Surfactant-Mediated Solubilization of Magnetically Separable Nanocatalysts for the Oxidation of Alcohols

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Scheme S1. Schematic representation of the synthesized ligands H$_2$L$_1$, H$_2$L$_2$ and H$_2$L$_3$.

Scheme S2. Schematic representation of the synthesized complexes 1-6.

Figure S1. ORTEP drawing (50% probability ellipsoid) of complex 2 (left) and complex 5 (Right).

Table S1. Crystallographic data and details of refinements for complexes 1, 2, 4 and 5.

Table S2. Coordination bond lengths (Å) and angles (°) for complex 1.

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Figure S4. Magnetization curves obtained by VSM at room temperature for (a) Fe$_3$O$_4$, (b) Fe$_3$O$_4$@dopa, (c) HCAT-1, (d) CHCAT-1.

Figure S5. Leaching of active metal species in absence of surfactant; (Left) HCAT-2(Right) CHCAT-2.

Figure S6. (Left) UV-vis spectral changes showing the conversion of [FeL$^{1}$] (1) (Blue) to [L$^{1}$Fe$_{III}$](OOH)] (Purple) in the reaction of [FeL$^{1}$](1 mM) and 10 equiv H$_2$O$_2$ (10 mM) in CH$_3$CN at –20 °C. (Right) Magnified image of the increment of peak around 530 nm.

Figure S7. UV-vis spectral changes showing the conversion of [Mn$^{I}$L$^{1}$] (4) (red) to [[L$^{1}$Mn$_{III}$](OOH)] (green) in the reaction of [MnL$^{1}$] (1 mM) and 10 equiv H$_2$O$_2$ (10 mM) in CH$_3$CN at –20 °C.

Figure S8. ESI-MS spectrum of 1. The ion peak at m/z 513. 9358 corresponds to [FeL$^{1}$]$^+$

Figure S9. Full range ESI-MS spectrum of [L$^{1}$Fe$_{III}$](OOH)] generated by adding H$_2$O$_2$ (10 equiv) to 1 in 1:1 CH$_3$OH/CH$_3$CN mixture. The peak at m/z 685.4332 corresponds to the [L$^{1}$Fe$_{III}$](OOH)]K species generated from FeL$^{1}$ Inset: Magnified spectra for [L$^{1}$Fe$_{III}$](OOH)]K with m/z = 685.4332.

Figure S10. ESI-MS spectrum of 4. The ion peak at m/z 512. 9406 corresponds to [MnL$^{1}$]$^+$

Figure S11. Full range ESI-MS spectrum of L$^{1}$Mn$_{III}$-OOH generated by adding H$_2$O$_2$ (10 equiv) to 4 in 1:1 CH$_3$OH/CH$_3$CN mixture. The peak at m/z 545.9350 corresponds to the
[L^1Mn^{III}(OOH)]K species generated from MnL^1. Inset: Magnified spectra for [L^1Mn^{III}(OOH)]K with m/z = 545.9350.

**Table S6.** Oxidation of alcohols catalysed by homogeneous catalysts (1-6)

**Figure S12.** (A) DFT optimized geometries of Fe(III) initial and (B) OOH complexes with low spin (2S +1 = 2) (at UB3LYP/6-31+G(d,p) (LANL2DZ pseudopotential for Fe, Cl, Br, and I.theoretical level).

**Figure S13.** (A) DFT optimized geometries of Fe (III) initial and (B) OOH complexes with high spin (2S +1 = 6) (at UB3LYP/6-31+G(d,p) (LANL2DZ pseudopotential for Fe, Cl, Br, and I.theoretical level).

**Figure S14.** (A) DFT optimized geometries of Mn(III) initial and (B) OOH complexes with low spin (2S +1 = 3) (at UB3LYP/6-31+G(d,p) (LANL2DZ pseudopotential for Fe, Cl, Br, and I. theoretical level).

**Figure S15.** (A) DFT optimized geometries of Mn(III) initial and (B) OOH complexes with high spin (2S +1 = 5) (at UB3LYP/6-31+G(d,p) (LANL2DZ pseudopotential for Fe, Cl, Br, and I.theoretical level).

