 = 1-(5-hydroxy-3-oxapentyliminomethyl)-3-ethoxyphenol, H_2L^7 = N,N′-ethylenebis(3-formyl-5-methylsalicylaldimine), H_2L^8 = N,N′-1-methylethylenebis(3-formyl-5-methylsalicylaldimine), H_2L^9 = N,N′-1, 1-dimethylethylenebis(3-formyl-5-methylsalicylaldimine), H_2L^{10} = N,N′-cyclohexenebis(3-formyl-5-methylsalicylaldimine), L^{11} = bis(picolyl)(N-methylimidazole-2-yl)amine, L^{12}= bis((1-methylimidazole-2-yl)methyl)((2-pyridyl)methyl)amine, L^{13} = ((1-methylimidazole-2-yl)methyl)((2-pyridyl)methyl)-(2-hydroxyphenyl)amine, H_5L^{14} = 2,6-bis((1-hydroxy-2-(hydroxymethyl)butan-2-ylimino)-methyl)-4-methylphenol, H_3L^{15} = 3-(3,3-bis(hydroxymethyl)pent-1-enyl)-2-hydroxy-5-methylbenzaldehyde, HL^{16} = 2-[(3-(dimethylamino)propylimino)methyl]-4-bromophenol, HL^{17} = 2-benzyl-6-((bis(pyridin-2-ylmethyl)amino)methyl)-4-chlorophenol, H_3L^{18} = 2,6-bis((1-hydroxy-2-methylpropan-2-ylimino)-methyl)-4-methylphenol, H_2L^{19} = 2-[(2-Hydroxy-1,1-dimethyl-ethylimino)-methyl]-phenol, L^{20} = tris(2-benzimidazolylmethyl)amine, H_2L^{21} = [2 + 2] condensation product of 2,6-diformyl-4-methylphenol and 2,2-dimethyl-1,3-diaminopropane, hmt = hexamethylenetetramine.

