

# Supporting Information

## Solvent-Controlled Morphology of Catalytic Monolayers at Solid-Liquid Interfaces

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In order to support the assignment that the two vibrational bands discussed in the main text ( $2025\text{ cm}^{-1}$  and  $2040\text{ cm}^{-1}$ ) do not originate from a cationic complex of the form  $\text{Re}(\text{CO})_3\text{MeCN}^+$ , we calculated the vibrational frequencies of the symmetric CO-stretching vibrations of the two complexes and looked for the CN stretching frequency of the MeCN ligand. The calculations have been performed on the DFT-level with the PBE exchange correlation functional, the DZVP-MOLOPT-GTH basis set and short-range (SR) correction for the Rhenium atom, using the cp2k program package.<sup>1</sup> Figure SI 1 shows two corresponding vacuum structures after geometry optimization. The axial MeCN ligand adopts a nearly linear coordination-geometry with respect to the Re-N-C-C axis.

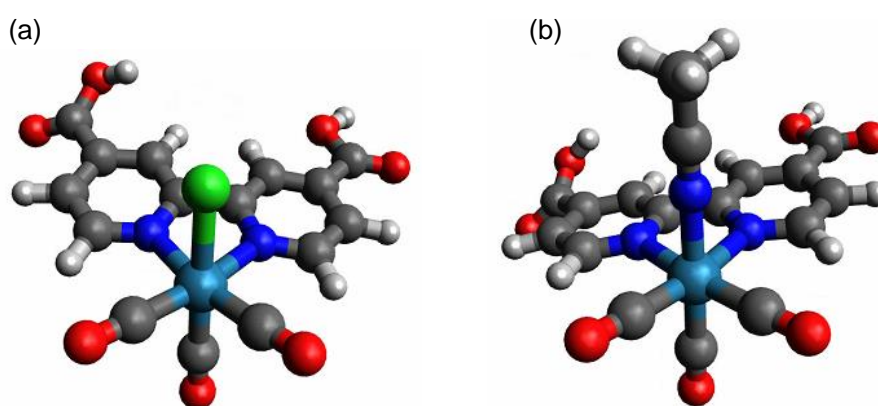


Figure S1. Optimized geometries for (a) the Cl-substituted complex  $\text{Re}(\text{CO})_3\text{Cl}$  and (b) the MeCN-substituted complex  $\text{Re}(\text{CO})_3\text{MeCN}$ . Color code for the atoms is hydrogen (white), carbon (grey), nitrogen (blue), oxygen (red), chlorine (green) and rhenium (cyan).

Subsequent normal mode calculations yielded the spectral positions of the symmetric CO-stretching vibration shown in Figure SI 2. For  $\text{Re}(\text{CO})_3\text{Cl}$  we find a band position of  $2015\text{ cm}^{-1}$ , and  $2044\text{ cm}^{-1}$  for  $\text{Re}(\text{CO})_3\text{MeCN}$ . Ligand substitution of  $\text{Cl}^-$  by MeCN thus slightly strengthens the CO bond and results in an upshift of the vibrational frequency by  $29\text{ cm}^{-1}$ . Similar spectral shifts have been observed experimentally for analogous samples in bulk solution.<sup>2-4</sup> However, the CN stretch vibration, which according to this calculation, is about a factor of 20 lower in intensity as compared to the carbonyl vibrations, should be clearly visible.

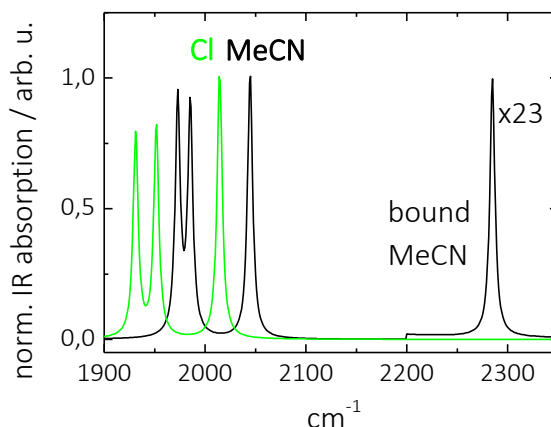


Figure S2. Calculated IR spectra of  $\text{Re}(\text{CO})_3\text{Cl}$  (green) and  $\text{Re}(\text{CO})_3\text{MeCN}$  (black) complexes in the spectral region of the symmetric CO-stretch vibration (after convolution with a Lorentzian lineshape of  $5\text{ cm}^{-1}$  FWHM).

Based on these calculations, we performed additional FT IR experiments on mesoporous ITO samples ( $1\text{ }\mu\text{m}$  thickness) to increase the absorbance of all species in the sample. Fig. SI 3 shows FT IR spectra covering also the CN stretch frequency region ( $>2200\text{ cm}^{-1}$ ) from samples identically prepared as the monolayer samples discussed in the main text. Also on the mesoporous ITO samples, the double band in the  $A'(1)$  region is clearly visible in MeCN, whereas only a single band is observed for the MeOH treated sample. However, no vibrational feature is observed in the CN stretching region ( $2200 - 2300\text{ cm}^{-1}$ ), thus ruling out any bound MeCN molecules at the complexes. Note that the line shape distortion stems from a Fano-interference<sup>5,6</sup> between the sharp IR resonance of the  $\text{ReCO}_3\text{Cl}$  and the broadband IR absorption of the highly conductive ITO layers.

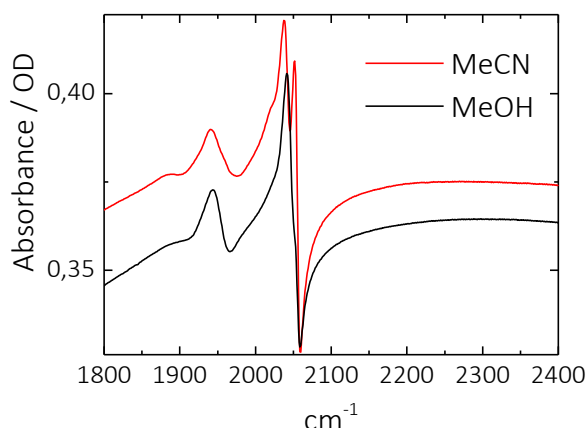


Figure S3. FT IR data of  $\text{ReCO}_3\text{Cl}$  on mesoporous ITO layers (about  $1\ \mu\text{m}$  thickness), prepared identically as the monolayer samples and treated overnight in MeOH (black) and afterwards in MeCN. The formation of the double band in the  $A'(1)$  region (ca.  $2000\ \text{cm}^{-1}$ ) is clearly visible for the MeCN treated sample. No CN vibration can be discerned above  $2200\ \text{cm}^{-1}$ . The lineshape distortions stem from a Fano-interference with the highly conductive ITO layer.

## References

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