

## Supporting Information for

# **Surface directed reversible imidazole ligation to nickel(II) octaethylporphyrin at the solution/solid interface: a single molecule level study**

Goutam Nandi, Bhaskar Chilukuri, K. W. Hipps,\* and Ursula Mazur\*

*Department of Chemistry and Materials Science and Engineering Program, Washington State University, Pullman, Washington 99164-4630*

**A. STM Imaging**

**B. Molecular DFT Calculations**

**C. Periodic plane-wave (PW) DFT calculations**

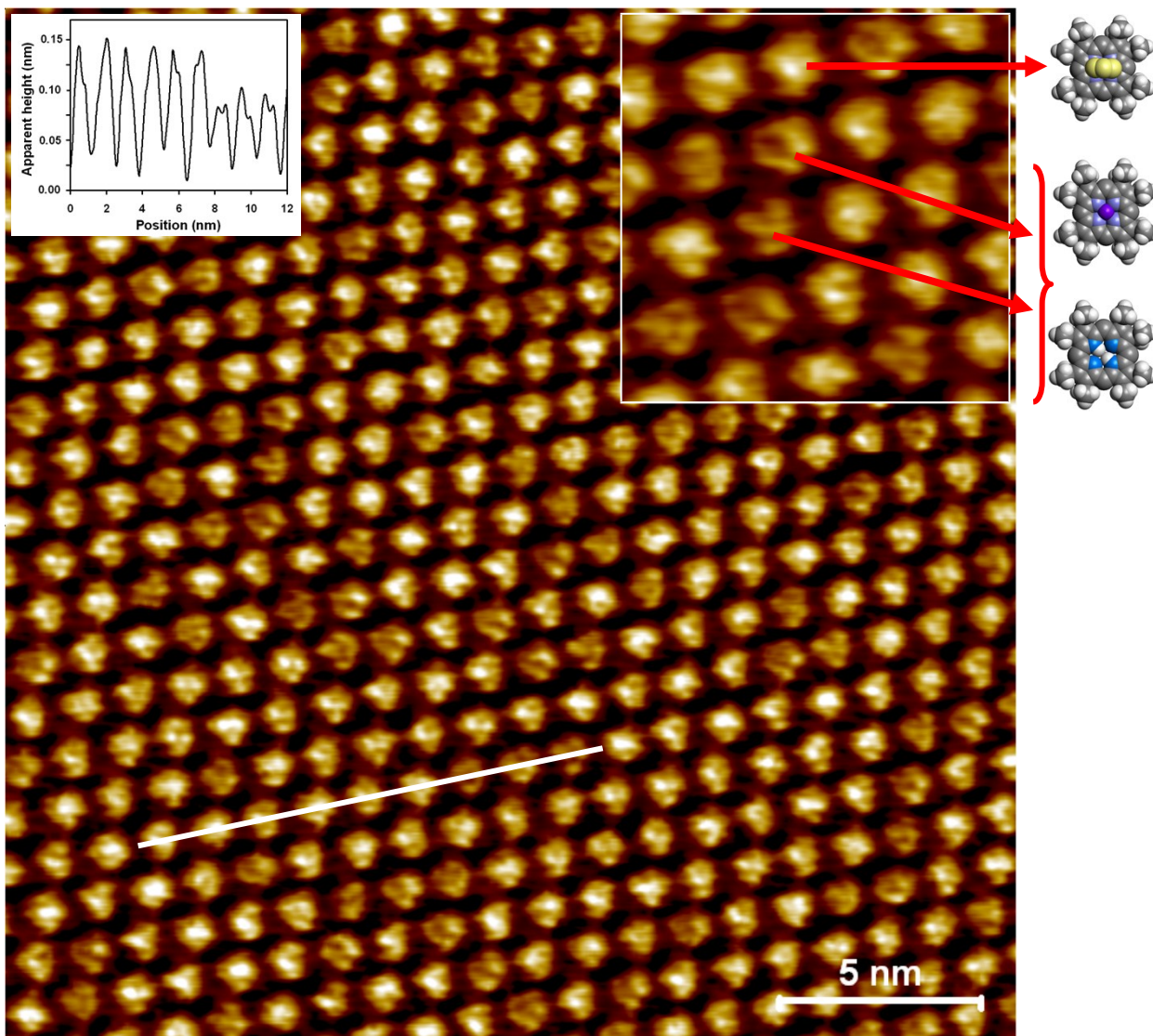
**D. Charge density and integration as a function of distance**

**E. Density of States**

**F. Entropy of binding/adsorption**

## A. STM Imaging:

The addition of H<sub>2</sub>OEP as a reference molecule to the NiOEP solution when following the kinetics of the binding of imidazole reaction to NiOEP provided a better contrast in the images of the ligated and unligated nickel ions in the STM. This is illustrated in Fig. SI-1 which depicts a STM image of 75% NiOEP and 25 % H<sub>2</sub>OEP on HOPG with  $1.1 \times 10^{-3}$  M Im in phenyloctane. Here one can easily distinguish the Im-NiOEP/HOPG species (bright molecules) as well porphyrins that are unligated (dark molecules). Some of the dark molecules have very distinct depression while others do not. In addition, some of the molecules with depressions exhibit a