**Table S7.** UB3LYP/6-31+G(d,p) (LANL2DZ pseudo potential for Fe, Cl, Br, and I) absolute electronic, E, and Gibbs, G, energies.
1. Synthesis of the homogeneous catalysts

![Scheme S1](image)

**Scheme S1** Schematic representation of the synthesized ligands H$_2$L$^1$, H$_2$L$^2$ and H$_2$L$^3$

**Synthesis of Complex 1 [FeL$^1$]**

5 mL ethanolic solution of 1,2-diaminocyclohexane (0.074 g, 1 mmol) was added slowly to a 10 mL ethanolic solution of 3,5-dichlorosalicylaldehyde (0.382 g, 2 mmol) which led to immediate precipitation of H$_2$L$^1$. 5 mL ethanolic solution of Ferric chloride hexahydrate (0.135 g, 0.5 mmol) was added slowly to the suspension of H$_2$L$^1$. Yellow precipitate of H$_2$L$^1$ disappeared readily transformed to give a wine red solution. The solution was allowed to stir for one overnight. Red colored micro crystals of 1 were formed from DMF after a few days. Yield: 82% (with respect to L$^1$). Anal. calculated. for 1: C, 44.44; H, 3.73; N, 6.76. Found: C, 43.15; H, 3.13; N, 6.43. IR (KBr): $\nu$(C=N) 1610.39 cm$^{-1}$; $\nu$ (skeletal vibration) 1577.58 cm$^{-1}$

**Synthesis of Complex 2 [FeL$^2$]**

Complex 2 was prepared by adopting the same procedure as that for 1 but in this case we used 3,5-dibromosalicylaldehyde (0.559 g, 2 mmol) in place of 3,5-dichlorosalicylaldehyde. Yield: 80% (with respect to L$^2$). Anal. calculated. for 2: C, 34.52; H, 2.90 ; N, 5.25. Found: C, 33.93; H, 1.94; N, 4.57. IR (KBr): $\nu$(C=N) 1600 cm$^{-1}$; $\nu$ (skeletal vibration) 1563 cm$^{-1}$

**Synthesis of Complex 3 [FeL$^3$]**

Complex 3 was prepared by adopting the same procedure as that for 1 and 2 but in this case we used 3,5-diiodosalicylaldehyde (0.748 g, 2 mmol). Yield: 75% (with respect to L$^3$). Anal. calculated. for 3: C, 27.95; H, 2.35; N, 4.25. Found: C, 26.98; H, 2.21; N, 4.33. IR (KBr): $\nu$(C=N) 1623 cm$^{-1}$; $\nu$ (skeletated vibration) 1526 cm$^{-1}$
**Synthesis of Complex 4 [MnL₁]**

To a 5 mL ethanolic solution of 1,2-diaminocyclohexane (0.074 g, 1 mmol) was added slowly to the 10 mL ethanolic solution of 3,5-dichlorosalicylaldehyde (0.382 g, 2 mmol) which led to immediate precipitation of H₂L₁. 5 mL ethanolic solution of manganese chloride hexahydrate (0.135 g, 0.5 mmol) was added slowly to the suspension of H₂L₁. Yellow precipitate of H₂L₁ disappeared readily transformed to give a deep brown solution. The solution was allowed to stir for 1 overnight. Black colored micro crystals of 4 were formed from DMF after few days. Yield: 88% (with respect to L₁). Anal. calculated. for 4: C, 44.37; H, 3.72; N, 6.75. Found: C, 43.21; H, 3.62; N, 6.81. IR (KBr): ν(C=N) 1614.63 cm⁻¹; ν (skeletal vibration) 1527.40 cm⁻¹.

**Synthesis of Complex 5 [MnL₂]**

Complex 5 was prepared by adopting the same procedure as that for 1 but in this case we used 3,5-dibromosalicylaldehyde (0.559 g, 2 mmol) in place of 3,5-dichlorosalicylaldehyde. Yield: 79% (with respect to L₂). Anal. calculated. for 5: C, 34.55; H, 2.90; N, 5.26. Found: C, 33.98; H, 1.99; N, 4.33. IR (KBr): ν(C=N) 1623 cm⁻¹; ν (skeletal vibration) 1526 cm⁻¹.

