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Paper:

Hierarchical transfer of chiral information from the molecular to the mesoscopic scale by Langmuir-Blodgett deposition of tetrasteroid-porphyrins

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Electronic Supplementary Information

ESI1. Synthesis of the tetrasteroid porphyrins investigated

TSP – [4-[10,15,20-tris[4-[4-[(3R,5R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethyl-2,3,4,5,6,7,8,9,11,12,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl]pentanoyloxy]phenyl]porphyrin-5-yl]phenyl], 4-[(3R,5R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethyl-2,3,4,5,6,7,8,9,11,12,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl]pentanoate.
4-[(3R,5R,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3-(2,2,2-trifluoroacetyl)oxy-2,3,4,5,6,7,8,9,11,12,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl]pentanoic acid was dissolved in toluene (15 ml), stirred and $COCl_3$ (2ml) added drop wisely. After 1.5 h the residual $COCl_2$ was removed by evaporation with toluene repeatedly and 67 mg of 5,10,15,20-tetrakis(4-hydroxy-phenyl)porphyrin (HTPP) dissolved in pyridine (10 ml) was added. The reaction mixture was heated to 75°C, evaporated and purified by column chromatography (silica gel, elution CH_2Cl_2). The desired fraction was evaporated, subsequently dissolved in THF:MeOH 1:1 (10 ml) and washed with saturated solution of $NaHCO_3$ (1 ml) to deprotect the lithocholic acid. Stirred for additional 2 hours, afterwards it was purified by flash chromatography (silica gel, CH_2Cl_2:MeOH 50:1). TSP (35mg) was obtained with 17% overall yield.
^{1}H NMR (300 MHz, CDCl3) -3.10 s (2 H) ,0.67 s (12 H), 0.94 s (12 H), 1.00 d (*J*=5.86 Hz, 12 H), 1.03 - 2.05 m (104 H), 2.29 - 2.61 m (8 H), 3.12 - 3.24 m (4 H), 7.20 - 7.28 dd (8 H), 7.90 – 7.98 dd (8 H), 8.60 – 8.64 s (8 H), 8; $C_{140}H_{182}N_4O_{12}$ calculated monoisotopic mass: 2111.3, found: MALDI-TOF 2112.3 [M+1].

TSPc - [4-[10,15,20-tris[4-[4-[(3R,5S,7R,8R,9S,10S,12S,13R,14S,17R)-3,7,12-trihydroxy-10,13-dimethyl-2,3,4,5,6,7,8,9,11,12,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl]pentanoyloxy]phenyl]porphyrin-5-yl]phenyl] 4-[(3R,5S,7R,8R,9S,10S,12S,13R,14S,17R)-3,7,12-trihydroxy-10,13-dimethyl-2,3,4,5,6,7,8,9,11,12,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl]pentanoate.
4-[(3R,5R,7R,8R,9S,10S,12S,13R,14S,17R)-7,12-dihydroxy-10,13-dimethyl-3-(2,2,2-trifluoroacetyl)oxy-2,3,4,5,6,7,8,9,11,12,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl]pentanoic acid (295mg, 6ekv.) was added to a mixture of HTPP (70mg, 0,1 mmol) (15 ml), EDC.HCl (115mg, 6ekv.) and DMAP (12mg, 1ekv) in DMF and stirred overnight, evaporated under reduced pressure and chromatographed (silica gel, CH_2Cl_2:MeOH 30:1). The desired fraction

was evaporated under reduced pressure, dissolved in THF:MeOH 1:1 (10 ml) and washed with saturated solution of $NaHCO_3$ (1 ml), stirred for 2 h, evaporated and chromatographed on column (silica gel, CH_2Cl_2:MeOH 10:1). The desired fraction was evaporated under reduced pressure. 24 mg of TSPc was obtained, overall yield: 9%.

^{1}H NMR (300 MHz, CDCl3) -3.10 s (2 H) ,0.67 s (12 H), 0.94 s (12 H), 1.00 d (*J*=5.86 Hz, 12 H), 1.03 - 2.05 m (104 H), 2.29 - 2.61 m (8 H), 3.12 - 3.24 m (4 H), 3.56-3.60 m (4 H), 3.76-3.80 m (4 H), 7.20 - 7.28 dd (8 H), 7.90 – 7.98 dd (8 H), 8.60 – 8.64 s (8 H), 8; $C_{140}H_{182}N_4O_{20}$ calculated monoisotopic mass: 2239.3 found: MALDI-TOF 2240.3 [M+1].

