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## **Do chemists control plane packing, *i.e.* two-dimensional self-assembly, at all scales?**

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### **Abstract**

Two-dimensional (2D) self-assembly (SA) is an efficient strategy to organize building blocks in a simple and efficient way. Actually, different communities of chemists or physicists use 2D SA, with different systems at different scales: molecules, nanoobjects, micron-sized colloidal particles, and even millimetric plastic shapes. Although, the cases of study and the perspectives are different, general trends and similar problems occur for all of them. In this Perspective, we combine mathematical considerations with experimental approaches in chemistry and physico-chemistry to draw general considerations on 2D SA. By building parallels between each field of study, global trends have been generalized for the elaboration of compact or porous single component SA, of binary saturated SA, and of quasiperiodic SA. Factors that influence the formation of superstructures are also rationalized, such as the control of defects, of the dynamics of formation, of the interaction potentials or of external driving forces.

## Introduction

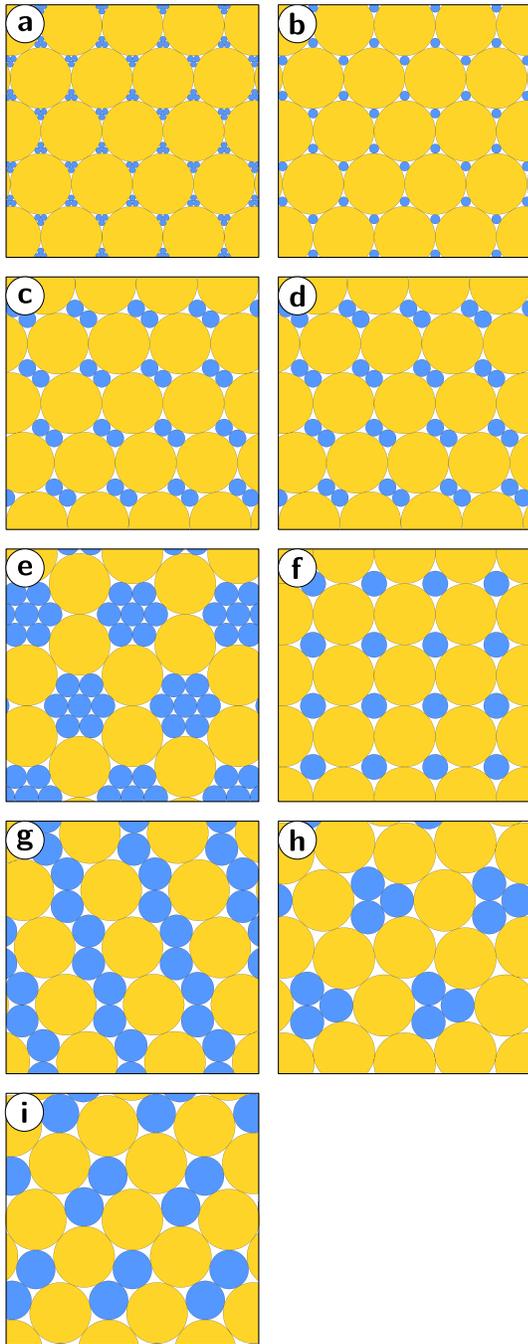
As soon as a surface is to be covered by elementary elements, the question of how to arrange the elements in relation to each other arises. Also, what shape, what symmetry, should these elements have in order to cover the surface perfectly, without any empty space, or with a controlled one? These kinds of questions are solved spontaneously when laying tiles or parquet, or when considering works of art, such as mosaic at Alhambra or graphic art of M. C. Escher, but are there general rules underlying such considerations? In mathematics, a tiling is defined as the covering of a surface, often a plane, using one or more geometric shapes with no overlaps and no gaps.<sup>1-3</sup> In the experimental world, the concept of packing is preferred, *i.e.* a set of non-overlapping objects (where gaps are allowed). If the objects have the capacity to move spontaneously, without the intervention of any external and intentional driving force, they can aggregate spontaneously to form assemblies, we speak then of self-assembly (SA). SA is a universal concept that can occur at all scales, from the molecular scale to the macroscale.<sup>4</sup> The aim of this perspective is to make connections between mathematical considerations and experimental SA, and to compare studies in different fields of research, from molecular chemistry and nanochemistry to granular physics. We will limit ourselves to the consideration of two-dimensional (2D) systems on substrates or interfaces. Tools for imaging exist at all scales in 2D thanks to adapted techniques, which facilitate comparisons. Four scales of interest will be chosen, which each correspond to different fields of research: the molecular scale (1 nm – 10 nm) with SA of molecules, the nanoscale (10 nm – 500 nm) with SA of nanoparticles, the microscale (500 nm – 1 mm) with SA of granular systems, and the macroscale (> 1 mm) as an ultimate extension of SA to bigger objects. First, we will briefly explain mathematical considerations on packing in 2D. Then, we will relate them to experimental compact SA with single component and binary systems, as well as porous SA. Finally, SA processes will be put into perspective in a discussion addressing quasiperiodic arrangements, structural defects, formation dynamics and tools to tune the SA, either internal (interaction potential) or external (force field or interaction with the substrate). Even if different scales, natures of objects, interactions, driving forces, and timescale of events are considered, global trends can be underlined from phenomenological behaviors. Establishing links between different fields of research opens up perspectives that could not have been imagined by staying in one's field of specialization. Here, we want to rationalize general concepts of SA, which occurs in any approach, and to make connections, conceptually, between facts, observations or problems that may have some similarities, even if they are encountered by independent scientific communities.