**Synthesis of Complex 6 [MnL₃]**

Similar procedure was adopted for synthesis of complex 6 but in this case we used 3,5-diiodosalicylaldehyde (0.748 g, 2 mmol). Yield: 74% (with respect to L₃). Anal. calculated. for 6: C, 27.98; H, 2.35; N, 4.26. Found: C, 27.48; H, 2.12; N, 4.74. IR (KBr): ν(C=N) 1623 cm⁻¹; ν (skeletal vibration) 1526 cm⁻¹.
2. X-ray data collection and structure determination

Diffraction data for complexes 1, 2 and 4, 5 were collected at room temperature (293 K) on a Bruker Smart CCD diffractometer equipped with graphite-monochromated MoK$_\alpha$ radiation ($\lambda$ = 0.71073 Å). Cell refinement, indexing and scaling of the data set were performed using Bruker SMART APEX and Bruker SAINT package. The structure was solved by direct methods and subsequent Fourier analyses and refined by the full-matrix least-squares method based on $F^2$ with all observed reflections using SIR-92 and SHELX-97, software. For the complex, all non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were fixed at their respective positions riding on their carrier atoms and refined anisotropically. All the calculations were performed using the WinGX System, Ver 1.80.05 PLATON99 ORTEP3 programs. Selected crystallographic data and refinement details of complexes 1, 2 and 4, 5 are displayed in Table S1.

3. Computational Method

All calculations were carried out with the Gaussian 09 series of programs. Full geometry optimization of all reactants and products has been carried out using Density Functional Theory with the UB3LYP$^{8,9,10}$ functional and the 6-31+G(d, p) basis set for C, N, O and H atoms as well as with LANL2DZ pseudopotential for Mn and Fe atoms. This theory level has rendered accurate results in previous studies of related systems.$^{11,12}$ Geometry optimizations were done with the Schlegel’s algorithm.$^{13,14}$ The located stationary points were checked to
be true minima by the analytical computation of the harmonic vibrational frequencies at the same theory level. Due to the open shell nature of the Mn complexes under study, the possible spin states have been calculated for non-oxidized and oxidized complexes and they showed practically no spin contamination at the theory level here used.

4. Crystal Structure Elaboration

The X-ray structure of Complex 1 shows that FeL₁ crystallizes in the monoclinic space group P2₁/n where the Fe (III) centre is hexa-coordinated with two phenolic oxygen and the two imine nitrogen atoms adorning the basal plane and with a chloride ion and a dimethylformamide molecule from the environment in the axial positions around the Fe(III) centre. The central metal atom is shifted 0.201 Å towards chloride ion. The bond distances in the equatorial plane of Fe(1)-O(1), Fe(1)-O(2), Fe(1)-N(1), Fe(1)-N(2) are 1.904(5), 1.890(5), 2.092(5), 2.085(5) Å and two axial bond distance of Fe(1)-O(3), Fe(1)-Cl(5) are 2.259(5), 2.314(3) Å respectively, and The \textit{trans} bond angles of N(1)-Fe(1)-O(2), N(2)-Fe(1)-O(1) and O(3)-Fe(1)-Cl(5) are 165.9(2), 160.5(2) and 175.38(15) respectively, indicating slightly distorted octahedral geometry of Fe(III) center (Figure 1 (left); (Main Manuscript)).

From the single crystal X-ray structure of complex 4, i.e MnL₁, it is evident that a mononuclear Mn(III) complex crystallizes in triclinic \textit{P}-1 space group (Figure 3). Here as well, the metal centre is hexa-coordinated with two phenolic oxygen and two imine nitrogen atoms occupying the basal plane and the oxygen atoms from two solvent molecules (dimethylformamide) in axial positions. One perchlorate ion is present as counter anions. The equatorial bond length of Mn(1)-O(1), Mn(1)-O(2), Mn(1)-N(1) and Mn(1)-N(2) are 1.880(3), 1.875(4), 1.978(5), 1.966(5) Å respectively and two axial bond length Mn(1)-O(3), Mn(1)-O(4) are 2.205(4) and 2.236(4) Å which are longer than two equatorial Mn-O bond length. The \textit{trans} angle of N(1)-Mn(1)-O(1), N(2)-Mn(1)-O(2) and O(3)-Mn(1)-O(4) are 173.13(18), 173.67(18), 174.67(17) respectively which indicates the slight distortion from octahedral geometry (Figure 1 (right); (Main Manuscript)).

