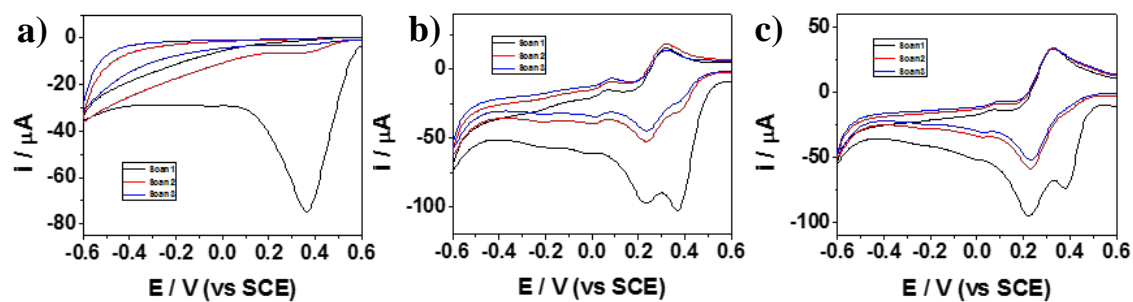
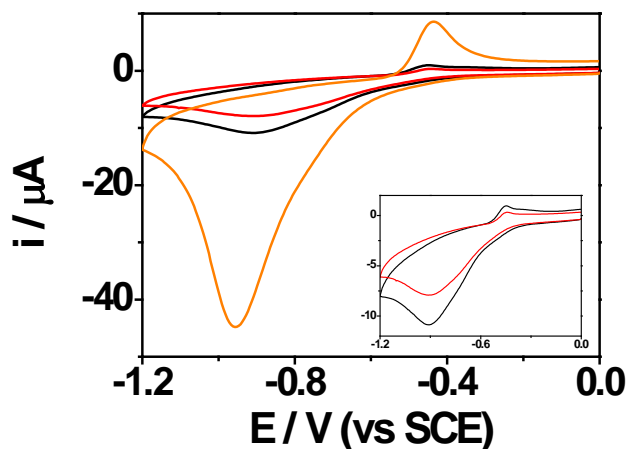


## ELECTRONIC SUPPLEMENTARY INFORMATION

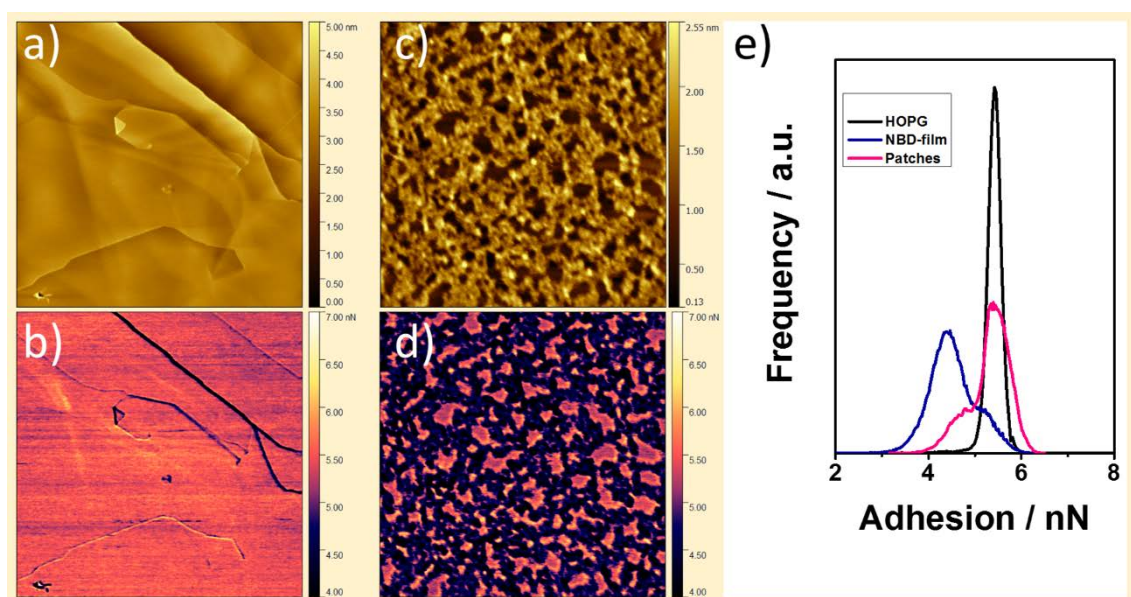


**S1.** Three consecutive voltammograms (1<sup>st</sup> black, 2<sup>nd</sup> red, 3<sup>rd</sup> blue) for a 1mM NBD + 0.1M TBABF<sub>4</sub> solution with (a) 0 mM, (b) 1 mM and (c) 2 mM of DPPH.



**S2.** First cyclic voltammogram recorded in 0.1 M NaOH of a modified HOPG electrode using a 1 mM NBD solution with 0 mM (orange), 1 mM (black) and 2 mM (red) DPPH ( $v = 0.05 \text{ V s}^{-1}$ ). The inset shows a detail of the response for modified electrodes using 1 mM and 2 mM DPPH.

Figure S2 shows cyclic voltammograms from 0 V to -1.2 V ( $v = 0.05 \text{ V s}^{-1}$ ) in 0.1 M NaOH recorded to estimate the surface coverage. A massive reduction of  $\text{NO}_2$  groups can be observed in all cases situated at -0.95 V without DPPH and at -0.9 V when DPPH is added. The reduction consists in the conversion of  $\text{NO}_2$  groups to -NHOH (a four-electron reaction) and to  $-\text{NH}_2$  (a six-electron reaction) implied at this irreversible cathodic wave. Moreover, at -0.4 V an oxidation peak is present related with the system NHOH/NO. Using the charges implied in these signals, an estimation of the surface coverage can be calculated.



**S3.** Topographic images ( $0.6\ \mu\text{m} \times 0.6\ \mu\text{m}$ ) for (a) bare HOPG and (b) film generated with 2 mM of DPPH. Simultaneous adhesion maps with  $F = 5\ \text{nN}$  corresponding to (a) bare HOPG and (b) NBD film. (e) Distribution for adhesion maps for bare HOPG (black line), NBD-covered areas (blue line) and uncovered areas (pink line). For the Peak Force QNM measurements, RTESPA-150 (6 N/m; 150 kHz) probes obtained from Bruker were used.

As it can be seen, bare HOPG shows an almost homogeneously adhesion map (S3b) obtained simultaneously to the topographic image (S3a). Surface steps shows a different adhesion related with adsorbates that can change some surface properties as previously reported despite contamination is almost avoided by cleavage of the HOPG substrate. (Lee et al.; *Nano Letters* **2015**, 9(4), 3814-3819). On the other side, two different areas can be observed in the adhesion map corresponding to the NBD film (S3d). Low/high adhesion values are related with NBD-covered/uncovered areas in the topographic map (S3c). A histogram for the values of this adhesion map can be seen in figure S3e. It is clear that higher values (flat patches, pink line) distribution perfectly matches with that

for bare HOPG (black line). In conclusion, these patches are uncovered areas and the adhesion response is the same than that of the bare HOPG, discarding the presence of adsorbed molecules due to the extreme dependence of the adhesion value on the nature of the surface.