

## Electronic Supplementary Information

# Inspecting the nonbonding and antibonding orbitals in a surface-supported metal-organic framework

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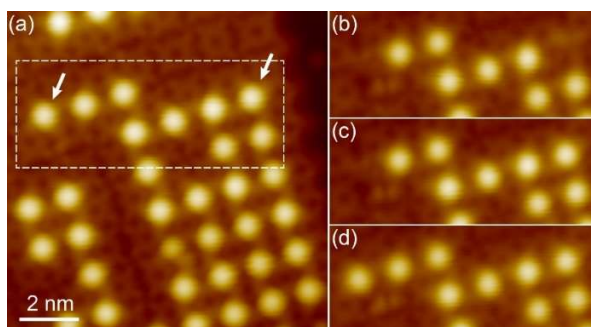
## Methods

All the experiments were carried out in a scanning tunnelling microscope (STM) system (Unisoku) at 4.9 K with a base pressure better than  $1 \times 10^{-10}$  mbar. The Au(111)/mica substrate was cleaned by cycles of Ar<sup>+</sup> sputtering and annealing. The 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) molecules were evaporated from a molecular beam evaporator (DODECON nanotechnology GmbH) at 640 K, and the Ni atoms were evaporated from an electron-beam evaporator (Scienta Omicron GmbH). The Au(111) substrate was held at room temperature during the deposition of TPyP molecules and Ni atoms, and was annealed at 373 K for 25 minutes to form Ni-TPyP frameworks. The  $dI/dV$  signals were acquired using a lock-in amplifier with a sinusoidal modulation of 1517 Hz at 10 mV.

The theoretical calculations were performed based on density functional theory (DFT) methods implemented in the Vienna *ab-initio* Simulation Package (VASP).<sup>1,2</sup> The exchange-correlation energy is in the form of Perdew-Burke-Ernzerhof (PBE) with the generalized gradient approximation (GGA).<sup>3</sup> A vacuum layer with thickness of 30 Å is used to minimize the interaction between the sample and its periodic images. The wave functions are expanded in plane waves up to a kinetic energy cutoff of 500 eV and a sum on a Monkhorst-Pack grid of  $10 \times 10 \times 10$  is used for integrals over the Brillouin zone.

## Manipulation of top-Ni atoms

The bright dots embedded in the Ni-TPyP network were vertically manipulated by the STM tip. As shown in Fig. S1, two bright dots, indicated by the arrows in Fig. S1(a), are first picked up by approaching the tip by 0.35 nm to the sample and applying a negative bias voltage of -2.2 V~-1.8 V [Fig. S1(b)], and then sequentially dropped to their original sites by approaching the tip by 0.4 nm to sample at a negative bias voltage of -1.0 V. Since each bright dot is manipulated as a whole, i.e., the bright dot cannot be separated during the manipulation, it is ascribed to one Ni atom sitting above the molecular plane (denoted as top-Ni). These results are reminiscent of the vertical manipulation of Fe atoms in the Fe-TPyP network with vertical dinuclear Fe centres.<sup>4</sup>



**Fig. S1** (a) STM image of Ni-TPyP network showing the top-Ni atoms and the underlying TPyP molecules (-1.0 V, 30 pA). (b-d) Sequential STM images of the dashed rectangle in (a) showing the vertical manipulation of top-Ni atoms (-1.0 V, 40 pA), (b) after picking up the two Ni atoms indicated by the arrows in (a), (c) after putting down the Ni atom on the right side, and (d) after putting down the Ni atom at the left side.

