Electronic Supplementary Material (ESI) for Nanoscale.

Induced circular dichroism from helicoidal nano substrates to porphyrins: The role of chiral self-assembly

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SUPPORTING INFORMATION

SI-1- Direct grafting on the silica surface.

Direct grafting of the porphyrins has been performed on the surface of the silica helices *via* electrostatic interactions for TPPS and metallo-TPPS and *via* covalent linkages for hemin.

a-Direct grafting in solution:

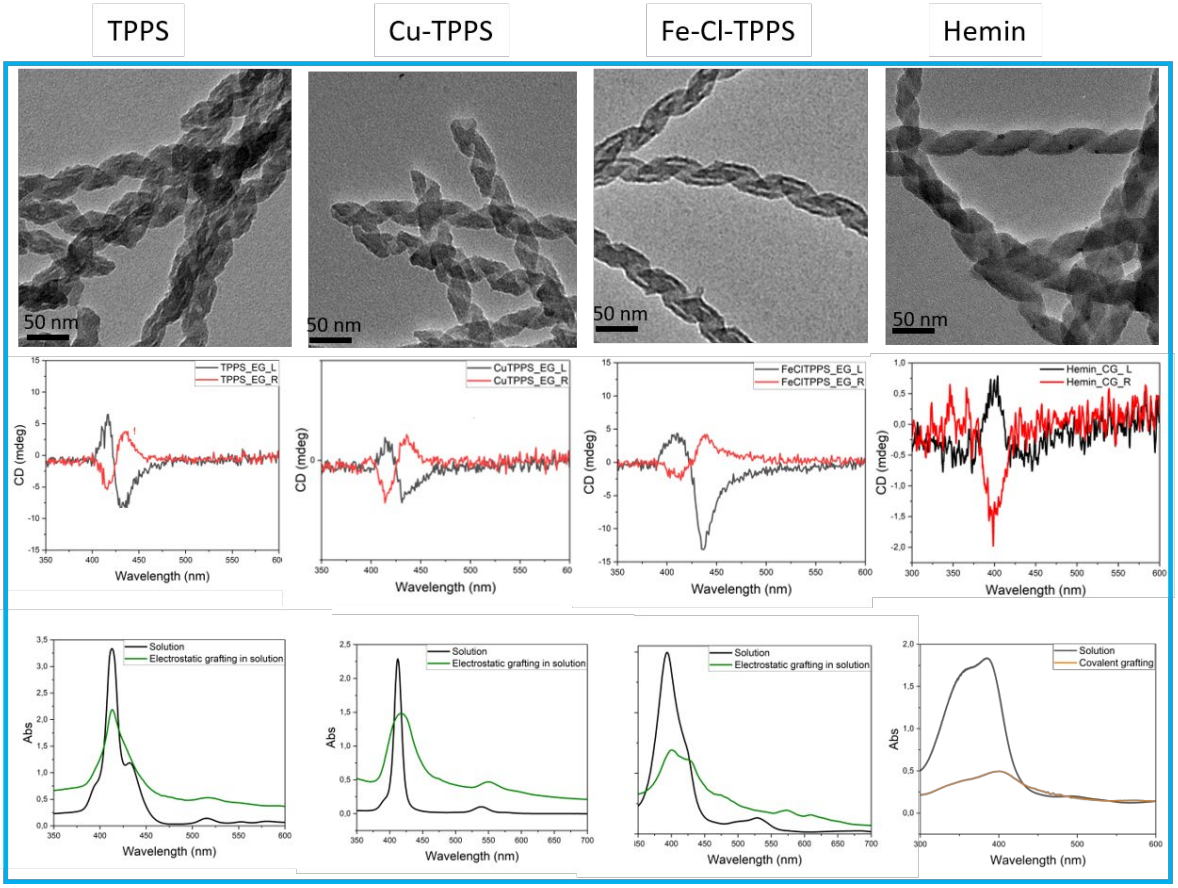


Figure S1-a: TEM images, CD spectra and UV/vis absorption spectra of the direct grafting in solution (electrostatic interactions for the TPPS and metallo-TPPS and covalent bond for the hemin). The path length used was 2 mm and the concentration of the suspensions was 1 mg/mL. The UV/vis spectra also show the TPPS, Fe-Cl-TPPS, Cu-TPPS and hemin in solution (without helices) at the concentration of 0.035 mM, 0.060 mM, 0.025 mM and 0.150 mM respectively.

b- Direct grafting after drop cast on a quartz plate:

