

# The Construction of Multichromophoric Assemblages: A Booming Field

Nasser Thallaj



**Abstract:** *The field of molecular photonics has witnessed significant advancements in the construction of multichromophoric assemblages, which play a crucial role in guiding and manipulating light energy at the molecular level. This paper provides an overview of the strategies and techniques employed in the design and synthesis of such assemblies, with a focus on covalent buildings. The concept of molecular photonic wires is introduced, where chromophores passively guide excitations between functional units. Various examples of covalent structures, including multiporphyrinic architectures, are presented, demonstrating precise control over energy transfer and propagation. Additionally, the polymerization of rigid porphyrinic precursors is explored as an alternative approach. The challenges and potential applications of these multichromophoric assemblies in the field of molecular photonics are discussed. The study highlights the importance of understanding the interactions between chromophores and offers insights into the applicative potential of organic compounds for emerging technologies.*

**Keywords:** *Multichromophoric Assemblages; Molecular Photonics; Covalent Buildings Energy Transfer; Excitons; Molecular Photonic Wires; Chromophores; Emerging Technologies*

## I. INTRODUCTION

The field of molecular photonics has witnessed significant advancements in recent years, particularly in the construction of multichromophoric assemblages. These assemblies, composed of multiple chromophores, play a crucial role in guiding and manipulating light energy at the molecular level. The ability to control and direct the flow of energy within these structures opens up exciting opportunities for various applications in emerging technologies. This paper aims to provide an overview of the strategies and techniques employed in the design and synthesis of multichromophoric assemblies, with a specific focus on covalent buildings [1].

Understanding the interplay between chromophores and their interactions is of paramount importance in the development of efficient multichromophoric systems. By harnessing the principles of molecular photonics, researchers aim to create molecular photonic wires that passively guide excitations between two functional units. These wires act as conduits for energy transfer and propagation, allowing for precise control over the movement of light energy.

Manuscript received on 15 May 2024 | Revised Manuscript received on 22 May 2024 | Manuscript Accepted on 15 June 2024 | Manuscript published on 30 June 2024.

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To achieve this, the field draws inspiration from nature's efficient structures, such as the photosynthetic systems found in plants and bacteria [2, 3]. The concept of molecular photonic wires is based on the idea of absorbing and migrating photons, or more specifically, induced electron excitations (excitons), within a precise arrangement of chromophores. Unlike classical optics, where miniature optical fibers conduct light, interactions between adjacent molecules, known as near-field interactions, become essential at the molecular scale. By confining the dimensions of the system to be smaller than the wavelengths of light, the behavior of photons can be controlled and guided at the molecular level [4, 5].

In a simplified manner, an elementary photonic "circuit" can be envisioned. When a photon with energy  $h\nu$  is absorbed at one end of the assembly, an electron excitation is generated. This excitation is then guided, via an energy gradient, to the opposite end of the system, where it is trapped and dissipated by the emission of a secondary photon with energy  $h\nu'$ . Importantly, the secondary photon has lower energy than the absorbed photon ( $h\nu' < h\nu$ ). The wire-like structure itself is composed of chromophores that act as conduits for the electronic excitation, while the functional units at the ends of the assembly play active roles in photon injection and extraction [3, 5, 6].

This concept of molecular photonic wires allows for the integration of two types of information carriers. Electromagnetic radiation serves as the medium for encoding and decoding data, while excitons, directly carried and processed by the molecules, facilitate energy transfer within the system. This integration of electromagnetic radiation and excitons offers a potential solution to the challenge of interfacing between the macroscopic and nanoscopic worlds. By directly converting photons into excitons and vice versa, the molecular photonic wires enable the processing of the same electrical signal in two distinct dimensions: the micrometric and nanometric realms [5, 6, 7].

Porphyrins, phthalocyanines, and perylenes are among the frequently employed chromophores in the construction of multichromophoric assemblies for molecular photonics applications. These chromophores exhibit unique properties that make them suitable for energy transfer and manipulation. Nature has already perfected the design and functionality of such systems in photosynthetic organisms. By precisely arranging pigments within protein complexes or lipid membranes, natural assemblies efficiently capture and guide light energy to specific points with high transfer efficiencies [7].



## The Construction of Multichromophoric Assemblages: A Booming Field

To mimic and expand upon nature's success, researchers employ various strategies to control the arrangement and form of unidirectional multichromophoric assemblies. These strategies can be broadly categorized as covalent and non-covalent buildings. Covalent buildings, relying on the rational design and synthesis of functional structures, offer precise control over the construction of multichromophoric assemblies [8]. Through the development of increasingly efficient synthetic tools, chemists can achieve precise control over the arrangement of artificial molecular architectures. Covalent buildings, based on a classical approach to molecular chemistry, have demonstrated their potential in the rational design of functional structures. Notably, the works of Lindsey and collaborators have made significant contributions in showcasing the potential of multiporphyrinic architectures for molecular photonics applications. By synthesizing edifices with multiple porphyrins, connected to distinct chromophores, researchers have observed and studied their photophysical behaviors in detail [6, 8]. These covalent buildings exhibit selective excitation of chromophores, such as boron dipyrromethene (BODIPY) or perylene, leading to cascades of energy transfers between the chromophores. The migration of excitation is dictated by the chromophores placed at the ends of the assembly, while the wire itself consists of zinc (II) porphyrins capable of conducting energy in both directions. The efficiency of each transfer step within these structures exceeds 90%, enabling efficient energy migration even in the longest compounds. Lindsey and colleagues have also successfully adjusted the energy levels of consecutive porphyrins to create a progressive energy gradient within the assembly, facilitating the unidirectional flow of energy [4, 8, 9]. Beyond simple covalent buildings, researchers have explored more complex architectures and strategies. For instance, the polymerization of rigid porphyrinic precursors has been investigated as an alternative approach to construct multichromophoric assemblies. By polymerizing porphyrin units, researchers can create extended structures with enhanced electronic communication between the chromophores. These polymeric assemblies offer opportunities for further tuning and control of energy transfer properties. The construction of multichromophoric assemblies presents both challenges and opportunities in the field of molecular photonics. Understanding the interactions between chromophores, optimizing the arrangement of functional units, and exploring the applicative potential of organic compounds are key areas of focus. By addressing these challenges, researchers aim to unlock the full potential of multichromophoric assemblies for diverse applications, including light-harvesting systems, photovoltaics, sensing devices, and optoelectronic technologies [5, 6].

In conclusion, the construction of multichromophoric assemblages represents a booming field within molecular photonics. The development of molecular photonic wires, composed of carefully arranged chromophores, enables the passive guidance of excitations between functional units. Covalent buildings, driven by precise design and synthesis strategies, offer control over energy transfer and propagation within these assemblies. Porphyrins, phthalocyanines, and perylenes are among the frequently employed chromophores, drawing inspiration from nature's efficient photosynthetic systems. Through the exploration of covalent and non-covalent strategies, researchers aim to advance the

field and leverage the applicative potential of multichromophoric assemblies in emerging technologies.

The following sections of this paper will delve into specific examples, experimental approaches, and findings in the construction of multichromophoric assemblies. By understanding the fundamental principles and advancements in this field, we can pave the way for further innovation and utilization of these structures in various technological applications [6, 9].

### II. MOLECULAR PHOTONIC WIRES

By moving to dimensions much smaller than the wavelengths used, it is no longer possible to conduct light according to the rules of classical optics such as "miniature optical fibers". We need to think in terms of interactions between adjacent molecules, also known as near-field interactions. The targeted structures are therefore not intended to conduct electromagnetic waves directly, contrary to what can be observed in certain organic microcrystals [5] or other molecular fibers of sufficient cross-section [6, 7]. It would be a question of absorbing and migrating the photons or, more precisely, the induced electron excitation (the exciton), in a precise assembly of chromophores.

Schematically, the simplest conceivable "photonic circuit" would work as follows:

A photon of energy  $h\nu$  is absorbed at one end of the building. The resulting electron excitation is guided (in an energy gradient) to the opposite end, where it is trapped and then dissipated by the emission of a secondary photon of energy  $h\nu'$ , with  $h\nu' < h\nu$  (Figure 1).



**Figure 1: Schematic Representation of an Elementary Photonic "Circuit" (Figure Inspired by Reference [8]).**

In this case, the wire itself is made up of all the chromophores that propagate the electronic excitation. The two ends, which have active functions (photon injection and extraction), are not part of it. Thus we could define molecular photonic wires by a set of chromophores that passively guide excitation between two functional units.