Like complex 1, complex 2, (Figure S1) and 5 (Figure S2) crystallizes in the monoclinic space group P2₁/n where the Fe(III) and Mn(III) centers are hexa-coordinated. For both complexes the central metal is coordinated to two phenolic oxygen and two imine nitrogen atoms in the basal plane, with a chloride ion and a dimethylformamide molecule in the axial position, and one lattice dimethylformamide molecule is present in the crystal structure. The central metal atom is shifted 0.196 and 0.151 Å for complex 2 and 5, respectively towards chloride ion. In the case of complex 2, Fe-O(phenoxo) and Fe-N bond lengths fall in the range 1.905(7)-1.894(7) Å and 2.081(7)-2.084(9) Å, respectively, whereas for complex 5 the
bond length range for Mn-O(phenoxo) and Mn-N are 1.871(5)-1.869(5)Å and 1.969(5)-1.976(6)Å, respectively. The *trans* bond angle of N(1)-Fe(1)-O(2), N(2)-Fe(1)-O(1) and O(3)-Fe(1)-Cl(1) are 166.0(3), 161.6(3), 175.5(2) respectively and bond angle of N(1)-Mn(1)-O(2), N(2)-Mn (1)-O(1) and O(3)-Mn(1)-Cl(1) are 172.4(2), 166.7(3), 174.21(18), respectively, which indicates the slight distortion in perfect octahedral geometry for complexes 2 and 5, respectively. The Crystallographic data and details of refinements for complexes 1, 2, 4 and 5 are delineated in Table S1.

**Figure S1.** ORTEP drawing (50% probability ellipsoid) of complex 2 (left) and complex 5 (Right).

**Table S1** Crystallographic data and details of refinements for complexes 1, 2, 4 and 5

| CCDC Number | Complex 1 (FeL¹) | Complex 2 (FeL²) | Complex 4 (MnL¹) | Complex 5 (MnL²) |
|-------------|------------------|------------------|------------------|------------------|
| Fw          | 695.64           | 871.42           | 758.73           | 870.51           |
| System      | Monoclinic       | Monoclinic       | Triclinic        | Monoclinic       |
| Space group | P21/n            | P21/n            | P-1              | P21/n            |
| a (Å)       | 11.652(3)        | 11.518(4)        | 9.287(4)         | 11.4987(10)      |
| b (Å)       | 17.782(4)        | 18.054(6)        | 11.100(4)        | 17.7354(16)      |
| c (Å)       | 15.870(4)        | 16.648(7)        | 16.408(6)        | 16.6060(15)      |
| α (°)       | 90.0             | 90.0             | 106.905(5)       | 90.0             |
| β (°)       | 107.297(6)       | 107.186(5)       | 96.627(5)        | 107.606(3)       |
| γ (°)       | 90.0             | 90.0             | 92.954(5)        | 90.0             |
| V (Å³)      | 3139.5(13)       | 3307(2)          | 1601.1(11)       | 3227.9(5)        |
| Z           | 4                | 4                | 2                | 4                |
| D(calcd) (g.cm⁻³) | 1.472           | 1.750            | 1.574            | 1.791            |
| μ (Mₒ-Kα)  (mm⁻¹) | 0.944           | 5.406            | 0.883            | 5.480            |
| F(000)      | 1428             | 1708             | 776              | 1704             |
| 0 range (°) | 1.8 - 20.3 | 1.7 - 19.8 | 1.3 - 26.8 | 1.7 - 24.0 |
|------------|------------|------------|------------|------------|
| Collected reflections | 9726 | 9247 | 11440 | 33321 |
| Indep. reflections | 3044 | 2982 | 5934 | 4995, |
| $R_{int}$ | 0.054 | 0.062 | 0.032 | 0.095 |
| Obs. reflections [I > 2σ(I)] | 2026 | 2042 | 3834 | 3112 |
| Parameters | 372 | 366 | 402 | 366 |
| $R_t$ [I > 2σ(I)]* | 0.0492 | 0.0462 | 0.0667 | 0.0555 |
| $wR_t$ [I > 2σ(I)]* | 0.1419 | 0.1147 | 0.2031 | 0.1336 |
| GOF on F² | 1.02 | 1.02 | 1.04 | 1.05 |
| Residuals (eÅ⁻³) | -0.23, 0.38 | -0.34, 0.50 | -0.57, 0.88 | -0.44, 0.69 |

