Recent Concepts for Supramolecular 2D Materials

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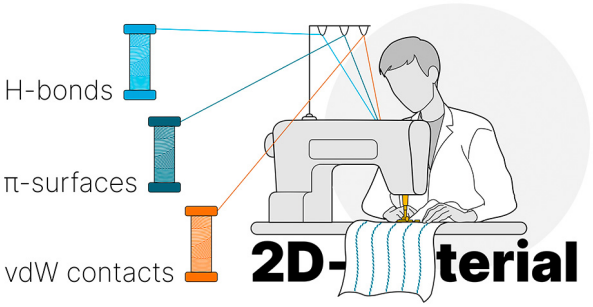

Received: 02.07.2022
Accepted after revision: 25.08.2022
DOI: 10.1055/a-1932-0463; Art ID: OM-2022-07-0017-SR

Abstract Bottom-up approaches are one strategy geared towards designing novel two-dimensional materials. Supramolecular polymerization has proven to be an effective way of obtaining these architectures due to the increasing control and tunability offered by different functional groups, which are not afforded by conventional polymerization. In this short review, we highlight examples of supramolecular assemblies held together by well-known non-covalent interactions, as well as new approaches that are becoming more relevant in recent years.

Key words: two-dimensional materials, supramolecular polymers, hydrogen bonding, π–π interactions, hydrophobicity, curvature

Introduction

Two-dimensional (2D) materials are a tantalizing area of research for materials scientists because of their potential applications in next-generation electronics, sensors and photovoltaics.[1] Interest in these systems arises from, amongst others, their large surface/volume ratio and tunable band gap, making them suitable candidates for energy storage and transport.[2] The ability to interact with light and to carry charge, as well as their thinness, offers potential to efficiently harvest energy, prompting appeal to photovoltaics.[3] 2D porous materials have shown capability to act as sensors and catalysts, allowing for specific adsorption of different guests on their thin surfaces.[4]

However, creating large, defect-free 2D lattices suitable for these purposes is nearly impossible. Graphene is a system that came close with its discovery in 2004 (Nobel prize 2010).[5] This landmark achievement was the result of a top-down approach where simple exfoliation of graphite yielded a single layer of covalently linked, conjugated carbon atoms.[5b] However, graphene cannot easily be modified – chemical changes occur randomly, if they occur at all – and its covalent build-up from smaller fragments remains challenging. Supramolecular approaches are a possible alternative,[6] where tailored fragments are made to assemble through weaker interaction forces rather than via the carbon–carbon bond. Early supramolecular materials used the hydrogen bond,[7] a particularly powerful tool, which showcased the reversibility and tunability of the formed polymers that is not achievable with regular covalently linked polymers.[8] These same interactions were then used to create soft 2D materials, where the directional nature of the hydrogen bond guides the assembly. Similar strides were made in the field of metal–organic frameworks, where incorporating directional coordination bonds between the metal and the ligand yielded thin 2D layers,[9,1e] although the suppression of layer-by-layer growth in the third dimension remains a challenge to this day. Despite the clear design approach, it is often not a sole interaction that drives the assembly, but a combination of several interactions, which leaves much room for serendipity. Within this short review, we detail recent conceptual approaches in hydrogen-bonded systems that have resulted in 2D supramolecular assemblies, as well as a brief overview of design principles that have succeeded in overcoming the necessity for strong directional interactions in such architectures.

Highly Directional Interactions

One of the most common methods to facilitate an assembly is to use monomers with components possessing strong dipoles that are therefore capable of sustaining a prolonged interaction between one another. This mandates that the interaction originates from specific sites within the monomer, acting as a focal point for the polymerization mechanism. Consequently, there is a clear preference for directionality

Biosketches

Lucía Gallego studied chemistry at the University of Zaragoza, where she worked with Prof. Santiago Franco on new organic dyes for Dye-Sensitized Solar Cells as a fellow of the Institute of Science of Materials of Aragón (ICMA). She then did her MSc studies in Organic Chemistry at the Autonoma University of Madrid, under the supervision of Prof. M. Victoria Martínez-Díaz and Prof. Tomás Torres, where she worked on new curved aromatic photosensitizers for Photodynamic Therapy. After this, she joined the lab of Dr. Michel Rickhaus at the University of Zurich where she is carrying out her PhD studies on exploring the reactivity and self-assembling properties of saddle-shaped compounds.

Joseph F. Woods studied chemistry (MChem) at the University of Oxford from 2015 to 2019 and spent a year in the group of Prof. Harry L. Anderson working on polyyne rotaxane chemistry leading towards new carbon allotropes. After graduating, he joined the group of Dr. Michel Rickhaus at the University of Zurich as a PhD student where he is currently investigating supramolecular assemblies of simple organic compounds with a particular focus on how shape can play a role in such systems.