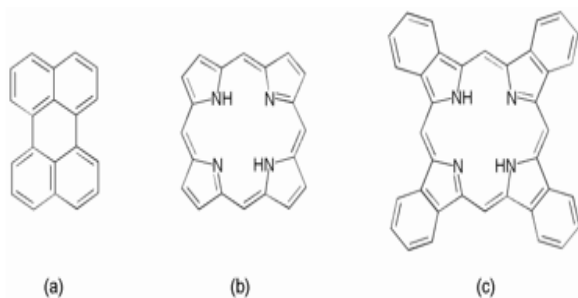
It is interesting to note that circuits based on this concept would involve two types of information carriers. On the one hand, the electromagnetic radiation used to encode the initial (programming) and final (reading) data, and on the other hand, the excitons directly carried and processed by the molecules.



In this case, the problem of interfacing between the macroscopic and nanoscopic worlds would be facilitated, since the conversion of photons into excitons and vice versa will be done directly by the elements of the circuit.

This would make it possible to circumvent the problem of the "bottleneck", which inevitably arises in molecular electronics, by processing the same electrical signal in two distinct "worlds", one of micrometric dimension and the other of nanometric dimension [8].

The construction of unidirectional multichromophoric assemblies is therefore a booming field. Among the most frequently used chromophores are porphyrins, phthalocyanines and perylenes (Figure 2) [9].



**Figure 2: Representation of Some Chromophores Proposed for Applications in Molecular Photonics (a) Perylene (b) Porphyrin (c) Phthalocyanine**

Long before scientists were interested in such systems, Nature developed and applied the most efficient structures known to date: the photosynthetic systems of plants and bacteria. Thanks to a precise arrangement of pigments, within protein complexes or lipid membranes, these assemblies make it possible to capture and guide light energy to precise points, with quantitative transfer efficiencies [10, 11, 12, 13, 14]. It is therefore clear that among the chromophores used, bacteriochlorine and porphyrin derivatives, key pigments of natural systems, occupy a prominent place.

Various strategies are employed to control their arrangement and form one-way chains. Many examples have been described in the literature and can be classified into two main types, which are covalent and non-covalent buildings.

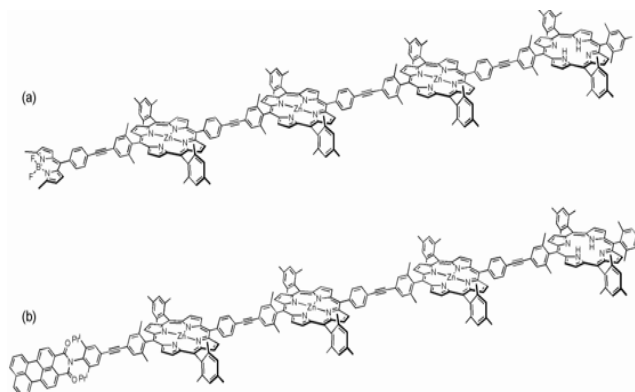
### III. COVALENT BUILDINGS

#### A. Simple Covalent Buildings

Thanks to the development of increasingly efficient synthetic tools, precise control of artificial molecular architectures has become possible. The limitation then remains the imagination of the chemist, confronted with the development of efficient synthesis strategies. A classical approach to molecular chemistry, it is obvious that the covalent pathway occupies a primary position in the rational design of functional structures.

Among the most instructive works of recent years, those developed by Lindsey and his collaborators have made a significant contribution to demonstrating the potential of multiporphyrinic architectures for applications in molecular photonics. Several examples of edifices with 1 to 3 identical porphyrins, connecting two distinct chromophores (Figure

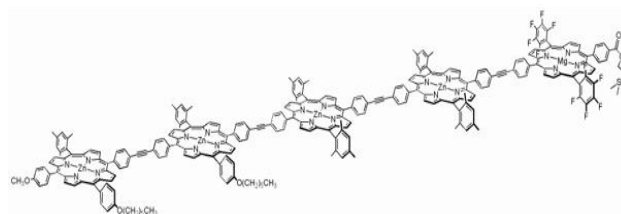
3), have been synthesized and their photophysical behaviors studied in detail [15, 16].



**Figure 3: Two Examples of "Molecular Photonic Wires" Studied in References [15] and [16]. In these Systems, Zinc (II) Porphyrins allow Energy to Migrate in Either Direction. The Direction of Excitation Propagation is Dictated by the Chromophores Placed at the ends of the Edifices, and is from a Boron Dipyrromethene (BODIPY) to a Free-Base Porphyrin (a), or from a Perylene to free-base Porphyrin (b). The Length of these Objects is Estimated to be 9 nm, and the Overall Quantum Energy Transfer Efficiencies are Greater than 75%**

In these structures, the selective excitation of boron dipyrromethene (BODIPY) or perylene induces a cascade of energy transfers from one chromophore to another, until the excitation is trapped and re-emitted by the terminal free base porphyrin. The direction of migration is imposed here by the two terminal groups. The "wire" itself is composed of zinc(II) porphyrins, which can conduct energy in either direction. Since the efficiency of each transfer step is greater than 90%, the energy migration is efficient even for the longest compounds (for the buildings shown in Figure 3, the estimated length is 9 nm and the overall efficiency is 76%).

Using a similar synthesis strategy, the same authors were able to adjust the relative energy levels of the HOMO-LUMO orbitals of the consecutive porphyrins, so as to impose a progressive energy gradient throughout the edifice (Figure 4). Since, in this case, a direction of propagation is imposed at each transfer step, the whole behaves more like a rectification element (diode) [17].



**Figure 4: Molecular "Photonic Diode" [17]. The HOMO-LUMO Levels of the Successive Chromophores Were Adjusted to Impose a Direction of Propagation at Each Transfer Step**

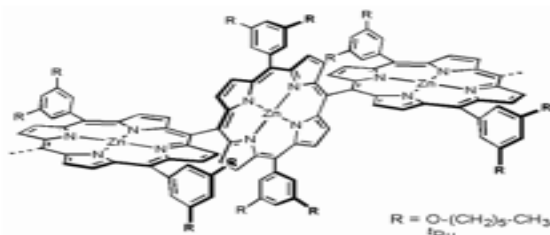
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These highly developed systems clearly demonstrate the finesse of organization that the covalent pathway can achieve, by offering a totally controlled construction method through multi-step synthesis. The examples of buildings prepared so far are too numerous to be presented in this introduction. The immense work of synthesis of oligomeric compounds (homo and heteromers) in recent years has been discussed in detail in various journals [18, 19, 20, 21][51].

The main problem with this approach, which is fundamentally motivating for the chemist, is that it often leads to low synthesis yields due to the multiplication of steps. Nevertheless, it makes it possible to obtain fantastic models, to study and rationalize the parameters that govern the interactions between chromophores; models, which themselves shed light on the applicative potential of organic compounds for new "plastic" technologies, at least conceptually.

A second possibility for preparing linear multi-porphyrinic systems is the polymerization of a rigid porphyrinic precursor; This polymerization can be done in the presence or absence of additives. Thus, conjugated oligomers of porphyrins, linked together by diethynyl [22], diethynyl-benzene [23], diethynyl-pyridine [24], diethynyl-anthracene [25], or involving longer conjugated spacers [19], have been prepared. In these different systems, a redward shift and an increase in the intensity of the least energetic porphyrin absorption bands are observed, which reflects the electronic communication between chromophores. It should be noted that this conjugation is rarely extended to the whole system, but limited to a certain number of repeated motifs, and is strongly dependent on the conformation of the chains of the polymer under consideration. This makes the photophysical behavior of such systems very complex and difficult to reconcile with their use as "molecular photonic wires" per se. Bonds that connect porphyrins to each other, without them being conjugated, have also been used, such as simple phenyl bridges [19-26]. However, the photophysical properties of such assemblages remain very complex because they depend on the uncontrolled orientations of the porphyrins between them. Moreover, in all of these examples, the buildings are obtained with a significant polydispersity.

Thus, while the polymerization yields are reasonable and the oligomers are obtained in one step from simple compounds, it should be noted that the final architecture of the molecules is much less controlled than by multistep synthesis. This route is therefore certainly better suited to the preparation of compounds for (opto)electronics or plastic photovoltaic cells. Indeed, in these applications, it will be the collective molecular properties that will be sought, within a material, and not those of a molecule in an "individual" way.



**Figure 5: Representation of an Oligomer of Porphyrins Coupled by their Meso Positions**

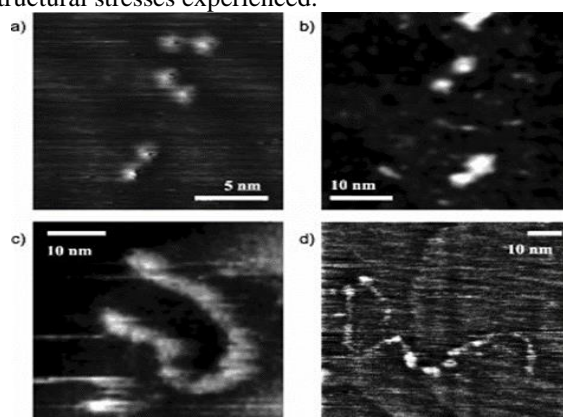
An elegant approach to circumventing the problem of polydispersity is the iterative strategy used by Osuka et al.