Table S2. Coordination bond lengths (Å) and angles (°) for complex 1

| Bond | Bond Length (Å) |
|------|-----------------|
| Fe(1) - Cl(5) | 2.314(3) |
| Fe(1) - O(1) | 1.904(5) |
| Fe(1) - O(2) | 1.890(5) |
| Fe(1) - O(3) | 2.259(5) |
| Fe(1) - N(1) | 2.092(5) |
| Fe(1) - N(2) | 2.085(5) |
| Cl(5) - Fe(1) - O(1) | 99.37(16) |
| Cl(5) - Fe(1) - O(2) | 95.54(16) |
| Cl(5) - Fe(1) - O(3) | 175.38(15) |
| Cl(5) - Fe(1) - N(1) | 92.40(18) |
| Cl(5) - Fe(1) - N(2) | 95.32(18) |
| O(1) - Fe(1) - O(2) | 101.0(2) |
| O(1) - Fe(1) - O(3) | 85.0(2) |
| O(1) - Fe(1) - N(1) | 89.2(2) |
| O(1) - Fe(1) - N(2) | 160.5(2) |
| O(2) - Fe(1) - O(3) | 85.13(19) |
| O(2) - Fe(1) - N(1) | 165.9(2) |
| O(2) - Fe(1) - N(2) | 90.3(2) |
| O(3) - Fe(1) - N(1) | 86.0(2) |
| O(3) - Fe(1) - N(2) | 80.1(2) |
| N(1) - Fe(1) - N(2) | 77.3(2) |
| Fe(1) - O(1) - C(1) | 131.5(4) |
| Fe(1) - O(2) - C(16) | 131.6(4) |
| Fe(1) - O(3) - C(24) | 117.2(6) |
| Fe(1) - N(1) - C(7) | 125.6(5) |
| Fe(1) - N(1) - C(8) | 113.3(5) |
| Fe(1) - N(2) - C(9) | 114.2(5) |
| Fe(1) - N(2) - C(14) | 124.7(4) |
**Table S3.** Coordination bond lengths (Å) and angles (°) for complex 2

| Bond                  | Length/Angle       |
|-----------------------|--------------------|
| Fe(1) - Cl(1)         | 2.307(4)           |
| Fe(1) - O(1)          | 1.905(7)           |
| Fe(1) - O(2)          | 1.894(7)           |
| Fe(1) - O(3)          | 2.247(9)           |
| Fe(1) - N(1)          | 2.081(7)           |
| Fe(1) - N(2)          | 2.084(9)           |
| Cl(1) - Fe(1) - O(1)  | 99.0(2)            |
| Cl(1) - Fe(1) - O(2)  | 95.2(2)            |
| Cl(1) - Fe(1) - O(3)  | 175.5(2)           |
| Cl(1) - Fe(1) - N(1)  | 93.0(2)            |
| Cl(1) - Fe(1) - N(2)  | 94.9(3)            |
| O(1) - Fe(1) - O(2)   | 100.1(3)           |
| O(1) - Fe(1) - O(3)   | 85.4(3)            |
| O(1) - Fe(1) - N(1)   | 89.8(3)            |
| O(1) - Fe(1) - N(2)   | 161.6(3)           |
| O(2) - Fe(1) - O(3)   | 85.1(3)            |
| O(2) - Fe(1) - N(1)   | 166.0(3)           |
| O(2) - Fe(1) - N(2)   | 90.5(3)            |
| O(3) - Fe(1) - N(1)   | 85.8(3)            |
| O(3) - Fe(1) - N(2)   | 80.6(3)            |
| N(1) - Fe(1) - N(2)   | 77.6(3)            |
| Fe(1) - O(1) - C(16)  | 132.2(7)           |
| Fe(1) - O(2) - C(4)   | 130.5(6)           |
| Fe(1) - O(3) - C(21)  | 115.4(9)           |
| Fe(1) - N(1) - C(13)  | 113.0(7)           |
| Fe(1) - N(1) - C(14)  | 124.8(7)           |
| Fe(1) - N(2) - C(7)   | 125.3(7)           |
| Fe(1) - N(2) - C(8)   | 114.0(7)           |

