

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Phase behavior of water soluble thermoresponsive porphyrin systems studied using BioSAXS (BM29)	Experiment number: MX-1921
Beamline: BM29	Date of experiment: from: 25 October 2017 to: 27 October 2017	Date of report: 17.08.2018
Shifts: 6	Local contact(s): Dr. Gabriele Giachin	<i>Received at ESRF:</i>

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Report:

1. Background and motivation

Porphyrins are widely studied functional dyes that can coordinate a great variety of metal cations. In biological systems, porphyrins play essential roles as photosynthetic antenna and reaction center. In our research we use porphyrin derivatives for various sensing applications such as enantiopurity sensing, selective detection of anions. Most of these sensing features are realized by non-covalent interactions (H-bond, electrostatic, π - π , etc.) between porphyrin and substrate. The sensing is unfortunately permitted only in organic solvents (CHCl_3 , THF, etc.). Therefore, we have introduced water soluble moieties such as m-tetraethylene glycol (**mTEG**) or poly(*N*-isopropylacrylamide) (**PNIPAm**) at the periphery of porphyrin (**TPP**) functional unit (Fig. 1a). These porphyrin/polymer systems exhibit response to whole range of stimuli (temperature, Fig. 1b; pH, Fig. 1c; solvent composition; etc.) and are potential candidates for various sensing applications, detection, separation and imaging purposes in aqueous media. In addition, these compounds can be also used in photodynamic therapy (PDT) or for heterogeneous catalysis.

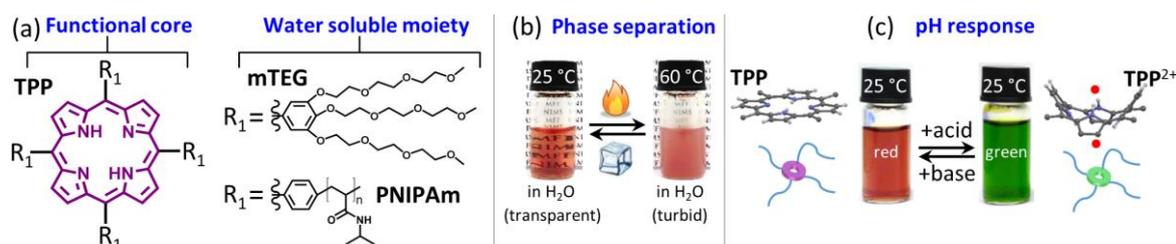


Figure 1. (a) Structures of two examples of water soluble porphyrins. (b) Phase separation of **TPP**-polymer/water system. (c) Colour change connected to pH response of **TPP**-polymer in water. Red/purple color represents uncharged **TPP** while green color represents diprotonated form of **TPP**.

2. Methods

SAXS experiments were performed on the beamline BM29 BIOSAXS using a pixel detector (Pilatus 1M). The X-ray scattering images were recorded at a sample–detector distance 2.867 m, using a monochromatic incident X-ray beam with an energy $E = 12,5$ keV, covering the range of momentum transfer of $0.025 \text{ nm}^{-1} < q < 5 \text{ nm}^{-1}$ ($q = 4\pi \sin \theta/\lambda$, where 2θ is the scattering angle). The solvent (deuterated water) scattering was subtracted prior to the fitting analysis. All data manipulations were performed using SASfit software.

3. Results

We have examined size and shape of **TPP**-polymer water-soluble molecules which are thermo- and pH-responsive. Experiments were performed in a broad range concentrations and temperatures in order to cover the phase separation phenomenon of various types of **TPP** derivatives. As an acid we have used (*S*)-camphorsulfonic acid, (*S*)-CSA. Figure 2a shows the scattering intensities for **TPP-PNIPAm(long)** [22.7 kDa, LCST = 27 °C]. Also scattering data in the presence of (*S*)-CSA acid are shown (Figure 2b).