Michel Rickhaus received his Master's degree in Organic Chemistry from the University of Basel. During that time, he was working with Prof. Lawrence T. Scott in Boston College as a visiting scholar, before beginning his PhD studies with Prof. Marcel Mayor at the University of Basel where he worked on helical polyaromatics. He then joined Dr. med. Johannes Beck as a research associate (Swiss Civil Service) working on depression predictors in sleep stages. From 2016 to 2019, Michel was an SNSF-funded postdoctoral researcher at Oxford University with Prof. Harry L. Anderson investigating non-planar π-conjugation in porphyrin rings and related topologies. In August 2019, Michel started his independent research career as group leader (SNSF Ambizione) at the University of Zurich and together with his team currently investigates the role of molecular topography in self-assembled systems.

through donor and acceptor components. It is well documented that not all types of non-covalent interactions are similar in strength and, although difficult to quantify, we may single out hydrogen bonding due to its highly directional nature.[10] Coordination bonds are another outstanding example of these strong directional interactions, but we see them outside the scope of this short review.

Hydrogen Bonding

In 2020, Montenegro et al. reported the assembly of a macrocyclic peptide that forms 2D layers in water by using a strategy where hydrogen bonding is supplemented by weaker interactions.[11] Initially, a one-dimensional (1D) assembly occurs, forming hollow columns of alternating D/L stacked monomers held together through hydrogen bonding between the residues. The conformation of the individual nanotubes is rigidified by complementary π–π interactions between tryptophan residues that allow alignment of the entire tube. Leucine residues flank the tryptophan and promote inter-tube hydrogen bonding, which generates a tertiary sheet structure in solution. The hydrophobicity of tryptophan is then used to create a flattened 2D sheet where the residue is buried within the structure to reduce exposure to the aqueous environment, resulting in the formation of thin sheets of lengths greater than 100 µm and with consistent thicknesses of 3.2 nm. This shows that combining hydrogen bonding with hydrophobicity is a potent method to create rigid, flat structures following a 1D-to-2D self-assembly approach (Figure 1).

A less elaborate example of building 2D sheets using a combination of hydrogen bonding and hydrophobicity was reported by Stevens and co-workers using linear instead of cyclic peptides (Figure 2).[12] Hydrogen bonding between phenylalanine groups occurs to knit the structure together in two dimensions, which allows for direct 2D assembly as there is no directional preference for interaction between rods within the plane of the sheet. By incorporating an alkyl chain which is linked to a phenylalanine segment, the pep-

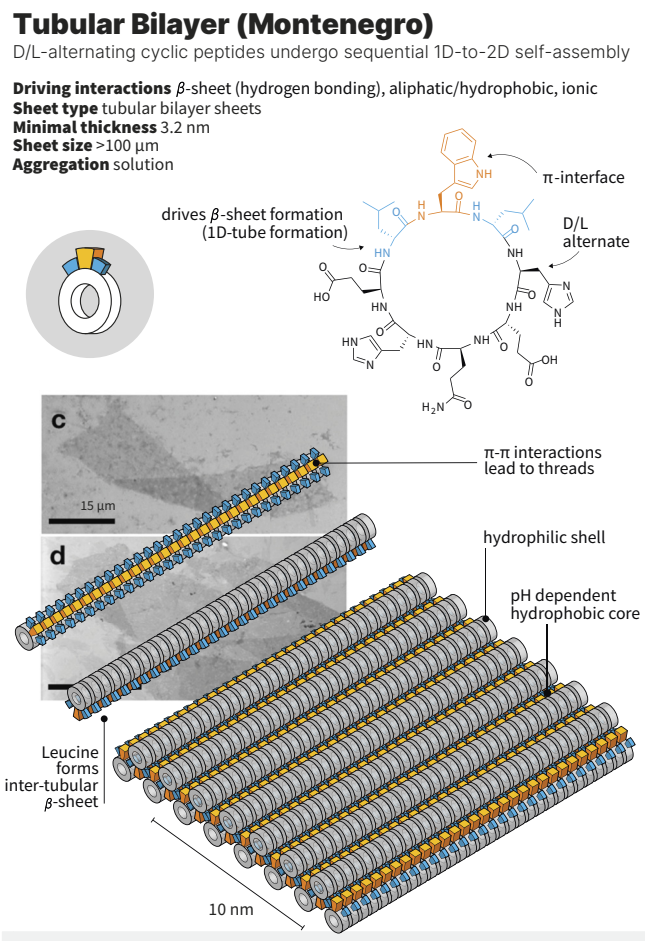

Figure 1 Schematic representation of a tubular bilayer reported by Montenegro et al. in which D/L-alternating peptides undergo one-dimensional self-assembly into hollow amphiphilic nanotubes that subsequently form tubular bilayer sheets through inter-tube hydrogen bonding. STEM images reprinted with permission from Ref. 11. Copyright 2020 American Chemical Society.

