Many-body transitions in a single molecule visualized by scanning tunnelling microscopy

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I. DETAILED RESULTS OF THE TDDFT CALCULATIONS

The many-body (MB) excited states \( |\Psi_k^{N(+1)}\rangle \) for the neutral (negatively charged) CoPC\(^0\) (CoPC\(^-1\)) are calculated using time-dependent density functional theory (TDDFT) and composed into single-particle (SP) excitations of the molecule’s ground state (GS) \( |\Psi_0^{N(+1)}\rangle \) by projecting them onto a chosen set of SP orbitals (here, the Kohn-Sham orbitals of neutral CoPC), i.e.

\[
|\Psi_k^{N(+1)}\rangle = c_{\text{virt}}^\dagger c_{\text{init}} |\Psi_0^{N(+1)}\rangle
\]

where \( c_{\text{virt}}^\dagger \) (\( c_{\text{init}} \)) is the electron creation (annihilation) operator. Supplementary Table 1 gives the excitation energies, as well as the dominant contributions upon projection onto the SP orbitals, of the first four (five) MB excited states of CoPC\(^0\) (CoPC\(^-1\)), calculated by TDDFT using the PBE functional\(^1\).

The local density of states (LDOS) measured in scanning tunneling spectroscopy (STS) is then given by the diagonal element of the many-body spectral function as

\[
A(\nu, E) = 2\pi \sum_k \left| \langle \Psi_k^{N+1} | c_\nu^\dagger | \Psi_0^N \rangle \right|^2 \delta(E - E_k^{N+1} + E_0^N)
\]

on the creation side of the spectrum (positive sample bias) and as

\[
A(\nu, E) = 2\pi \sum_k \left| \langle \Psi_k^N | c_\nu | \Psi_0^{N+1} \rangle \right|^2 \delta(E - E_k^N + E_0^{N+1})
\]

on the annihilation side of the spectrum (negative sample bias). Here, \( E \) denotes the energy of the states involved and \( \nu \) is an index referring to the SP basis used. In order to observe the transitions into the MB excited states in STS, the excited state must be obtainable by injecting (removing) a single electron into (from) the ground state of the neutral (negatively charged) CoPC.

For the excited states of CoPC\(^0\), i.e. the removal of an electron from CoPC\(^-1\) at negative bias, the first three MB excited states \( |\Psi_1^N\rangle, |\Psi_2^N\rangle, |\Psi_3^N\rangle \) can be reached simply by tunneling out of either the HOMO-2, HOMO-1 or HOMO-3. The fourth excited state \( |\Psi_4^N\rangle \) has two main contributions, which contain an additional electron in the LUMO+1/ LUMO+2. For the tunneling event to end up in this state, there should also be a second excitation, i.e. the tunneling electron would be removed from the LUMO and a simultaneous transition from the HOMO/HOMO-1 to the LUMO+1/LUMO+2 should occur. Since this presents
a second order tunneling process, its probability should be much smaller than for the first three excited states and thus, it is not expected to be observed in STS.

In case of electron injection into CoPC\(^0\) at positive bias, i.e. transitions into the excited states of CoPC\(^-1\), the first, third and fourth MB excited state \(|\Psi_{1+}^{N+1}\rangle, |\Psi_{3+}^{N+1}\rangle, |\Psi_{5+}^{N+1}\rangle\) all correspond to second order tunneling processes, i.e. in addition to the occupation of the LUMO, a simultaneous transition from the HOMO-2 or HOMO-1 into the LUMO+1 would be necessary to end up in this state. These cases are similar as for \(|\Psi_{4}^{N}\rangle\) and thus, these transitions should not occur in our STS experiments. The situation is different for the second and fifth excited state \(|\Psi_{2}^{N+1}\rangle, |\Psi_{5}^{N+1}\rangle\); their dominant contribution can be reached by simply tunneling into the LUMO+1 of the neutral molecule and therefore can be observed in STS. The transitions from CoPC\(^0\) to CoPC\(^-1\) and vice versa including the MB excitations are summarized in Supplementary Figure 2.

**Supplementary Figure 1.** Transitions from CoPC\(^0\) to CoPC\(^-1\) and vice versa taking MB excited states into account. The schematic indicates only the dominant contributions for the MB excited states upon projection onto the Kohn-Sham orbitals of neutral CoPC. The dashed vertical line marks filling up to charge neutrality. Dashed arrows indicate transitions which are not expected to be observable in STS, as the corresponding MB excited states, marked as semi-transparent, represent second-order tunneling processes.
**Supplementary Table 1.** Excited states for CoPC\(^0\). Energies are given with respect to the ground state.

