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Supplementary Information for

# Simple Lattice Model of Self-Assembling Metal-Organic Layers of Pyridyl-Substituted Porphyrins and Copper on Au(111) Surface

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**DFT calculations**

The energies of Cu-Py coordination ($w_{CB}$) were calculated using two software packages: Quantum Espresso – accounting for the Au (111) surface and Orca – in vacuum. Results of the calculations on the Au(111) surface are summarized in Table S1. To calculate the Cu-Py coordination energy in vacuum we used the geometries of the molecules obtained by their geometric optimization on the Au(111) surface. Further we just optimize the coordinates of the copper atom relative to the molecule (Table S2). To parametrize the lattice model, we used the value of $-90$ kJ/mol that is close to the average value of the $w_{CB}$ energy obtained in such way.

Table S1 – Results of the $w_{CB}$ energy calculations on Au(111) surface obtained from DFT-GGA/PBE calculations with dispersion correction DFT-D3.

| Energy, kJ/mol | P-4 | P-3 | P-$2_1$ | P-$2_2$ |
|---|---|---|---|---|
| Total Energy | -23047467 | -22877582 | -22707673 | -22707690 |
| Energy without one Cu | -22886501 | -22716606 | -22546693 | -22546707 |
| | -22886494 | -22716601 | -22546694 | -22546707 |
| | -22886497 | -22716606 | - | - |
| | -22886501 | - | - | - |
| Energy of Cu | -160572 | | | |
| Optimal adsorption energy of Cu | -298 | | | |
| Coordination energy $w_{CB}$ | -96 | -105 | -109 | -112 |
| | -102 | -110 | -109 | -112 |
| | -99 | -105 | - | - |
| | -96 | - | - | - |
| Average coordination energy $w_{CB}$ | -98 | -107 | -109 | -112 |

Table S2 – Results of the $w_{CB}$ energy calculations in vacuum obtained from DFT-GGA/PBE calculations with dispersion correction DFT-D3 and the basis set with valence triple-zeta polarization (def2-TZVP).

| Energy, kJ/mol | P-4 | P-3 | P-$2_1$ | P-$2_2$ |
|---|---|---|---|---|
| Total Energy | -22414933 | -18066269 | -13717631 | -13717635 |
| Energy without one Cu | -18108382 | -13759688 | -9411076 | -9411085 |
| | -18108381 | -13759697 | -9411076 | -9411085 |

| | | | | |
|---|---|---|---|---|
| | -18108381 | -13759713 | - | - |
| | -18108382 | - | - | - |
| Energy of Cu | -1640 | | | |
| Coordination energy $w_{CB}$ | -89 | -118 | -92 | -88 |
| | -90 | -110 | -92 | -88 |
| | -90 | -94 | - | - |
| | -89 | - | - | - |
| Average coordination energy $w_{CB}$ | -90 | -107 | -92 | -88 |

Figure S1 demonstrates the examples of the molecule-molecule interaction potentials calculated with DFT-GGA/PBE method using DFT-D3 dispersion correction and the basis set with valence triple-zeta polarization (def2-TZVP).

