How self-assembly of amphiphilic molecules can generate complexity in the nanoscale

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HIGHLIGHTS

- Only some selected chemical compounds are capable to lead to useful self-assembled structures.
- Amphiphilic molecules offer a rich scenario of intermolecular interactions giving surprising complex structures.
- The bottom-up design of molecular complex systems is a fascinating challenge for nanotechnology.

GRAPHICAL ABSTRACT
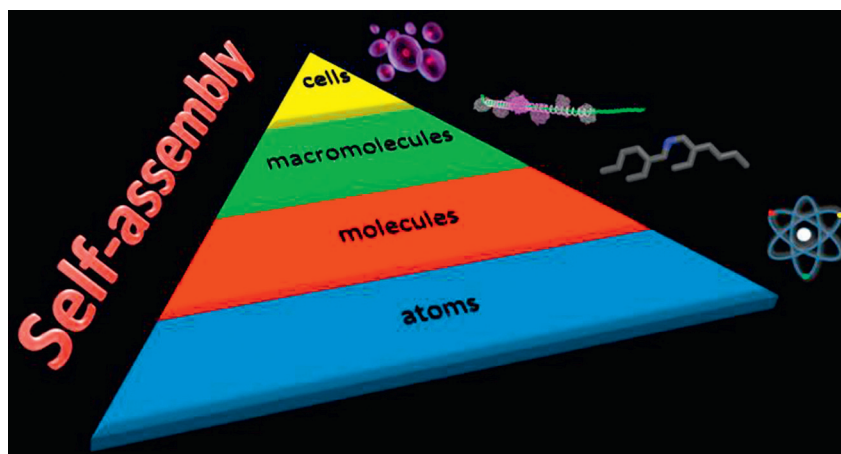
ABSTRACT

Given the importance of nanomaterials and nanostructures in modern technology, in the past decades much effort has been directed to set up efficient bottom up protocols for the piloted self-assembly of molecules. However, molecules are generally disinclined to adopt the desired structural organization because they behave according to their own specific intermolecular interactions. Thus, only some selected classes of chemical compounds are capable to lead to useful self-assembled structures. Amphiphiles, simultaneously possessing polar and apolar moieties within their molecular architecture, can give a wide scenario of possible intermolecular interactions: polar–polar, polar–apolar, apolar–apolar interactions, eventual directional H-bonds, steric hindrance and so on. This peculiarity efficiently triggers the possibility of originating complex behavior, i.e. the formation of interacting structures at hierarchical length-scales characterized by emerging and specific properties and functions. However, if one places in a becher the molecules constituting a living cell, he does not observe the formation of a living cell even after vigorous and prolonged stirring and/or heating. This consideration suggests that the building up of complex structures is not only an affair of molecular structure, system composition and self-assembling processes but additional subtle features can contribute to the overall process. The aim of this contribution is to furnish to the reader a panoramic view of this exciting problematic clarifying what is meant with

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the concept of complexity and how the rich world of amphiphilic molecules are employed for obtaining complex nanostructure-based systems with novel characteristics for applications in nanotechnology. While the literature is full of contributions focusing on specific aspects of self-assembly and complexity, the present work constitutes an easy to read critical point of view which tries to interact with the imagination of readers hopefully leading to the discovery of novel aspects and interconnections and ultimately stimulating new ideas and research.

1. Introduction

While there is plenty of works covering all the specific aspects involved in molecular self-assembly and complexity, in our opinion there is a substantial need for a philosophical and critical easy to read review which would furnish a panoramic view of the problematic. A critically speculative treatment, in fact, would give a sight from the top of all the aspects involved in chemical self-assembly, a view which can be of benefit for the idealization and construction of novel devices with desired properties and functionalities for advanced specific applications. From a general point of view the possibility that simple elements can assemble or be assembled to form complex structures would trigger the emerging of novel properties which cannot be predicted from the characteristics of each single constituent and which can ultimately give rise to *complex* behaviour. In the present work we will try to give an original and easy to read contribution released from weighty technical details, referring the reader to the literature for the details of all the specific aspects which from time to time are faced. We aimed to be suggestive more than comprehensive, tickling more than exhaustive. To do this, we will first introduce the concept of complexity and how it originates. We will emphasize that complexity is often present in natural and artificial structures and it is not exclusively present in chemical systems. We will show how this concept can be beneficial in nanotechnology.

Then, in Section 2, we will focus on chemical systems and we will show some strategies that molecules can adopt to assemble to form complex structures and to give complex behaviour at the nanoscale. In Section 3, we will go deeper into details focusing on amphiphilic systems and showing that "amphiphilicity" is not only a characteristic exclusively possessed by molecules but it is a property that can characterize many other chemical systems and that can occur at various length scales. Micellar systems, mixtures of pure amphiphiles, block copolymers and liquid crystals will be investigated as examples of different self-assembled complex structures at different length scales. Finally, in Section 4, we will show how all these concepts have been recently used to design and construct complex nano-devices with desired properties and functionalities. We will show the parallel, sometimes interacting strategies to form complex devices of use in modern nanotechnology, as well as interesting modern examples. Of course all the examples are not exhaustive but only indicative in order to be exploratory and suggestive: we will try to stimulate the reader's curiosity and we refer to the bibliography for eventual in-depth analysis.

1.1. Complexity: what is it?

Complexity is something we are currently, sometimes unconsciously, involved in. It deals with the organization of units to form bigger entities which are ultimately constituted by the opportune arrangement of those sub-units. Even at a first glance we understand that the principle of organizing smaller sub-units to form a more complex assemble, or alternatively, to look at a complex entity as a combination of simpler sub-units, is at the basis of every kind of disciplines: from chemistry to computer programming to sociology. Just to introduce the topic by an example, elementary particles are somehow assembled to form atoms, atoms are assembled to form molecules, molecules can be assembled to form living cell, opportunely organized living cells can constitute tissues, and insisting with such a kind of reasoning we can consecutively consider organs, human beings, society ...in an escalation which can have a big number of levels. This is shown in Fig. 1 (left panel) where the structure of a living cell is schematically represented as an organized structure of sub-building blocks.

From this example it can be envisioned that what we call "constituent" can be a building block to be assembled to form a bigger and more complex object; on the other side, the same "constituent" is in turn the rearrangement of smaller sub-units. In this framework, complexity is based on a hierarchical relationship between constituents and objects. So, the "constituents" refer to a specific "level", but when they are assembled to form a "bigger" object, a successive level is reached. These are what are called levels of complexity; for this reason it can be misleading to deal with "bigger" or "smaller" systems, because it is not a matter of size: it is correct to deal with different levels of complexity. In the aforementioned example, each level of complexity is the topic of a specific discipline: elementary particles are fertile field of investigation in physics, molecules are studied by chemistry, cells by biology and so on, landing to medicine and sociology. In fact each level of complexity is characterized by specific characteristics and therefore a specific approach is needed for its investigation. With reference to the above cited example of a cell and reported in Fig. 1, the pertinent disciplines are shown in the right panel. The peculiar features possessed by the elements belonging to each level of complexity are the consequence of novel emerging and unexpected properties that can arise when passing from a level to the successive. Let's try to shed light on the origin of this phenomenon.

If a system was the bare collection of independent and non-interacting constituents, it would be just a "simple" assembly of its constituents. Most of its characteristics would be foreseen starting from the characteristics of its constituents. A pile of potatoes can hardly be used in a different way than the potato itself. The same holds for a pile of sand or whatever. There may be some argument about the validity of these examples, since concepts like "critical mass" needed for triggering nuclear reactions or for forming a super-nova, for example, should also be taken into account. However let us introduce the problematic from a general prospect firsts, referring to more specialized works when specific systems or examples are faced. If the constituents are interacting, instead, the complex system is not any more the mere collection of its building blocks and the overall properties cannot be obtained by simple extrapolation of the characteristics of their constituents. Interestingly, novel and unexpected emerging properties can arise when passing from a level to the successive. This happens at every length-scale:

1. In the nano-world: opportunely assembled supra-molecular structures, proteins and DNA can form living cells;
2. In the man-size world: in some school of fish each single fish is a prey, but if all the fishes arrange to form a dense assembly
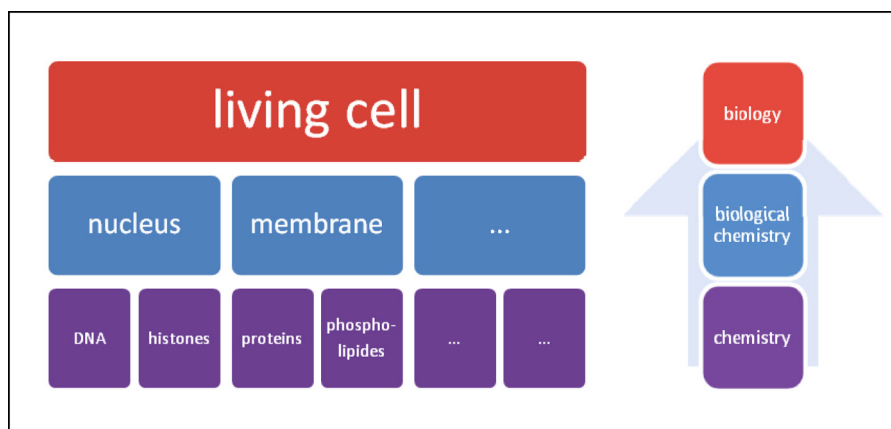
Fig. 1. Increasing levels of complexity generate systems with emerging properties and novel functionalities. In the case of a cell, it is constituted by supra-molecular aggregates, which, in turn, are constituted by molecules/polymers. In the right panel are reported the specific disciplines studying the pertinent levels.

they can look like a single big predator, in a well-known natural strategy used for self-defense;

3. In the astral scale: planets are grouped to form a solar systems, solar systems to form galaxies and star clusters and so on.

What lies at the origin of such a behavior? The following paragraph will focus on this.

1.2. The origin of complexity

At the origin of complex behaviour holds the possibility of establishing interactions between the "constituents". The term "interaction" is necessarily used in the most general sense, and can include, in principle, every kind of dealing: not only physical interactions like electric or magnetic or gravitational, but also every mean allowing exchange of information. If the physical/chemical or gravitational interactions are clear in the aforementioned examples, there are some examples of extensive correlation like the formation of a wave in a stadium or the (sometimes detectable) synchronization of the clappings of hands in an applause, which are far from being understood. Some women can guarantee that in confined working ambient with other women, a synchronization of their menstrual cycle takes place. All this well shows the "complexity" of the problematic and the fact that much is still needed to comprehensively rationalize all the aspects involved.

Coming back to what is known, it is clear that interactions or same sort of information exchange between the constituents are necessary. This does not mean that they are sufficient. Some interactions can occur but they may not be suitable for generating complex behaviour. At least for a specific property.

This concept is schematically depicted in Fig. 2 which in few words shows that a mere blending of all the building blocks are not sufficient if they do not interact, because their mutual interactions permit their spontaneous organized self-assembly.

In a school of fish of course steric interactions are presents but this is not the cause of their disposition to look like a big predator, whereas it is clear that a wide scenario of possible interactions are concurrently needed to assemble molecules and supra-molecular aggregates to form a living cell. On the other hand, what is certain is that even the most trivial interaction, like the excluded volume interactions between different molecules in a liquid, can give origin to emerging properties: the apparent negative excess volume observed when two liquids are mixed can be, even at a zero-order approximation, be interpreted in terms of excluded volumes of differently-sized molecules [1]. When two liquids are mixed, in fact, the smaller molecules tend to occupy the interstitial holes generated by the bigger ones, giving rise to a negative mixing volume. It

is usually accepted that an ideal behaviour in mixing two liquids is obtained when they share the same interactions, both in type and entity. So this example lets us to conclude that even excluded volume effects, coming from the simple hard sphere model, can be dealt with effective interactions in the same way as more complex interactions.

