

Supramolecular Chirality Transfer to Large Random Aggregates of Porphyrins

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ELECTRONIC SUPPORTING INFORMATION

Experimental Details.

Chemicals. 5,15-bis(N-methylpyridinium-4-yl)-10,15-bis-diphenylporphine (t-H₂Pagg) was purchased from Mid-Century Chemicals as the chloride salt and used as received. Its copper(II) derivative (t-CuPagg) was prepared via previously reported procedures.¹ Porphyrins stock solutions were prepared from the solids in Millipore purified water and stored in the dark. Solution concentrations were determined from known molar extinction coefficient at the Soret maximum (t-CuPagg: $2.34 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$).²

Sodium salts of poly-D- and poly-L-glutamic acid (FW ~ 17 kD) were obtained from Aldrich Chemicals Co. Stock solution of the polypeptides were prepared by dissolving the solids in Millipore purified water, and dialyzing exhaustively against acetate buffer at pH 4.2 and ionic strength (*IS* = 5 mM). Concentrations of the peptides solutions were determined spectrophotometrically, using $\epsilon_{205} = 2240 \text{ M}^{-1} \text{ cm}^{-1}$.³

All other reagents were supplied by Aldrich Chemicals Co. and used without further purification.

Methods. Mixing of the reactants was carried out in methacrylate cuvettes at room temperature, by using two protocols: (i) *protein first*, where a small volume of porphyrin stock was added initially to polyglutamate (PGA) in a 5 mM acetate buffer at pH 4.2, successively adding NaCl up to *IS* = 0.1 M; (ii) *protein last*, where a small volume of porphyrin stock was added initially to NaCl, successively adding PGA in a 5 mM acetate buffer at pH 4.2 (final *IS* = 0.1 M).

Extinction measurements were conducted on a Jasco mod. V-550 spectrophotometer, and resonance light scattering (RLS) experiments were performed on a Jasco mod. FP-750 spectrofluorimeter, adopting a synchronous scan protocol with a right angle geometry.⁴ RLS spectra were not corrected for the absorption of the samples. Whenever possible, plastic cuvettes were used to reduce porphyrin staining of the cuvette surface. Quartz cuvettes were employed only in the case of measurements in the UV region, or for circular dichroism experiments carried out on a Jasco mod. J-710 spectropolarimeter.

Light scattering experiments were performed by using a He–Ne laser source ($\lambda=632.8 \text{ nm}$) at a power of 10mW, linearly polarized orthogonally to the scattering plane. The scattering angle was changed by a computer-controlled home-made goniometer apparatus in the range 30–140°.⁵

For the Dynamic Light Scattering measurements, the scattered light was analyzed using a MALVERN 4700 correlator which builds up the normalized intensity autocorrelation function, $g_2(t)$, which is related to the electric field correlation function, $g_1(t)$, through the Siegert relation:⁶

$$g_2(t) = 1 + \beta |g_1(t)|^2$$

with β a spatial coherence factor depending on the geometry of the detection optics.

In the case of dilute solutions of monodispersed particles, $g_1(t) \sim \exp(-DQ^2t)$, D being the translational diffusion coefficient and Q the exchanged wavevector ($Q = [(4\pi n)/\lambda] \sin(\theta/2)$, with n the refractive index of the sample, λ the wavelength of the incident light in the vacuum, and θ the scattering angle).^{6, 7} From the diffusion coefficient, the hydrodynamic radius of diffusing particles can be calculated using the Einstein–Stokes equation:

$$R_H = \frac{k_B T}{6\pi\eta D}$$

where k_B is the Boltzmann constant, T the absolute temperature, and η the viscosity of the solvent.

For the Static Light Scattering measurements, the collected scattered intensity profile was corrected for the contribution of the solvent and fitted with the power law describing fractals:^{8, 9}

$$I(Q) \propto Q^{-D_f}$$

where D_f (< 3 and not integer) is called fractal dimension and represents the parameter relating the mass of the cluster, M , to its radius R ($M \propto R^{D_f}$).