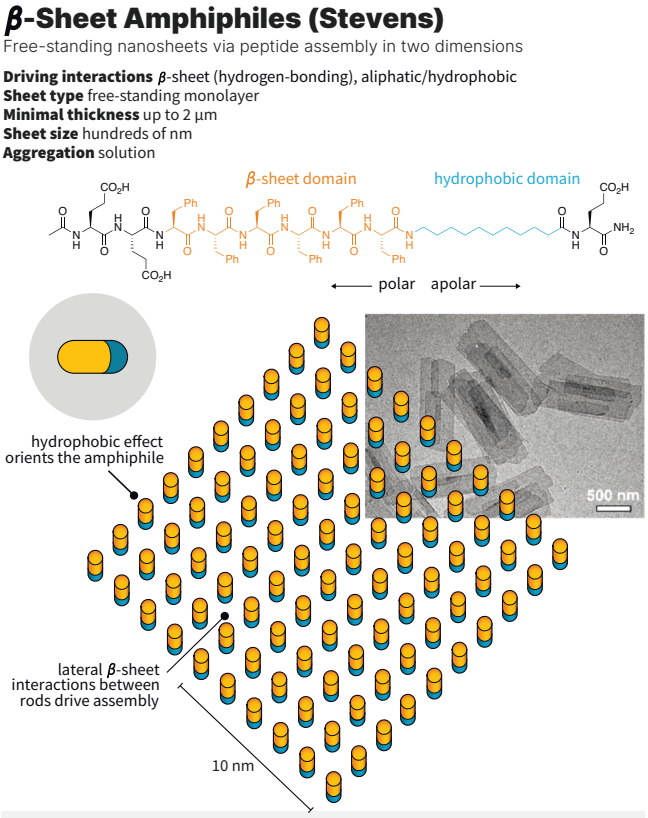

Figure 2 Schematic representation of free-standing nanosheets formed via hydrogen-bonded peptide assembly in two dimensions supplemented by hydrophobic effects from aliphatic chains. TEM image reprinted from Ref. 12 published under a creative commons licence (CC BY).

tides undergo self-sorting in the assembly process where separation based upon hydrophobicity occurs, providing single-layer sheets of micrometer length and with thicknesses of approximately 5 nm. Furthermore, the acyclic nature of the monomer allows for functionalization of the sheets from the respective N- or C-termini, increasing the potential application of the created surface in fields such as catalysis, drug delivery and sensing.

Work from De Yoreo's group has further shown that peptides are a strong choice for 2D assemblies.[13] A peptide containing seven amino acid residues acylated at the N-termini and amidated at the C-termini with high binding affinity to MoS_2 assembles when incubated on this inorganic surface. Sheets of 0.7 nm thickness and 1 μm in length are formed and appear to have a bias of direction for assembly that can be explained by their affinity to sulfur. The peptides first form dimers through hydrogen bond pairing at the C-terminus, which are then propagated through further hydrogen bonding and van der Waals interactions between internal residues of the dimers to form a 2D assembly. These sheets orient preferentially in three directions within the plane of the MoS_2 surface with an offset of 60° between one another, which relates to the densest sulfur packing axes of the MoS_2. In contrast to the previous example, peptides align themselves parallel to the surface to maximize association with sulfur and between one another.

Following a more generalized approach, Li et al. reported in 2021 that a hydrogen-bonded organic framework (HOF) can assemble to create layers with micrometer dimensions and a thickness of around 1 nm.[14] A double imidization reaction on a napthalenic dianhydride with two diaminotriazoles forms imide monomers, which can then self-assemble in solution through hydrogen bonding. The network is propagated through free amino groups on the triazole moiety interacting with the carbonyl groups on the naphthalenes, showcasing the importance of the repeating unit structure. Like many hydrogen-bonded structures, treatment with a strong acid or base disassembles the HOF into its monomers, highlighting the reversibility of these non-covalent interactions. The sheets are reinforced with π–π in-

teractions between the naphthalene groups to generate thin layers.

Weaker Interaction Modes

Unlike strong directional interactions, which originate from a specific site, weaker interactions arise from a fragment within the molecule and often have a lower directionality than hydrogen bonding. This results in a less defined conformation of assembly and a weaker association across the structure due to the variability in constituency. Thus, these approaches are often labelled as non-conventional methods for self-assembly as they usually rely more on cooperative forces that emerge as a function of the tertiary structure or the environment, lacking the strength to hold together suprastructures.

However, recent advances in supramolecular chemistry, illustrated by the examples included in this short review, showcase 1D and 2D supramolecular structures formed from monomers that have to date not been classical choices for self-assemblies.

Preorganized π–π Interactions

Molecules with an abundance of π-electrons can interact with one another to provide a driving force for assembly, usually in tandem with another weak interaction. Whilst we acknowledge that the strength of these interactions is size-dependent and may not always be sufficient to be termed as "π–π interaction", we include π-systems of any size that exhibit coplanar arrangement in this section of the review.[15] Preorganization of the monomers via covalent bonding to a rigid backbone that holds the π-surfaces in close proximity can greatly contribute to a successful assembly, forming highly ordered 2D structures.

One reported example of 2D sheets includes the supramolecular "push–pull" synergetic strategy used by Huang and co-workers in which an attractor/(steric)repeller monomer adopts a propeller structure (Figure 3).[16] This approach suppresses the interlayer 3D stacking through sterics between repellers while maintaining the assembly of the intralayer for 2D growth, driven by π–π interactions between pyrene units. Formation of well-defined 2D nanosheets obtained from a solution of THF was observed, with a side-length ratio of 1.93 and a height of 56 nm. In addition, a different assembly was obtained as a 2D crystal film from surface-assisted layer-by-layer assembly from a bilayer solution (toluene/water) with a thickness of 25 nm. These self-assembled 2D materials show notable charge mobility, a high photoluminescence quantum yield and deep-blue laser characteristics.

