Electronic Supplementary Information

Porphyrin anchoring on Si(100) using a β-pyrrolic position

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I- ^{1}H-NMR spectrum of compound 5

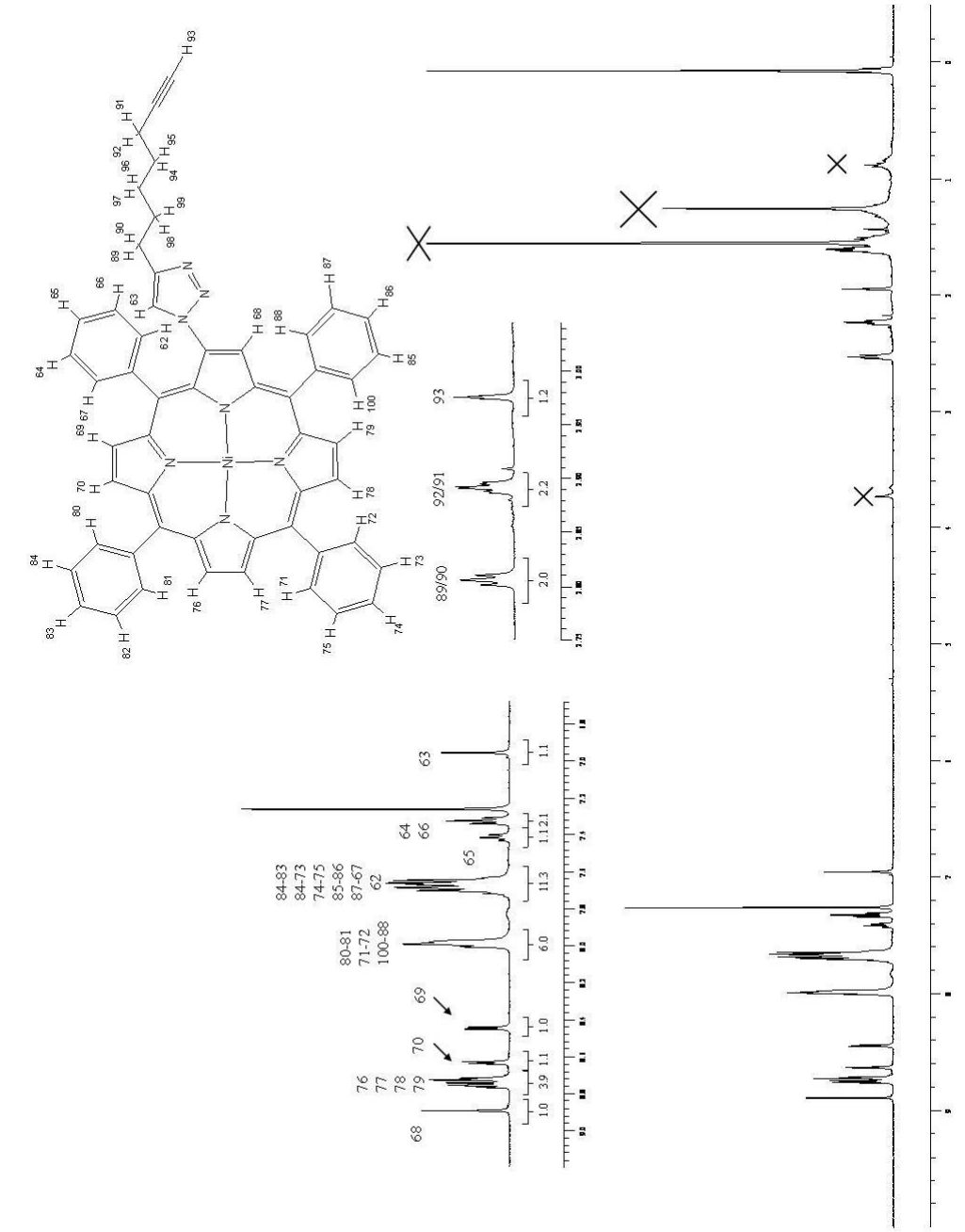

Figure 1: ^{1}H NMR of compound **5**

The peak observed at 3.7 ppm corresponds to a residual amount of EtOH. The peak observed at 1.55 ppm comes from the H_2O contained in the NMR solvent. The peaks at 1.26 and 0.88 ppm are deuterated solvent impurities.

