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

*Zakaria Anfar<sup>1</sup>, Balamurugan Kuppan<sup>1</sup>, Antoine Scalabre<sup>1</sup>, Rahul Nag<sup>1</sup>, Emilie Pouget<sup>1</sup>,  
Sylvain Nlate<sup>1</sup>, Gabriele Magna<sup>2</sup>, Ilaria Di Filippo<sup>2</sup>, Donato Monti<sup>3</sup>, Mario L. Naitana<sup>2</sup>,  
Manuela Stefanelli<sup>2</sup>, Tatsiana Nikonovich<sup>4</sup>, Victor Borovkov<sup>4</sup>, Riina Aav<sup>4</sup>, Roberto Paolesse<sup>2</sup>,  
Reiko Oda<sup>1,5\*</sup>*

<sup>1</sup>*Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248, 33600 Pessac, France;*

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

<sup>3</sup>*Department of Chemistry, Sapienza, University of Rome, piazzale Aldo Moro 5, 00185 Rome, Italy*

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

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

## **Abstract**

The development of chiral receptors for discriminating the configuration of the analyte of interest is increasingly urgent in view of monitoring the pollution in water and waste liquids. Here we investigate an easy protocol to immobilize desired non-water soluble receptors inside a water-dispersible chiral nano platform made of silica. This approach induces chirality in the receptors and at the same time makes the dye@nanohelix system dispersed in suspension of water without aggregation. We noted strong induction and amplification of chiroptical activity in both achiral or chiral (proline-based or hemicucurbituril-based) porphyrin derivatives with and without zinc ions once confined and organized in nanometric silica helices. The results clearly demonstrated that the organization-induced chirality amplification of porphyrins dominates the molecular chirality and the amplification is more efficient for more flexible porphyrins (especially free-base and achiral).

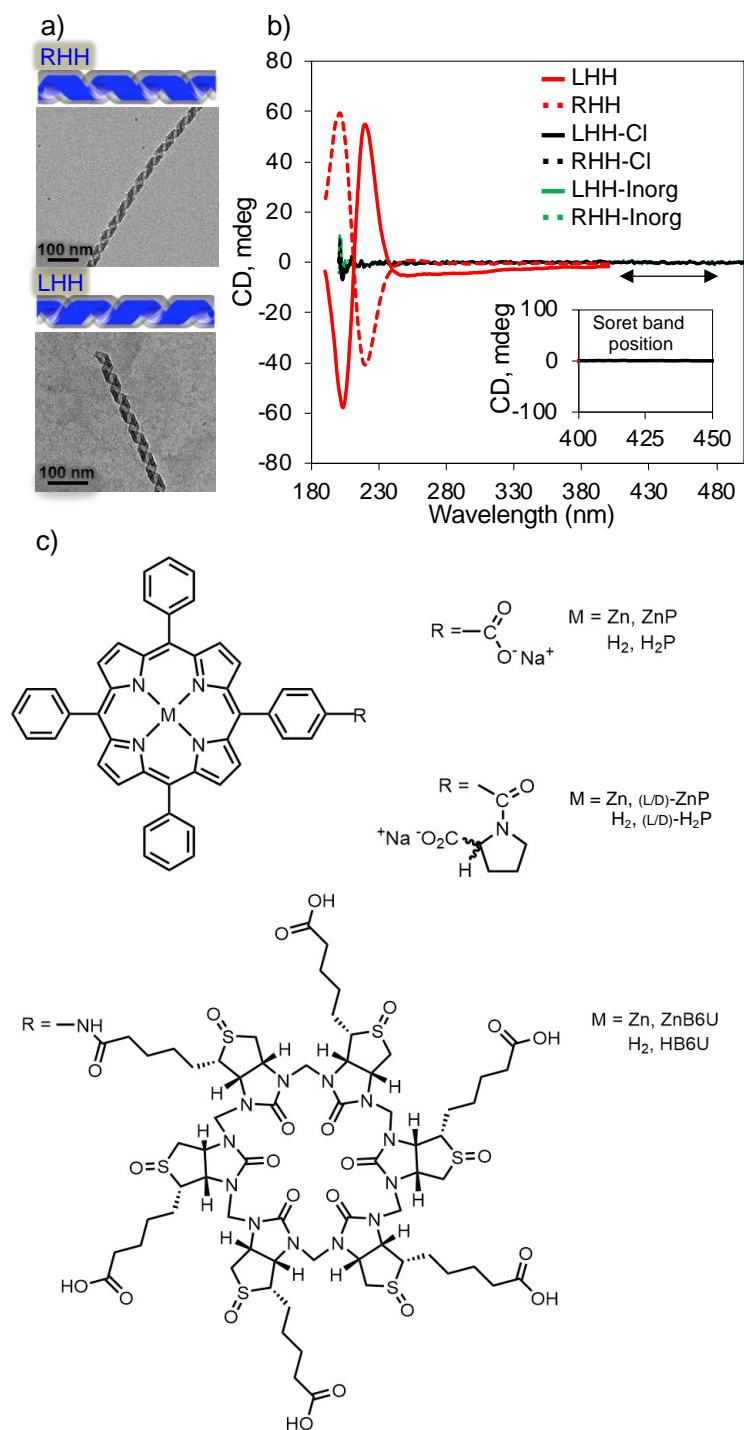
**KEYWORDS** : hybrid chiral materials, silica nanohelices, chiral porphyrins, hemicucurbiturils, chiral induction.