<table>
<thead>
<tr>
<th>Exc. state</th>
<th>Orbitals</th>
<th>Weight</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(</td>
<td>\Psi^N_1\rangle)</td>
<td>HOMO-2 LUMO</td>
<td>0.985</td>
</tr>
<tr>
<td>(</td>
<td>\Psi^N_2\rangle)</td>
<td>HOMO-1 LUMO</td>
<td>1.000</td>
</tr>
<tr>
<td>(</td>
<td>\Psi^N_3\rangle)</td>
<td>HOMO-3 LUMO</td>
<td>0.988</td>
</tr>
<tr>
<td>(</td>
<td>\Psi^N_4\rangle)</td>
<td>HOMO LUMO+1</td>
<td>0.521</td>
</tr>
<tr>
<td>(</td>
<td>\Psi^N_5\rangle)</td>
<td>HOMO-1 LUMO+2</td>
<td>0.476</td>
</tr>
</tbody>
</table>

**Supplementary Table 2.** Excited states for CoPC\(^{-1}\). Energies are given with respect to the ground state.

<table>
<thead>
<tr>
<th>Exc. state</th>
<th>Orbitals</th>
<th>Weight</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(</td>
<td>\Psi^{N+1}_1\rangle)</td>
<td>HOMO-2 LUMO+1</td>
<td>0.982</td>
</tr>
<tr>
<td>(</td>
<td>\Psi^{N+1}_2\rangle)</td>
<td>LUMO LUMO+1</td>
<td>0.997</td>
</tr>
<tr>
<td>(</td>
<td>\Psi^{N+1}_3\rangle)</td>
<td>HOMO-2 LUMO+1</td>
<td>0.991</td>
</tr>
<tr>
<td>(</td>
<td>\Psi^{N+1}_4\rangle)</td>
<td>HOMO-1 LUMO+1</td>
<td>0.984</td>
</tr>
<tr>
<td>(</td>
<td>\Psi^{N+1}_5\rangle)</td>
<td>LUMO LUMO+1</td>
<td>0.994</td>
</tr>
</tbody>
</table>

**II. COMPARISON BETWEEN DFT AND TDDFT**

Many STM experiments studying the electronic properties of molecules on surfaces focus on the frontier molecular orbitals, i.e. the first resonance below and above the Fermi level. These constitute usually transitions between neutral and singly-charged ground states of the molecule, where re-ordering of the HOMO and LUMO orbitals involved in the tunneling events is unlikely to occur. The MB effects would then result in only slight distortions of the SP wave functions\(^2\), which would be very difficult to detect experimentally. Thus, consideration of the standard Kohn-Sham picture is usually sufficient.

Going beyond the frontier resonances in STS and probing transitions into excited states of the molecule, MB effects in principle always play a role. This is due to the strong confinement...
of the electrons, which increases the significance of electron-electron interactions on the electronic properties. However, their impact, i.e. how much the resulting MB transitions deviate from the SP picture, will depend on the molecule under study. Toroz et al.\(^3\) noted that the energy-spacing of the different orbitals plays a role, as correlation effects are favoured for electronic states closer in energy.

As we demonstrate in our manuscript, identification and quantification of these effects experimentally requires spatial mapping of the transitions (i.e. the involved orbitals), as the transitions energies alone might not be sufficient to unambiguously identify MB states. In addition, our study shows that these MB transitions that are an intrinsic property of the molecule persist if the molecule adsorbs on a surface. This holds at least as long as the general electronic structure is preserved by use of e.g. an ultrathin insulating layer to electrically isolate the molecule from the substrate. It is important to note that our conclusions also apply to other systems characterized by strong electron confinement, such as nanoclusters (so-called artificial atoms or molecules)\(^4\), where mixing of SP transitions due to MB effects has been predicted by TDDFT as well\(^5,6\).