II- IR spectrum of compound 5

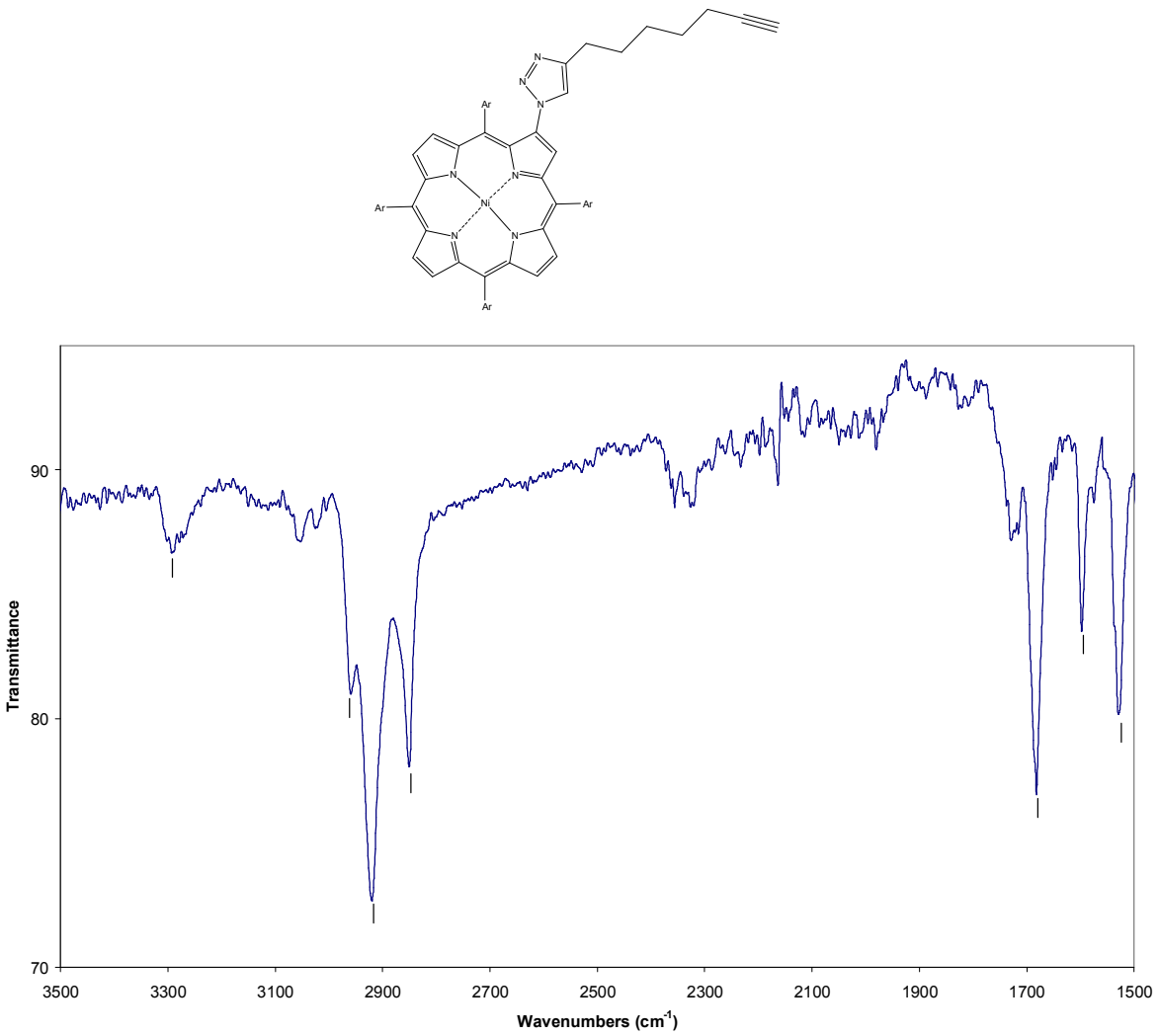

Figure 2: IR spectra of compound **5**.

The main bands are visible at 3288 cm^{-1} H-C(≡C), 2957, 2918 and 2849 cm^{-1} (alkyl, aryl C-H stretches) and 1682, 1597 and 1527 cm^{-1} (alkyl, aryl C-H deformations). As expected the N_3 vibration band at 2100 cm^{-1} is absent.