In a mathematical language we can describe a simple behaviour when an overall system property (P_l, where the subscript refers to the level of complexity labelled "l") is the mere sum of the properties of all its i constituents obviously lying at a lower (l-1) level of complexity. (See Eq. (1)) To this category lies the mass (simply additive) or other extensive properties. Instead, a complex behaviour is observed when, in addition to the sum of the properties of all the constituents, there is a further contribution which specifically depends on the presence of (in principle) all the building blocks. Excess volume or any other excess property is explicitly defined in these terms. This further contribution, shown in Eq. (2), originates just because of the simultaneous presence of the constituents. With the term "simultaneous" we refer to the fact that the constituents must somehow be aware of their concurrent presence, which is the same as to say that they are interacting.

$$\text{simple system:} \quad P_l = \sum_i P_{l-1}(i) \tag{1}$$

$$\text{complex system:} \quad P_l = \sum_i P_{l-1} + f[1, 2, 3, \ldots n] \tag{2}$$

Having introduced the topic, in the present study we will focus on the complex behavior at a molecular scale which ultimately results in self-assembly phenomena in chemical systems. In the next paragraph we will first give the scientific justification of this interest with special reference to applications in modern technology.

1.3. Why is complexity useful? Complexity for nanotechnology

Recently, the trend in technology has been typically to obtain materials with new properties by the reduction of the dimensionality of already known materials. The use of nanoparticles, nanowires, nanoplates and nano-objects gave thus origin to a novel development of technology, the so-called nanotechnology, which is becoming pivotal for progress in society.

The use of nano-objects has in fact a double role:

1. On the one hand the use of nano-sized materials permits to access truly novel materials. In fact finely divided matter can exhibit size-dependent properties that are different from those of the same material in the bulk state: the simple reduction in size of a well-known material down to the nano-scale originates
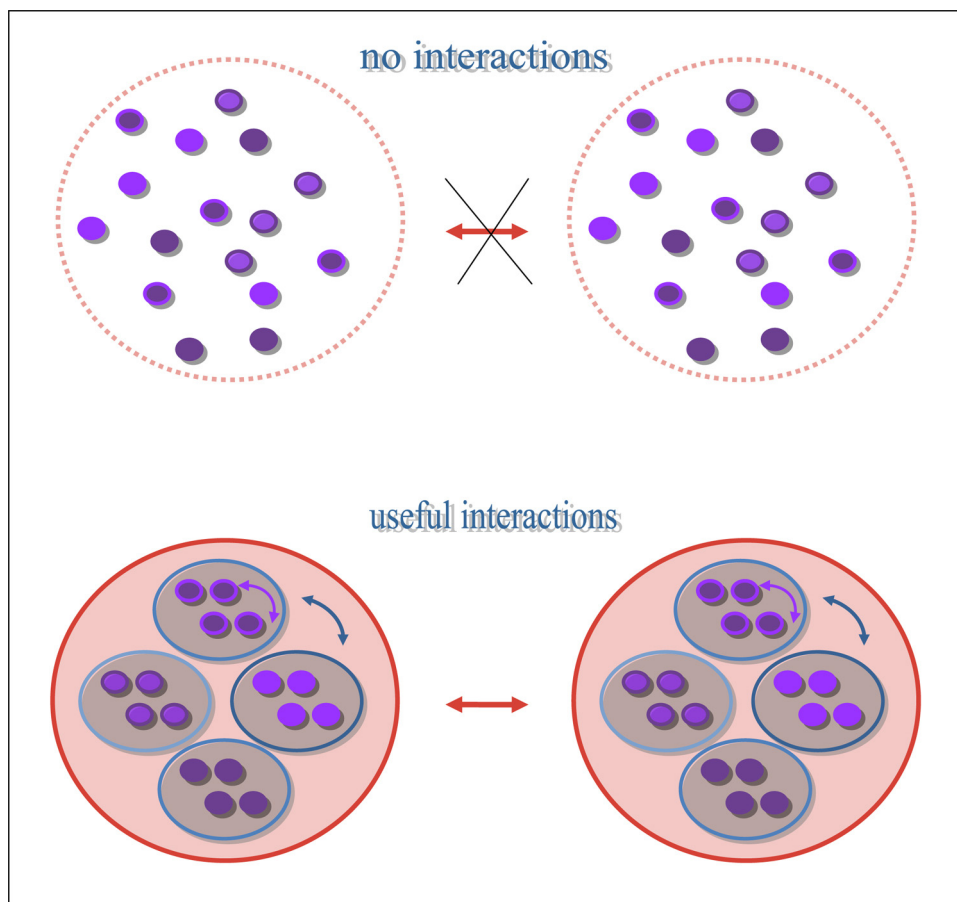
Fig. 2. If a system was the bare collection of independent and non-interacting constituents (upper panel), it would be just a "simple" assembly of its constituents, with no structure. On the other hand, interactions among all the sub-building blocks (lower panel) allows the formation of structures and their organization to form other entities at higher levels of complexity. Interactions open the door to complexity.

itself new effects giving the sample novel characteristics. This is primarily due to quantum size effects, giant surface-to volume ratio and peculiar properties of surface atoms;

2. On the other hand, the use of nano-objects is, by definition, the optimal answer to the ever increasing need in miniaturization.

These two roles have made the use of nanostructured materials a winning approach in most aspects of modern technology, supporting the two older and well established strategies: (i) the synthesis of new molecules (synthetic chemistry, giving new molecules) and (ii) the blending of already known materials (composites). Interesting comments in this regards can be found in Ref. [2]. In that work it has been discussed about the fact that the most efficient strategies imply a hybrid mix of the three exploiting all their advantages. In this ambit, an example is given by the recent attention in nanocomposites, systems which are heterogeneous at the nanoscale and where nanoparticles are mixed with some selected or novel materials. Even more, the realization of nanocomposites chemically far from equilibrium looks a powerful tool to enlarge the potentialities in the preparation of materials and highly miniaturized devices with specific functionalities. Actually this ideal approach is the one used by nature: it is enough to look at biological systems where a wide range of molecules spontaneously self-assemble in concert with others which are synthesized, blended, and assembled by preexisting living nanostructures to form novel living nanostructures and complex supra-nanostructures. This is, in few word, exploiting complexity in the nanoworld. It is worth of note that in case of living structures, the role of a preexisting living entity to drive the process is fundamental: never it has been observed the formation of a living nanostructure through the spontaneous self-assembling of biomolecules.

The construction of a modern complex system can be thought as the result of two somehow inter-penetrating processes: the construction of suitable materials or novel ones with emerging properties, and the building up of their assemblies showing higher level of complexity. Obviously these processes can be repeated in several steps in order to have higher and higher levels of complexity.

The aim of the present work is to focus on the generation of complexity at the nano-scale i.e. the spontaneous self-assembly of molecules as well as the molecular assembly directed by a mold-system pointing out that the self-assembly by amphiphilic species is not necessarily a property exclusive of molecules and therefore it can take place at various length scales.

Given the importance in living structures and in modern applications the emphasis will be given to a very interesting and fascinating class of molecules, amphiphiles, i.e. those possessing the simultaneous presence of polar and apolar parts within their molecular architecture. This field, in fact, offers in our opinion the best example of how complex behavior is generated at the molecular level and how novel materials with interesting properties can be prepared and exploited. Moreover, we will refer specifically to applications in modern technology giving, in this way, the scientific justification of this interest.

In the next section, we will start by trying to understand the basic factors responsible for the triggering of molecular self-

assembly to constitute entities with emerging properties and functionalities.

2. From single molecules to assemblies: some strategies the molecules use to self-assemble

The advantage of the small molecules is in their inherent individuality. This is missing, for example, in the case of more extended molecular structures like polymers that are always represented by mixtures of components with different molecular weights. In fact preparation of particularly purified polymers is a complicated task: traditional methods such as chromatography on silica, distillation, or gradient sublimation cannot be applied. This is a reason why quality of extended molecular structures is difficult to control and there is often some batch to batch variation in their physical and electronic properties. On the other hand, small molecules can be extensively purified and they have fully reproducible physical and electronic properties. This is major reason why the latest research is largely focused on small molecules.

The morphology control in the case of small molecular system is a bottleneck issue. This makes a challenge for supramolecular chemists to design well ordered self-assembling small molecular donor/acceptor composites performing efficiently in devices. Interactions between the building blocks are the link between molecules and their assemblies. Here follows some comments on the strategies adopted by molecules to self-assemble, giving particular emphasis on the interactions responsible for this. This is an important point, since a deep understanding of these principles allows the piloted preparation of novel materials with emerging properties and specific functionalities.

2.1. triggering molecular self-assembly I: soft interactions

In general, supra-molecular assemblies are multi-body systems whose integrity is kept by non covalent bonds. The non-covalent interactions may be H-bonds, van der Waals interactions, π–π ones, electrostatic effects and so on. A more detailed description of the entities of such interactions is reported in Ref. [3]. All these interactions are much less intense than the covalent bond, so the consequent supra-molecular assemblies are less stable and are much more susceptible to ruptures and/or changes at small variations of the physical parameter (temperature…) or chemical conditions (pH…).

Usually the association among the various parts of the supra-molecular aggregate is based on the interaction between two sites: generally one of them is named "donor" and the other, consequently, is called "acceptor". In this framework, the complementariness between donor and acceptor is an important requisite for association and efficiently responds to the requirements that the interactions must be effective in order to allow complexity generation. This peculiarity determines the high selectively in the formation of supra-molecular systems. In bio-chemistry this is known as the lock-and-key principle first postulated by Emil Fischer in 1894. Of course this model needs to be interpreted, in modern times, in terms of specific interactions between parts which are obviously dependent on physical and chemical conditions. Moreover, rather than imagining a binary result (interaction occurs, interaction does not occur) it is better to start thinking of a continuum of possible intermediate situations. Last, dealing with chemical entities, which can be of a certain "complexity" a wide conformational space can be explored by each molecule: some conformers can interact, others may not and the equilibrium between all the conformers as well as their dynamical features are obviously temperature-dependent.

We like therefore to think of self-assembly as in terms of statistical averages in space and in time within the whole sample. For example, micelles, which are usually dealt with closed structures with specific characteristics (size, shape) are in reality evanescent and living for milliseconds [4]. This aspect is very important since, just to quote a mere example, its comprehension allowed the exploitation, among the innumerable methods of synthesis of nanoparticles (see the huge literature available), of surfactant-based techniques to soft-coat nanostructures [5–6], to prepare ionic clusters with novel characteristics [7], to prepare composite nanoparticles [8] and metal-semiconductors nanocomposites with interesting optical properties [9].

Even effects like crystallizations in polymers can be interpreted as related to conformational dynamics [10].

Generally speaking, since the interactions involved are usually soft the resulting structures give rise to the so-called soft-matter, which, of course, is a very general term including polymeric materials, membranes, quaternary structures of proteins, colloids, foams, detergents [11–12].

Since the interactions are weak, they are all comparable to the $K_B T$ factor at room temperature, so very interesting effects can be envisaged by changes in temperature. However the driving force is usually thermodynamic and lies on the enthalpic term which drives a self-assembly process which is in general entropically unfavorable. This can drive the system to the equilibrium which is always to be intended as a dynamic equilibrium.

Given this dynamic aspect, self-assembly of molecules can give rise at short time-scales to assemblies different from those desired, but the soft interactions permit their quick disassemble to restore the original building blocks which become then ready again for successive reversible reactions. Now one of these reactions can give the final desired assemble. In this continuous breaking and reforming process the overall structure must then be considered only just the mere time- and space- averaged structure.

This reversibility is one key-characteristic of supra-molecular synthesis in soft matter which contrasts the conventional molecular synthesis of novel materials which involves the formation of covalent bonds.

The mechanism is schematically depicted in Fig. 3a.

In this ambit, an interesting aspect is offered by the behavior of liquid surfactants: the pure amphiphile possesses structure and dynamics typical of structured liquids and glass formings. In this framework, the opportune mixture of different liquid surfactants can trigger therefore the arising of striking emerging properties which can be used for specific technological applications [13].

