# Electronic supplementary information (ESI) for:

## Pt-Dipyridyl Tetrazine metal-organic network on the Au(100) surface: Insights from first principles calculations

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#### **1** Pt—DT on the Au(100) surface

To survey the favorable registry of the Pt—DT chain with the reconstructed Au(100) surface, we use an  $8 \times 5 \times 5$  reconstructed Au(100) slab. The 9 different registries considered in this survey are shown in Figure S. 1. We found that their formation energies are very close to each other, with about 100 meV maximum variation between that the most favored (Figure S. 1a) and the least so (Figure S. 1i). We then increased the Au slab size to  $9 \times 5 \times 5$  to further separate the Pt—DT chain for the highest and lowest formation energy structures, reducing interaction between them. Analysis done and described in the manuscript are obtained these structures.



Figure S. 1 Pt-DT chain on  $(5\times1)$  reconstructed Au(100) surface considered in this work. Au atoms in the topmost layer is color code to highlight the reconstruction (the darker color is, the higher Au atoms is). Red, blue, black, and magenta circles represent Pt, N, C, and H, respectively. The green lines connect the Pt atoms to guide the difference between the structures.

### 2 Adsorption of DT on Au(100)

To find the absorption configuration of DT molecule on the reconstructed Au(100) surface, we placed DT molecule near the highest Au row, at a distance of about 3 Å, of a ( $8 \times 6 \times 5$ ) reconstructed Au(100) slab. Results of relaxations suggest that the binding energy of DT in the lowest energy configuration (Figure S. 2) is -1.90 eV. In this configuration, the tetrazine ring rotates so that two N atoms form bonds with surface Au atoms with N—Au bondlengths of ~2.48 Å.



Figure S. 2 The lowest energy configuration of DT on the reconstructed Au(100) surface. Yellow, blue, black, and magenta balls represent Au, N, C, and H atoms, respectively.

## **3** Pt monolayer on Au(100)

Results from experiments by Skomski *et al.*<sup>1</sup> suggest that Pt form atomistic layer on the reconstructed Au(100) surface. To mimics this structure, we prepared a slab with  $(1 \times 6 \times 1)$  Pt layer adsorbed on the reconstructed  $(1 \times 6 \times 5)$  Au(100) slab so that one Pt initially placed on the hollow sites near the lowest Au row, resulting two structures. After relaxation, the two structures converge to one which is shown in Figure S. 3. The average binding energy of one Pt atom is found to be - 5.45 eV.



Figure S. 3 Atomistic model of single layer Pt on the reconstructed Au(100) surface. The insert rectangular indicate the surface unitcell. Gray and yellow balls represent Pt and Au atoms, respectively.

#### **4** Oxidation number of Pt atoms

To determine approximately the oxidation number of Pt atoms in the Pt—DT chain on the Au(100) surface, we used Bader analysis<sup>2, 3</sup> to evaluate the charge states of the Pt atoms and compared them with charge states of Pt in platinum oxide ( $Pt_xO_y$ ) for which the oxidation number of Pt atoms is known. We obtained Pt oxide structures from Material Project<sup>4</sup> (two PtO, four PtO<sub>2</sub>, and two Pt<sub>3</sub>O<sub>4</sub> structures). As seen in Figure S. 4, charge of Pt atoms in Pt—DT chain on the reconstructed Au(100) surface is closest to that of PtO, suggesting that Pt atoms in Pt—DT have oxidation state of +2. Moreover, charge of Pt atoms in Pt monolayer on the reconstructed Au(100) surface is close to 0 (-0.06 e), suggesting that they have oxidation states of 0.



Figure S. 4. Charges of Pt atoms in some Pt oxide compounds evaluated using the same method described in the main text. The magenta line indicate charges of Pt atoms in Pt—DT chain on the reconstructed Au(100) surface.

#### **5** References

(1) Skomski, D.; Tempas, C. D.; Smith, K. A.; Tait, S. L. Redox-Active on-Surface Assembly of Metal-Organic Chains with Single-Site Pt(Ii). J. Am. Chem. Soc. **2014**, *136*, 9862-9865.

(2) Bader, R. F. W., *Atoms in Molecules: A Quantum Theory*. Oxford University Press: New York, 1994.

(3) Tang, W.; Sanville, E.; Henkelman, G. A Grid-Based Bader Analysis Algorithm without Lattice Bias. *J. Phys.: Condens. Matter* **2009**, *21*, 084204.

(4) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; et al. Commentary: The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. *Apl Mater* **2013**, *1*, 011002.