III- IR surface analysis

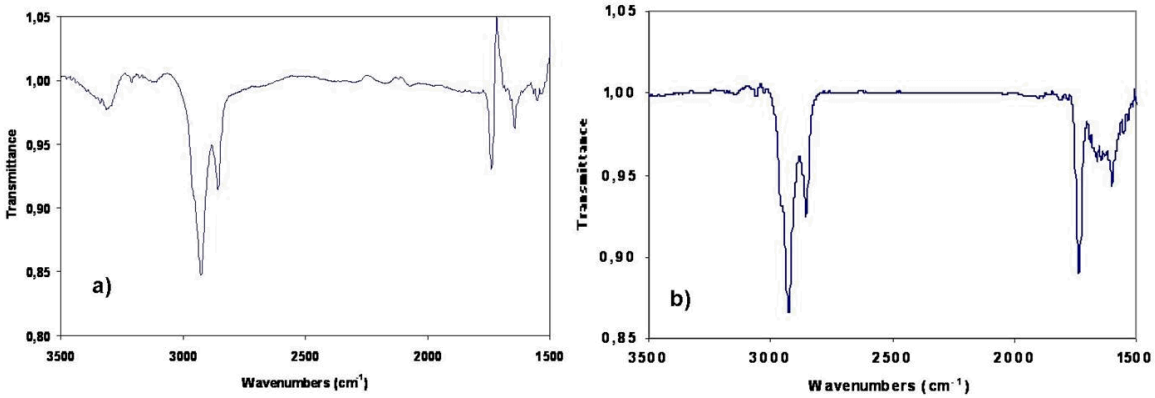

Figure 3: MIR-IR spectra of **surface 2** after linker immobilization (a) and **surface 3** after coupling to the porphyrin (b).

IV- XPS surface analysis

Step 1. The alkyne-terminated monolayer.

The global spectrum (Fig. 4a) of surface showed that the substrate was not contaminated by other elements than those expected. The C 1s spectrum (Fig. 4c) did not allow discriminating sp^3 and sp C atoms. The Si 2p spectrum did not reveal a significant oxidation of the substrate (Fig. 4b), which indicated that the grafted monolayer was densely packed and prevented the substrate oxidation by air.