ESI2. Definition of the torsional angles minimized in the Molecular Mechanics calculations.

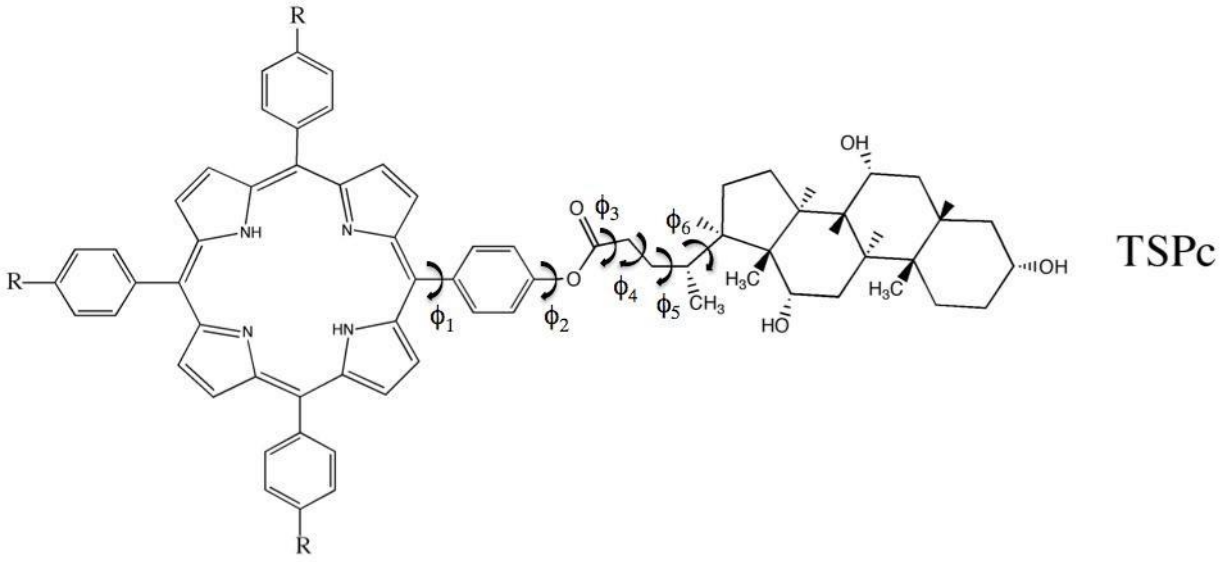

Figure S1. Torsional angles minimized in the MM calculations using the rotational isomeric state approximation.

ESI3. Absorption and fluorescence emission spectra of TSP and TSPc in DMSO and DMSO/H_2O solutions.