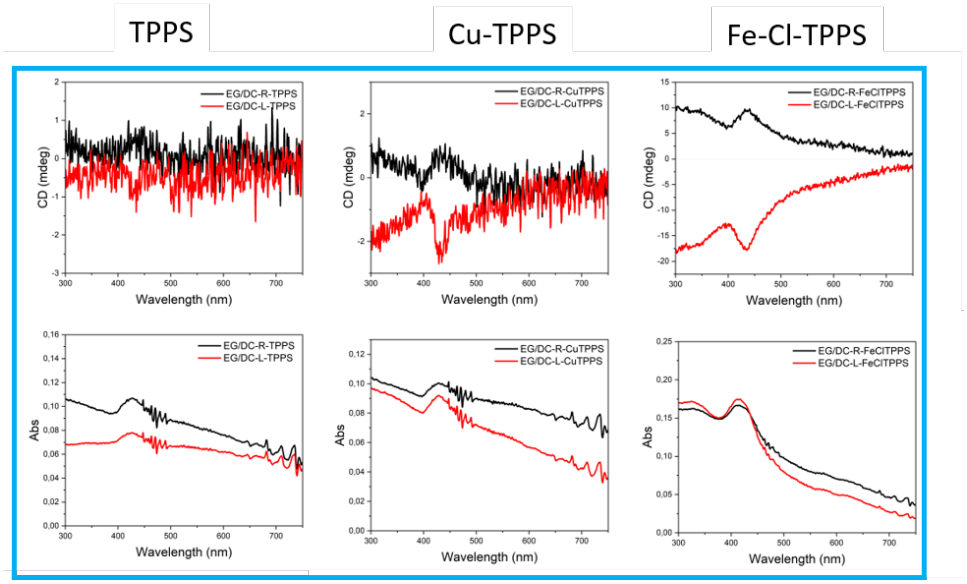


Figure S1-b: CD and UV/vis absorption spectra of the direct grafting drop casted on quartz plates.

c- Direct grafting after drop cast on quartz plate + drop cast of porphyrins:

Being the most promising sample, this test has been done with the free base TPPS. We drop casted a solution of TPPS onto helices previously grafted with TPPS (CD spectra in SI1-b). Here the ICD was 10 times weaker than when TPPS was drop casted onto naked helices (g-factor is $1{,}3.10^{-3}$ vs $1{,}2.10^{-2}$). This suggests that the grafted TPPS hinders the growth of J-aggregates parallel to the helix.

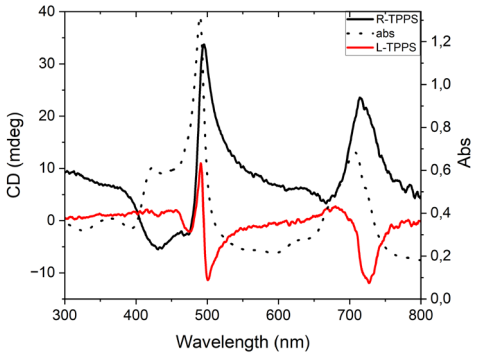


Figure S1-c: CD and UV/vis absorption spectra of the TPPS direct grafting drop casted on quartz plates followed by TPPS drop cast. Left and right signals are not perfectly opposite because of the concentration deposited on the quartz plate but the g-factors are similar.

SI-2- Definition of the *g*-factor

Electronic circular dichroism is defined as the difference

$$\Delta A = A^l - A^r \qquad (1)$$

where A^l and A^r are the absorptions of left and right circularly polarized light. For historical reasons, the output of CD instruments is usually measured as ellipticity θ (in mdeg), related to CD through Δθ (mdeg) = 32982 ΔA.[i] In analogy to Beer-Lambert law, one can define a molar quantity

$$\Delta\varepsilon = \varepsilon^l - \varepsilon^r = \frac{\Delta A}{\mathrm{c \cdot b}} \qquad (2)$$

which is dependent on concentration *c*, expressed in mol/L, and on pathlength *b*, expressed in cm.

The definition of equation (1) immediately tells us that *CD* can be measured only in correspondence to absorption bands. It is worth observing that *CD* is a signed quantity, because, ε^l may be smaller or larger than ε^r (and consequently A^l and A^r); it is easy to show that for each absorption band, the *CD* of two enantiomers are always exactly opposite.

