In the figure S1 reflection spectra of ZnPP Langmuir film spread on an ultrapure water subphase are reported. [26]

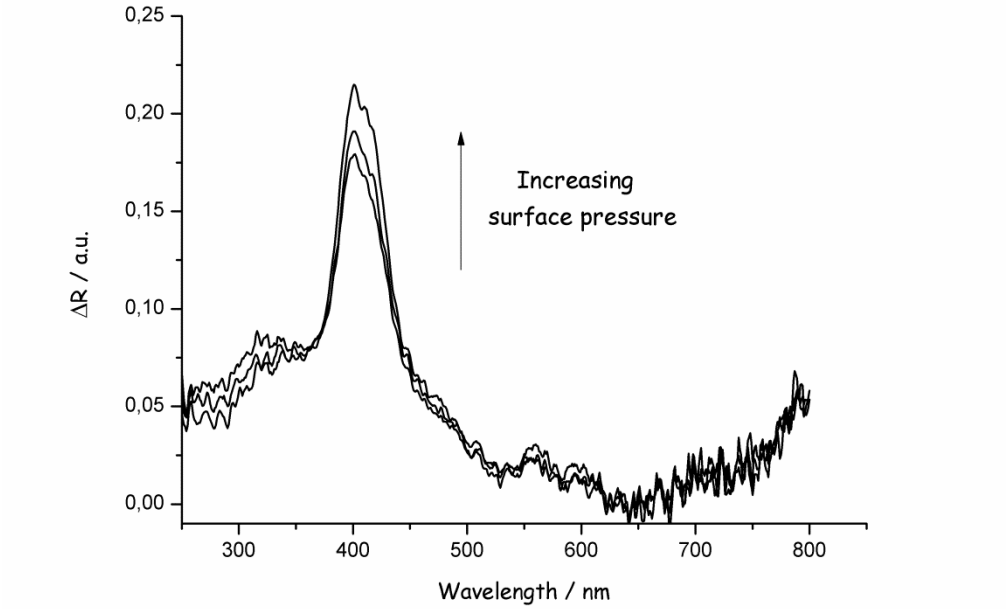

Figure S1 Reflection spectra of the floating film of 80 µl of ZnPP spread onto ultrapure water subphase (surface pressure: 6 mN/m, 10 mN/m, 20 mN/m). The spectra suggest the simultaneous presence of both syn- and anti-conformers, with absorption bands located at 398 nm and 420 nm (as a shoulder), respectively.

Morphology of floating film was monitored during compression by means of a NIMA® Brewster Angle Microscope (BAM) installed onto the Langmuir trough with a lateral resolution of 2 µm. BAM pictures show the simultaneous presence of large aggregates of spread molecules and regions of the interface not covered by ZnPP floating layer (images a and b of figure S1). The motion of the barriers induces a better packing of the floating film with a most uniform covering of the subphase surface (figure S2 c and d). For very high surface pressure values, the floating film forms a uniform layer upon the aqueous subphase.

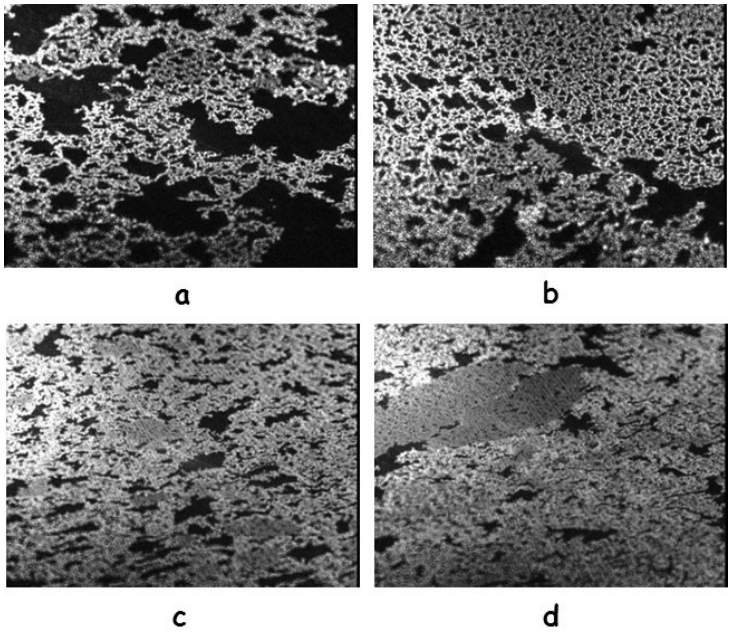

Figure S2 BAM images of the floating film of ZnPP spread on a water subphase containing 10^{-6} M aniline. Width of images is 430 µm. The increasing surface pressure, induced by the motion of the barriers of the Langmuir trough, causes a better covering of the surface and, whereupon, a higher ZnPP average density. Image **a** was taken for a surface pressure of 1 mN/m, image **b** surface pressure reached from the floating film was 10 mN/m. **c** and **d** images are respectively related to 18 and 28 mN/m.