## Introduction

The design and synthesis of chiral materials of diverse types<sup>1</sup> are continuously pursued for their use in various fields such as chiral induction, recognition or amplification. Based on small chiral selectors of natural or synthetic origin, there has been important progress in recent years in the development of chiral inorganic materials<sup>2,3</sup>, which often display enhanced optical activities strictly related to their easily tunable morphology<sup>4</sup>. While still in its infancy, the line-up of different soft-templating assembly methods allowed the preparation of materials with potential use in optoelectronic devices<sup>5</sup>. Other inorganic materials have also shown enantioselective recognition and sensing properties<sup>6,7</sup>. One of the hottest topics concerning the use of chiral recognition is undoubtedly found in environment preservation and health security fields, where the development of sensing devices being able to discriminate the enantiomers of potentially harmful substances represents an urgent task. In this context, our focus is to develop chiral chemical sensors based on rationally designed sensing materials, intending to fill the existing gap between the production of enantioselective receptors and the realization of macroscopic devices being able to work in real scenarios. As an example of such sensors, we have recently reported that sensing layers consisting of metalloporphyrins combined with chiral cyclohexanohemicucurbit[8]urils deposited on quartz microbalances efficiently recognize vapor samples of limonene and 1-phenylethylamine enantiomers by application of a novel normalization procedure and multivariate analysis techniques to improve the classification performances<sup>8</sup>. In this manuscript, we report new chiral nano systems by integrating porphyrin-based receptors into silica nano helices. Indeed, nano scale siliceous materials offer a number of potential advantages for sensing applications thanks to their stable structural and functional properties<sup>9-11</sup>, also in combination with organic dyes like porphyrins<sup>12-17</sup>. The selectivity towards a target analyte can be tuned by adequately decorating

the pore walls and/or channels with porphyrin receptors, giving an easily readable analytical signal thanks to the extraordinary photochemical properties of these macrocycles.

We have previously reported how achiral gemini-type dialkyl diammonium amphiphilic molecules complexed with chiral tartrate counterions self-assemble to helical nano ribbons. The coverage of these structures with silica gives rise to organic-inorganic chiral nano structures called hybrid nano helices (HH, **Figure 1a**)<sup>18-21</sup>. When tartrate anions as an origin of chirality are replaced with other anions, the confinement in the nano metric chiral space given by the solid silica walls may induce a chiroptical activity in the new guest molecules. Thus, hybrid nano helices provide a versatile chiral nano space where achiral molecules can enter and organized in a chiral way (see CD signal of hybrid nano helices, HH in **Figure 1b**)<sup>20,21</sup>. In the present work, we extend this approach to study chiral porphyrin derivatives. The environment of these organic macrocycles can be analyzed thanks to their rich spectroscopic features, which are markedly sensitive to self-aggregation and local microenvironment<sup>22</sup>, such as supramolecular chirogenesis<sup>23</sup>. In addition, having an excellent host-guest complexing ability, it can be used for a variety of selective separations<sup>24</sup>. We selected a set of water insoluble porphyrins composed of two achiral (H<sub>2</sub>P and ZnP) and six chiral [(L)H<sub>2</sub>P, (D)H<sub>2</sub>P, (L)ZnP, (D)ZnP, HB6U and ZnB6U] porphyrin derivatives (**Figure 1c**).



**Figure 1.** a) TEM images of right-handed hybrid nano helices (RHH) and left-handed hybrid nano helices (LHH), b) CD signals of different prepared nano structures based on hybrid silica nano helices and c) structures of achiral ZnP and H<sub>2</sub>P and chiral (L or D)-ZnP, (L or D)-H<sub>2</sub>P, ZnB6U and HB6U and guest molecules used in this work, where letters L and D are expressing handedness of chiral porphyrins, Zn stands for zinc metal in metalloporphyrins and all others are free base porphyrin derivatives. LHH and RHH represent left handed helices and

right handed helices, respectively. Whereas, -Cl and -inorg acronym present right or left handed nano helices modification.