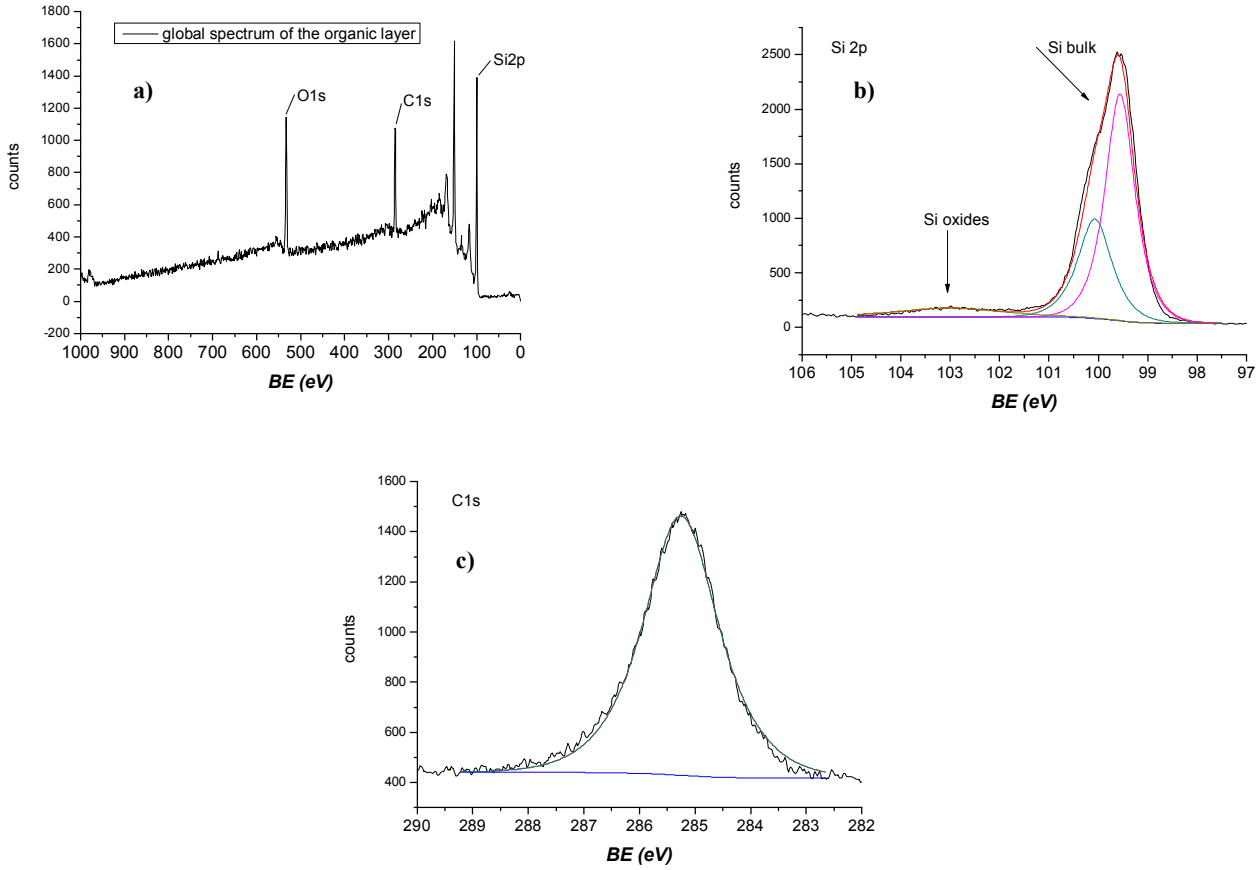

Figure 4. Global XPS spectra (a); Si 2p HR spectra of surface (b) and C 1s HR spectra (c) of **surface 2**.

Step 2. The porphyrin-terminated monolayer.

The global spectrum (Fig. 5a) revealed the presence of all the elements as expected for the porphyrin-terminated monolayer. More importantly, the presence of the N 1s (Fig. 5e) and Ni $2p_{3/2}$ (Fig. 5d) confirmed that the porphyrin molecules were covalently assembled on silicon surface. The Si 2p spectrum showed the silicon substrate was oxidized by air, which might be due to the disruption of the spacer monolayer by the massive porphyrin molecules (Figure 5b).