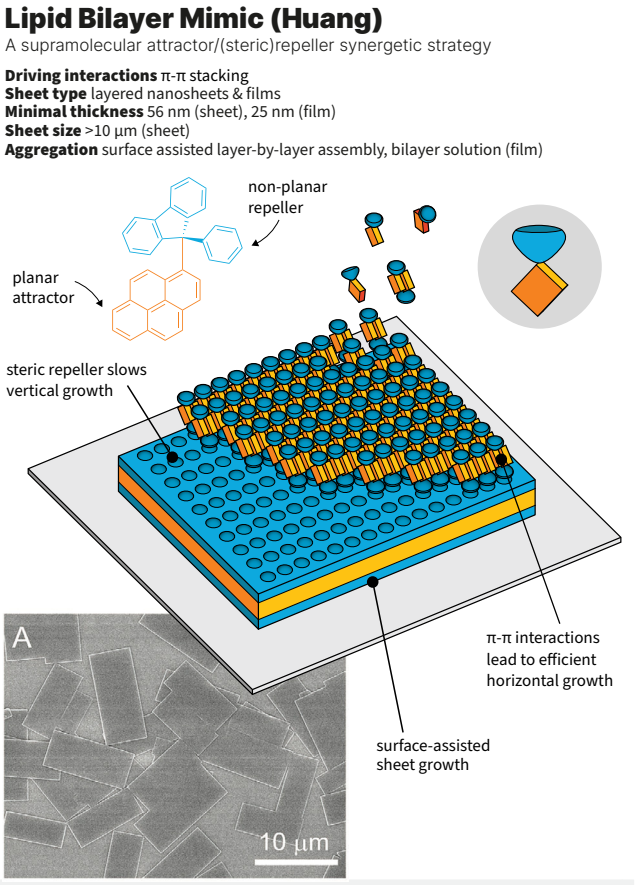

Figure 3 Schematic representation of a lipid bilayer mimic reported by Huang and co-workers. Well-defined crystal nanosheets and millimeter-sized crystal films with layered amphiphile-like packing were observed from the assembly of propeller-shaped monomers. SEM image reprinted with permission from Ref. 16. Copyright 2021 John Wiley and Sons.

Another example of preorganized π–π interactions using a covalent linkage was reported by Wennemers et al. in 2016.[17] Formation of hierarchical supramolecular self-assemblies occurs from the π–π association of sterically demanding perylene monoimides (PMIs) connected to an oligoproline backbone acting as an insulating shell, and the effect of structural modifications on these monomers is studied. Formation of fibers was observed in the case of two repeating units of the monomer and sheets in the case of three, which were obtained from a solution of THF/water with widths up to 200 nm. In 2017, the same group reported a triaxial supramolecular weave consisting of organized organic threads formed by self-assembly of building blocks containing a rigid oligoproline backbone with additional residues between two PMI π-surfaces (Figure 4).[18] π-Stacking of chromophores leads to spatially defined threads stabilized by cross CH–π interactions between adjacent PMI groups leading to further assembly of the threads into a triaxial woven structure. The self-assembled weave was pre-

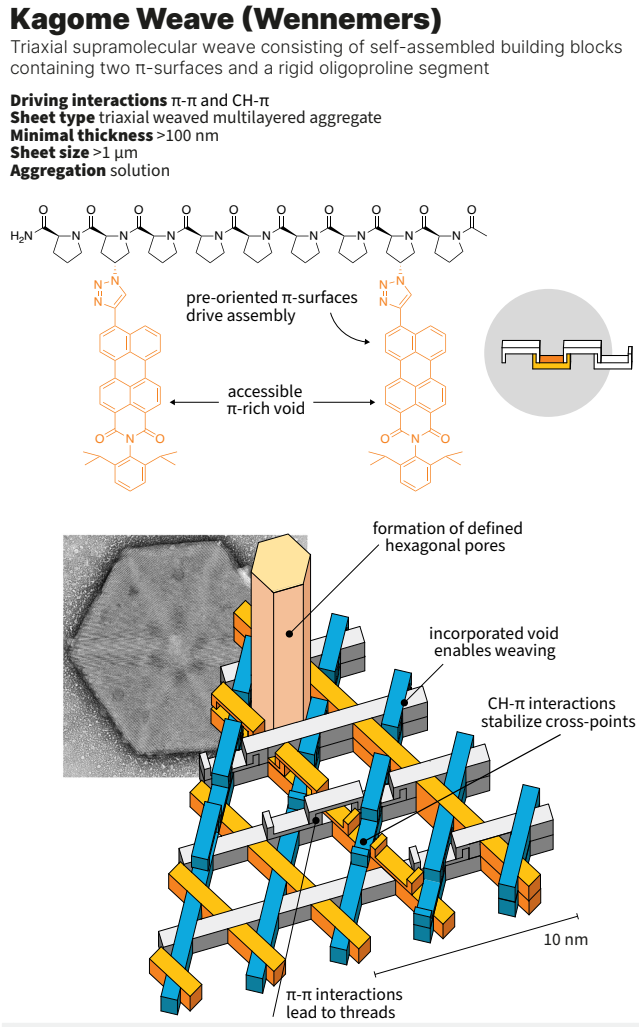

Figure 4 Schematic representation of a Kagome weave reported by Wennemers et al. prepared from organic threads formed by π–π self-assembly of building blocks containing two π-surfaces connected to a rigid oligoproline backbone. TEM image adapted with permission from Ref. 18. Copyright 2017 Springer Nature.

cipitated from a THF/water solution of the monomer, revealing a highly ordered morphology of flat hexagonal structures. These sheets showed diameters over 1 µm and thicknesses over 100 nm, with formation of defined hexagonal pores within the interwoven network. Iridium nanoparticles, which are of interest in catalysis and gas storage, can be prepared from Ir(cod)acac that acts as a guest to the pores.