[27]. By successive sequences of oxidative couplings, in the presence of silver salt, of the size oligomers were obtained and separated by steric exclusion chromatography. Subsequent couplings between the oligomers then allow for a Rapid size increment (from single to double),

This makes it easier to purify the products. Using this method, edifices with 2 - 8, 10, 12, 16, 20, 24, 32, 40, 48, 64, 96, 128, 192, 256, 384, 524, 768 and 1024 zinc(II) porphyrins were synthesized and characterized, making them the longest compounds obtained

with precise control of the number of associated chromophores [28]. Directly related by their meso positions (Figure 5), porphyrins cannot arrange themselves in a planar manner due to steric stresses, and the resulting edifices are therefore not conjugated. In addition, the chromophores develop a strong excitonic coupling between them, which should allow efficient energy transfers from one cell to another. Nevertheless, the measurement of the hydrodynamic radii of chains of different sizes by  $^1\text{H}$  NMR as well as AFM and STM images showed the relative flexibility of such assemblies, both in solution and on solid support. Indeed, chains with more than a dozen porphyrins fold visibly and present various conformations when deposited on a surface (conformational polydispersity, Figure 6). The absorption and fluorescence of each of the porphyrins is identical, as their geometric arrangement is well determined. This allows for the transfer energy efficiency between them. However, with the increase in the number of bound porphyrins, and therefore their size, buildings are subject to more and more external stresses.

Some studies Extensive spectroscopic studies have been used to evaluate the effect of this structural inhomogeneity on the photophysical behaviour of isolated chains [29]. In particular it has been shown that beyond from 8 porphyrins consecutively linked, some Phenomena non-radiative relaxation methods induce significant energy losses, due to deformation some Buildings. Until 8 porphyrins behaviour in terms of These stresses result in the adoption of various conformations by the chains, in order to minimize the structural stresses experienced.



**Figure 6: STM Images of Zinc (II) Porphyrin Chains Coupled by their Meso Positions. The buildings are Deposited on HOPG and Include: (a) 6; (b) 9; (c) 48; (d) 128 Units [28,29]**

Thus, the direct environments of the porphyrins are no longer necessarily identical in the building. Some conformations can result in the trapping and non-radiative dissipation of energy, blocking its migration within extended assemblies. The precise mechanisms of dissipation are still hypothetical, but could be related to vibrational relaxation and conformational transitions.

Finally, it is interesting to note that these buildings can, after treatment with strong oxidants, form much more rigid ribbon structures, totally conjugated (Figure 7) [30].



**Figure 7: Formation of Bands of Fused Porphyrins from Mesoconnected Oligomers**

In this case, the geometry of the buildings is better defined and since the porphyrins are totally conjugated, they should no longer be considered as separate interacting elements, but as constituting a single chromophore of large size. Therefore, the presence of microenvironments disrupting energy migration is not to be considered, as the whole by definition adopts a single state. However, by increasing the size of the edifices, and thus by extending the conjugation, the separation of the HOMO-LUMO levels decreases rapidly, which limits the optical activity of these compounds at very long wavelengths (IR). These "ribbons", as well as other so-called fused porphyrin derivatives, are therefore more suitable for electronic conduction than photon conduction [31].

Finally, it should be noted that the iterative strategy is simply a particular type of multi-step synthesis that allows the size of objects to be rapidly increased by "symmetrical" couplings of increasingly long fragments. The problem of poor yields, due to the multiplication of stages, is therefore posed in the same way as before.

As we have seen in all these systems, even for the most rigid ones, geometric control is only carried out over limited distances, since as the size of the buildings increases, the external constraints are more and more important. This "flexibility" of one-dimensional covalent assemblies is found in all large-scale organic systems [32, 33]. A solution to this problem could be to take advantage of secondary interactions, such as those used in natural systems (proteins, RNA, etc.), to obtain very well-defined architectures of large size.

### B. Secondary Structuring of Covalent Buildings

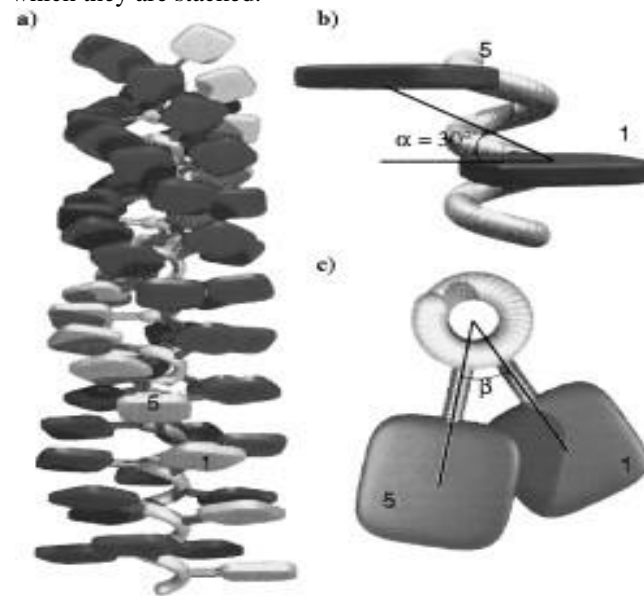
The structuring of molecular systems involves three levels of organization:

(i) the primary structure which corresponds to the direct chain of chemical bonds

covalent and defines the skeleton of the molecule ii) the secondary structure which corresponds to the three-dimensional folding of the primary structure, due to the non-covalent or reversible interactions that may develop between particular elements or motifs of the molecular backbone iii) finally, the tertiary structure which corresponds to the association between the elements

Reorganized.

Thus, by accumulating certain secondary interactions within a judiciously constructed covalent assembly, it should be possible to reinforce, or even force, the mode of organization of the linked elements. An interesting example in this regard is that of polyisocyanides functionalized by porphyrins [34]. In this case, the chromophores are bound to a polymeric core, through amino acid derivatives [9]. The characteristic helical arrangement of polyisocyanide chains is stabilized by the development of intramolecular hydrogen bonds between the opposite amino acids. The porphyrins themselves are forced to adopt a helical arrangement, in which they are stacked.



**Figure 8: Representation of the Arrangement of Porphyrins in a Functionalized Polyisocyanide Chain. The Helicity of the Core Allows the Partial Stacking of Porphyrins Separated from 4 Monomers. The Porphyrin-Porphyrin Distance is 4.2 Å. They are Arranged in 4 Helical Rows, Along the Axis of the Polymer [9]**

in four separate rows (Figure 8). Since the distance between chromophores is 4.2 Å, it is more of an organization to minimize steric discomfort than an aromatic stack. Nevertheless, the helical structure of the core and the stacking of chromophores lead to an extremely well-organized and very rigid multichromophoric ensemble with a persistence length greater than 70 nm. This allows the excitonic coupling to be extended to 25 consecutive porphyrins and ensures a very efficient energy transfer between them. Indeed, the doping of the polymer, with 0.05% zinc porphyrins, leads to the total extinction of the fluorescence of the system.

If in the case of the simple covalent structures, presented above, the smaller species are the most rigid and therefore the best defined, in the case of these particular edifices, the structuring of the porphyrins is only reached beyond the chaining of a certain number of monomers (at least 8) [35].

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Here, the structure is only expressed through the accumulation of weak interactions (hydrogen bonding and steric exclusion) and the collective aspect is the key element of these systems. Nevertheless, based on a classical polymerization of the monomer, the prepared edifices once again show a high polydispersity.

Nevertheless, with a persistence length of more than 70 nm and an excitonic coupling extended to 25 consecutive porphyrins, these edifices are the longest artificial "photonic wires", geometrically well defined, known to date. Nevertheless, their peculiar helical structure makes them more sets of (four) twisted wires than real isolated molecular wires...

### IV. NON-COVALENT BUILDINGS

As we have seen, the covalent approach makes it possible to obtain very interesting systems from the point of view of structure/function control, but often at the expense of synthesis yields. In addition, access to large, single-disperse assemblies (in terms of size and conformity) remains a challenge. Ultimately, the most efficient geometric control results from the reinforcement of the primary structuring of the molecular backbone by so-called secondary or weak interactions, such as aromatic stacking, coordination bonds, hydrogen bonds, electrostatic interactions, hydrophobic interactions, and Van der Waals forces.