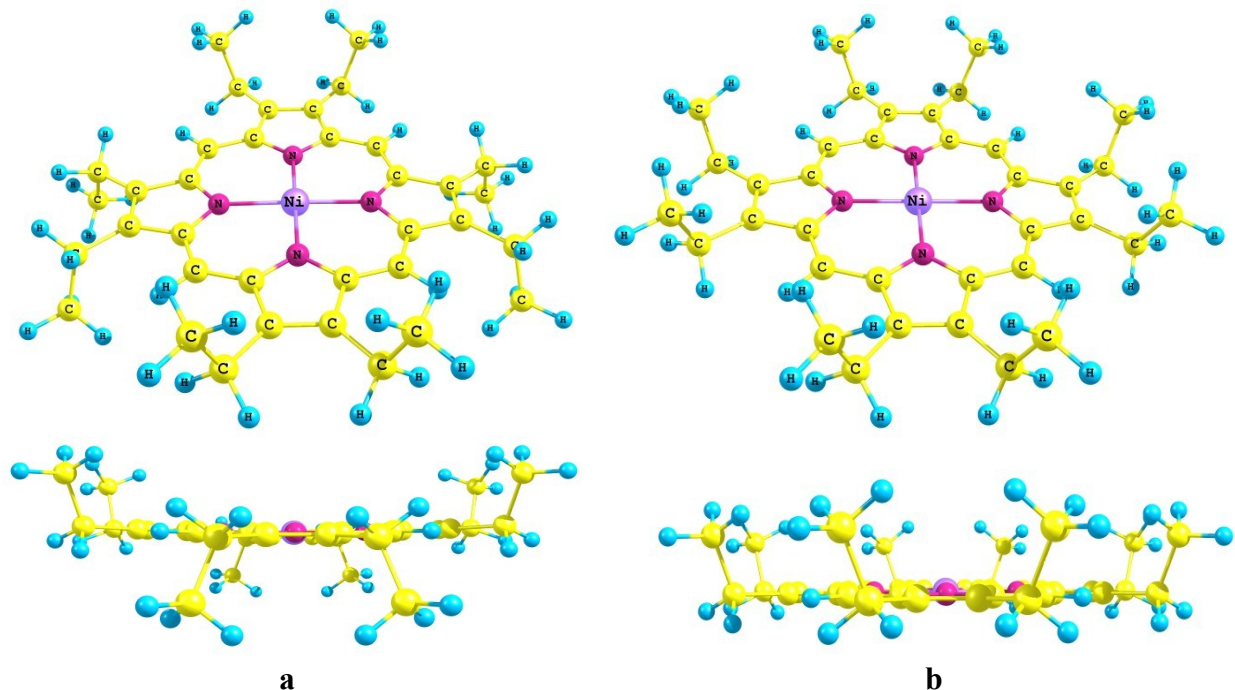


**Fig. SI-1** Constant current STM image of the phenyloctane/(75% NiOEP + 25 % H<sub>2</sub>OEP)/HOPG interface with less than 50% of the NiOEP surface adsorbate ligated to Im at 25 °C. Data was acquired at 0.2 V and 50 pA set point. A cross-sectional diagram and an enlarged surface section are also shown. Different porphyrin surface species are identified with CPK models of H<sub>2</sub>OEP, NiOEP, and NiOEP-Im.

brighter edges. This artifact at times interfered with the precise counting the number of bright and dark molecules. Addition of a small amount of H<sub>2</sub>OEP better accentuated the minima and maxima in the contrast level of images and improved our counting accuracy. We also prepared some samples of both NiOEP/HOPG and (0.9 NiOEP + 0.1 H<sub>2</sub>OEP)/HOPG and exposed them to high Im concentrations. The surface coverages measured from both sets of samples agreed within experimental error.

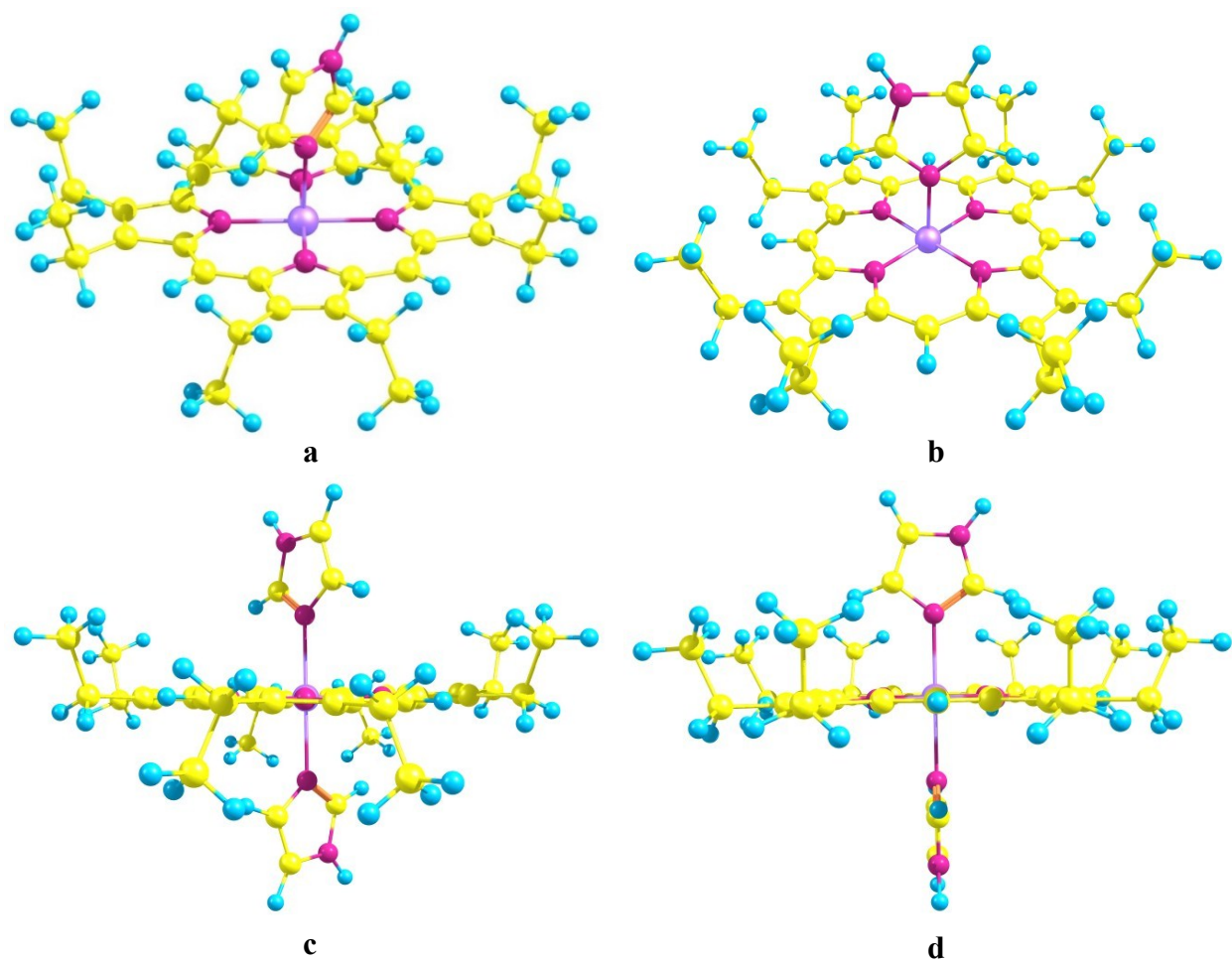
## B. Molecular DFT calculations:

Density functional theory (DFT) calculations with Gaussian 09 package were performed on 4 molecules including imidazole (Im), NiOEP, NiOEP-Im and NiOEP-Im<sub>2</sub> complexes. The ethyl groups in NiOEP are found to have an alternating up and down orientations (Fig. SI-2a) with respect to the porphyrin plane in the crystal structure.<sup>1</sup> But on HOPG surface, all the ethyl groups of NiOEP monolayer face above the porphyrin plane (Fig. SI-2b) away from the HOPG surface.<sup>2</sup> Hence, we considered both orientations for molecular DFT calculations. Optimizations performed on both singlet and triplet spin states of Im and NiOEP (on both configurations in Fig. SI-2) indicated that both Im and NiOEP molecules have a singlet ground state.



**Fig. SI-2** Top and side views of molecular models of NiOEP (a) in crystal structure configuration with alternating up and down ethyl groups and (b) on HOPG surface with all ethyl groups pointing up.

