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# Nucleosides as Organizing Agents

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**ABSTRACT:** In the present review, we discuss the results of the research we have done over the last decade on multi-porphyrinic architectures bearing a nucleotidic backbone, compare all the data, offer a novel overview and emphasize common capabilities of nucleosides appearing in various systems, providing a new insight on the pre-organizing capabilities of nucleosidic backbones. The efficiency of nucleosides as preorganizing agents was investigated through the synthesis and study of various bis-porphyrins bearing nucleosidic linkers, as well as through the investigation of the conformation of linear and arborescent multi-porphyrins constructed on a nucleosidic backbone. The capacity of these molecules to complex guests with a high association constant was used as a tool to evaluate their degree of pre-organization, as well as the investigation of the electronic coupling existing between their chromophores and their photo-chemical capacities. Such an overview of one decade of scientific investigations documents the fact that rigid linkers between chromophores are not necessary for their spatial pre-organization, and open new routes to the faster synthesis of flexible highly pre-organized molecular architectures avoiding the long and tedious synthesis of rigid tweezers, especially for the preparation of rigid linkers which may bring solubility and stability problems.

**KEYWORDS:** porphyrins, nucleosides, supramolecular interactions, pre-organization, molecular recognition.

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## INTRODUCTION

Exerting control over the position and distance of the porphyrins along our specifically designed oligonucleotidic scaffold was our main goal over the past years. Elaboration of non-covalent multiporphyrinic assemblies represents an important challenge in relation to the mimicry of bacterial photosynthesis [1-4] and the design of functional molecular materials.[5] Axial coordination to the central metal ions of porphyrins by suitable ligands is an effective and widespread strategy for the assembly of non-covalently bound multi-component systems. Zn(II) derivatives have been extensively used for this purpose,[6-8] and examples based on Ru(II), Co(II), Rh(III) porphyrins can be found in the literature.[9-12]

In the present review, we discuss the results of the research we have done over the last decade on multiporphyrinic architectures bearing a nucleotidic backbone, compare all the data, offer a novel overview and emphasize common capabilities of nucleosides appearing in various systems, providing a new insight on the pre-organizing capabilities of nucleosidic backbones. All along this review, we try to highlight how nucleosides determine both conformation and properties of various molecular architectures where porphyrins are held together by nucleosidic backbone. Tweezers as well as star-shaped and linear multi-porphyrinic arrays are discussed.

Over the years, we first focused on cofacial bis-porphyrin tweezers and host/guest interactions to investigate the possibility to obtain self-coordinated molecular systems with predictable spectral and redox characteristics. We reported some years ago the synthesis of a bis-porphyrinic tweezers bearing a tris-anthracenic spacers.[13] Specifically, a tris-anthracene spacer was chosen in order to facilitate a cofacial orientation of the chromophores while allowing free rotation around the acetylene axis, thus adjusting the cavity to a large variety of guests. Indeed, this adjustable tweezers is able to complex both small and large bidentate bases, as well as photoactive guests such as bipyridyl-porphyrins.[14] However, synthesis of rigid tweezers can be long and tedious, especially for the preparation of rigid linkers which may bring solubility and stability problems. Considering that properly functionalized nucleosides adopt a more or less blocked conformation,[15-16] we decided to synthesize three bis-porphyrins using either uridine or 2'-deoxyuridine derivatives as spacers, expecting to bring the porphyrins in a face-to-face orientation.[17] These three dimers differ by the positions where the chromophores are attached, either on the ribose or on the nucleic base. For two of these three bis-porphyrinic nucleosides, their binding studies with the bidentate base DABCO showed that the nucleoside confer sufficient preorganization to the dimers to enhance the association constants, documenting the fact that rigid dimers are not necessary for preorganization, and opening up new routes to the faster synthesis of flexible tweezers capable of complexing guests with a high association constant.

Such a capacity of nucleoside to pre-organize the porphyrins attached to it was also observed in a star-shaped multi-porphyrins with chiral and enantio-pure nucleosidic linkers we synthesized in the past.[18] If the configuration is indeed a star-shaped nanomolecule, it appears that the induced conformation is nothing as expected. The four peripheral Zn(II) porphyrins collapse over the free-base central one, what induce totally different photo-physical properties. Due to this induced conformation and despite a minor expected light energy harvesting behavior, the principal capability of this system is to quench the collected light energy.