The last set of examples in this section highlights work from Schlüter and co-workers, which results in 2D materials after photo-irradiation of a preorganized π–π network to form covalent bonds. Whilst we would consider these materials to no longer be supramolecular in nature, the underlying design principle is supramolecular and highly relevant. In several works, tripodal monomers with blades containing π-surfaces (anthracenes, alkynes) stack face-to-face to form a hexagonal lattice to favor maximized packing (Figure 5).[19] The π–π interactions are sufficient to hold these layers in place, but do not prevent growth in a third dimension, affording a crystalline material. Following photo-irradiation to induce cycloaddition between adjacent monomers and exfoliation from 1-methyl-2-pyrrolidone, 2D covalent sheets are obtained. In a more recently developed method with the purpose of avoiding the exfoliation process, extended triptycenes with a hydrophilic group at one end were used at an air/water interface.[20] Single-layer supramolecular preorganization into a hexagonal packing array followed by photocyclization and compression at the interface directly yielded a 2D covalent sheet.

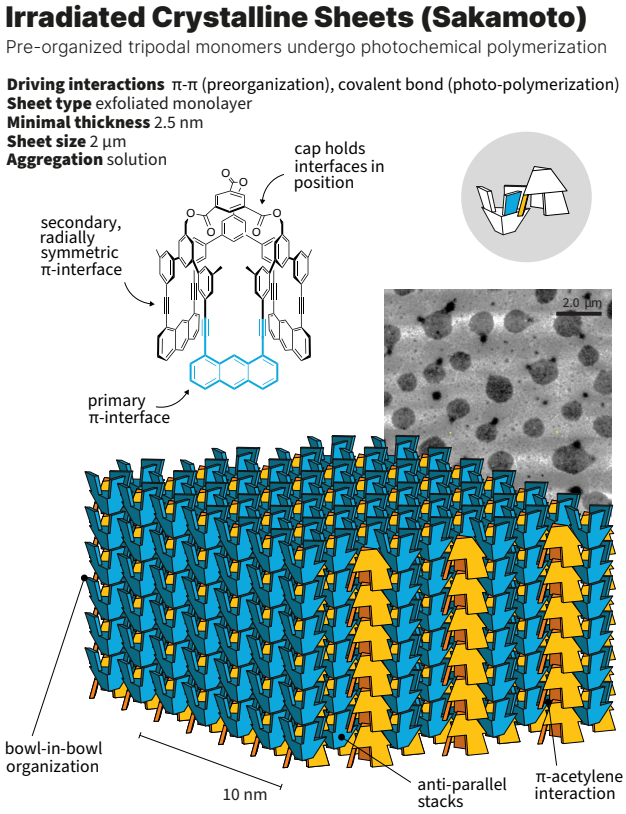

Figure 5 Model of a π–π preorganized 3D crystal composed of tripodal monomers that is later photo-irradiated and exfoliated to yield 2D covalent sheets. AFM image adapted with permission from Ref. 19a. Copyright 2012 Springer Nature.

Hydrophobic Interactions

Another approach to build 2D supramolecular materials in the absence of strong directional interactions is based on the hydrophobicity of the monomers. Hydrophobic interac-

tions can become the driving force to build self-assemblies of different dimensions and properties when association of a monomer containing a hydrophobic core with the appropriate side chains takes place in a hydrophilic solvent.

In 2016, Lee et al. reported the self-assembly of monomers based on a design combining anthracene units (hydrophobic π-core) and polyethylene glycol chains (hydrophilic outer shell) that gives rise to the formation of static and dynamic sheets prepared from two separate geometric isomers.[21] Aggregation takes place in a two-step process from an aqueous solution. The weak π–π association between anthracenes yields primary nanofibers that then undergo lateral association driven by hydrophobicity in order to reduce contact between aromatic units and water (Figure 6). The *cis*-isomer yields static planar sheets and the *trans*-isomer forms dynamic sheets, which can be reversibly rolled as a result of thermal dehydration of dendrimer side chains that causes twisting of adjacent macrocyclic cores. The mixed solution of both isomers exhibits self-sorting behavior.