Since most applications require recognizing chiral target analytes in water or aqueous solutions, such as pollutants or contaminants, the scarce or no solubility in water of most of the porphyrin-based receptors may hinder their practical applications. The incorporation of porphyrin derivatives into water-dispersible silica nano helices (**Figure S1-a**) allows to overcome this problem, hence enabling their use as chemical probes to detect various analytes in water.

## **Experimental**

All solvents and chemicals are of the highest purity grade available from Sigma Aldrich and used without further purification. We previously reported the preparation and self-assembly behavior in solution for porphyrin derivatives ZnP, H<sub>2</sub>P, (D/L)ZnP, and (D/L)H<sub>2</sub>P<sup>25</sup>. Synthetic procedures for HB6U and ZnB6U was presented in SI. Transmission electron microscopy (TEM) was performed with CM 120 (Philips) at 120 kV. For TEM experiments, samples were applied to carbon-coated copper 300 mesh grids. Circular dichroism (CD) and absorption spectra were measured by a J-815 (JASCO) CD spectrometer. FTIR spectra were recorded with a Thermo-Nicolet Nexus 670 FTIR spectrometer, at a resolution of 4 cm<sup>-1</sup>, by recording 50 scans.

*Porphyrin aggregation procedure.* 1 mM stock solutions were prepared for each porphyrin derivative in the proper organic solvents (DMSO for ZnB6U, THF for HB6U and DMF for the two enantiomeric pairs of ZnP and H<sub>2</sub>P). An aliquot of 200 μL of porphyrins in the respective organic solvent was added to 2.8 mL of water to reproduce the ion exchange protocol. Finally, CD and UV-Vis spectra were acquired after 8 hours. Due to the intense

absorbance of samples, a 1 mm cuvette optical path length was utilized for these experiments to maintain the corresponding optical density below 1.5.

*Synthesis of hybrid silica nano helices using chloride.* *N,N'*-Dihexadecyl-*N,N,N',N'*-tetramethylethylenediammonium L- (and D-) tartrate (16-2-16 L- (and D-) tartrate) were synthesized by the previously reported procedure<sup>26–28</sup>. The powder of 16-2-16 gemini tartrate was dissolved into water at 60 °C (1 mM) and then aged for 4 days at 20 °C with the typical used quantities being 20 mg of powder for 28 mL of ultrapure water. Then, the 16–2–16 L- or D-tartrate self-assemblies are used as templates to prepare corresponding silica nano structures like helices through a sol–gel transcription procedure. In a typical preparation, 0.5 mL of tetraethoxysilane (TEOS) was added to 10 mL of 10<sup>−4</sup> M aqueous solution of D- or L-tartaric acid and prehydrolyzed at 20 °C by stirring on a roller mixer for 7 h. Then, 5 mL of prehydrolyzed TEOS was mixed with 5 mL of organic gels and stirred at 20 °C in a roller mixer overnight. Once the transcription was completed, the mixture was thoroughly washed five times by centrifugation in ultrapure water (4 °C). In order to insert the porphyrins' molecules in the structure, the counterions of D- or L- 16-2-16 hybrid silica were first replaced by chloride ions by washing eight times with KCl (100 mM) at 4 °C until no tartrate was detected using CD and followed by washing five times with ultrapure water (4 °C)<sup>29</sup> (**Figure 1b**). Then, the concentration of prepared right or left hybrid helix chloride (RHH-Cl or LHH-Cl) was adjusted to the desired value (0.5mg/mL) using ultrapure water and kept at 4 °C.

*Porphyrin molecules insertion procedure.* To insert porphyrin molecules by ion exchange, we made it to interact with hybrid silica helices chloride (RHH-Cl or LHH-Cl) dispersed in water at 20 °C with a molar ratio of 1:1 in THF:H<sub>2</sub>O (1:14, v/v) (for HB6U), DMSO:H<sub>2</sub>O (1:14, v/v) (for ZnB6U) and DMF:H<sub>2</sub>O (1:14, v/v) (for other molecules). Each initial solution contains 1 mM concentration of a desired molecule in the corresponding solvent. Then, 200 μL of each solution was poured in 2.8 mL of hybrid helices chloride dispersion in water