This exponent is not only a structural parameter, being connected to the density of the clusters, but it is also a signature of the mechanism of aggregation depending on the sticking probability of the monomers and small clusters in solutions. Statistical physics and computer simulations have related its value to different growth processes: $D_f=2.5$ indicates percolation and diffusion-limited aggregation (DLA); $D_f=1.75$ diffusion-limited cluster-cluster aggregation (DLCCA); $D_f=2.1$ reaction limited aggregation (RLA).^{9, 10}

References

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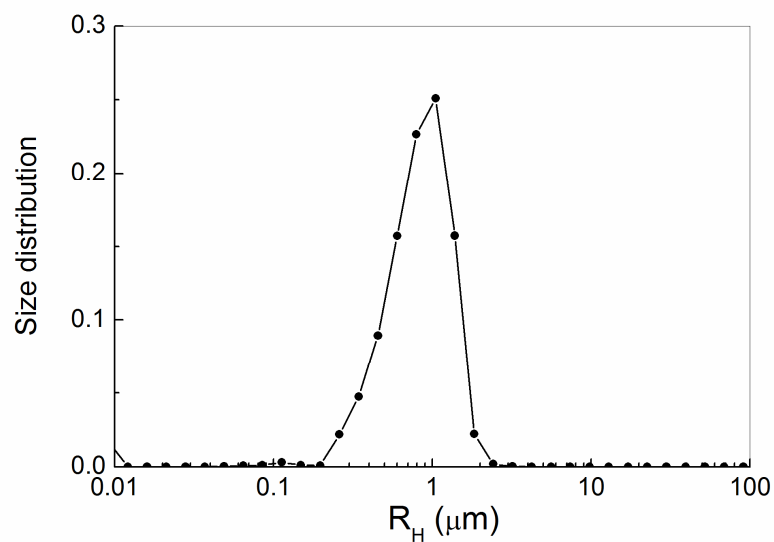


Figure S1. Size distribution of the t-CuPagg aggregates. Experimental conditions: [t-CuPagg] = 5 μ M; $IS = 0.1$ M.

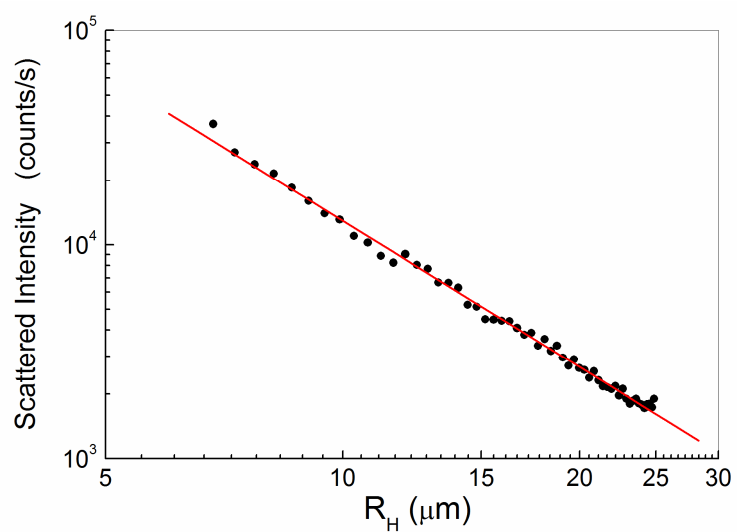


Figure S2. Scattered intensity profile of the t-CuPagg aggregates in the same experimental conditions as in Figure S1. The continuous line is the fit according to the fractal power law ($D_f \sim 2.4$)

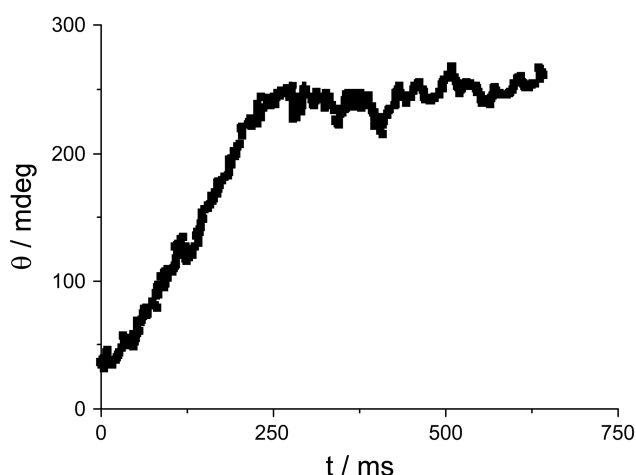


Figure S3. Change in ellipticity at fixed wavelength (453 nm) monitored through a stopped-flow kinetic experiment where pre-aggregated t-CuPagg is added to L-PGA. Experimental conditions: [t-CuPagg] = 5 μ M; [Glu] = 500 μ M; $IS = 0.1$ M; [buffer] = 5 mM, pH 4.2.

