Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2020

# Supplementary Information

## Quantifying reversible nitrogenous ligand binding to Co(II) porphyrin receptors at the solution/solid interface and in solution

Kristen N. Johnson, K. W. Hipps* and Ursula Mazur*

Department of Chemistry and Materials Science and Engineering Program, Washington State University, Pullman, WA 99163-4630

**Contents** **Page**

## DFT computational details

Gaussian[1] (ub3lyp/6311g for the cobalt complexes and b3lyp/6-311G for all singlet state species) were performed on all species reported here. VASP[2,3] calculations were performed with the optB88-vdW functional[4] with PAW potentials optimized for the PBE functional for all calculations.

In both the free molecule and adsorbed state calculations, the low energy configuration of the MeOPy-CoOEP was the one shown in Figure S1 with the Pyridine ring bisecting the N-Co-N angle. Also shown in S1 is the supercell use bin the VASP calculations but expanded by two in the a and b directions to aid understanding of the system calculated. The graphite layer is colored yellow for clarity. The 2-layer graphite was first optimized and then the bottom layer fixed in all subsequent optimizations. The top layer and all atoms of adsorbates were optimized to an energy of 1 mV or better. VASP calculations were performed for MeOPy, MeOPy–CoOEP, and CoOEP in in 2x2x1 (otherwise empty) supercells in order to more correctly calculate free molecule energies.

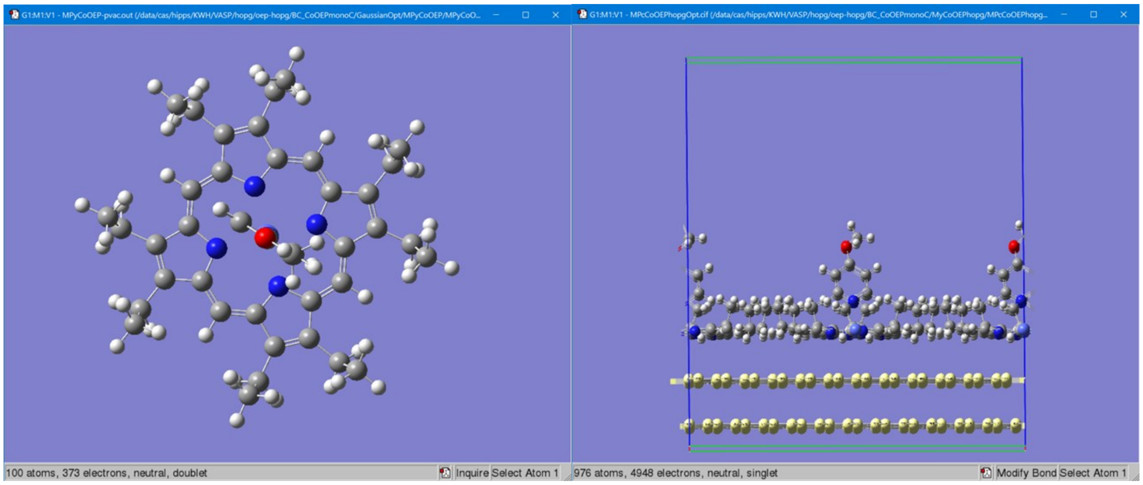

Figure S1. Molecular models of systems used in calculations. Left, MeOPy–CoOEP molecule is shown in the lowest energy configuation. Right, supercell used for VASP calculations is shown.

**Table S1.** B88-vdW VASP energies of indicated species.

| **System** | **eV** |
|---|---|
| HOPG | -1150.6446 |
| CoOEP M | -472.9750 |
| CoOEP BigBox | -472.6469 |
| CoOEP hopg | -1627.0814 |
| MPyCoOEP M | -556.6455 |
| MPyCoOEP Big Box | -556.4028 |
| MPyCoOEPhopg | -1710.9419 |
| Mpy big box | -82.7643 |
| CoOEP/G = G + CoOEP | 3.79 |
| MPyCoOEP/G = G + MPyCoOEP | 3.89 |

Table S1 presents the computed energies of the various systems with "Big Box" indicating that a 2x21 supercell was used to minimize communication between molecules in cells. The M notation indicates that the same monolayer structure as for the HOPG supported system was used, but the HOPG was not included. For example, the condensation of the CoOEP into the monolayer structure in the absence of HOPG (CoOEP M) is predicted to be 328 meV more stable than when HOPG is present (CoOEP BigBox). The last two entries in the table are the electronic desorption energies into the gas phase. It is useful to note that the gas phase electronic energy difference predicted for the reactions (where s designates adsorbed in the HOPG surface):

$$\mathbf{MeOPy(g) + CoOEP(s) = MeOPy\text{-}CoOEP(s) \qquad rxn\ 1}$$

$$\mathbf{MeOPy(g) + CoOEP(g) = MeOPy\text{-}CoOEP(g) \qquad rxn\ 2}$$

are **$\Delta E_1$ = –106 kJ/mole for rxn1** and **–96 kJ/mole for rxn 2.**

This is a small difference and indicates that the HOPG surface is not significantly affecting the reaction energetics.

