#### **Supporting Information**

# A DFT and experimental study of the host-guest interactions effect on the structure, properties and electro-catalytic activities of N<sub>2</sub>O<sub>2</sub>-Ni(II) Schiff-base complex/zeolite

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## 1. Preparation of H<sub>2</sub>{salnptn(4-OH)<sub>2</sub>}

To a stirred ethanolic solution (20 ml) of 2,2-dimethylpropylenediamine (0.102 g, 1 mmol), 2,4-dihydroxyacetophenone (0.304 g, 2 mmol) is added. The bright orange solution is stirred and heated to reflux for 1 h. The resulting orange precipitate is filtered off, washed with warm ethanol and diethyl ether (Yield (90%), Melting point 120 °C) and analyzed by <sup>1</sup>HNMR, UV-vis, FT-IR (see Fig. S1.A, B and C in supporting information section) and elemental analysis techniques. Anal. Calc. for C<sub>21</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub> (370.44): C, 68.08; H, 7.07; N, 7.56. Found: C, 68.21; H, 7.16; N, 7.49%. FT-IR data,  $\nu$  (cm<sup>-1</sup>): 3467 (O-H), 2993 (C-H), 1637 (C=C), 1562, 1491 (C=N), 1244 (C-O). <sup>1</sup>HNMR ( $\delta$ ): 1.04 (s, 6H, NCH<sub>2</sub>C(*CH*<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>N), 2.26 (s, 6H, *H*<sub>3</sub>*C*=NCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>N=*CH*<sub>3</sub>), 3.42 (s, 4H, N*CH*<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>*CH*<sub>2</sub>N), 6.05- 7.39 (m, 6H, ArH), 9.07 (br, 2H, *OH*), 17.01 (s, 2H, *OH*). The absorption spectrum of the Schiff-base ligand consists of a higher energy band at 371 nm (Fig. S1.B) that are attributable to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively.



Fig. S1.A. <sup>1</sup>HNMR spectrum of the Schiff-base ligand in DMSO solvent



Fig. S1.B. UV-vis spetrum of the Schiff-base ligand in DMF solvent.



Fig. S1.C. FT-IR spectrum of the Schiff-base ligand

## 2. Preparation of Ni<sup>II</sup>{salnptn(4-OH)<sub>2</sub>} complex

 $H_2$ {salnptn(4-OH)<sub>2</sub>} (0.37 g, 1 mmol) dissolved in 30 ml of ethanol is added to an ethanolic solution of Ni (II) acetate.4H<sub>2</sub>O (0.245 g, 1 mmol) and the mixture is refluxed for 3 h. The colored solution is concentrated to yield an orang powder. The product is washed with diethylether and dried in air.

# 3. Preparation of poly-Ni<sup>II</sup>{salnptn(4-OH)<sub>2</sub>}/Pt electrode

In order to prepare a modified Pt surface with, the electrode (geometric area of 0.064  $\text{cm}^2$ ) is immersed in a 2×10<sup>-3</sup> M solution of the free complex in aqueous 1 M NaOH solution and the potential is cycled between 0 and 1 V (at 100 mV s<sup>-1</sup>). Prior to each experiment, the Pt electrode is dipped in 1:1 ratio of water concentrated nitric acid solution for a couple of minutes and washed thoroughly with water. The electrode is subsequently polished to a mirror-like finish with 0.05 µm alumina slurry on a Buelher polishing cloth with distilled water as lubricant and rinsed with water. The electrode is then placed in distilled water and sonicated for about 5 min to eliminate any trace of polishing paste from the surface.

## 4. Electrochemistry of the Ni<sup>II</sup>{salnptn(4-OH)<sub>2</sub>} Schiff-base complex

The electrochemical oxidation of  $Ni^{II}$ {salnptn(4-OH)<sub>2</sub>} is carried out at a Pt electrode in aqueous 1 M NaOH using multiple scan cyclic voltammetry. A tipycal cyclic voltammogram obtained for poly-Ni<sup>II</sup>{salnptn(4-OH)<sub>2</sub>} film growth on a Pt electrode is

shown in Figs. S2.A and B. During the first scan, the anodic peak corresponds to the oxidation of the monomer and further scans clearly show the anodic and cathodic peaks of redox reaction of the Ni<sup>II</sup>/Ni<sup>III</sup> couple. Film growth is accompanied by increasing current for the latter peaks.

The voltammetric responses as well as their evolution during the polymerization process are qualitatively similar to those observed for analogous Ni- and Cu-salen complexes<sup>1-3</sup> although the peaks assigned to the deposited film are detected at much less positive potentials. The current rise following the anodic scan wave is the result of the oxygen evolution reaction. The thin polymeric film, which is formed, demonstrates a high degree of adherence to the Pt electrode. This polymer film is visible to naked eye, and is of yellow color. The modified electrode is very stable in alkaline solutions. The electrode coating is also stable when the electrode is removed from the solution for modification and stored for a long time (up to two weeks) in "dry" conditions or in alkaline solutions. The cyclic voltammogram observed in 1 M NaOH for freshly prepared poly-Ni<sup>II</sup>{salnptn(4-OH)<sub>2</sub>} film electrodeposited on a Pt electrode is illustrated in Fig. S2.C where a similar cyclic voltammogram curve has been observed.