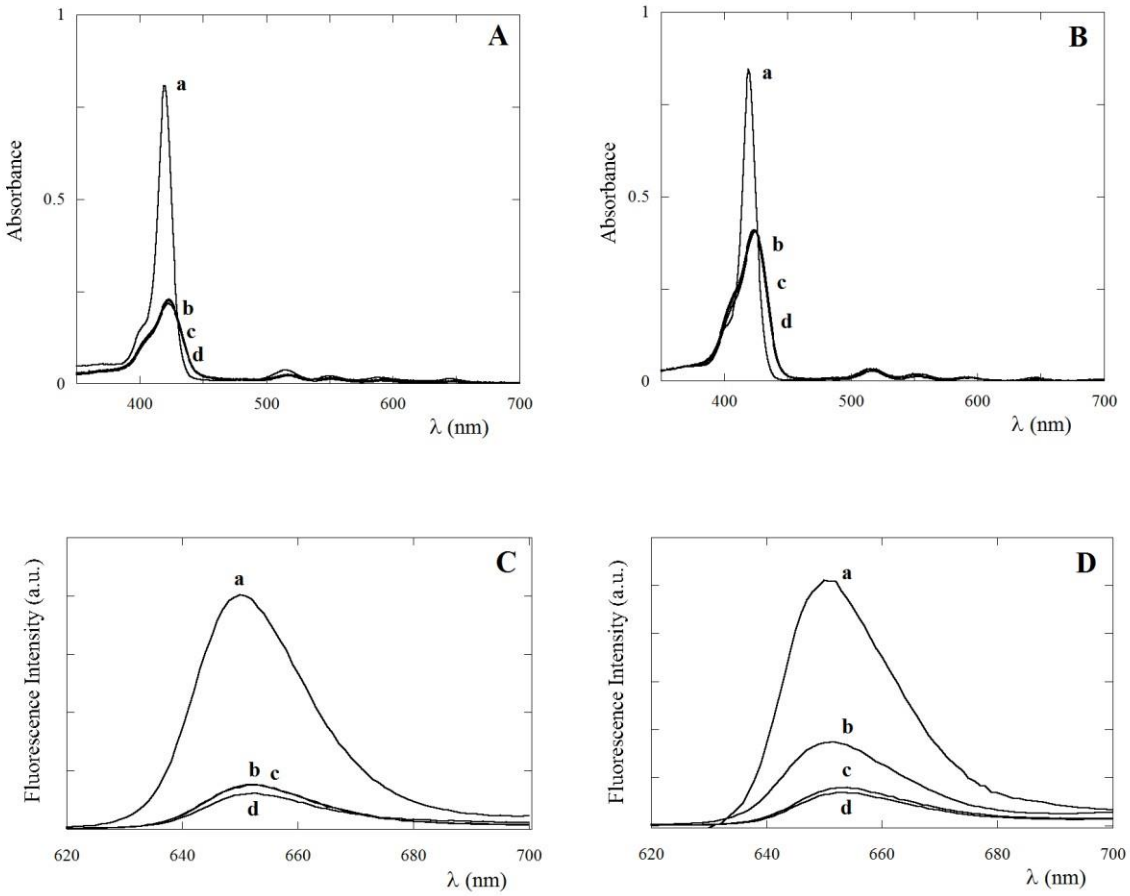

Figure S2. UV-Vis absorption and fluorescence emission spectra of TSP (A, C) and TSPc (B, D) in DMSO (a) and in DMSO/H_2O 70/30 (b), 50/50 (c) and 30/70 v/v (d).

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ESI4. Circular dichroism spectra of TSP and TSPc in DMSO and DMSO/H_2O mixtures.

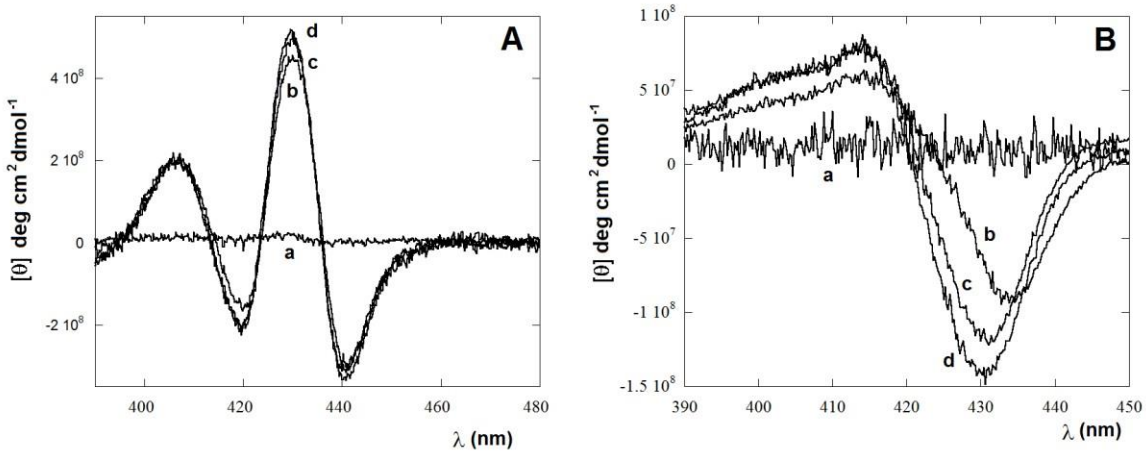

Figure S3. CD spectra of TSP (A) and TSPc (B) in DMSO/H_2O for different mixture compositions: a) DMSO; (b) 70/30, (c) 50/50 and (d) 30/70 DMSO/H_2O v/v.