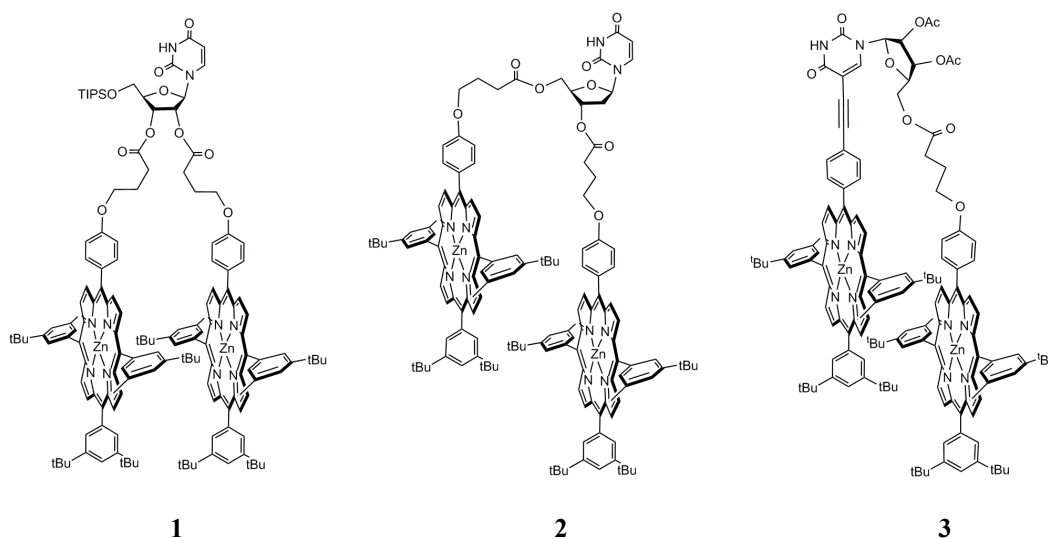
The gain in stability and the enhancement of the association constants observed for the complexation of bidentate base such as DABCO by bis-porphyrins using either uridine or 2'-deoxyuridine derivatives as spacers can be even greater when a dinucleotide linker is used. These results document the fact that dinucleoside confer an even greater preorganization to the dimers to enhance the association constants. Our last challenge was thus to synthesize an oligonucleotide with pendant porphyrins, using a modified oligonucleotidic backbone to target a parallel conformation of the porphyrins appended to each deoxy-uridine moiety. To provide a rigid environment for the porphyrins, the

uridine units were coupled in 3'-5' stepwise fashion using ether-ester type of spacer of suitable length, and porphyrins were anchored to the uridine by means of robust carbon-carbon bonds. The investigation of the conformation of the four specifically designed uridine-porphyrin conjugates (a monomer, dimer, tetramer and octamer) was realized through a comprehensive conformational analysis by NMR spectroscopy. The obtained results testify in favor of the existence of an anti glycosidic angle and suggest a slipped cofacial conformation for the porphyrin macrocycles.[19]

## RESULTS AND DISCUSSION

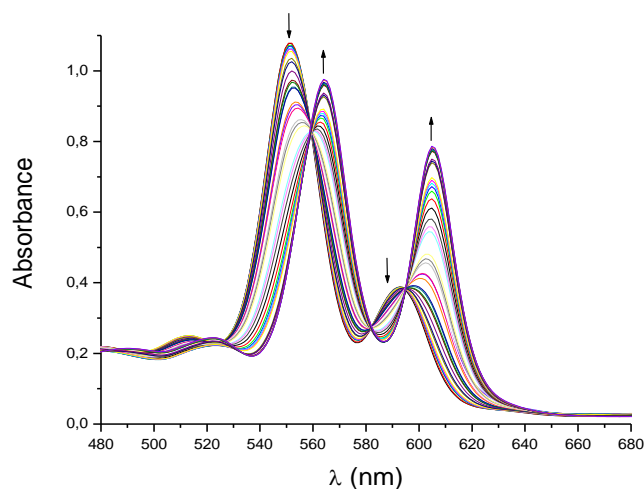
### BIS-PORPHYRIC TWEEZERS WITH A SIMPLE NUCLEOSIDIC LINKER

As part of our studies concerning the elaboration of pre-organized systems, we synthesized some years ago three new bis-porphyrins bearing a flexible nucleosidic linker (**1**, **2** and **3** in Figure 1.) expected to adopt a tweezer like conformation which should facilitate the complexation of bidentate Lewis bases. These dimers differ by the attachment positions of the two porphyrins. For bis-porphyrinic dimers **1** and **2**, both porphyrins are attached to the ribose, in the O-2' and O-3' positions of uridine for dimer **1** and in the O-3' and O-5' positions of 2'-deoxyuridine for dimer **2**. [20-21] For dimer **2** and **3**, the anchoring position of one Zn(II) porphyrin at the O-3' position of the sugar moiety is conserved, while the second chromophore is attached either at the O-5' position of the 2'-deoxyuridine for dimer **2** or at the C-5 position of the nucleic base for dimer **3**.



**Fig. 1.** Three new bis-porphyrins bearing a flexible nucleosidic linker and differing by the attachment positions of the two porphyrins.

The ability of tweezers **1**, **2** and **3** to accommodate guests of various size was investigated through binding studies carried out in dichloromethane with DABCO or 4,4'-bipyridine as bidentate bases. The complexations were monitored by UV-visible spectrophotometric titration of a solution of tweezers in CH<sub>2</sub>Cl<sub>2</sub> ([**1**] = 2.7x10<sup>-5</sup> M, [**2**] = 3.0x10<sup>-5</sup> M, [**3**] = 2.4x10<sup>-5</sup> M), which resulted as expected in a significant red-shift of the Soret and Q bands in the porphyrin (Figure 2).[22-23]



