Supplementary material of:

Electronic band structure of 1D π-d hybridized narrow-gap metal-organic polymers

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Experimental Techniques:

- Sample Preparation: For all experiments, the samples were prepared in-situ in UHV conditions. The single-crystalline Au(111), Au(788) substrates were prepared by repeated cycles of Ar⁺ sputtering and annealing. The 2,5-diamino-1,4-benzoquinonediimine (2H-QDI) molecules were sublimed from a tantalum pocket heated to 115°C. The chains were grown by co-deposition of precursor molecule with Co metal atoms from an electron-beam evaporator onto the Au substrates kept at 250°C.
- <u>LT-STM/STS:</u> All experiments were performed in commercial ultrahigh vacuum (UHV) low-temperature microscopes with combined STM/AFM capabilities (Specs-JT Kolibri: PtIr tip) at 4K. All STS data were acquired in constant height mode (open feedback loop) using the lock-in technique with a bias modulation amplitude of 10 mV, frequency f=723.1Hz and a magnetic field of B=0.5T. Prior to STS data acquisition, the tips were calibrated with reference to the Au(111) Shockley surface state.
- <u>ARPES</u>: ARPES measurements were performed with a lab-based experimental setup using a display-type hemispherical electron analyzer (SPECS Phoibos 150, energy/angle resolution of 40 meV/0.1°) combined with a monochromatized Helium I α (hv = 21.2 eV) source. Measurements were acquired with the sample at 200 K by moving the polar angle, which is set to be parallel to the average step direction (i.e. [$1\overline{10}$] direction).
- **XPS:** X-ray light (monochromatized Al K_{α}, hv=1486 eV) was produced from a Specs microfocus setup μ FOCUS600. The experimental resolution was determined to be 500 meV. Measurements were acquired with the sample at 200 K at 65° incidence and 40° emission angle. All energy positions are referred to the Fermi level measured at the same sample under the same experimental conditions.

Theoretical Calculations:

DFT Calculations: DFT calculations were carried out for the isolated chain in the periodic supercell approach with projector augmented wave potentials and a plane-wave basis set as implemented in VASP ^{1,2}. The atomic positions were set to those previously found by GGA+U (U= 5eV) calculations³, leaving 7 Å between replicas. The basis set was built with an energy cut-off of 280 eV and a 6 × 1 × 1 sampling of the first Brillouin zone⁴. The total energies were converged with a tolerance of 10⁻⁶eV.

Wavefunctions were calculated for the HSE03 hybrid functional^{5,6}, confirming the *S*= 3/2 ground state found by GGA+ U^3 . Subsequently, the eigenenergies were renormalized by the partially self-consistent *GW* method $(GW_0)^{7,8}$, where the Green function is updated by solving the Dyson equation and the screened Coulomb interaction is kept at the value given by DFT. Additionally, the possibility of further renormalization by interaction with the Au substrate was explored with an image potential model, as described in Ref.⁹. For this, the total potential of a Au(111) slab of 9 atomic planes was calculated with the PBE functional¹⁰. The final bandstructures were obtained by interpolation with 21 maximally localized Wannier functions (MLWF)^{11,12}, using projections on the Co(*d*), N(p_z) and C(p_z) orbitals, and three interstitial *s* additional functions in the aromatic ring. This interpolation scheme was applied to GGA+*U*, HSE03, and *GW*₀ bands for comparison (see Figure S9 in SI).

The effect of paramagnetism on the bandstructure was mimicked by superposing the bands for spin spirals along the chains with different wavevectors *q* taking values in Γ Y. For each *q* value the eigenenergies were approximated by interpolation of a non-collinear Hamiltonian *H*(*q*) in the MLWF basis, which was constructed by rotation of the original Hamiltonian. To do so, $i\sigma^{qR}$

with the MLWFs treated as spinors, we add a phase $e^{i\sigma \frac{1}{2}}$ to the σ = ±1 spin component of the functions corresponding to the Co(*d*) projections at position *R* in the chain.