Taking these interactions into account as a proper means of organizing matter has been a major revolution in recent decades. Conceptualized in the context of supramolecular chemistry, "the chemistry of interactions beyond the molecule" [36], the use of non-covalent bonds alone to build precise molecular architectures seems very promising. In this case, the "assembly tools" used preserve the integrity of each component of the building. In addition, due to the reversibility of the connections involved, the formed objects remain dynamic. This mode of organization therefore plays on thermodynamic equilibria, with the system evolving towards the most stable assembly under the experimental conditions applied. This could allow molecular edifices prepared in this way to adapt to changes in their environment, or even spontaneously eliminate any structural defects they may have.

By taking advantage of the precise structural control that is accessible for the synthesis of small molecules, and some weak directional interactions (hydrogen bonds and coordination), it is possible to prepare highly specific artificial recognition patterns. The latter should then make it possible to "program" the more complex molecules that would integrate them, to spontaneously form a determined structure in a particular environment. In the long term, the objective would be to prepare relatively simple elements, possessing both their own physicochemical characteristics (a known behaviour in the face of a given stimulation) and structuring information that would guide their precise positioning in a complex and functional building.

This strategy can be applied to the unidirectional organization of chromophores but inevitably leads to more or less polydispersed species. Due to thermodynamic factors, it is difficult to force the monodispersity of equilibrium sets, especially in the case of open objects such as the molecular

threads under consideration. However, the spontaneous selection of suitable objects, during the formation of more complex structures (circuits or molecular components) could make it possible to circumvent the problem. It must be seen that final objects are not necessarily intended to pre-exist in solution, but rather in fixed phases outside equilibrium (solid matrices, surfaces, etc.). The selection of basic constituents can very well be done, or be induced, under heterogeneous conditions. The first step is to prepare systems capable of forming unidirectional multi-porphyrin edifices and then, secondly, to find ways to stabilize them and allow them to be studied in depth.

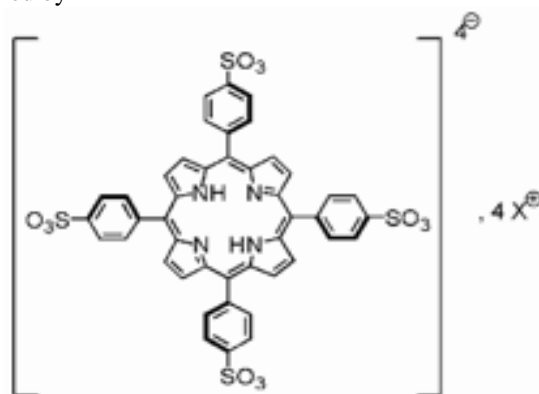
Many examples of non-covalent unidirectional assemblies have been reported so far, but we will limit ourselves to those that retain a molecular character. Concerning coordination or other "polymers", obtained and characterized only in the crystalline state, some reviews offer a fairly complete vision [37-39][50].

#### A. Self-Assembly in Aqueous Media

##### a. Assembly of Ionizable Derivatives

One of the simplest ways to obtain self-assembled multiporphyrinic edifices is to play on the electrostatic and hydrophobic interactions that porphyrins carrying ionizable groups can develop. Thus, the spontaneous organization of cationic and anionic porphyrins has been extensively studied in aqueous solution, in particular the case of 5,10,15,20-tetra(4-sulfonatophenyl) porphyrin (Figure 9).

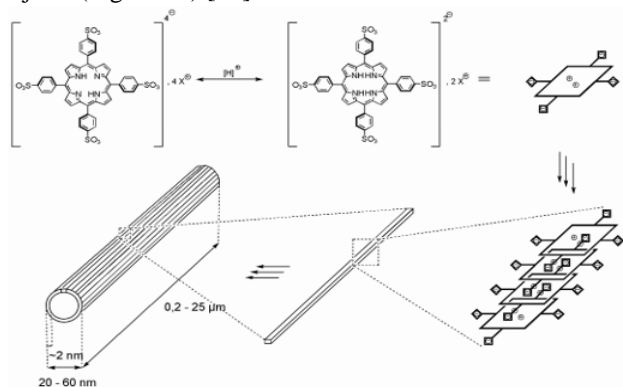
This compound, which is well soluble in water, tends to form rigid linear aggregates, up to several tens of microns, after protonation of the porphyrin core [40]. By playing with the sample preparation temperature, it is possible to promote the appearance of larger or smaller aggregates, thus allowing a certain control over the assemblies. Moreover, it has been shown that these structures are relatively robust and can be obtained by



**Figure 9: 5,10,15,20-tetra(4sulfonatophenyl) Porphyrin**

presence of different counterions and in a wide range of ionic strengths. Finally, the association of these objects into fibres, which can be up to several millimetres long, is possible in high-concentration solutions [41].

Recently, the observation of the polarization of the fluorescence of such fibers, aligned by an intense magnetic field, has made it possible to deduce the molecular structure of the assemblies and to propose a growth pattern of these objects (Figure 10) [42].



**Figure 10: Representation of the Proposed Assemblage Mode for 5, 10, 15, 20-tetra(4-sulfonatophenyl) Porphyrin, in Acidic Aqueous Solution [42]**

It is interesting to note that 5,10,15,20-tetra(4-carboxylphenyl) porphyrin forms very similar structures in an acidic environment. However, in this case, the counterions have a large influence on the geometry of the aggregates, as the nitrites can induce tubule cyclization [43].

The equimolar mixture of a di-protonated tetrasulfonated porphyrin and a cationic tin porphyrin also makes it possible to obtain very homogeneous tubular structures, whose walls are "multi-layered" [44]. Surprisingly, these nano-objects fuse into dense aggregates when exposed to light, but the initial tubular structures re-form as soon as the medium is placed in darkness. This behavior is a remarkable example of the stimulated evolutionary capacity of self-assembling buildings and the principle of "self-repair" that makes dynamical systems fascinating objects.

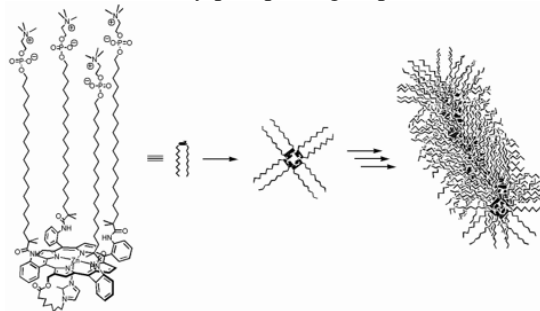
It should also be noted that, in these examples, it is the tube superstructure that makes it possible to obtain extremely rigid and well-defined joints. The subcomponents (shown as linear rods in Figure 10) have never been observed in isolation. Moreover, it is quite unlikely, starting from symmetrical compounds such as 5,10,15,20-tetra(4-sulfonatophenyl) porphyrin, to obtain such rods in solution. It seems more likely that the formation of tubular objects is the result of a phenomenon of collective growth or the folding of porphyrin sheets.

#### b. Micelle Formation

Amphiphilias are molecules that are well known for being able to assemble in a variety of ways in solution. Depending on the ionic strength and concentration of the medium, different structured phases have been observed, ranging from simple globular micelles to complex lamellar phases [45]. Bipolar compounds, amphiphiles generally combine a hydrophilic head with a long, hydrophobic, often flexible part. Their behaviour in solution generally tends to minimise the contact of the hydrophobic part with water, resulting in the formation of well-defined structures. This mode of assembly derives from the overall morphology of the molecules and not from a specific recognition pattern, and can therefore be applied to any derivative with a bipolar appearance. Under certain conditions, a particularly

interesting fibrous structure can appear, the vermicular micelle, which can reach macroscopic dimensions!

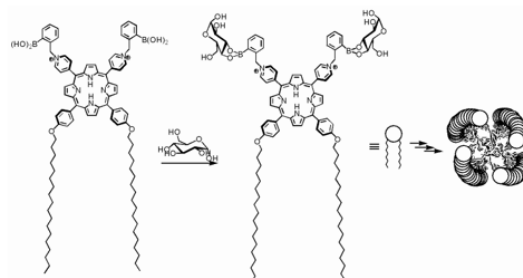
In order to exploit this original mode of association, amphiphilic porphyrins, such as the one shown in Figure 11, have been synthesized [46]. In the example above, one side of the macrocycle is functionalized by four fat chains terminated by phosphate groups.



**Figure 11: Formation of Porphyrin Fibers by Assembly of an Amphiphilic Compound [46]**

In aqueous solution, the optimal arrangement to minimize hydrophobic interactions is the formation of micelles, the core of which has four porphyrins "per section" (Figure 11).

