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# Interface-Interactive Nanoarchitectonics: Solid and/or Liquid

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The methodology of nanoarchitectonics is to construct functional materials using nanounits such as atoms, molecules, and nanoobjects, just like architecting buildings. Nanoarchitectonics pursues the ultimate concept of materials science through the integration of related fields. In this review paper, under the title of interface-interactive nanoarchitectonics, several examples of structure fabrication and function development at interfaces will be discussed, highlighting the importance of architecting materials with nanoscale considerations. Two sections provide some examples at the solid and liquid surfaces. In solid interfacial environments, molecular structures can be precisely observed and analyzed with theoretical calculations. Solid surfaces are a prime site for nanoarchitectonics at the molecular level. Nanoarchitectonics of solid surfaces has the potential to pave the way for cutting-edge functionality and science based on advanced observation and analysis. Liquid surfaces are more kinetic and dynamic than solid interfaces, and their high fluidity offers many possibilities for structure fabrications by nanoarchitectonics. The latter feature has advantages in terms of freedom of interaction and diversity of components, therefore, liquid surfaces may be more suitable environments for the development of functionalities. The final section then discusses what is needed for the future of material creation in nanoarchitectonics.

## 1. Introduction

Humanity is confronted with energy problems,[1] environmental issues,[2] development of devices for the information society,[3] and biomedical problems.[4] Many of these solutions have been brought about by the development of useful functional materials and functional systems. They are supported by diverse scientific research. In some aspects, these approaches are being pursued independently and disorganized. It seems that the integration of fields under a more comprehensive concept will lead to the development of shared values among the fields. For example, under the concept of nanotechnology, molecular chemistry and quantum physics have developed along with various nanostructure sciences.[5] The concept of "post-nanotechnology," the next step after nanotechnology, is needed. This is the new concept of "nanoarchitectonics" that is now emerging.[6] The background and significance of this concept are described below, based on the flow of material development.

Originally, humans processed naturally occurring materials to make tools and buildings with some techniques for creating alloys and modifying materials. Later, the development of the field of chemistry related to materials created ways of full-fledged methodologies for creating desired materials. Since the inception of various chemical fields, many functional materials have been created until today. At present, functional materials have been reported one after another in the fields of organic chemistry,[7] inorganic chemistry,[8] polymer chemistry,[9] coordination chemistry,[10] supramolecular chemistry,[11] various material chemistry,[12] and biochemistry,[13] and their functions have been investigated. At the same time, progress in physics, which examines the structure and physical properties of chemically created new materials, has also greatly contributed to the development of functions of these materials.[14] Such developments in chemistry and physics (and biology as well) have led to the discovery of one common fact. It is not only the material itself, but also its internal and external structure in nano-level that determines its properties. It is important not only to create a materials, but also to precisely control their structures.[15]

A decisive impetus for the importance of such structural control has been the progress of nanotechnology. Phenomena at the nanometer level involve the physical properties of atoms and molecules in their aggregates and nanostructures. They are also compatible with quantum phenomena.[16] The development of nanotechnology has also had a significant impact on recent technological developments in science. These include techniques that allow precise observation of atomic and molecular structures,[17] and characterization of extremely small objects and nanoscopic spaces.[18] Functional materials are increasingly being developed based on this nano-scale knowledge. It is important to propose such a trend as a new methodology for the unified development of functional materials. Nanoarchitectonics plays this role.[19]

Following Richard Feynman's initiation of nanotechnology in the middle of the 21st century,[20] nanoarchitectonics was proposed by Masakazu Aono in the beginning of 21st century.[21] The methodology of nanoarchitectonics is to assemble functional materials using nanounits such as atoms, molecules, and nanoobjects, just like architecting buildings (Figure 1). However, the methodology of creating functional materials by assembling molecules can be seen in the other disciplines. These include the formation of functional molecular assemblies in supramolecular chemistry[22] and thin film fabrication such as self-assembled monolayer (SAM),[23] Langmuir-Blodgett (LB) film,[24] and layer-by-layer (LbL) assembly.[25] Alternatively, mesoporous materials can be created by template synthesis,[26] metal-organic frameworks (MOFs) by coordination chemistry,[27] and covalent-organic frameworks (COFs) by polymer chemistry.[28] Nanoarchitectonics incorporates them all. Rather than advocating a new concept, nanoarchitectonics pursues the ultimate concept of materials science through the integration of related fields. It even integrates nanotechnology with various material chemistries, microfabrication technologies, and bio-related sciences.[29]

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The nanoarchitectonics methodology combines various elemental technologies. Select from atomic and molecular manipulation, synthesis of nanomaterials, organic molecules, and polymers, physical and chemical material transformation, self-assembly and self-organization, alignment by external fields and forces, fabrication at the nano and micro level, and biological processes,[30] in combination, they develop functional material systems from nano-units. Compared to self-assembly based on a single equilibrium,[31] nanoarchitectonics, which can be multi-step, is more suited to the fabrication of hierarchical and asymmetric functional structures.[32] In addition, nano processes will encompass uncertainties such as thermal fluctuations, stochastic distributions, and quantum effects. Nanoarchitectonics can also include such ambiguities, and structures can be built up as the effects are harmonized.[33] Features such as hierarchy and harmonization share characteristics with the construction of advanced functional structures in biological systems.[34]

These characteristics of nanoarchitectonics are not limited to one particular material or function. The range of applications is extremely broad. An overview of recent research papers advocating nanoarchitectonics reveals its wide application. It is used in basic fields such as material synthesis,[35] structure control,[36] exploration of physical phenomena,[37] and basic biochemistry.[38] At the same time, it is used in highly applicable fields such as catalysis,[39] sensor,[40] device,[41] environmental applications,[42] energy production,[43] energy storage,[44] cell engineering,[45] drug delivery,[46] and medical applications.[47] Originally, all materials are made of atoms and molecules. If the theory of everything is the ultimate goal of physics,[48] then nanoarchitectonics can be the method for everything in materials science.[49] Many examples that have not been advocated as nanoarchitectonics can, in fact, be considered as one output from nanoarchitectonics approaches.