- Surface Potential Model: We find that, upon van der Waals interaction with the Au substrate, the bands close to the Fermi level with in-plane and out-of-plane orbital characters undergo a slightly different renormalization. The energy difference is estimated to be of the order of a few tenths of eV using an image potential model for the substrate, which contributes a self-energy correction. Although the PBE functional fails to describe the Au(111) potential Coulomb tail at typical van der Waals adsorption heights ($z_{ad} \cong 3$ Å), we can extrapolate this behavior by matching it at a common slope point to the

$$V_{im}(z) = -\frac{1}{4(z-z_0)}$$

expression, as shown in SI Figure S10(a). For this surface, we find z_{im} = 0.93 Å. The correction of the ϵ_{nk} eigenergy (*n* is the band index and *k* the wavenumber) is given by⁹

$$\Delta \epsilon_{nk} = -Z_{nk} \int dz (\bar{\rho}_{nk}(z))^2 V_{im}(z)$$

where $\bar{\rho}_{nk}(z)$ is the plane-averaged density distribution of the eigenstate. The band with $Co(d_{xy})$ character has a narrow spread in *z* close to z_{ad} , while the ones with $N(p_z)$ show peaks $\cong 1$ Å above and below a nodal plane at z_{ad} . SI Figure S10(b) shows the densities at Γ for the five relevant bands below the Fermi level. The other source of a difference in the renormalization is in the spectral weight Z_{nk} that multiplies the GW_0 self-energy. It takes values $\cong 0.70$ and $\cong 0.75$ for $Co(d_{xy})$ and $N(p_z)$ states, respectively. For $z_{ad}=3$ Å, this analysis shows that the latter states will undergo a downshift 50 meV larger than the $Co(d_{xy})$ band.



Figure S1: Overview STM image of Co-QDI chains synthesized on Au(111) (STM parameters: V= 100 mV, I= 16 pA).



Figure S2: LEED pattern comparison between Co-QDI/Au(788) and the pristine Au(788). (a) Co-QDI/Au(788) LEED pattern obtained at 40 eV of the preparation shown in Figure 1(a) of the main text. (b) LEED pattern corresponding to the pristine Au(788) case prior to the Co-QDI deposition. Here only the substrate spots are visible, which appear splitted due to the herringbone reconstruction and step periodicity.



Figure S3: XPS survey (monochromized Al K_{α}) spectra of 2H-QDI and Co-QDI on the Au(788). One mainly observes the strong substrate emissions from Au. The important transitions of the molecules and the chains are marked by small rectangles. Note the background slope from the Au emissions for the molecular core levels.



Figure S4: XPS spectra fitting for C 1s and N 1s core level peaks for Co-QDI and 2H-QDI depositions on Au(788). For 2H-QDI deposition, the sample was held at room temperature. (top) Original XPS spectra. (middle) Co-QDI peak fits. For the C 1s core level two Doniaj-Sunic lines of identical width, asymmetry and backround have been used for C-C and C-N emissions. The relation from the fit resulted in C-C: C-N =1:2.08, very close to the 1:2 amount of the atom sites. The N 1s spectra of the peak fit was Au 4d background subtracted. Here a single peak for the N-Co site was used. (bottom) 2H-QDI peak fits. One notes in both, C 1s and N 1s that the theoretical 1:1 mix of NH₂:NH is not fulfilled. We interpret the N 1s peak fit results as an uptake of additional H⁺ leading to a conversion of one or even both NH sites to NH₂. This possibility was already discussed in ref.¹³. Peak intensity relation from the fit is NH₂:NH=4:1. The proton uptake leads to a charge uptake that affects the C 1s emission that was now fitted with three identical peaks (width, asymmetry, background) for C-C, C-C+, and C-N emissions. The relation of the peak integrals from the fit was 0.26:0.74:1.97.



Figure S5: High-resolution LEED pattern obtained at 50 eV corresponding to a similar Co-QDI/Au(788) preparation to the one shown in Fig. 1 of the main manuscript. From the LEED pattern we can extract information from the Au(788) substrate (i.e., herringbone and step periodicities) as well as from the Co-QDI chains (i.e., their unit cell). This confirms the 1D MO chain formation.



Figure S6: High-resolution LEED pattern obtained at 25 eV and 40 eV and STM image (V=1.3 V and I = 300 pA) corresponding to the Co-QDI/Au(788) preparation in a higher coverage regime. The loss of chain alignment is evident by the attenuation of the chain diffraction in LEED as well as in STM images where the chains start to grow along directions perpendicular to the steps.



