

Electronic Supporting Information

for

Counter-anions role on the kinetics and chirality of porphyrin J-aggregates

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Experimental section

The porphyrin meso-tetrakis(4-sulfonatophenyl)porphyrin (TPPS₄) was purchased from Aldrich Co. as the tetrasodium salt. Aqueous stock solutions of this porphyrin (200 μM) were prepared in dust-free Millipore water, stored in the dark in glass vials, and used within a week of preparation. The concentration of the porphyrin samples was determined spectrophotometrically using $\epsilon_{414} = 5.33 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ in water. High purity inorganic acids (H₂SO₄, HCl, HBr, HNO₃, HClO₄) were purchased from Aldrich Co. Samples of J-aggregated TPPS₄ were prepared following the porphyrin first (PF) mixing protocol: (PF) consists of the addition of a predetermined volume of acid stock solution to a diluted porphyrin sample. Aggregation was carried out in 0.5 M acid solution. UV/Vis spectra were collected with a Hewlett-Packard 8453 diode array spectrophotometer using 1 cm pathlength quartz cells. Kinetic experiments were carried out in the thermostated compartment of the spectrophotometer at 298K, with a temperature accuracy of ± 0.1 K. The analysis of the kinetic profiles was performed using a non-linear fit of the extinction data according to equation 1:

$$\text{Eq. 1} \quad \text{Ext} = \text{Ext}_{\text{inf}} + (\text{Ext}_0 - \text{Ext}_{\text{inf}}) (1 + (m - 1)\{k_0 t + (n + 1)^{-1} (k_c t)^{n+1}\})^{-1/(m-1)}$$

(Ext, Ext₀ and Ext_∞ are the extinction at time t, at starting time and at the end of aggregation, respectively).

The circular dichroism (CD) spectra were recorded on a JASCO J-720 spectropolarimeter, equipped with a 150 W xenon lamp. The ellipticity was obtained by calibrating the instrument with a 0.06% aqueous solution of R-camphorsulfonic acid. CD spectra were corrected both for the cell and

solvent contributions. To quantify the sign and magnitude of the supramolecular chirality we used the dissymmetry factor $g = \Delta\varepsilon/\varepsilon = \Delta A/A$, $\Delta A = \Theta/32980$, where: ΔA in absorbance units, Θ is ellipticity in mdeg).

The values for the parameter ΔG_{HB} (used in Figs 3 and 4) have been calculated from the values of the changes of entropy associated with the structural variations, ΔS_{struct} , reported in Table 7 of ref. 19 for the various anions, according to the following equation:

$$\Delta G_{HB} = -0.18 - 1.022 \times 10^{-2} \times (\Delta S_{struct} / \text{J K}^{-1} \text{ mol}^{-1})$$