Supporting Information

Selectively addressing plasmonic modes and excitonic states in a nanocavity hosting a quantum emitter.

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1- Methods.

Sample and tip preparation. All the experiments were performed with an Omicron Low-Temperature Scanning Tunnelling Microscope (LT-STM), operated at 4.5 K, in Ultra-High-Vacuum (UHV) conditions (P ∼ 10^{-11} mbar), and equipped with a custom-built light detection setup. Ag(111) single crystals (MaTecK) were cleaned by repeated cycles of sputtering with 1.5 keV Ar⁺ ions followed by thermal annealing at 500 K. The nanocrystallites were grown by deposition of C_{60} fullerenes (Sigma Aldrich) on top of a NaCl covered Ag(111) sample. The NaCl template (2-3 mono-layers) was grown by sublimation of NaCl (Sigma Aldrich) onto the clean Ag(111) surface held at room temperature. Au tips were used in all the experiments. After
electrochemical etching in a solution of HCl (37%) in ethanol, the tips were cleaned in UHV by sputtering with 1.5 keV Ar$^+$ ions.

**Data acquisition.** All the topography images and luminescence spectra were acquired in the constant current mode of the STM. The topography images were processed with the WSxM software. The luminescence spectra were recorded with an Andor Shamrock 500 spectrometer equipped with a Peltier cooled Charge Coupled Device (CCD). The CCD was operated at -85 C. The acquisition time of each spectrum in figure 2a and 3d was 100 seconds, and the spectra were recorded in the voltage range from 1.5 to 5.5 V in steps of 0.1 V.

2- Effect of the dielectric layer on the tunnelling characteristic curves.

The existence of a dielectric layer separating the molecules at the surface of the crystallites from the metal substrate implies that only a fraction of the applied voltage drops between the STM tip and the C$_{60}$ molecules, while the other part of the voltage shifts the charge neutrality level of the crystallite surface with respect to the Fermi level of the Ag(111) substrate. In order to estimate this fraction, we model the junction as a capacitor filled in part by vacuum and in part by an effective dielectric that includes the underlying C$_{60}$ molecules and the NaCl film. The capacitance of the junction can thus be considered to result from the association in series of two capacitors, one filled with vacuum and the other one filled with the dielectric. We can thus state that

$$C_T V_B = C_{ins} V_{ins}(S1)$$

where $V_B$ is the total bias voltage applied between the Ag(111) surface and the Au tip, $C_T$ is the total capacitance of the junction, $V_{ins}$ is the voltage that drops between the surface of the crystallite and the Ag(111) interface and $C_{ins}$ is the capacitance associated to the effective dielectric composed of the C$_{60}$ layers behind the surface and the NaCl film. Thus, the voltage drop in the dielectric layer is simply proportional to the applied total voltage with a proportionality constant given by $\alpha = C_T / C_{ins} \leq 1$. $\alpha$ depends on the tip-surface separation, and thus, comparing curves recorded with different stabilization bias would in principle require to calculate $\alpha$ for both conditions. Within a $dI/dV$ or $I(V)$ curve, however, since the feedback loop is open, the distance between tip and surface remains constant and, thus, one can assume a single value of $\alpha$ for all the curves.

3- Occupied electronic states

While our $dI/dV$ curves show clear features at positive voltages attributed to the unoccupied orbitals of C$_{60}$, on the negative bias side no particular feature can be observed that can be attributed to the HOMO orbital, only a sharp increase in the tunnelling at voltages below -2V. This is not surprising, because the electronic gap in C$_{60}$ crystallites is of 3.5 eV, and thus, given that the LUMO is found at about 0.5 eV above the Fermi level, the HOMO could be expected to be found below -3 V. The situation is however even worse due to the dielectric spacer. As discussed in the main text, the energy levels are expected to shift with the bias voltage as $E_i + \alpha eV_B$, where $E_i$ is the energy position of the $i^{th}$ orbital at zero bias. On the other hand, the position of the tip Fermi level with respect to the Fermi level of the sample is just $eV_B$. The molecular energy levels will thus be observed in $dI/dV$ curves at the voltages corresponding to the intersection of these straight lines. Figure S1 a) shows the evolution of the HOMO, LUMO and LUMO+1 orbitals (blue lines) and the position of the tip’s Fermi level (black line) with the applied voltage. Notice that, at negative voltages, the LUMO orbital meets the sample Fermi level at -2
V, while a higher negative voltage would be required for the tip’s Fermi level to reach the HOMO orbital. We thus expect that the molecules charge negatively by transferring electrons from the metal substrate to the $C_{60}$ LUMO, rendering the HOMO level of the neutral molecule unobservable.