Just as an example, under anhydrous condition, self-assembled acid–base composites formed by the acidic surfactant monodo-decyl phosphate and the basic surfactant 2-undecylimidazole molecules have showed a high proton conductivity of about 10^{-3} S cm^{-1} at 150 °C. This has been explained in terms of two-dimensional proton-conducting pathways within the polar domains of highly ordered lamellar structures [14] and this effect has been obtained even at room temperature in Bis(2-ethylhexyl) phosphoric acid/bis(2-ethylhexyl) amine [15] and Octanoic acid/Bis(2-ethylhexyl) amine mixtures [16].

The liquid crystal-like structure in mixtures of pure amphiphiles can give peculiar structural properties which give exotic behaviour, especially due to the interplay between local molecular rearrangement and partially/selectively arrested dynamics, like 1-D molecular diffusion, anti-Arrhenian behaviour of conductivity etc. [17–18].

All these are examples of how soft interactions can tune self-assembly (and therefore the dynamical properties and functions of the material) in concert with temperature due to the reversible
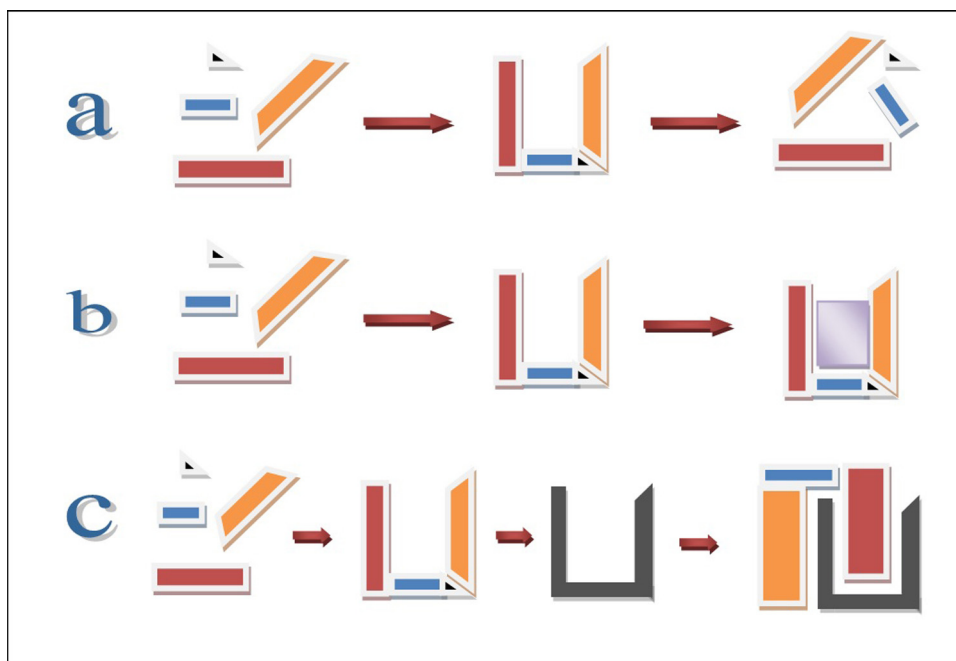
Fig. 3. Different mechanisms for complexity generation. (a) the building blocks are assembled through soft interactions. The structure formation is reversible and usually temperature-dependent. The assemblies show emerging properties with respect to those possessed by their constituents. (b) the building blocks are assembled in such a way to template or to drive the formation of successive structures. See for example nanoparticle synthesis through the use of microemulsions. (c) the building blocks are assembled through strong interactions. Such structures are less sensitive to temperature changes and may be needed for the preparation of building blocks for the formation of complex structures of successive level of complexity.

character of the interactions involved. However, such self-assembly can also be used for the nanoparticle and nanostructures synthesis, because they act as templating agents driving nanostructure synthesis, as it will be better highlighted in the following paragraph.

2.2. triggering molecular self-assembly II: soft interactions as templates for strong interactions

As a consequence of the natural tendency to adopt particular structures, amphiphiles can be used for preparing templates to actively host nanoparticles. In this way, nanoparticles more or less affected by the surroundings are spatially disposed according to the structure imposed by the chemical system hosting them. The principle is reported in Fig. 3b as compared to panel a. For instance, ternary water/surfactant/oil systems can possess different local structures according to the relative amount of the three substances such as lamellar, globular, cylindrical, bicontinuous and so on. See Fig. 4 for a schematic description of the possible structures.

Generally, the amount of amphiphilic molecules influences the morphology of the self-assembled structures. While at very low concentration the molecules will be dispersed randomly without any ordering, due to the entropic driving force, at the higher amphiphile concentrations the self-assembled nano-structures can order themselves, since the enthalpic driving force overcomes the negative entropic one.

For the appearance of liquid crystal phases the major prerequisite is anisotropy. In the case of amphiphiles, the anisotropy is assured by the different solubility properties of the different ends of the amphiphiles together with a subtle balance of intermolecular interactions and steric interactions [19–21]

At higher concentrations hexagonal phases and lamellar phases are encountered and at extremely high concentrations of amphiphile reversed (or inverted) liquid crystal phases are often observed. Generally, more complex phase behavior are observed in nonionic amphiphiles [22] and the appearance of a cloud point can

occur due to the interplay with collective phenomena involving a large number of macromolecules [20,23,24] together with temperature effects that cannot be neglected. So, such systems can be used as templates in the nanoparticle synthesis and are involved simultaneously in their spatial arrangement. Nanoparticles are generally formed in the aqueous regions of the system and they are subjected to remain localised there as a consequence of the spatial confinement imposed by the surfactant. Diffusion of the nanoparticle out of aqueous regions would require a very high energy contribution and is enthalpically disadvantageous and does not occur.

This has allowed the control of the size, shape and spatial distribution of a wide number of inorganic nanoparticles. Interestingly, the mutual interactions among nanoparticles could allow the emergence of novel features which are absent in the isolated ones [25].

Interestingly, the opportune treatment of microemulsion-based systems has also allowed the preparation of salt-soluble substances, both organic [26–27] and inorganic [7]. This technique has proved to be successful in governing nanoparticle size and shape and in arranging nanoparticles in defined 2D and 3D arrangements. Moreover it is also worth noting that such methods, in high surfactant concentration conditions, are able to control the crystal morphology, probably due to specific surfactant adsorption on crystal faces as already seen in crystals of organic compounds [28].

It is important to point out that very interesting situations can be explored when the amphiphile concentration increases to such an extent to become the most abundant species in the system. In this situation the amphiphilic molecules arrange themselves to maximize their polar–polar and apolar–apolar interactions while minimizing the steric hindrance. The low-content of solvent makes the structure more rigid with a partially arrested dynamics. The amphiphile forms strong templating hosting structures and the remaining solvent molecules are confined in their region with same polarity [29–30].
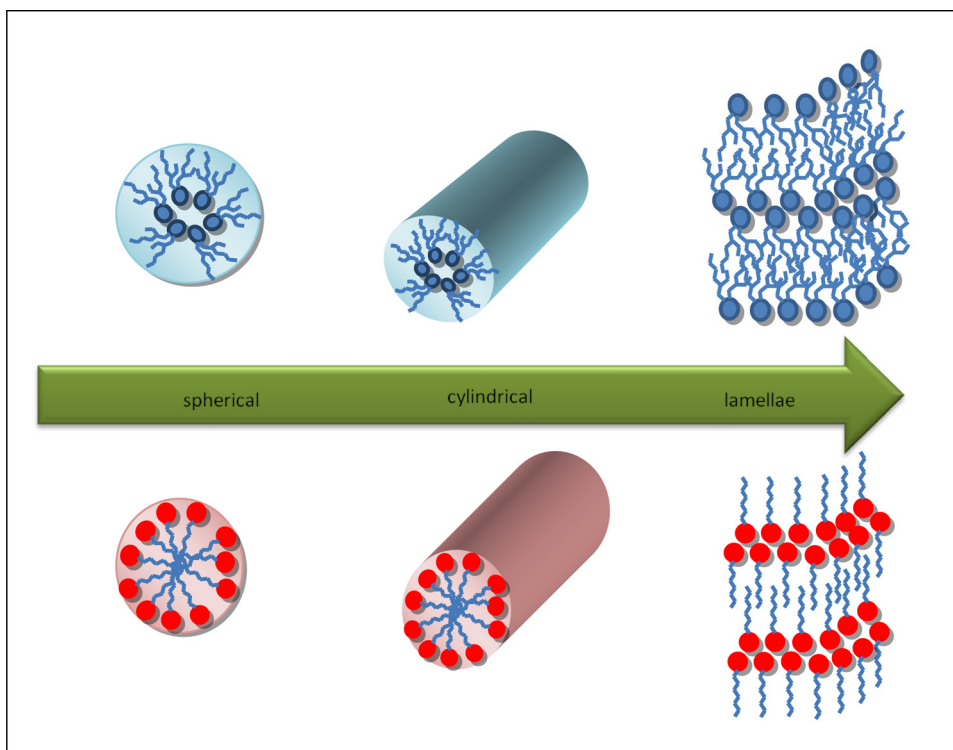
Fig. 4. The aggregation of amphiphiles can give supra-structures with various dimentionalities: 0D (micelles) 1D (cylinders or cylindrical micelles), 2D (lamelles). These structures can be reversed (upper panel) or direct (lower panel) depending on the polarity of the solvent. In apolar solvent reversed structures are formed, in polar solvent direct structures are the stable ones.

Bringing to extreme the amphiphile concentration, we can consider pure amphiphiles. We must say that they have not generally taken much into account since many of them are ionic amphiphiles (anionic and cationic surfactants) and therefore they are solid. So, rather being studied in the pure state, they are generally dissolved in opportune solvents. Instead, the case of non-ionic liquid amphiphiles can give interesting examples. In this case, the amphiphile, in the pure state is liquid and therefore possess structure and dynamics typical of structured liquids and glass formings. The presence of polar and apolar regions in such systems, together with the liquid nature of the medium, has proven to be effective for the synthesis of nanoparticles [31].

2.3. triggering molecular self-assembly III: strong interactions

Sometimes the self-assembly can also involve strong interactions. This kind of interaction is of course different from the aforementioned interactions, since they would lead to irreversible, long-lasting structures. This is not a drawback, because in a complex structure with specific and peculiar properties and functions, also "rigid" parts may be needed: parts which are more insensitive to changes in temperature and/or external stimuli and which can be of help in the piloted synthesis and hosting of a complex object. See Fig. 3c and the schematic comparison with the aforementioned strategies shown in panels a and b.

Generally such a kind of self-assembly can be induced by means of suitable compounds that are able to strongly bind nanoparticle or a solid substrate. In this case the surfactant polar head must possess a binding functional group as thiol. Following this strategy one can imagine linear molecules with such a kind of functional group at the two extremes: in this case both extremes can bind nanoparticles and the molecule truly acts as linker. Owing to the nanoparticle-molecule-nanoparticle bond, a given nanoparticle is forced to stay assembled with other nanoparticles at a certain dis-

tance and geometries dictated by these molecular linkers. Some compounds that have recently been used for this purpose are 4-aminobenzenthiol, alkanethiol, DNA. As a rule of thumb thiols link noble metals like Au and Ag but also Cu, Hg, GaAs and InP, whereas carboxylic acids can be useful for several oxides like silver oxide, titanium oxide and indium tin oxides (ITO). It is interesting to note that even if the binding is not irreversible, novel interesting properties can however emerge: as an example TiO_2/octanoic acid have shown interesting electro-rheological effect (i.e. an increase in apparent viscosity induced by an electric field) even at very low fields like hundreds of V/mm thanks to the soft adsorption of the carboxylic acid onto the nanoparticle surface [32]. In this case, in fact, it is not important to have strong solvent-particle interactions, but rather the existence of a variety of dynamical processes able to assure a certain amount of solvent interacting with the particles even at different regimes of shear rates.

Films with desired thickness have also been prepared using alkanethiol as molecular linkers, and spherical nanoparticle aggregates have been synthesised using aminobenzenthiol and DNA [33–34].