**Table S4.** Coordination bond lengths (Å) and angles (°) for complex 4

| Bond                  | Length/Angle       |
|-----------------------|--------------------|
| Mn(1) - O(1)          | 1.880(3)           |
| Mn(1) - O(2)          | 1.875(4)           |
| Mn(1) - O(3)          | 2.205(4)           |
| Mn(1) - O(4)          | 2.236(4)           |
| Mn(1) - N(1)          | 1.978(5)           |
| Mn(1) - N(2)          | 1.966(5)           |
| O(1) - Mn(1) - O(2)   | 94.84(15)          |
| O(1) - Mn(1) - O(3)   | 92.06(17)          |
| O(1) - Mn(1) - O(4)   | 91.81(17)          |
| O(1) - Mn(1) - N(1)   | 173.13(18)         |
| O(1) - Mn(1) - N(2)   | 91.44(18)          |
| O(2) - Mn(1) - O(3)   | 92.35(18)          |
| O(2) - Mn(1) - O(4)   | 90.97(17)          |
| O(2) - Mn(1) - N(1)   | 91.94(17)          |
| O(2) - Mn(1) - N(2)   | 173.67(18)         |
| O(3) - Mn(1) - O(4)   | 174.67(17)         |
| O(3) - Mn(1) - N(1)   | 88.79(19)          |
| Bond                  | Length (Å) |
|----------------------|------------|
| O(3) - Mn(1) - N(2)  | 88.2(2)    |
| O(4) - Mn(1) - N(1)  | 86.94(18)  |
| O(4) - Mn(1) - N(2)  | 88.0(2)    |
| N(1) - Mn(1) - N(2)  | 81.8(2)    |
| Mn(1) - O(1) - C(4)  | 129.2(3)   |
| Mn(1) - O(2) - C(20) | 129.3(3)   |
| Mn(1) - O(3) - C(24) | 127.5(4)   |
| Mn(1) - O(4) - C(21) | 124.5(4)   |
| Mn(1) - N(1) - C(13) | 112.0(4)   |
| Mn(1) - N(1) - C(14) | 126.2(4)   |
| Mn(1) - N(2) - C(7)  | 127.0(4)   |
| Mn(1) - N(2) - C(8)  | 110.8(5)   |

**Table S5. Coordination bond lengths (Å) and angles (°) for complex 5**

| Bond                  | Length (Å) |
|----------------------|------------|
| Mn(1) - Cl(1)        | 2.457(3)   |
| Mn(1) - O(1)         | 1.871(5)   |
| Mn(1) - O(2)         | 1.869(5)   |
| Mn(1) - O(3)         | 2.398(6)   |
| Mn(1) - N(1)         | 1.969(5)   |
| Mn(1) - N(2)         | 1.976(6)   |
| Cl(1) - Mn(1) - O(1) | 98.5(2)    |
| Cl(1) - Mn(1) - O(2) | 94.02(19)  |
| Cl(1) - Mn(1) - O(3) | 174.21(18) |
| Cl(1) - Mn(1) - N(1) | 91.67(18)  |
| Cl(1) - Mn(1) - N(2) | 93.5(2)    |
| O(1) - Mn(1) - O(2)  | 91.62(19)  |
| O(1) - Mn(1) - O(3)  | 87.3(3)    |
| O(1) - Mn(1) - N(1)  | 92.5(2)    |
| O(1) - Mn(1) - N(2)  | 166.7(3)   |
| O(2) - Mn(1) - O(3)  | 86.2(2)    |
| O(2) - Mn(1) - N(1)  | 172.4(2)   |
| O(2) - Mn(1) - N(2)  | 93.3(2)    |
| O(3) - Mn(1) - N(1)  | 87.6(2)    |
| O(3) - Mn(1) - N(2)  | 80.7(3)    |
| N(1) - Mn(1) - N(2)  | 81.3(2)    |
| Mn(1) - O(1) - C(4)  | 130.1(5)   |
| Mn(1) - O(2) - C(16) | 128.6(4)   |
| Mn(1) - O(3) - C(21) | 112.9(7)   |
| Mn(1) - N(1) - C(7)  | 125.0(5)   |
| Mn(1) - N(1) - C(8)  | 112.6(4)   |
| Mn(1) - N(2) - C(13) | 111.9(5)   |
| Mn(1) - N(2) - C(14) | 124.5(5)   |
Figure S2. FT-IR spectrum of (Left) HCAT-1 (right) CHCAT-1

Figure S3. PXRD pattern of (A) HCAT-1 (B) CHCAT-1
Figure S4. Magnetization curves obtained by VSM at room temperature for (a) Fe₃O₄, (b) Fe₃O₄@dopa, (c) HCAT-1, (d) CHCAT-1.

