# Supplementary Information for: Electron-phonon coupling in engineered magnetic molecules $^{\dagger}$

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### **1** TPyP adsorption on Au(111) and the metalation of porous structures

TPyP self-assembly on Au(111) substrates yields a variety of structures that can be categorized in close-packed structures and porous structures. At room temperature substrate deposition the molecules self-assemble in close-packed structures predominantly with a square lattice but not always (see Fig. 1(a) in the main article). The schematic structure of the two arrangements of CoTPyP close-packed layers pictured in Fig. 1 and discussed in the main article is presented in FigS. 1. Upon subsequent annealing to around 250 °C the molecular structure undergoes a phase transformation and the molecules form porous structures having four-fold or six-fold symmetries.<sup>1</sup> An alternate way to create the porous structure is to perform the molecular deposition on substrates held at temperatures slightly above room temperature (see FigS. 2(a)). The six-fold symmetry structure, also known as the Kagome lattice, shows a preferential orientation of the pores along the <211> directions of the substrate. These porous structures were previously reported for similar molecules and their formation was explained through metal-ligand interactions, i.e., these structures are organo-metallic structures where metallic atoms coordinatively binds to the molecules.<sup>1.2</sup> In our present work the metal atoms that coordinate the molecules can only be Au atoms extracted from the surface, which explains the higher temperatures (increased mobility of surface atoms) needed for the formation of such networks.



FigS. 1 Schematic drawing of the CoTPyP close-packed molecular arrangements discussed in the main text and illustrated in Fig. 1(a).

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**FigS.** 2 (a) STM image (120 nm×80 nm, -1.5 V, 0.1 nA) of porous TPyP molecular assemblies on Au(111). The porous TPyP structures are obtained here by TPyP depositions at substrate temperatures above room temperature. (b) STM image (50 nm×50 nm, -1.5 V, 0.05 nA) taken after Co deposition of 0.09 ML at room temperature.

Contrary to the close-packed structures, the porous structures are easily affected by the impinging magnetic atoms. The Cr and Co atoms were electron-beam evaporated from a Co rod (99.9996%, Alfa Aesar) and Cr granules (99.999 %, Alfa Aesar), respectively. FigS. 2 (b) presents an STM images recorded after 0.09 ML Co deposition onto the porous TPyP layers pictured in FigS. 2 (a) kept at room temperature. The porous structures are destroyed and molecules are forming irregular structures. Subsequent annealing up to 250 ° for several hours failed to restore the previous molecular assemblies, indicating the formation of strong intermolecular bonds after Co interaction.

#### 2 Additional scanning tunnneling spectroscopy (STS) data for CoTPyP networks

FigS. 3 presents a schematic of the initial and final states in the tunneling mechanisms that give rise to the zero-bias (top panel) and the vibrational Kondo resonances (bottom panel) for single phonon interaction. Recent theoretical work<sup>3</sup> indicates that in the presence of electron-phonon interactions, in addition to the zero-bias Kondo resonance, multiple replica of the Kondo resonance are expected to appear shifted from the Fermi level by multiples of the phonon energy. This effect is observed only for the in-situ engineered CoTPyP molecules and discussed in detail in the article.

In general, the Kondo temperature varies exponentially with the spectral density of the conduction states ( $\rho$ ) and the exchange coupling (*J*) between the magnetic impurity and the conduction electrons as<sup>3</sup>

$$T_K = \exp(-1/\rho J). \tag{1}$$

The exchange coupling as a function of the hybridization potential,  $V_K$ , is defined as



**FigS. 3** Schematic drawing of the initial and final states in the tunneling mechanisms that give rise to the zero-bias (top panel) and the vibrational Kondo resonances (bottom panel) for single phonon interaction.

$$J = 2|V_K|^2/(\varepsilon_F - E_d), \tag{2}$$

where  $\varepsilon_F$  and  $E_d$  are the Fermi level and the energy of the localized level, respectively.

According to Ref. 3 the electron-phonon interactions ( $\lambda$ ) lead to a renormalization of the hybridization  $V_K$ , which depends on the electron-phonon coupling constant ( $\lambda$ ) and on the phonon frequency ( $\omega_0$ ) as shown below. Thus an increase in electronphonon interactions leads to a reduction of the  $T_K$ .

$$\frac{\tilde{V}_K}{V_K} = exp\left[-\frac{(\lambda/\omega_0)^2}{2}\right]$$
(3)

Consequently, the renormalized  $T_K$  is defined as

$$T_K \sim exp\left[-1/[2\rho|\tilde{V}_K|^2/(\varepsilon_F - \tilde{E}_d)]\right].$$
(4)

FigS. 4 ((a) and (b)) presents two instances of CoTPyP self-organization on Au(111). Panel (a) illustrates a square-like arrangement of CoTPyP molecules whereas panel (b) illustrates a small molecular island comprised of both CoTPyP and TPyP molecules. The dI/dV spectra measured at two locations on the Co-TPyP molecule as well as on its surroundings are presented in FigS. 4(c). The Kondo peak and its 80-mV spaced replicas are observed up to four-phonon frequencies at the center of the marked CoTPyP molecule. This suggests that Kondo replicas are measured in CoTPyP molecules independent of their arrangement or immediate surroundings. Note that a dip-like zero-bias feature is observed at the junction of the four molecules, i.e. on the protrusion, which we believe is a Co particle. More STS details of similar intermolecular junctions created after deposition of Cr

will be presented in the next section.