Another derivative for the formation of fibre in the presence of sugars was prepared by Arimori et al. [47]. In this case, the condensation of glucose (or galactose) on the two boronic acids carried by the porphyrin reinforces the amphiphilic character of the compound, which then aggregates in an original way (Figure 12).



**Figure 12: Micelle Formation in the Presence of Sugars [47]**

The micelles are also made up of four molecules per "section", and the porphyrins tend to stack face to face, defining four columns whose helicity is modular by the nature of the sugars present in the medium.

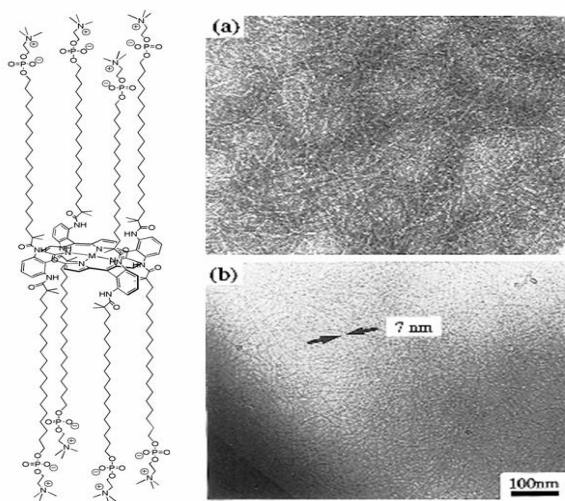
Nevertheless, in these two systems, if the assemblies obtained are indeed unidirectional and if a certain degree of excitonic coupling exists between the chromophores, the structures remain quite complex, associating several filaments of porphyrins in the same fiber.

An interesting compound has been proposed by Fuhrhop et al. to form filaments of single-stranded porphyrins [48]. To do this, eight fat chains were introduced, symmetrically, on either side of the macrocycle (Figure 13).

## The Construction of Multichromophoric Assemblages: A Booming Field

As these chains are themselves terminated by polar groups, the derivatives obtained have a lipophilic core with porphyrin at its center, and a very hydrophilic periphery. Due to this original morphology, the compounds have a strong tendency to aggregate laterally in an aqueous medium, leading to the appearance of fibers several hundred nanometers long. However, within blends, due to a high steric size, porphyrins cannot develop specific structuring interactions with each other (such as aromatic stacking, for example). They therefore orient themselves in a more or less random to each other, while remaining aligned in the axis of the micelle.

In general, micellar assemblages remain very dynamic and are constantly evolving in solution. They don't have a truly fixed structure, but a tendency to assemble into fibers under given conditions, and are therefore difficult to implement "directly". However, they can be used to preorganize chromophores carrying polymerizable groups, in order to obtain large linear covalent assemblages, after polymerization of the micelles [49][52].



**Figure 13: Formation of Single-Stranded Porphyrin Fibres. Observation of Micelles, by Transmission Electron Microscopy [48]**

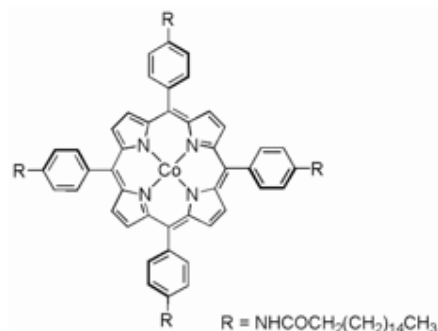
### B. Self-Assembly in an Organic Medium

A limitation encountered in the development of non-covalent systems in aqueous media is often the introduction of solubilizing groups. Indeed, these are generally ionizable or polar (protic or not), and are themselves likely to develop relatively strong non-covalent interactions. Thus, if these groups do not directly carry structuring information as in the case of 5,10,15,20-tetra(4-sulfonatophenyl) porphyrin, they can easily interfere with the patterns initially intended to organize the molecular bricks. In the absence of designing extremely elaborate architectures, such as those found in biological systems, which ultimately isolate the specific recognition patterns in an organic matrix, it remains easier to use general modes of association such as the formation of micelles, to structure small water-soluble compounds. From this point of view, the design of supramolecular assemblies in an organic medium is simpler, as it does not require the introduction of solubilizing groups likely to interfere with the recognition patterns used. In addition, it is very easy to modulate the physicochemical characteristics of organic

media (protic character, polarity, ionic strength, pH,...) to specifically promote one or the other of the interactions. In comparison, in aqueous media, only pH, ionic strength and temperature are easily adjustable. Thus, a greater number of interactions, of different kinds, can be used to organize artificial compounds in an organic environment.

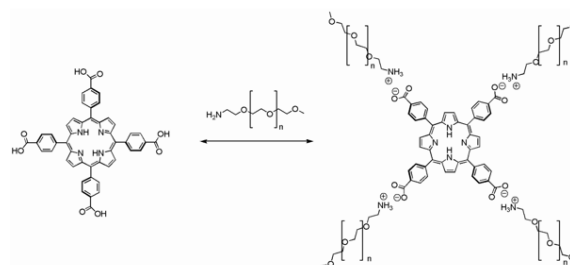
#### a. Aromatic Stacking

The p-stacking of conjugate planar systems has been widely used to organize chromophores unidirectionally [49], mainly in liquid crystals and gels, some of which incorporate porphyrins. Nevertheless, the macroscopic structures obtained in this case are complex and result from the more or less anarchic lateral aggregation of many fibrils with each other.



**Figure 14: Cobalt (II) Porphyrin, 5,10,15,20-tetra(4-Heptadecanamido-Phenyl)**

The introduction of long movable chains on the edge of the porphyrins avoids or limits lateral aggregation, due to the steric discomfort they cause (dispersive forces). Thus, the formation of single-stranded fibers of cobalt(II) 5,10,15,20-tetra(4heptadecanamidephenyl)porphyrins has been studied in an alcoholic environment (Figure 14). By light scattering measurements, the size of the aggregates present in solution was estimated to be 205 nm long, which would correspond to about 800 porphyrins stacked face to face (assuming "rigid" linear assemblies). Similarly, the addition of oligomers of the polyethylene oxide type, carrying an amine function, makes it possible to stabilize isolated columnar aggregates of 5,10,15,20tetra(4-carboxyphenyl)porphyrin in chloroform. In this case, the polymer chains bind to the carboxyls by developing salt bridges, after proton exchange (Figure 15).



**Figure 15: Introduction of Polyethylene Oxide Chains by Electrostatic Bonding**

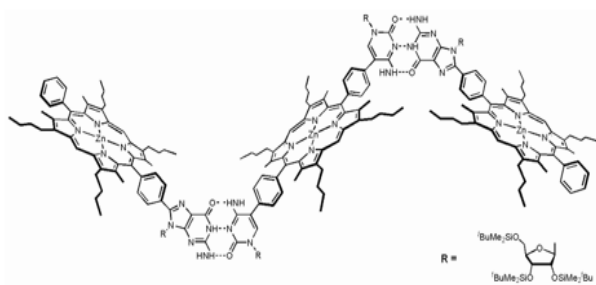




In both systems, a widening of the UV-Visible absorption bands, compared to those of the isolated monomers, was observed. It has been attributed to a slight excitonic coupling that would develop between the porphyrins, and make these structures potentially interesting for photon conduction. It should be noted, however, that these assemblages are very similar to the micelles described above. They are therefore also difficult to implement because they are very dynamic and rather poorly defined in solution. Until now, it has not been possible to observe them directly.

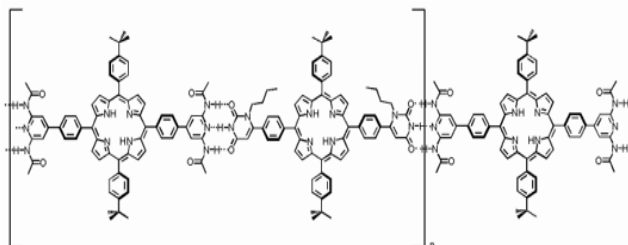
*b. Hydrogen Bonds*

Hydrogen bonds were one of the first assembly tools used to form unidirectional chains of chromophores. Thus, the functionalization of porphyrins by nucleic bases has made it possible to take advantage of the selectivity and the high stability constant of the guanosine-cytosine pairing, to obtain trimeric oligomers (Figure 16).



**Figure 16: Use of Guanosine-Cytosine Pairing**

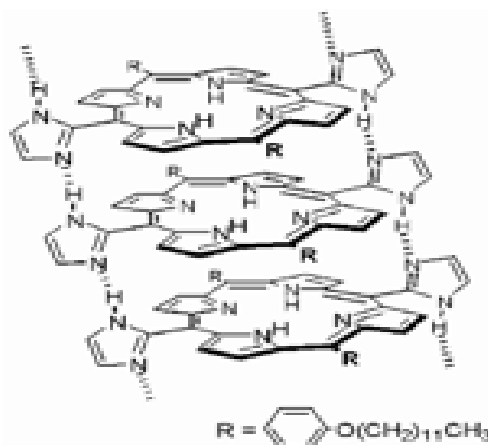
Other systems have been based on the complementarity between uracil and diacetamidopyridine derivatives, to obtain more extensive linear edifices (Figure 17).