Figure S15. Leaching of active metal species in absence of surfactant; (Left) HCAT-2(Right) CHCAT-2.
**Figure S6.** (Left) UV-vis spectral changes showing the conversion of [FeL$^{1}$] (1) (Blue) to [L$^{1}$Fe$^{III}$](OOH)] (Purple) in the reaction of [FeL$^{1}$](1 mM) and 10 equiv H$_2$O$_2$ (10 mM) in CH$_3$CN at –20 °C. (Right) Magnified image of the increment of peak around 530 nm.

**Figure S7.** UV-vis spectral changes showing the conversion of [Mn$^{1}L^{1}$] (4) (red) to [[L$^{1}$Mn$^{III}$(OOH)] (green) in the reaction of [MnL$^{1}$] (1 mM) and 10 equiv H$_2$O$_2$ (10 mM) in CH$_3$CN at –20 °C.
Figure S8. ESI-MS spectrum of 1. The ion peak at m/z 513.9358 corresponds to [FeL1]+.

Figure S9. Full range ESI-MS spectrum of [L¹Fe³⁺(OOH)] generated by adding H₂O₂ (10 equiv) to 1 in 1:1 CH₃OH/CH₃CN mixture. The peak at m/z 685.4332 corresponds to the [L¹Fe³⁺(OOH)]K species generated from FeL¹. Inset: Magnified spectra for [L¹Fe³⁺(OOH)]K with m/z = 685.4332.
Figure S10. ESI-MS spectrum of 4. The ion peak at m/z 512.9406 corresponds to \([\text{MnL}^1]^+\)
Figure S11. Full range ESI-MS spectrum of $L^1\text{Mn}^{\text{III}}\cdot\text{OOH}$ generated by adding $\text{H}_2\text{O}_2$ (10 equiv) to 4 in 1:1 CH$_3$OH/CH$_3$CN mixture. The peak at m/z 545.9350 corresponds to the $[L^1\text{Mn}^{\text{III}}(\text{OOH})]K$ species generated from MnL$^1$. Inset: Magnified spectra for $[L^1\text{Mn}^{\text{III}}(\text{OOH})]K$ with m/z = 545.9350 amu.

Catalytic measurements
We investigated the catalytic activity of the homogeneous catalysts (1-6) and heterogeneous catalysts CHCAT-1 and CHCAT-2 for a wide variety of organic transformation reactions.

Control Experiment for oxidation reactions
To assess the capability of $\text{H}_2\text{O}_2$ to directly oxidize the organic substrates without any aid of the catalysts, control experiments were performed taking only the corresponding substrate and $\text{H}_2\text{O}_2$. A solution of each of the substrate (1 mmol) and $\text{H}_2\text{O}_2$ (2 mmol) was taken in acetonitrile medium and magnetically stirred till reaction was complete. Diethyl ether was used to extract the organic products (4 mL × 3) at the end of the reactions. $^1\text{H}$-NMR analysis was performed. Extremely low conversions (<5%) were found at the end of the analysis.

Catalytic Alcohol Oxidation by Homogeneous catalysts 1-6
The homogeneous catalysts 1-6 (2 mmol), alcohol (1 mmol) and $\text{H}_2\text{O}_2$ (3 mmol) were subjected to stirring at room temperature in CH$_3$CN (10 mL) for 4 h. The progress of the reaction was
surveilled by TLC. After 4h, an aqueous solution of NaHCO$_3$ (20 mL) and CH$_2$Cl$_2$ (20 mL) was added to the reaction mixture. As a consequence of layer separation, the aqueous layer was extracted with CH$_2$Cl$_2$ (3×5 mL). The organic layers were dried on MgSO$_4$ and concentrated under vacuum furnishing the products. The products were identified through $^1$H-NMR Spectroscopy.

**Catalytic Alcohol Oxidation by Heterogeneous catalysts CHCAT-1 and CHCAT-2**

Catalyst (120 mg), alcohol (1mmol) and H$_2$O$_2$ (3mmol) were subjected to stirring at room temperature in H$_2$O (10 mL) for 6h. The progress of the reaction was surveilled by TLC. After 4h, the catalyst was removed with the help of a magnet and to the resulting solution, an aqueous solution of NaHCO$_3$ (20 mL) and CH$_2$Cl$_2$ (20 mL) was added to the reaction mixture. As a consequence of layer separation, the aqueous layer was extracted with CH$_2$Cl$_2$ (3×5 mL). The organic layers were dried on MgSO$_4$ and concentrated under vacuum furnishing the products. The products were identified through $^1$H-NMR Spectroscopy.