**FigS. 4** (a) High-resolution STM image (8 nm×8 nm, -1 V, 0.1 nA) of a small molecular island formed by four-fold pyridyl binding. (b) STM image (6 nm×6 nm, -0.3 V, 0.1 nA) of a small molecular island comprised of both magnetic and non-magnetic molecules. In addition, at the junction of four molecules there is a Co particle bridging the molecules. (c) dI/dV spectra taken at the locations marked in panel (b) (color coded). Spectroscopy set points: -1 V and 1 nA; 1 mV lock-in amplitude.

<b>Table 1</b> Selected vibrational modes and energies of CuTPP, ZnTPP and CoTPP from experimental data and theoretical calculations. The
results listed for CoTPP are in agreement with Fourier transform infrared spectroscopy results obtained from a CoTPP layer on Au(111) in
Ref. 4.

Molecule	$E_{exp}$ (meV)	$E_{th} (\mathrm{meV})$	band assignment	reference
CuTPP	153.5	153.9	59% ν $C_m C_{ph}$ ; 15% ν $C_\alpha N$	5
	153.1	153.9	78% νC <sub>α</sub> N; 14% νC <sub>α</sub> C <sub>β</sub>	
	157.3	154.9	$48\%  \mathrm{vC}_m \mathrm{C}_{ph}; 27\%  \mathrm{vC}_\alpha  \mathrm{N}$	
ZnTPP	153	153.1	$49 \% \nu C_m C_{ph}$	5
	155.2	154.9	85% vC <sub><math>\alpha</math></sub> N; 11% vC <sub><math>\alpha</math></sub> C <sub><math>\beta</math></sub>	
CoTPP	154.3	-	$\nu C_{\alpha} N$	6
	168.1	-	$\nu C_{\beta}H + \nu C_{\alpha}N$	
CoTPP	41.9	-	γ pyr swiv	7
	49.6	-	$vCo-N_{pyr}$	
	110.35	-	δpyr def	
	167.1	-	vpyr 1/2	

## 3 STS of metallic intermolecular junctions formed after Cr deposition

In general, metalation of the TPyP close-packed structures with either Cr or Co gives overall similar results on the Au(111) substrate. The molecules are successfully doped and metalation of the network happens at coverages exceeding one atom per molecule. Depending on the adatom coverage we observe different occupation of the hollow sites (intermolecular junctions) in the molecular structures. For instance, the occupation can vary from a single atom to three or more atoms. However, to be able to distinguish between different occupations of the hollow sites is not trivial. For this task we rely on high-resolution STM imaging with functionalized tips<sup>8</sup>, STS, and previous experimental work by Crommie *et al.*<sup>9</sup>.



**FigS. 5** (a) and (b) High-resolution STM images of CrTPyP molecular islands formed by four-fold pyridyl binding showing intermolecular junctions with different occupation. The junctions are labeled as I, II, and III as discussed in the text. Chemical structure of the molecule is superimposed for eye guidance. Image parameters are: 0.3 V, 0.2 nA for (a) and -0.3 V, 0.5 nA for (b). (c) dI/dV spectra measured at the center of CrTPyP and at the three junctions.

FigS. 5 presents two high-resolution images that illustrate three types of intermolecular junctions marked by I, II, and III obtained after Cr deposition of 0.05 ML. Chemical structure of the molecules is superimposed on the image for eye guidance. Apparent height analyses carried out using high-resolution STM images yield  $3.1 \pm 0.2$  Å,  $2.7 \pm 0.2$  Å and  $2.0 \pm 0.2$  Å for the heights of junctions III, II and for the CrTPyP molecules, respectively, when one uses a tunneling junction of few  $G\Omega$ . Note that at this Cr coverage the type I and II junctions are more predominant whereas the type III junctions are very few. The type I junction shows either a protrusion of similar height as the surrounding molecules (see FigS. 5 (b)) or just a hollow depending on the nature of the tip apex or on the tunneling parameters. Most often the single atom insertion at the intermolecular junction can go undetected in the STM images and therefore we believe that this type of junction is a single Cr atom bounded to four molecules as seen in Ref. 10. FigS. 5(c) displays representative spectra from each of these junctions measured for a small energy window around the Fermi level. The spectra measured at the center of a CrTPyP molecule is added for comparison. Zero bias (ZB) depressions are detected on two of these junctions, i.e junction I and III. The ZB features are fitted with Fano-line shapes<sup>11</sup> and the Kondo temperatures are  $76\pm10$  K, and  $133\pm11$  K for junction I and III, respectively, and  $105\pm15$  K for CrTPyP. Based on these analyses and on previous experimental work on Cr atoms, dimers and trimers<sup>9</sup> we propose that these three junctions are formed by Cr monomers, dimers and trimers bounded to four molecules. The fact that we do not detect a Kondo resonance on the medium height features, assigned here to Cr dimers, can be explained by the antiferromagnetically coupled atoms in the dimer forming a singlet state. A detailed description of the magnetic properties of Cr monomers, dimers and trimers adsorbed on Au(111) is presented in Ref. 9.

In conclusion, controlled addition of magnetic atoms (Cr and Co in this study) to the TPyP molecular structure has the potential to create magnetic networks with two types of magnetic centers. One type consists of magnetic molecules and the other consists of magnetic monomers or trimers. In the case of Cr metallation, the two magnetic particles interact differently with the underlying substrate giving rise to either peaks or dips in the local density of states of the particles.

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