![Figure S1](image)

**Figure S1.** a) Dependence of the energies corresponding to the $C_{60}$ frontier orbitals (blue lines) and the tip Fermi level (black line) with the bias voltage (the energies are referred to the substrate Fermi level). The voltages at which the molecular orbital features show in the curves correspond to the intersections between these lines. The position of the HOMO at zero voltage is estimated as the position of the LUMO minus 3.5 eV, which corresponds to the electronic gap of crystalline $C_{60}$. Notice that for negative voltages below 2 eV, the LUMO level crosses the Fermi level of the surface, and the molecule will receive charge from the metal. The hypothetical crossing between the blue line corresponding to the HOMO of the molecule with the tip Fermi level occurs at more negative voltages and it is, thus, unobservable. b) and c) STM image and simultaneously recorded plasmonic luminescence map recorded with $V_B = -3.0$ eV and $I_t = 500$ pA. The intensity of the plasmonic light depends on the molecular orientation, but the spatial distribution of the bright molecules corresponds to the double-lobe, butterfly shape identified with the LUMO orbital.

The charging of the molecules is further supported by the spatial mapping of the tunnel electroluminescence signal at negative voltages. In this range of bias voltage, only plasmonic luminescence is observed. The spatial maps of the intensity of such plasmonic light on the $C_{60}$ crystallites show intramolecular resolution, with a characteristic two-lobes, butterfly shape that corresponds to the LUMO orbital or molecules with two hexagons pointing towards the tip. Notice that this is only possible if the LUMO orbital is occupied, so that electrons can tunnel inelastically from the LUMO to empty states in the tip, which supports our idea that the pinning of the LUMO to the Fermi level and the concomitant charging of the molecule occurs for less negative voltages than those for which the HOMO feature would be observed.

4- Derivation of Equations (1) and (2)

As previously discussed in Ref [], when both tip and sample are metals, the rate of inelastic tunnel events creating an excitation of energy $\hbar \omega$ with an applied bias voltage of $eV_B$ can be obtained through the expression:

$$R_{\text{inel}}(\hbar \omega, V_B) \propto \int_{-\infty}^{+\infty} \rho_T(E + \hbar \omega - eV_B) f(E + \hbar \omega - eV_B) \rho_S(E) [1 - f(E)] T(E, V_B, \hbar \omega) dE$$

(S1)

where, $\rho_T$ and $\rho_S$ are the densities of electronic states of tip and sample respectively, $f$ is the Fermi-Dirac distribution and $T$ is the transmission factor. When all the energies involved are
much larger than the electronic thermal energy $k_B T_{el}$, the previous expression can be obviously approximated by

$$R_{\text{inel}}(\hbar \omega, V_B) \propto \int_0^{eV_B - \hbar \omega} \rho_T(E + \hbar \omega - eV_B) \rho_S(E) T(E, V_B, \hbar \omega) dE$$

(S2)

When comparing the previous expression with the traditional Bardeen approach to calculate the elastic tunnel current, given by

$$I_t(V_B) \propto \int_0^{eV_B} \rho_T(E - eV_B) \rho_S(E) T(E, V_B) dE$$

(S3)

we conclude that

$$R_{\text{inel}}(\hbar \omega, V_B) \propto I_t(V_B - \hbar \omega/e)$$

(S4)

for photon energies lower than the applied bias voltage.

In the presence of an insulating spacer, we consider (as discussed in the main text) that the tunnelling events occur predominantly between the tip and the surface of the $C_{60}$ nanocrystallite, and the voltage that drops between the tip and the surface of the crystallite is only $(1 - \alpha)eV_B$. In this case, expressions (S2) and (S3) become

$$R_{\text{inel}}(\hbar \omega, V_B) \propto \int_0^{(1 - \alpha)eV_B - \hbar \omega} \rho_T(E + \hbar \omega - (1 - \alpha)eV_B) \rho_S(E) T(E, (1 - \alpha)V_B, \hbar \omega) dE$$

(S5)

and

$$I_t(V_B) \propto \int_0^{(1 - \alpha)eV_B} \rho_T(E - (1 - \alpha)eV_B) \rho_S(E) T(E, (1 - \alpha)V_B) dE$$

(S6)

corresponding to expressions (1) and (2) in the main text. Finally, comparison of (S5) and (S6) shows that

$$R_{\text{inel}}(\hbar \omega, V_B) \propto I_t(V_B - \hbar \omega/(1 - \alpha)e)$$

(S7)

This final expression corresponds to Equation (3) in the main text.