**Table S2.** Gaussian calculations for molecules in toluene.
* indicates entropy correction for free volume of solution

| **System: ub3lyp/6-311G(d,p)** | | **H (eV)** | **G(eV)** | **$E_{elect}$ (eV)** | **St+r J/mole-K** | **S J/mole-K** |
|---|---|---|---|---|---|---|
| | | 6-311Gdp | | | | |
| MeOPyCoOEP vacuum G09 | | -3362.676206 | -3362.815198 | -3363.5734 | 353.0 | 1,223.9 |
| MeOPyCoOEP toluene G09 | | -3362.715866 | -3362.851957 | | 353.0 | 1,198.4 |
| Delta of immersion in kJ/mole | | -107.5 | -107.8* | | | |
| | | | | | | |
| MeOpy vacuum | | -362.77493 | -362.81358 | -362.90363 | 283.8 | 340.4 |
| MeOpy in toluene | | -362.78333 | -362.82224 | | 283.8 | 342.6 |
| Delta of immersion in kJ/mole | | -22.0 | -34.1* | | | |
| | | | | | | |
| CoOEP vacuum G09 | | -2999.88388 | -3000.00124 | -3000.65081 | 348.3 | 1,033.4 |
| CoOEP toluene G09 | | -2999.91123 | -3000.02616 | | 348.3 | 1,012.0 |
| Delta of immersion in kJ/mole | | -72.0 | -76.6* | | | |
| | | kJ/mole | kJ/mole | | | |
| **Δ(RXN) Gas (rxn 2)** | | -45.6 | -0.96 | -49.7 | -279.1 | -149.9 |
| **Δ(RXN) Solution (rxn 1)** | | -55.9 | -20.6* | | -241.1* | -118.4* |

Table S2 collects the results of the Gaussian calculations. Note that the predicted electronic energy change for rxn 2 is of the same order but about half that from the VASP calculation. It should be noted that the functionals used in the two methods are quite different in that b3lyp has no dispersion term but does partially account for HF exchange. The vdW-B88 functional does contain a significant dispersion term but is not account for HF exchange. We believe that the energy difference between gas phase and surface energy calculations in VASP (10.1 kJ/mole) should be representative of the desorption energy because the porphyrin-HOPG interaction is primarily dispersive.

**Table S3.** Solvent accessible areas for porphyrin complexes and for a monolayer of the complex on HOPG. The derived heat of immersion based on proportion of surface exposed and heat of immersion of free complex is also provided.

| ub3lyp/6-311G(dp) | SAS ($A^2$) | Surface SAS ($A^2$) | $\Delta H_I$ surf kJ/mole |
|---|---|---|---|
| CoOEP/HOPG into toluene | 1148.1 | 574.1 | -36.0 |
| MPyCoOEP/HOPG into toluene | 1267.4 | 693.4 | -59.0 |

An additional pair of Gaussian calculations were performed in order to obtain a heat of immersion for HOPG that would be internally consistent with the other heats of immersion. We created an hydrogen terminated slab of graphite from the 2 layers used in the calcualtion but containing a total of 164 carbons ($C_{164}H_{48}$) and used the SCRF(SMD) model to calculate the heat of imemrsion. The result was –249.086 kJ/mole of the flake. To convert this to per mole of CoOEP (and therefore MeOPy-CoOEP) we used carbon area of the flake (4.25 $nm^2$) and that of the CoOEP (1.61 $nm^2$) to get a ***heat of immersion of HOPG of –94.55 kJ/mole of CoOEP area.***

Two other thermodynamic issue must be addressed. The Gaussian calculation of entropy and free energy in solution treats the system as if it has the full volume of a mole of gas at 298K. Obviously, this is not appropriate for a solution. One way to correct for this is to simply compress that gas from 24.45 L to the 1 mole/L standard state. This is often done.[5] Clearly, it leaves too much free volume since the space occupied by the solvent is not considered.[4] In this work we chose to compute the free volume in one liter of toluene by first computing the effective volume of a toluene molecule (0.132 nm$^2$) and the volume available per molecule based on the density (0.178 nm$^2$) and taking the difference to get 0.0455 nm$^2$/molecule of toluene or 250 cm$^3$ per L of toluene. The entropy correction for going from STP as a gas to 1 mole/L is therefore Rln(24.45/.25) = 38.10 J/mole K reduction in entropy and 298*Rln(24.45/.25) = 11.35 kJ/mole increase in G.

Second, when the standard free energy and entropy of a reaction with a surface is considered, the standard state is usually taken to be one half monolayer. There is configurational entropy of Rln(2) that must than be added to the entropy of the adsorbed system.

With these computed values, the following analysis was applied.

--------------------------------------------------------------------------------

Consider the reaction **A + B = C**, where each component is treated as ideal in the gas and solution phase and the total energy is assumed to be a sum of electronic, vibrational, rotational, and translational parts.

Suppose $F_i^p = F(int)_i^p + F(t,R)_i^p$ where ***F*** is a function of state and ***t, R*** is the translational and rotational contributions referenced in the ***p*** phase. Because these are ideal systems, we have $H(t,R)_i^{g,l} = 3RT$ and also $S_i^l = S(int)_i^l + S(t,R)_i^g - Rln(\frac{24.45}{Vf})$ where Vf is the free volume available for solute in 1 L of solution.