## Planar packing in mathematics, the case of compact packing

In mathematics, a *packing* is a set of non-overlapping objects. The fraction of the plane or the space covered by such objects defines the *density* of the packing. For example, the density of the hexagonal disk packing in 2D (disks centered on the hexagonal grid in the plane) is about 91%,<sup>5</sup> and the density of the hexagonal close packing (HCP) or cubic close packing (FCC) of spheres in 3D is about 74%.<sup>6</sup> 2D packings of disks are usually called *hard disk mixtures* in physics. A specific case is that of *compact packings*, which are packings of disks in the plane in the way that any hole between the disks is always bounded by exactly three disks. For example, the above-mentioned hexagonal disk packing is a compact packing, as well as the disk packings depicted in Figure 1, obtained by binary systems composed of disks of two different sizes. The constraint “being compact” is strong, and if the number of different sizes that the disks can have is fixed, then there is only a finite number of size ratios that allow a compact packing.<sup>7</sup> For example, with two sizes of disks, it has been demonstrated that there are only 9 possible ratios,<sup>8</sup> namely those depicted in Figure 1 (they already appeared in reference<sup>9</sup> except h). For three sizes of disks, there are only 164 possible ratios.<sup>5</sup> The notion of compact packing extends to sphere packings in 3D: a packing of spheres is compact if there are only tetrahedral sites. For example, HCP is not compact, but if we insert in each octahedral site of HCP a small sphere in contact with the six neighboring spheres, we then obtain a compact sphere packing.<sup>6</sup> Back in 2D, intuitively, a compact packing is a packing of disks such that the disks “arrange themselves well around each disk”, and one expects its density to be particularly high and therefore potentially favored during an experimental synthesis or SA. Indeed, the hexagonal compact packing is the densest among all the packings with disks of the same size.<sup>10</sup> Similarly, each of the 9 compact packings depicted in Figure 1 is, among the packings with two disks in the same size ratio, the densest one.<sup>11</sup> However, one should notice that the compact packings are not always the densest for more than three disk sizes.<sup>12</sup>

From a mathematical point of view, little has been proven beyond compact packing. Lower and upper bounds on the maximum density of disk packings are known for any ratio of two disk sizes.<sup>13</sup> As a particular case study, the densest packings have been characterized in the size ratio leading to the square lattice depicted in Figure 1f, when the stoichiometry of each type of disk is moreover imposed: an interesting transition occurs, depending on whether the disks in excess are the large ones (the densest packings then mix both disks in a rather uniform way) or the small ones (the densest packings then follow a phase separation: one phase is formed by equal proportions of large and small disks organized like the packing depicted in Figure 1f, while the remaining small disks form a second phase, organized in a hexagonal compact packing).<sup>14</sup> Beyond the mathematical point of view, simulations have provided a more complete picture of what the phase diagram of disk packings of two different sizes might look like, although apart

from the nine magic ratios, it is still an open mathematical problem to prove which is the densest structure for a given composition and size ratio.<sup>15</sup>



**Figure 1.** The nine possibilities that allowed a compact packing of a 2D plane with disks of two sizes: a)  $p = 6$ ,  $q \approx 0.10$ ; b)  $p = 2$ ,  $q \approx 0.15$ ; c)  $p = 2$ ,  $q \approx 0.28$ ; d)  $p = 6$ ,  $q \approx 0.34$ ; e)  $p = 3.5$ ,  $q \approx 0.38$ ; f)  $p = 1$ ,  $q \approx 0.41$ ; g)  $p = 2$ ,  $q \approx 0.53$ ; h)  $p = 1$ ,  $q \approx 0.54$ ; i)  $p = 1$ ,  $q \approx 0.63$ ; with  $p$  the number ratio and  $q$  the size ratio between the small and the large disks.

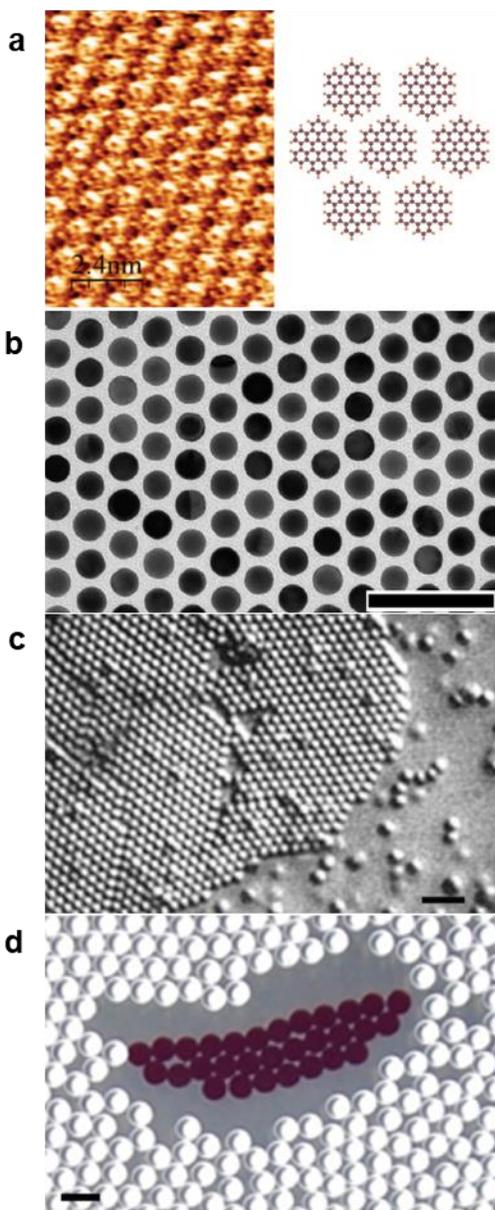
## Two-dimensional self-assembly: comparisons at four scales

