Supporting Information

Ligation of Carbon Monoxide at Iron and Cobalt Single Metal Atom Sites: Competition for the +1 Oxidation State in a Surface-Confined Organic Network.

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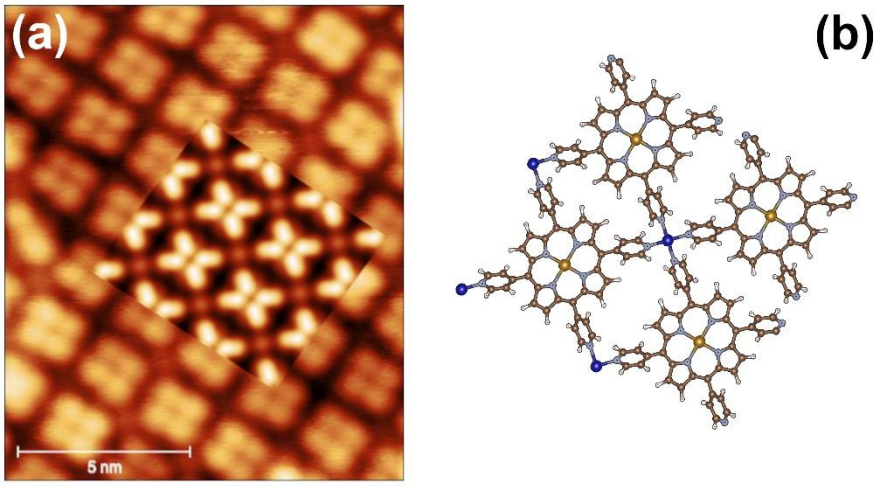


Figure S1. (a) Experimental STM image of the FeTPyP-Co/Gr/Ir(111) system at full Co coverage (Co:FeTPyP coverage ratio 1:1) yielding a (2 × 2) unit cell: the inset depicts the superimposed simulated image as obtained by the Tersoff-Hamann approach[1] from the structure optimized within the DFT calculation framework;[2] (b) DFT best structure geometry of the metalorganic network (underlying graphene is not shown for clarity) represented by a sticks-and-balls model (color map: Fe – gold, Co – blue, N – gray, C – brown, H – white). Further details about the geometric and electronic structures of the layer can be found in our recent work.[2]

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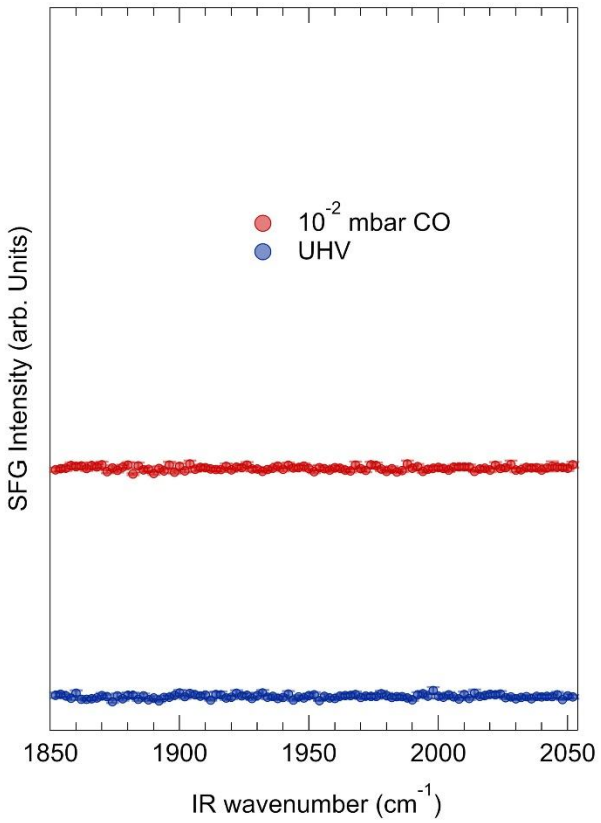


Figure S2. IR-Vis SFG spectra collected in the internal C-O stretch energy region at room temperature (*ppp* polarization combination) for the as-prepared FeTPyP/Gr/Ir(111) monolayer in UHV (bottom) and in 10^{-2} mbar CO. The layer is inert, at least up to this pressure value, showing no evidence for CO ligation at the Fe sites.

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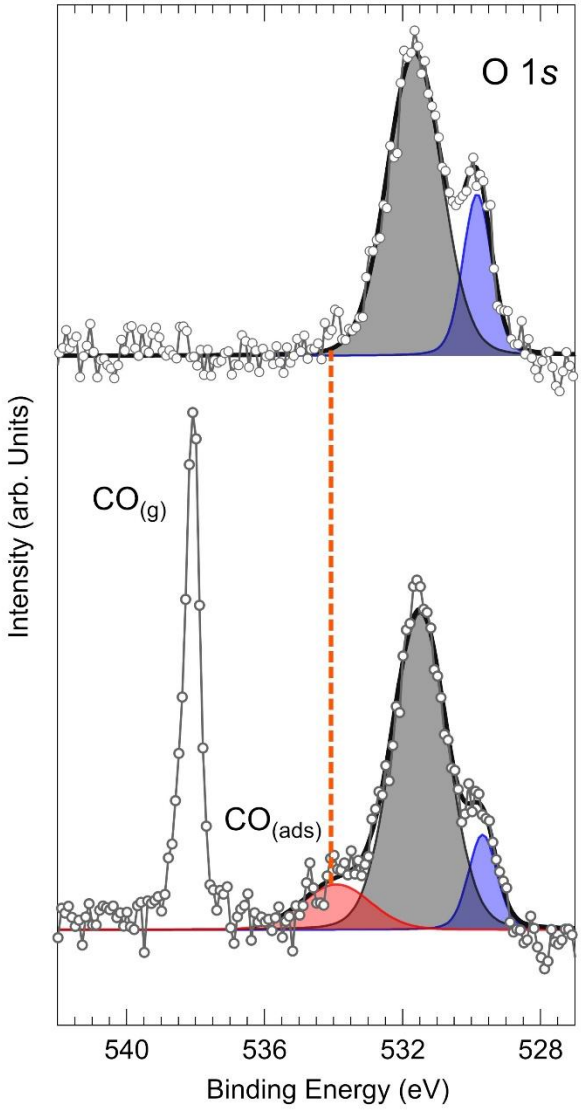


Figure S3. O 1*s* XPS spectra collected *in situ* in 10^{-2} mbar CO (bottom) and after recovering UHV conditions (top).

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References.

(1) Tersoff, J.; Hamann, D. R. Theory of the Scanning Tunneling Microscope. *Phys. Rev. B* **1985**, *31* (2), 805–813. https://doi.org/10.1103/PhysRevB.31.805.

(2) Namar, A.; Roondhe, B.; De Col, M.; Baronio, S.; Jugovac, M.; Scardamaglia, M.; Frampton, E.; Vinogradov, N. A.; Giannozzi, P.; Vesselli, E. Stabilization of Strongly Reduced Fe(I)-like Single Atom Species Coordinated in a 2D Self-Assembled Metalorganic Network.

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