For a reaction:

$$\Delta S^l = \sum(\Delta S(int)_i^l + \Delta S(t,R)_i^g - Rln(\frac{24.45}{Vf}))$$

Since the correction term is the same for all components, one product and two reactants results in:

$$\Delta S^l = \sum\left(\Delta S(int)_i^l + \Delta S(t,R)_i^g\right) + Rln(\frac{24.45}{Vf})$$

The value in () is the calculated value of S for the solution phase provided by the Gaussian program. Thus

$$\Delta S^l = \Delta S_{G09}^{\,l} + Rln(\frac{24.45}{Vf}) \qquad \text{a1}$$

Since $\Delta H^l = \Delta H_{G09}^{\,l}$ we have

$$\Delta G^l = \Delta G_{G09}^{\,l} - RTln(\frac{24.45}{Vf}) \qquad \text{a2}$$

Or more generally for a reaction with a **net loss of n moles**:

$$\Delta G^{l} = \Delta G_{G09}^{\ l} - nRTln(\frac{24.45}{Vf})$$

$$\Delta H^{l} = \Delta H_{G09}^{\ l} \qquad \text{a3}$$

Now consider the reaction with mixed phases:

A(g) + B(g) = C(g) a4

A(g) + B(s, g) = C(s, g) a5

A(l) +B(l) = C(l) a6

A(l) +B(s, l) = C(s, l) a7

Where (s, g) designates a surface supported monolayer in contact with gas and (s, l) is the same monolayer in contact with liquid.

$\Delta E_4$(electronic)and $\Delta E_5$(electronic) were computed from VASP while all the thermodynamic variables were computed for eqn a4 and a6 using Gaussian. We will now combine this information to derive $\Delta H_7$ and $\Delta S_7$, from which $\Delta G_7 = \Delta H_7 - T\Delta S_7$. Three approximations will be used:

1) The entropy and enthalpy of the adsorbed species B and C associated with the 6 frustrated translations and rotations cancel. This is a good approximation for the case where the adsorbates have similar physisorption forces and similar masses (as is the case here).

2) The heats of wetting of the adsorbed species are proportional to the solvent accessible surface area (SAS). [6]

3) The internal motions of the adsorbed molecules are little changed by adsorption to the thermodynamic functions associated with internal motions are the same in solution as on the surface.

Thus:

$\Delta H_5 = -\varepsilon + \Delta H_4 - H_{T,R}(C; g) + H_{T,R}(B; g)$ where $H_{T,R}(B; g)$ is the translational and rotational enthalpy of species B in the gas phase. The later 2 terms cancel at 298 K.

$\Delta H_7 = \Delta H_5 + \Delta H_I(C; s) - \Delta H_I(B; s) - \Delta H_I(A)$

Where $\Delta H_I(C)$ is the enthalpy associated with transporting a mole of C in the gas phase at 1 atm to a monolayer of C on an HOPG surface. $\Delta H_I(A)$ is the enthalpy of immersion for A. That is, the enthalpy associated with transferring 1 mole of gas A at 1 atm to a 1 M solution.

$\Delta S_7 = \Delta S_6 - S_{T,R}(C; l) + S_{T,R}(B; l) + S_{config}$

The last term, $S_{config}$, is the configurational entropy of a half filled monolayer that is the standard state for the Langmuir adsorption and is equal to Rln(2).

