

Porphyrin-based Hybrid Nano Helices: Cooperative Effect Between Molecular and Supramolecular Chirality on Amplified Optical Activity

Zakaria Anfar¹, Balamurugan Kuppan¹, Antoine Scalabre¹, Rahul Nag¹, Emilie Pouget¹, Sylvain Nlate¹, Gabriele Magna², Ilaria Di Filippo², Donato Monti³, Mario L. Naitana², Manuela Stefanelli², Tatsiana Nikonovich⁴, Victor Borovkov⁴, Riina Aav⁴, Roberto Paolesse², Reiko Oda^{1,5}*

¹*Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248, 33600 Pessac, France;*

²*Department of Chemical Science and Technologies, University of Rome Tor Vergata, via della Ricerca Scientifica 1, 00133 Rome, Italy*

³*Department of Chemistry, Sapienza, University of Rome, piazzale Aldo Moro 5, 00185 Rome, Italy*

⁴*Department of Chemistry and Biotechnology, School of Science, Tallinn University of Technology, Akadeemia tee 15, SCI-421A, 12618 Tallinn, Estonia*

⁵*WPI-Advanced Institute for Materials Research, Tohoku University, Katahira, Aoba-Ku, 980-8577 Sendai, Japan*

Definition of the g-factor

Electronic circular dichroism is defined as the difference

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

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 $\Delta\theta$ (mdeg) = 32982 ΔA . In analogy to Beer-Lambert law, one can define a molar quantity,

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

which is dependent of concentration c , expressed in mol/L, and of 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).

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 factor¹:

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

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 path-length.

Procedure for preparation of HB6U

To the solution of biotin-L-sulfoxide[6]uril (0.178 mmol, 3 equiv., 290 mg), HATU (0.065 mmol, 1.1 equiv., 24.8 mg) and DIPEA (0.065 mmol, 1.1 equiv., 11.3 μ l) in anhydrous DMF (3.6 ml) a solution of *para*-monoamino-tetraphenylporphyrin H2TPP-NH2 (0.059 mmol, 1 equiv., 37.3 mg) in anhydrous DMF (3.6 ml) was added during 6 hrs followed by overnight stirring at r.t. The obtained reaction mixture was then concentrated under reduced pressure, the residue was then transferred to the filter with H2O (20-30 ml), washed with H2O (3 \times 10 mL), with H2O:Methanol mixture (1:4, 3 \times 10 mL), then with pure methanol (3 \times 10 mL) and dried in air to give HB6U mono-amide (90 mg, 68% isolated yield, HPLC purity 77%).

Procedure for preparation of ZnB6U

To the solution of HB6U (0.02 mmol, 1 equiv., 45 mg) in the mixture of chloroform:methanol=5:3 (8 ml) Zn(OAc)2 (0.20 mmol, 10 equiv., 37 mg) was added, the resulting reaction mixture was refluxed for 2 hours and then cooled to room temperature. After concentration under reduced pressure the residue was transferred with water (10-15 ml) to the filter, washed with H2O (3 \times 5 mL), with H2O:Methanol mixture (1:1, 3 \times 5 mL), then with pure methanol (3 mL) and dried in air to give ZnB6U (40 mg, 86%, HPLC purity 87%).