**Figure 17: Use of Complementarity between Uracil and Diacetamidopyridines**

In addition, the development of hydrogen bonds between imidazole substituents has also been considered to obtain unidirectional multiporphyrinic assemblies in nonpolar organic solvents (Figure 18). In this example, an energy transfer between the chromophores was demonstrated by the addition of an acceptor in solution (the fluorescence being completely extinguished for a ratio of 2.9 between the concentrations of the monomer and the acceptor). However, the structure of the buildings present in the solution could not be precisely determined.

Many other grounds for recognition have been proposed and implemented to form self-sustaining chains. extensive assemblies of chromophores and are described in some recent reviews.

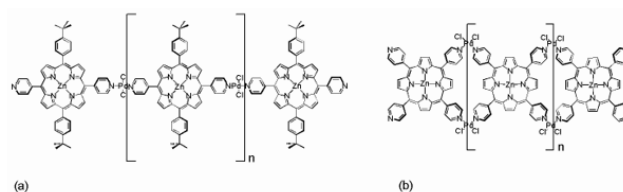


**Figure 18: Use of Imidazoles**

*c. Exocyclic Coordination Links*

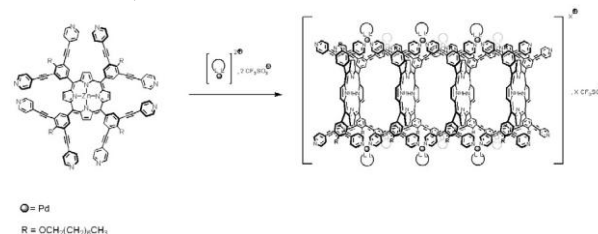
Coordination bonds have also been shown to be an efficient and modular tool to form isolated linear architectures, after the introduction of complexing groups on porphyrin.

For example, a zinc(II) porphyrin disubstituted by pyridines can coordinate with trans-dichloro-palladium(II), to form linear assemblies that retain some conformational freedom (Figure 19a).



**Figure 19: Multiporphyrinic Assemblages Employing Pyridine Coordination on Dichloro-Palladium (II) Centres. (a) Trans-Dichloro-Palladium(II). (b) cis-Dichloro-Palladium(II)**

The use of zinc(II)-tetra(4-pyridyl)-tetra(4-pyridyl)porphyrin as a structuring agent leads to more rigid and flat edifices (Figure 19b). Finally, again based on the use of pyridines and *cis*diphosphonato-palladium(II) complexes, large-pored zinc(II) porphyrin fibers, capable of accepting host diamines, have been obtained.



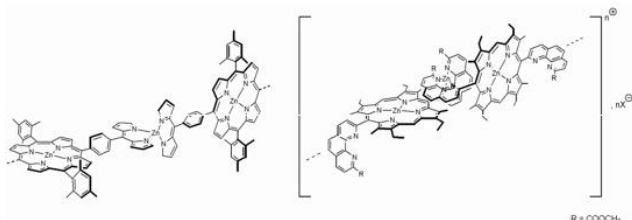
**Figure 20: Formation of zinc (II) Porphyrin Fibers with Large Pores**

In this case, the introduction of a metal center carrying a chiral ligand, such as BINAP, makes it possible to impose helicity on the fibers, taking advantage of cooperative induction.

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The appearance of a chiral center at a point in the edifice forces the orientation of the adjacent centers due to the high rigidity of the monomers and the strong steric discomfort between the substituents of the porphyrins [34]. Thanks to their highly efficient mode of association, these compounds form macroscopic structures that have been characterized by transmission electron microscopy.

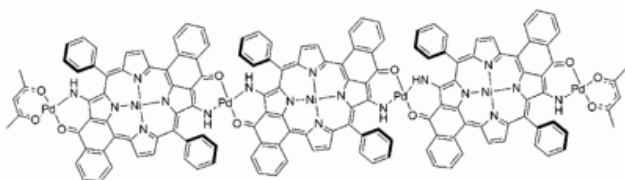
The use of dipyrines [35], or phenanthrolines [36], associating around a zinc(II) center has also been considered to obtain coordinating polymers (Figure 21).



**Figure 21: Use of zinc (II) Bis-Dipyrine and Zinc (II) Bis-Phenanthroline Complexes**

In the case of phenanthroline derivatives, original photophysical studies have shown that treatment with zinc(II) acetate of micromolar solutions of these compounds leads to the formation of oligomers incorporating an average of twelve units. By increasing the initial concentration of non-metallated monomers (millimolar solutions), a solid precipitates rapidly. These are probably larger buildings, but it has not been possible to characterize them precisely.

The functionalization of porphyrins by two enamino-ketone-like groups, at opposite positions, resulted in linear, planar and conjugated coordinating oligomers after treatment with palladium(II) salts (Figure 22) [37].

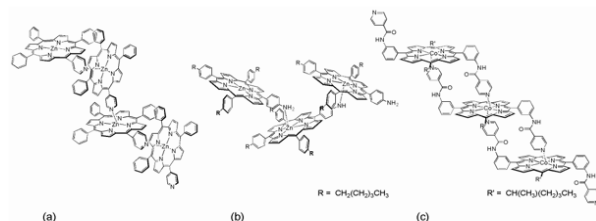


**Figure 22: Use of palladium (II) Bis-Enamino-ketone Complex**

In this example, it was possible to control the number of monomers incorporated into the buildings by the ingenious use of the acetylacetonate ligand to protect the ends of the assemblies. The exchange of this ligand with a simple (more labile) acetate allows the terminal metal centers to be "reactivated", which can then react with new porphyrinic ligands. In this way, it is possible to increase the size of buildings by two units per cycle.

### d. Endocyclic Coordination Links

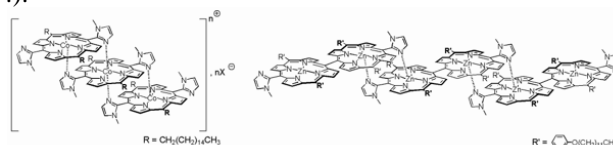
When metal cations with more than four coordination sites (Zn(II), Fe(II/III), Co(II/III), Ga(III)...) are inserted into the porphyrin core, they can be directly used to form intermolecular complexes. Thus, zinc(II) metallation of 5-pyridyl-10,15,20-triphenylporphyrin leads to the formation of solution-detectable coordination polymers (UV-Visible, NMR) [38]. The structure of these edifices was assumed to be close to that observed in the solid state, i.e. formed by unidirectional chains of porphyrins (Figure 23 a).



**Figure 23: Various Polymers Obtained by Endocyclic Metal Coordination. (a) zinc(II), 5,10,15-Triphenyl-Pyridylporphyrin. (b) zinc(II) 5,10,15-tri(4-pentylphenyl)-1-Anilyporphyrin. (c) cobalt(II) Complex of a Porphyrin Carrying Two Phenyl-Amidopyridine Groups**

Similarly, soluble oligomers were obtained by zinc(II) metallation of 1a5,10,15-tri(4-pentylphenyl)-1-anilyporphyrin (Figure 23b) [39], or cobalt(II) metallation of a porphyrin carrying two phenyl-amidopyridine substituents (Figure 23c) [40].

In both examples, the presence of oligomers in solution, the size of which depends on concentration, was demonstrated by <sup>1</sup>H NMR and gel permeation for the cobalt(II) compound. It is interesting to note that the formation of buildings is promoted in a totally different way in the two systems. For the cobalt(II) compound (Figure 23c), the pendant groups were arranged in such a way as to optimize the interaction between the metal and pyridine while minimizing steric repulsions. This results in the formation of very stable complexes and oligomers can reach 100 units in solution. On the contrary, for zinc(II) derivatives (Figure 23b), the position of the amine group in the macrocycle plane does not allow a strong association between two porphyrins that would be perfectly aligned. Indeed, this configuration would result in significant steric repulsions between the monomers. However, if this method of assembly were favourable, it would tend towards the simple dimerisation of porphyrins in a head-to-toe configuration. It is therefore the destabilization of the system due to a particular geometry that favors oligomerization. However, if the buildings obtained in solution are assumed to be unidirectional, no precise characterization could be obtained. The insertion of hexavalent metals (Co(III), Ga(III)) into a bis(imidazolyl)porphyrin or a pentavalent metal (Zn(II)) into a bis(imidazolylporphyrin)-type derivative, has been studied in detail by Kobuke et al. (Figure 24). In these examples, the double coordination of the central metal or the use of a dimeric pattern to assemble the zinc(II) porphyrins, lead to particularly stable edifices (Log K<sub>ass</sub> > 9!).