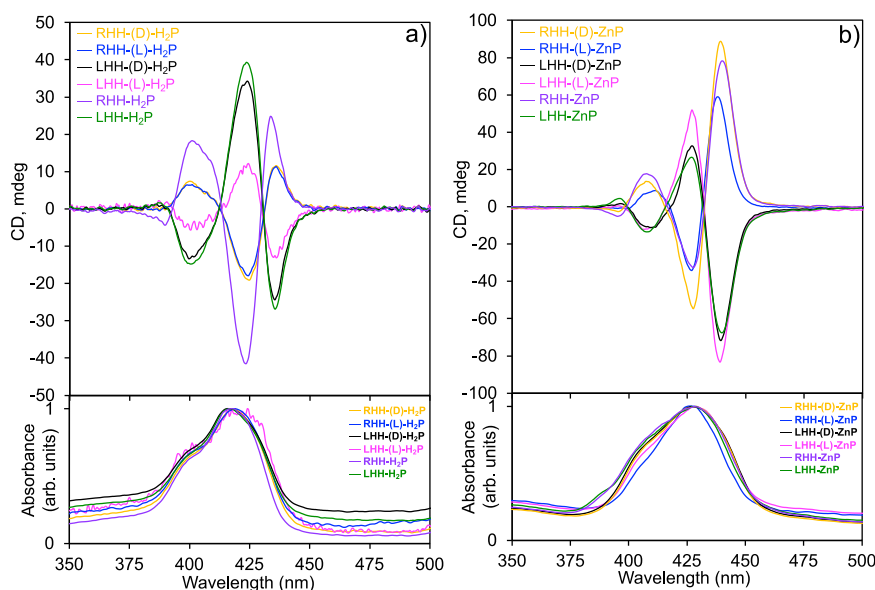
(RHH-Cl or LHH-Cl), then the mixture was aged for 1 hour on a roller mixer at 20 °C followed by four washings using centrifugation (12 min at 4500 rpm) at 4 °C. The insertion of porphyrin molecules was confirmed using FTIR analysis as presented in SI (See **Figure S2** with discussion).

## **Results and Discussion**

*Porphyrins in solutions.* While solubilized in the respective organic solvents as described in experimental section, porphyrins are not aggregated as evidenced by their spectral invariability. Additionally, even with the presence of chiral appended groups, (L or D)-H<sub>2</sub>P and (L or D)-ZnP do not show detectable CD signals in the visible region of the spectra. The addition of antisolvent, such as water, induces aggregation of the porphyrins, which can lead to the formation of stereospecific supramolecular structures that often display very intense CD signals in the visible region. The aggregation mechanisms and protocols to stereospecifically organized chiral and achiral porphyrins by supramolecular interactions have extensively been investigated<sup>25,30</sup>. The efficiency in chiral induction of these systems depends on many different parameters, such as solvent, concentration, pH, temperature, and even preparation protocol of samples<sup>31,32</sup>. In the present case, as expected, water induced aggregation of pristine achiral H<sub>2</sub>P and ZnP does not show CD signals proving the absence of unwanted potential chiral effectors during the procedure (**Table S1**). On the other hand, the aggregates of all the chiral porphyrin derivatives herein studied at the same condition show supramolecular CD signals with dissymmetric *g*-factors (normalized optical activity, which defined as  $\Delta\epsilon/\epsilon$ ) in the range of  $10^{-5}$  (see **Table S1, Figures S3, and S4**).

*Hybrid silica nano helices with achiral porphyrins.* In agreement with our previous report, right- (RHH) and left-handed hybrid helices (LHH) (before ion exchange) show mirror-image CD signals at 200-250 nm, which correspond to the tartrate's carboxylic groups (**Figure 1b**).

When porphyrins are incorporated into the hybrid silica nano helices via the ion exchange procedure as described above, the UV-Vis spectra of the hybrid systems display the typical visible features imputable to porphyrins. Additionally, the change in contrast on TEM images with FTIR analysis (**Figure S1-b and Figure S2**) confirms the insertion of porphyrin molecules into the chiral nano space of hybrid silica nano helices without modification of the helical morphology of the latter (similar observation was reported in our previous work<sup>20-21</sup>). In the cases for which two achiral porphyrins (namely H<sub>2</sub>P and ZnP) are introduced into the chiral nano spaces of RHH or LHH, the solet band region shows the CD spectra features with oppositely signed Cotton effects, depending on the handedness of the helices (**Figure 2**). Thus, RHH induced exciton-coupled CD shows a +/-/+ pattern, while in the presence of LHH, corresponding mirror image CD spectrum was observed (**Figure 2**). The effect of the presence of a coordination metal ion, Zn<sup>2+</sup>, was investigated. ZnP in hybrid silica nano helices shows a slightly lower *g*-factor compared to H<sub>2</sub>P in hybrid silica nano helices ( $\sim 2.0 \times 10^{-3}$  for H<sub>2</sub>P at 424 nm and  $\sim 0.6 \times 10^{-3}$  for ZnP at 427 nm). Unlike the free base macrocycles, Zn-porphyrins have a possibility to axially coordinate a ligand, and zinc ion has a good oxophilicity that may confer an additional interaction mechanism with silica and gemini moieties. This coordination could result in an increased distance between electronic transitions and less favorable dihedral angles for exciton coupling. Hence, these additional interactions may account for the lower *g*-factor.