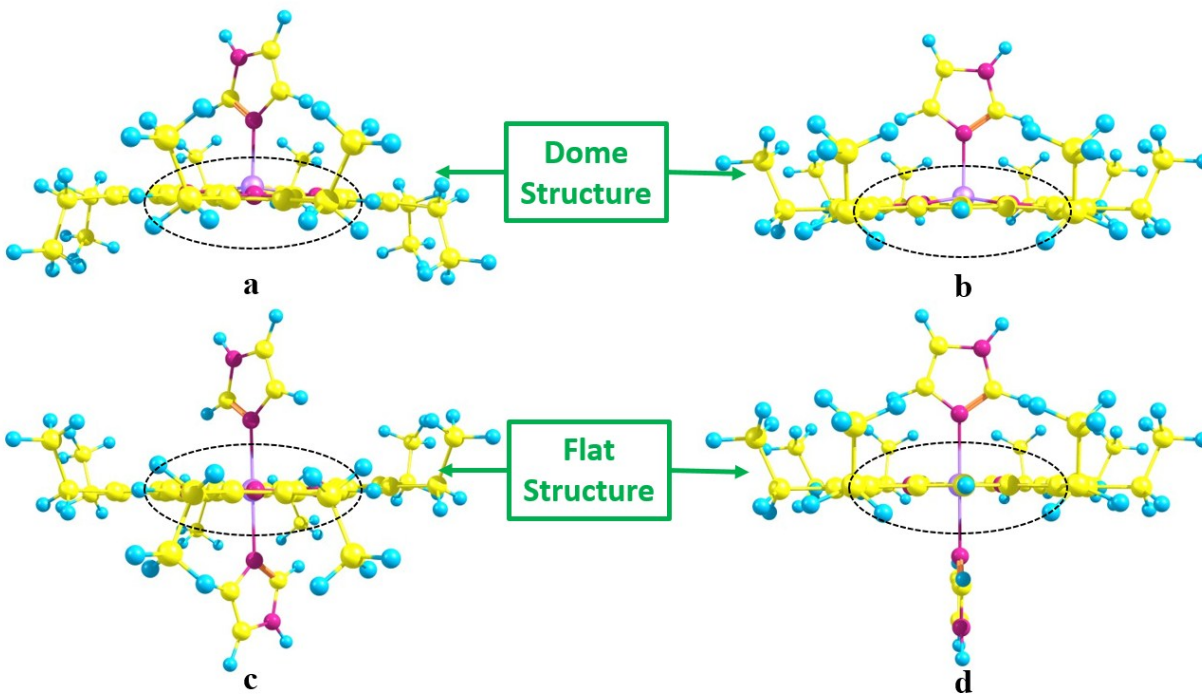
Using the optimized geometries of NiOEP and Im, molecular models of NiOEP-Im and NiOEP-Im<sub>2</sub> complexes were built and fully relaxed each in their singlet and triplet spin states. In all NiOEP-(Im/Im<sub>2</sub>) calculations both configurations of NiOEP (Fig. SI-2) were used. Upon relaxation, it was found that in singlet spin state NiOEP *does not* bind to imidazole either as a NiOEP-Im complex (Fig. SI-3a,b) or as NiOEP-Im<sub>2</sub> complex (Fig. SI-3c,d). We noticed that imidazole molecules are being pushed away from Ni atom as the optimization progressed with singlet NiOEP-Im and NiOEP-Im<sub>2</sub> complexes.



**Fig. SI-3** Molecular models of NiOEP-Im (a, b) and NiOEP-Im<sub>2</sub> (c, d) complexes with NiOEP in crystal structure configuration (a, c) and on HOPG surface configuration (b, d).

In triplet spin state, it was found that imidazole molecule binds to Ni<sup>2+</sup> ion both as a 5-coordinate NiOEP-Im and 6-coordinate NiOEP-Im<sub>2</sub> complex. Calculations also showed that orientation of ethyl groups has no significant effect on the coordination of imidazole ligand(s) to

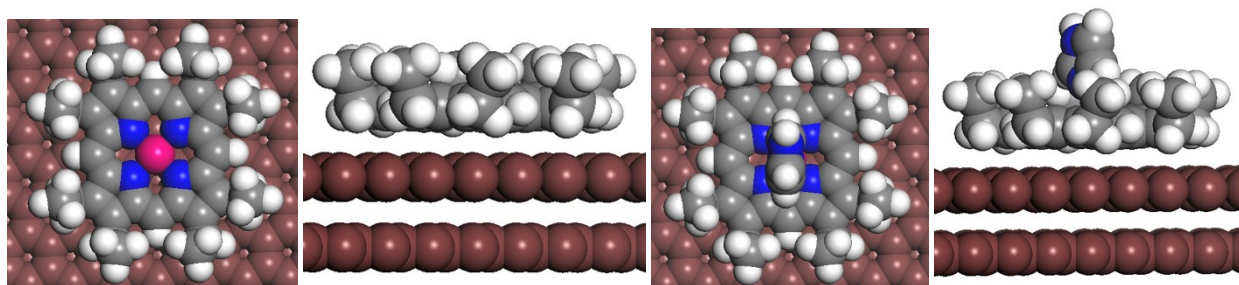
NiOEP in either spin state. The optimized geometries of imidazole ligated NiOEP complexes are shown Fig. SI-4. The NiOEP-Im complex has a characteristic dome shape (Fig. SI-4a,b) with Ni atom being raised above the porphyrin plane. The dome shape is also consistent with literature studies<sup>3</sup> of nickel porphyrins ligated to nitrogenous bases in triplet spin state. On the other hand, The NiOEP-Im<sub>2</sub> are complexes have a completely flat porphyrin core (Fig. SI-4b,c).



**Fig. SI-4** Optimized structures of NiOEP-Im (a, b) and NiOEP-Im<sub>2</sub> (c, d) complexes with NiOEP in crystal structure configuration (a, c) and on HOPG surface configuration (b, d).

### C. Periodic plane-wave (PW) DFT calculations:

To model the interface interactions between the NiOEP and NiOEP-Im complexes with HOPG substrate, appropriate initial geometries are necessary. The optimized structures of imidazole, NiOEP and NiOEP-Im molecules obtained from molecular DFT calculations are used as initial structures for building monolayers and interfaces in PW-DFT simulations. A detailed description of how the initial structures were built is given below.



**Fig. SI-5** Listed from left to right are optimized geometries of NiOEP/HOPG and Im-NiOEP/HOPG with alternating top (along  $c$ -axis of unit cell) and side ( $ab$ -plane) views respectively. Atom colors: nickel-pink, porphyrin and imidazole carbons-grey, nitrogen-blue, hydrogen-white, HOPG-brown.

**a) *Au(111) Surfaces*:** Crystal structure unit cell<sup>4</sup> of HOPG was optimized with plane-wave DFT and were used to build the respective (0001) surface. The primary surface of HOPG is multiplied  $5 \times 5 \times 1$  in  $a$ ,  $b$ ,  $c$  directions as substrate for NiOEP and Im-NiOEP monolayer respectively. The chosen dimensions of the HOPG substrate are based on the lattice parameters of NiOEP monolayer on HOPG obtained from STM images reported in the literature.<sup>2</sup> The obtained super cells with lattice parameters listed in Table SI-1. A vacuum of  $\sim 15$  Å is added along the  $c$  direction for creating a more realistic slab structure for HOPG(0001).