$\Delta G_7 = \Delta H_7 - T\,\Delta S_7$

## Equilibrium constant determination in toluene solution

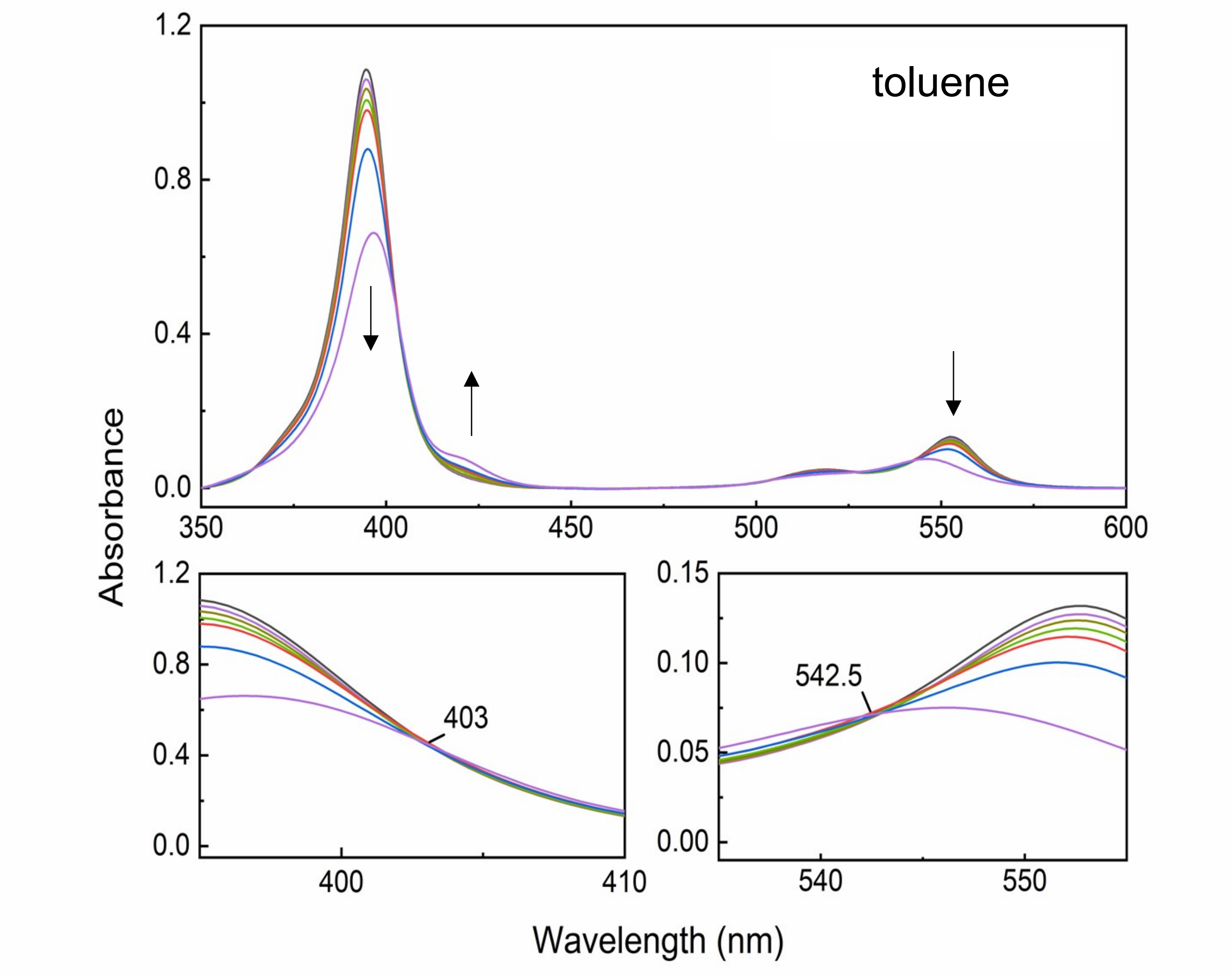

**Figure S2**. UV-Vis spectra of MeOPy–CoOEP in toluene. The initial concentration of CoOEP was 5.2 μM and the concentration of MeOPy was consecutively larger in each spectrum from 8.2 μM to 0.066 M. Arrows indicated the direction of spectral changes to each peak. Upper chart shows the full spectrum while lower charts show zoomed in regions of the spectrum that include isosbestic points at 403 and 542.5 nm.

## Absorbance curve fitting derivation for titration of MeOPy and CoOEP in toluene

Definitions: $P$ = CoOEP; $L$ = MeOPy; $PL$ = MeOPy–CoOEP; $\varepsilon_P$ = extinction coefficient of $P$; $\varepsilon_{PL}$=extinction coefficient of $PL$; $A$=absorbance at 394.5 nm. The electronic spectra above shows the solution phase complexation of CoOEP and MeOPy following the reaction:

$$P + L \leftrightarrow PL \tag{b1}$$

$$K = \frac{[PL]}{[P][L]} \tag{b2}$$

At equilibrium:

$$[P] = [P]_0 - [PL] \tag{b3}$$

$$[L] = [L]_0 - [PL] \tag{b4}$$

where $[P]_0$ is the initial concentration of the porphyrin and $[L]_0$ is the initial concentration of the ligand which is much greater than the concentration of the complex and we will use the approximation $[PL] \ll [L]_0$. Combining the above equations (b2-b4) gives:

$$[PL] = \frac{K[L]_0[P]_0}{1 + K[L]_0} \tag{b5}$$

The complexed ($PL$) and the unbound porphyrin ($P$) have differing extinction coefficients, and each follows beer's law. Here, the path length is 1 cm and the ligand alone does not absorb light at the wavelength of interest. Therefore, the total absorbance of the system in equilibrium is given by:

$$A_{tot} = A_p + A_{PL} = \varepsilon_P[P] + \varepsilon_{PL}[PL] \tag{b6}$$

Initially, absorbance is only due the unbound porphyrin:

$$A_0 = \varepsilon_P[P]_0 \tag{b7}$$

$$\Delta A = A_{tot} - A_0 = \varepsilon_P[P] + \varepsilon_{PL}[PL] - \varepsilon_P[P]_0 = \varepsilon_P([P]_0 - [PL]) + \varepsilon_{PL}[PL] - \varepsilon_0[P]_0$$

$$= (\varepsilon_P - \varepsilon_{PL})[PL] + \varepsilon_P[P]_0 - \varepsilon_0[P]_0 = \Delta\varepsilon[PL] \tag{b8}$$

$$\Delta A = \Delta\varepsilon\frac{K[L][P]_0}{1 + K[L]} \tag{b9}$$

The titration shown in Figure S2 and Figure 2 provides a series of absorbance values at 394.5 nm. Subtracting these absorbance values from that of the initial absorbance of CoOEP in toluene gives data points of ΔAbs versus the MeOPy concentration are shown in Figure 3. Curve fitting the plot with the equation b9, shown above, we get $K_{s,\ toluene}$=890 ± 65 $M^{-1}$. Taking $\Delta G = -RT \ln K$, gives $\Delta G_{soln,\ toluene}$(298 K)= -16.8 ± 0.2 kJ/mol. Derivation was adapted from [7].