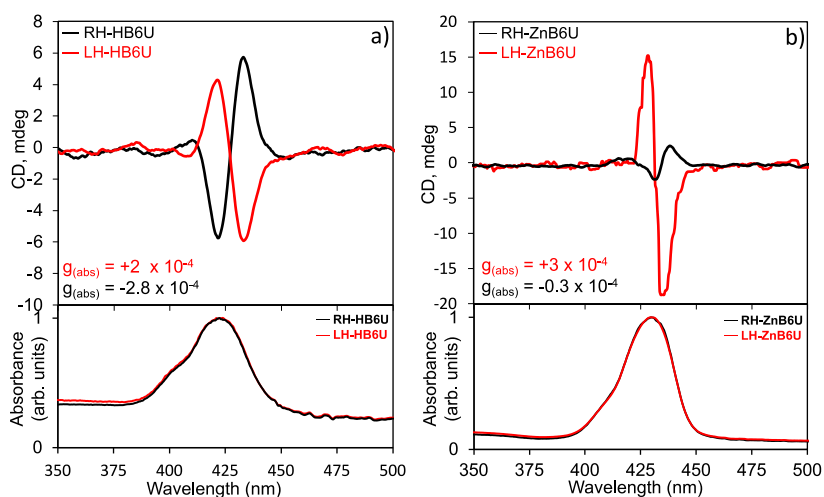
**Figure 2.** CD and UV-Vis spectra obtained from nano structured porphyrin derivatives (chiral and achiral) with and without different combinations of LHH and RHH. (a) and (b) are CD and normalized absorbance spectra (at the peak position) for free base and zinc-based porphyrins (respectively).

*Hybrid silica nano helices with chiral porphyrins.* Subsequently, we investigated if the presence of the chiral proline group covalently attached to the porphyrins [(L)-H<sub>2</sub>P, (D)-H<sub>2</sub>P, (L)-ZnP, and (D)-ZnP] may influence the overall CD features once inserted into the helices. In this case, it is interesting to note that the chiroptical features of these chiral porphyrins confined into RH- or LHH are determined by the handedness of nano helices, disregarding the appended proline configuration (**Figure 2**). This indicates that the effect of the mesoscopic handedness of hybrid silica nano helices is a determining factor of the CD signals, which predominates over the molecular chirality of porphyrin. The **Table S1** shows that CD spectra of hybrid porphyrin-silica nano structures based chiral/achiral free bases H<sub>2</sub>P and ZnP generally have one or two orders of magnitude higher *g*-factors of the corresponding supramolecular assembly (from  $\sim 5 \times 10^{-4}$  up to  $\sim 2 \times 10^{-3}$ ). In these systems, the crystalline packing of gemini surfactants and the resulting chiral environment inside HH are responsible for the chiral organization of anionic molecules trapped inside, which leads to the appearance

or amplification of chirality of the anions which is in good agreement with our previous reports in which hybrid silica nano helices were used to induce chirality to various anionic dyes and monoanions<sup>21,29,33,34</sup>. The amplitude of the CD spectra of chiral porphyrins@hybrid silica nano helices decreases slightly in the case of porphyrin free bases ((L)- or (D)-H<sub>2</sub>P), whereas for chiral ZnPs they are similar to achiral ZnP (*g*-factors  $\sim 0.6 \times 10^{-3}$  for both chiral and achiral ZnP) (see **Table S1**). Remarkably, the amplification of CD signals by the porphyrins' incorporation into silica nano helices is much more effective than the aggregation induced amplification probably due to the presence of water antisolvent. Apparently, it is due to the chiral arrangement of porphyrins induced by an electrostatic interaction with chiral and crystalline gemini surfactants confined in the chiral nano space of silica helices as compared to randomly aggregated porphyrins (**Table S1**).