Incidentally, DNA is going to play a peculiar role: the potential of combining nucleotide specificity in binding one another and their capability to bind solid nanoparticles as well as their peculiar electron transport properties, is of course generating much interest.

An interesting use of this strategy has been shown by Boal et al. [35], who developed a "bricks and mortar" strategy to prepare spherical aggregates of nanoparticles achieving also a fine aggregate size control. This strategy is based on the use of nanoparticles functionalised with polymers bearing complementary recognition elements. Nanoparticles are then attached with polymers bearing particular functionalised groups at the ends; in this way the interactions, mostly H-bond (but also π–π interactions) between the various free functionalised ends of the polymeric chains attached to the various nanoparticles dictate nanoparticle disposition in the aggregate.

Another interesting example of self-assembly was offered by the work of Bizdoaca et al. [36] on the rearrangement of magnetic nanoparticles induced by a magnetic field. They observed that in absence of magnetic field the particles are randomly distributed and the system has not net magnetic dipole moment. When a magnetic field is applied, the magnetic moments of the particles align and eventually tend to overcame the Brownian thermal motion so that the systems shows ordering. It has been assumed that the ordering process starts as a small number of particles are aligned so that they originate a local inhomogeneous magnetic field that tends to align other particles thus forming a one-dimensional chain. The length of such chains and the distance between one chain and another are dictated by the particle concentration and the strength of the magnetic field.

3. Amphiphilic systems

In this section we will go deeper into details focusing on amphiphilic systems. It is important to point out that "amphiphilicity" is a characteristic not exclusively possessed by molecules. We would like to go beyond the idea that an "amphiphile" can be dealt with only as a molecule. We want to show that the self-assembly, driven by chemical amphiphilicity, can take place at different length scales and with various modalities. We will investigate micellar systems, mixtures of pure amphiphiles, block copolymers and liquid crystals just as mere examples of different self-assembled complex structures at different length scales and occurring with various modalities.

Far from being a complete review of all the methods, for which we refer to the bibliography and to specialized literature, for the following we will just present and comment the most common amphiphile-based materials to give an idea about the philosophy beneath their preparation giving the first hint to the strategy adopted for their manipulation at the nanoscale.

3.1. amphiphile-based systems I: surfactants in solution

In surfactants the simultaneous presence of hydrophilic and hydrophobic moieties within the molecular structures drives the formation of nano-segregated polar and apolar domains giving different mesophases. These materials therefore have very interesting physico-chemical properties, thus constituting an interesting class of materials as a direct consequence of the peculiar amphiphilic properties of the molecules involved. Such systems are characterized by locally ordered structures that exist for a system-dependent time scale; at the same time, they are characterized by a molecular diffusion taking place on a longer time scale.

The properties of these ordered structures can be characterized in terms of their mean size, lifetime, and dynamics and are important because they control the macroscopic physicochemical properties and are at the basis of specialized biological and technological applications.

As an example, the well-known aggregates of amphiphilic molecules called "micelles" experience a wide variety of dynamical processes, each one with a characteristic time-scale. Due to the simultaneous presence of all these dynamical processes, and in particular the breaking and reforming of such aggregates occurring in the milliseconds timescale, such structures are evanescent and the system can be defined as characterized by such structures only if time- and space- averaged (see Section 2.1). Fig. 5 shows a schematic picture of some processes taking place in a reversed micelle.

In some cases the inter-molecular interactions (polar–polar, apolar–apolar, and polar–apolar interactions, eventual H-bonds, steric hindrance etc.) can drive molecular self-assembly to form

supra-molecular structures of different levels of complexity [37,38].

It must be said that the use of surfactant dissolved in solvents is not new: their self-assembly has been studied both experimentally and theoretically [38] and smart non-invasive techniques have been set-up which have highlighted spinodal decompositions and multi-step self-assemblying processes giving various levels of complexity [39–40]. Stimuli-responsive supramolecular micelles with sharp intelligent response to intracellular environmental stimuli, such as pH-change, redox, enzymes, temperature-change, and so on, are promising anticancer drug carriers. Among various intelligent delivery systems, pH sensitive drug delivery has received greater attention due to their site-specific targeting release of payloads, leading to aggressive anticancer activity and maximal chemotherapeutic efficacy with fewer side effects [41–42].

As an example of application of this pH-responsive host–guest molecular recognition, we can report the work by Chen and co-workers [43] who masterfully designed a pH-responsive supramolecular amphiphile comprising benzimidazole (BM) functionalized poly(ϵ-caprolactone) (BM-PCL) and β-cyclodestrin(CD) modified dextran (Dex-β-CD) giving supramolecular micelles utilized as nanocarriers to encapsulate hydrophobic anticancer drug doxorubicin. A nice review on host-guest interaction based supramolecular amphiphiles has recently been published by Guocan et al. [44].

3.2. amphiphile-based systems II: mixtures of liquid surfactants

In comparison with the above examples, less usual is instead the use of a pure liquid surfactant, which itself shows self-segregation. The fact that the pure surfactant may be in the liquid state at room temperature is obviously a big advantage because the absence of any solvent to get a liquid state maximizes the properties specific of the surfactant and coming from its amphiphilicity. Further, the mixing of two (or more) different amphiphilic substances allows the preparation of systems characterized by composition-dependent structures and properties amenable to specialized applications such as nano-heterogeneous solvents, templating agents, electrorheological fluids, specialized non-aqueous reaction media and anti-corrosion films [14,45,46].

Recently it has been shown that the simple mixing of two appropriately chosen amphiphilic substances allows the preparation of blends with enhanced proton conductivity which can be of utmost interest in dedicated applications such as in anhydrous proton-conducting media for fuel cells [47].

In the specific, our recent studies have been devoted to understand the reason why the mixing of two low-conducting molecular liquids can give a blend characterized with an enhanced proton conductivity and at the present the cause can be ultimately addressed to two concomitant factors: (i) the increase of number density of charge carriers and (ii) the establishment of preferential pathways for proton mobility.

In fact, just a simple chemical reasoning suggests that if an acid surfactant is mixed with a basic one, the resulting acid-base interaction triggers the formation of H-bonds which can increase significantly the concentration of less bound protons and/or their mobility. As examples, the benzimidazole/monododecyl phosphate acid system shows a high proton conductivity exceeding 10^{-3} S cm^{-1} above 100 °C [48], and the addition of *N*-methyl formamide to the surfactant Bis(2-ethylhexyl) phosphoric acid causes an increase of proton conductivity of more than four orders of magnitude [49].

Moreover, when mixing amphiphilic substances, the delicate equilibrium of several, sometimes opposing, factors, specifically steric effects, van der Waals interactions between hydrophobic tails, polar interactions among the heads, formation of H-bonds etc.
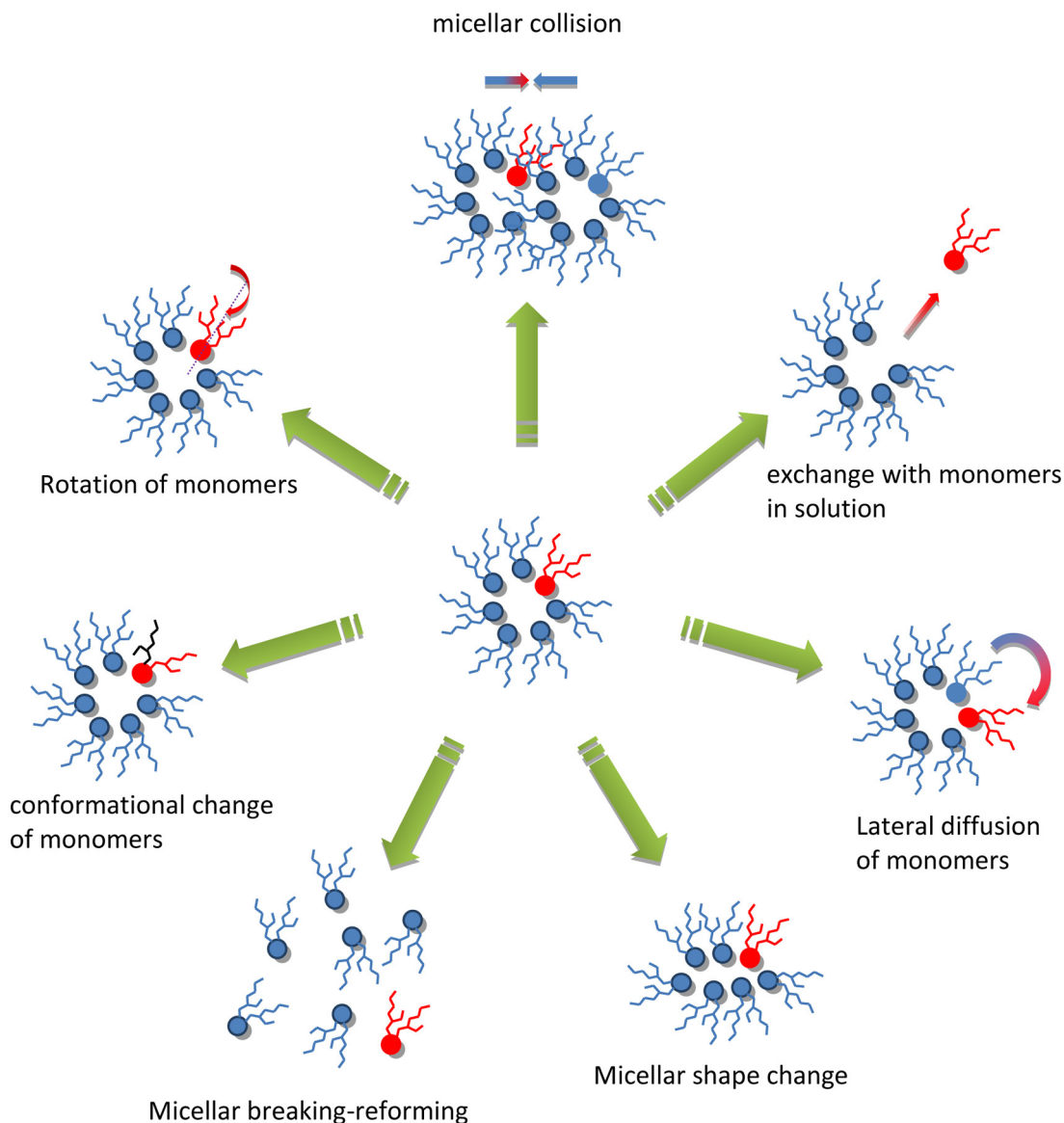
Fig. 5. Some dynamical processes taking place in a reversed micelle. Each of them is characterized by a specific timescale and varies from nanoseconds for conformational dynamics to milliseconds for breaking and reforming the aggregate.

can cause the formation of medium-range structures with the formation of coexisting insulating and conductive nanoregions whose spatial organization could generate pathways for significant charge transport, actually constituting conductive channels for the charge migration through the whole system.

As an example, under anhydrous condition high proton conductivity (about $10^{-3}\,\mathrm{S\,cm^{-1}}$) has been found at 150 °C in acid–base composites formed by mixing the acidic surfactant monododecyl phosphate and the basic surfactant 2-undecylimidazole. This has been rationalized in terms of presence of self-assembled lamellar structures offering 2D pathways for proton conduction [14].

So, the appropriate choice of surfactants allows, in principle, the preparation of blends of surfactant molecules possessing, thanks to the concomitant exploitation of both effects, enhanced conductivity already at room temperature and whose conductivity can also be tuned in a wide range (several orders of magnitude) by simply changing the composition. For example, we have studied the structural and conductometric properties of liquid mixtures composed of bis(2-ethylhexyl) amine (BEEA) and bis(2-ethylhexyl) phosphoric acid (HDEHP) [15]. We found that while both pure

components exhibit very low proton conductivities, their mixtures are characterized by an increase in structural order and a huge enhancement of conductivity. We recognized that these features are mainly driven by acid–base interactions between PO_4H (of HDEHP) and NH (of BEEA) groups.