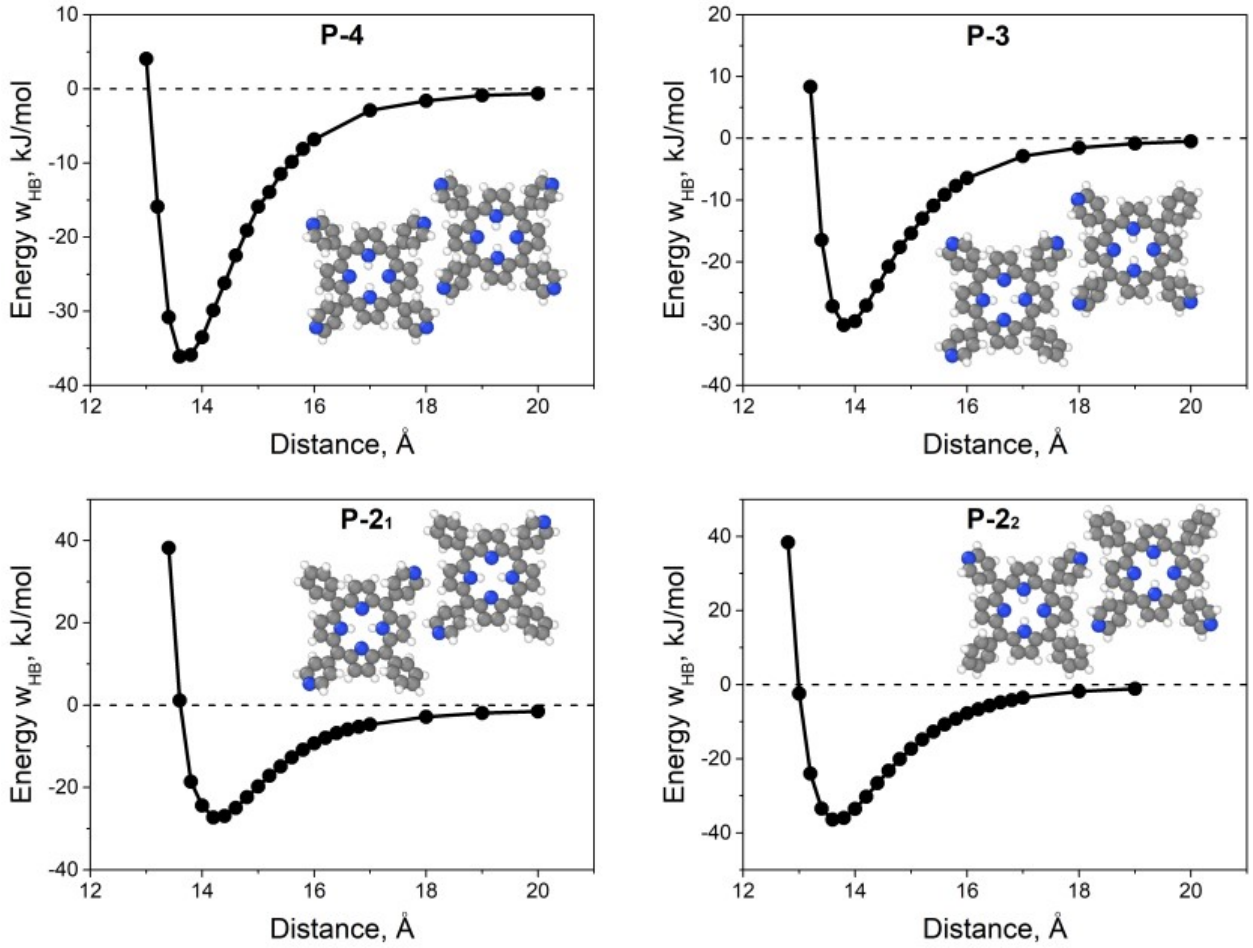


Figure S1 – Interaction energy between two molecules ($w_{HB}$) vs. Distance between the centers of mass of the molecules for some pair configurations shown in the inserts.

**Ground state analysis**

Based only on the experimental data, we have calculated the ground state phase diagrams of the SMONs lattice models differing by the number of pyridyl-groups in the porphyrin core (Figure S2). Here, we take into account that the considered molecules cannot adsorb into the 2D pores of the metal-organic network due to steric hindrances.