SA is a phenomenon that spans several areas of research in chemistry. In molecular chemistry (1 – 10 nm), 2D SA is mostly studied using flat molecules on substrates. They can be assembled from solution either at the solid-air interface after the solvent evaporation, or directly at the solid-liquid interface. The experimental systems can also be prepared by chemical vapor deposition, electrospray, or sublimation. They are generally characterized by scanning probe microscopy, either scanning tunneling microscopy (STM) or atomic force microscopy (AFM). Such systems are called molecular or supramolecular networks, packings, lattices, or tilings. In nanochemistry (10 nm – 500 nm), 2D SA is made from nanoobjects dispersed in colloidal solutions. They are assembled during the solvent evaporation, either on a substrate or at the liquid-liquid interface between two immiscible solvents. They are generally characterized by electronic microscopy, either transmission electronic microscopy (TEM) or scanning electronic spectroscopy (SEM), and are also suitable for characterization by X-ray diffraction techniques, such as grazing incidence small angle X-ray scattering (GISAXS). SA of nanoparticles are called superlattices, supercrystals, *i.e.* crystals made of nanocrystals, or supracrystals. At the micron scale (500 nm – 1 mm), SA is formed from a suspension of micron-size particles dispersed in a solvent. They are generally confined between two glass slips, the spacing between the slips being adapted to produce a monolayer of the particles. They are characterized by optical microscopy and are called colloidal crystals. Finally, SA at the macro scale (> 1 mm) is more anecdotic, but can be good phenomenological models for microscopic behaviors.<sup>16–18</sup> It is obtained by shaking millimetric plastic objects on surfaces, or by floating them at a liquid-liquid interface. They are characterized by simple photography. As illustrations, we will detail four systems: compact SA with isotropic objects, compact SA with elongated objects, saturated SA with binary systems, and porous SA with single components.

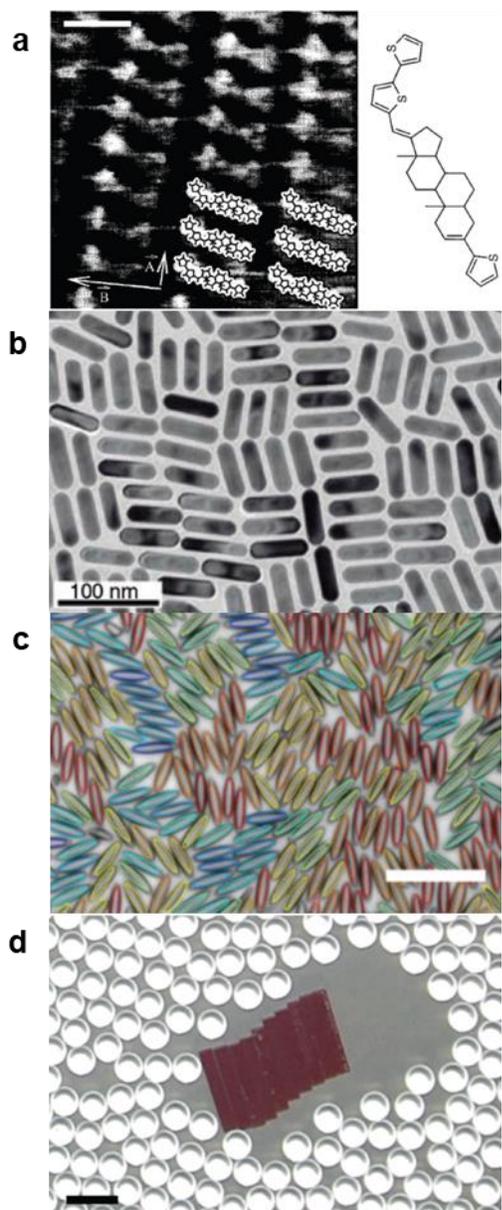
### *Compact SA with single components*

Compact SA offers compacity at least higher than the one of a hexagonal compact arrangement. When realized with single-component systems in 2D, and as soon as the building blocks have small aspect ratios – and are therefore assimilated to isotropic objects – a hexagonal packing is obtained. Even if such a hexagonal organization can be seen as extremely simple, it has been the scope of intense research at all scales. Figure 2 shows examples of compact SA with isotropic objects – spheres or disks: hexabenzocoronene at the molecular scale,<sup>19</sup> gold nanoparticles at the nanoscale,<sup>20</sup> polystyrene latex particle at the microscale,<sup>21</sup> and plastic disks at the macroscale. In this last example, the disks – which are the objects of interest – are dispersed in a bath of free spheres; the system is shaken by a randomized agitation and SA results from non-equilibrium phase separation.<sup>18,22</sup> At all scales, hexagonal arrangements are obtained, where a given object is surrounded by six other ones. As soon as the aspect ratio of the objects increases, they can no longer be considered as disks and the shape anisotropy raises the question of the object

orientation. Figure 3 reports examples of the ultimate case of rods, where one dimension of the objects is significantly higher than the other: oligothiophene steroid at the molecular scale,<sup>23</sup> gold nanorods at the nanoscale,<sup>24</sup> polystyrene ellipsoid particles at the microscale,<sup>25</sup> and plastic rectangles at the macroscale. In all cases, the objects aligned side-to-side. Most of the time, such an alignment is driven by favorable attractive interactions between the objects where side-to-side arrangement maximizes the contact between them. At the molecular scale, the most influential interactions are van der Waals interactions.<sup>26,27</sup> At the nanoscale, the same forces are considered,<sup>28</sup> both between the core of the nanoobjects, but also between the ligands that stabilize them.<sup>29</sup> In addition to attractive interactions, internal pressure should also be considered, as seen during the formation of nematic domains by increasing the density of microscopic systems.<sup>25</sup> Similarly, phase segregation in the macroscopic granular system causes a local pressure induced by shocks between the objects.<sup>22</sup> Then, the anisotropic building blocks will necessarily tend to align side-to-side to minimize the free space in the systems. Making compact SA is a way of obtaining well-organized systems, with regular distances and orientations between the building blocks. It is thus of particular interest to cover surfaces by dense monolayers forming regular patterns. On another hand, it can also be a simple mean for the study of collective behaviors between objects that interact with each other.