The influence of scan rate in a wide range of 5–1000 mV s<sup>-1</sup> on the electrochemical behavior of poly-Ni<sup>II</sup>{salnptn(4-OH)<sub>2</sub>} film is represented in Fig. S3.A and C. A pair of well-defined peaks, indicating the presence of Ni(II)/Ni(III) species appears in the voltammograms. Furthermore, plots of the anodic and cathodic peaks currents (I<sub>p</sub> and I<sub>c</sub>) are linearly dependent on *v* at the scan rates below 100 mV s<sup>-1</sup> (Fig. S3.B), which indicate a surface-confined redox process. Based on the slope of cathodic line as well as benefiting from eq. (2) [Ref. 65] (in the text) the value of  $\Gamma$  has been obtained to be around 7.05×10<sup>-8</sup> mol cm<sup>-2</sup>. At *v*>100 mV s<sup>-1</sup>, the peaks currents become directly proportional to the square root of the potential scan rates (Fig. S3.D). The linear dependence of the peaks currents with *v*<sup>1/2</sup> can explain the fact that the charge transfer is controlled by the diffusion of OH<sup>-</sup> ions towards the film. In addition, the relationship between  $I_p/v^{1/2}$  and *v* (Fig. S3.E) indicates the independence of  $I_p/v^{1/2}$  on *v* at higher scan rates (>100 mV s<sup>-1</sup>) which, in turn, corroborates a diffusion controlled process.

Furthermore, for this polymeric film ( $\Gamma = 70.5 \text{ nmol cm}^{-2}$ ) and for all scan rates, a linear dependence of anodic and cathodic peak current on the scan rate is observed (log I<sub>p</sub>

versus log v plots) have slopes close to half, (Fig. S3.F), which indicates a semi-infinite diffusion regime for charge transport. This regime has been observed for nickel and other polymer modified electrodes<sup>4,5</sup> and as suggested by Bartlett,<sup>6</sup> is determined by the interplay between scan rate and kinetics of charge transport throughout the film. Plots of  $E_p$  versus log v (Fig. S3.G) in the region where diffusion control is predominant (v > 100 mV s<sup>-1</sup>) show the anticipated increase in peak separation ( $\Delta E$ ).



**Fig. S2.** (A) Consecutive cyclic voltammogram of  $Ni^{II}$ {salnptn(4-OH)<sub>2</sub>} complex at Pt electrode in 1 M NaOH comprised of first and fiftith cycle during the modification of the electrode surface at the scan rate of 100 mV s<sup>-1</sup>. (B) The ten early cycles of the



modification. (C) The Cyclic voltammogram of  $Ni^{II}$ {salnptn(4-OH)<sub>2</sub>} modified electrode in 1 M NaOH solution at the scan rate of 100 mV s<sup>-1</sup>.

**Fig. S3.** Cyclic voltammograms of poly-Ni<sup>II</sup>{salnptn(4-OH)<sub>2</sub>} in 1 M NaOH solution. Potential sweep rates from inner to outer are : (A) 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 and (C) 150, 200, 300, 400, 500, 600, 700, 800, 900, 1000 mV s<sup>-1</sup>. Fig. 9B and 9D shows the dependency of anodic and cathodic peak currents on the potential sweep rate at lower

values of 20–100 mV s<sup>-1</sup> and on the square roots of sweep rate at higher values of 150– 1000 mV s<sup>-1</sup>, respectively. The Fig. 4C show plot of  $I_{pa}/v^{1/2}$  vs. v for cyclic voltammograms represented in panels A and C for the anodic and the cathodic peaks. Plot of Log I vs. Logv (panel F) and Ep vs. Logv (panel G) for cyclic voltammograms represented in the main panel for the anodic and the cathodic peaks.



**Fig. S4.** Cyclic voltammograms showing catalytic oxidation of (a) ethanol; (b) 1-propanol; (c) 2-propanol at  $Ni^{II}$ {salnptn(4-OH)<sub>2</sub>}-Y/CPEin 1 M NaOH solution; scan rate 20 mV/s. (d-f) variation of the logarithm of alcohol oxidation peaks currents with the logarithm of alcohol bulk concentration.



**Fig. S5.** Cyclic voltammograms showing catalytic oxidation of (a) ethanol; (b) 1-propanol; (c) 2-propanol at poly-Ni<sup>II</sup>{salnptn(4-OH)<sub>2</sub>}/Pt electrode in 1 M NaOH solution; scan rate 20 mV/s. (d-f) variation of the logarithm of alcohol oxidation peaks currents with the logarithm of alcohol bulk concentration.

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Note: Ref. (65) is given in text.

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