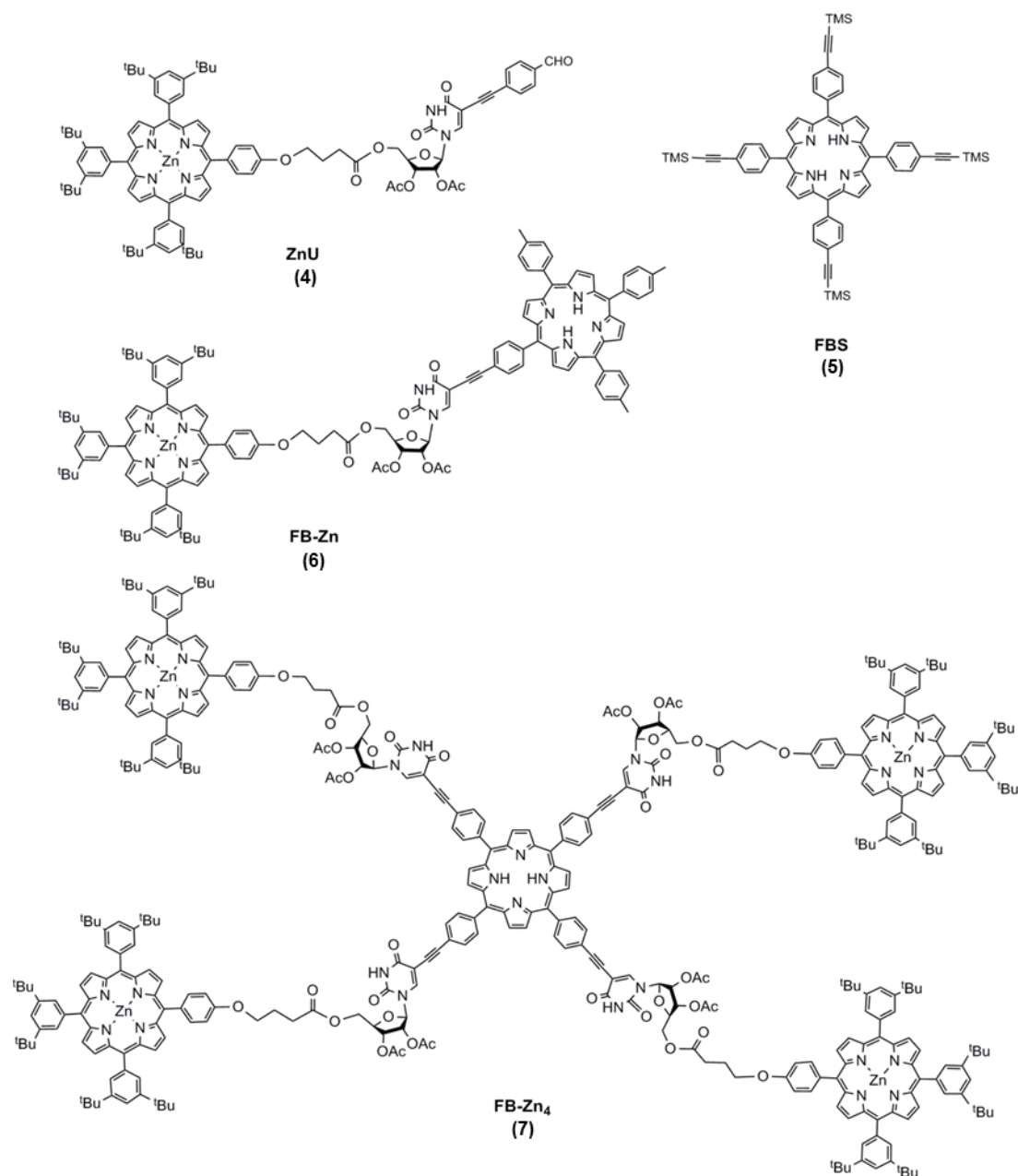
**Fig. 2.** UV-Vis spectroscopic titration of dimer **2** with DABCO in  $\text{CH}_2\text{Cl}_2$  at rt. Spectral changes of **2** on addition of DABCO at rt:  $[\mathbf{2}] = 3.10 \times 10^{-5} \text{ M}$ , concentration ratio  $[\text{DABCO}] / [\mathbf{2}] = 0$  to 100.

The association constants for the formation of the complexes were calculated from UV-visible spectroscopic data. A value of  $2.5 \times 10^4 \text{ M}^{-1}$  was found for tweezers **1**, which is similar to the association constant of DABCO with a reference Zn(II) porphyrin 5,10,15,20-tetra-di-tert-butyl-phenyl-porphyrin  $\text{A}_4$  ( $2.5 \times 10^4 \text{ M}^{-1}$ ), thus indicating as expected that no well-defined pre-organized conformation exists for bis-porphyrin **1**. However, much higher binding constants were found for the formation of host/guest complexes between tweezers **2** and **3** and DABCO. Values of  $6.3 \times 10^5 \text{ M}^{-1}$  and  $2.0 \times 10^6 \text{ M}^{-1}$  were found. These association constants are increased by 1.5 or 2 orders of magnitude as compared to the association constants of the same bidentate ligand with the above cited reference Zn(II) porphyrin. This enhanced stability of the complex may be ascribed to a pre-organization of the bis-porphyrinic tweezers **2** and **3** forming a cavity and provides convincing evidence that the bidentate base is inserted into the cavity of both dimers via host/guest interactions. Such results were expected for tweezers **3** since it is known that the anti-conformation is blocked for uridine in the presence of bulky substituents on the nucleic base, providing more favorable conditions for the second porphyrin to come in a face-to-face orientation. However, no explanation could be found to explain such a high complexing capability of tweezers **2**.