**Figure 2.** Compact self-assembly with isotropic objects: spheres/disks. a) molecular scale: hexabenzocoronenes – scale bar: 2.4 nm,<sup>19</sup> b) nanoscale: gold nanoparticles – scale bar: 100 nm,<sup>20</sup> c) microscale: polystyrene latex particles – scale bar: 5  $\mu\text{m}$ ,<sup>21</sup> d) macroscale: plastic disks (red) in a bath of spheres (white) – scale bar: 1 cm. Adapted with permission from: ref 19 Copyright 2012 IOP, ref 20 Copyright 2020 Wiley-VCH, ref 21 Copyright 1999 AAAS.

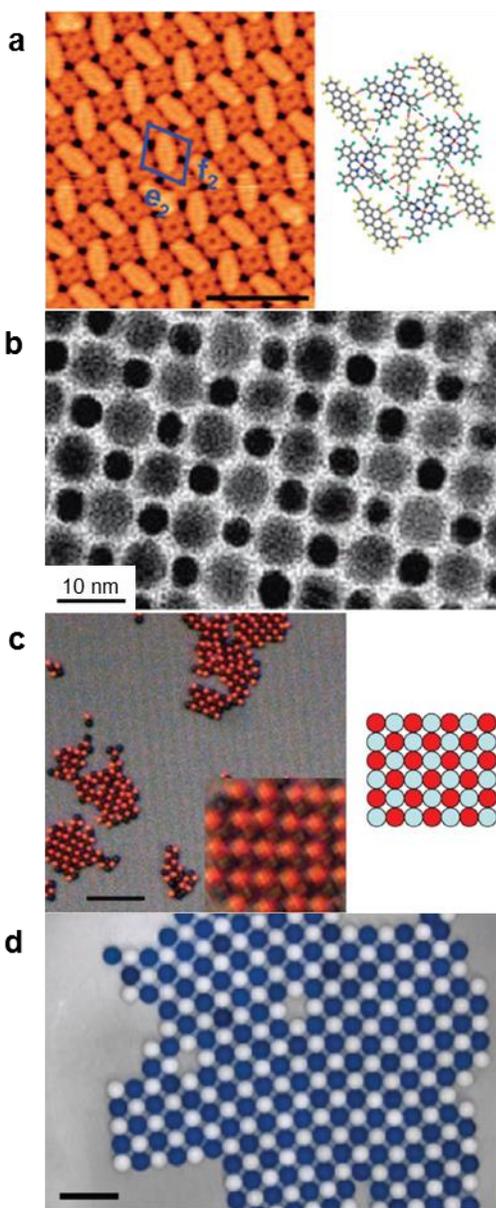


**Figure 3.** Compact self-assembly with elongated objects: rods. a) molecular scale: oligothiophene steroids – scale bar: 2 nm,<sup>23</sup> b) nanoscale: gold nanorods – scale bar: 100 nm,<sup>24</sup> c) microscale: polystyrene ellipsoid particles – scale bar: 20  $\mu\text{m}$ ,<sup>25</sup> d) macroscale: plastic rectangles (red) in a bath of spheres (white)– scale bar: 1 cm. Adapted with permission from: ref 23 Copyright 1999 Wiley-VCH, ref 24 Copyright 2017 AAAS, ref 25 Copyright 2021 RSC.

### *Saturated SA with binary systems*

For the scope of this perspective, we have chosen to define a packing as saturated when the free spaces between the building blocks are too small to accommodate a new one. On the contrary, if the free spaces are large enough to host a new object, the packing is defined as porous. All the compact systems described above are thus saturated according to this definition. Binary systems are composed of two types of components, different either by the size or by the composition, uniformly mixed – we exclude the case of phase segregation. The consideration of binary systems brings an important complexity in the possibility of arrangements. For example, we have explained above there is only one possibility of compact packing of disks with a single component system, whereas there are nine possibilities with a binary system. Looking at other saturated – non-compact – binary systems, the number of possible arrangements explode. However, if we look closer at the interactions between the elements of a binary systems, called A and B, three main configurations can happen: 1/ repulsive interactions between all the elements, 2/ attractive interactions between all the them, 3/ attractive interactions between A / B but repulsive between A / A and B / B. Case 1/ can be set aside because no stable static SA will occur if all the building blocks repel each other. Both case 2/ and case 3/ can lead to binary SA. In case 2/ A (respectively B) can touch A and B indifferently. When all the interactions are similarly attractive, SA will tend to form compact packing, to minimize the free energy of the system. The situation where A and B have the same size lead to system randomly distributed as there is no way to differentiate A from B during the SA process. If A and B have different sizes, compact packing occurs if the size ratios fit the nine possibilities detailed in Figure 1. These ratios are strict, as phase segregation occurs rapidly if one deviates from them.<sup>13</sup> That is why the control of the average size and the size dispersion is crucial to obtain binary SA. Considerations on size dispersion are meaningless with molecules as they are identical. Size dispersion is negligible at the micro and macro scale as the processes of fabrication are precise. It is however a critical issue at the nanoscale, where variations of few atomic layers will be significant compared to the size of the objects. It is commonly admitted that the size dispersion should be less than 10 % to obtain good SA. For hard inorganic nanoparticles, the size dispersion of the core is compensated by the adaptability of the soft shell of ligands. As examples of compact structures, Paik et al. reported four of the nine binary systems, by realizing SA of nanodisks (namely systems c, d, f and i in Figure 1).<sup>30</sup> In case 3/ when interactions are attractive between A / B but repulsive between A / A and B / B, A (respectively B) can touch only B (respectively A) but cannot touch A (respectively B) within the SA. Competition between attractive and repulsive forces thus leads to specific binary structures that are not necessarily compact. Most common examples are based on objects that can be negatively or positively charged. Some reports of structures stabilized by differential magnetic interactions are also documented.<sup>31</sup> Finally, the last option to form binary SA is to use building blocks with directional interactions, such as hydrogen or coordination bonds at the molecular scale.<sup>32,33</sup> As examples, Figure 4 reports pictures of binary