ESI5. Circular dichroism spectra of TSP and TSPc films obtained by casting

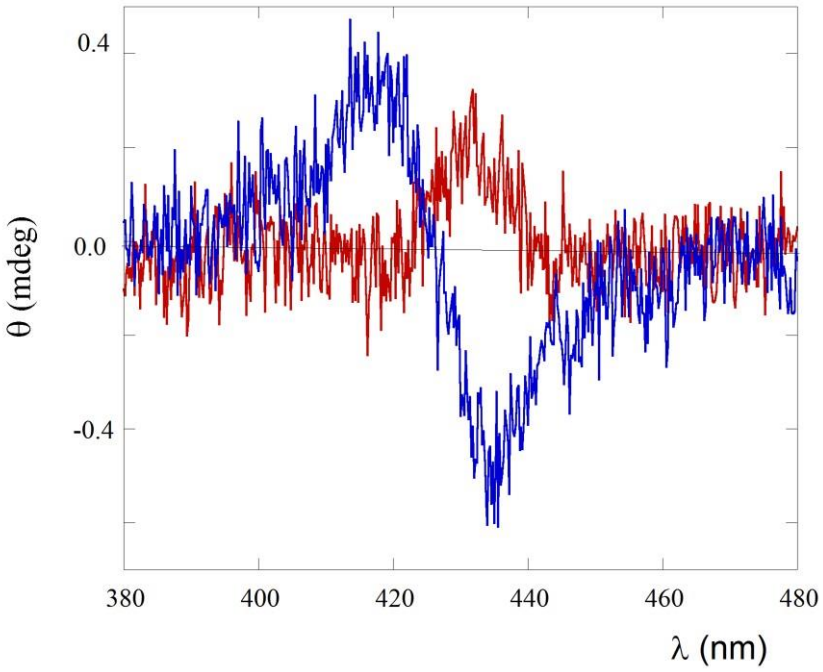

Figure S4. CD spectra of TSP (red) and TSPc (blue) films obtained by casting deposition of micromolar chloroform solutions.

ESI6. Fluorescence microscopy imaging of TSP and TSPc films obtained by casting

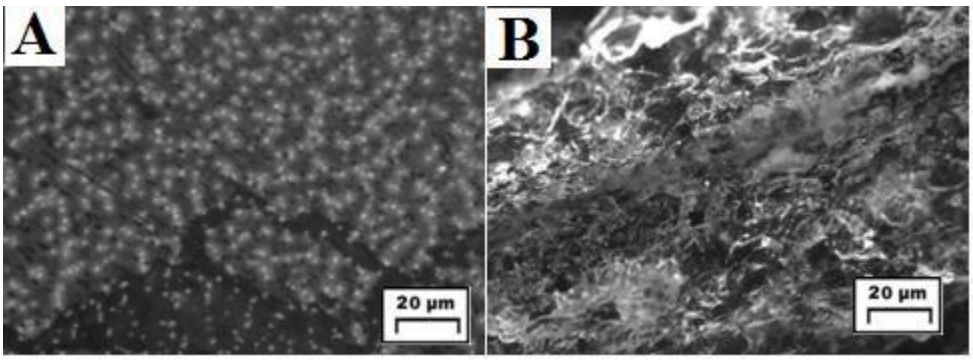

Figure S5. Fluorescence microscopy imaging of TSP (A) and TSPc (B) films obtained by casting deposition of micromolar chloroform solutions.

ESI7. Fluorescence microscopy imaging of a TSP monolayer

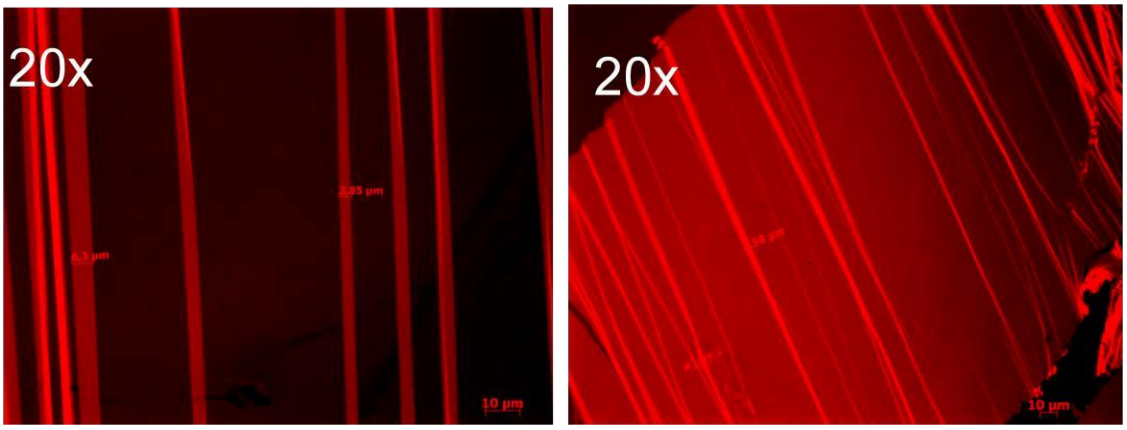

Figure S6. Fluorescence imaging of a TSP monolayer at a surface pressure above the LE→LC transition.

ESI8. AFM imaging of TSP and TSPc films on mica at π=60 mN/m.