## UV-Vis CoOEP + MeOPy in n-octylbenzene solution

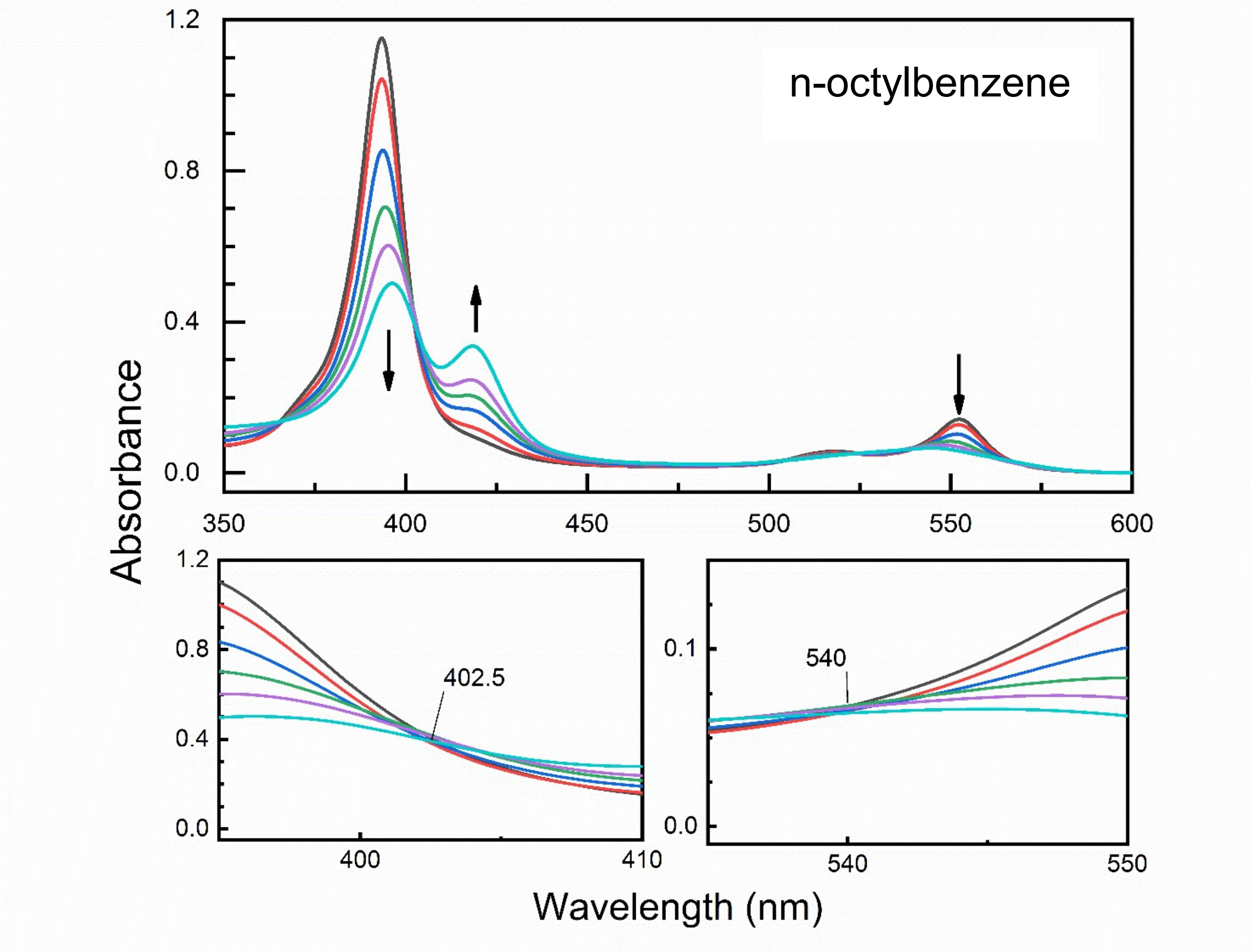

**Figure S3**. UV-Vis spectra of MeOPy–CoOEP in n-octylbenzene. The initial concentration of CoOEP was 5.2 µM and the concentration of MeOPy was consecutively larger in each spectrum from 50 µM to 0.023 M. Arrows indicated the direction of spectral changes to each peak. Upper chart shows the full spectrum while lower charts show zoomed in regions of the spectrum that include isosbestic points at 402.5 and 540 nm. The peak at 420 nm is more prominent in n-octylbenzene solution than in toluene solution otherwise no significant differences are observed.