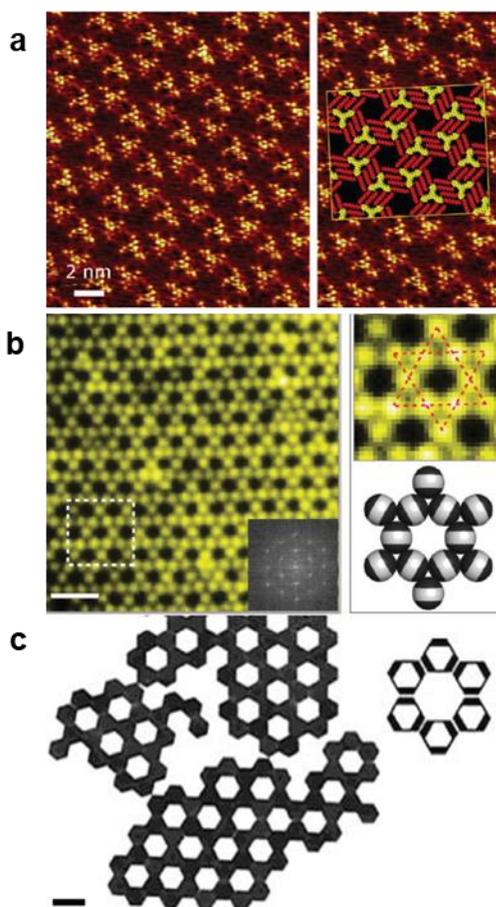
systems organized in structures that alternate the two components in square lattices. Each element A (respectively B) occupies a square site formed by the lattice of the B (respectively A) elements. At the molecular scale, phthalocyanine and perylene formed SA through the formation of directional intermolecular C-F...H-C hydrogen bonds.<sup>34</sup> At the nanoscale, PbSe and Au nanoparticles interacted through attractive van der Waals interactions to form the compact SA represented in Figure 1f.<sup>35</sup> At the microscale, Ising interactions between spherical magnetic and non-magnetic beads, which behave as paramagnetic or diamagnetic dipoles when immersed in a ferrofluid, led to intricate square lattices.<sup>31</sup> Finally, at the macroscale, plastics beads positively and negatively charged by tribocharging formed square binary lattices.<sup>36</sup> In the last two examples, no contact occurs between components of the same nature. Beyond SA in square lattice, the stoichiometry between components A and B can vary, both for compact packing (Figure 1) and for competing attractive and repulsive interactions (adapting the number of the building blocks or of their relative charge, in the case of charged objects). Making binary systems is an efficient strategy to obtain organized structures that combine the properties of each component.<sup>37</sup> For example, at the nanoscale, SA can be a tool to make structures where energy is transferred from fluorescent CdSe nanoparticles to Au nanoparticles.<sup>38</sup> Tuning the structure of the SA can also be a way to tune the final properties of the obtained system. For example, magneto-transport properties were modified depending if 11-nm Fe<sub>3</sub>O<sub>4</sub> and 4.5-nm FePt nanoparticles formed binary AlB<sub>2</sub> or ico-AB<sub>13</sub> structures.<sup>39</sup> Finally, another interest of binary structures is to use them as templates for lacunar organization, provided that one type of object can be removed but not the other. Such a strategy has been successfully used for selective removal of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, while letting Au nanoparticles intact.<sup>40</sup>



**Figure 4.** Non-compact self-assembly with binary systems, example of alternance of the two components in square lattices: a) molecular scale: phthalocyanine and perylene – scale bar: 5 nm,<sup>34</sup> b) nanoscale: PbSe and Au nano-particles – scale bar: 10 nm,<sup>35</sup> c) microscale: magnetic and non-magnetic particles – scale bar: 10 μm,<sup>31</sup> d) macroscale: positively and negatively charged plastics beads – scale bar: 1 cm.<sup>36</sup> Adapted with permission from: ref 31 Copyright 2012 Springer Nature, ref 34 Copyright 2010 Wiley-VCH, ref 35 Copyright 2006 ACS, ref 36 Copyright 2012 RSC.

### *Porous SA with single components*

The binary systems presented so far were made by construction, but one can imagine the elaboration of a structure made of a single component where a second element could be added on demand. To do so, it is first necessary to elaborate single component porous SA, *i.e.* SA with free cavities in the same size range as the building blocks. In order to obtain porous SA, whatever the form of the object itself is anisotropic or not, anisotropy must be present in the structure to form directional interactions between the building blocks.<sup>41</sup> Figure 5 reports three examples of porous SA with single components. At the molecular scale, the threefold symmetry of tristylbene led to a honeycomb network on highly ordered pyrolytic graphite (HOPG) thanks to van der Waals interactions between well oriented alkyl chains.<sup>42</sup> At the microscale, polystyrene spheres decorated on opposite poles by gold led to Kagome lattices thanks to directional interactions: electrostatic repulsion in the middle and hydrophobic attraction at the poles formed threefold local contacts between the twofold decorated building blocks.<sup>43</sup> Finally, at the macroscale, a honeycomb lattice has been obtained by mixing anisotropic hexagonal plates floating at a perfluorodecalin / interface.<sup>44</sup> There, capillary forces differentiated the interactions between hydrophobic and hydrophilic faces, and a honeycomb structure was obtained thanks to twofold interactions between objects with a threefold symmetry. To our knowledge, there is still no example of 2D-porous SA at the nanoscale. Indeed, even if several studies report SA of anisotropic objects, they generally describe saturated SA.<sup>45,46</sup> The big challenge of the field is to synthesize shaped nanoobjects that form directional interactions at the nanoscale. A strategy can be to organize the ligand arrangement at the surface of the nanoparticles, to form patchy particles.<sup>47</sup> Such anisotropic functionalization of nanoobjects has already been reported, *e.g.* on nanorods by differential functionalization of different crystalline face,<sup>48</sup> on isotropic nanoparticles by phase segregation of ligands at their surface or by differential densities,<sup>49,50</sup> or even on triangular gold nanoparticles by asymmetric polymer grafting on the apexes,<sup>51</sup> but no well-organized 2D porous arrays have been reported with these systems. There is therefore a clear space for research in this perspective. Predicting the shape and the anisotropic functionalization of the building blocks is however not sufficient to predict the final structure of the SA, as they can arrange in several ways, such as honeycomb *vs.* hexagonal packing with triangular molecular units.<sup>52</sup> An interest of making 2D porous SA is to use them as host systems, *e.g.* as a matrix for organizing functional guests,<sup>53-55</sup> as a tool for size segregation between different hosts,<sup>56</sup> or as a scaffold for *in-situ* reactions.<sup>57</sup>