The same behaviour was found also in bis(2-ethylhexyl) amine/n-octanoic acid (OA) mixtures [16] for which it has been suggested that, driven by OA-to-BEEA proton transfer, the formation of hetero-adducts with peculiar physico-chemical properties occurs. This was recognized to be a key ingredient for the slowing down of molecular dynamics and the increase in charge carrier mobility and number density leading to a composition dependent striking conductivity enhancement (more than seven orders of magnitude).

Instead, in bis(2-ethylhexyl) phosphoric acid/n-octylamine mixtures the conductivity is suppressed with respect to the pure components but, interestingly, a peculiar unidirectional pathway for diffusion of surfactant molecules is established thanks to the formation of unidirectional self-assembled structures (see Fig. 6A) [17,50]. It is interesting to note that the building of unidirectional structures causes an obvious increase in viscosity but also
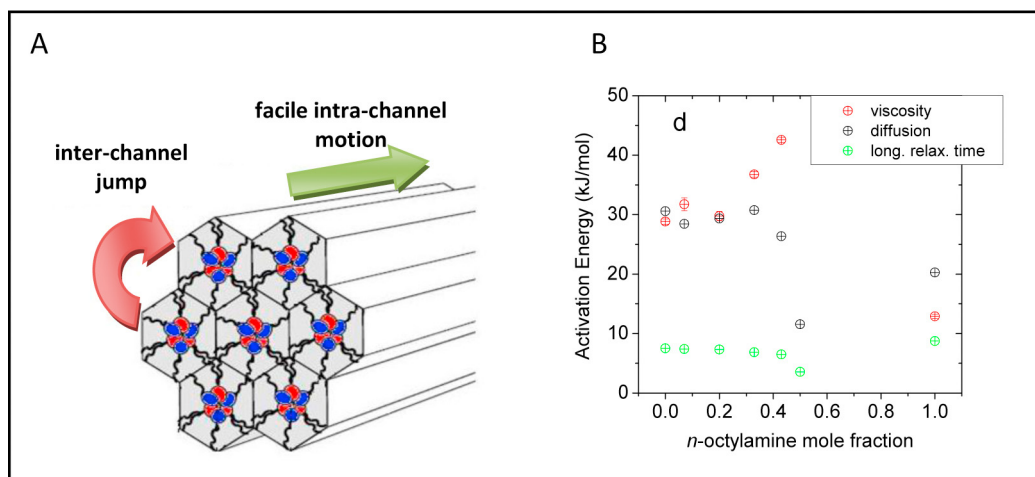
Fig. 6. Self-assembly of amphiphilic molecules in the liquid phase, can give very peculiar behaviour especially when two liquid amphiphiles are mixed. bis(2-ethylhexyl) phosphoric acid/*n*-octylamine mixtures form peculiar unidirectional pathways for diffusion of surfactant molecules thanks to the formation of unidirectional self-assembled structures. Panel B reports the activation energy for the viscosity, diffusion and longitudinal relaxation time as a function of *n*-octylamine mole fraction.

an unexpected reduction of the activation energy of the diffusion and longitudinal relaxation time as reported in the graph of Fig. 6B.

Even an anti-Arrhenian behaviour of conductivity has been found in *n*-octanoic acid–bis(2-ethylhexyl) amine systems (see the structure of the locally assembled amphiphiles responsible for this behaviour in Fig. 7A together with the Arrhenius plot of the conductivity in Fig. 7B). This was given by the presence of local structures facilitating proton migration whose lifetime and integrity are sensitive to temperature [18].

It turns out that the peculiar dynamical processes observed in surfactant mixtures appear as emerging properties as a consequence of a rich scenario of possible inter-molecular interactions which allows the formation of supramolecular structures at different levels of complexity and the formation of energetic barriers of different heights and at different lengths. These aspects remain to be clarified in surfactant-based liquid mixtures. So part of recent literature is being opening to these directions because such systems constitute a new class of materials and can have a high impact in specialized applications.

3.3. Block copolymers

Block copolymers form a group of materials which is very attractive from the morphological point of view. They are special kind of copolymer which are made up of blocks of different polymerized monomers. The presence of two blocks with different chemical composition and physical properties governs self-assembling of block copolymers into well-organized 3D structures [51]. For this reason we like to deal with such a kind of polymeric system as an interesting example of self-segregation to form self-assembled structures which can have novel and useful final properties. This is then an alternative example of amphiphilicity at a longer scale than that of molecular systems above illustrated, and are then nice candidates for giving complex behaviour. Conceptually, the physical principle triggering self-assembly in such systems is the same as in the other reported example, i.e. the equilibrium between steric and repulsing forces and attractive stabilizing forces taking place among parts of same affinity (polar or apolar).

For instance, styrene–isoprene–methyl methacrylate block copolymer undergoes self-assembling with the formation of highly periodical 3D grid-like nanostructures [52–53].

Very similar organization behavior is expected for all conjugated block copolymers [54]. Therefore, they were envisioned to be excellent materials for devices: the key idea is to organize block copolymer on a substrate in a vertical multicolumn fashion resulting in a perfect morphology for charge generation and transport toward respective electrodes [55].

The application in optoelectronics of block copolymers was recently reviewed [56,57].

Sommer et al. [58] have developed a wide group of diblock copolymers incorporating perylene diimide units. Such morphology in this material enables its relatively efficient photovoltaic operation particularly facilitating charge generation and transport to the electrodes. A detailed overview of block copolymers designed for photovoltaics appeared recently [59].

Self-assembly of block copolymers in selective solvents can be viewed in strong analogy to low molecular weight surfactant in water. On the other hand, since a block copolymer chain may consist of more than 400 monomeric units, the free energy per micelles is much larger for block copolymers than for traditional surfactants in water.

The use of block copolymer self-assembly has been demonstrated to be one of the promising bottom-up methods for the design and construction of hybrid (inorganic–organic) functional nanomaterials. In these systems, in fact, the thermodynamic incompatibility between the different blocks causes a microphase separation that gives rise to a spatial organization of morphologies starting from the nanonanometer scale.

See Fig. 8 where the scheme of the process is depicted: this nano- or micro- phase separation can take place in a wide variety of modes. Since the interactions involved in the self-assembly at long range are generally soft, temperature can have a crucial role and, by modifying the system volume fraction and solution conditions, novel structural transitions can be induced, as demonstrated by different studies [60,61].

In this respect the combination of supramolecular interactions and the ability to control both the length scale and the structural morphologies make block copolymers particularly attractive templates in the synthesis of nanoporous materials with new characteristics and properties [62,40].

Block copolymers are able to produce various kinds of morphologies ranging from micelles or vesicles to lamellae. In particular, amphiphilic block copolymers are known to form polymersomes that are analogous to liposomes but with different
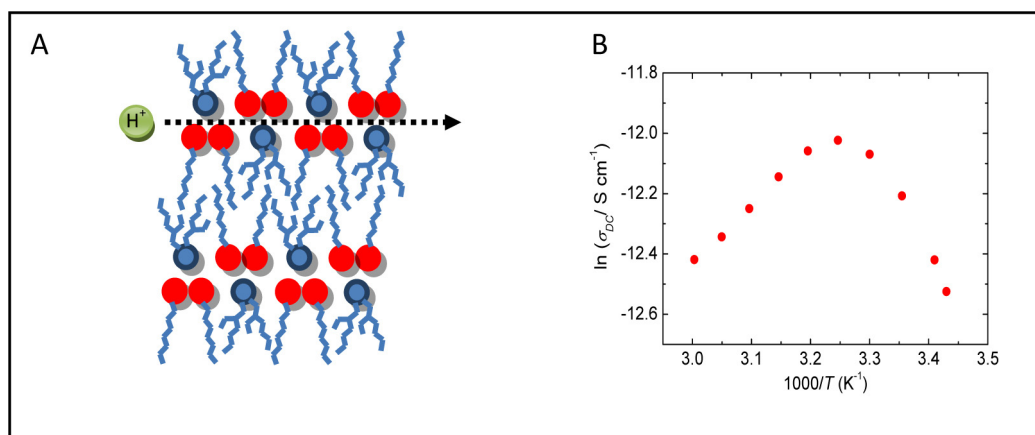
Fig. 7. In n-octanoic acid–bis(2-ethylhexyl) amine systems local structures facilitate proton migration but such structures are local and evanescent, so changes in temperatures causes dramatic changes in the conductivity behaviour. Panel B reports the Arrhenius plot.
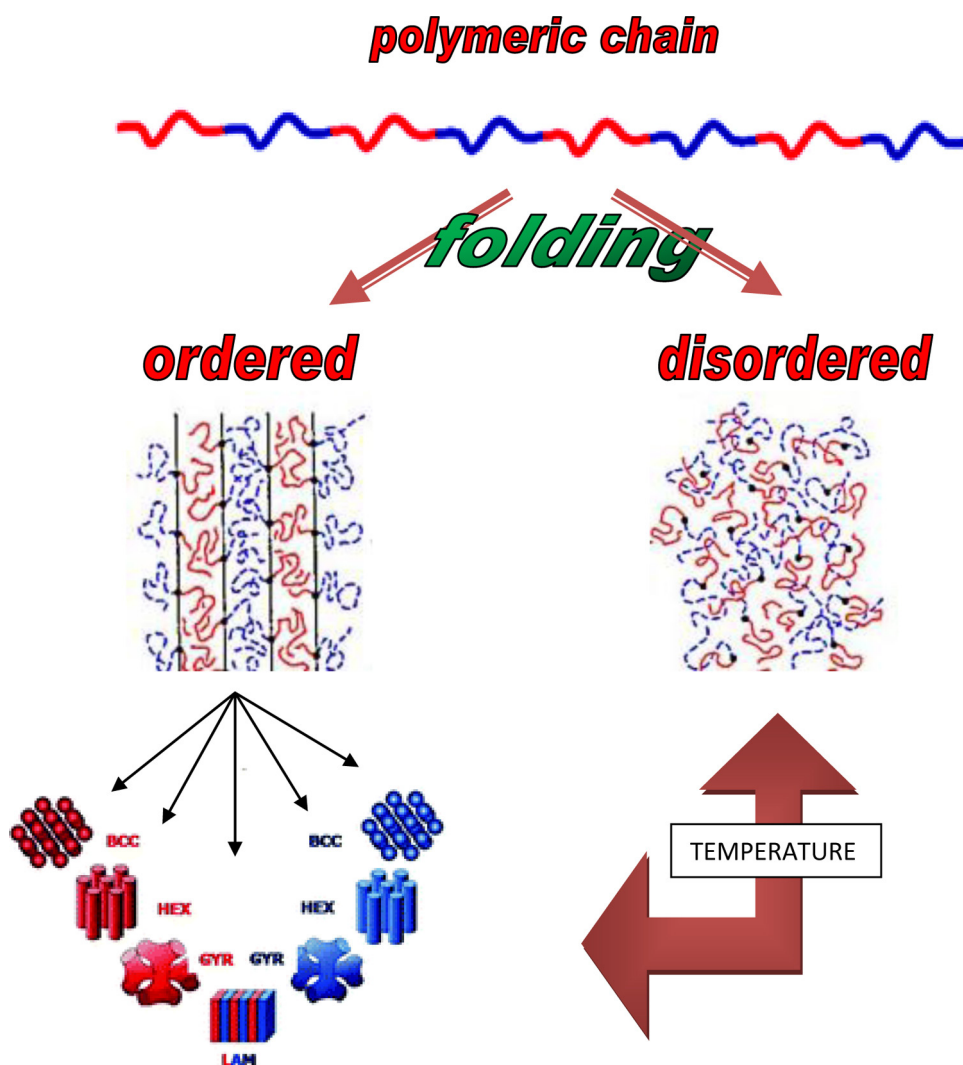
Fig. 8. Schematic depiction of the self-assembly processes taking place in block copolymers.

properties associated with their larger size. In 2007, the groups of Vriezema et al. [63] reported the use of such structures to encapsulate enzymes for producing a nanoreactor capable of performing one-pot multistep reactions. Other examples can be found in Ref. [64].
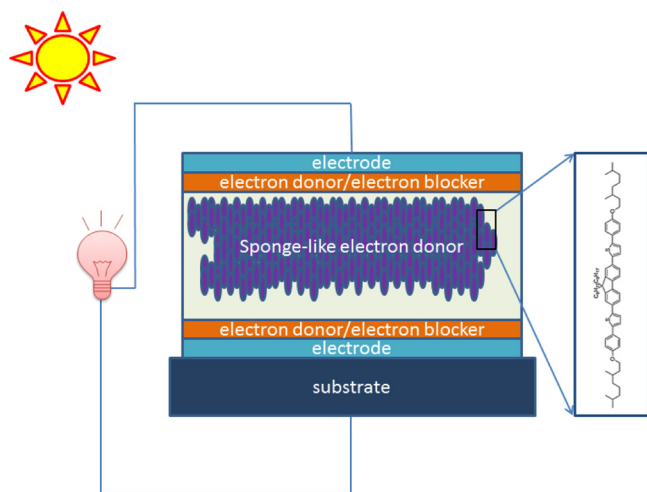
Fig. 9. Representative scheme of an ideal Liquid Crystal (LC) composite photovoltaic cell.