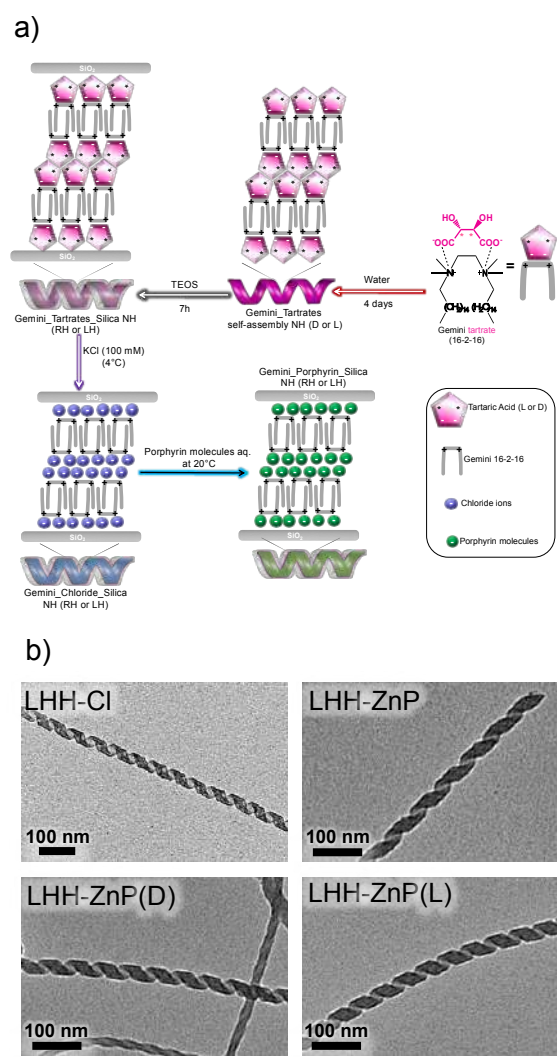


Figure S1. a) Schematic representation showing insertion of porphyrin molecules into the chiral nano spaces of silica nano helices by ion exchange and b) TEM images of different prepared LH-nano structures with porphyrins based Zn

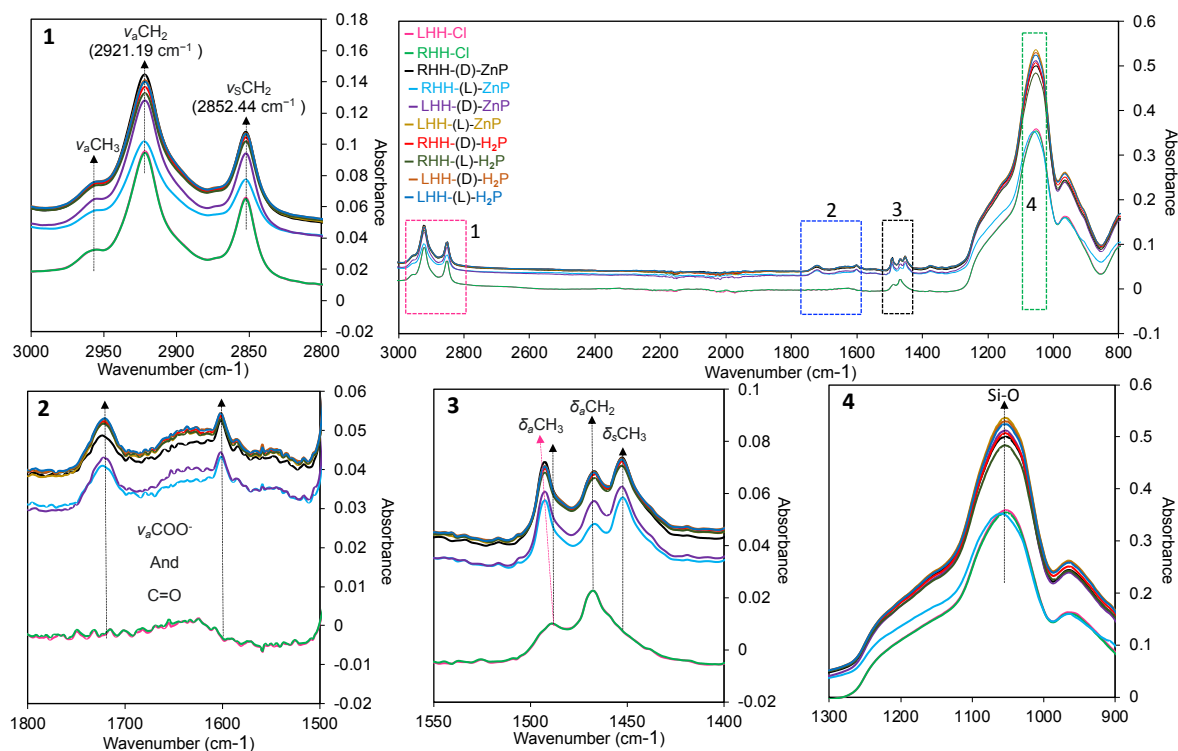


Figure S2. FTIR analysis of hybrid silica nano helices chloride and different prepared nano structures with porphyrins molecules