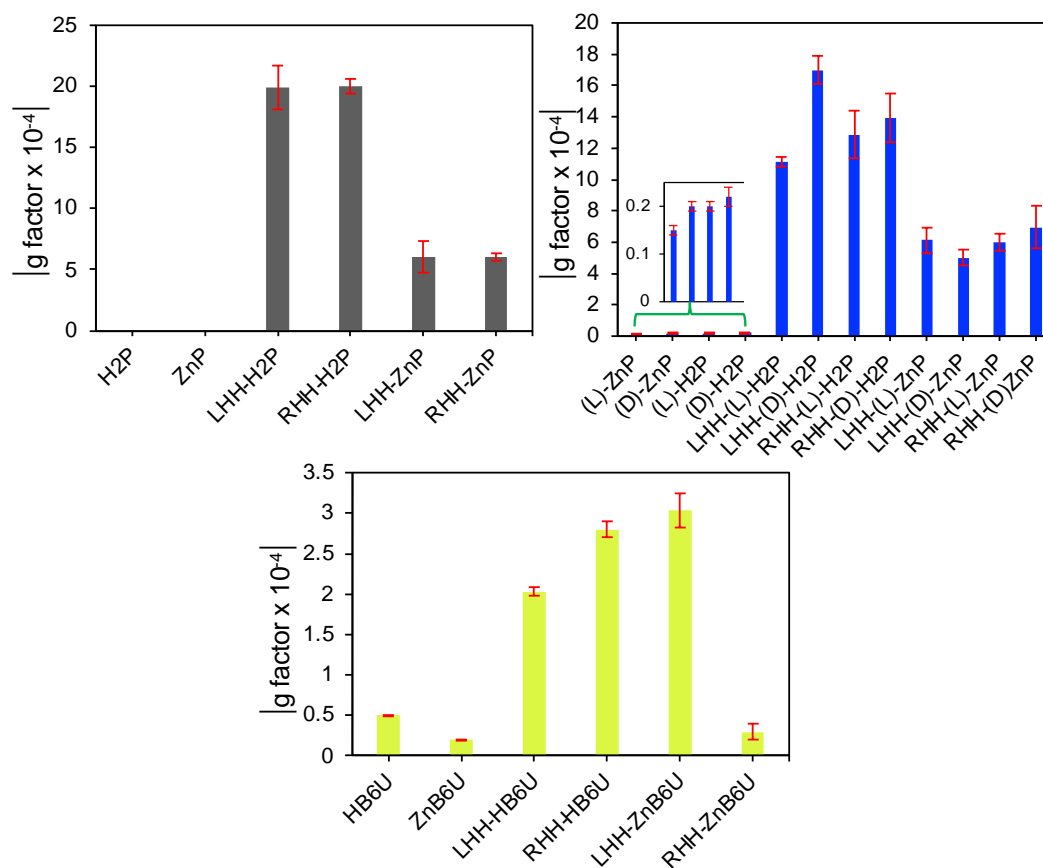
*Hemicucurbituril appended porphyrins.* We then studied the system for which the porphyrins (free base and zinc complex) are covalently linked to D-biotin-L-sulfoxide[6]uril<sup>35</sup>, (B6U) macrocycle<sup>36</sup>, giving mono porphyrin substituted D-biotin-L-sulfoxide[6]urils (HB6U and ZnB6U, respectively). These systems allow us to investigate the effect of much larger chiral moieties capable of molecular recognition<sup>37</sup>. In addition, porphyrin and B6U have similar dimensions close to a nano meter, making this combination very appealing at the supramolecular level. Both HB6U in THF and ZnB6U in DMSO solutions gave a bathochromic shifts of the porphyrin Soret band. These spectral features are similar to the UV-Vis absorption reported for zinc porphyrin complexes with enantiopure cyclohexanohemicucurbit[*n*]urils (*n* = 6, 8)<sup>38</sup>. When HB6Us are incorporated inside the chiral nano space of hybrid silica nano helices, a noticeable increase of the corresponding *g*-factors ( $|2-3 \times 10^{-4}|$  (**Figure 3**) for both RHH- and LHH compared to  $5 \times 10^{-5}$  for the molecular solution of HB6U, Figures S3 and S4) was observed. The signs of these CD signals adhere to the handedness of the hybrid silica nano helices, which agrees with what was observed in the

case of H<sub>2</sub>P (L and D) molecules, again showing that the helical chirality of hybrid silica nano helices dominates over molecular chirality. For the zinc complex of biotinuril-porphyrin macrocycle, ZnB6U, on the other hand, while a similar chirality amplification was observed with LHH i.e.,  $g$ -factors  $|3.0 \times 10^{-4}|$ , the observed CD signal shows very little amplification with RHH,  $|3 \times 10^{-5}|$  (**Figure 3 and S4**). The amount of HB6U and ZnB6U molecules interacting with the RHH and LHH chiral templates was quantified by recording the UV-Vis absorbance of supernatant solutions after the functionalization process (**Figure S5**). About  $3.2 \times 10^{-7}$  moles of HB6U is incorporated in 1 mg of hybrid silica nano helices (corresponding to  $1.6 \times 10^{-6}$  moles of gemini surfactants) both for RHH and LHH. A similar value of the occupancy was observed for ZnB6U bound to LHH. On the other hand, in the case of the ZnB6U-RHH system, only  $1.0 \times 10^{-7}$  moles of ZnB6U was incorporated, suggesting that ZnB6U molecule has much weaker interaction with RHH. Such results suggest that while the chiral moieties of HB6U have little effect on the organization of the porphyrins in the chiral nano space of the helices, ZnB6U has a different organization in LHH or in RHH. This is again probably due to the lower in-plane flexibility of Zn porphyrin, which results in the B6U moieties being more intimately linked with the Zn porphyrin, and having an additional interaction with the silica and gemini moieties<sup>39,40</sup>. Nevertheless, the  $g$ -factor amplification is rather modest for the B6U complex with helix, compared to smaller porphyrins, as shown in **Figure 4a and 4b**. We suggest that the relatively large biotinuril macrocycle suppresses the ability of porphyrins to penetrate hybrid silica nano helices. Clearly, in the case of ZnB6U, additional interactions by zinc cation have an effect on diastereoselective binding to the inorganic helix. This highlights the generation of the matching effect between ZnB6U and LH helix (larger  $g$ -factor), whereas the mismatching impact can be seen with RHH (lower  $g$ -factor) (**Figure 4c**).