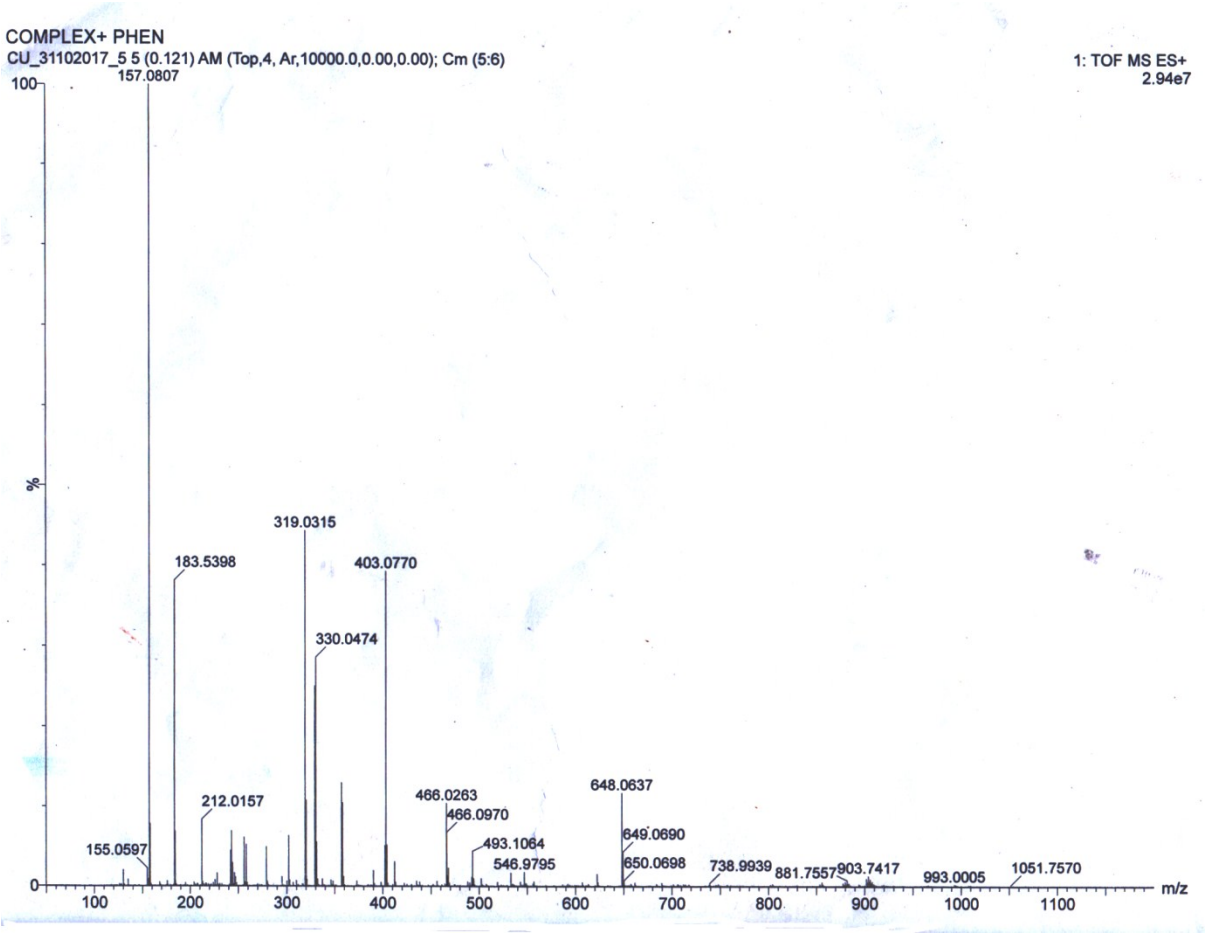

Fig. S16 Representative ESI mass spectrum of complex **1** with OAPH.