**b) *Isolated NiOEP and Im-NiOEP Molecules*:** Based on the experimental topography of NiOEP<sup>2</sup> on HOPG, we generated initial structures for isolated NiOEP molecule. The NiOEP molecule was built with all the 8 ethyl substituents on the porphyrin stay in an “all up” or “crown” configuration instead of the packing seen in the crystal structure.<sup>1</sup> The optimized geometries obtained from gas phase molecular DFT calculations were used as the starting geometries for the PW-DFT study. The lattice parameters for modeling the isolated imidazole, NiOEP and Im-NiOEP molecules are listed in Table SI-1, where the NiOEP and coronene molecules were placed at the center of the cubic box.

**Table SI-1.** Lattice parameters used in PW-DFT simulation models.

System	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)
HOPG	14.74	14.74	30	90	90	120
NiOEP/HOPG	14.74	14.74	30	90	90	120
Im-NiOEP/HOPG	14.74	14.74	30	90	90	120
Isolated Imidazole	30	30	30	90	90	90
Isolated NiOEP	30	30	30	90	90	90
Isolated Imidazole- NiOEP	30	30	30	90	90	90

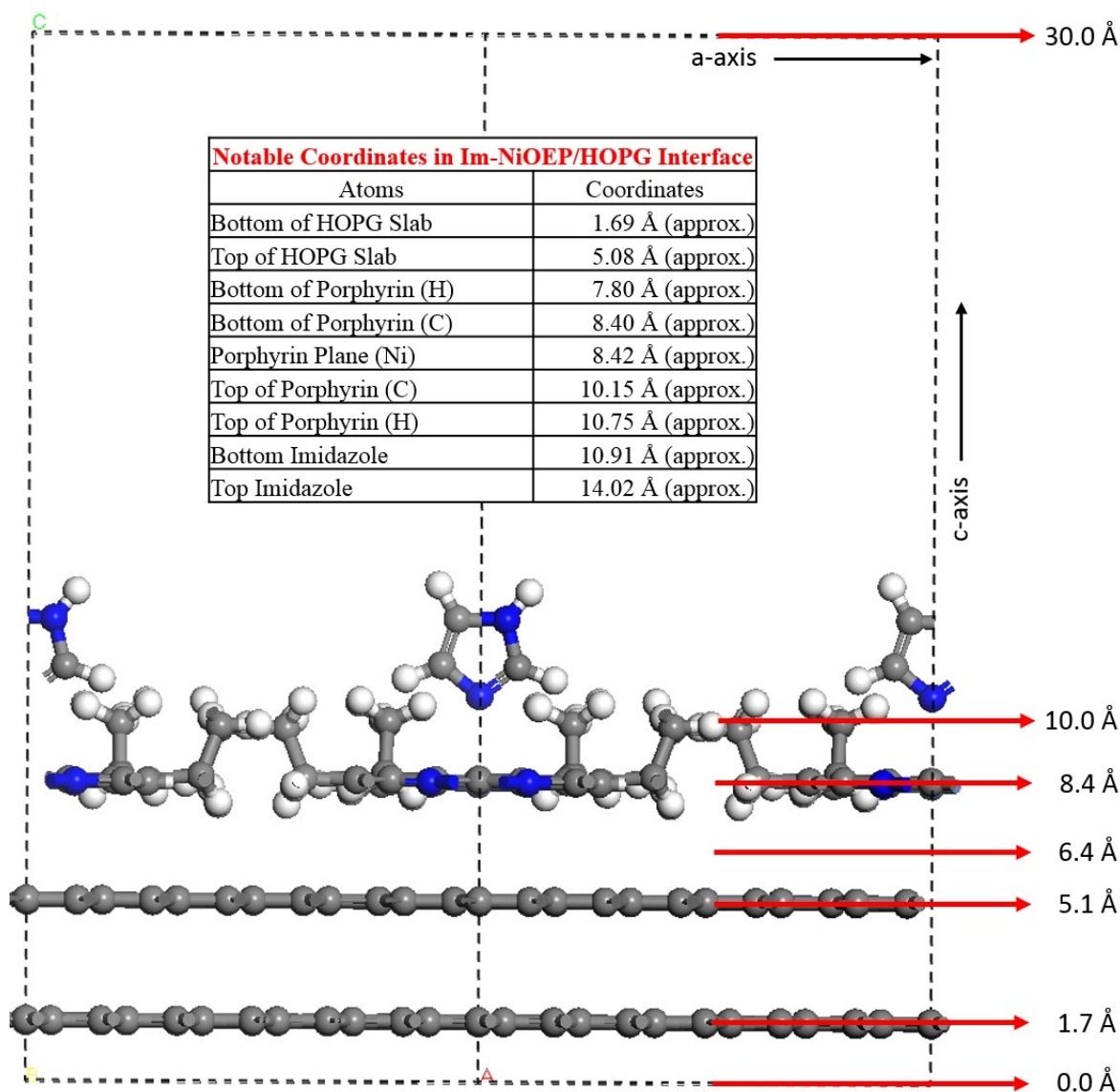
c) *NiOEP/HOPG and Im-NiOEP/HOPG Interfaces*: A single NiOEP molecule with Ni atoms centered on the c-axis is placed top of optimized 5×5×1 slab of HOPG, thus transferring the cell parameters of the slabs to the interfaces (Table S1). Although the exact size of the unit cell of the proposed model differs slightly from experiment, the effect of this difference should be negligible considering weak intermolecular repulsions between hydrogen atoms from neighboring molecules in the observed monolayers of NiOEP on HOPG from experiment. Imidazole molecule is added on top of optimized NiOEP/HOPG interface using orientation obtained from molecular DFT calculations of Im-NiOEP complex.

**Table SI-2:** Absolute energies obtained using DFT calculations with hybrid-B3LYP functional.

System	Molecular DFT			Periodic PW-DFT		
	Singlet (S0) (Hartrees)	Triplet (T1) (Hartrees)	S0-T1 (kJ/mole)	Singlet (S0) (eV)	Triplet (T1) (eV)	S0-T1 (kJ/mole)
<b>Isolated Imidazole (Im)</b>	-226.28	-226.14	<b>372.02</b>	-120.00	-116.12	<b>372.15</b>
<b>Isolated NiOEP</b>	-3126.22	-3126.20	<b>42.57</b>	-1023.60	-1022.96	<b>61.59</b>
<b>Im-NiOEP</b>	-3352.48	-3352.51	<b>-87.80</b>	-1143.54	-1143.82	<b>-27.58</b>
<b>NiOEP-HOPG</b>				-3684.53	-3684.04	<b>47.04</b>
<b>Im-NiOEP/HOPG</b>				-3804.88	-3804.68	<b>19.08</b>

#### D. Charge density and integration as a function of distance:

The charge redistributions at the NiOEP/HOPG ( $\rho_{diff}$ ) and Im-NiOEP/HOPG ( $\rho_{diff}'$ ) interfaces are obtained as discussed in the manuscript. Now the redistributed charge in each system is integrated as a function of distance along c-axis of the Im-NiOEP/HOPG lattice (Table SI-1). The interval for distance along c-axis is 0.07 Å. The positive and negative charge components with corresponding planes of integration are tabulated as a function of distance in Tables SI-3 and SI-4. The c-axis distances listed in these tables can be referred to Fig. SI-6.