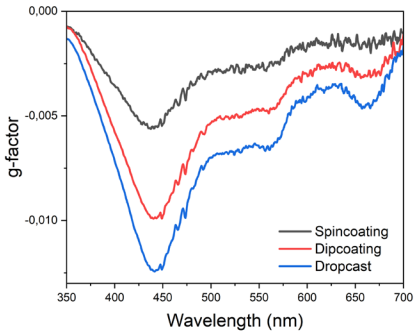
To discard the problem of the dependence on the sample concentration on the measured CD, optical activity of chiral system is often measured through the dimensionless g factor[ii]:

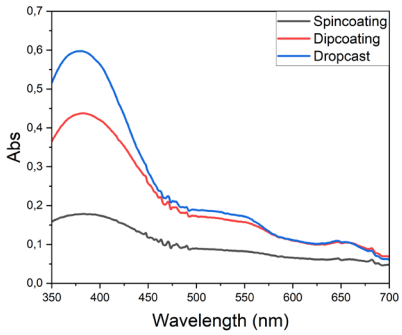
$$\mathrm{g} = \frac{\Delta\varepsilon}{\varepsilon} = \frac{\varepsilon^l - \varepsilon^r}{\varepsilon} = \frac{A^l - A^r}{A} = \frac{\Delta\theta}{32982A} \qquad (3)$$

where, ε^l and ε^r are the molar absorption coefficients for left and right polarized light, $\Delta\varepsilon$ and ε are the molar circular dichroism and molar absorptivity, A is conventional absorbance of non-polarized light (equivalent with the average of A^l and A^r). Thanks to the g-factor, chiroptical properties can be estimated and compared independently of the concentration and the pathlength.

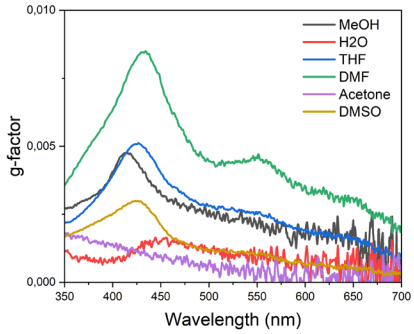
SI-3- Optimization of the drop cast parameters with hemin

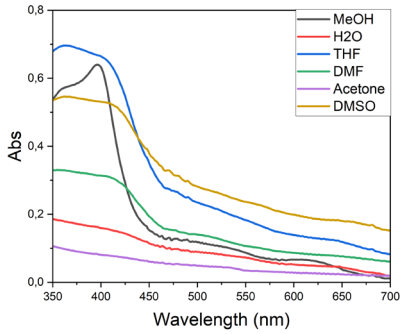
a) Technique used: spin coating, dip-coating and simple drop-casts have been compared for hemin, always showing maximum g factors for the simple drop-casts.





b) Solvent used for the dilution of hemin before drop-cast.

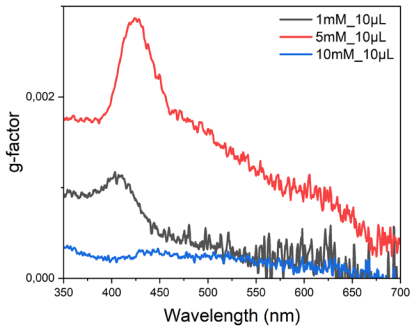


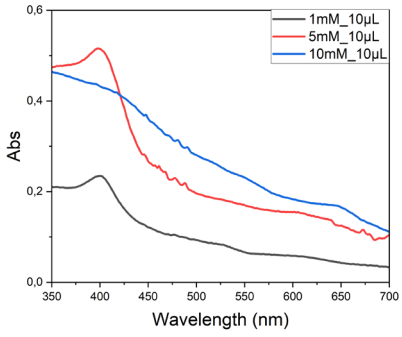


MeOH: Methanol; H_2O: Water; THF: Tetrahydrofurane; DMF: N,N-dimethylformamide; DMSO: Dimethylsulfoxide

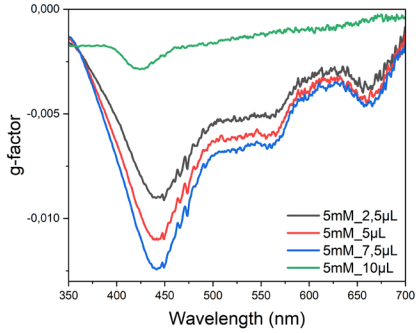
c) Ratio $m_{helix}/n_{molecule}$ used

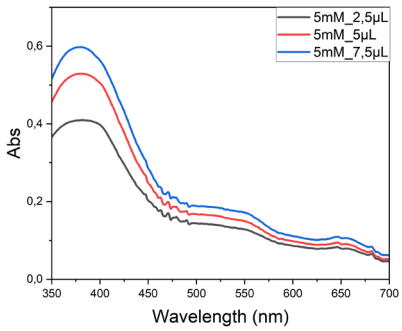
I. Test concentration for fixed volume (preliminary tests to estimate the right number of moles of hemin needed for 100 µg of helices for optimized CD induction)



