ESRF	Experiment title: STUDY OF DYNAMICAL AND STRUCTURAL PROPERTIES OF METAL BIS-PORPHYRINS IN AQUEOUS SOLUTIONS	**Experiment number**: HD-338
Beamline: ID10A	**Date of experiment**: from: 19/06/2009 to: 23/06/2009	**Date of report**: 25/08/2009
Shifts: 12	**Local contact(s)**: Chiara Caronna	*Received at ESRF:*

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Report:

The main aim of the experiment carried out on ID10A was measuring the correlation function as a function of concentration of aqueous solutions of the Cobalt(II) bis-porphyrin system (tweezers) with two different bridge lengths (m=1 and m=7, as sketched in Figure 1) and at different pH. Moreover, we intended to study the change in the tweezers dynamics and structure upon amino acid binding[1]. Such an experiment should have been performed at QR<1 in order to extract the diffusion coefficient and, from that, the hydrodynamic radius of the molecule, which along with the form factor could give information on the conformation of the tweezers. In the opposite limit, QR>1, conformational dynamics (relative motion) of the two porphyrin residues had to be investigated and correlated with internal motions allowed by the different bridge length. Unfortunately, the signal-to-noise ratio was so small, even for the most concentrated solution, that no correlation function could be measured. Therefore, we tried to collect SAXS data by using the 2D detector. The low excess scattering does not allow for an unambiguous interpretation of the intensity profile especially for what concern the comparison between the two Cobalt(II) bis-porphyrins with different bridge length.

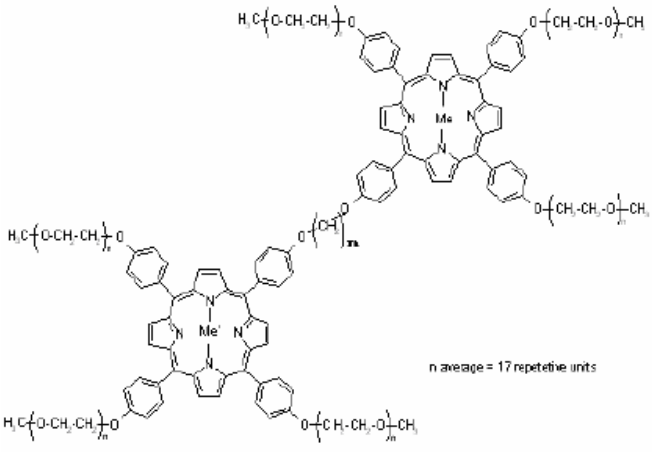

Figure.1 Structure of Cobalt bis-porphyrins: Bis{5,10,15-tri[p(ω-methoxy-polyethyleneoxy)phenyl]-20-[p-(phenylene) Cobalt-porphyrin]-1,1-dioxy-methane (with m=1) and Bis{5,10,15-tri[p(ω-methoxy-polyethyleneoxy)phenyl]-20-[p-(phenylene) Cobalt-porphyrin]}-1,7-dioxyhepthane (with m=7).

A tentative approach consists in comparing the intensity profiles collected at different concentration values for same Cobalt(II) bis-porphyrin (see Figure 2a and 2b). The collected intensity profile seems to suggest the presence of aggregate whose radius of gyration, R_g, is about 15 nm for both bis-porphyrins, as obtained by using the Guinier law in the Q range 0.0065-0.01 $Å^{-1}$. However, due to the unfulfillment of the Guinier limit

in the mentioned Q region, the value of R_g is underestimated. It cannot be excluded that smaller aggregates of Cobalt(II) bis-porphyrins are also present, as suggested by the slope of Guinier plot of the intensity profile at the higher Q values.

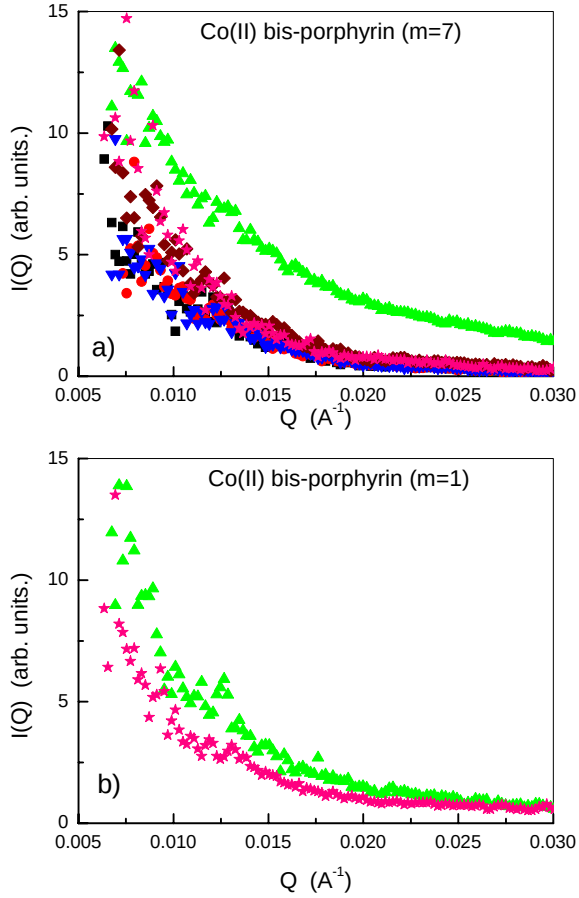

Figure 2. Excess scattered intensity at pH=7 and at different concentration values (square: 0.7 mM, circles: 1.5 mM, up triangles: 2mM, down triangles: 5 mM, diamonds: 10 mM, stars: 20mM).

As far as the bis-porphyrin solution with amino acid is concerned, a clear evidence of the effect of the molecular recognition between the two species is obtained. The binding process between L-thryptophane and Cobalt(II) bis-porphyrins causes the progressive disruption of the aggregates, indicating the existence of a kinetic process favouring the formation of stable tweezers/amino acid complex in water solution also at moderately high porphyrin concentration.

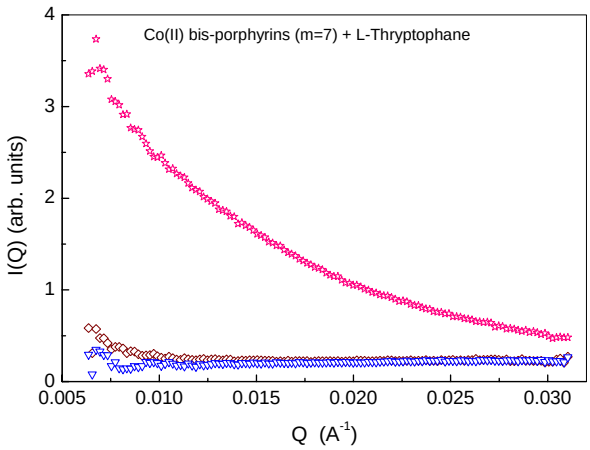

Figure 3. Excess scattered intensity at pH=9 for the solution at 2mM in the absence (stars) and in the presence of L-Thryptophane at tweezer/amino acid 1:10 molar ratio, freshly prepared (diamonds) and after six hours (down triangles).

In summary, although the main aim of the experiment could not be achieved, the obtained information will be certainly useful together with other results that will come from specific experiments to be performed in our laboratories. Therefore, we are confident that the data can be subject of a future publication on an international journal.

References

[1] Villari V, Mineo P, Micali N, Angelini N, Vitalini D and Scamporrino E 2007 *Nanotechnology* **18,** 375503 (13pp).