

## AQUEOUS SUPRAMOLECULAR POLYMER FORMED BY AN AMPHIPHILIC PERYLENE DERIVATIVE

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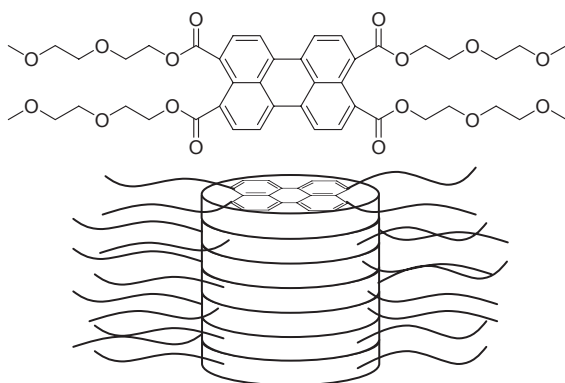


Figure 1: Structure of **Pery-2**.

Supramolecular polymers are reversible one-dimensional assemblies, driven by dynamic non-covalent intermolecular interactions.<sup>1</sup> Apart from biological systems, such self-assemblies are mostly known in organic and non-polar solvents, and interesting material properties have been demonstrated in the case of specific monomers such as ureido-pyrimidones or bis-ureas that can self-organize into very long chains. These materials combine conventional polymer properties with reversibility and responsiveness. It is a challenging objective to expand this innovative theme to aqueous medium. Thus, we designed an amphiphilic molecule affordable in large scale, via easy synthesis and purification.<sup>2</sup> This perylene derivative exhibits a large hydrophobic aromatic core, surrounded by four hydrophilic arms (Figure 1). Such a design provides one-dimensional assembly in water, through intermolecular  $\pi$ -stacking and/or hydrophobic interactions. The four hydrophilic arms are expected to hinder side aggregation of such assemblies and to ensure their water-solubility.

### Qualitative evidence of self-assembly

Spectroscopic evidence (<sup>1</sup>H NMR, UV absorption and fluorescence) show that **Pery-2** is molecularly dissolved in chloroform, but self-associated in more polar solvents such as ethanol and water (Figure 2). Moreover, the relative viscosity of aqueous solutions increases significantly with the concentration of **Pery-2**.<sup>2</sup> This macroscopic

observation is in agreement with a polymer-like behavior of **Pery-2** in water.

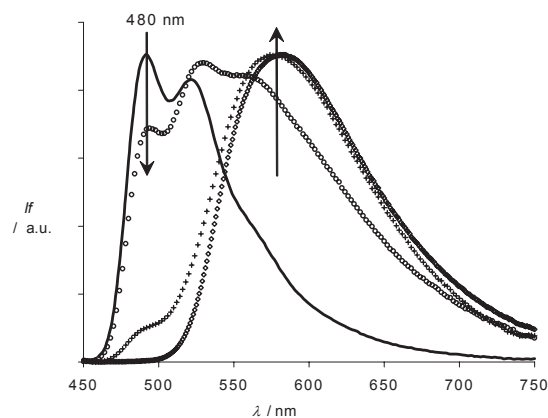


Figure 2. Fluorescence spectra of **Pery-2** in water, at 25°C (—:  $4 \cdot 10^{-7}$  M,  $\circ$ :  $10^{-5}$  M,  $+$ :  $10^{-4}$  M,  $\diamond$ :  $10^{-2}$  M). Excitation at 425 nm. Arrows indicate the direction of change with increasing concentration.

### Shape of the supramolecular aggregates

Solutions of **Pery-2** (in D<sub>2</sub>O at 25°C) were studied using small-angle neutron scattering (SANS) to demonstrate the expected wire-like structure. For the three concentrations, the scattered intensity is proportional to the concentration (Figure 3a). Therefore, it is reasonable to assume that no inter-object correlations are visible: the signal is proportional to the signal of one single object in this  $q$  range. At intermediate scattering vector, the  $qI$  product shows a plateau corresponding to a  $q^{-1}$  dependence well known as the signature of rod-like objects (Figure 3b). However, when  $q$  tends towards zero, the  $qI$  product increases. This shows a stronger  $q$  dependence for  $I$ , attributed to larger additional aggregates.