Orbital re-ordering due to a change in the charge state is to some extent also captured in standard DFT, as it treats many-body effects in a mean-field approach. Thus, for the measurements on the negatively charged CoPC\(^-1\), an alternative approach would be to compare with the orbital order calculated from DFT for the anionic ground state of the molecule. Indeed, those calculations yield an orbital order different from the neutral ground state, but it also differs from the order of the TDDFT calculations. In terms of the SP wave functions of the neutral ground state, the anionic ground state gives the order (occupied DOS, in decreasing order) LUMO, HOMO-2. HOMO-3, and HOMO/HOMO-1, while the TDDFT transitions give LUMO, HOMO-2, HOMO-1, HOMO-3, i.e. the second and third resonance below the LUMO are swapped. For the anionic ground state, these two are very close in energy to each other (difference less than 30 meV), and the simulated LDOS map at the peak energy is dominated by the HOMO/HOMO-1. However, even when measuring the dI/dV map at the rising edge of the experimental resonance \(A_4\), we did not find any indication of the HOMO-3 orbital predicted by DFT. Instead, when comparing the experiments for both charge states of CoPC with the different simulations, it is clear that the MB transitions from TDDFT yield overall a better agreement than the individual ground state calculations of either the neutral or anionic GS.
While we do not currently have a quantitative explanation for the difference between the experimental energies and those calculated energies by TDDFT, the orbital energies are not always reproduced faithfully in DFT. In particular in the case of transition metal complexes, there is a problem of correctly describing the C-Co bond lengths and strengths. The usual hybrid functionals of choice for small molecules (e.g. B3LYP) do not do so well in describing these bonds, and the pure exchange-correlation functionals (e.g. BP86 or PBE) give results that better match the experimental values (see, e.g. ref\textsuperscript{7}). We have shown earlier that PBE reproduces the correct orbital order for neutral CoPC\textsuperscript{8} in contrast to the hybrid functional PBE0 (or B3LYP). The fact that the energy difference between the first and second excited state for spectra on CoPC\textsuperscript{−1} (Supplementary Figure 2 b) is better reproduced with the ground-state DFT than the TDDFT calculations is most likely due to the limited accuracy arising from the present approximation to the exchange-correlation functional, thus the exchange-correlation potential (DFT, TDDFT) and kernel (TDDFT). This work therefore adds to the database of test cases for future approaches addressing the approximations to the exchange-correlation term.

Finally, from the theoretical point of view, DFT is a reliable tool for ground state properties but TDDFT is a more accurate method for the excited states needed here for the many-body calculation of the STS spectra.

III. COMPARISON BETWEEN EXPERIMENTAL STS AND SIMULATED STS FROM DFT AND TDDFT

In Supplementary Figure 3 we show the experimental point spectra and MB-based simulated spectra already presented in the main manuscript in Figure 3 and 4, along with the simulated spectra based on the different ground states of CoPC from standard DFT. For CoPC\textsuperscript{−1} (Supplementary Figure 3a and b), the variations in the relative peak intensities of resonance A3 and A4 is captured well by TDDFT and the GS calculation for the negatively charged CoPC\textsuperscript{−1}, while the GS calculation for the neutral CoPC\textsuperscript{0} shows in fact the reverse trend. The ground state DFT for CoPC\textsuperscript{0} shows only one peak above in the LUMO within a large energy range, while the MB-derived STS gives a reasonable explanation for the unusual large intensity of N1\textit{uv} via the two close-lying MB transitions.
Supplementary Figure 2. Comparison of the predicted orbital order between DFT for differently charged ground states, MB excited states from TDDFT and experiment. (a) Simulated DOS and LDOS maps for the MB transitions and the neutral ground state of CoPC, along with experimentally measured dI/dV maps. (b) Simulated DOS and LDOS maps for the MB transitions and the neutral and anionic ground state of CoPC, along with experimentally measured dI/dV maps. The maps were simulated using the same parameters as for the ones shown in the main manuscript in Figure 3d and Figure 4c, i.e. using a broadening of 30 meV. The orbital maps shown in addition for the anionic ground state correspond to the LDOS of the individual orbital without any broadening.

IV. VARIATIONS IN THE PEAK ENERGIES FOR DIFFERENT MOLECULES

The negatively charged CoPC\textsuperscript{−1} molecule shown in the main manuscript in Figure 3 displays some deviation from the perfect fourfold symmetry of the chemical structure, with one of its four lobes showing increased intensity in the dI/dV maps in Figure 3c. This is simply related to the molecule adsorbing off-centre in the pore of the h-BN moiré\textsuperscript{9}, resulting in a slight tilt of the molecule, which can be also seen from the constant-current STM image in Figure 3d. In the constant-height dI/dV maps, such a tilt causes a variation in the tip-sample distance for the different lobes, and thus a higher intensity on one of them. Below in Supplementary Figure 4a and b, we show data on another negatively charged molecule that has a more planar adsorption geometry. As can be seen, the important aspects of the molecule’s electronic structure is essentially the same as for the molecule presented in the main manuscript, i.e. the tilting does not play a role in the interpretation of our results.
**Supplementary Figure 3.** Comparison between experimental dI/dV spectra and simulated STS from DFT and TDDFT. (a) The experimental dI/dV point spectra for CoPC$^{-1}$ as shown in the main manuscript in Figure 3a. (b) Simulated STS based on the ground state of neutral and anionic CoPC from DFT (solid and dotted lines) and on the MB excited states from TDDFT (dashed line). (c), (d) Same for CoPC$^0$. (e) STM topography and overlaid structural model of CoPC indicating the positions of the experimental and simulated point spectra. Shown is the negatively charged molecule from Figure 3d in the main manuscript.