The adjustment of the cavity to bidentate guests of various size was investigated for tweezers **2** and **3** through binding studies realized in dichloromethane between these dimers and 4,4'-bipyridine. The complexations were monitored by UV-visible spectrophotometric titration of a solution of tweezers in  $\text{CH}_2\text{Cl}_2$  ( $[\mathbf{2}] = 2.9 \times 10^{-5} \text{ M}$ ,  $[\mathbf{3}] = 2.2 \times 10^{-5} \text{ M}$ ), which resulted as expected in a significant red-shift of the Soret and Q bands in the porphyrin. The association constants for the formation of the complexes were calculated from UV-visible spectroscopic data. Values of  $1.3 \times 10^5 \text{ M}^{-1}$  and  $3.2 \times 10^5 \text{ M}^{-1}$  were found for tweezers **2** and **3** respectively. These binding constants are increased by 1 or 1.5 order of magnitude as compared to the association constants of the same bidentate ligand with a reference Zn(II) porphyrin 5,10,15,20-tetra-di-tert-butyl-phenyl-porphyrin  $\text{A}_4$  ( $7.9 \times 10^3 \text{ M}^{-1}$ ), indicating an enhanced stability of the complex, which may be ascribed to a pre-organization of the bis-porphyrinic tweezers **2** and **3** forming a cavity. These results document the insertion of the bidentate base into the cavity of the dimers via host/guest interactions, and clearly demonstrate the adjustment of the cavity to the size of the complexed guest.

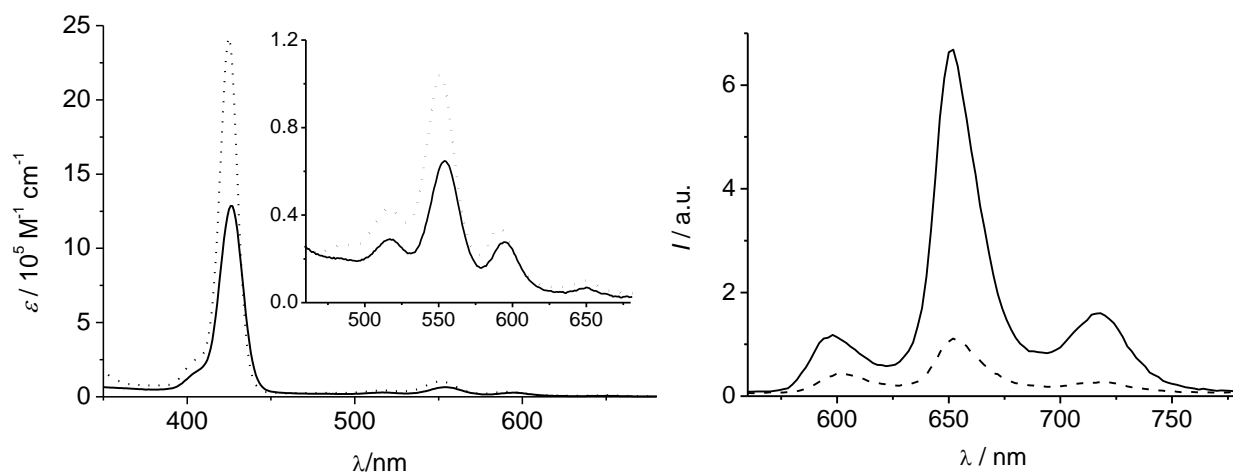
## STAR-SHAPED PENTA-PORPHYRIN WITH CHIRAL AND ENANTIOPURE NUCLEOSIDIC LINKERS

The study of a pentaporphyrin structure FB-Zn<sub>4</sub> (7) with a central free-base porphyrin and four peripheral zinc porphyrins connected *via* a chiral and flexible nucleosidic linker was undertaken in order to determine its potential use as an antenna system, able to collect light energy and to convey it to the energy sink in the central position.[18, 24] The peripheral zinc porphyrin chromophores can extensively absorb light throughout all the visible range and convey the stored energy to the central free-base porphyrin. The system can effectively work as an antenna if the absorbed light energy is efficiently conveyed to the central porphyrin and no competitive loss of the absorbed energy occurs. The model systems ZnU (4), FBS (5) and the dyad FB-Zn (6), reported in Figure3, were synthesized to help in the elucidation of the photo-physical behavior of the pentad system FB-Zn<sub>4</sub> (7).