**Fig. SI-6** Optimized model of Im-NiOEP/HOPG interface. The dotted line represents the periodic lattice. Two adjacent cells along a-axis are shown for clarity. The table in the figure lists important Cartesian coordinates along the c-axis. Some corresponding values are also depicted in the figure next to the red arrows.



**Table SI-3:** Positive and negative charges as a function distance along c-axis of lattice after charge redistribution in NiOEP/HOPG ( $\rho_{diff}$ ) and Im-NiOEP/HOPG ( $\rho_{diff}'$ ) interfaces.<sup>a, b</sup>

	c-axis position	Without Imidazole ( $\rho_{diff}$ )			With Imidazole ( $\rho_{diff}'$ )		
		+	-	Difference	+	-	Difference
<b>Plane of Integration-1</b>							
HOPG Substrate	0 to 7.5 Å	1.89	-1.37	<b>0.52</b>	0.97	-0.93	<b>0.03</b>
Monolayer & Vacuum	7.5 to 30.0 Å	0.39	-0.90	<b>-0.52</b>	1.18	-1.21	<b>-0.03</b>
		2.28	-2.27		2.14	-2.14	
<b>Plane of Integration-2</b>							
HOPG Substrate	0 to 6.7 Å	1.18	-1.28	<b>-0.11</b>	0.97	-0.57	<b>0.40</b>
Monolayer & Vacuum	6.7 to 30.0 Å	1.10	-0.99	<b>0.11</b>	1.18	-1.57	<b>-0.40</b>
		2.28	-2.27		2.14	-2.14	
<b>Plane of Integration-3</b>							
HOPG Substrate	0 to 6.4 Å	0.97	-1.28	<b>-0.31</b>	0.92	-0.57	<b>0.35</b>
Monolayer & Vacuum	6.4 to 30.0 Å	1.31	-0.99	<b>0.32</b>	1.22	-1.57	<b>-0.35</b>
		2.28	-2.27		2.14	-2.14	

<sup>a</sup> Different planes of integration (1 to 3) in the table gives charges at different distances along c-axis. Based on the atomic positions of HOPG substrate and NiOEP/Im-NiOEP molecules shown Fig. SI-6 and their respective covalent/van der Waals radii, plane of integration-2 gives the most relevant charge redistribution data at the molecule-substrate interface.

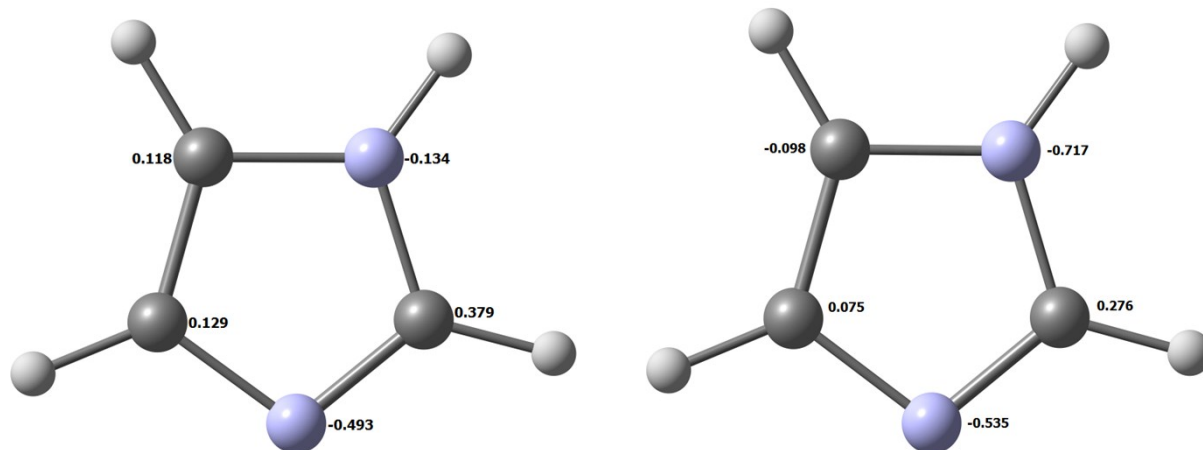
<sup>b</sup> Note that each integration plane is divided to 2 components with charge distribution on each component. Observation of charge in each component shows whether the substrate (HOPG) and molecule (NiOEP/Im-NiOEP) are acting charge acceptors or donors.

**Table SI-4:** Positive and negative charges as a function distance along c-axis of lattice after charge redistribution in NiOEP/HOPG ( $\rho_{diff}$ ) and Im-NiOEP/HOPG ( $\rho_{diff}'$ ) interfaces.<sup>c, d</sup>

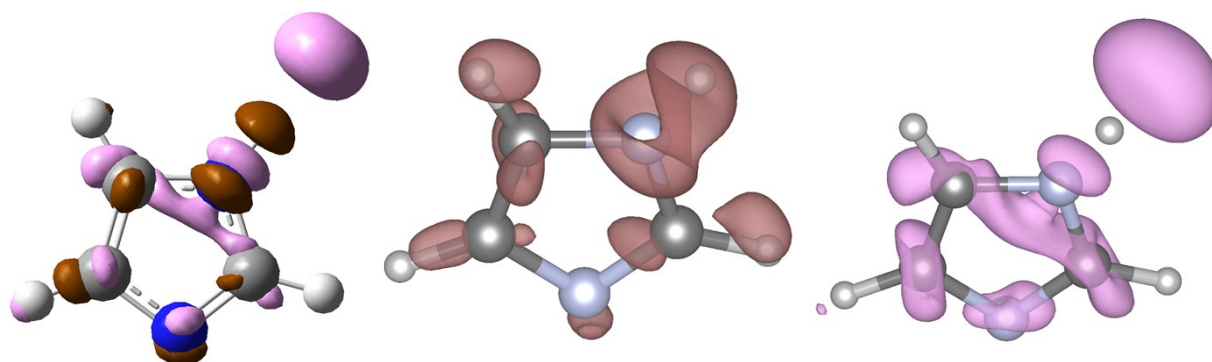
	c-axis position	Without Imidazole ( $\rho_{diff}$ )			With Imidazole ( $\rho_{diff}'$ )		
		+	-	Difference	+	-	Difference
<b>Plane of Integration-1</b>							
HOPG	0 to 7.5 Å	1.89	-1.37	<b>0.52</b>	0.97	-0.93	<b>0.03</b>
Porphyrin Plane	7.5 to 10.0 Å	0.34	-0.77	<b>-0.44</b>	0.73	-0.47	<b>0.26</b>
Above Porphyrin Plane (Ethyl groups, Im, Vacuum)	10.0 to 30.0 Å	0.05	-0.13	<b>-0.08</b>	0.45	-0.74	<b>-0.29</b>
<b>Total</b>		2.28	-2.27		2.14	-2.14	
<b>Plane of Integration-2</b>							
HOPG	0 to 6.7 Å	1.18	-1.28	<b>-0.11</b>	0.97	-0.57	<b>0.40</b>
Porphyrin Plane	6.7 to 10.0 Å	1.05	-0.86	<b>0.19</b>	0.73	-0.84	<b>-0.11</b>
Above Porphyrin Plane (Ethyl groups, Im, Vacuum)	10.0 to 30.0 Å	0.05	-0.13	<b>-0.08</b>	0.45	-0.74	<b>-0.29</b>
<b>Total</b>		2.28	-2.27		2.14	-2.14	
<b>Plane of Integration-3</b>							
HOPG	0 to 6.4 Å	0.97	-1.28	<b>-0.31</b>	0.92	-0.57	<b>0.35</b>
Porphyrin Plane	6.4 to 10.0 Å	1.25	-0.86	<b>0.39</b>	0.78	-0.84	<b>-0.06</b>
Above Porphyrin Plane (Ethyl groups, Im, Vacuum)	10.0 to 30.0 Å	0.05	-0.13	<b>-0.08</b>	0.45	-0.74	<b>-0.29</b>
<b>Total</b>		2.28	-2.27		2.14	-2.14	