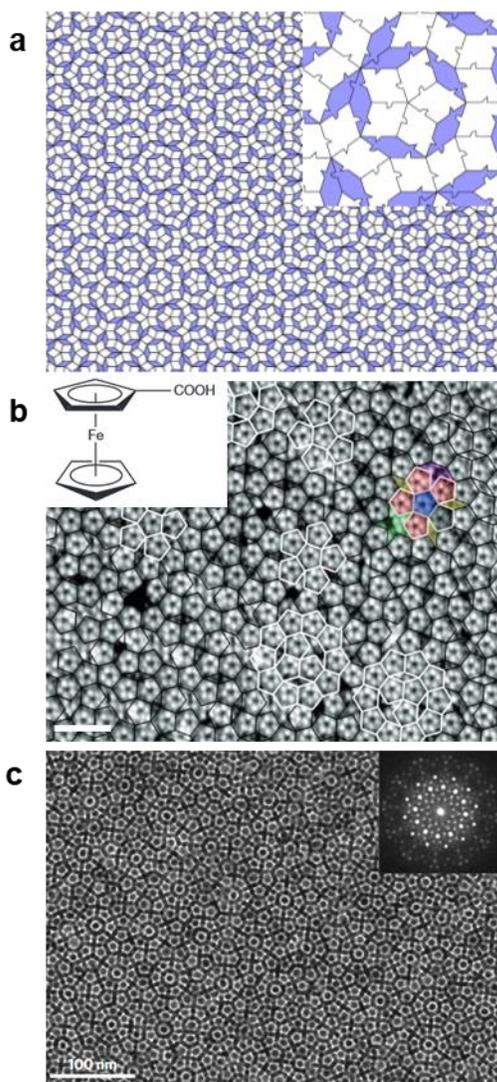


**Figure 5.** Porous self-assembly with single components. a) molecular scale: tristyrene – scale bar: 2 nm,<sup>42</sup> b) microscale: hydrophobic/hydrophilic Janus spheres – scale bar: 4 mm,<sup>43</sup> c) macroscale: hydrophobic/hydrophilic plates – scale bar: 1 cm.<sup>44</sup> Adapted with permission from: ref 42 Copyright 2007 Wiley-VCH, ref 43 Copyright 2011 Springer Nature, ref 44 Copyright 2000 ACS.

## Discussion

### *Complexifying 2D assemblies*

All the 2D SA presented so far are periodic, *i.e.* which recurs at regular intervals. They are invariant by translation. However, plane packing can be realized by more complex features, such as fractal patterns, “exactly the same at every scale or nearly the same at different scales,” as defined by Benoit B. Mandelbrot.<sup>58</sup> For example, fractal patterns have been successfully obtained thanks to synergistic halogen and hydrogen bonds between two aromatic bromo compounds,<sup>59</sup> or thanks to coordination of cyano molecules to Fe atoms.<sup>60</sup> By construction, fractals show scale invariance. If we want to consider a saturated but non-periodic packing with scale invariance, we must look at the quasiperiodic packing. Quasiperiodic packing is not periodic as it is not invariant by translation, but still shows some order, as any pattern of the packing ends up reappearing everywhere. That is why a Fourier transform of a quasiperiodic packing image displays a defined pattern. The Penrose tiling is the best-known examples of quasiperiodic packing (Figure 6a).<sup>61</sup> By combination of two kinds of tiles, it exhibits a fivefold symmetry. Considering quasiperiodic tiling, one should make the difference between “it is possible to pave non-periodically” and “the only way to pave is to pave aperiodically”. Indeed, the ingenuity of Penrose was to induce a local constraint of the tiles (defining asymmetrical notches on the edges of the tiles as seen in the inset of Figure 6a in order to force a global property of the assembly (a five-fold quasiperiodic arrangement). Figure 6b and c show examples of quasiperiodic systems obtained both at the molecular scale with an assembly of ferrocenecarboxylic acid,<sup>62</sup> or at the nanoscale with a binary assembly of 6.2 nm FePt and 11.5 nm Fe<sub>3</sub>O<sub>4</sub> nanocrystals.<sup>63</sup> Most of the time in experimental systems, periodic and aperiodic SA coexist. Even if the description of quasiperiodic systems is very stimulating, they are obtained more by chance than by design, as it is still very difficult to control the local rules to obtain a quasiperiodic arrangement experimentally (whereas simple algorithms have shown this feasibility in mathematical simulations).<sup>64</sup> This is especially true when quasiperiodic systems are realized using single component systems.<sup>65</sup> Indeed, the question of whether there is a single tile that paves non-periodically is still considered as open mathematically; the biggest advance in this direction is the so-called Socolar-Taylor tile,<sup>66</sup> and it is still subject of debate. In addition, even more for quasiperiodic SA than for periodic SA, the presence and correction of defects is of primary importance.