FTIR spectra measurements were used not only to confirm the total elimination of gemini-chloride, but also to have a clear idea about the structure of the prepared inorganic silica and confirm the preservation of the chemical nature of the surface. FTIR analysis of hybrid-chloride systems reveals the presence of two characteristic bands of Gemini-tartrates around 3000–2800 cm^{-1} regions, corresponding to vibrational information of hydrocarbon chains of the gemini surfactant. In addition, the bending modes of methyl ($\delta_a\text{CH}_3$, $\delta_s\text{CH}_3$ and $\delta_s\text{CH}_3$) and methylene (δCH_2) groups of the amphiphilic cations in the 1490–1410 cm^{-1} region were observed. We can also extract 3 principals peaks around 960 cm^{-1} , 1100 cm^{-1} , 1630 cm^{-1} and 3000–4000 cm^{-1} region, corresponding to Si-OH, asymmetric Si–O–Si stretching, O–H bending (molecular water, δHOH) and O–H stretching, respectively. The presence of a strong pic of C=O groups and COO- after porphyrin insertion confirm the process of ions exchange. In addition,

significant change was observed in the bending modes of methyl ($\delta_a\text{CH}_3$, $\delta_s\text{CH}_3$ and $\delta_s\text{CH}_3$) of the alkyl chain of 16-2-16 surfactant. These results confirm the fact that porphyrin disorder the gemini structure.

Table S1. g factor of molecules alone and with hybrid silica nano helices (420-425 nm@peak)

Molecules	g factor x 10 ⁻⁴		
	Alone	With RHH	With LHH
H₂P	0	-20	20
(L)-H₂P	-0.2	-13	11
(D)-H₂P	0.22	-14	17
ZnP	0	-6	6
(L)-ZnP	-0.15	-6	6
(D)-ZnP	0.2	-7	5
HB6U	0.5	-2.8	2
ZnB6U	0.2	-0.3	3

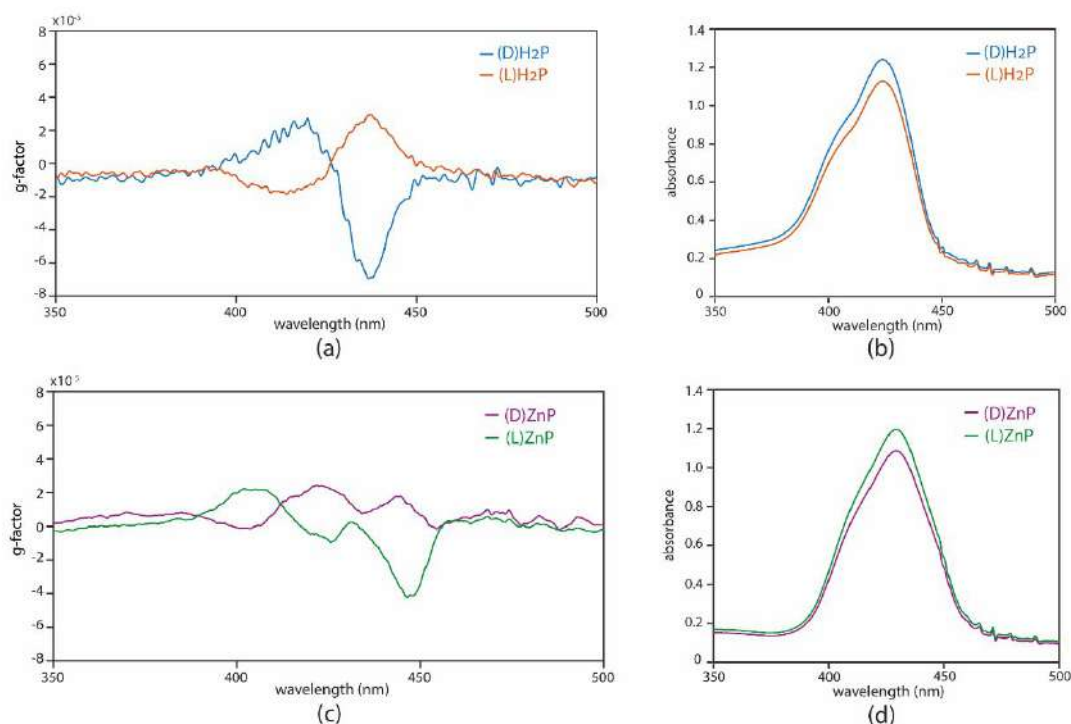


Figure S3. (A) CD and (B) UV-Vis spectra of (D)-H₂P and (L)-H₂P at 66 μM concentration in 1:14 DMF:water solutions. Spectra were recorded after 8 hours from the preparation with 1 mm cuvette. (C) CD and (D) UV-Vis spectra of (D)-ZnP and (L)-ZnP at 66 μM concentration in 1:14 DMF:water solutions. Spectra were recorded after 8 hours from the preparation with 1 mm cuvette.