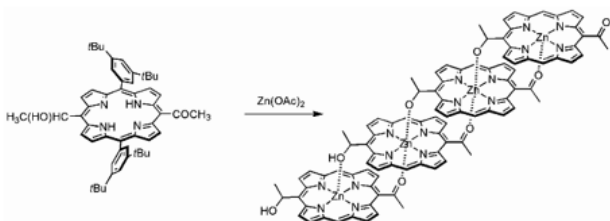


**Figure 24: Use of Imidazole Complexes. (a) Cobalt Bis (Imidazolyl) Porphyrin; (b) Zinc Bis (Imidazolylporphyrin)**

For example, for cobalt(III) compounds (Figure 24a), oligomers of more than 30 units were detected in solution by gel permeation [40]. It should also be noted that the strong excitonic coupling observed between the associated porphyrins is promising for photonic conduction applications. In addition, the use of unmethylated imidazoles has made it possible to form neutral polymers of the same type after the introduction of gallium(III) into the macrocycle [40]. In this case, one of the axial imidazoles is deprotonated before it coordinates with the central metal. Zinc(II)(imidazolylporphyrin) bis(imidazolylporphyrin) edifices, on the other hand, have been used to obtain systems involving up to 400 units (800 porphyrins) in solution (Figure 24b).

Recently, manganese(III) porphyrins, carrying only one imidazole, have been used to functionalize free ends of the latter systems [41]. It is possible to obtain these mixed architectures, without destabilizing the initial zinc(II) edifices, by matching the relative values of the stability constants of the different conceivable assemblies. The association of zinc(II) compounds with each other ( $K_{ass} = 10^{11} M^{-1}$ ) is favoured compared to the formation of a heterogeneous manganese(III)-zinc(II) system ( $K_{ass} = 10^8 M^{-1}$ ), which is itself more stable than the manganese(III) homodimer ( $K_{ass} = 10^3 M^{-1}$ ). The conditions used make it possible to obtain functionalized polymers involving up to 600 units. In these buildings, the probability of energy transfer from any zinc(II) porphyrin to one of the terminal manganese(III) porphyrins was estimated to be greater than 67%. Photonic conduction in these supposedly linear systems is therefore relatively efficient. Nevertheless, the actual geometry adopted by these objects remains difficult to access in the studies conducted so far.

Finally, assemblages close to natural chlorosomes have been obtained from zinc(II) porphyrin derivatives by Balaban et al. [41]. These systems are capable of forming mesoscopic aggregates in a nonpolar environment, and their intense fluorescence in solution reflects a high degree of organization within the assemblies. Thus, the arrangement adopted by the latter was assumed to be identical to that observed in the solid state, i.e. in extended chains of porphyrins, linked together by the double coordination of oxygenated substituents on zinc(II) (Figure 25) [42].



**Figure 25: Use of Zinc (II)-Oxygen Bonds. The 1,3-di (Tertbutyl) Phenyl Substituents Were Omitted for Clarity of the Representation of the Extended Assembly**

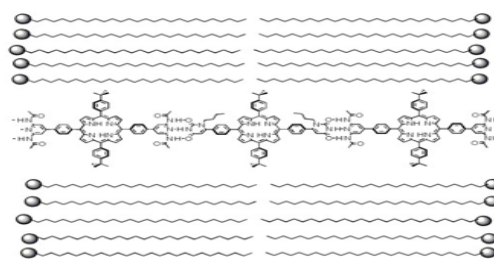
## V. TOWARDS THE CONTROL OF THE POLYMORPHISM OF DYNAMIC SPECIES?

As we have just seen, many derivatives have been proposed to obtain unidirectional self-assembled systems in solution, and for some, the physicochemical and photophysical behaviors observed are encouraging.

However, in most cases, the architecture of the buildings was characterized indirectly and the objects were therefore described by the most likely geometry, i.e. their assumed equilibrium geometry. The lack of exact knowledge of the species present in the environment does not allow an unambiguous interpretation of the results, which therefore remain qualitative. Apart from some very well-defined assemblies due to their tertiary structuring (tubes), and for the shorter buildings, which are also at first glance better defined, the precise control of the morphology of the assemblies remains an open question. It is also possible to question the relevance of such a question for systems which, in equilibrium, are necessarily polymorphic. Nevertheless, their dynamic nature could be used to circumvent the problem, by the application of external constraints capable of partly directing the equilibrium. Over the past five years, a number of strategies have been developed in this direction.

### A. Structuring of Buildings in Confined Environments and in Solutions

The use of external matrices, of precise size, capable of stabilizing or inducing the formation of buildings has been proposed to control their dimension. Thus, the organization of porphyrins in the DNA double helix has been considered and studied in detail [42-45]. While well-defined arrangements of porphyrins have been obtained and exhibit excitonic coupling between chromophores, this hybrid architecture seems difficult to use due to the photo-cutting of DNA induced by porphyrins. Other hybrid systems playing on their organization induced by carbon nanotubes have recently been described [44]. In this work, once again, the precise structure of the assemblies remains difficult to assess precisely. In addition, these compounds appear to be more interesting for photovoltaic applications, due to an efficient capture of the excited state of porphyrins, by electron transfer to carbon nanotubes. An original means proposed to control the size of porphyrin fibers, while isolating them from each other, is to confine them in a lipid bilayer of known thickness (and modular by the size of the surfactants used) [45]. In these systems, which use hydrogen bonds as a means of assembly, the association of porphyrins is clearly favored in the nonpolar space defined by surfactants, whereas hydrogen bonds are destabilized in the vicinity of the polar heads. Thus, although the presence of small oligomers, trapped in the lipid bilayer, cannot be excluded, the maximum size of transverse species is limited (Figure 26).

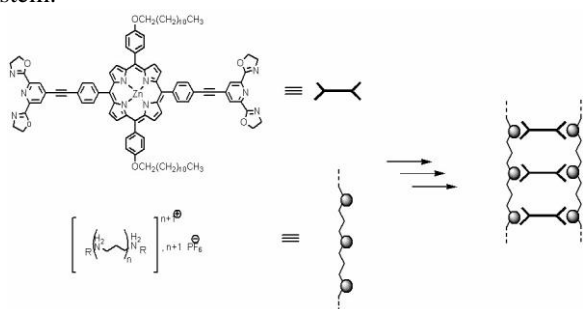


**Figure 26: Use of Lipid Bilayers to Control the Size of Porphyrin Oligomers**

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The generation of a photocurrent between two electrochemical cells separated by a membrane doped in this way seems to show that such molecular "wires" make the junction between the two compartments. However, the actual geometry adopted by the buildings has not been precisely determined, and it cannot be ruled out that large oligomers, oriented parallel to the median plane of the membrane, are trapped in the center of the bilayer.

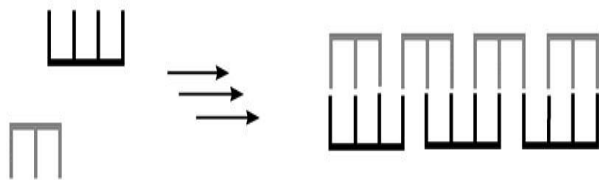
The use of protonated polyamines as a matrix allowed the assembly of porphyrins carrying the 2,6-bis-oxazolopyridine groups, in a scale-like geometry (Figure 27) [46]. In this example, the orientation of the porphyrins is very well defined due to their stacking, and their number is determined by the size of the matrix used. The formation of these structures takes place in a cooperative manner: the interaction of the two polyamine strands with a porphyrin leads to the preorganization of the association site according to which favors the insertion of a new porphyrin into the system.



**Figure 27: Use of a Polyammonium Matrix to Control Porphyrin Assembly**

In addition, the strong electrostatic repulsions between the polyammonium strands prevent lateral aggregation of the buildings in solution. For the time being, this strategy has been applied to the formation of trimeric aggregates, but it should be possible to extend it to larger buildings.

Recently, the so-called "vernier" assembly principles have made it possible to obtain multiporphyrinic buildings of controlled size, in a very elegant way [47]. These assemblies are based on the mixture of two rigid strands with complementary patterns but whose number differs. The system will tend to evolve towards buildings in which all the association sites are used, which will mostly lead to the appearance of a species of very specific size (Figure 28).