<sup>c</sup> Different planes of integration (1 to 3) in the table gives charges at different distances along c-axis. Based on the atomic positions of HOPG substrate and NiOEP/Im-NiOEP molecules shown Fig. SI-6 and their respective covalent/van der Waals radii, plane of integration-2 gives the most relevant charge redistribution data at the molecule-substrate interface.

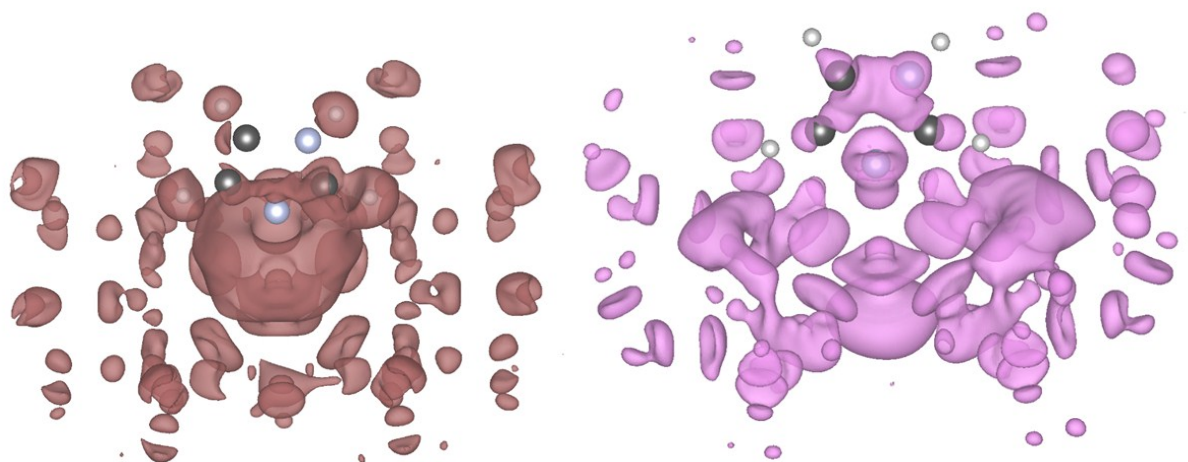
<sup>d</sup> Note that each integration plane is divided to 3 components with charge distribution on each component. Observation of charge in each component shows whether HOPG, NiOEP and imidazole molecules are acting charge acceptors or donors.



**Fig. SI-7** Natural charges summed with nearest hydrogens of neutral (left) and anion (right) of imidazole molecules obtained from molecular DFT calculations. Atom colors, grey-carbon, blue-nitrogen, white-hydrogens.



**Fig. SI-8** Valence charge difference between imidazole anion and neutral molecules. Positive charge is colored in brown and negative charge in pink. Figure on left obtained from molecular DFT. Figures in middle and right obtained from PW-DFT calculations.

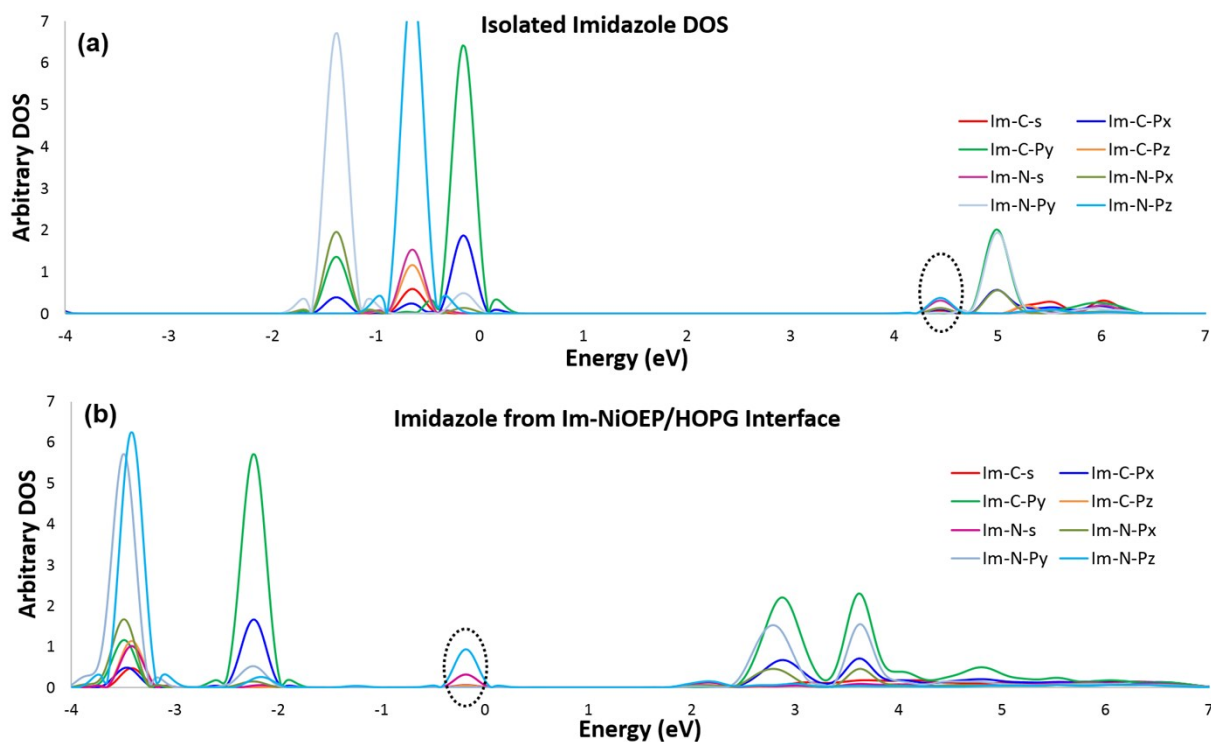


**Fig. SI-9** Valence charge redistribution in Im-NiOEP/HOPG interface. Charge on HOPG is masked for clarity. Positive charge is colored in brown and negative charge in pink.