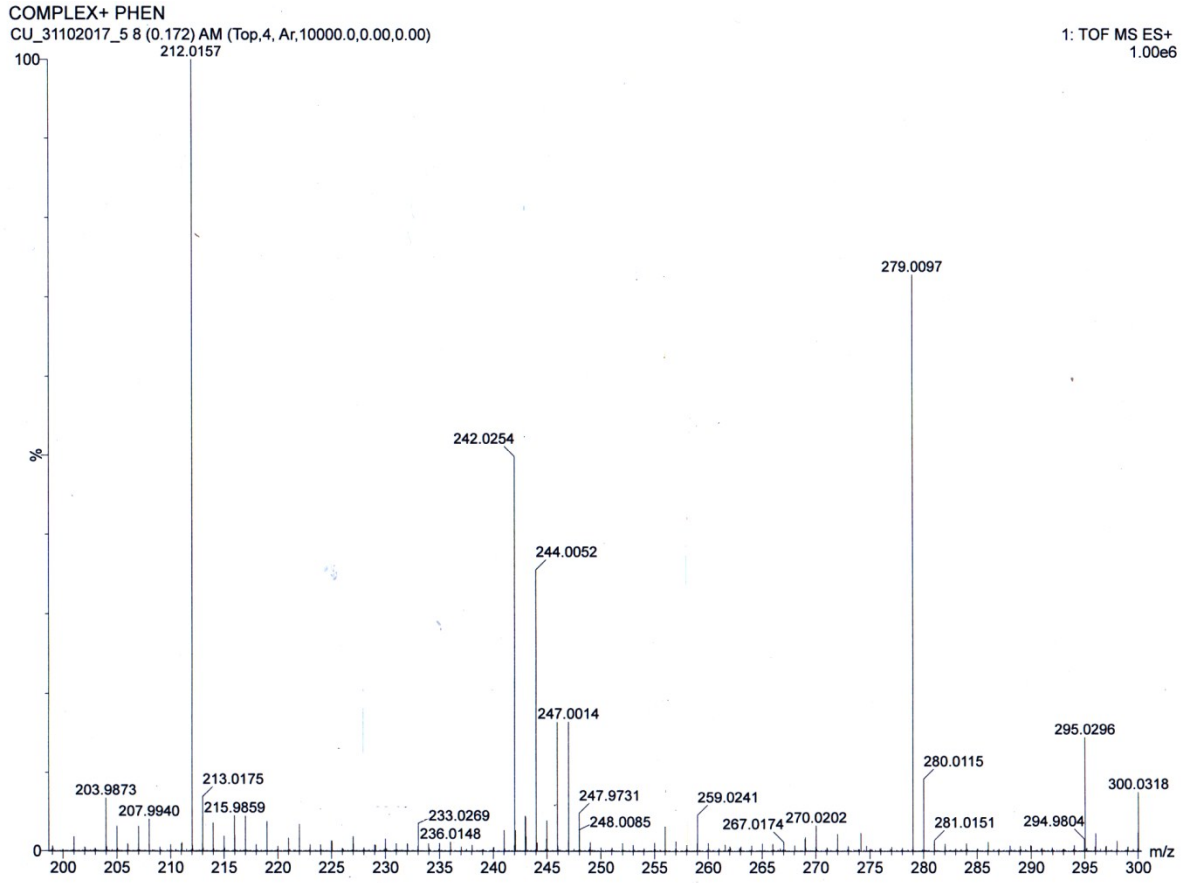

Fig. S17 Representative ESI mass spectrum of complex **1** with OAPH.

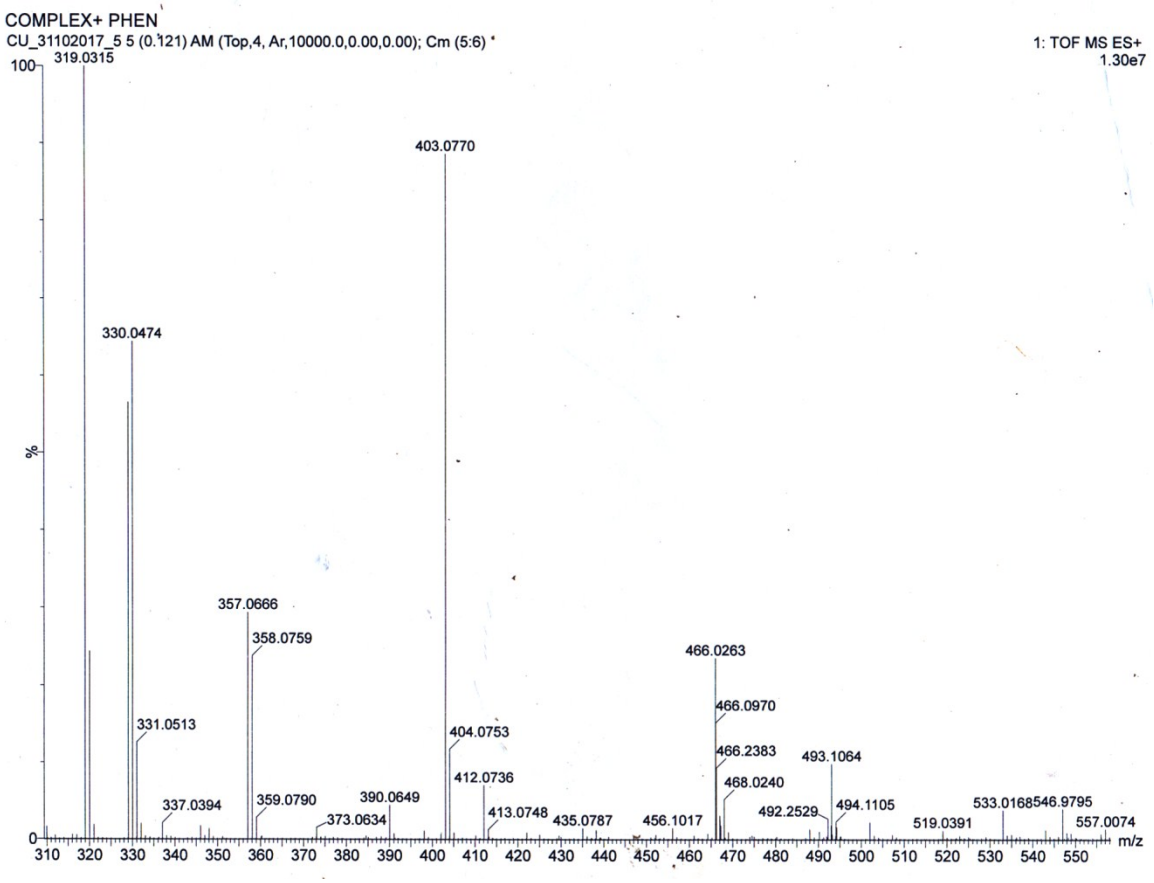

Fig. S18 Representative ESI mass spectrum of complex **1** with OAPH.