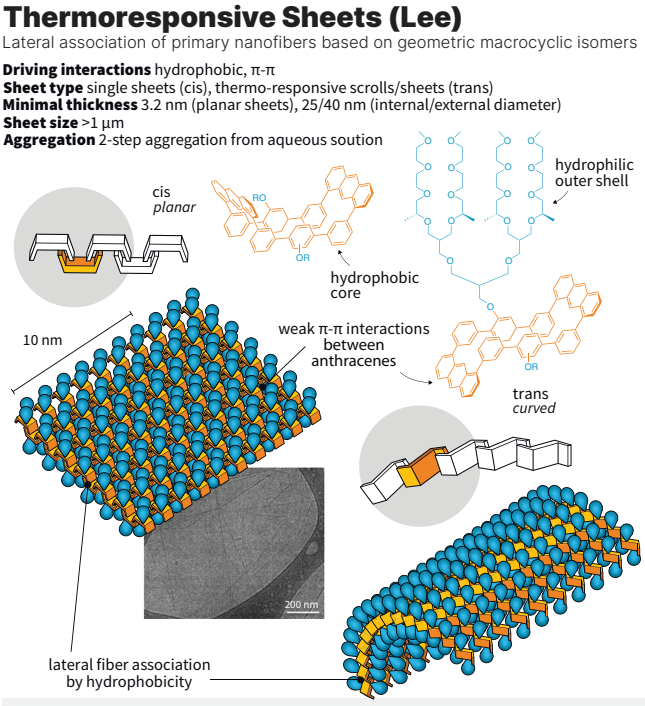

Figure 6 Schematic representation of thermoresponsive sheets reported by Lee et al. where lateral association of primary nanofibers is based on geometric macrocyclic isomers and driven by hydrophobicity of the aromatic cores in an aqueous solution. Cryo-TEM image reprinted with permission from Ref. 21. Copyright 2016 John Wiley and Sons.

Stupp et al. reported in 2014 the formation of self-assembling hydrogel scaffolds for photocatalytic hydrogen production in which the design of the monomer is based on a PMI unit connected to a carboxylic acid through a five-carbon linker.[22] This has shown to pack in an anti-parallel fashion into a highly interdigitated bilayer, forming supramolecular ribbons of around 40 nm in width and several micrometers long. The formation of these 2D structures takes place in aqueous solution and is a result of the hydrophobic collapse of the aromatic core. Additionally, when an aqueous solution of the nanoribbons was doped with different salts, formation of a gel was observed with a network of flat sheet-like structures.

Space-Filling Design

Formation of large-area molecular films with long-range 2D structural integrity up to the centimeter length scale was reported in 2015 by Fukushima et al. relying on a space-filling design (Figure 7).[23] By taking advantage of the C_3 symmetry of a triptycene monomer, previously reported for its liquid crystalline properties,[24] and its inherent geometry, three-fold interdigitation of π-surfaces for 2D growth is permitted. The three-bladed propeller shape of the monomer, with benzene rings at 120° to one another, allows for interpenetration of propeller parts in a 2D hexagonal packing array. In a second step, these assemblies stack vertically to form multilayers with long-range structural order. The assembled structures were observed by vacuum evaporation, spin-coating and cooling of the isotropic liquid of the triptycene.

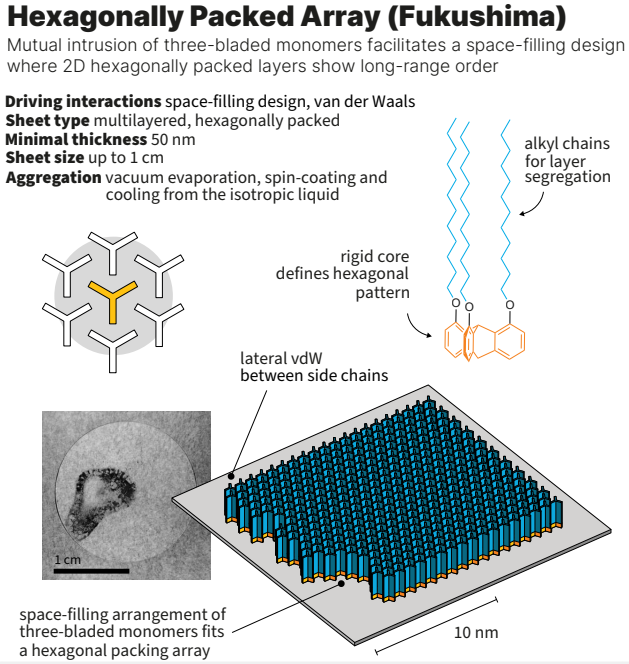

Figure 7 Model of a hexagonally packed 2D array of three-bladed monomers held together through a space-filling design and segregating alkyl chains. Image adapted with permission from Ref. 23. Copyright 2015 American Association for the Advancement of Science.

Curvature-Assisted Interactions

The influence of curvature in an aggregation-competent monomer has not been studied systematically to a large extent. With the improved access to non-planar π-systems in recent years, π-bowls[25] have found their way into the supramolecular world. They are mostly biased scaffolds that facilitate growth in one direction, where they can be functionalized at specific points to optimize polymerization; however, little consideration has been given to the shape as an ordering factor in self-assembly. Saddles have been studied to a much lesser degree in self-assembling systems due to their challenging syntheses. In the rare cases where their assembly was carefully studied, mainly 1D stacks were observed. Itami and co-workers have shown that warped nanographenes can stack into nanofibers solely based on dipolar π–π stacking and are assisted by a negative curvature.[26]

We have recently reported the first example of a saddle-shaped monomer able to self-assemble into monolayered 2D nanosheets of over 1 µm in length and single-molecule thickness formed from a solution of toluene (Figure 8).[27] This example showcases the impact topography can have to enforce order within assemblies through restriction of rotation and translation between monomers. The simplicity in the monomer design implies that association into 1D stacks is primarily driven by π–π interactions and assisted by shape, such that the individual effects alone would be insufficient. Weak van der Waals interactions then drive the lateral association of linear stacks into sheets and short alkyl chains enable layer segregation. Pairing these modes of association results in highly defined sheets, demonstrating that the curvature should not be overlooked as a possible approach towards supramolecular polymers.