**Supplementary Figure 4.** dI/dV measurements on a second set of molecules. (a), (b) Point spectra (a) and corresponding maps (b) for a second negatively charged CoPC. (c), (d) Same for a second neutral CoPC.

The exact adsorption position only affects the position of all the molecular resonances through the work function of the substrate, which is continuously modulated by the moiré pattern (the molecular resonances are pinned to the vacuum level of the substrate system)$^9,^{10}$. 
Note that all h-BN pores are not equal as h-BN/Ir(111) is actually an incommensurate structure. Except for the slight changes in the energies of the resonances (up to 100 - 200 mV), the basic features and their order do not change between different molecules. This is also demonstrated in Supplementary Figure 4c and d, which shows a second set of measurements for another neutral molecule. For both molecules presented in Supplementary Figure 4, CoPC0 and CoPC−1, the overall characteristics of the spectra and the symmetry of LDOS maps are identical to those presented in the main manuscript in Figure 3 and 4, except for the slight changes in the energies of the resonances.

It is important to note that despite the fact that CoPC on h-BN/Ir(111) forms a double-barrier-tunneling junction, the fraction of the bias that drops between the molecule and the substrate is only very small. This is demonstrated in Supplementary Figure 5a, where we plot some example spectra of the LUMO resonance of fluorinated CoPC (F16CoPC) adsorbed on a wire, measured at different tip-sample distances. F16CoPC has a very similar electronic structure compared to CoPC and the depicted resonance corresponds to the N2 resonance of CoPC. As the tip-sample distance is decreased, the peaks shift to higher bias corresponding to the usual case in a double barrier-tunnel junction where occupied (unoccupied) levels are probed at negative (positive) bias. This corresponds to the tip Fermi level aligning with the molecular resonances. The full data set (false-color plot in Supplementary Figure 5b) allows us to estimate the bias drop over the h-BN layer. The peaks shift by ca. 50 mV as the tip is moved in by 3 Å, i.e. 7 % bias drops between molecule and substrate at closest approach. The shifts are small and at the set-points corresponding to the spectra in the paper (corresponding roughly to a vertical approach of 1 Å in Supplementary Figure 5b), this effect is negligible.

V. DIFFERENCES BETWEEN EXPERIMENTAL AND SIMULATED LDOS MAPS

The experimental dI/dV maps of resonances A3 and A4 presented in the main manuscript in Figure 3c show larger intensity on the central cobalt ion than predicted by the simulated LDOS maps. There are two main reasons for this: Partially, this is due to the vibronic replica of the resonances, which are not included in the simulation and partly overlap with the elastic transitions, which is in particular the case for resonance A3.
Supplementary Figure 5. $dI/dV$ measurements on a second set of molecules. (a), (b) Point spectra (a) and corresponding maps (b) for a second negatively charged CoPC. (c), (d) Same for a second neutral CoPC.

Supplementary Figure 6. LDOS maps for different simulation parameters. The broadening refers to the width of the resonances in energy space, and the distance in the plane above the molecule at which the square of the wavefunction is evaluated.

The other relevant factor is that different orbitals decay differently into the vacuum and the DFT calculations are evaluated at a smaller tip height than the experimental results. This is due to the technical limitations of extending the basis sets far outside the molecular plane. The figure below shows how the relative intensities of the theoretical $dI/dV$ signal on the carbon backbone and on the central ion change with the simulation parameters, while the overall symmetry remains unaltered. In general, the orbitals localized on the central
metal atom decay more slowly than the delocalized \( \pi \) orbitals. Hence, at larger tip-sample distances, there is more intensity on the central part of the molecule. The experimental tip-sample distance is difficult to quantify, but is likely to be of the order of 7 Å. In addition, the theoretical maps in the manuscript were simulated using the same parameters as for the theoretical spectra, for reasons of consistency. The experimental maps were recorded in an open-feedback configuration, while for the point spectra the feedback loop was closed when moving from one point to the other. Hence, differences in the absolute tip-molecule distance between point spectra and maps can be expected, but are difficult to quantify.

Finally, the N1 and N1v resonances in the main manuscript in Figure 4c have different symmetries in the \( dI/dV \) images, which should not occur for the simple vibronic replica. There are a couple of plausible reasons for this behaviour. One is the splitting of degenerate orbitals induced by the substrate that breaks the four-fold symmetry of the molecule. However, it is unlikely that this splitting would be as large as \( \sim 100 \) meV. Another possible effect is coherent coupling of two electronic levels in a molecule by a molecular vibration\(^\text{11}\). In this case, the intensities, symmetries and energies of molecular resonances are modified and this would at least semi-quantitatively match our experiments on the wire CoPC.

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