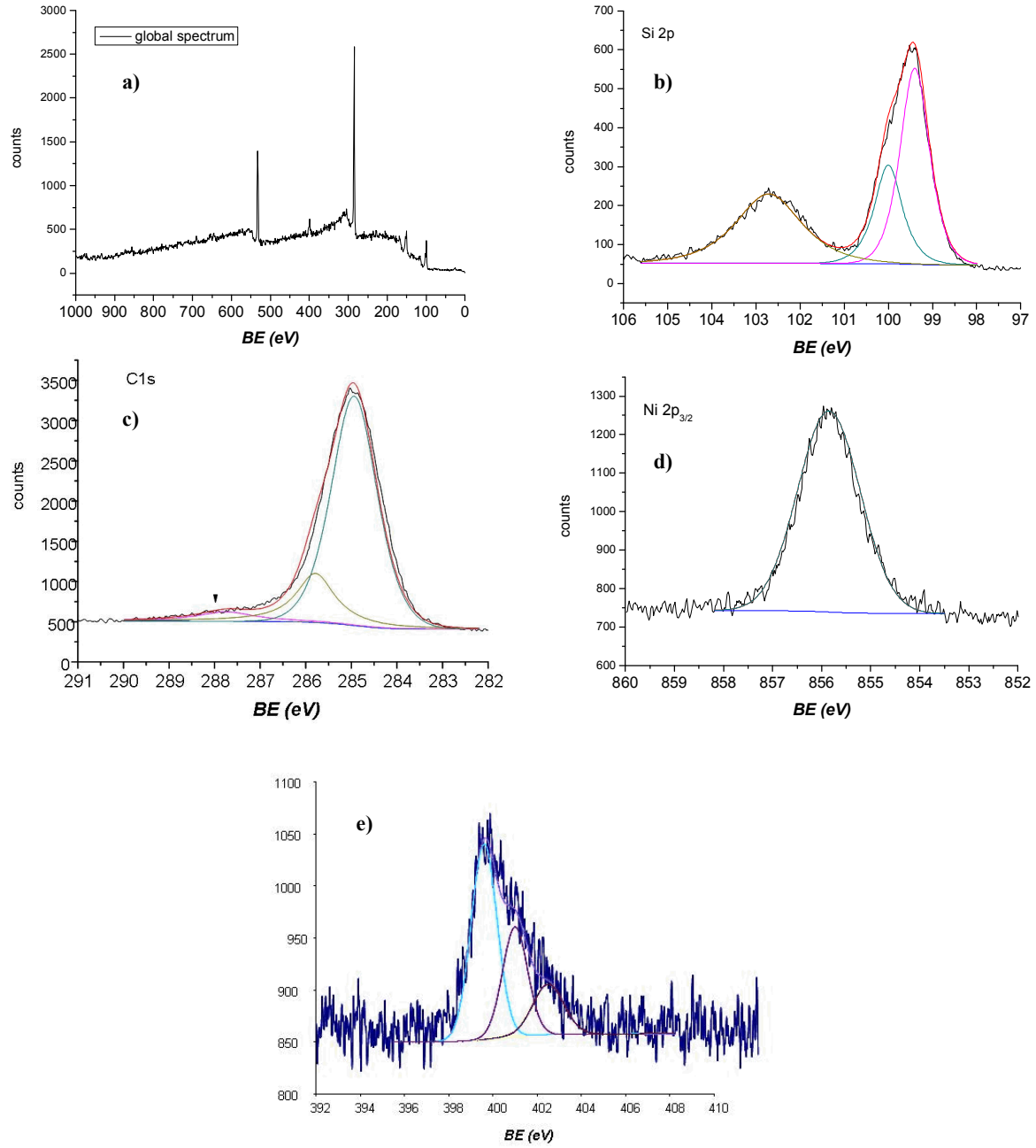

Figure 5. Global XPS spectra (a); Si 2p HR spectra of surface (b); C 1s HR spectra, Ni $2p_{3/2}$ (d) and N 1s HR spectra of **surface 3**.

V- Cyclic voltammetry study of surface 3

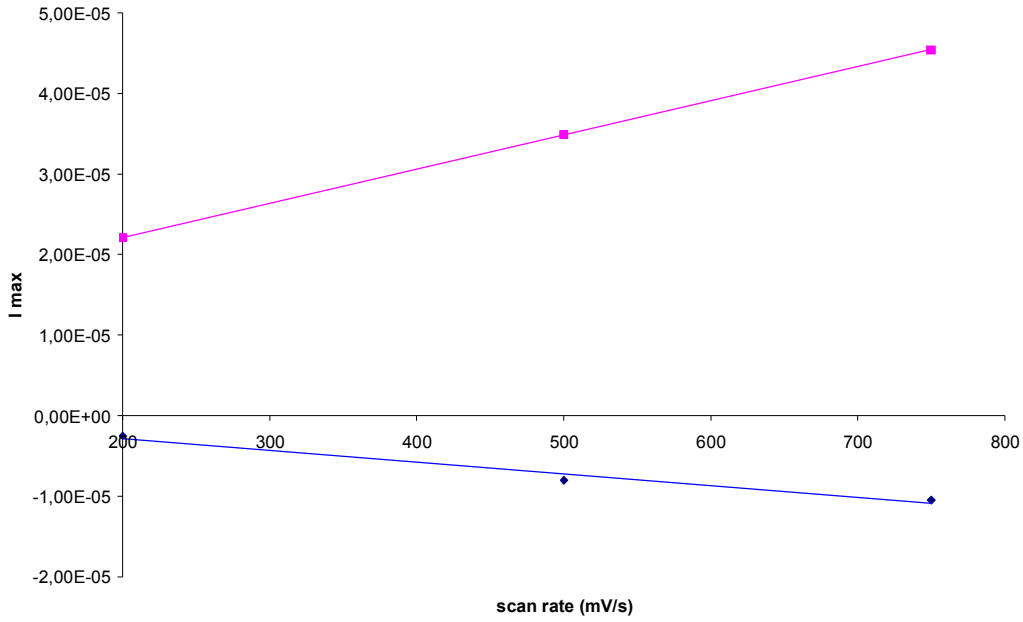

Figure 6 : Plot of Imax vs scan rate.

The variation of the I_{max} has been recorded in function of the scan rate. Both I_{max} for the oxidation and the reduction peaks were recorded. For both sets of data it is noticeable that the I_{max} is linearly proportional to the scan rate.