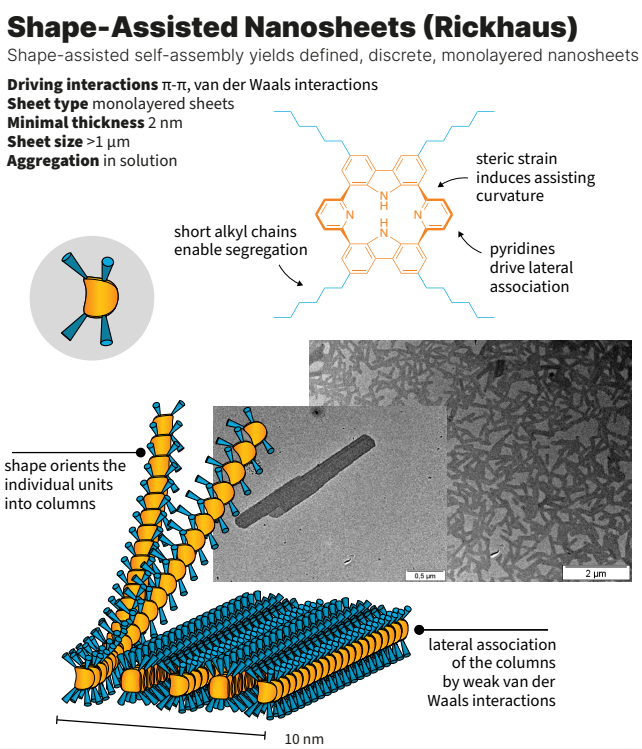

Figure 8 Shape-assisted nanosheet formation reported by Rickhaus and co-workers where monomers are forced into columnar stacks by π–π interactions that are assisted by the shape of the monomer. Lateral association of the columns into nanosheets takes place through van der Waals interactions. TEM images reprinted from Ref. 27 published under a creative commons licence (CC BY).

Complementary Interaction Modes

Successful assemblies are dependent on many factors, of which the encoded "strongest" interaction is one of them. Sometimes, however, multiple interactions are introduced in a balanced design, as exemplified by the following examples. On almost all occasions, a combination of most of the previously mentioned interactions within the same monomer allows access to suprastructures that would not be possible with a single interaction alone. However, this can be most clearly seen with the following assemblies.

One such case is a porphyrin-based monomer reported by Sugiyasu and co-workers in 2017 incorporating hydrogen bonding motifs and alkyl chains on the periphery (Figure 9).[28] The authors observed formation of fibers following a nucleation–elongation model with hydrogen bonding between amide groups and π–π stacking between porphyrin cores being the main driving forces. Although the influence of the alkyl chain length was considered negligible for 1D assembly, van der Waals forces among the alkyl chains play a vital role leading to the formation of 2D self-assemblies. The thermodynamic pathway for forming sheets was facilitated through the use of longer alkyl chains for lateral assembly, overcoming the kinetic preference of fiber formation. This example showcases the drastic change in assembly morphology at the expense of one methylene group.

Feng et al. reported in 2013 the formation of 2D nanostructures by the assembly of *n*-type thiophene-armed tetraazaanthracene molecules with peripheral alkyl chains of different lengths.[29] π–π stacking, S–S interactions and weak hydrogen bonding from electron-rich N heteroatoms in the molecular backbone primarily lead to assembly, which is then further enhanced by van der Waals interactions arising from the side chains to form 2D layers (Figure 10). Self-assemblies of these layers in binary solvent systems yield alkyl-length-dependent 2D nanosheet morphologies (sheets obtained from C_6H_{13} and $C_{12}H_{25}$ alkyl chains, spherical aggregates obtained from $C_{18}H_{37}$, and rods obtained from a branched C_8H_{17}).

Finally, the last example that highlights the power of orthogonal interactions is an amphiphilic hexa-*peri*hexabenzocoronene (HBC) derivative that was reported by Aida et