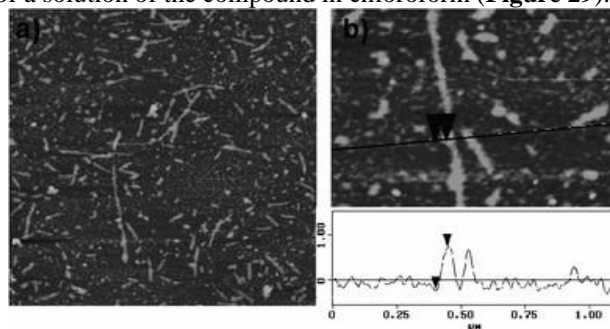
**Figure 28: Diagram of Vernier's Principle. An assembly of Complementary Strands with A Different Number of Complementary Sites**

In their work, the authors modified this principle slightly by using segments with two dihydroxylated tin(IV) porphyrins, and segments with three consecutive zinc(II) porphyrins. Since axial hydroxyl ligands can complex at zinc(II) centers, very stable edifices with three parallel chains of six porphyrins have been obtained.

### B. Structuring of Buildings on Solid Support

Even if a partial control of self-assembled linear architectures seems possible in solution, in the long term, objects developed for molecular photonics should find their application in structures frozen in solid phase. On the other hand, thanks to currently available microscopy techniques, the observation of isolated species on a surface allows their direct study (as in the case of mesocoupled porphyrin oligomers described in reference [28]) and a precise assessment of their physicochemical behaviour. The spontaneous organization of unidirectional organic structures on surfaces is therefore a very important issue and should allow easier control of morphologies. Indeed, by moving to a two-dimensional space (the surface) the degrees of freedom of the molecules are necessarily reduced. Taking advantage of the experience gained in the organization of structures in solution and applying them to liquid-solid interfaces, very interesting edifices were obtained.

In particular, linear assemblages of cobalt(III) bis(imidazolyl)porphyrins several hundred nanometers to one micrometer long have been observed by atomic force microscopy (AFM), on mica carriers, after direct evaporation of a solution of the compound in chloroform (Figure 29).



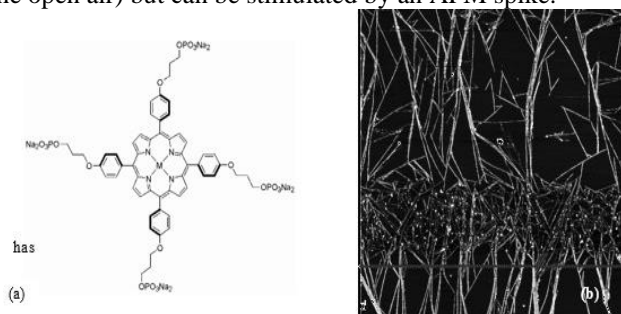
**Figure 29: Assemblages of Cobalt (III) bis(imidazolyl) Porphyrins on Mica. a) AFM image 3 µm x 3 µm. b) Detail (1 µm x 0.8 µm) and Image Profile**

The authors present these images as representative of rigid and linear species initially present in solution. However, caution should be exercised in this interpretation, especially since these dynamic buildings can assemble directly at the interface during solvent evaporation. In any case, this example clearly shows that it is possible to induce the formation of precise structures from tools from supramolecular chemistry, by a surprisingly simple implementation: the evaporation of a solution.

The autonomous assembly of filamentous structures on a gold crystal (111), by sublimation of porphyrins carrying cyano or carboxylic acid groups, has recently been described [48,49]. In these systems, the subtle balance between molecule/molecule and molecule/surface interactions leads to the formation of intermolecular aggregates that are organized according to the reconstruction lines of the gold surface. By playing with the position and number of substituents of porphyrins, various patterns can be generated and the control of these structures seems predictable!

It should be noted, however, that their formation and maintenance require ultra-high vacuum conditions, to avoid restructuring of the surface of the gold crystal in contact with air.

Finally, a tetraphosphate porphyrin, soluble in water, exhibits a particularly interesting behaviour (Figure 30) [49]. After adsorption of a uniform monolayer of this porphyrin onto a mica support, the film is rearranged into totally linear fibers, up to several micrometers long, and whose thinnest cross-section corresponds to the diameter of a single porphyrin. This transition takes place over several days (in the open air) but can be stimulated by an AFM spike.



**Figure 30: Formation of Tetraphosphate Porphyrin Fibres on Mica. (a) Representation of Porphyrin. (b) Fibers Formed on the Substrate after One Week (3  $\mu\text{m}$  x 3  $\mu\text{m}$ )**

This phenomenon has been studied in detail and can be explained in the following way. After the aqueous solution is deposited on the substrate, a monolayer of porphyrins is formed at the air/water interface, with the macrocycles orienting themselves parallel to the surface of the droplet. The rapid absorption of the excess solution (with paper!) allows the film to be deposited directly, without modifying it, on the surface of the mica (the porphyrins are finally laid flat on the support). Weakly stabilized by electrostatic interactions developed between phosphate substituents and cations present on mica, the film is metastable and rearranges itself in such a way as to minimize unfavorable hydrophobic interactions between mica and porphyrins. These straighten and aggregate face to face, forming large fibres. The saline character of the resulting buildings gives them this impressive rigidity and they remain stable for several weeks in the air.

As we have seen, the self-assembly of organic compounds on surfaces can take various paths that are often disconcertingly easy to implement. In particular, the formation of predetermined structures from molecules in solution is very attractive. A gentle method, it tolerates a wide range of compounds and provides access to extremely varied deposition conditions. However, if we hope to be able to combine the richness of the assemblies in solution with the structuring capacities of the surfaces, there is still a long way to go.

It is surprising that so few unidirectional porphyrinic edifices, self-assembled on solid supports, have been described so far. This is all the more surprising in view of the many possibilities envisaged to obtain such systems as a solution. However, as we have also pointed out, the majority of them have been indirectly characterized and described by the geometry they would preferentially adopt at equilibrium. For many of them, it is easy to imagine non-linear, angled or

connected structures that would result from kinetic aggregation. This kind of more or less anarchic association can take place in particular with systems using coordination links, since the latter do not by themselves impose a particular orientation on the ligands. To get around this problem, one possibility would be to multiply the weak interactions between the ligand and substituents preorganized around the porphyrin center, in order to guide the approach of this ligand during its complexation on the metal. Several examples of such "multi-interacting" receptors have been reported, but curiously they have not yet been used in any assembly strategy to obtain better-defined multiporphyrinic edifices.

## VI. CONCLUSION

The construction of multichromophoric assemblages represents a rapidly advancing field in molecular photonics. This article has provided an overview of the strategies and techniques employed in the design and synthesis of these assemblies, with a particular emphasis on covalent buildings. The concept of molecular photonic wires, where chromophores passively guide excitations between functional units, has been introduced and explored.

The study has highlighted the importance of understanding the interactions between chromophores and their role in guiding and manipulating light energy at the molecular level. Various examples of covalent structures, including multiporphyrinic architectures, have been presented, demonstrating precise control over energy transfer and propagation. Additionally, the polymerization of rigid porphyrinic precursors has been discussed as an alternative approach. Nature's photosynthetic systems have provided inspiration for the development of efficient and precise arrangements of pigments, which serve as a guide for capturing and directing light energy. Key pigments such as bacteriochlorine and porphyrin derivatives have been extensively used in multichromophoric assemblies. The article has outlined two main types of strategies employed in the construction of multichromophoric assemblies: covalent and non-covalent buildings. The focus has been on covalent buildings, which offer controlled construction methods through multi-step synthesis. Examples of simple covalent buildings have been provided, showcasing the potential of multiporphyrinic architectures for molecular photonics applications. The controlled arrangement of chromophores and the establishment of energy gradients have been achieved, enabling efficient energy transfer and propagation.

While covalent buildings offer precise control over molecular architectures, their synthesis often involves multiple steps and can lead to lower yields. On the other hand, the polymerization of rigid porphyrinic precursors offers a one-step approach but results in less controlled final architectures. Both approaches have their advantages and are suitable for different applications within the field of molecular photonics.



# The Construction of Multichromophoric Assemblages: A Booming Field

Overall, the construction of multichromophoric assemblies holds great promise for emerging technologies. The precise control over energy transfer and propagation, as well as the understanding of chromophore interactions, offer valuable insights for the development of organic compounds in various fields, including (opto)electronics and photovoltaic cells. Continued research and advancements in this booming field will contribute to the realization of innovative and efficient molecular photonics systems.

## DECLARATION STATEMENT

Funding	No, I did not receive
Conflicts of Interest	No conflicts of interest to the best of our knowledge.
Ethical Approval and Consent to Participate	No, the article does not require ethical approval and consent to participate with evidence.
Availability of Data and Material	Not relevant.
Authors Contributions	I am only the sole author of the article.

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