3.4. Self-assembling of liquid crystalline and crystalline-conjugated materials

Liquid crystalline (LC) materials have been used to create, directly from solution, thin films with structures optimized for specific applications. The discotic liquid crystal hexa-perihexabenzocoronene was used in combination with a perylene dye to produce thin films with vertically segregated perylene and hexabenzocoronene, with large interfacial surface area.

This nematic LC gels can be incorporated in diode structures [65] to generate a vertically separated distributed interface between electron donating and accepting materials for improved device efficiency. This could represent an attractive new approach to organic photovoltaics, solar cells or, in general, power supplies for electronic applications.

Liquid crystalline materials were further explored in order to design self-assembled bulk heterojunction solar cells. The presented examples suggest how the reduction in scale-length of the building blocks generating a complex photoelectrochemical complex device, together with their fine control, can show large potential for the design of higher stability and efficiency.

The liquid crystalline conjugated polymers, like, for example, poly(p-phenylene vinylene), polyfluorene, polythiophene are classified into two types: conjugated main chain polymers with long alkyl side chains, namely main-chain type LC polymers, and conjugated polymers grafting with mesogenic side groups, namely side-chain type LC conjugated polymers (see for example the representative scheme of an ideal Liquid Crystal (LC) composite photovoltaic cell in Fig. 9). In general, the former shows higher transition temperature and only nematic phase; the latter possesses lower transition temperature and more mesophases, for example, smectic and nematic phases, depending on the structure of mesogenic side chains. The fully conjugated main chain promises them as good candidates for polarized electroluminescent or field effect devices. The polarized emission can be obtained by surface rubbing or thermal annealing in liquid crystalline phase, with maximum dichroic ratio more than 20 [66].

4. Future perspectives: self-assembly for generating complex devices

The smallest building blocks for assembling complex structures are obviously constituted by stable components of matter i.e. atoms and molecules which need, in their first step, to be organized to form definite nanoparticles. At the nanoscale, below a substance-specific size threshold, the properties of many solids becomes strongly size-dependent due to quantum size effects. Moreover, it cannot be neglected that a considerable fraction of surface atoms are in contact with the surrounding medium: surface adsorption of suitable molecules besides stabilizing the nanoparticles, offer a chemical modification (functionalization) which is the first step for their piloted assembly.

As a consequence of all these considerations, the preparation of a material with desired characteristics is based on a simultaneous exploitation of the following strategies:

1. The synthesis of new molecules (synthetic chemistry);
2. The blending of already known materials;
3. The reduction of the dimensionality of already known materials to the state of nanoparticles, nanowires, nanoplates which simultaneously takes into account the need in miniaturization.

These three complementary strategies are schematically depicted in Fig. 10: the first one is based on the fact that the properties of molecular solids are basically those of the constituent molecules so the synthesis of a material with innovative properties is achieved through the synthesis of new molecules. This is the fertile field of all synthetic chemists both organic and inorganic. The second strategy is conceptually different from the first one, since it is based on the blending of already known substances at particular doses. The simultaneous presence of different compounds in the mix confers to the resulting material novel properties that come not only from the mere combination of single contributions but also from novel and sometimes unexpected synergic effects. Incidentally this is an approach exploiting the emergence of novel properties in complex systems. In this background the reduction of well-known materials to the state of nanoparticles has represented a new and parallel possibility to synthesize materials with novel properties. This has been primarily due to the fact that finely divided matter can exhibit properties that are different from those of the same material in the bulk state, due to quantum size effects, giant surface-to volume ratio and peculiar properties of surface atoms.

The recent attention in nanocomposites, systems homogeneous at the macro-scale, but heterogeneous at the nanoscale, where the use of nanoparticles is coupled with the mixing of some selected materials is a really good example.

Once organization at the supramolecular level has been achieved by covalent synthesis of appropriate building blocks, the supramolecular entities should self-assemble (or be assembled) into structures that can bridge length scales from nanometers to macroscopic dimensions. As an example, when the building blocks have particular shapes, sizes, and capacity to give hydrogen bonds or π–π interactions, they can self-assemble to give light harvesting and/or charge separation phenomena [67–69].

In this ambit, we cannot but seeing now that in the aforementioned examples of amphiphile self-assembly, and specifically (i) amphiphiles in solution, (ii) mixing of amphiphiles, and (iii) block copolymer, the strategies of preparation of novel materials introduced in this paragraph are somehow implied. In fact:

i) the self-assembly process of a surfactant in solution is dictated by the molecular structure. the microscopic characteristics of the amphiphile govern its self-assembly pattern as a function of concentration and temperature;
ii) the mixing of two (or more) different amphiphiles gives emerging properties that cannot be extrapolated from the characteristics of each single component;
iii) in the example of block copolymers, the coexistence of "blocks" with different chemical characteristics within the lin-
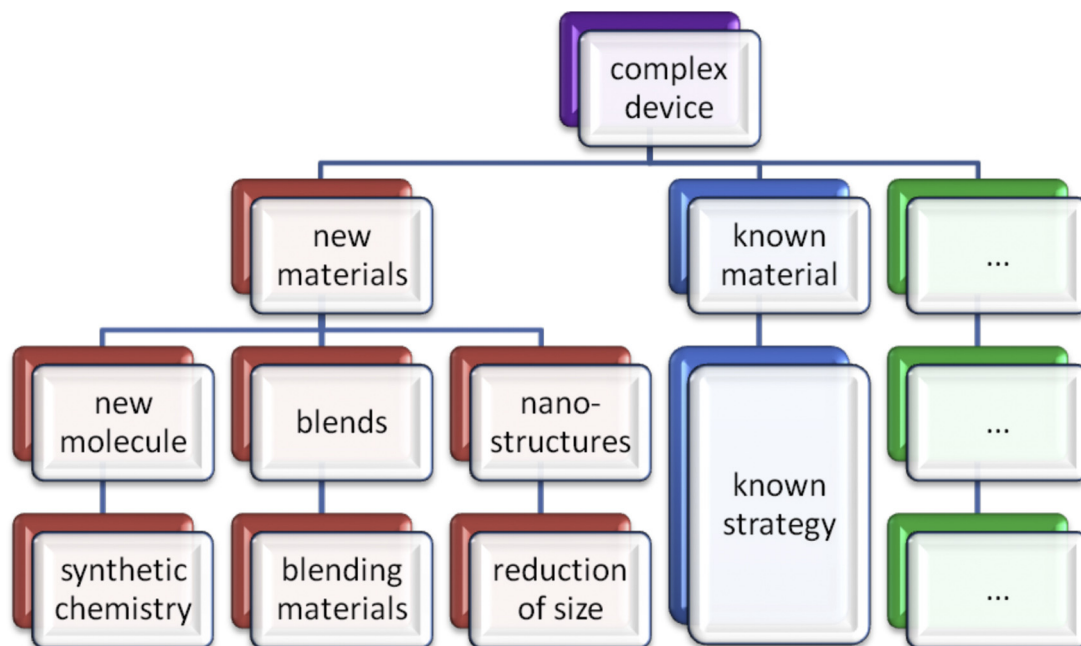
Fig. 10. Scheme of the strategies used to build up new devices.

ear sequence in the polymeric chain gives polymer folding with the formation of local nanostructures. Each local nanostructure has thus specific characteristics and the supra-aggregation pattern at a higher level of complexity is automatically dictated by the opportune sequence of the original blocks along the polymeric chain.

Once novel materials have been prepared, it is possible to build a wide variety of useful machineries with specific applications and of different complexity. So, the methods for the synthesis of such novel materials building blocks must take into account for the factors governing their properties (material, size, shape, surface) and be finalised to the their subsequent use to form assemblies of higher level of complexity and device with specific properties and functions. Moreover, since bare nanoparticles are thermodynamically unstable toward an unlimited growth, any synthetic method should devise a molecular process able to hinder their spontaneous coalescence such as spatial segregation, electrostatic repulsion or nanoparticle surface coating. These aspects have been outlined in a recent review so we refer the reader to that article [2].

We have already mentioned that our opinion is that the realization of specific materials chemically far from equilibrium looks an effective tool to access specific functionalities, an ideal approach already used by nature. Nature, once more, shows excellent examples of how a wide range of molecules are synthesised, blended, and self-assembled to form complex supra-nanostructures with emerging properties and specific functionalities.

Currently, miniaturization is pursued by the top-down approach, which consists in manipulating progressively smaller pieces of matter by photolithography and related techniques. Such an approach does not seem capable of exploiting the "plenty of room at the bottom" offered by the nanometre world of molecules. Therefore, the alternative bottom-up approach for the construction of molecular devices, emerged in the late 1970s and fully suggested in this paper, can exploit the supramolecular chemistry approach to efficiently gain, in our opinion, ever increasing levels of complexity.

Having roughly presented the strategies we are now finally pleased to introduce how they have been exploited giving some examples of a modern devices. We have chosen the following examples as merely representative (even though not exhaustively) of

a state-of-the-art level of complexity, furnishing, in our opinion, interesting models and promising patterns for future engineering organized in the nano-scale.

4.1. Device categorization

It may be useful to categorize molecular devices and machines according to the nature of the cause (electronic, photonic, or chemical input) and the nature of the effect (electronic, photonic, or chemical process that follows, output). In the simplest case, input and resulting process have the same nature: an electronic input can generate release of an electron (molecular electronics), absorption of a photon can generate emission of a photon (molecular photonics), and a chemical input can generate a chemical reaction (molecular chemionics).

It is also possible, however, to have molecules that convert an input into a process of different nature. For example, a chemical reaction can generate emission of a photon, and an electronic input can generate a chemical reaction. Furthermore, it is possible to stimulate a molecule (even better a supramolecular system) with a sequence of inputs of the same or different nature and obtain processes of the same or different types. For example, a chemical reaction of a molecule followed by absorption of a photon can generate emission of a photon that would not have been emitted by the original molecule. Therefore, besides molecular electronics, molecular photonics, and molecular chemionics, at least six cause/effect crossing couples can be considered, corresponding to electro-photonics, electro-chemionics, photo-electronics, photo-chemionics, chemio-photonics, and chemio-electronics.

In the last few years, many supramolecular systems capable of transferring, switching, collecting, storing, and elaborating light signals for information processing at the molecular level have been constructed and investigated. Examples are wires for photoinduced electron and energy transfer, plug-socket systems, electrical extension cables, memories, light harvesting antennas, logic gates, and a variety of machines (*vide infra*).

4.2. Molecular machines

Molecular machines are chemical systems and therefore operate by means of chemical reactions that, broadly speaking, imply both electronic and nuclear rearrangements.

The functions that could be performed by molecular devices and machines are various. They may be related to signal transfer (in the form of energy, electrons, protons, etc.) [70,71], information processing (e.g. by molecular-level logic gates) [72], energy conversion, about which many examples have been given throughout this manuscript, or a chemical fuel [73]

Molecular rotary motors are systems capable of undergoing unidirectional and repetitive rotations under the action of external energy inputs. The construction of molecular rotary motors poses several challenges, particularly because it is difficult to satisfy the unidirectional rotation requirement [74–76].