Figure S7: ARPES band structure of the pristine Au(788) and Co-QDI/Au(788). The second derivative treatment of the data is shown for both cases. (a-d) ARPES band structure measurements of the pristine Au(788) crystal. (b) ARPES band structure ($E vs k_y$) obtained in the direction parallel to the steps (k_x integrated = -0.15 ± 0.08 Å⁻¹). The well-known Shockley surface state at Γ and the highly-dispersive sp-bands crossing the Fermi level at ~1.1 Å⁻¹ can be seen. (a, c) Band structure ($E vs k_x$) obtained at $k_y = 0$ Å⁻¹ and 1.63 Å⁻¹. (d) Constant energy surfaces ($k_x vs k_y$, extracted at -0.8 eV and -1.3 eV). (e-h) Band structure of Co-QDI chains on Au(788). (f) ARPES band structure ($E vs k_y$) of the Co-QDI chains parallel to the direction of the chains and steps ($k_x integrated = -0.15 \pm 0.08$ Å⁻¹). A combination of weakly dispersive and dispersive bands becomes clear. (e, g) Band structure ($E vs k_x$) obtained at $k_y = 0$ Å⁻¹ and 1.63 Å⁻¹. (h) Constant energy cuts ($k_x vs k_y$) extracted at the bottom of the dispersive band (-0.8 eV) and second nearly-flat band (-1.3 eV). Their one-dimensional character becomes evident due to their non-dispersive features along k_x . The second derivative of the intensity is shown in a linear color scale (highest intensity being red). ARPES parameters: hv = 21.2 eV, T_{sample} = 200K.



Figure S8: ARPES band structure of the pristine Au(788) and Co-QDI/Au(788) (in raw data). (a-d) ARPES band structure measurements of the pristine Au(788) crystal. (b) ARPES band structure (*E* vs k_y) obtained in the direction parallel to the steps (k_x integrated = -0.15 ± 0.08 Å⁻¹). The well-known Shockley surface state at Γ and the highly-dispersive sp-bands crossing the Fermi level at ~1.1 Å⁻¹ can be seen. (a, c) Band structure (*E* vs k_x) obtained at k_y = 0 Å⁻¹ and 1.63 Å⁻¹. (d) Constant energy surfaces (k_x vs k_y , extracted at -0.8 eV and -1.3 eV). (e-h) Band structure of Co-QDI chains on Au(788). (f) ARPES band structure (*E* vs k_y) of the Co-QDI chains parallel to the direction of the chains and steps (k_x integrated = -0.15 ± 0.08 Å⁻¹). (e, g) Band structure (*E* vs k_x) obtained at k_y = 0 Å⁻¹ and 1.63 Å⁻¹. (h) Constant energy cuts (k_x vs k_y) extracted at the bottom of the dispersive band (-0.8 eV) and second nearly-flat band (-1.3 eV). ARPES parameters: hv= 21.2 eV, T_{sample}= 200K.



Figure S9: DFT bandstructure of the high-spin Co-QDI chain calculated by three different methods and interpolated with MLWFs: (a,b) GGA+U (U=5 eV), (c,d) HSE03 and (e,f) GW₀. Top and bottom panels highlight the states with predominant (a,c,e) Co(d_{xy}) or (b,d,f) N(p_z) orbital character. Red (blue) curves indicate majority (minority) spin. The Fermi level has been set in the middle of the gap in each case.



Figure S10: (a) The dotted curve shows the planar average of the total potential of a 9-layer Au(111) slab (i.e., sum of electrostatic and exchange and correlation terms) calculated with the PBE functional. The topmost atomic plane lies at z=0 Å. The green curve is a Coulomb image potential, where the common slope condition yields z_{im} =0.93 Å. (b) Planar average of the charge distributions of the five GW₀ states at Γ below the Fermi level. The solid line, peaked at the adsorbate height (z_{ad}), is the Co(d_{xy}) state and the double-peaked dashed lines are the N(p_z) ones. Red (blue) color indicates majority (minority) spin.



Figure S11: Model of the effect of Co spin disorder on the GW₀ bands. Panels (a,b) show the bundles of Wannier-interpolated bands after applying a superperiodic rotation to the MLWF spinors with wavectors *q* taking values in Γ Y. Panels (c,d) reproduce the data in a spectral-intensity format. In the top panels, the eigenenergies directly obtained from diagonalization of the H(*q*) hamiltonian are surperposed, i.e., the Fermi level of H(*q*=0) is used for all the spirals. In the bottom panels, the energy of the highest occupied state of each H(*q*) is set to zero, i.e. each spiral is added to the average with its own Fermi level. In panels (e,f), the contribution of states with weight on Co(d_{xv}) is singled out. The same for N(p_z) states in panels (g,h).



Figure S12: dl/dV map of a Co-QDI chain of the onset of the valence band (VB) at V = -0.37V.

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