## STM time dependent imaging of MeOPy binding to CoOEP

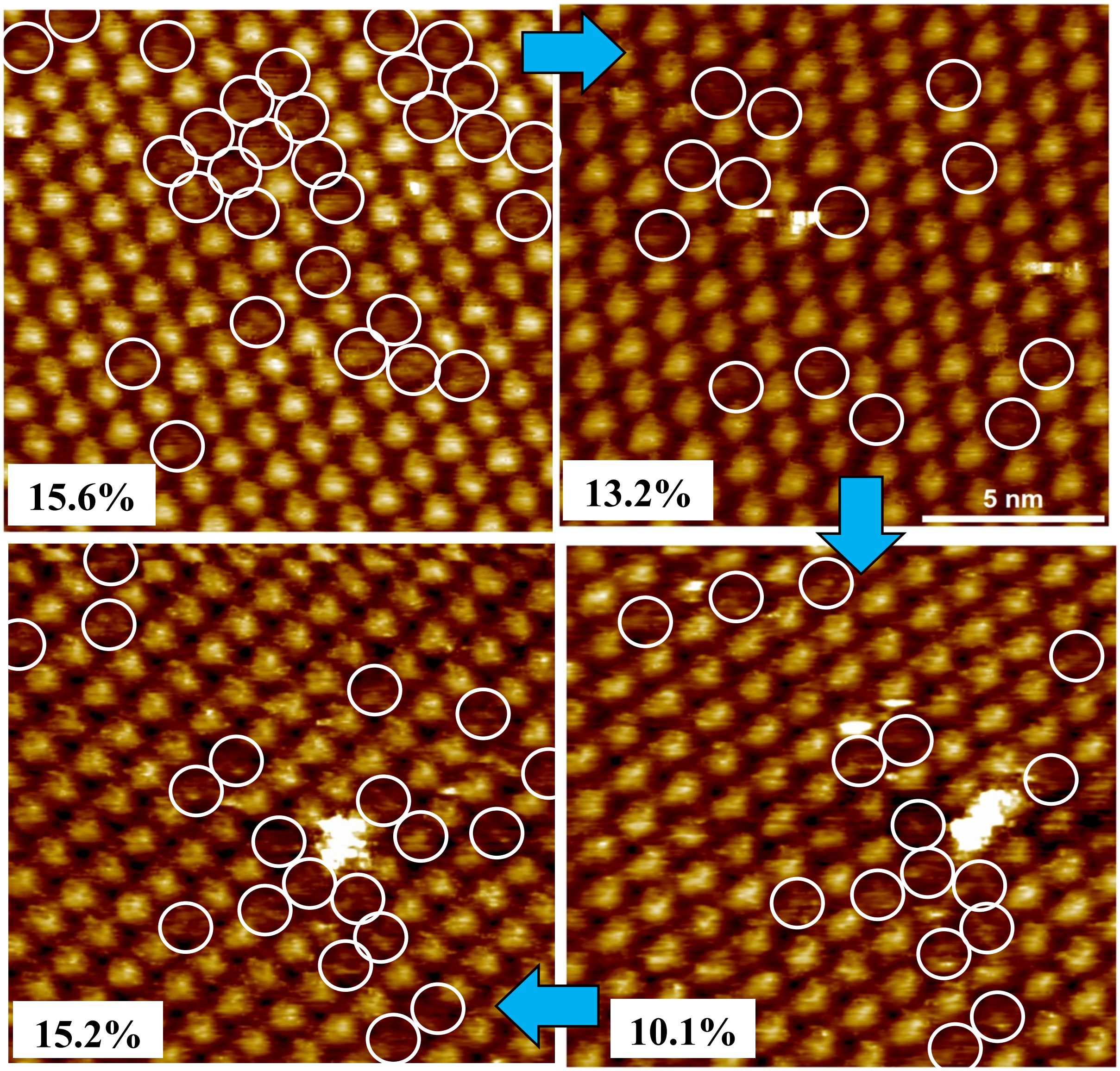

**Figure S4.** Representative STM images collected sequentially with [CoOEP] = 10 μM and [MeOPy] = 500 μM. These images are a part of the sequence of STM images that were used to create Figure 6. Values for θ are overlaid on each image. Images are 15x15 nm in size, were collected at −600 mV, 10 pA and collection time was 85 sec/image.