**Fig. 3.** The component models ZnU (4) and FBS (5), the dyad FB-Zn (6) and the pentad FB-Zn<sub>4</sub> (7).

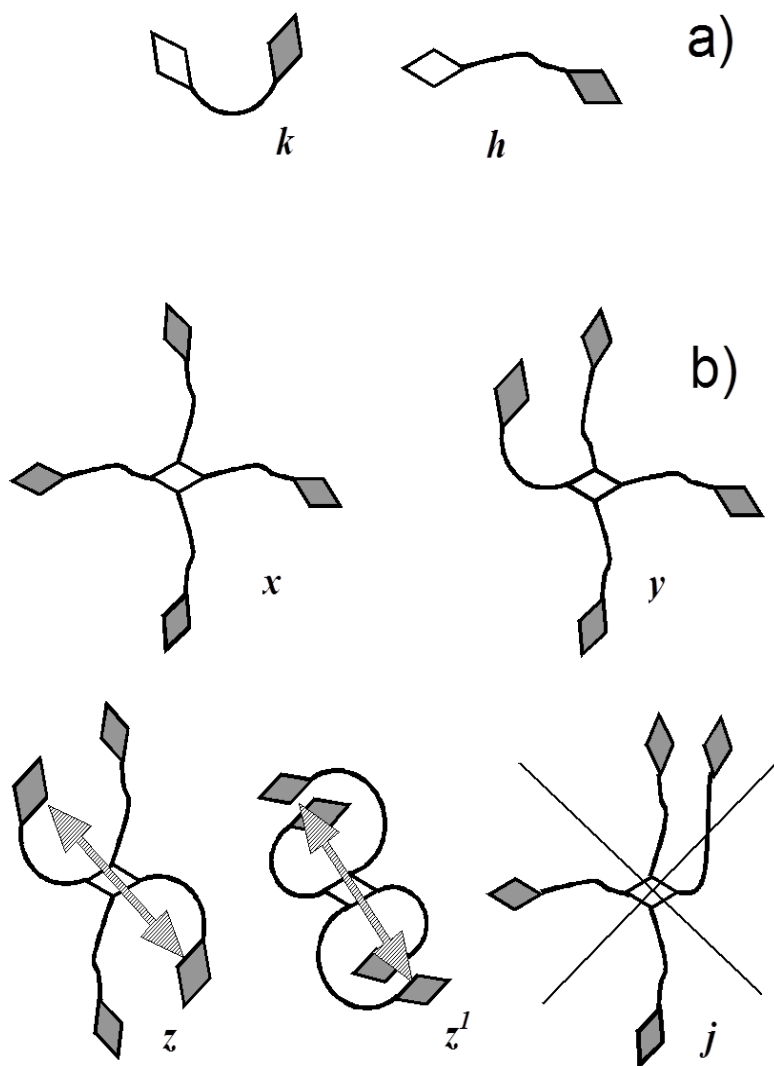
The absorption spectrum of the dyad FB-Zn (**6**) closely matches the superposition of the two model components. This is indicative of a very modest interaction between the components, as expected from the length and the type of bridging ligand. Unlike what found for the dyad, the absorption spectrum of the pentad FB-Zn<sub>4</sub> (**7**), appears different from the simple superposition of components unit. Figure 4a reports the absorption spectrum of the pentad compared with the sum of the components. Large effects on the Soret band, namely broadening, decrease in epsilon and a minor red shift are observed and in addition, a rather important change in epsilon, a red shift and a change in spectral shape in the Q bands region are also detected. Whereas some change in the Soret band region is generally encountered whenever porphyrins are connected to other species, the effect on the Q band region is rather unusual. This fact can be taken as indication of a rather important coupling between components. Since the type and length of the bridge is not expected to couple the components to such an extent, a through space interaction can be envisaged to explain the observation. This must occur in a conformation where the components are in close contact and which can only be possible in FB-Zn<sub>4</sub> (**7**) and not in FB-Zn (**6**), since in the latter no such interaction was evidenced.



**Fig. 4.** a) Molar absorption coefficient of FB-Zn<sub>4</sub> (**7**) in toluene solution (solid line). The sum of the molar absorption coefficients of the components, one FBS (**5**) and four ZnU (**4**) units, is also reported (dotted line). b) Emission detected from optically matched ( $A = 0.18$ ) toluene solutions excited at 550 nm of FB-Zn (**6**) (solid line) and FB-Zn<sub>4</sub> (**7**) (dashed line).

The emission spectrum of the dyad FB-Zn (**6**), when excited at a wavelength where only FBS (**5**) absorbs, i.e. at  $\lambda > 625 \text{ nm}$ , displays the emission of the FBS (**5**) model, with a quantum yield identical within experimental error. Selective excitation of the ZnU unit (**4**) is not possible, but excitation where both components absorb yields an emission spectrum which shows the features of both the free base component ( $\lambda \text{ max} = 652 \text{ and } 718 \text{ nm}$ ) and of the zinc component ( $\lambda \text{ max} = 598 \text{ nm and } 646 \text{ nm}$ ). Nonetheless, if the emission is compared to those of the component models absorbing the same number of photons as they do in the dyad, it is clear that in the array the emission of the zinc porphyrin unit is quenched whereas the emission of the free base porphyrin moiety is increased, i.e. sensitized. Time resolved experiments with picosecond resolution, allow to determine that the dyad is made of two populations of conformers which equilibrate on time scales which are slow, compared to the photo-induced processes and therefore they behave as independent species. With respect to the theoretical results in the gas phase, which indicates a folded structure as shallow minimum conformer, the solution experimental results indicate that a more displaced conformation

has been stabilized by solvent interactions and accounts for the 70% of the population. A schematic illustration of the two conformers, compatible with both the experimental findings and the theoretical results, is reported on Figure 5a. Both conformers are in a bent configuration, but whereas in isomer *k*, the two porphyrins are nearly overlapping, with a distance between the donor-acceptor couple of the order of 20-23 Å, sufficient to promote a dipole-dipole type energy transfer process. In the conformer in the open conformation, *h*, the planes containing the porphyrins are displaced and the center to center distance is increased to value of ca. 32 Å, distance which does not allow the energy transfer to take place effectively.



**Fig. 5.** Cartoon representation of the different conformations for FB-Zn (6) (a) and FB-Zn<sub>4</sub> (7) (b). White diamonds represent the free-base porphyrin energy acceptor and grey diamonds the Zn porphyrin energy donor. The arrows indicate exciton interactions.

