## Tuning the chiroptical and morphological properties of steroidalporphyrin aggregates. A mechanistic, structural, and MM investigation.

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## **Electronic Supplementary Material (ESI)**

The conformational properties of the porphyrin **H<sub>2</sub>CholP** were investigated by Molecular Mechanics (MM) calculations adopting the following procedure: a) the conformers arising from internal rotation around the torsional angles of the side chains linking the steroid to the porphyrin (Fig. ESI 1) were built up by making use of the rotational isomeric state model; b) the conformational energy was then optimized by varying all torsional angles associated to both the steroid side-chains. The potential energy comprised electrostatic, nonbonding, hydrogen bond, and torsional interactions, was calculated by using standard bond angles and lengths, as implemented in the MM4 force field. [1. Allinger NL, Chen K, Lii J-H. An Improved Force Field (MM4) for saturated hydrocarbons. *J. Comp. Chem.* 1996; **17**, 642; Nevens N, Chen K, Allinger K. Molecular Mechanics (MM4) calculations on alkenes. *J. Comp. Chem.* 1996; **17**, 669-694; Nevins N, Lii J-H, Allinger NL. Molecular Mechanics (MM4) vibrational frequency calculations for alkenes and conjugated hydrocarbons. *J. Comp. Chem.* 1996; **17**, 642; Neven S, MM4) vibrational frequency calculations of alkenes and conjugated hydrocarbons. *J. Comp. Chem.* 1996; **17**, 675; Nevins N, Allinger NL. Molecular Mechanics (MM4) vibrational frequency calculations for alkenes and conjugated hydrocarbons. *J. Comp. Chem.* 1996; **17**, 730]



Fig. ESI 1. Molecular drawing of the porphyrin  $H_2CholP$  indicating the torsional angles used for generating the starting conformations in the MM calculations.

The apparent dielectric constant of the solvent mixture, implicitly taken into consideration in the calculations, is  $\varepsilon_r = 70.5$ . The value has been calculated by using the  $\varepsilon_r$  of the pure solvents, weighted by their molar fractions.

The MM calculations indicate that the structure with the deepest energy minimum shows a saddled distorted geometry, and is stabilized by two non-conventional H-bonds among the hydroxyl groups of the steroid moieties and the  $\pi$ -orbitals of the meso-phenyl groups of the porphyrin.

This structural arrangement is characterized by a hydrophobic surface (Fig. ESI 2) which makes it particularly suitable for non-bonding interactions with other molecules having similar features, favoring the formation of extended supramolecular structures.



Fig. ESI 2. Surface of  $H_2$ CholP monomer (chromatic legend of the atoms: Oxygen (red); Nitrogen (bleu); Carbon (ochre); Hydrogen (white)).

The modelling was also carried out by explicitly considering the solvent molecules. In particular, we have analyzed the two limit cases in which the monomer is surrounded by molecules of DMA or water. The results have been reported in Table ESI1 and in Figure ESI3.

	d (O centroid) (Å)	angle (deg)
implicit solvent	2.93	168
DMA	2.89	170
H <sub>2</sub> O	3.10	156

Table ESI1. C	Calculated	distance a	nd angles	for the	O-aromatic	centroid



Figure ESI3. Molecular structures of the porphyrin in the presence of DMA (A; porphyrin in red) and water (B; porphyrin in light brown).

In the case of the good solvent (DMA) were not observed significant structural variations. With the water, as expected, was noted the formation of a cage-like structure of the solvent which must carry the cavity able to accommodate the molecule substantially hydrophobic.

The distance O ... phenyl centroid is only slightly increased because the hydroxyl interacts with vicinal water molecules. As a general consideration, we can conclude that even in the extreme case (not real) in which are present only water molecules, the overall structure is retained because of the steric hindrance of the steroid. Of course, water plays a pivotal role in the aggregation process but, in our opinion, for our system the effect is mainly entropic. As reported in the paper, the J-aggregate is favored overwhelmingly by the spatial arrangement of the two side-chains because we did not observe significant structural differences in the dimer when the two solvents were explicitly considered.



Fig. ESI 4. Plot of the energy per monomer vs number of porphyrin monomer.