## STM Images of premixed CoOEP and MeOPy

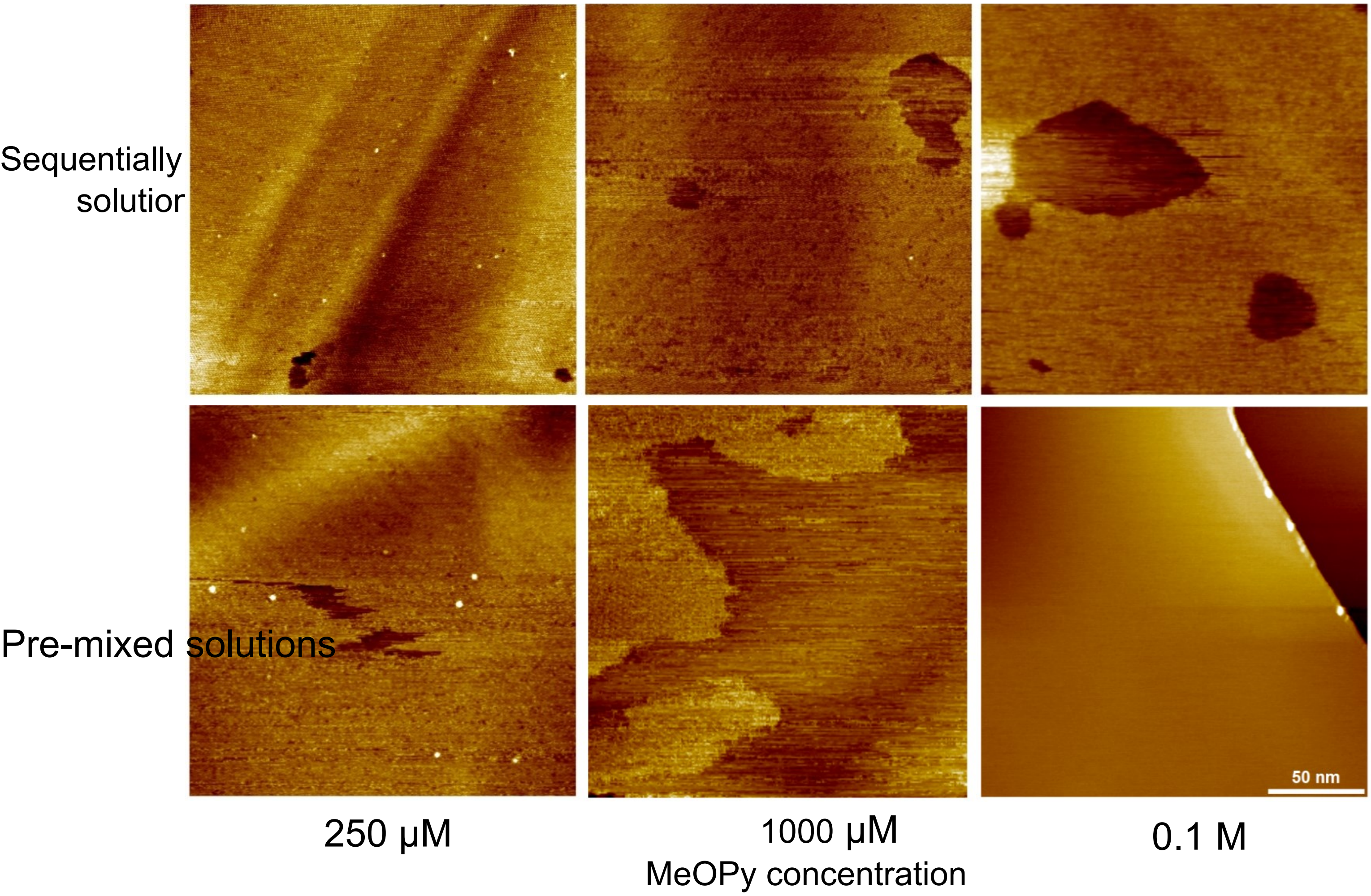

**Figure S5.** Large scale (200 x 200 nm) STM images illustrate the difference between two sample preparation methods. The top row shows samples that were prepared first adding 10 µL of 20 µM CoOEP solution to the HOPG substrate and then adding 10 µL methoxypyridine solution with the desired concentration. All images shown in the main paper were created in this way. The lower row shows the samples that were prepared by first mixing the CoOEP and MeOPy solutions and adding 20 µL of the mixed solution to the HOPG substrate. Initially, we observe a difference in the amount of HOPG that is covered by organized adsorbed porphyrin molecules depending on the concentration of MeOPy and method of sample preparation. However, in the sequentially added solution case after sufficient equilibration time (~10 hrs) the results begin to match the results from the pre-mixed solution preparation method.