Asakawa [77] and Balzani [78] reported some examples of a molecular catenane in which the electron-acceptor tetracationic cyclophane is "symmetric", whereas the other ring contains two different electron–donor units, namely, a tetrathiafulvalene (TTF) and a 1,5-dioxynaphthalene (DON) unit. This supra-molecule is considered as a first step to set up a device which exploits alternated electrical potential energy to perform a molecular-level mechanical rotation.

Light can be used as the external energy input for a nano-motor. Molecular devices that can use light energy and process light signal are termed *photochemical molecular device.* Photochemical molecular devices designed to obtain extensive conformational changes upon photoexcitation are called *photochemical molecular machines.* Sometimes, they are dealt with "Light powered molecular machines".

Of course, understanding the interaction between light and molecules, would expand the potentialities of using light as an energy supply (to sustain energy expensive functions) or as an input signal (to be processed and/or stored).

The first examples of light-driven molecular machines reported in the literature are the molecular tweezers based on photoisomerizable units [79] and nowadays they have reached a high level of sophistication. Photoinduced ring shuttling in a rotaxane containing two different recognition sites in the axle component has been achieved using a compound consisting of six molecular components suitably chosen and assembled to achieve the devised function [80].

Example of molecular shuttles relying on the photoisomerization of azobenzene or stilbene units [81] or nano-muscle [82], where reversible photoisomerisation of the stilbene units causes the cyclodextrins to move off and on the stilbene units, contracting and extending the distance between the blocking groups have also been reported. Interesting reviews on this kind of device can be found in Ref. [83–84].

A very interesting example of molecular machine is that controlled by pH conditions. An assembly of dibenzo[24]crown-8 (DB24C8) macrocycle and a dumbbell-shaped component containing a dialkylammonium center and a 4,4′-bipyridinium unit behaves as a chemically controllable molecular shuttle where it is possible to switch the position of the ring between the two 'stations' by an external stimulus which causes pH variation [85] (see Fig. 11 for the schematic representation). In this system, the incorporation of appropriate chemically-, electro-chemically- and/or photochemically-responsive units into either the host or guest components of supramolecular complexes creates conditions under which the pH variation, acting as external stimulus, can effect decomplexation/complexation processes.

The basic principle of pH-operated method is to change the chemical properties of components in the system by adjusting pH of the solution via adding acid/base compounds, to realize the movements of components, which belongs to chemical stimulation mode. The acid/base controlled method has been one of the most useful energy-driven modes for artificial molecular machines [86–87].

4.3. Logic functions (Molecular computing)

Molecular computing is a promising development of modern solid-state computing: despite they are usually much less stable and they cannot be easily interconnected, however molecules show several advantages: they (i) are very small (nanometre, or sub-nanometre scale) enabling a very high density of information storage, (ii) can integrate highly complex functions on a single platform, (iii) can be reconfigured in situ by changing inputs and outputs, or by manipulating the substrate by an external input, and (iv) can work in confined environments, like cells, and even in vivo, where silicon-based technology is unlikely to prove useful. A representative scheme of a nanostructured logic port is shown in Fig. 12.

Within the field of molecular logics there are two distinct approaches: the first one, aiming at developing nanoelectronics, is based on molecules as solid-state nanocomponents of electric circuits to enhance density of information storage. The second approach is inspired by information processing in biology and is based on functions performed by an ensemble of molecules in solution, which can selectively respond to a variety of chemical, photochemical or electrochemical stimuli. The chemical approach may take advantage of the potentiality of molecules to perform complex functions and give rise not only to binary outputs, but also to multi-valued outputs with increased density of information. It can even result in the construction of analogic devices and systems capable of using fuzzy logic.

By suitable combinations of writing and reading processes it is indeed possible to perform logic functions and also to make complicated operations [88]. Amphiphilic structures, again, give nice examples of their potentialities also in this field: for example a three-component system consisting of a potentially fluorescent anthracene unity linked to a crown ether and an amine function has been used. The quenching action of the amine and crown ether moieties on the fluorescent excited state of anthracene can be deactivated by addition of protons and sodium ions, thereby allowing the system to play the AND logic function [89].

4.4. Memories

Molecules that can be interconverted by stimulation between two different states may be used to store information, thereby playing the role of memories.

There are three different types of molecular memories: shallow (or weak) memories when the bit of information is erased spontaneously, vacant memories when the written information is erased by the reading process and deep (or stable) memories. The latter result can be obtained by using a second input that locks the written information and allows reading without erasing. In suitably designed systems, the information can be unlocked when necessary and then erased to reset the system.

In 1998, it has been developed a system based on *cis-trans* photoisomerization of 4′-hydroxyflavilium [90] with the two isomers that can be locked and unlocked through a variety of acid–base reactions (see Fig. 13 for the schematic representation of the processes).

Starting from the *trans* isomer at pH 4, it is possible to write a bit of information by 365 nm light which leads to the *cis* isomer. Going to pH 1 the written information can be locked as the protonated form that, being not photosensitive, can be read by recording its absorption spectrum without erasing (deep memory). The pro-
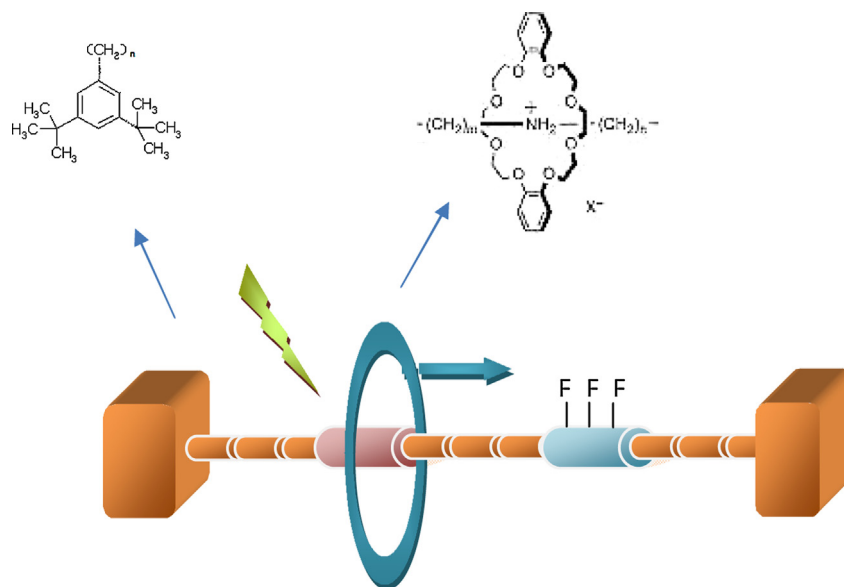
Fig. 11. Scheme of the working principle of a molecular machine. The molecules shown are those involved for the realization of a pH-responsive molecular machine as reported in Ref. [85].
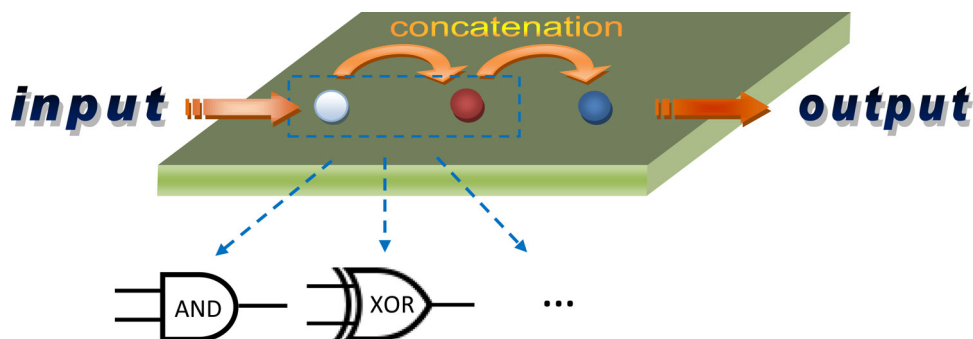
Fig. 12. Representative scheme of how opportunely concatenated molecules or nanoparticles can work as logic port.

tonated form can then be unlocked by a jump to pH 12, which yields a metastable *cis* form (shallow memory) that can be written by light at 313 nm to yield the stable—trans form (deep memory). When necessary, the information stored into the stable-trans can be unlocked by means of a pH jump, resetting the system.

4.5. Encoding and decoding

Encoding and decoding solid state macroscopic devices are widely used in everyday life for data communication, networking and information storage. An encoder is a device that compresses information according to a known code, while a decoder translates encoded inputs into readable outputs. Recently, it has been found that the supramolecular system consisting in a dithienylethene (DTE) photochrome covalently linked to two fulgimide (FG) photochromic moieties be isomerized independently by different wavelengths of light between closed forms, which are colored in the visible range, and open, UV absorbing, forms. These properties allow the triad to act as either a 4-to-2 encoder or a 2-to-4 decoder, depending upon the nature of the photonic inputs and outputs [91].

4.6. Sensors

A requirement for the application of supramolecular chemistry in building recognition devices is that the binding of the analyte

to the receptor, or in other words the host-guest interaction, must trigger an observable response through a reporter molecule.

The nature of the response will depend upon the analytical method used to detect the signal but will typically be colorimetric, electrochemical or fluorescent. An appropriate signaling mechanism may be designed to incorporate, for example, changes in conformation or molecular orbital energies that in turn affect the reporter molecule electronic or spectroscopic signature upon analyte binding.

Finally, the receptor must be linked to the reporter molecule so that the effect of binding directly affects the latter without compromising the observable response. The schematic scheme is reported in Fig. 14

A known class contains the arginine-like reside that plays the role of an anion transferring species in biological systems [92].

Another example is porphyrin (the structure is reported in Fig. 14, entry a) and its derivatives which bind magnesium, manganese, cobalt and nickel cations, in natural processes [93].

For example, Wang prepared porphyrin as nanotube [94]: this geometrical motif is particularly appealing for sensor applications, because it can potentially show a dramatic increase in sensitivity/selectivity performances with respect to the individual subunits.

Moreover, the variation of peripheral substituents of porphyrins, such as for example chiral appended functionalities, can result in the formation of porphyrin aggregates featuring high
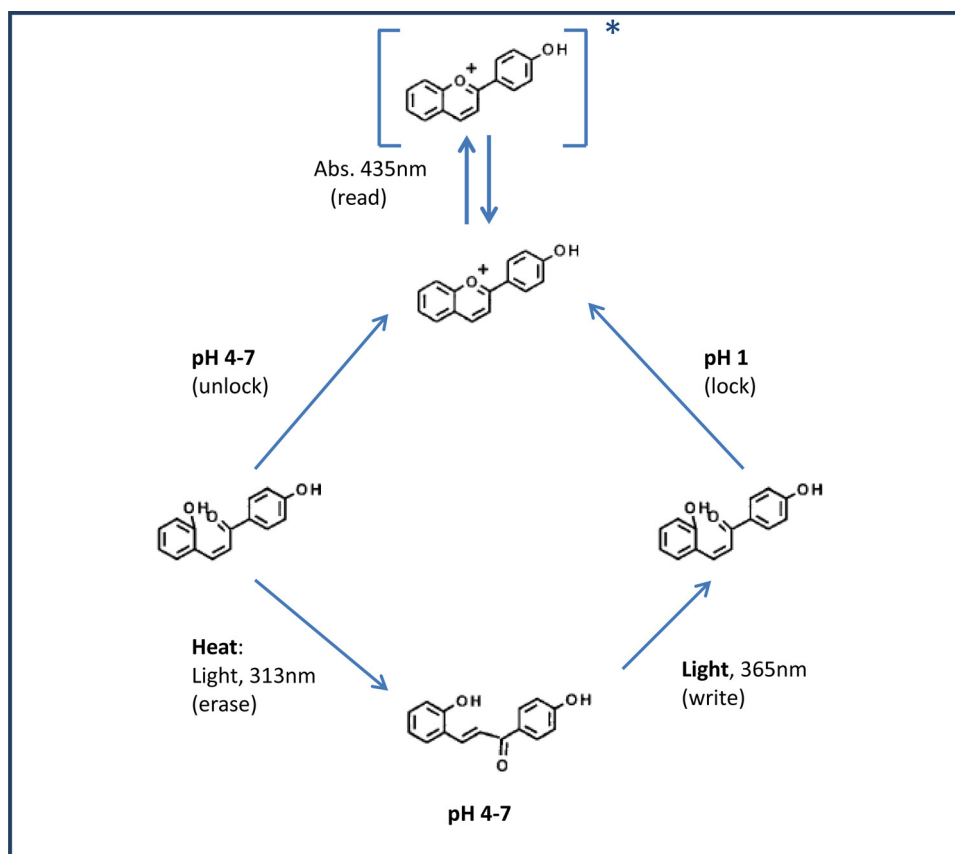
Fig. 13. Write-lock-read-unlock-erase cycle involving 4′-hydroxyflavilium (see Ref. [90]).

supramolecular chirality. This would allow the achievement of porphyrin layers characterised by different chiroptical and molecular recognition properties [95].