NH_3 and n-butylamine were dissolved in subphase in order to evaluate their effect on the ZnPP molecules. Bis-porphyrin molecules appear to be principally as syn-conformers, confirming the key role of the π-π interaction between the aromatic amines and the porphyrin moieties of ZnPP.

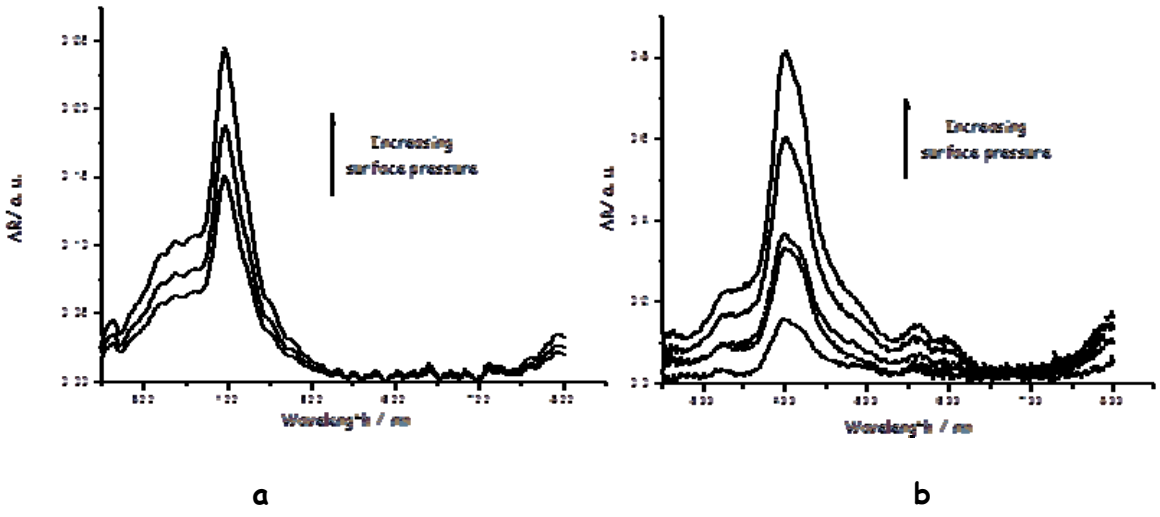

Figure S3 ZnPP reflection spectra acquired when n-butylamine (a) and NH_3 (10^{-3} M) (b) are dissolved in subphase. Both spectra point out that bis-porphyrin appears preferably in the syn-form.

Isotherm curves were recorded by means of a NIMA instrument at 293 K. A barrier constant speed of 5 mm/min was set to compress the floating film; the surface pressure was measured by means of a platinum Wilhelmy balance. The limiting area per molecule of ZnPP, obtained by the extrapolation of the linear portion of the Langmuir curve to 0 mN/m, in the case of water subphase containing 10^{-6} M aniline (black line of figure S4) is ~158 $Å^2$/molecule. Such a value is very close to the theoretical one (that is 160 $Å^2$/molecule) calculated for an anti-form organization of ZnPP molecules. A kink can be observed near 25 mN/m and an area per molecule equal to 120 $Å^2$/molecule can be extrapolated from the isotherm curve. It cannot be ascribed to a switch from anti- to syn- conformer (theoretical value is about 80 $Å^2$/molecule), but it is most probably due to the formation of a multilayers floating film.

The isotherm curve registered after spreading 80 µl of ZnPP chloroform solution on water subphase containing 10^{-6} M *tert*-butylamine is shifted towards smaller area per molecule, and a limiting area per molecule of 130 $Å^2$/moleculeindicates the simultaneous presence of both syn- and anti- ZnPP conformers.