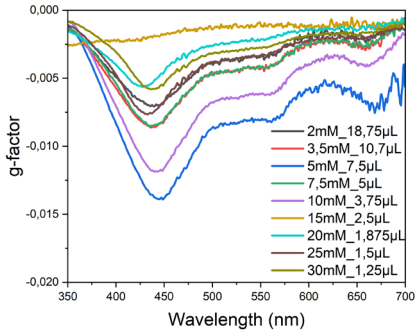


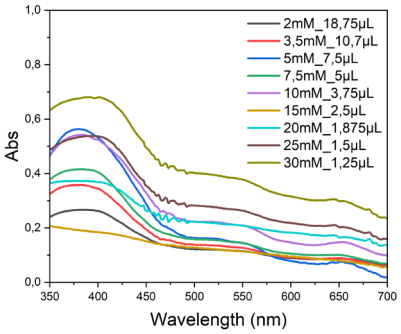
II. Test volume for fixed concentration (to get a more accurate value)





III. Test solvent evaporation kinetics: for a fixed hemin molarity, the deposited volumes are optimized (so the hemin concentration is modified to keep the fixed amount of hemin molecules).

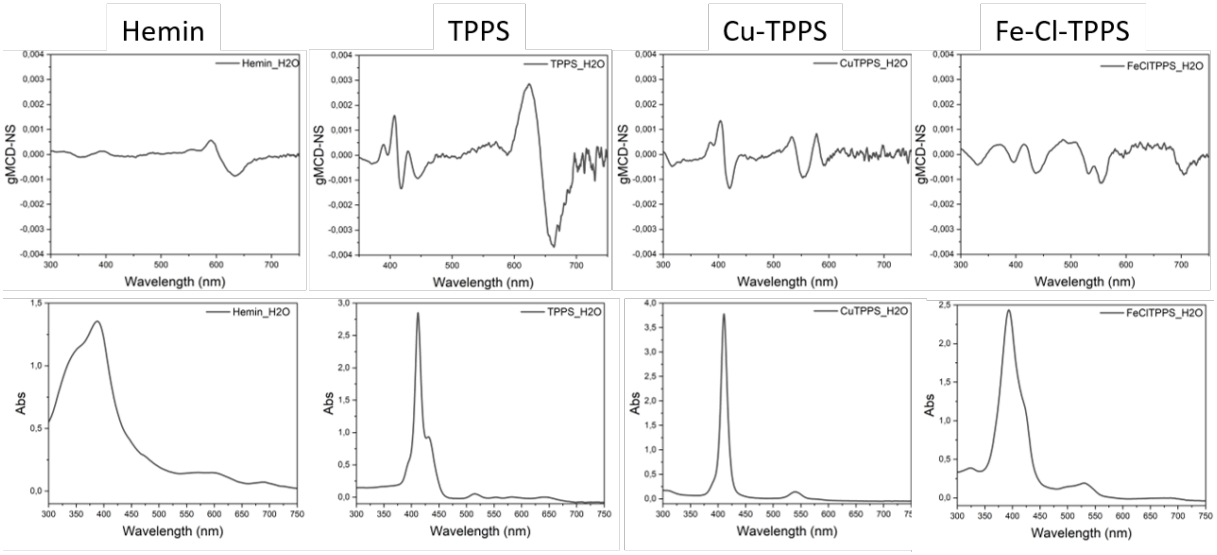




The best parameters are: 1- deposit via drop-cast 100 µg of silica nanohelices. 2- Add via drop-cast 7.5 µL of a solution of porphyrin in DMF at 5 mM.

SI-4 : MCD of the pure solutions of porphyrins

MCD has been measured for the porphyrins in H_2O under a magnetic field oriented North-South (NS). Because the porphyrins in solution do not have any CD signal, no data treatment was necessary. The multiple peaks seen in Fe-Cl-TPPS likely correspond to the monomer and the µ-oxo dimer.