**Table SI-5** Work function data from PW-DFT calculations.

System	WF ( $\phi$ ) (eV)
HOPG Substrate	4.70
NiOEP on HOPG Substrate	4.52
Imidazole ligated to NiOEP on HOPG Substrate	3.21

### E. Density of States



**Fig. SI-10** Comparison of (a) isolated and (b) ligated imidazole density of states (DOS). NiOEP and HOPG bands in the DOS are masked for appropriate comparison. The black dotted oval in the figure indicates an unoccupied band (upper panel, a) in isolated imidazole molecule but moved to being occupied band (lower band, b) in imidazole-NiOEP/HOPG interface.

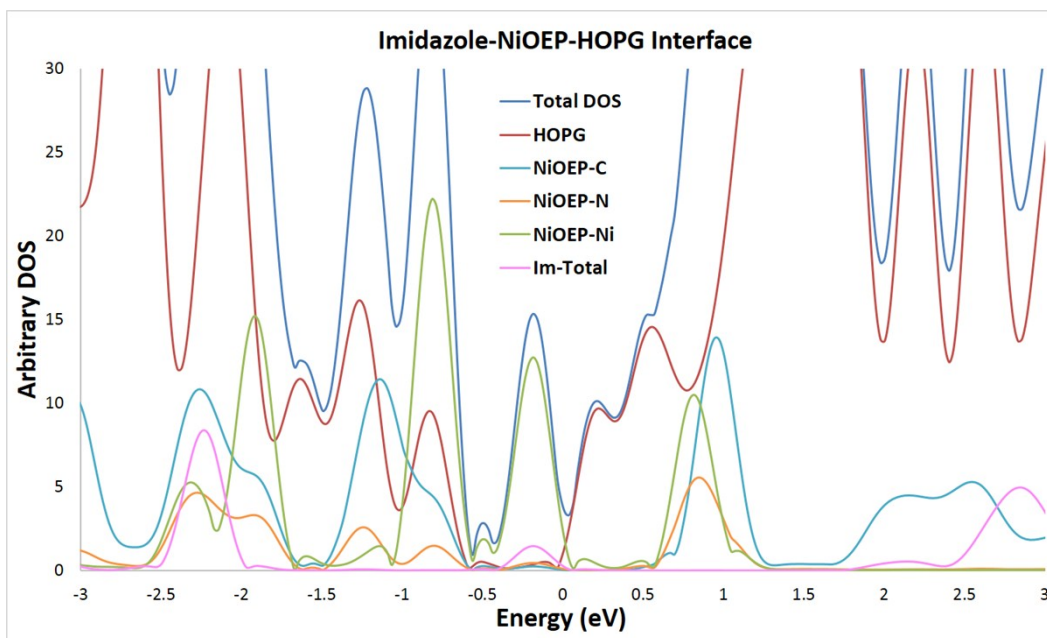


Fig. SI-11 Density of states of Im-NiOEP/HOPG interface.

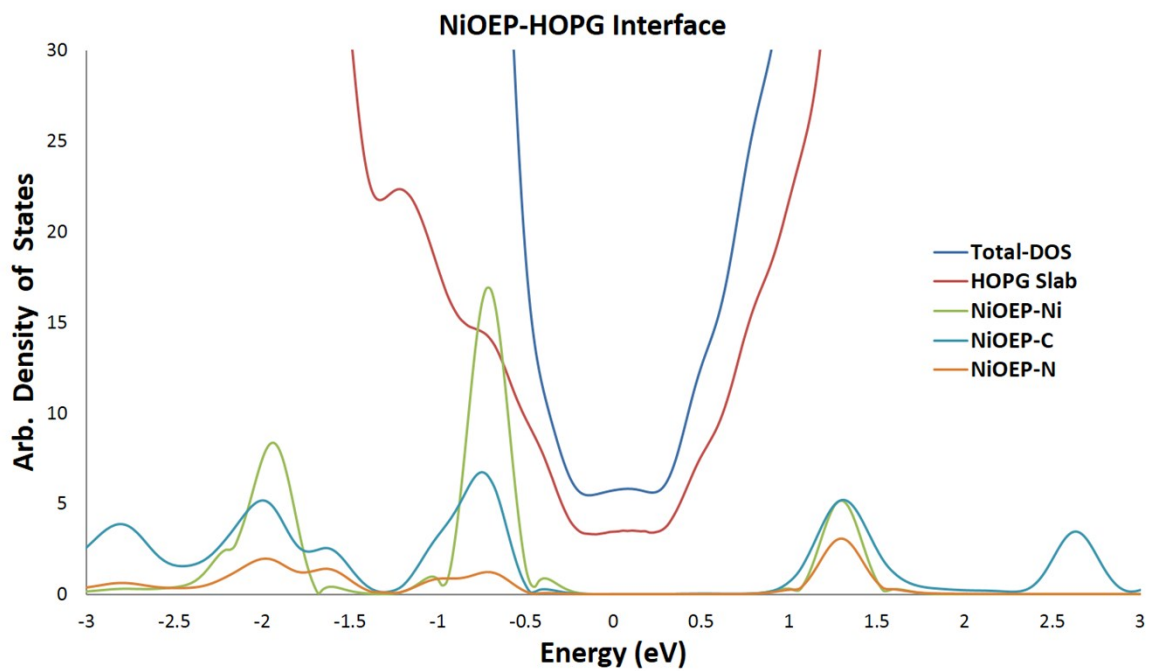
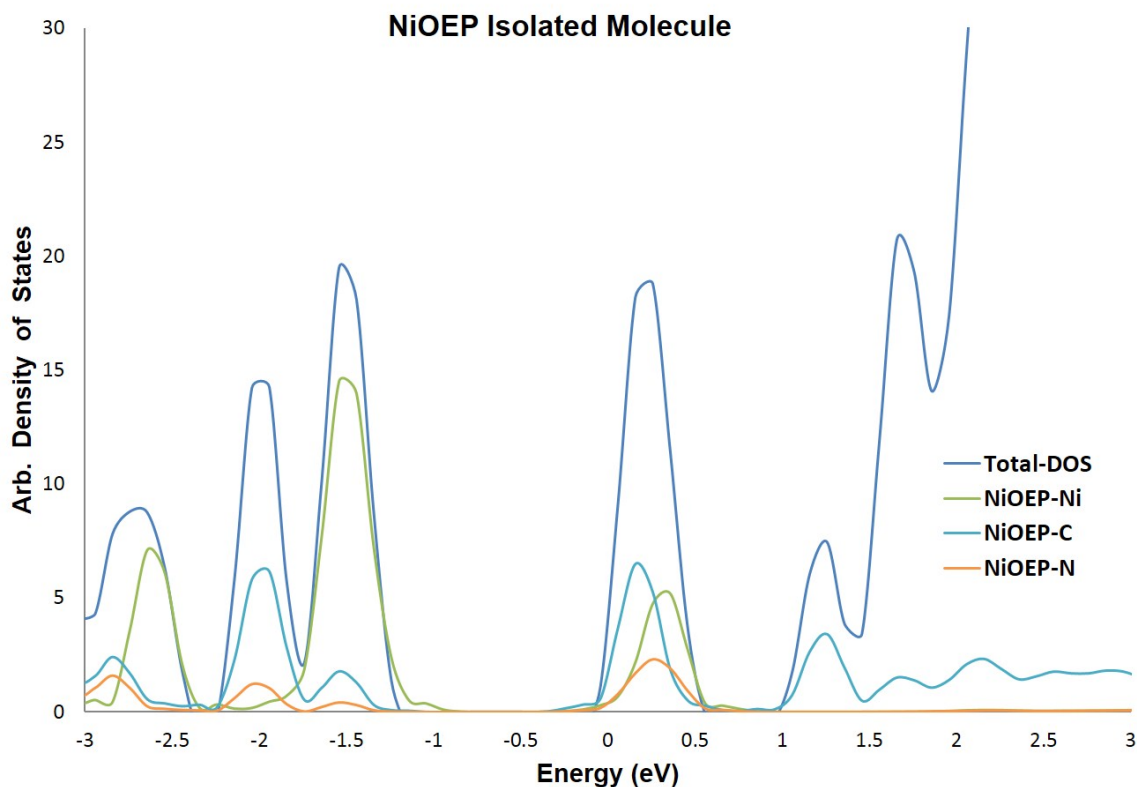