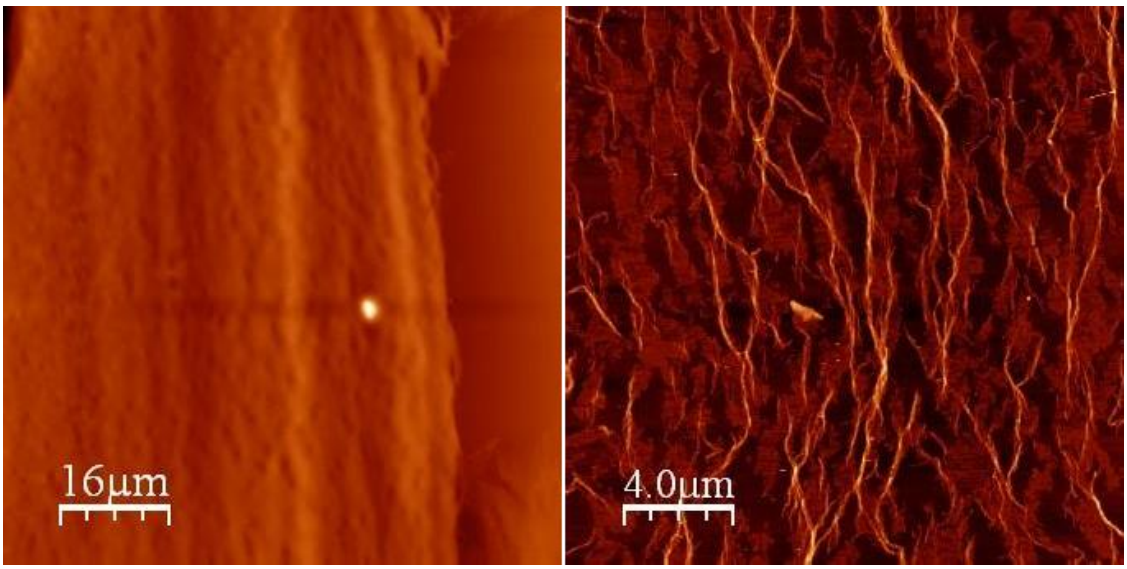

Figure S7. AFM images of TSP (left) and TSPc (right) films deposited on mica at a surface pressure π = 60 mN/m.

ESI9. Minimum energy conformers of TSP and TSPc dimers.

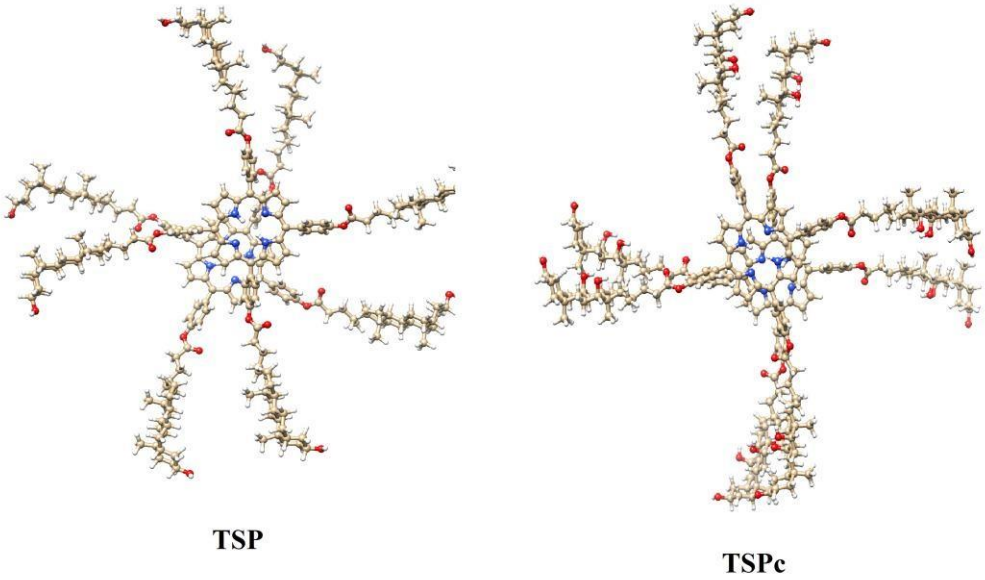

Figure S8. Minimum energy conformers of the TSP and TSPc dimers. Red: Oxygen atoms; Blue: Nitrogen. Note the anticlockwise (P-helicity) winding of the four steroid substituents in both compounds.