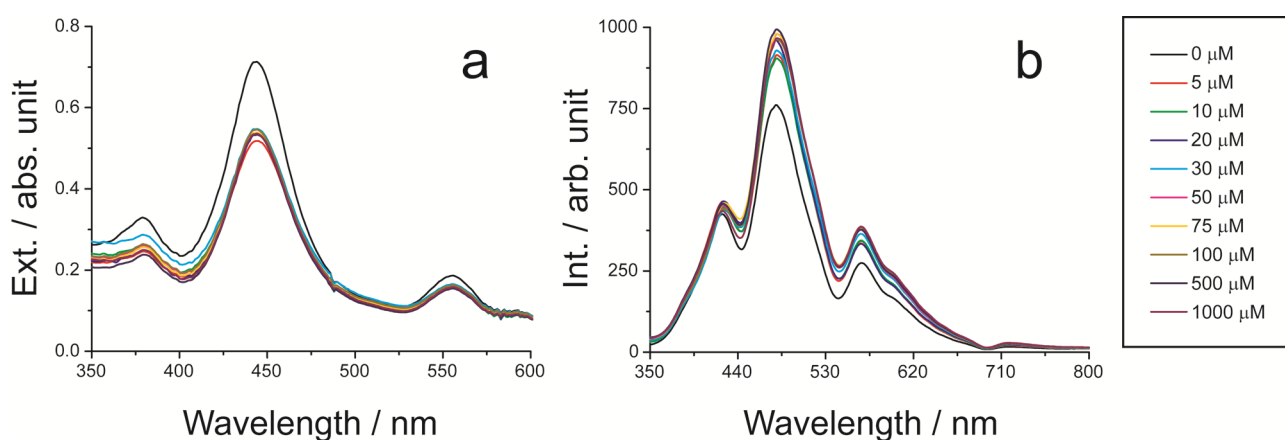


Figure S4. UV/vis extinction (a) and RLS (b) spectra of a batch titration experiment where increasing amounts of L-PGA (as indicated by the legend) have been added to fully-aggregated solutions of t-CuPagg. [t-CuPagg] = 5 μ M; $IS = 0.1$ M; [L-PGA] = 0-1000 μ M; [buffer] = 5 mM, pH 4.2; mixing protocol: *protein last*.

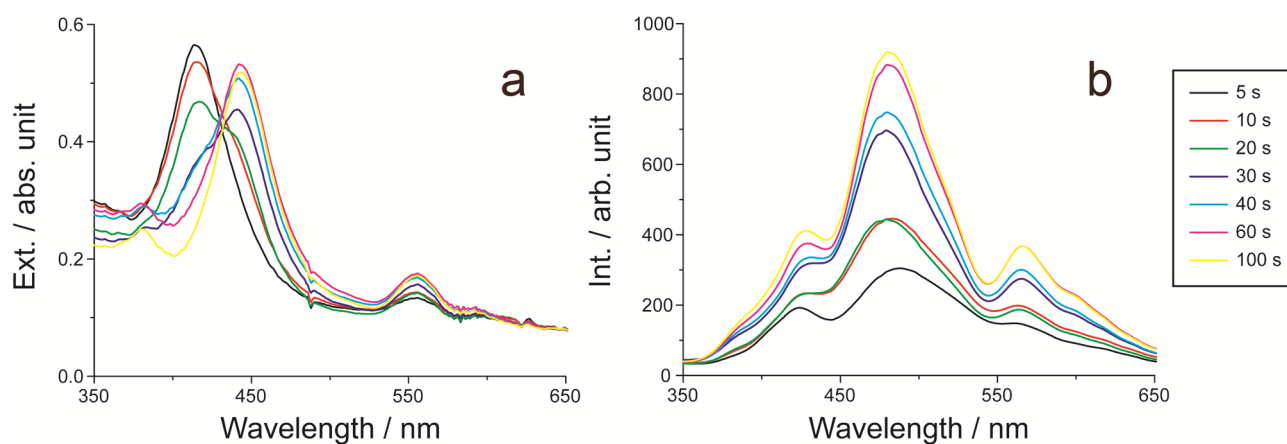


Figure S5. Comparison between the UV/vis extinction (a) and RLS (b) spectra of the t-CuPagg aggregating solutions after injecting L-PGA at the different time delays (as indicated by the legend). Experimental conditions: [t-CuPagg] = 5 μ M; IS = 60 mM; [L-PGA] = 200 μ M; [buffer] = 5 mM, pH = 4.2; mixing protocol: *protein last*.