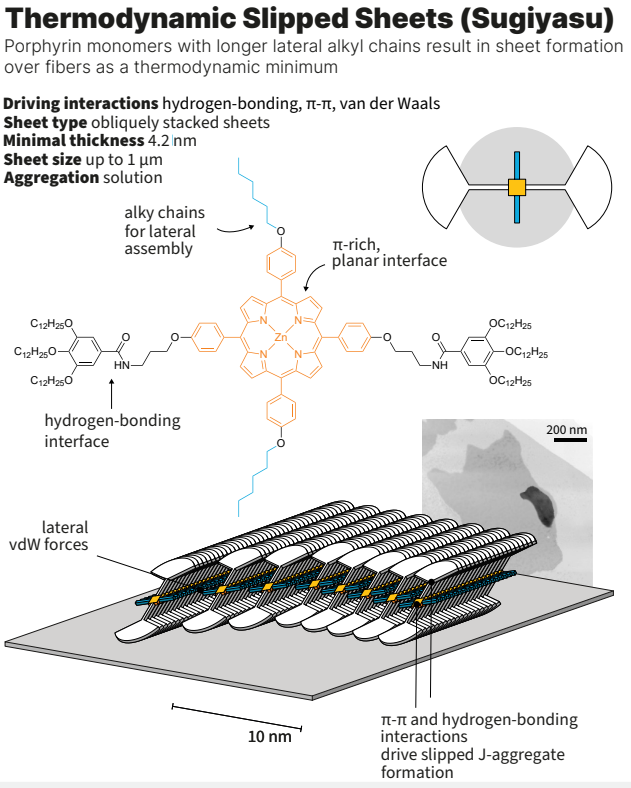

Figure 9 Model of oblique porphyrin layers obtained by Sugiyasu et al. When the alkyl chain is shorter than hexyl, fibers are obtained as the thermodynamic minimum, whereas sheets are obtained with longer side chains. AFM image adapted with permission from Ref. 28. Copyright 2017 Springer Nature.

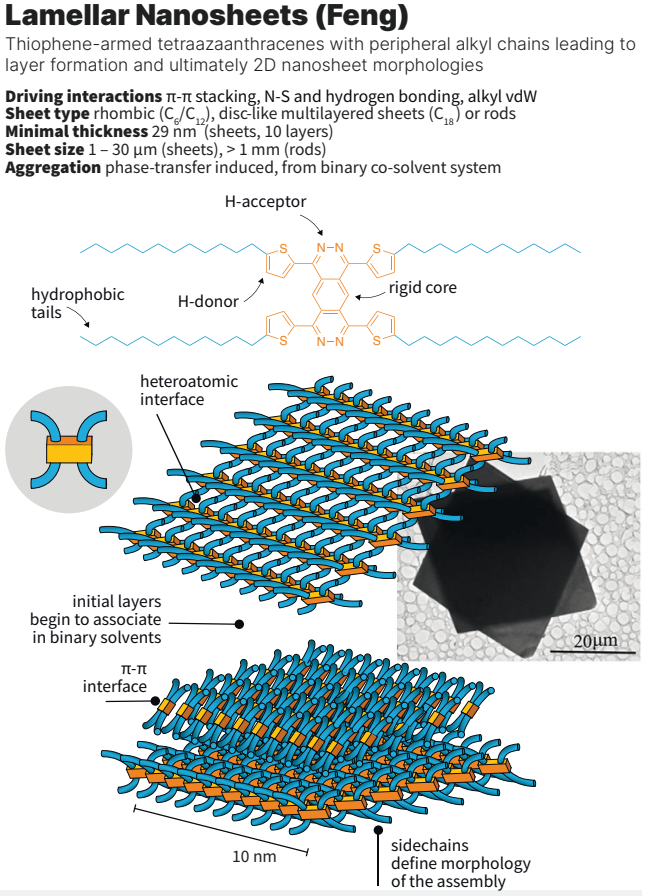

Figure 10 Schematic representation of lamellar sheets obtained by Feng et al. from π–π stacking of a tetraazaanthracene monomer in which electron-rich heteroatoms create multiple weak intermolecular interactions and alkyl chains define the morphology of the sheets by van der Waals interactions. TEM image reprinted with permission from Ref. 29. Copyright 2013 John Wiley and Sons.

al. in 2004.[30] The monomer bears two long alkyl chains on one side of the aromatic core and two triethylene glycol chains on the other side. Assembly of this derivative from THF and THF/water was studied, affording 1D columns of π-stacked HBC units which form graphitic layers that further stack onto a bilayer tape connected by interpenetration of the alkyl chains. Tight rolling-up of the 2D structure results in nanotubes where both the internal and external surfaces are covered by the hydrophilic triethylene glycol chains.

Conclusions and Outlook

In summary, the examples presented above show how hydrogen-bonded supramolecular polymers are amongst the most studied 2D materials, which is attributed to the highly directional interactions they possess. However, this does not mean that other modes of association should be overlooked. With advances in synthesis and greater understanding of weaker interactions, new routes towards 2D materials have been uncovered using π–π stacking, hydrophobicity and the effects of curvature or topography. Combining a number of these weaker effects provides a powerful toolkit to balance competing interactions in order to form new materials we would otherwise think impossible. With these design concepts, greater effort can be put to preparation of new 2D materials with the purpose of expanding their scope and accessibility. It is not unimaginable that novel 2D organic electronics may one day be used to replace more scarcely available resources (e.g., yttrium, neodymium), that porous 2D materials may help to capture and catalytically remove harmful agents (e.g., CO_2, CFCs, pathogens) and that 2D devices may be prototypes for more efficient renewable energy production (e.g., photovoltaics).

Funding Information

M.R. gratefully acknowledges funding from the Swiss National Science Foundation (grant PZ00P2_180101).

Acknowledgements

We thank K. Gademann for generously hosting and supporting our research group.

Conflict of Interest

The authors declare no conflict of interest.

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