Carbon monoxide ligation at single metal atom sites in a 2D manganese-cobalt coordination network: equilibrium at room temperature.

Michela De Col,[a,†] Danilo Comini,[a,†] Stefania Baronio,[a,†] Asha Yadav,[b] Basant Roondhe,[b] Alessandro Namar,[a] Davide Bidoggia,[a] Mattia Scardamaglia,[c] Paolo Giannozzi,[b,d,*] Erik Vesselli[a,e,f,*]

[a]Department of Physics, University of Trieste via A. Valerio 2, Trieste 34127, Italy

[b]Department of Mathematics, Computer Science, and Physics, University of Udine, Udine, I-33100, Italy

[c]MAX IV Laboratory, Lund University, Lund, 22100, Sweden

[d]CNR – Istituto Officina dei Materiali, SISSA, Trieste 34136, Italy

[e]CNR – Istituto Officina dei Materiali (IOM) S.S. 14 km 163.5, Area Science Park, Basovizza, Trieste 34149, Italy

[f]Center for Energy, Environment and Transport Giacomo Ciamician, University of Trieste, Trieste 34127, Italy

*corresponding authors' e-mails: evesselli@units.it, paolo.giannozzi@uniud.it

[†]These authors contributed equally to the experiments

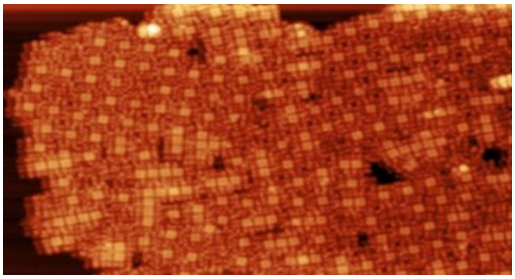

Figure S1. STM image collected at LN_2 temperature of the MnTPyP-Co network at low coverage (about 0.75 ML MnTPyP), so to put in evidence each different possible coordination structure, depending on the local Co coverage, yielding (2 × 2), (2 × 1), and (1 × 1) geometries for Co:Mn = 0.25, 0.5, and 1.0 ratios, respectively. Further details can be found in our recent paper.[1] Image parameters: 60 × 30 nm^2, V_{bias} = 2.20 V , I = 90 pA.

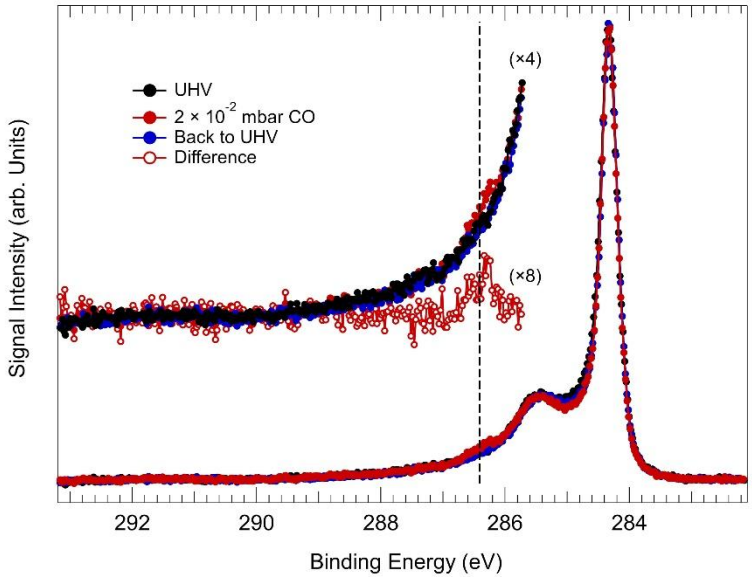

Figure S2. C 1*s* core level spectra of the pristine MnTPyP-Co/Gr system collected in UHV (black filled markers), in 2 × 10^{-2} mbar CO (red filled markers) and after recovering UHV conditions (blue filled markers). The high binding energy tails of the spectra have been magnified and offset in the inset for better clarity, evidencing the presence of a peak at 286.4 eV (difference spectrum, red empty markers), associated with the CO species ligated at the Co sites (hν = 400 eV).