**Figure 6.** Quasiperiodic structures. a) Penrose tiling (inset: zoom showing the non-symmetric character of the tiles), and quasicrystalline self-assemblies: b) molecular scale: assembly of ferrocenecarboxylic acid – scale bar: 5 nm,<sup>62</sup> c) nanoscale: binary assembly of 6.2 nm FePt and 11.5 nm Fe<sub>3</sub>O<sub>4</sub> nanocrystals – scale bar: 50 nm.<sup>63</sup> Adapted with permission from: ref 62 Copyright 2014 Springer Nature, ref 63 Copyright 2017 Springer Nature.

## *Errors and defects*

In experimental systems, errors of packing or the presence of defects always end up during the SA process. Two scenarios of trials and errors can be considered for SA. First, SA development can occur in a nucleation and growth process, similar to that of crystal or quasicrystal formation, in which building blocks are added and organized one by one on a pre-formed nucleus.<sup>67</sup> For compact packing of isotropic objects, the mechanism is trivial, but a dynamic exchange becomes necessary when a building block should be replaced by another as *e.g.* in binary systems, or should be reoriented as *e.g.* in quasiperiodic SA. A bad local packing will create a defect, either local or which can be propagated. Second, another mechanism can be a global prearrangement of the building blocks in a prenucleation state, where they interact with each other without any precise relative position and orientation. The final SA occurs within such a preformed system, as observed with atomic species for the formation of gold ultra-small nanoparticles.<sup>68</sup> Here too, defects can be included in the final structure. In both cases, mechanisms of defect repair are possible, either by local reorganization of the building blocks or by global annealing (either thermic, or by solvent vapors).<sup>69,70</sup> Relaxations processes then tend to stabilize the system by “flipping” – reorganizing – the building blocks in a pre-organized assembly, as was theoretically detailed.<sup>71</sup> The nature of defects in SA is similar to the ones described for classical crystals. For example, random tiling and topological defects have been described in a molecular network,<sup>72</sup> edge dislocation, stacking faults, grain boundaries, as well as point defects have been observed in nanoparticle supercrystal.<sup>73,74</sup>

## *Dynamics of formation*

In the scope of this perspective, we do not consider dynamic SA, *i.e.* SA that occurs if the system is dissipating energy, but only static SA, *i.e.* SA that forms as the system approaches equilibrium, reducing its free energy. However, to reach such an equilibrium experimentally, the building blocks have to move and reorganize from each other, in a trial-and-error process. A competition between an aleatory movement of the building blocks and some ordering driving forces is thus necessary in all SA process. At the molecular, nano, and microscale, aleatory movement is provided by Brownian motion, whereas at the macroscale, whether the shaking is random or not,<sup>16</sup> chocks between the elements are the primary source of aleatory events. When the objects are not self-propelled – which leads to dynamical SA,<sup>75,76</sup> the motion is ensured by the random agitation of the surrounding environment. In order to form SA, the building blocks must somehow come together and arrange themselves in relation to each other. Even if some examples report SA without attractive interactions,<sup>22</sup> most of the time, attractive forces brings the elements in proximity to each other.<sup>77</sup> When they are close to each other, repulsive forces prevent the elements to merge. Even if the nature of such attractive and repulsive forces is fundamentally different at each scale, basic principles remain

constant. First, the balance between attraction and repulsion should be equilibrated.<sup>28</sup> Indeed, if the repulsion is too strong, the system never assembles. On the contrary, if the attraction is too strong, the system jams without any organization.<sup>78</sup> Second, attraction and repulsion should be in the same energy range as the kinetic energy of the objects. Otherwise, the trial-and-error process could not occur and the system would not organize. Finally, for practical reasons, the time of SA should stay in reasonable ranges for conducting experiments. Typical times are few seconds for SA of molecules at a liquid-substrate interface, few hours for SA of nanoparticles at a liquid-liquid interface, few minutes for SA of microparticles between two glass slides, and between few minutes and few hours for SA at the macroscale.