Table S4. k_{cat} Values for the oxidation of OAPH to 2-aminophenoxazine-3-one catalyzed by complex 1 and other reported Manganeese complexes.[c]

	Complexes	**k_{cat} (h^{-1}) in CH_3OH**	**k_{cat} (h^{-1}) in CH_3CN**	**k_{cat} (h^{-1}) in DMF**	**References**
Mn^{II} complexes	$[Mn^{II}(HL^1)(H_2O)_2(CH_3CN)](ClO_4)_2$	Not performed	Not performed	2.916	34a
	$[Mn^{II}(L^2)Cl_2]$	11.90	Not performed	Not performed	35a
	$[Mn^{II}(L^3)Cl_2]$	9.66	Not performed	Not performed	35a
	$[Mn^{II}(L^4)Cl_2]$	8.32	Not performed	Not performed	35a
	$[Mn^{II}(L^5)Cl_2]$	26.32	Not performed	Not performed	35a

	$[Mn^{II}(L^6)_2(OH_2)_2]$	315	Not performed	Not performed	35a
	$[Mn^{II}(HL^7)_2]\cdot 2ClO_4$	138.62	Not performed	Not performed	33c
	$[Mn^{II}(HL^7)(N(CN)_2)$	64.07	Not performed	Not performed	33c
	$[Mn^{II}(HL^7)(SCN)_2]$	14.2	Not performed	Not performed	33c
Mn^{III} complexes	$[Mn^{III}(L^8)_2]ClO_4$	Not performed	60	Not performed	35b
	$[Mn^{III}(L^9)(NCS)(H_2O)]$.DMSO	Not performed	308.13	Not performed	35b
	$[Mn^{III}(L^{10})Cl(H_2O)].H_2O$	35.24	Not performed	Not performed	35c
	$[Mn^{III}(HL^{11})_2(CH_3OH)_2][Mn^{III}(HL^{10})_2(N_3)_2]$	Not performed	215.58	Not performed	34d
Mn^{IV} complexes	$[Mn^{IV}(L^{12})_2](ClO_4)_2\cdot 0.88H_2O$	Not performed	65.82	Not performed	35d
	$[Mn^{IV}(HL^{12})_2(N_3)_2](ClO4)_2\cdot 2H_2O$	Not performed	68.46	Not performed	35d
	$[Mn^{IV}(HL^{13})(L^{12})(NCS)]_n$	Not performed	280.4	Not performed	33f
	$[Mn^{IV}(HL^{14})_2(OH)Cl]$	Not performed	166.2	Not performed	33f
Mixed valence $Mn^{II/III}$ complexes	Complex **1**	738	Not performed	Not performed	Present Study

[c] Where L^1 = 1,3-Bis(6′-methyl-2-pyridylimino)isoindoline,L^2 = 2-(tetrahydro-2-(pyridin-2-yl)pyrimidin-1(2H)-yl)-N-((pyridin-2-yl)methylene)ethanamine, L^3 = N-(methoxy(pyridin-2-yl)methyl)-2-(2-(pyridin-2-yl)imidazolidin-1-yl)ethanamine, L^4 = 2-(2-(6-methylpyridin-2-yl)imidazolidin-1-yl)-N-((6-methylpyridin-2-yl)methylene)ethanamine, L^5 = hexahydro-1-(2-(tetrahydro-2-(pyridin-2-yl)pyrimidin-1(2H)-yl)ethyl)-2-(pyridin-2-yl)pyrimidine, L^6 = 3-

methoxy-4-hydroxy-benzaldehyde,HL^7 = 4-tert-butyl-2,6-bis-[(2-pyridin-2-yl-ethylimino)-methyl]-phenol, HL^8 = 3-(N,N-dimethylamino)propyliminomethyl-6-ethoxyphenol, H_2L^9 = N,N′-bis(3-ethoxysalicylidene)ethane-1,2-diamine, H_2L^{10} = (E)-6,6′-((1E,1′E)-(ethane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(2-methoxy-4-((E)-p-tolyldiazenyl)phenol)], H_2L^{11} = 1-(5-hydroxy-3-oxapentyliminomethyl)-3-ethoxyphenol, HL^{12} = 2-[(3-(dimethylamino)propylimino)methyl]-4-bromophenol, H_2L^{13} = 1-(5-hydroxy-3-oxapentyliminomethyl)-3-ethoxyphenol, H_2L^{14} = 1-(5-hydroxy-3-oxapentyliminomethyl)-4-chlorophenol.