Editorial

Dimensionality in Chemistry

There are different views on the meaning of 'Dimensionality' depending on who is asked and the context in which this term is used must therefore be transparent. Some use dimensionality when referring to the mere size of an object, the physical space in which we live or the water surface reflecting the rising sun. Others use it when speaking about the complexity of a sociological process or the functional depth of a building.

In the realm of chemistry, dimensionality often concerns the topological dimension of the molecules under consideration, with small molecules being zero-dimensional (0D), linear polymers one-dimensional (1D) and macroscopic materials such as crystalline or glassy metals three-dimensional (3D).

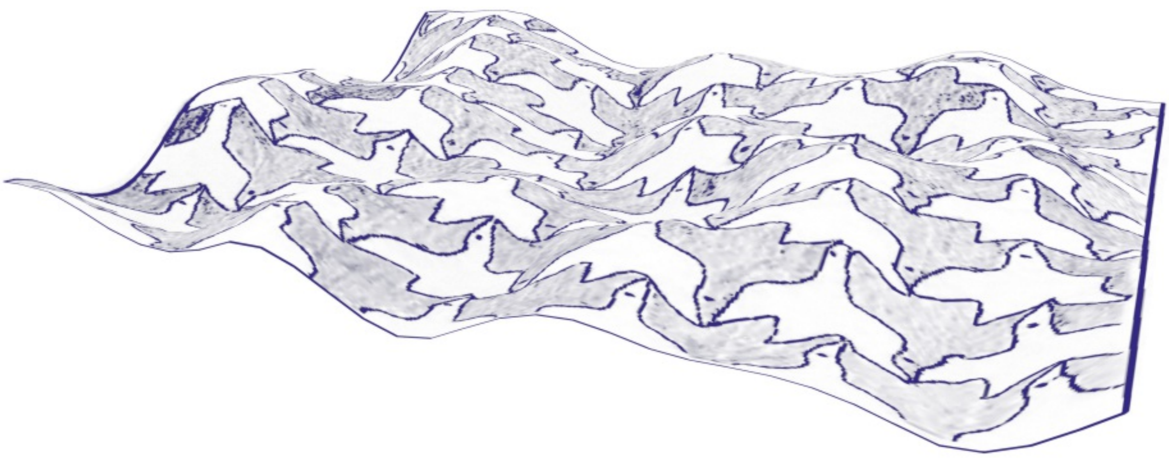
Enormous progress for humankind has been achieved by developing chemistry in zero, one or three dimensions. While the (somewhat rough) two-dimensionality of catalytic surfaces, for example, played a vital role in this development, synthetic 2D materials such as molecular-scale sheets or interwovens have not been greatly explored. This surprising fact has something to do with the high sophistication the measures require to suppress the intrinsic tendency of growth processes to depart into the third dimension rather than to confine themselves to two.

2D materials have always been available in Nature. Graphene, layered silicates or dichalcogenites are famous examples. Only recently, chemists and physicists have begun, however, to develop synthetic procedures that provide access to such materials under conditions mild enough to ensure the structural integrity of the molecularly defined two-dimensional objects obtained.

2D materials differ greatly from the known 3D materials even for similar atom compositions. This is due to their 'infinitely' large aspect ratio, which results in the absence of a bulk phase, the simultaneous presence of two surfaces (on both sides of the sheet) and the existence of a 1D circumference. Graphene, a naturally occurring 2D polymer, in comparison to graphite is a perfect example for how the dimensionality affects properties. While a single graphene sheet behaves like a soft but strong tablecloth that bends easily without breaking, its 3D congener, graphite, is a solid lubricant.

The high expectations resulting from such remarkable differences explain why CHIMIA has decided to devote a special issue to this topic. This issue highlights examples for how to access 2D materials, to deal with the challenging analytical and separation issues, and what properties to expect. Given the early phase of development, the emphasis is naturally more on the fundamentals than on applications.

In terms of analysis, one should always bear in mind that when going from 0D chemical compounds *via* 1D polymers to 2D polymers, the complexity in structural analytics increases exponentially. In terms of isolation, it is important to be aware that most 2D materials are obtained as stacks of sheets (exceptions from that are included in the examples selected), from which – depending on the application in mind – the individual sheets or thin sheet stacks have to be isolated.



Adapted from M. C. Escher's 'Two Birds' to show the flexibility of thin 2D materials. By ADS and Gregor Hofer.

The current issue does not strive for completeness but rather tries to provide a collection of enticing appetizers. The subject is opened up by the beautiful articles by ***Helma Wennemers and coworkers*** and ***Alfredo Di Silvestro and Marcel Mayor*** providing insight into the thrilling topic of molecular 2D interwovens. While there is mileage still to go, only few years ago such considerations would have been shrugged off as hopeless. Times have changed.

These articles are then followed by the article of ***Catherine Housecroft*** and ***Edwin Constable*** nicely illustrating the interplay between the second and third dimensions. It provides a fascinating view into coordination networks and stresses how slight changes in ligand structure steers whether 2D- or 3D products are obtained.

Moving from coordination networks to covalent 2D networks ***Robert Häner and coworkers*** describe an exceedingly elegant approach how to exploit DNA self-assembly to create a precursor network in which photochemically linkable anthracene units are positioned such that simple photochemical treatment allows for covalent fixation.

Subsequently, physicist ***Andrey Turchanin*** shows that the field is not entirely in the hands of chemists. He presents a versatile and simple method how to create covalently connected sheets that present pre-selected substituents on both sheet faces and how to create organic/inorganic hybrid structures. While an electron beam is used to weld the initial monolayer constituents together, this method is still much closer to a controlled synthesis than chemical vapour deposition, for example.

Xinliang Feng and his co-authors present their impressive method on order formation between complementary monomers at an air/water interface, which eventually will enable them to obtain monolayer 2D polymers with large lateral scale. This work has also led to the first Selected Area Electron Diffraction (SAED) benchmark study confirming crystallinity in a few-layer covalent sheet.

Dieter Schlüter then explains genuine two-dimensional polymerization through which nm-sized monomer molecules are converted into μm^2- and mm^2-sized long range ordered covalent monolayers (2D polymers) under room temperature conditions.

Now time is ripe for state-of-art analysis. ***Renato Zenobi and co-authors*** took on this challenge and acquaints the reader mainly with the power of tip-enhanced Raman spectroscopy (TERS) in the context of monolayer analysis. The beauty of this extremely sensitive technique is that it not only provides information about bond formation and reaction conversion but does so with spatial resolution.

Finally, ***Claudia Backes*** shows impressively how to master the wet-chemical exfoliation of inorganic 2D materials all the way down to single layers by a combination of ultrasound treatment and ultracentrifugation. Interestingly, this technique can be applied to synthetic organic 2D materials as well, which is likely to give the field of 2D polymers obtained in single crystals a significant push.

I would like to cordially thank the colleagues for their insightful contributions to this issue. I hope you will enjoy this excursion into the fascination of dimensionality aspects in chemistry.

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Front cover: Dimensionality also plays an important role in the arts, as the cover picture based on the fascinating M. C. Escher drawing 'Two Birds' nicely illustrates. This piece combines two-dimensionality with pattern regularity, features that we will recognize again in some of the contributions of this issue.

It is with great pleasure that the Editorial Board of CHIMIA warmly thanks Prof. A. Dieter Schlüter for his great efforts in the successful realisation of this exciting issue on 'Dimensionality in Chemistry'.