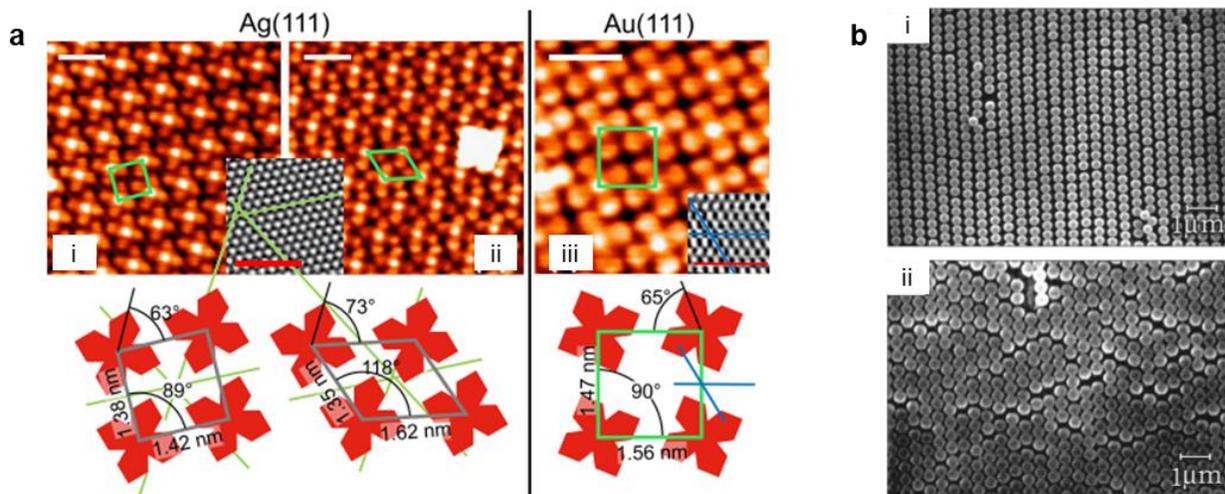
### *Tuning the interaction potential*

As chemists, the primary tool for controlling SA is the design of the building blocks and of their interactions. For example at the molecular scale, the geometric and chemical nature of the porphyrin substituents that mediate the interactions between individual adsorbed molecules allows a controlled formation of monomers, trimers, tetramers or extended wire-like structures.<sup>79</sup> For 2D SA, various interactions must be taken into account: adsorbate-substrate interactions governing adsorption sites, adsorbate-adsorbate interactions favoring close packing, and steric hindrance inhibiting certain otherwise energetically beneficial molecular arrangements.<sup>80</sup> In addition, competition between various parameters may favor an organization over another and may lead to a phase transition within the same system. For example at the molecular scale, the final structure can be influenced by temperature,<sup>81</sup> surface defects,<sup>82</sup> concentration,<sup>83,52</sup> or force competition.<sup>84</sup> At the nanoscale, the ratio between the core radius and the ligand chain length is an efficient tool to control the final structure of binary nanocrystal superlattices.<sup>85</sup> On another hand, computer simulations shown that a tuning of structural descriptors, such as pressure, compressibility, or diffusion coefficients can lead to a rich phase diagrams where hexagonal, rhomboid, honeycomb and stripe phases as well as hierarchical self-assembly coexist,<sup>86</sup> as well as quasicrystals.<sup>87</sup>

### *Driving the SA by external parameters*

External parameters can have a drastic influence on the SA process and the final structure. First, the substrate on which the SA is conducted is far to be innocent, either because of its chemical nature that tunes the interactions with the building blocks,<sup>88</sup> or because of some pre-patterning. Figure 7 reports two examples of substrate effects: at the molecular scale, ruthenium phthalocyanines form square and hexagonal structures on gold, whereas they form square structures only on silver;<sup>89</sup> at the microscale, polystyrene colloidal spheres form 1D stripe structure, or 2D centered-rectangular lattice, depending on the ratio between the

diameter of the sphere and the period of the grating of the patterned substrates.<sup>90</sup> With molecular systems, the surface can also be reactive, and *e.g.* can provide nonbonded adatoms that will embed in the molecular array.<sup>91</sup> For some systems, it is the epitaxy on the substrate that drives the 2D SA; in the absence of the substrate, it is then shown that such a superstructuration is unlikely to be stable.<sup>92</sup> Besides, 2D SA can be stabilized on some substrate, but not on others, depending on the relative strength of adsorption energy.<sup>93</sup> On the other hand, at the nanoscale and micro scale, the use of external fields can help to improve the overall organization and minimize defects, as *e.g.* electrical field,<sup>94</sup> magnetic field,<sup>25</sup> dielectrophoresis,<sup>95</sup> or magnetophoresis.<sup>96</sup> Indeed, independent objects that respond similarly to an external excitation are collectively influenced by a directed driving force that pushes them to order, in competition with the randomization induced by Brownian motion.



**Figure 7.** Influence of substrate on the self-assembly of isotropic objects. a) molecular scale: ruthenium phthalocyanine on metal surface, the structure depends on the chemical nature of the surface: i, ii, on gold, formation of square and hexagonal structures ; iii, on silver, formation of square structures only – scale bars: 2 nm,<sup>89</sup> b) microscale: polystyrene colloidal spheres on patterned substrates, the structures strongly depend on the ratio between the diameter of the sphere  $d$  and the period of the grating  $p$ : i, 1D stripe structure,  $d/p = 0.74$ ; ii, 2D centered-rectangular lattice,  $d/p = 1.05$  – scale bars: 1  $\mu\text{m}$ .<sup>90</sup> Adapted with permission from: ref 89 Copyright 2020 ACS, ref 90 Copyright 2001 AIP.

## Conclusion

In this perspective, after describing planar packing in mathematics, we considered specific descriptions of compact, saturated binary and porous self-assemblies at the molecular, nano, micro and macro scales. We noticed that no example of 2D porous SA has been reported at the nanoscale, because of the difficulty to synthesize and assemble nanoobjects with anisotropic decoration. Chemists thus do not fully control plane packing, *i.e.* two-dimensional self-assembly, at all scales, yet. Succeeding in realizing such SA would thus be of primary importance towards the elaboration of hierarchical superstructures at the nanoscale on substrates. Research efforts should then be directed toward the two main reported porous structures, namely the honeycomb structure with twofold interactions between threefold symmetry objects, and the Kagome network with threefold local contacts between twofold symmetry building blocks. Regardless of scale, general considerations run through 2D SA: the formation of more complex systems such as quasiperiodic stacking, the importance of defects and formation dynamics, which combine competition between attractive and repulsive interactions and random motion, and the means of tuning these interactions through building block design, or through the use of external driving forces. The organization of a repetitive pattern in 2D is of interest for various fields of application, as for example plasmonics,<sup>97</sup> strain gauges,<sup>98</sup> or surface patterning.<sup>99</sup> SA is also a tool towards the elaboration of complex systems, like binary systems that combine two properties (*e.g.* hyperthermia and catalysis, charge transport and luminescence), porous systems that can host guest molecules (*e.g.* for gas storage or sensors applications). Finally, this perspective reports works from four different communities, which work at four different scale ranges. Each of them corresponds to different natures of objects, of characterization techniques, implying different conceptual and experimental problems. But all of them tackle similar questions on SA, thus soliciting similar concepts. Drawing inspiration from other communities can be helpful in broadening the scope of thinking. Moreover, the rationalization of plane packing has been widely studied in mathematics, by specialists in geometric tiling. This is why we think it is essential to be interested in other areas of research and to understand the problems of others and how to solve them. We are convinced that a multidisciplinary culture, and interactions between actors from different fields, will be beneficial to solve the challenges of today's science.

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