Supporting Information

Adsorption, ordering and metalation of porphyrins on MgO nanocube surfaces: the directional role of carboxylic anchoring groups

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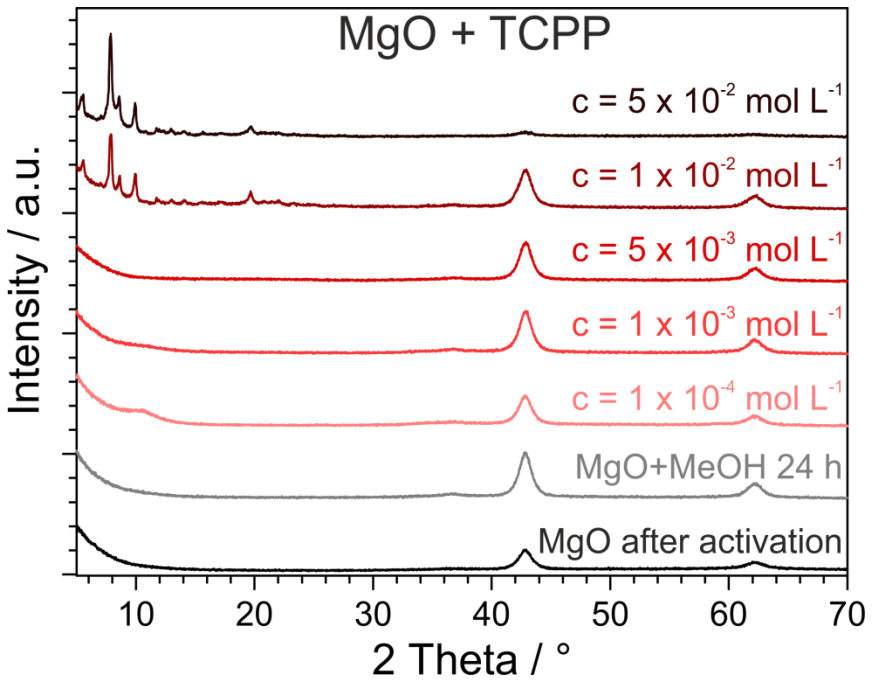

Figure S1: X-ray diffractograms of MgO (black line) after thermal activation, (grey line) treated with pure methanol and (red lines) after contact with 2H TCPP/MeOH solution. For higher concentrations, Bragg reflexes in the range below 2Θ ≤ 25° attributed to the ordered adsorption of 2H TCPP on the MgO nanocube surface occur.

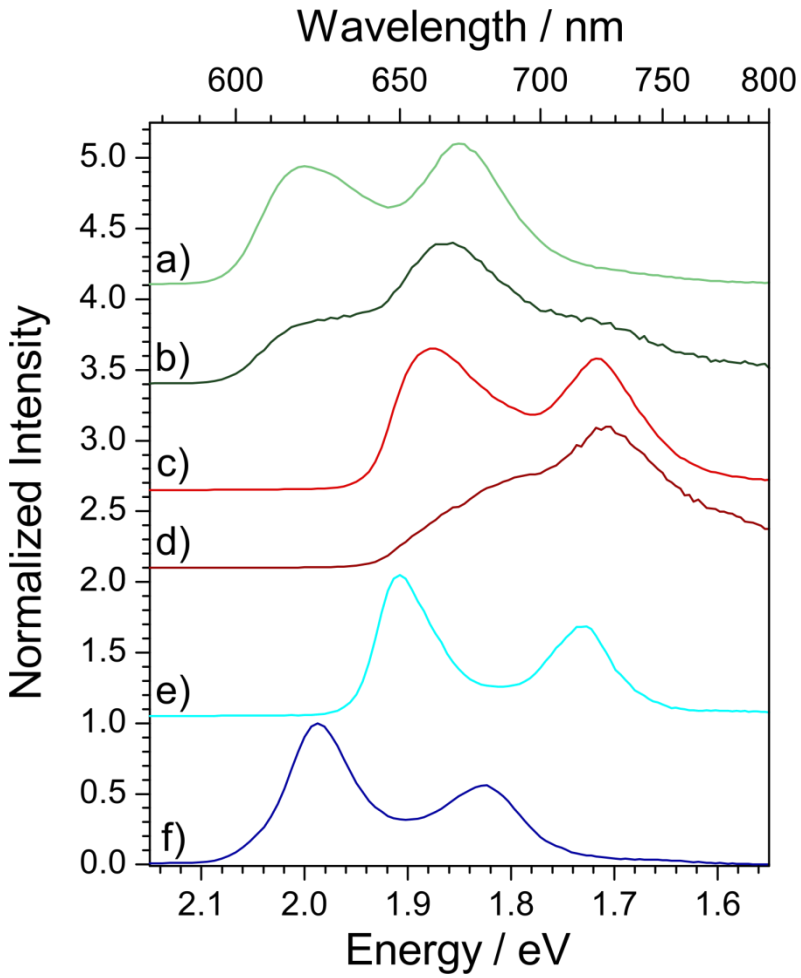

Figure S2: Photoluminescence emission spectra of MgO nanocubes after 2H TPP adsorption from toluene solutions of different concentration: a) $1 \cdot 10^{-4}$ mol·L^{-1} and b) $1 \cdot 10^{-2}$ mol·L^{-1}. Spectra of MgO nanocubes after 2H TCPP adsorption from methanol solutions of different concentration: c) $1 \cdot 10^{-4}$ mol·L^{-1} and d) $1 \cdot 10^{-2}$ mol·L^{-1}. Emission spectra of 2H TCPP e) and Mg TCPP f) dissolved in methanol are shown for comparison. For better conspicuity the spectra were normalized and provided with an offset.

Photoluminescence emission measurements were performed to complement DR-UV/Vis data. The spectra of 2HTPP adsorbed on MgO nanocubes are shown in Figure 2a and b, whereas the spectra of adsorbed 2HTCPP are shown in Figure 2c and d. Solution spectra of non-metalized 2HTCPP and metalized MgTCPP are shown in Figure 2e and f. 2HTCPP in methanolic solution shows two emission bands at 650 nm and 715 nm. The emission spectrum of dissolved MgTCPP features two bands at 625 nm and 680 nm. By comparing the spectra in solution with those of the adsorbed porphyrins, one can clearly see that the band positions in the spectra of

adsorbed 2HTPP (Figure 2a and b) resemble those of the metalized porphyrin (MgTCPP) in solution showing only a minor hypsochromic shift together with a band broadening. On the other hand there is a good match of band positions observed for adsorbed 2HTCPP and 2HTCPP in solution. Upon adsorption only a slight bathochromic shift is observed in this case together with band broadening. The small band shifts as well as the broadening of the emission band upon porphyrin adsorption most probably result from porphyrin-porphyrin or porphyrin-surface interactions. The change of the relative band intensities most probably results from the re-absorption of emitted photons at high surface coverages.