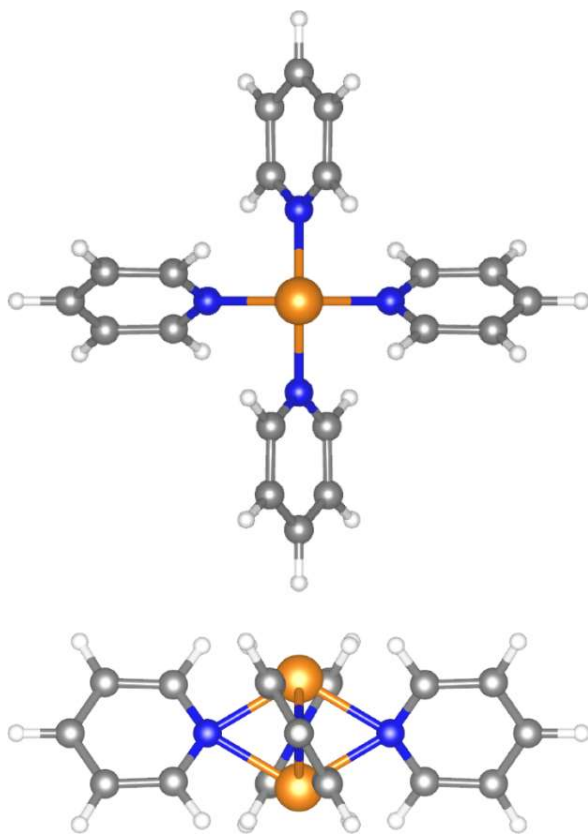
#### The representations of $\Gamma_\sigma$ in the $C_{4v}$ point group

$C_{4v}$	$E$	$2C_4$	$C_2$	$2\sigma_v$	$2\sigma_d$		
$A_1$	1	1	1	1	1	$z$	$x^2+y^2, z^2$
$A_2$	1	1	1	-1	-1	$R_z$	
$B_1$	1	-1	1	1	-1		$x^2-y^2$
$B_2$	1	-1	1	-1	1		$xy$
$E$	2	0	-2	0	0	$(x, y), (R_x, R_y)$	$(xz, yz)$
$\Gamma_\sigma$	4	0	0	2	0	$A_1+B_1+E$	

**Table S1** The character table of  $C_{4v}$  point group and the representations of  $\Gamma_\sigma$  in the  $C_{4v}$  point group.

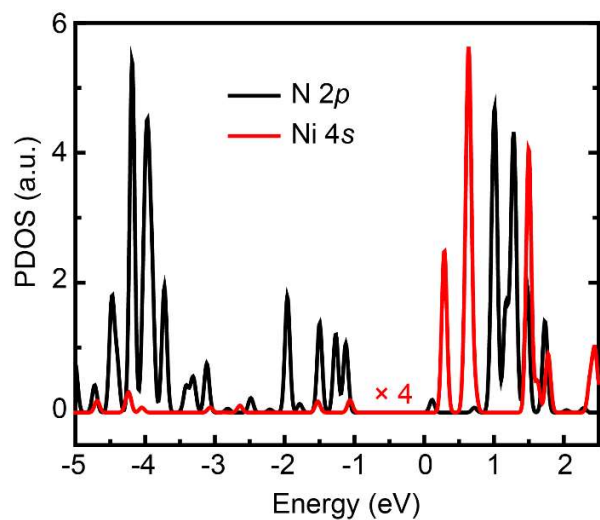
#### DFT optimized coordination structure

The coordination between dinuclear Ni centres and TPyP molecules is modelled by two vertically arranged Ni atoms coordinated to four pyridine molecules. In the initial structural model, the lateral distance between the Ni atom and N atom is determined from the period of the Ni-TPyP network and the optimized molecular structure in our previous work.<sup>5</sup> The dihedral angle of pyridyl rings with respect to the plane containing four N atoms is set to be 60°. All the H and Ni atoms are allowed to relax until the forces on each atom are less than 0.05 eV/Å, while the positions of the N and C atoms are fixed during relaxation. The top and side views of the DFT optimized coordination structure is shown in Fig. S2. In the optimized structure, the top-Ni atom lies in a ligand field with  $C_{4v}$  symmetry.



**Fig. S2** The top (up) and side (down) views of the DFT optimized coordination structure of a dinuclear Ni centre coordinated to four pyridine molecules (C, gray; H, white; N, blue; Ni, orange).

**The PDOS overlap between Ni 4s and N 2p orbitals**



**Fig. S3** Calculated PDOS of the 4s orbital of top-Ni atom and the 2p orbitals of the surrounding N atoms. The PDOS of the Ni 4s orbital is multiplied by 4 for clarity.

## References:

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