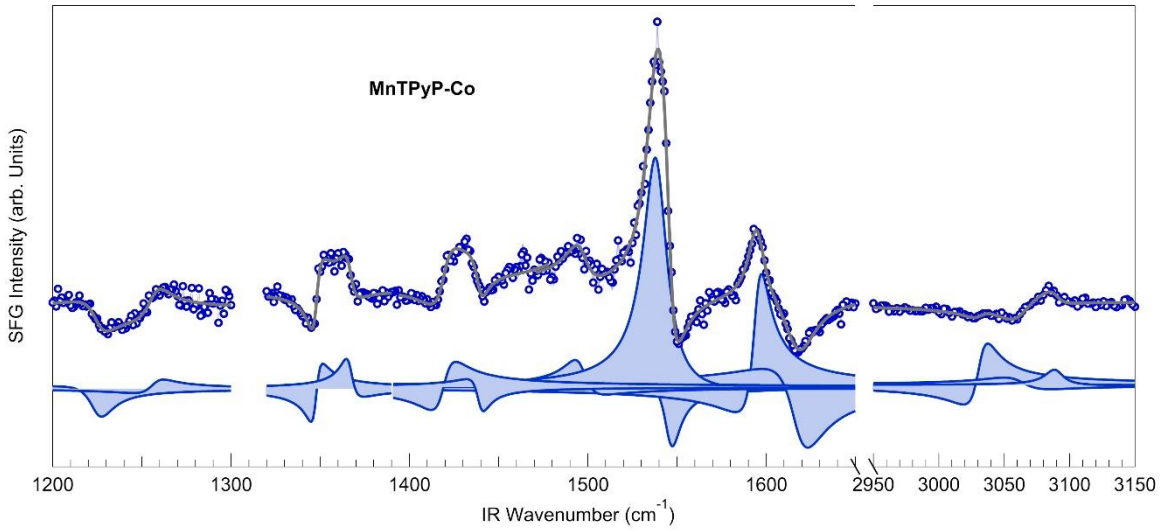

Figure S3. IR-Vis SFG spectra, best fit and deconvolution of 0.7 ML MnTPyP-Co on Gr/Ir(111) at about half Co saturation. The low-energy resonances are associated to pyridinic modes, the range 1320-1550 cm^{-1} exhibits prevalently macrocycle modes, while the most intense pyridinic fesatures are observed at 1500-1650 cm^{-1}. The peaks at higher wavenumbers (2900-3200 cm^{-1}) originate from the C-H stretching modes. More details about the UHV characterization of the pristine layer can be found in our previous paper.[1]

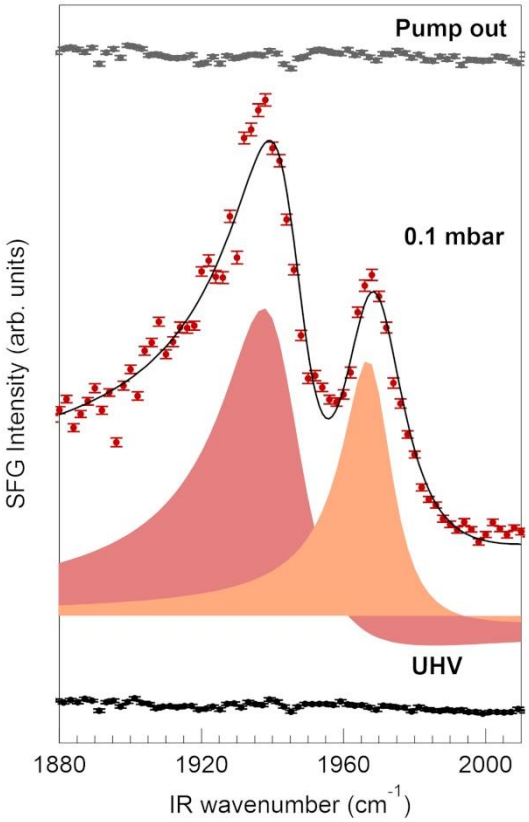

Figure S4. IR-Vis SFG ppp spectra collected in the internal C-O stretch region for the pristine MnTPyP-Co layer in UHV (bottom), in 0.1 mbar CO (center), and after recovering UHV conditions (top).