Path length was 2 mm. Concentrations for the hemin, TPPS, Cu-TPPS and Fe-Cl-TPPS solutions were respectively of 0.110 mM, 0.031 mM, 0.040 mM and 0.097 mM

SI-5 : MCD of the DC samples

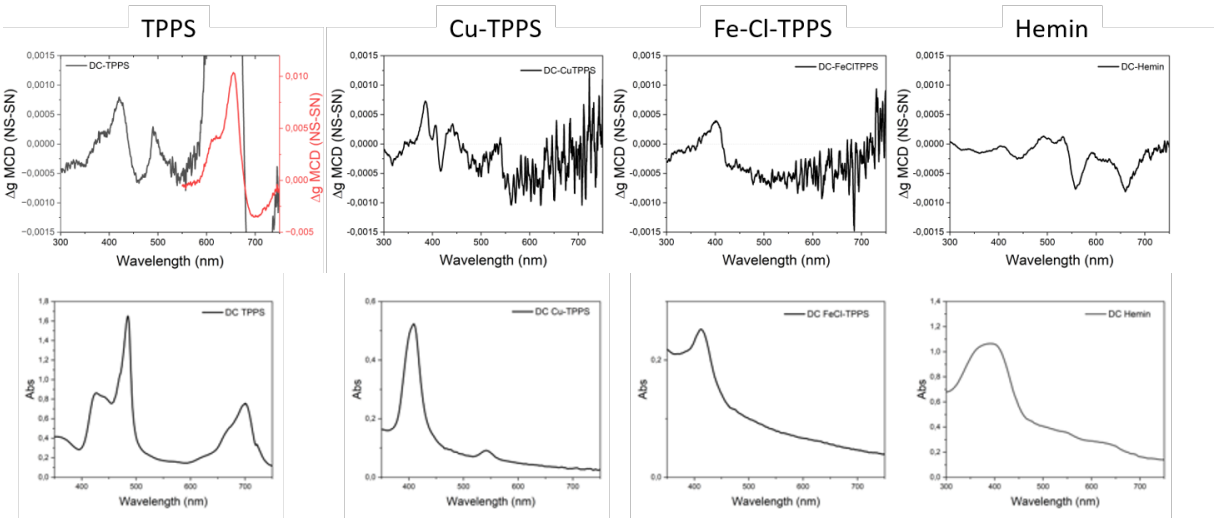
Because both MCD and ICD signals are detected when a sample is irradiated with polarized light under an external magnetic field, it was mandatory to recalculate MCD values simply by subtracting the measured signal with magnetic field by the same measurement without a magnetic field:

$$ICD(B \neq 0) = ICD(B = 0) + MCD$$

$$MCD = ICD(B \neq 0) - ICD(B = 0)$$

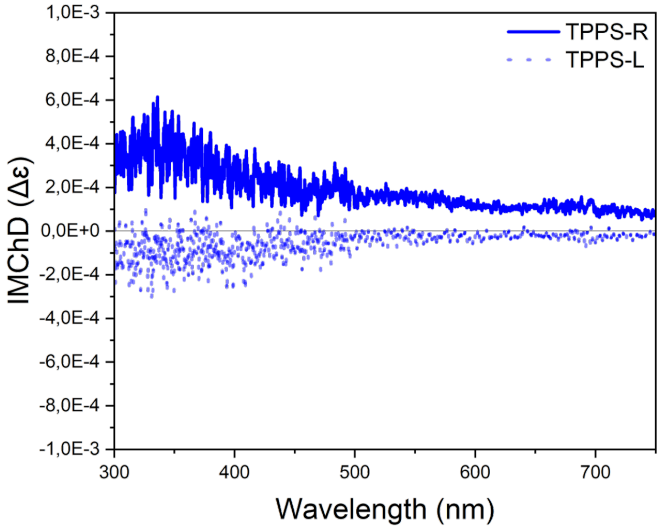
Moreover, those calculations were made with g values, in order to be able to subtract comparable numbers, because absorbance values slightly change between the two setups (standard ICD and the one with magnetic field).

Finally, in order to avoid a maximum of noise and artifacts that can appear during the subtraction, particularly for very low intensity signals, the graphs presented here show the differential MCD signal under the parallel (NS) and antiparallel (SN) magnetic field.



SI-6 : MChD of the TPPS DC sample

Typical MChD spectrum for the drop-casted samples investigated in this study. This data refers to TPPS (both Right and Left) at T = 4.0 K under an alternating magnetic field B of ±2.0 T.



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[i] An introduction to circular dichroism spectroscopy: https://www.chem.uci.edu/~dmitryf/manuals/Fundamentals/CD%20spectroscopy.pdf

[ii] N. Berova, et al, Application of electronic circular dichroism in configurational and conformational analysis of organic compounds, Chem. Soc. Rev., 2007, 36, 914-931.