A model of infinite rigid rods with circular cross section and a uniform scattering length density profile was used. Fitting the scattering curves according to equations (1) and (2) provides the characteristics of the fibrillar objects.

$$I = \frac{\pi}{q} \overline{\Delta b^2} M_L \left[ 2 \cdot \frac{J_1(qr)}{qr} \right]^2 \quad (1)$$

$$(qI)_{q \rightarrow 0} = (qI)_o \exp\left(-\frac{r^2 q^2}{4}\right) \quad (2)$$

$c$  is the rod concentration ( $\text{g}\cdot\text{cm}^{-3}$ ),  $M_L$  is the mass per unit length of the rod ( $\text{g}\cdot\text{\AA}^{-1}$ ),  $\Delta b$  is its specific

contrast (i.e. the difference in density of scattering length between **Pery-2** and the solvent  $\text{D}_2\text{O}$ ),  $r$  is the radius of the cross section, and  $J_1$  is the Bessel function of the first kind.

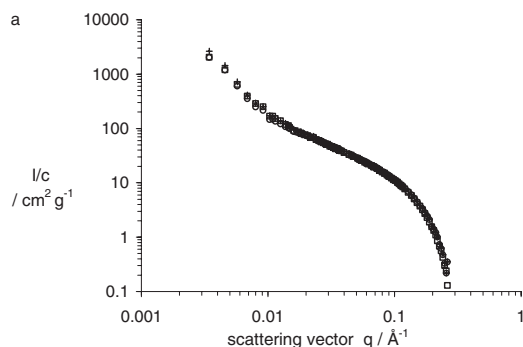


Figure 3a. SANS data (PACE) for solutions of **Pery-2** in  $\text{D}_2\text{O}$ , at 0.5% (o), 1% (+) and 2% (□) at  $25^\circ\text{C}$ . (a):  $I/c$  vs.  $q$ , (b):  $qI$  vs.  $q$ , curves were fitted according to equation (1).

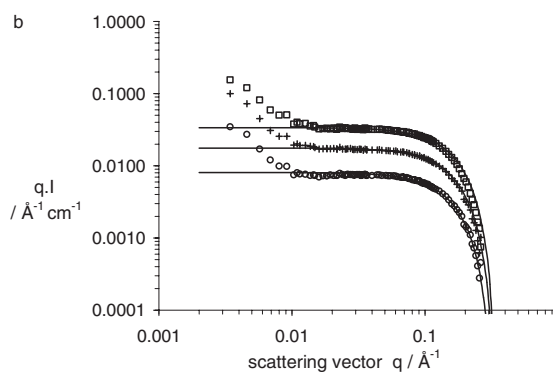


Figure 3b. shows satisfying fits for  $q \geq 0.01 \text{ \AA}^{-1}$ , establishing a constant rod diameter ( $2r = 24 \text{ \AA}$ ) over this range of concentration. A  $24 \text{ \AA}$  diameter is coherent with the largest dimension of **Pery-2**. This confirms that the rod is a one-dimensional assembly of stacked molecules of **Pery-2**, i.e. a supramolecular polymer in water.

### Strength of the association

A model involving an infinite number of equilibria has been used to describe the formation of the long supramolecular chains, with a dimerization ( $K_2$ ) and multimerization ( $K$ ) constant.<sup>2</sup> Then, the free monomer concentration ( $M_1$ ) can be numerically calculated from the mass balance equation. NMR and fluorescence data were used to determine these association constants. The knowledge of the association constants makes it possible to compute the degree of polymerization of the supramolecular polymer versus concentration (Figure 4). Average chains of 50 to 100 units can be obtained at reasonable concentrations.

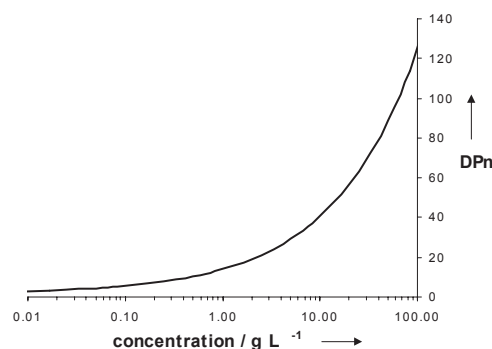


Figure 4. Calculated number average degree of polymerization of **Pery-2** versus concentration, in water.

### References

1. L. Brunsveld, B. J. B. Folmer, E.W.Meijer, R.P.Sijbesma, *Chem. Rev.* **2001**, *101*, 4071-4097
2. A. Arnaud, J. Belleney, F. Boué, L. Bouteiller, G. Carrot, V. Wintgens, *Angew. Chem. Int. Ed.* **2004**, *43*, 1718-1721