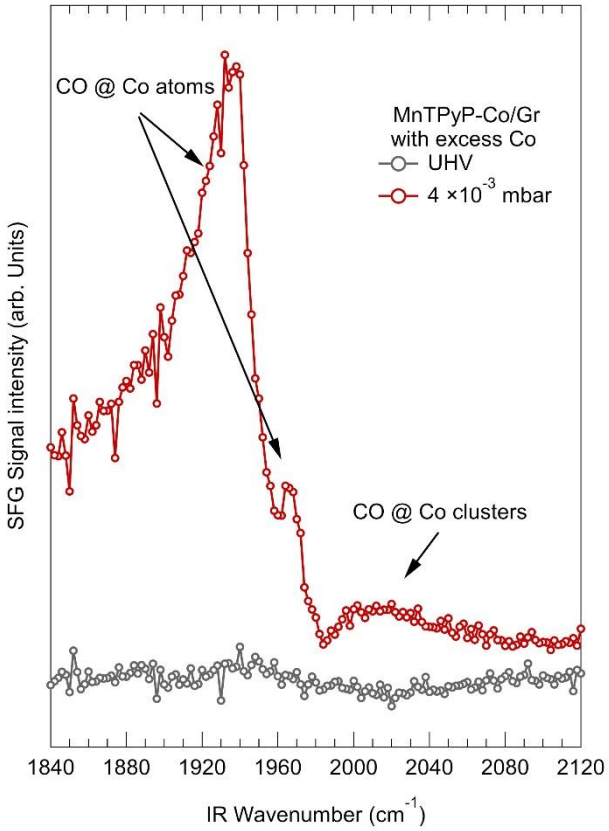

Figure S5. IR-Vis SFG spectra in the internal C-O stretching energy region of a MnTPyP-Co/Gr layer with excess Co, yielding the nucleation of Co clusters at defective sites and on the moiré pattern of the clean graphene domains. Introduction of CO evidences a spectra contribution above 2000 cm^{-1} associated with CO adsorption at the metal nanoparticles.[2–4]

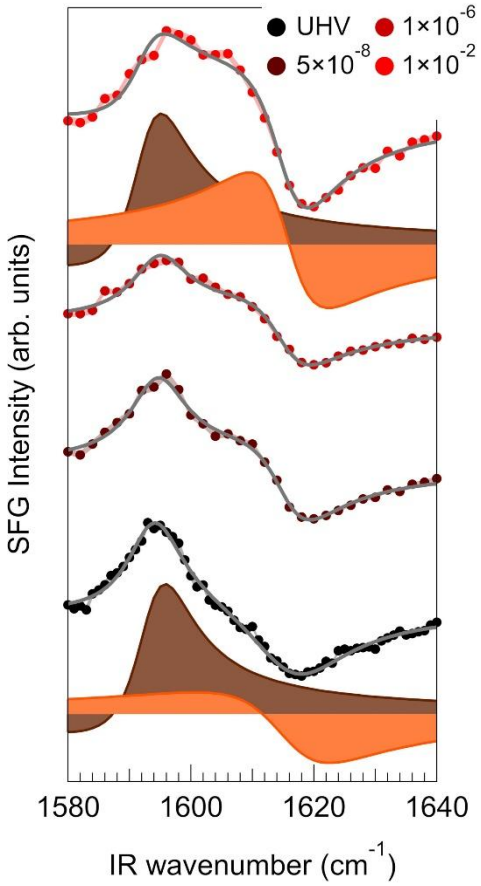

Figure S6. IR-Vis SFG spectra (ppp polarization combination) of a pristine MnTPyP-Co/Gr layer evidencing two modes at 1594 and 1616 cm^{-1}, associated with C-C stretching and δ modes of the pyridyl moieties, respectively (bottom spectrum, see Figure S3 for the complete spectrum). The phase evolution (of the order of 20°) for increasing CO background pressure is evident from the plot of the single resonances (filled profiles). Dots: experimental data; gray continuous lines: best fit. Since both geometric distortion and charge doping affect the resonances phase, this observation further supports that ligation of CO occurs at the Co sites.

	Spin	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}
MnTPyP-Co/Gr (Pristine)						
Mn1	**Up**	0.465	0.975	0.982	0.984	0.990
	Down	0.045	0.054	0.058	0.336	0.977
Mn2	**Up**	0.465	0.975	0.982	0.984	0.990
	Down	0.047	0.052	0.058	0.337	0.977
Co1	**Up**	0.987	0.989	0.993	0.995	0.996
	Down	0.024	0.138	0.978	0.984	0.990
Co2	**Up**	0.987	0.990	0.994	0.996	0.996
	Down	0.024	0.138	0.977	0.985	0.990
CO@MnTPyP-Co/Gr (CO ligated at the Co site)						
Mn1	**Up**	0.466	0.975	0.982	0.983	0.989
	Down	0.046	0.053	0.059	0.338	0.977
Mn2	**Up**	0.466	0.975	0.982	0.983	0.989
	Down	0.047	0.053	0.058	0.338	0.977
Co1	**Up**	0.971	0.972	0.988	0.994	0.996
	Down	0.126	0.143	0.936	0.938	0.990
Co2	**Up**	0.988	0.990	0.994	0.995	0.996
	Down	0.024	0.137	0.977	0.986	0.989

Table S1. Spin-resolved orbital populations (d_{z^2}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, d_{xy}) for Mn1, Mn2, Co1, and Co2 atoms in the MnTPyP-Co/Gr systems under pristine conditions and upon CO adsorption. Both spin-up and spin-down states are shown. Notable changes in orbital occupancy upon CO coordination are highlighted in red, indicating electronic redistribution.

References

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