## MeOPy–CoOEP nearest neighbor distribution analysis

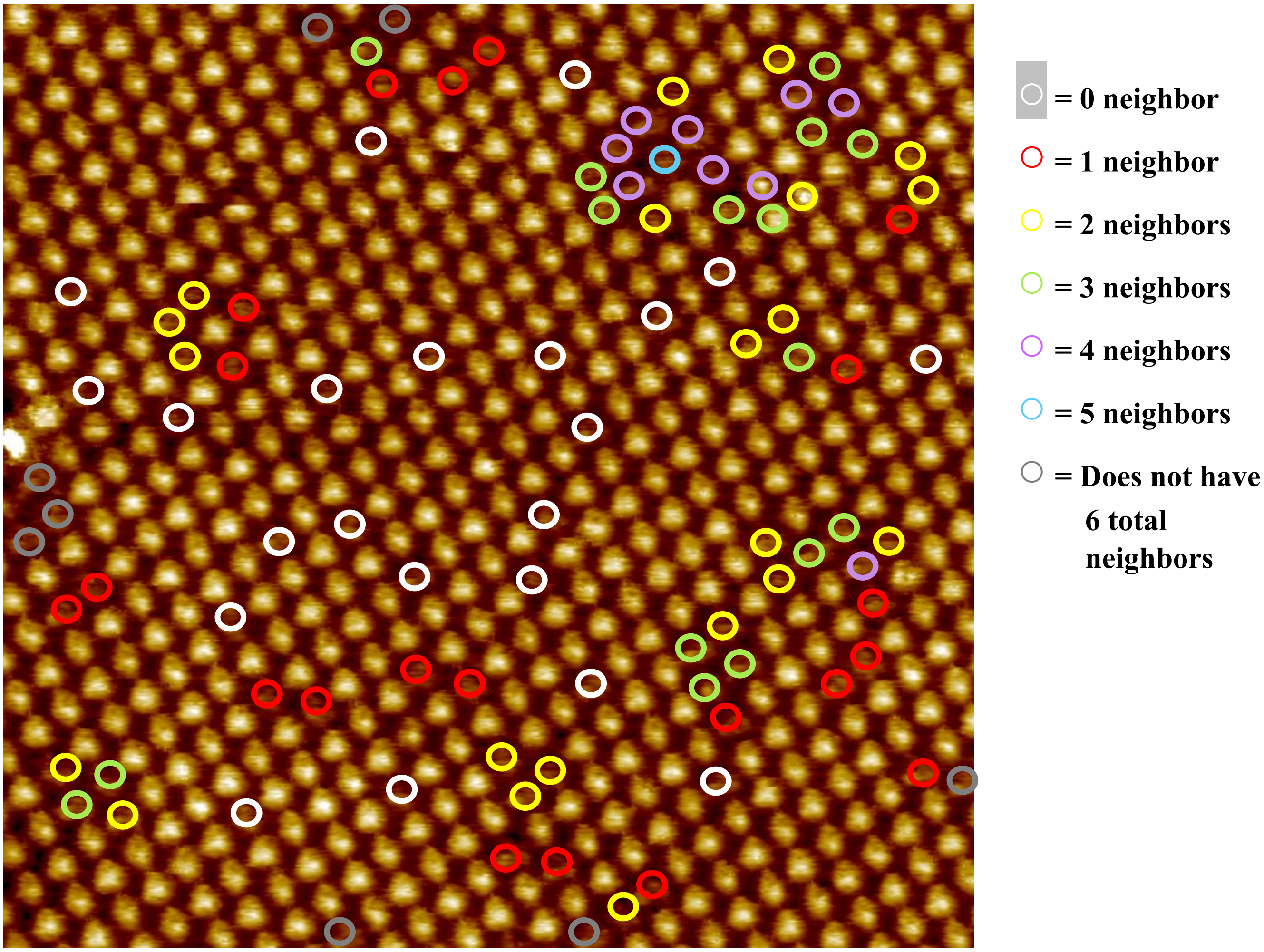

**Figure S6.** Representative STM image used for nearest neighbor distribution analysis, bias is +500 mV and setpoint is 20 pA. Image collected at 22° C and 500 μM MeOPy concentration in Ar atmosphere. Total porphyrin molecules in image is 610, total ligated porphyrin molecules (dark spots) in image is 95; therefore, $\theta$ is 15.6%. Circles denote all ligated porphyrins in the imaging area, and they are color coded based on number of adjacent ligated porphyrins. Each CoOEP has a total of 6 neighbors when incorporated into the monolayer. The molecules near the edges of the image that do not have 6 total visible neighbors are colored grey they are used in determining number of neighbors for any adjacent porphyrins that do have 6 visible neighbors, but are not, themselves, included in the analysis.

**Table S4.** Completed Nearest Neighbor Analysis for Representative STM Image

| **Counting type** | **Number of Ligated Neighbors** | | | | | | |
|---|---|---|---|---|---|---|---|
| | **0** | **1** | **2** | **3** | **4** | **5** | **6** |
| Experimental count | 21 | 19 | 21 | 16 | 9 | 1 | 0 |
| Experimental fraction | 0.24 | 0.22 | 0.24 | 0.18 | 0.10 | 0.01 | 0.00 |
| Random Fraction (θ=15.6%) | 0.36 | 0.40 | 0.18 | 0.05 | 0.01 | 0.00 | 0.00 |

## Nearest Neighbor Statistics

To investigate the correlation of the ligation of porphyrin molecules and their distribution within the monolayer statistical analysis in the style of Hulsken et al was undertaken.[8] In the case where all ligated porphyrins are randomly distributed throughout the monolayer, each porphyrin molecule has equal probability of complexing with MeOPy, and ligation events are independent of neighboring porphyrin molecules. Then at any given time the ligated porphyrins in the monolayer follow a binomial distribution. In general, the binomial distribution goes as:

$$f(n,k,p) = \binom{n}{k} p^{k}(1-p)^{n-k} \quad \text{c1}$$

$$\binom{n}{k} = \frac{n!}{k!(n-k)!} \quad \text{c2}$$

Where *n* is the number of independent trials, *k* is the number of successes, and *p* is the probability of success. The CoOEP monolayer has a pseudo-hexagonal lattice in which each porphyrin is surrounded by 6 nearest neighbors, so in this case $n$=6. The probability of success will be related to the fraction of ligated molecules, $p=\theta$, and the number of successes, $k$, will be the number of ligated nearest neighbors each porphyrin in the imaging area has. So, the chance of having $i$ ligated direct neighbors goes as:

$$f_i = \binom{6}{i} \theta^{i}(1-\theta)^{6-i} \quad \text{c3}$$

In Figure S6 and Table S4 analysis of one representative image is shown. To get Figure 11 in the main text a total of 12 individual STM images were used for a total of 3990 porphyrin molecules of which 630 were ligated to give an overall $\theta$ = 15.7%, this $\theta$ was used in determining the bars labeled random in Figure 11. The individual images had local $\theta$'s ranging from 14.1% to 16.8%.

## References

---

1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09 (Revision D.01), Gaussian, Inc., Wallingford CT, 2013.

2 G. Kresse and J. Furthmüller, *Phys. Rev. B.*, 1996, **54**, 11169−11186.

3 G. Kresse and D. Joubert, *Phys. Rev.,* 1999, **59**, 1758−1775.

4 M. Mammen, E. I. Shakhnovich, J. M. Deutch and G. M. Whitesides, *J. Org. Chem.*, 1998, **63**, 3821–3830.

5 J. B. Foresman and Æ Frisch, *Exploring Chemistry with Electronic Structure Methods*, *3rd edn.*, Gaussian, Inc.: Wallingford, CT, 2015.

6 S. Conti and M. Cecchini, *Phys. Chem. Chem. Phys.*, 2016, **18**, 31480–31493.

7 H. Tsukube, H. Furuta, A. Odani, Y. Takeda, Y. Kudo, Y. Inoue, Y. Liu, H. Sakamoto and K. Kimura, in *Comprehensive Supramolecular Chemistry, Volume 8: Physical Methods in Supramolecular Chemistry*, ed. J. E. D. Davies, and J. A. Ripmeester, Pergamon, Tarrytown, NY, 1st edn., 1996, vol. 8. pp. 425−441.

8 B. Hulsken, R. Van Hameren, J. W. Gerritsen, T. Khoury, P. Thordarson, M. J. Crossley, A. E. Rowan, R. J. M. Nolte, J. A. A. W. Elemans and S. Speller, *Nat. Nanotechnol.*, 2007, **2**, 285–289.