In the pentad, FB-Zn<sub>4</sub> (7), selective excitation of the free-base component at 650 nm, indicates a decrease of the emission quantum yield of this component compared to the model. Under these strong coupling conditions, quantitative consideration on the emission quantum yield of the single components in the pentad as done for the dyad (6), is rather unreliable. This type of determination, in fact, strongly relies on the fact that the components do not substantially change their properties when bound in the arrays. This is not the case, as evident both from the ground state absorption



spectrum of Figure 4a and from the free base porphyrin emission yield, which appears decreased in the pentad. Nonetheless, a qualitative experiment comparing the overall emission quantum yield of optically matched solutions of the dyad and the pentad is reported in Figure 4b. It shows that the emission in the higher order array is strongly diminished both on the zinc porphyrin band and on the free base band, so it cannot be ascribed to an increased efficiency of the intramolecular energy transfer process, but rather to an overall increase in the non-radiative component decay involving both components of the pentad, i.e. the free base- and the Zn porphyrin. In spite of the fact that the overall yield of the luminescence of the pentad is extremely low, sensitization of the free base by the zinc component still occurs, as evidenced by the excitation spectrum registered at 720 nm, a wavelength of free-base porphyrin emission. In this excitation spectrum there is a clear contribution to the free base emission from the zinc porphyrin donor band at 550 nm, its extent is partial as in the dyad FB-Zn (6), and should be ascribed to the fact that some conformations in Fb-Zn<sub>4</sub> (7) do not contribute to energy transfer. Though, in presence of sensitization of some free-base emission, as proved by the excitation spectrum, the overall emission of the free-base porphyrin does not appear to be sensitized but rather to decrease. At the same time we determined a quenching of the zinc porphyrin, without detecting a corresponding sensitization in the free base acceptor.[25] In order to explain the observation we have to assume that a remarkable loss of emission from the zinc porphyrin component, as well as from the free-base porphyrin unit, must take place through some non-radiative path.

Some strong interacting conformer could account for the observed phenomena, namely non additivity of absorption, dramatic decrease in emission quantum yield of the pentad compared to the dyad and a new fast component (110 ps) in the quenching of the luminescence. This conformation should be precluded in the dyad, where the above effects were not observed. For the pentad a series of different conformations can be envisaged, some are reported in Figure 5b. Whereas conformation x (fully extended) and conformation y (partially bent) are resembling and should behave similarly to the conformations of the dyad, the conformation resulting from the concomitant bending of two (or even more) Zn porphyrins over the free base component, denoted as z or z1, is unique to the pentad. Other types of conformations unique to the pentad, as the j, with the Zn porphyrins in a parallel arrangement, can be ruled out. It seems, in fact, unlikely that this type of conformation could affect the radiative parameters of the free base component which is not involved in the interaction. Type z conformers appear therefore as the most probable candidates responsible for the strong interaction detected in the pentad and this will gain further support from the data presented in the following sections. The interpretation of the data can be attempted in a rather simplified frame as follows. The pentad is assumed to take (at least) the three different types of conformations denoted as x, y and z. Whereas conformation x and y behave “regularly” i.e. similarly to the corresponding bent or extended conformations in the dyad, as confirmed by the similar lifetimes detected in the luminescence quenching of the Zn porphyrin donor, the z type conformations can be responsible for the different behavior of this array compared to the dyad. To this type of conformation is assigned the short luminescence lifetime of the zinc porphyrin component (110 ps) which, unlike the 240 ps component assigned to an energy transfer process in conformation y, has to be regarded as a fast, non-radiative decay of the excited state. In this type of conformation, an electronic, exciton type interaction involving also the free-base component can occur, and this induces a strong perturbation of the individual parameters of the components, resulting in a greatly increased non radiative decay. Since it accounts for about half of the excited population, as derived from the luminescence components, its behavior will dominate the observed phenomena. The ensemble Zn-FB-Zn in z, or Zn-Zn-FB-Zn-Zn in z1, typical of the pentad, is therefore deemed responsible for the new properties, brought about by the strong electronic coupling between components. Deactivation of the excited ensemble Zn-FB-Zn (or Zn-Zn-FB-Zn-Zn) proceeds rapidly, through non radiative paths, without producing any sensitization localized on the free base. The free-base porphyrin itself, when selectively excited, displays a decreased emission quantum yield in

the pentad. This indicates that, irrespective of the excited component, the Zn-FB-Zn ensemble seems to follow non radiative decay paths.