A nice example of a macro-amphiphile has been reported by Ogoshi et al. [96] who synthesized carbon nanotube-cyclodextrins (SWCN-CD) hybrids for the construction of novel chemically-responsive supramolecular hydrogel systems (schematic structure is reported in Fig. 14, entry b) [96].

Another nice example of amphiphile at a level of complexity higher than that of a single molecule, is given by Mutihac [97] in 2011 who designed calixarenes able to form interactions (so-called cation-interactions) with polar cationic molecules, such as amino acids and neurotransmitters, which can thus bind the nonpolar core—in essence serving as a 'nonpolar anion'.

Various studies [98–100] have shown the self-assembling, through hydrogen bonding of the hydroxyl units or functionalized rims, of calixarene (structure shown in Fig. 14 entry c) or resorcinarene (resorcinol-derived) molecules into cages with spherical or oblong cavities for recognition purpose.

Finally, Rotello and co-workers have used the reversible character of supramolecular complexes between charged nanoparticles and oppositely charged fluorescent conjugated polymers to elaborate "chemical noses" for the detection and identification of proteins [101].

4.7. Molecular based magnets

Molecule-based magnets are a broad, emerging class of magnetic materials that expand the materials properties typically associated with magnets to include low density, transparency, electrical insulation and low-temperature fabrication.

Molecular magnets are single molecules consisting of a magnetic core and an organic ligands, that have a moiety able to link the metal magnetic core and an aliphatic part with shielding function. They possess magnetic anisotropy and show ferromagnetic behavior when cooled sufficiently [102]. This makes them interesting for data storage purposes but to finally use Molecular magnets as bits in a binary System an implementation to a medium is required [103].

In the last years, increasing attention has been paid in searching for new molecule based magnets: in particular materials with d-orbital spin sites connected via covalent bonds have been explored by using organic synthetic methods [104–107].

An interesting class of "*magnetic molecular composite*" is represented by the transition metal(II) phosphonates, $M(II)[RPO_3] \cdot nH_2O$ and bis(phosphonates), $M(II)[O_3P-R-PO_3] \cdot 2H_2O$ (M is a divalent metal, Cd, Mn, Fe, Ni, Co, Zn; and R is an alkyl/aryl group) that feature magnetic long-range ordering at low temperatures [108–113].

In general the structure of these compounds is lamellar and presents alternating organic and inorganic layers where the organic group R of the phosphonate lies in the interlayer space forming a bilayer (thanks to van der Waals contacts) that is interspersed between the inorganic ones. See Fig. 15 for the representative structure.

The magnetic behavior at low temperatures is related to the 2D character of the inorganic sublattice, with alternation of polar and apolar layers whose assembly is dictated by the amphiphilic nature of the alkyl-phosphonate. Such a peculiar structure favours next-neighbour exchange magnetic interactions in phosphonates containing paramagnetic ions [114–116].

The length of the organic R-group, that may include additional tailored chemical and/or physical properties, determines the interlamellar distance, depending on the number of carbon atoms. This implies that by increasing the number of carbon atoms of
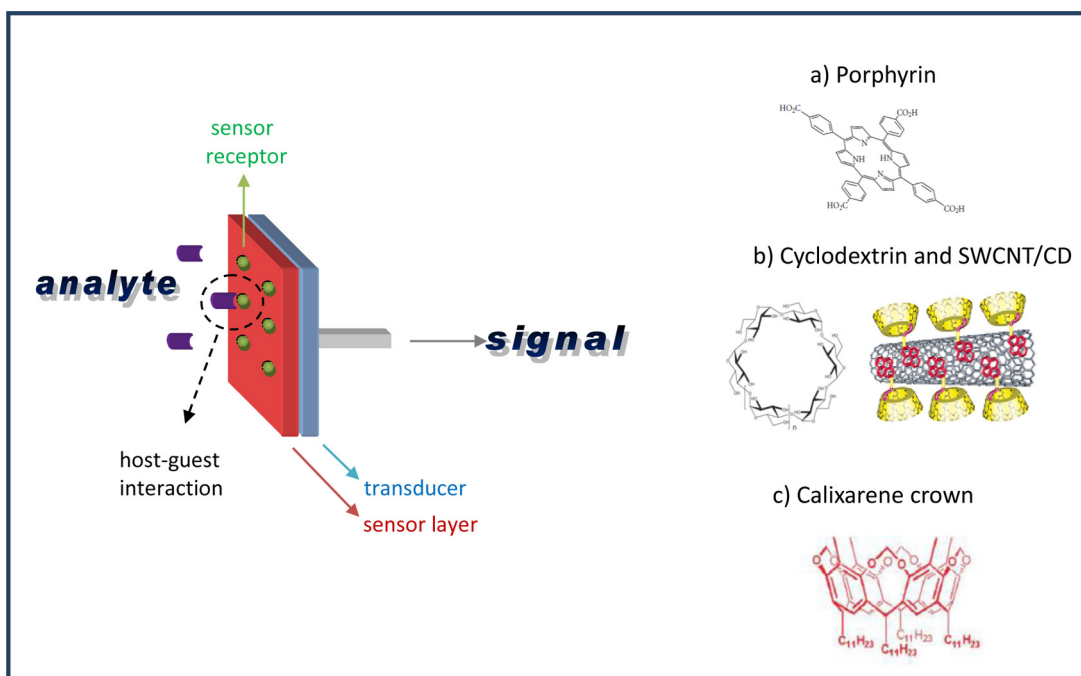
Fig. 14. Scheme of the working principle of a sensor. The chemical species (a–c) involved are mentioned in the text.
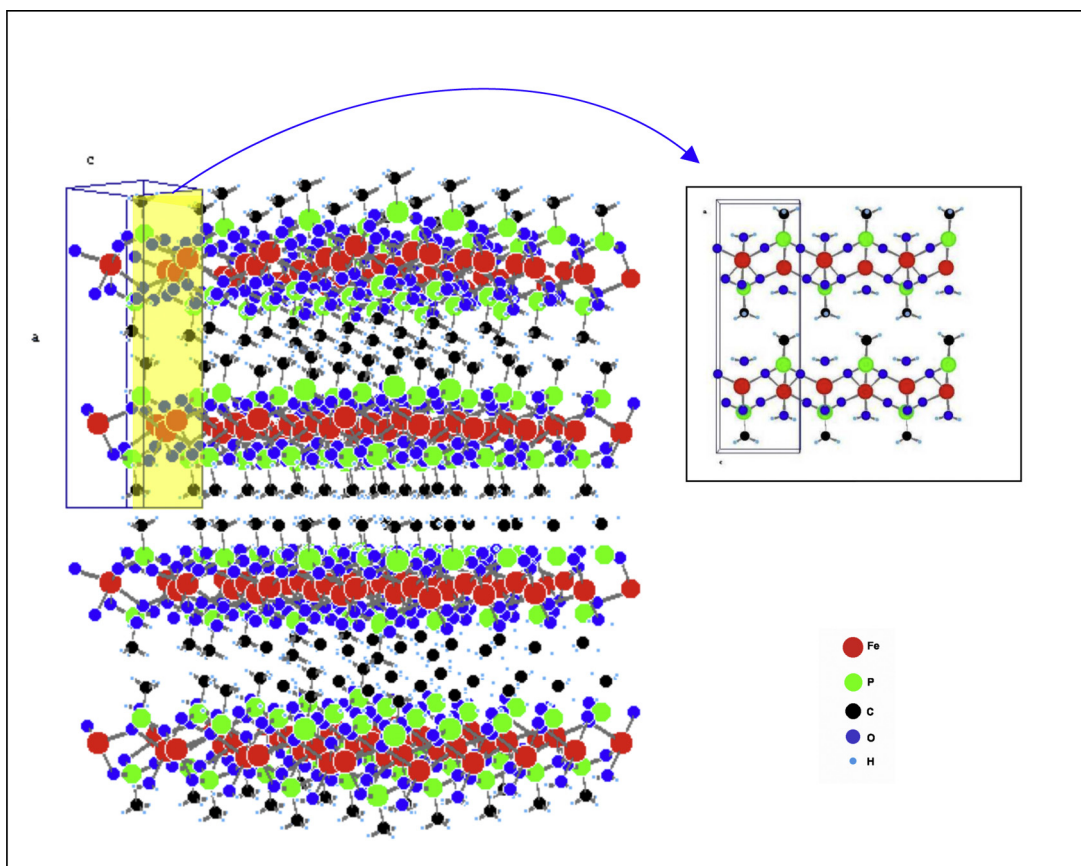

Fig. 15. Overall 3D view of the packing with alternated parallel layers of $Fe[(CH_3PO_3)H_2O]$; the inset shows the projection of the crystalline structure along the b axis [143].

the ligand, it is possible to increase the interlayer distance in the mentioned systems and therefore the thickness of the organic layers. The inorganic layer, which mimics the metal oxide layers, is then well separated from the others by the organic layer, thus

reducing the magnetic interactions along the third direction of the lattice.

In contrast with intercalation compounds [117], where the organic molecules between layers of the inorganic lattice form only

van der Waals interactions, in "molecular composite" solids, the organic molecules are covalently or ionically bound to the inorganic layers [118]. This has the effect of fixing the orientation of the ligand in the lattice, thus giving often fully ordered crystals.

This is a proof of the fact that, again, the opportune assembly of materials with different properties (the organic part and the inorganic one) can give synergic effects and emerging properties due to the merits of the two constituents. The design and the synthesis of this class of compounds in fact have provided examples of novel multifunctional materials, such as multiferroics, ferromagnetic conductors, chiral magnets, porous magnetic materials, chiral molecular conductors, paramagnetic superconductors, etc., that are difficult to find in classical inorganic materials conductors [119–124].

5. Concluding remarks

The rational assembling of specifically chosen nanoscaled building blocks to form an organized network constitutes a novel philosophy to enlarge the potentialities of nano-sized systems because it allows the emerging of new functionalities. This is what is called nanoscale complexity. This philosophy allows to reach ever higher levels of complexity by changing the size, shape, composition of the building blocks together with their spatial distribution and physico-chemical interconnections. Together to current approaches, novel methodologies are currently being developed and are still needed to accomplish this task, taking into account that nature often shows good examples. The up-to-date state-of-the-art shows that we have enough knowledge to manage the problematic dealing with the preparation as well as the characterization of nanoscaled building blocks. A lot towards the controlled assembling of these building blocks has been done but much more is required to exploit the huge potentialities of complexity in nanoworld. The horizon of this exciting research field is the building up of "artificial" systems that could improve the human life by realizing novel complex materials/systems/devices amplifying the range of their capabilities in every desired field.

We have given a easy to read and critical contribution showing the fascinating problematic involved in complexity at the nanoscale. We tried to furnish a panoramic and speculative sight of the topic hoping this view could interact with the imagination of readers to stimulate the discovery of novel aspects and interconnections and ultimately new ideas and research

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