A fitting model of polydisperse ellipsoids (PELs) was chosen for samples at low temperatures (below phase separation). At higher temperatures (from 35 °C) polydisperse spheres (PSs) were found in the solution (Figure 2a). The effect of addition of acid ((*S*)-CSA) into the solution increases the size of PSs above phase separation temperature (i.e. 55 °C) almost twice (Figure 2b).

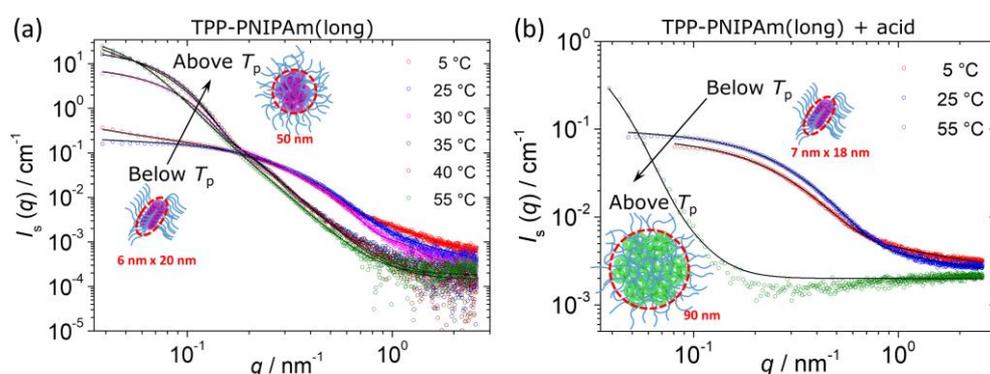


Figure 2. Plots of scattered intensities I_s as a function of temperature for (a) **TPP-PNIPAm(long)** (0.43 wt.%) and (b) **TPP-PNIPAm(long)** (0.43 wt.%) with excess of (*S*)-CSA.

4. Conclusions

Based on these preliminary findings we could make a model of phase separation as seen schematically in Figure 3. There are several new and unusual effects of these studied systems: (1) the phase separation temperature is almost unchanged after addition of acid (i.e. at low pH) and (2) the size of spherical aggregates is about twice larger above separation when acid is added (which is counterintuitive since one would expect opposite due to electrostatic repulsion of charged **TPP** cores). These effects build the link between intrinsic structure of **TPP** derivatives in various conditions which can be exploited for fabrication of nano-/micro-gels with intended dimensions and subsequently use them, for example, as a drug delivery systems or photodynamic sensitizers.

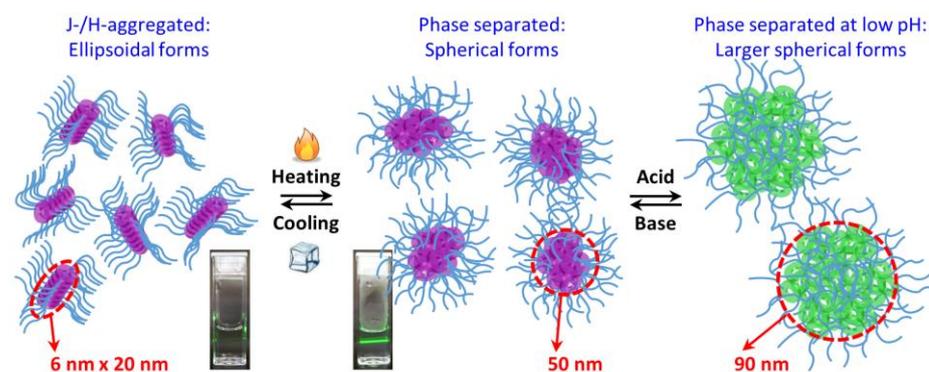


Figure 3. Schematic visualization of **TPP**-polymer units as they behave below (J-/H-aggregated structures) and above (globular structures) phase separation, and after addition of (*S*)-CSA acid. The dimensions indicated are for **TPP-PNIPAm(long)**/water system. Red/purple color represents uncharged **TPP** while green color represents diprotonated form of **TPP**.

Photos of cuvettes with diluted sample irradiated by green laser pointer are also shown.