**Figure 3.** CD and UV-Vis spectra obtained from HB6U and ZnB6U molecules with and without different combinations of LHH and RHH. (a) and (b) are CD and normalized absorbance spectra (at the peak position) for free base and zinc-based B6U, respectively.

The ensemble of the  $g$ -factors (measured at 420-425 nm) observed from the Soret bands of porphyrins as described above is summarized in **Figure 4**.



**Figure 4.** Comparison of  $g$ -factors (at 420-425 nm) of studied systems with a) achiral porphyrin (H<sub>2</sub>P and ZnP), b) chiral porphyrin ((D or L)-H<sub>2</sub>P and (D or L)-ZnP) and c) hemicucurbituril appended porphyrin (HB6U and ZnB6U)

## Conclusions

In this work, we demonstrated that the chiral nano environment, the absolute configuration, and the nature of porphyrin molecules cooperatively affect the chirality amplification process upon confinement in the chiral nano space of hybrid silica nano helices.

Both chiral and achiral porphyrins [(L or D)-H<sub>2</sub>P, (L or D)-ZnP, H<sub>2</sub>P and ZnP] confined in hybrid silica nano helices show opposite Cotton effects at the corresponding Soret band, the sign of which is determined solely by the handedness of hybrid silica nano helices. The amplification of the  $g$ -factors due to the aggregation of porphyrin derivatives in the nano helical environment was largely dominant with respect to the molecular chirality being negligible. Indeed, the  $g$ -factors of (L or D)H<sub>2</sub>P, (L or D)ZnP increased by 25-80 times when they are incorporated in the nano helices compared to when they are free in solution.

The chirality amplification was more efficient for achiral and free base porphyrins compared to chiral and Zn complex counterparts. Zn ion may coordinate some external (achiral) ligands that can enlarge the distance between the electronic transitions and/or make the dihedral angles less favorable for exciton coupling. For the covalently linked biotinuril-porphyrins, the chirality amplification was again more efficient for the free-base porphyrins HB6U and the induced CD signals were dependent only on the handedness of the hybrid silica nano helices. Interestingly, for ZnB6U, the chirality amplification was observable only for LHH, while no chirality amplification was found in the case of RHH with much less incorporated amount of ZnB6U (< 25%).

The smaller the anionic moieties the higher the chirality amplification, with free base porphyrins showing stronger amplification. As a consequence, the order of chirality

amplification is follows:  $H_2P@HH > (L)\text{-}H_2P@HH$  or  $(D)\text{-}H_2P@HH > ZnP@HH > (L)\text{-}ZnP@HH$  or  $(D)\text{-}ZnP@HH > HB6U@HH \approx$  matched  $ZnB6U@HH \gg$  mismatched  $ZnB6U@HH \approx$  chiral  $H_2P$  in solution  $\approx$  chiral  $ZnP$  in solution, HH represent “hybrid silica nano helices”

The ensemble of the data indicates that two factors may be the dominant origin of chirality induction to porphyrins. The first is the flexibility of the confined porphyrin ring, which influences the ability of the ring to accommodate the chiral induction enforced by the chiral environment. The second is an exciton coupling of corresponding electronic transitions. In the case of the second effect, the distance and dihedral angle between the coupling electronic transitions are the main controlling factors.

The structural deviation of porphyrin can induce changes in the spatial, physical, and electronic structure, which in turn can change its electronic transitions and properties, thus leading to differences in interaction with hybrid silica nano helices. Such observation can shed light on how chiral molecules organize and assemble into chiral nano space resulting in induction and amplification of their chiroptical behaviors and can help the design of new chiral hybrid systems based on porphyrin and robust inorganic nanostructures for specific chiral applications.

## **ASSOCIATED CONTENT**

The Supporting Information is available free of charge.