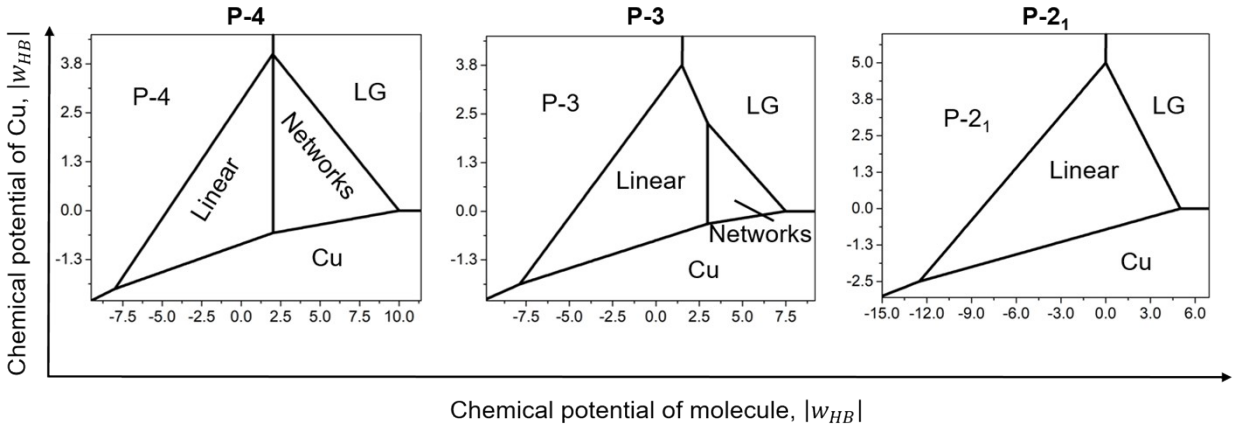


Figure S2 – Ground state $(\mu_{mol}, \mu_{Cu})$ phase diagrams ($RT/|w| = 0$) of the models accounting for only the experimentally observed SMONs based on P-4, P-3, P-$2_1$ pyridyl-substituted porphyrins and Cu atoms. The diagrams calculated at $w_{HB}/|w_{HB}| = -1$, $w_{CB}/|w_{HB}| = -2.5$.

Figure S3 presents the structures of pure organic layers comprising pyridyl-substituted porphyrins and the pure copper phase appearing in the ground state of the considered models.

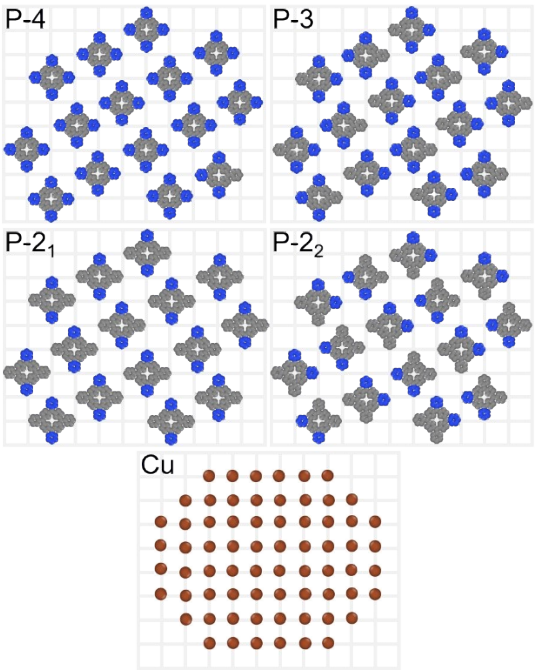


Figure S3 – Lattice models of the organic phases comprising the P-4, P-3, P-$2_2$ pyridyl-substituted porphyrins and copper phase. Functional groups are marked in blue.

**Monte Carlo simulation**

The structures of the ground state phase diagrams were verified by the Grand Canonical Monte Carlo simulations (GCMC). On the diagrams we have marked the $(\mu_{mol}, \mu_{Cu})$ points, where the simulation was performed (Figure S4). The colors indicate the phase we observed in this area of the diagram.