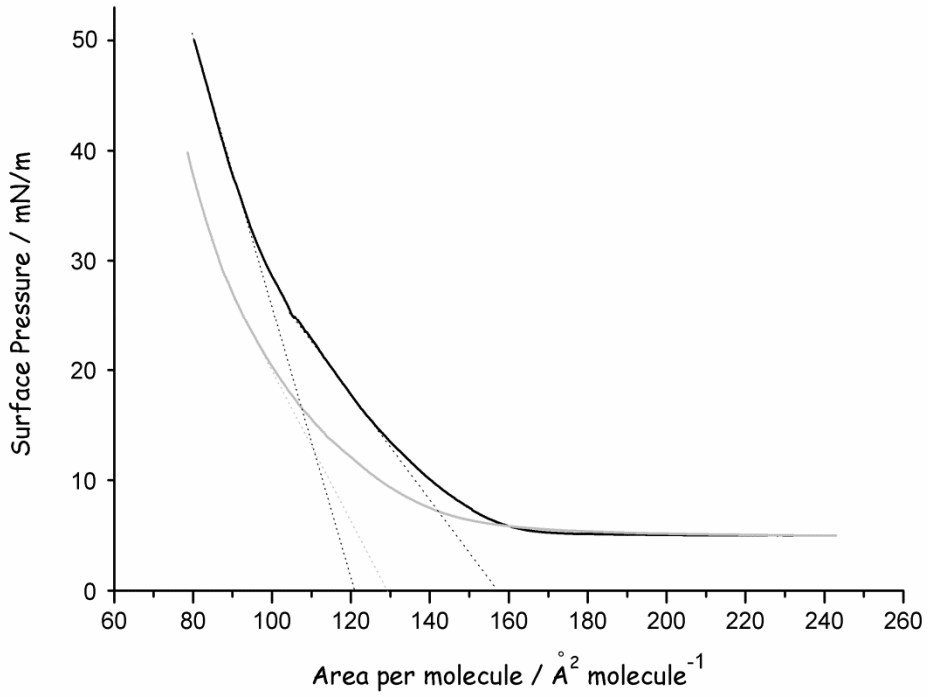

Figure S4 Isotherm curves after spreading 80 µl of ZnPP chloroform solution on the water subphase containing aniline 10^{-6} M (black line) and tert-butyl amine (10^{-6} M), respectively. The intercepts of dotted lines with Area per molecule axis indicate the limiting area per molecules.

The deposition method strongly influences the conformation arrangement of the ZnPP layer. In figure S5, ZnPP molecules within the LS film obtained by 10 horizontal runs appear essentially in the syn- conformation; even though the shoulder at 420 nm suggests the coexistence of syn- and anti- conformers. When the ZnPP is transferred on solid supports by means of spin-coating method, the visible spectrum indicates a preferential anti-conformation arrangement.