### **Corresponding Author**

**Reiko Oda** - Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248, 33600 Pessac, France; WPI-Advanced Institute for Materials Research, Tohoku University, Katahira, Aoba-Ku, 980-8577 Sendai, Japan; <https://orcid.org/0000-0003-3273-8635>; Email: [reiko.oda@u-bordeaux.fr](mailto:reiko.oda@u-bordeaux.fr)



## Authors

**Zakaria Anfar** - Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248, 33600 Pessac, France; <http://orcid.org/0000-0001-8840-7160>; Email: [zakaria.anfar@gmail.com](mailto:zakaria.anfar@gmail.com)

**Balamurugan Kuppan** - Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248, 33600 Pessac ; France. <https://orcid.org/0000-0002-2131-1233>

**Antoine Scalabre** - Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248, 33600 Pessac, France; <https://orcid.org/0000-0001-7304-1960>

**Rahul Nag** - Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248, 33600 Pessac, France; <https://orcid.org/0000-0001-8562-8793>

**Sylvain Nlate** - Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248, 33600 Pessac, France; <https://orcid.org/0000-0002-0300-9081>

**Emilie Pouget** - Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248, 33600 Pessac, France ; <https://orcid.org/0000-0002-3175-6201>

**Gabriele Magna** - Department of Chemical Science and Technologies, University of Rome Tor Vergata, Via Della Ricerca Scientifica 1, 00133 Rome, Italy ; <https://orcid.org/0000-0003-2140-0110>

**Ilaria di Filippo**- Department of Chemical Science and Technologies, University of Rome Tor Vergata, Via Della Ricerca Scientifica 1, 00133 Rome, Italy ; <https://orcid.org/0009-0002-1723-6573>

**Mario L. Naitana** - Department of Chemical Science and Technologies, University of Rome Tor Vergata, Via Della Ricerca Scientifica 1, 00133 Rome, Italy; <https://orcid.org/0000-0001-8443-4831>

**Tatsiana Nikonovich** - Department of Chemistry and Biotechnology, School of Science, Tallinn University of Technology, Akadeemia tee 15, 12618 Tallinn, Estonia

**Manuela Stefanelli** - Department of Chemical Science and Technologies, University of Rome Tor Vergata, Via Della Ricerca Scientifica 1, 00133 Rome, Italy; <https://orcid.org/0000-0001-8563-8043>

**Donato Monti** - Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, I-00185 Rome, Italy; <https://orcid.org/0000-0002-6166-8536>

**Victor Borovkov** - Department of Chemistry and Biotechnology, School of Science, Tallinn University of Technology, Akadeemia tee 15, 12618 Tallinn, Estonia; <https://orcid.org/0000-0001-7898-0457>

**Riina Aav** - Department of Chemistry and Biotechnology, School of Science, Tallinn University of Technology, Akadeemia tee 15, 12618 Tallinn, Estonia; <https://orcid.org/0000-0001-6571-7596>

**Roberto Paolesse** - Department of Chemical Science and Technologies, University of Rome Tor Vergata, Via Della Ricerca Scientifica 1, 00133 Rome, Italy; <https://orcid.org/0000-0002-2380-1404>; Email: roberto.paolesse@uniroma2.it

**Reiko Oda** - Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248, 33600 Pessac, France; WPI-Advanced Institute for Materials Research, Tohoku University, Katahira, Aoba-Ku, 980-8577 Sendai, Japan; <https://orcid.org/0000-0003-3273-8635>; Email: reiko.oda@u-bordeaux.fr

### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### **Notes**

The authors declare no competing financial interest.

### **Supporting Information**

The Supporting Information is available free of charge at XXXXXXXXX

Schematic presentation of porphyrins in chiral nano spaces. UV-Vis, CD signals and  $g$ -factors, TEM characterization, of nano structures with porphyrins.

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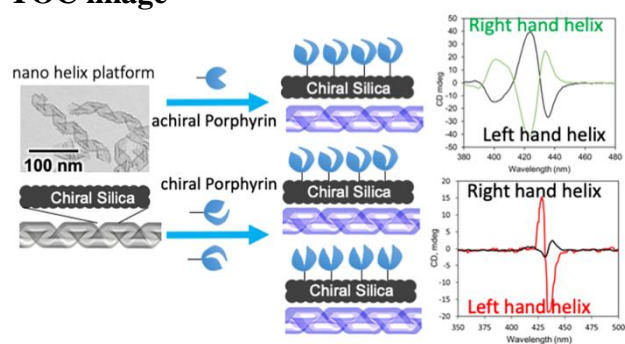
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### TOC image



**Induction and amplification of chirality and enantioselective interaction between chiral silica platform and chiral or achiral porphyrin**