Fig. SI-12 Density of states of NiOEP/HOPG interface.



**Fig. SI-13** Density of states of isolated NiOEP molecule.

## F. Entropy of binding/adsorption

The technique described by Whitesides was used to estimate the change in translational and rotational entropy resulting from the binding of imidazole to NiOEP.<sup>5</sup> The Pauling radii were used to estimate the actual molecular,  $V_m$ , volume of phenyloctane and the value found was 232 Å<sup>3</sup>. Using a value of 0.858 g/cm<sup>3</sup> for the density of phenyloctane, 368 Å<sup>3</sup> was found for the available volume per molecule,  $V_a$ . The free volume,  $V_f$ , was determined by the equation:  $V_f = 8(V_a^{1/3} - V_m^{1/3})^3 = 8.18$  Å<sup>3</sup> and the ratio,  $r$ , of  $V_f/V_a = 0.022$ . The translational entropy is then given by:

$$St := -R \cdot \ln \left[ \left( \frac{1}{c \cdot N} \right) \cdot \left( \frac{2 \cdot \pi \cdot m \cdot k \cdot T \cdot e^{1.667}}{h^2} \right)^{1.5} \right]$$

where  $c$  is  $M/(r \times 1000 \text{ cm}^3/\text{L})$ , and  $M$  is the concentration of imidazole in moles per liter and  $m$  is the molecular weight of imidazole (68.08 g/mole) divided by Avogadro's number. Taking the

standard reference state to be that concentration at which half the surface is covered, one finds from the Langmuir fit that  $c = 1.7 \times 10^{-3}$  M, and thus at 298 K,  $S_t = -156$  J/mole-K.

The rotational entropy is given by the formula,

$$S_r := -R \cdot \ln \left[ \left( \frac{\sqrt{\pi}}{\gamma} \right) \cdot \left( \frac{8\pi^2 \cdot k \cdot T \cdot e}{h^2} \right)^{1.5} \cdot (I_1 \cdot I_2 \cdot I_3)^{0.5} \right]$$

where the  $I$ 's are the moments of inertia and were determined from optimizing the structure of imidazole in Gaussian03 at the HF/6-31g level.  $R_f = -101$  J/mole-K

Once imidazole binds to NiOEP (either in solution or on the surface), there is a small increase in entropy due to the three vibrations resulting from rotations and three translational vibrations. We estimated these in two different ways (that gave nearly the same result). First, the three frustrated rotations were assigned as having a  $50 \text{ cm}^{-1}$  energy (each) and the other three were estimated as  $275$ ,  $275$ , and  $200 \text{ cm}^{-1}$  because reported imidazole-metal complexes have vibrational bands assigned to this region.<sup>6,7,8</sup> Using these value one finds  $S_v = +40$  J/mole-K. Alternatively, we did DFT optimization frequency calculation on Im-CoOEP (a stable species) and found all the relevant vibrational modes lay between  $60$  and  $126 \text{ cm}^{-1}$ . Using three modes at  $70 \text{ cm}^{-1}$ , two at  $100 \text{ cm}^{-1}$ , and one at  $126 \text{ cm}^{-1}$ , we found  $S_v = 43$  J/mole-K. Thus, summing all three terms, we found:  $\Delta S \approx -216$  J/mole-K and  $T\Delta S \approx -64$  kJ/mole

<sup>1</sup>Meyer Jr., E.F. The crystal and molecular structure of Nickel(II)octaethylporphyrin. *Acta Cryst.* **1972**, B28, 2162-2167.

<sup>2</sup>Bhattarai, A.; Mazur, U.; Hipps, K.W. Desorption Kinetics and Activation Energy for Cobalt Octaethylporphyrin from Graphite at the Phenyloctane Solution–Graphite Interface: An STM Study. *J. Phys. Chem. C* **2015**, 119, 9386–9394.

<sup>3</sup>Dommaschk, M.; Schütt, C.; Venkataramani, S.; Jana, U.; Näther, C.; Sönnichsen, F.D.; Herges, R. Rational design of a room temperature molecular spin switch. The light-driven coordination induced spin state switch (LD-CISSS) approach. *Dalton Trans.* **2014**, 43, 17395–17405.

<sup>4</sup>Wyckoff, G., R. W. *Crystal Structures*. 2 ed.; Interscience Publishers: New York, New York, 1963; Vol. 1, p 7-83.

<sup>5</sup>Mammen, M.; Shakhnovich, E.; Deutch, J.M.; Whitesides, G.M. Estimating the Entropic Cost of Self-Assembly of Multiparticle Hydrogen-Bonded Aggregates Based on the Cyanuric Acid-Melamine Lattice. *J. Org. Chem.* **1998**, 63, 3821-3830

<sup>6</sup>Taylor, C.; Underhill, A.; Complexes of Cobalt(II) and Nickel(II) Halides with Imidazole. *J. Chem. Soc. A* **1969**, 368-372.

<sup>7</sup>Goodgame, D.; Goodgame, M.; Hayward, P.; Rayner-Canham, G. Vibrational spectra of Imidazole Complexes. *Inorg. Chem.* **1968**, 7, 2447-2451.

<sup>8</sup>Naumov, P.; Grupce, O.; Jovanovski, G. Experimental and theoretical Raman study of binuclear

---

copper(II) imidazole saccharinato complex. *J. Raman Spec.* **2000**, *31*, 475-479.