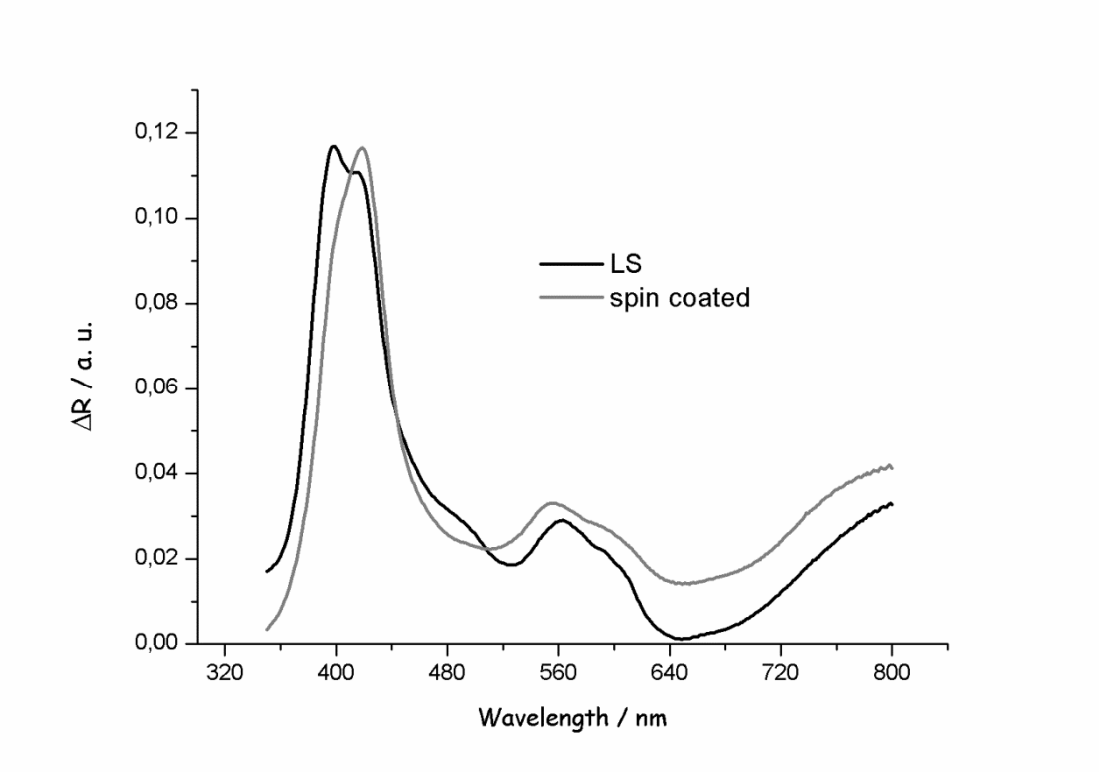

Figure S5 Normalized absorption spectra of deposited ZnPP films. Black line reports the absorption spectrum of the LS ZnPP layer transferred by 10 horizontal runs. The ZnPP appears preferentially packed in syn-form. Grey line is related to the absorption of spin coated ZnPP film. The presence of EtOH as stabilizer of the chloroform solvent induces a preferential anti-conformation arrangement.

Response of 10 layers of ZnPP LS film after 1 cycle (continuous lines) and 7 cycles of 10^{-7} M 1-(1-naphtyl)ethylamine injection and recover (dotted lines) is reported in figure S6. The spectra indicate that the reduction is proportional as for the *syn*- and for the *anti*- forms that indicates removing the deposited LS films from the solid support rather than changing the sensor activity. A further confirmation supporting that the sensing activity does not change comes from the stability of the syn/anti absorption ratio.

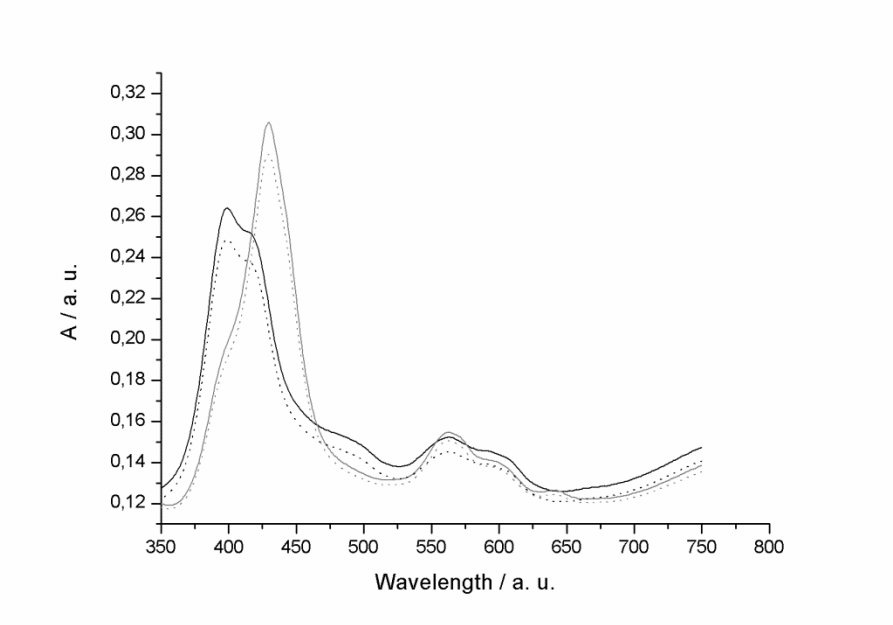

Figure S6 Continuous black line represents the visible spectrum of the as-deposited LS film (10 horizontal runs) and continuous grey line is the spectral profile of the response of the active layer to 10^{-7} M 1-(1-naphtyl)ethylamine. Dotted line are the spectra of the LS film after 7 cycles of amine injection and recovery by means of the temperature effect. The loss in the signals (about 4% of the original absorbance values) can be attributed to the mechanical action of the water solutions fluxed on the film during the 7 cycles.