**Table S6. Oxidation of alcohols catalyzed by homogeneous catalysts (1-6)**

| Entry | Alcohol | Product | Yield (%) | 1 | 2 | 3 | 4 | 5 | 6 |
|-------|---------|---------|-----------|---|---|---|---|---|---|
| 1     | ![Alcohol](image1.png) | ![Product](image2.png) | 90 85 80 88 80 72 |
| 2     | ![Alcohol](image3.png) | ![Product](image4.png) | 87 82 76 84 80 73 |
| 3     | ![Alcohol](image5.png) | ![Product](image6.png) | 85 80 72 85 76 70 |
| 4     | ![Alcohol](image7.png) | ![Product](image8.png) | 95 93 90 92 90 88 |
**Reaction conditions:** 10 mL CH₃CN, 1 mmol alcohols, Catalysts 1-6 (2 mmol), H₂O₂ (3 mmol); 6h at room temperature under stirring.

\(^a\) Isolated Yield
Figure S12. (A) DFT optimized geometries of Fe(III) initial and (B) OOH complexes with low spin \( (2S + 1 = 2) \) (at UB3LYP/6-31+G(d,p) (LANL2DZ pseudopotential for Fe, Cl, Br, and I) theoretical level).
Figure S13. (A) DFT optimized geometries of Fe (III) initial and (B) OOH complexes with high spin \(2S + 1 = 6\) (at UB3LYP/6-31+G(d,p) (LANL2DZ pseudopotential for Fe, Cl, Br, and I.theoretical level).
Figure S14. (A) DFT optimized geometries of Mn(III) initial and (B) OOH complexes with low spin (2S +1 = 3) (at UB3LYP/6-31+G(d,p) (LANL2DZ pseudopotential for Fe, Cl, Br, and I. theoretical level)).
Figure S15. (A) DFT optimized geometries of Mn(III) initial and (B) OOH complexes with high spin \(2S +1 = 5\) (at UB3LYP/6-31+G(d,p) (LANL2DZ pseudopotential for Fe, Cl, Br, and I. theoretical level).
Table S7. UB3LYP/6-31+G(d,p) (LANL2DZ pseudo potential for Fe, Cl, Br, and I) absolute electronic, E, and Gibbs, G, energies.

|                  | E (a.u.) | G (a.u.) | E (a.u.) | G (a.u.) |
|------------------|----------|----------|----------|----------|
| OOH⁻             | -151.072711 | -151.081236 |          |          |

**Cl axial**

|                  | E (a.u.) | G (a.u.) | E (a.u.) | G (a.u.) |
|------------------|----------|----------|----------|----------|
| Fe-cl- low spin  | -1214.893708 | -1214.627835 | -1195.381575 | -1195.114608 |
| Fe-br- low spin  | -1207.759553 | -1207.500458 | -1188.244413 | -1187.981617 |
| Fe-i- low spin   | -1200.636518 | -1200.382084 | -1181.129734 | -1180.872503 |
| Fe-cl- high spin | -1214.906731 | -1214.641089 | -1195.436899 | -1195.169483 |
| Fe-br-high spin  | -1207.771424 | -1207.512414 | -1188.301728 | -1188.040877 |
| Fe-i-high spin   | -1200.647081 | -1200.392668 | -1181.177053 | -1180.920465 |

**OOH axial**

|                  | E (a.u.) | G (a.u.) | E (a.u.) | G (a.u.) |
|------------------|----------|----------|----------|----------|
| Fe-OO-cl-low spin| -1366.049160 | -1365.766737 | -1346.54467 | -1346.263361 |
| Fe-OO-br-low spin| -1358.913173 | -1358.637070 | -1339.408425 | -1339.133788 |
| Fe-OO-i-low spin  | -1351.787185 | -1351.515527 | -1332.282567 | -1332.012221 |
| Fe-OO-cl-high spin| -1366.056704 | -1365.781456 | -1346.559401 | -1346.283258 |
| Fe-OO-br-high spin| -1358.920556 | -1358.650609 | -1339.423622 | -1339.154145 |
| Fe-OO-i-high spin | -1351.794971 | -1351.531482 | -1332.298157 | -1332.032740 |

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