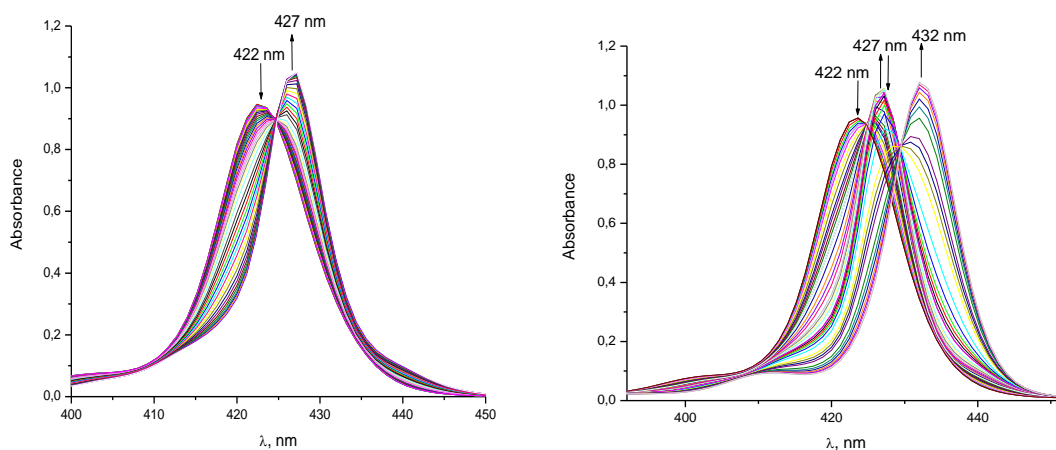
## DINUCLEOTIDE: PARTICULARLY HIGH ASSOCIATION CONSTANT FOR THE FORMATION OF A SANDWICH TYPE MOLECULAR COMPLEX.

The gain in stability and the enhancement of the association constants observed for the complexation of bidentate base such as DABCO by bis-porphyrins using either uridine or 2'-deoxyuridine derivatives as spacers can be even greater when a dinucleotide linker is used. Indeed, we recently synthesized bis-porphyrinic dimer **8** based on a di-nucleosidic linker (Figure 6) and studied its complexation capabilities by UV-Vis spectroscopy.[26] The gain in stability for the formation of sandwich type host-guest complex with DABCO can be even greater when a dinucleotide linker is used. Such pre-organization increases the association constants by one to two orders of magnitude when compared to the association constants of the same bidentate ligands with a reference Zn(II) porphyrin.

### 8

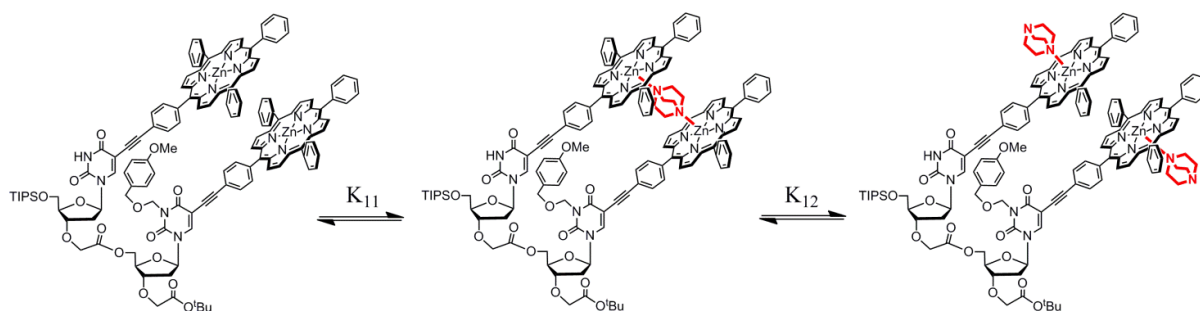
**Fig. 6.** Rigid cofacial bis-porphyrinic tweezers with di-nucleosidic spacer **8**.

The ability of di-nucleotide **8** to accommodate guests was investigated through binding studies carried out in dichloromethane with DABCO as bidentate base. As reported in some of our previous publications (Solladie et al., 2008), it was assumed that the di-nucleosidic bis-porphyrin could be pre-organized and thus facilitate the coordination of this rigid bifunctional ligand. The synthesized molecular system is amenable to preorganization, because its architecture is based on combination of rigid and flexible linkers. The architecture of multi-porphyrinic systems is important because the covalent connectivity between the interacting centers commands the geometry of resulting assembly and the relative orientation of chromophores dictates the strength of the interaction with ligands. As already noted, the geometry of porphyrins in supramolecular assembly is crucial in design of artificial light-harvesting complexes.[27-33] Data obtained by UV-visible titrations were analyzed by using the values of the absorbance at fixed wavelengths, which method is exclusively valid for the complexes with stoichiometry 1/1, and by simultaneous fitting of the whole series of spectra collected at 1 nm intervals using the software SPECFIT. [34-35]



**Fig.7.** UV-visible titration of bis-porphyrinic tweezer **8** with DABCO in CH<sub>2</sub>Cl<sub>2</sub> at rt. On the left hand side first part of the titration and on the right the complete titration.

After examining the complexation of the simple porphyrin with DABCO, we studied the binding of the same base to dimer **8**, the bis-porphyrinic tweezer appended to an appropriate position of the flexible uridinic scaffold by the rigid acetylene group. The titration of the dimer with DABCO was measured by using the coordination shift of the Soret absorption as well as the Q-bands. The Soret band absorption was measured at the concentration of  $1.04 \times 10^{-6}$  M which corresponds to an absorbance of 0.95 at 422 nm. The titration was performed in two parts to be analyzed in terms of two-state equilibria. The first part of the titration was processed until 2 equivalents of DABCO were added per porphyrin. The complete titration that involved an addition of DABCO until 6000 equivalents per porphyrin was performed separately, Figure 7. The clean isosbesticity of spectra obtained in the first part of the titration demonstrates that the only colored species present in solution are free dimer **8** and one type of its complex with DABCO. The observed spectral changes are quite similar to those obtained in the titration of the monomer. However, there are some minor spectral changes, i.e. smaller red shift of the Soret peak, from 422 to 427 nm, as well as intensified and sharpened form of the titration spectrum. A shift in the Soret band of 5 nm is exactly two times smaller than the shift obtained for the 1/1 monomer/DABCO complex. Accordingly, it was reasonable to anticipate formation of the intramolecular 1/1 sandwich complex. On addition of more DABCO, intensity of the absorption band at 427 nm decreased, and a new absorption band appeared at 432 nm. As observed in the titration spectrum of the monomer, the Soret absorption at 432 nm is typical for the simple 1/1 porphyrin/DABCO complex. On the basis of the changes in absorption spectra, the possible two consecutive two-state equilibria with corresponding stepwise constants in the binding of DABCO to bis-porphyrinic tweezer **8** are shown in Figure 8.