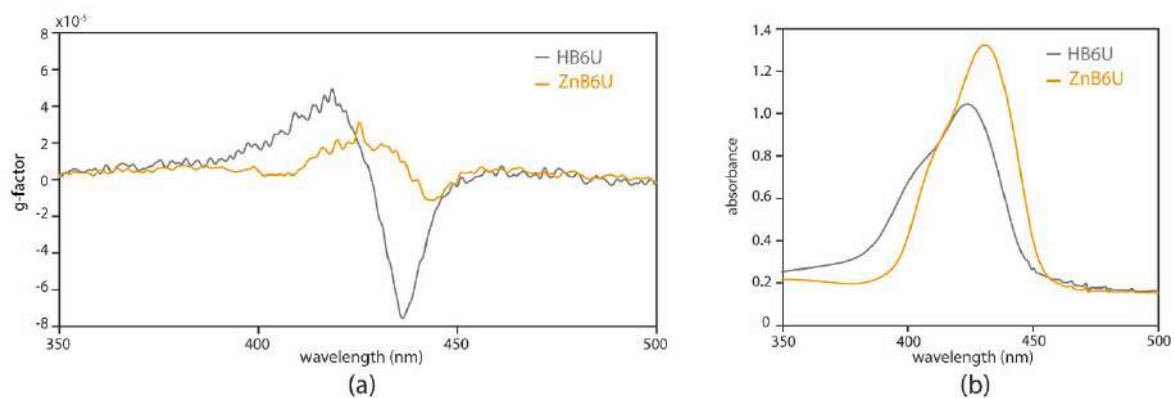


Figure S4. (a) CD and (b) UV-Vis spectra of HB6U and ZnB6U at 66 μ M concentration in 1:14 THF:water or DMSO:water solutions, respectively. Spectra were recorded after 8 hours from the preparation with 1 mm cuvette.

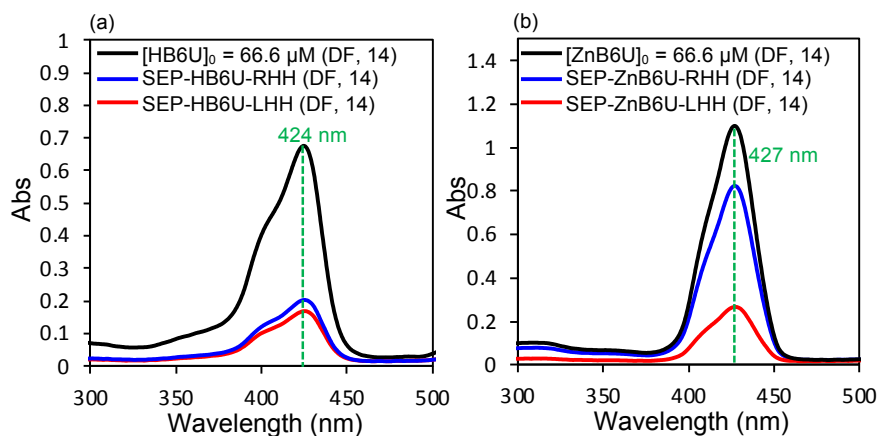


Figure S5. Adsorption spectra of supernatants of a) HB6U-RHH and HB6U-LHH, and b) ZnB6U-RHH and ZnB6U-LHH. Analyzed solution were diluted 14 times (DF, 14).

References

- (1) Berova, N.; Bari, L. Di; Pescitelli, G. Application of Electronic Circular Dichroism in Configurational and Conformational Analysis of Organic Compounds. *Chem. Soc. Rev.* **2007**, *36* (6), 914. <https://doi.org/10.1039/b515476f>.