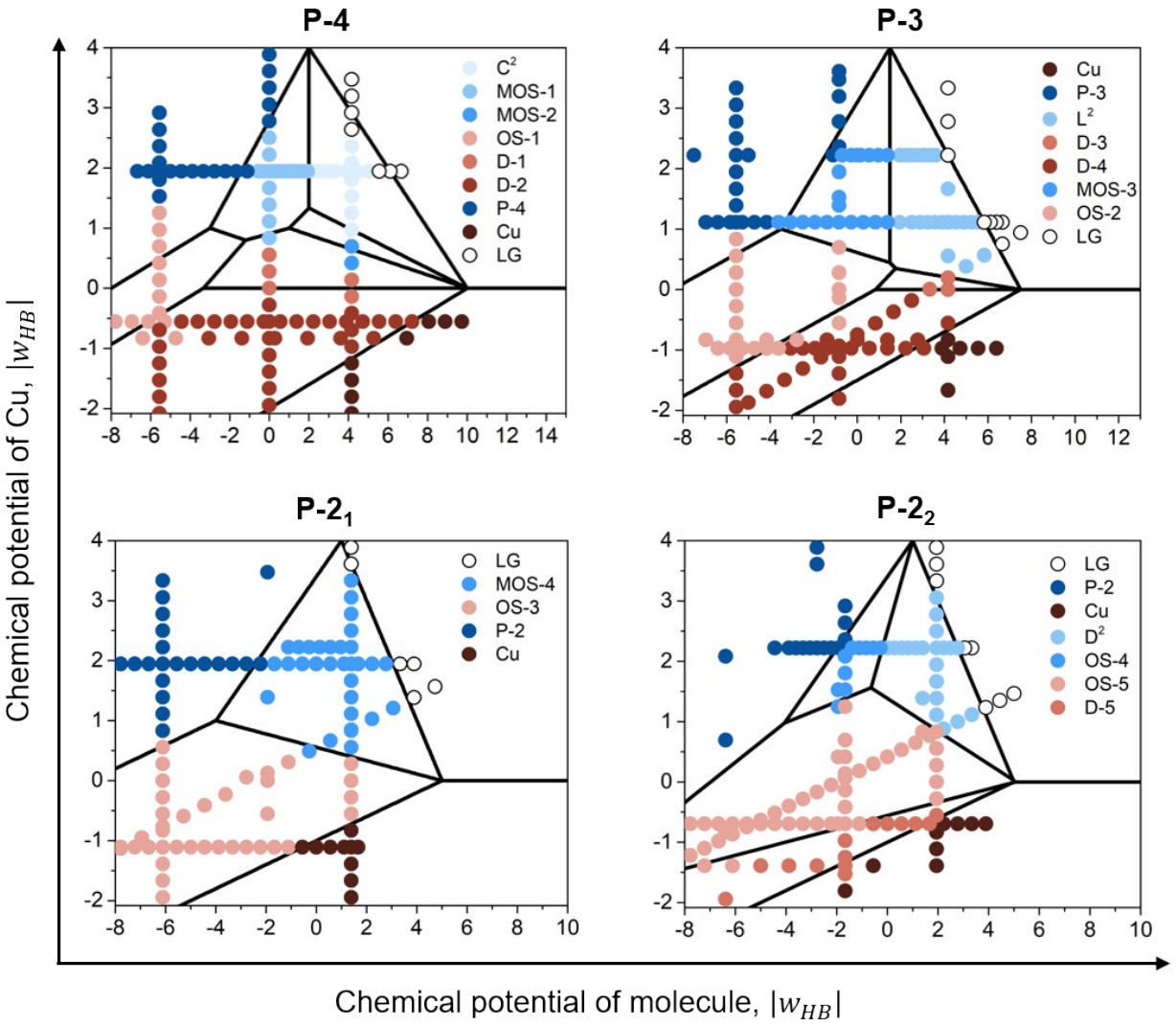


Figure S4 – $(\mu_{mol}, \mu_{Cu})$ phase diagrams ($RT/|w| = 0$) of lattice models of the SMONs based on P-4, P-3, P-$2_1$ pyridyl-substituted porphyrins and Cu atoms calculated at $w_{HB}/|w_{HB}| = -1$, $w_{CB}/|w_{HB}| = -2.5$. Colored symbols show the $(\mu_{mol}, \mu_{Cu})$ points at which we observed the phases in the GCMC simulation at $RT/|w_{HB}| = 0.07$.