**Fig. 8.** Representation of the proposed equilibria involved in the binding of DABCO to bis-porphyrinic tweezer **8**. For clarity reasons tert-butyls on meso-phenyls are omitted.

The first method for calculation of the binding constant by using titration data at selected wavelengths was applied only to the first part of the titration characterized by sharp isosbestic point. This analysis could be performed because the complexation by 1/1 binding model was envisaged in the first equilibrium. The binding constant for the 1/1 dimer/DABCO complex was found to be  $7.4 \times 10^6 \text{ M}^{-1}$  ( $\log K_{11} = 6.9$ ). The formation of this type of a complex was verified by analysis of the whole set of spectra which correspond to the first part of the titration by using SPECFIT. The analysis resulted with only one possible 1/1 complex with corresponding binding constant  $\log K_{11} = 6.42 \pm 0.03$ . It is interesting to note that calculated  $\log K_{11}$  for 1/1 dimer/DABCO complex is more than one order of magnitude higher than  $\log K_{11}$  for 1/1 monomer/DABCO complex. Taken together, these results strongly support formation of 1/1 dimer/DABCO sandwich complex through the chelate effect. The whole spectra obtained by the complete titration was

analyzed in terms of three possible colored species: free dimer **8**, 1/1 sandwich complex, and 1/2 open complex (Figure 8). Fitting of the titration data revealed that 1/1 and 1/2 binding models for dimer/DABCO are only possible.

Fitting to 1/1 binding isotherm yielded the stoichiometric binding constant  $\log K_{11} = 6.65 \pm 0.08$ , while the fit to 1/2 binding model provided  $\log K_{12} = 3.21 \pm 0.10$ . The calculated  $\log K_{11}$  is almost identical to  $\log K_{11}$  value obtained in the analysis of the first part of the titration. Moreover, calculated  $\log K_{12}$  value is three orders of magnitude lower than  $\log K_{11}$  value. Therefore, dissociation of the more stable chelated 1/1 complex is followed by coordination of second DABCO and by that formation of the 1/2 complex in which two DABCO molecules are coordinated to two porphyrins of the dimer. Both, 1/1 and 1/2 complexes involved in these consecutive two-state equilibria are in agreement with the species represented in Figure 8.

Similar formation of sandwich complexes was evidenced by Sanders, Hunter, Anderson and co-workers.[36-39] These studies show that sandwich complex formation is in concert with the parallel orientation of two porphyrin macrocycles. In this respect, the shifts in titration spectra are caused by proximity of the porphyrins and in this line increased interporphyrinic electronic interaction. The Soret band of the free dimer **5** has full width at half maximum (fwhm) 15 nm, and the Soret band of the dimer/DABCO sandwich complex 11 nm. It is believed that this narrowing indicate a significant increase in the center-to-center distance between the two porphyrins, due to the insertion of DABCO into the bis-porphyrinic cavity. This hypothesis is in great agreement with the half width at half maximum of 13 nm for the 1/2 dimer DABCO open complex. The outer coordination of DABCO allows a shorter center-to-center distance between the porphyrins.

These results thus document the fact that the choice of rigid spacers is not the only way to pre-organize bis-porphyrins, and that some well-chosen nucleosidic linkers offer an interesting option for the synthesis of such devices. Furthermore, the chirality and enantio-purity of the nucleosidic linkers paves the way toward the selective complexation of enantio-pure bidentate guests and the resolution of racemates.

## CONCLUSION

In the present review, we discuss the results of the research we have done over the last decade on multi-porphyrinic architectures bearing a nucleotidic backbone, compare all the data, offer a novel overview and emphasize common capabilities of nucleosides appearing in various systems, providing a new insight on the pre-organizing capabilities of nucleosidic backbones. The efficiency of nucleosides as preorganizing agents was investigated through the synthesis and study of various bis-porphyrins bearing nucleosidic linkers, as well as through the investigation of the conformation of linear and arborescent multi-porphyrins constructed on a nucleosidic backbone. The capacity of these molecules to complex guests with a high association constant was used as a tool to evaluate their degree of pre-organization, as well as the investigation of the electronic coupling existing between their chromophores and their photo-chemical capacities. Such an overview of one decade of scientific investigations documents the fact that the choice of rigid spacers is not the only way to pre-organize bis-porphyrins, and that some well-chosen nucleosidic linkers offer an interesting option for the synthesis of such devices. Furthermore, the chirality and enantio-purity of the nucleosidic linkers paves the way toward the selective complexation of enantio-pure bidentate guests and the resolution of racemates.

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