However, it is not easy to achieve this ultimate methodology in one fell swoop. It may be advisable to start thinking about material architecture within a limited space, rather than building a group of materials spread out three-dimensionally. For example, the interface environment is a good medium to start. At the interface, the spread of materials and the range of their activities are restricted to the two-dimensional plane. At the interface, the chemistry and physics of material interactions often differ from those in bulk space. Specificities unique to the interface also emerge. It is a very interesting medium for the creation of materials through nanoarchitectonics.[50] Interfacial environments, such as solid surfaces, also provide an excellent opportunity to investigate the structure and properties of materials in detail. The structure and properties of molecules and nanomaterials on solid surfaces can be studied with great precision.

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Nanoarchitectonics based on specific interactions at interfaces is a very interesting subject in terms of observation and evaluation, structure fabrication, and functional exploration. In this review paper, under the title of interface-interactive nanoarchitectonics, several examples of structure fabrication and function development at interfaces will be discussed, highlighting the importance of architecting materials with nanoscale considerations. In terms of mobility and degrees of freedom, surface environments can be broadly classified into solid and liquid surfaces. This review paper discusses interface-interactive nanoarchitectonics, broadly following such a classification. The examples of research discussed, while recent, are not necessarily representative of the field as a whole. However, even in such limited examples, the characteristics of nanoarchitectonics are evident. Following this introduction, two sections provide some examples at solid and liquid surfaces. The final section then summarizes their characteristics and discusses what is needed for the future of material creation in nanoarchitectonics.

## 2. On Solid Surface

At solid surfaces, the movement of adsorbed molecules is restricted. Possible conformations may also be limited. Adjacent molecules may also contact each other in their preferred orientation. Molecules often assemble in two dimensions to form controlled assembly structures. Those phenomena can be observed in detail by scanning tunneling microscope (STM) and atomic force microscope (AFM).[51] As such, solid surfaces are an ideal site for molecular-level nanoarchitectonics. Various supramolecular structures can be nanoarchitectonized in a two-dimensional surface. Phenomena that can occur are not only due to non-covalent bonding. Reactions involving covalent bonds also occur. Molecules interact with each other in specific orientations, and selective molecular couplings and polymerizations occur. It is also possible to observe these phenomena in detail. This series of studies is often referred to as on-surface synthesis.[52] It is also possible to use the tip of a probe microscope to carry specific molecules to react with a certain site. This is in turn called local probe chemistry.[53] Intentional polymerization reactions can also be induced by stimulating certain positions in a supramolecular array structure with a tip.[54] These phenomena are organic and macromolecular synthesis, but their reactivity and reaction selectivity are very different from those of conventional solution science. It seems that a new page in organic chemistry is about to be opened. Thus, the solid interfaces control the structure and reactions at the most bottom part of nanoarchitectonics.[55] This section explores this by looking at some recent examples.

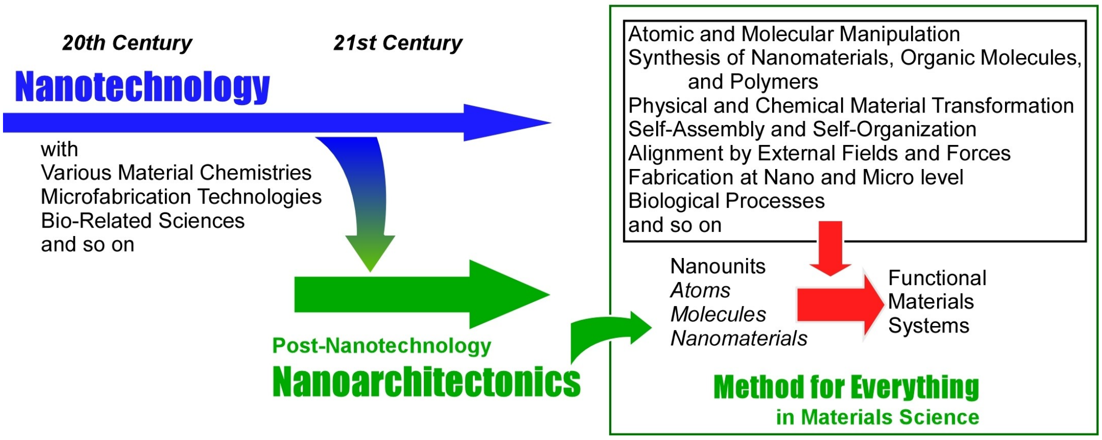

**Figure 1.** History and outline of nanoarchitectonics concept.

The introduction of Si atoms into organic compounds is a useful method for diversifying the reactions of organic molecules, creating a variety of functionalities and facilitating further applications. Sun, Foster, Kawai, and co-workers investigated the reaction of bromo-substituted molecules with silicon atoms on Au(111).[56] Synthesis of nanoribbon structures with silole derivatives and 8-membered sila-cyclic rings was demonstrated. It is synthesized from brominated molecules at the bay and peri positions on Au(111). In addition to confirming its structure, its electronic properties were also investigated. This was done by a combination of scanning tunneling microscopy/spectroscopy (STM/STS) and density functional theory (DFT) calculations, as shown in Figure 2. In addition to the $C_5Si$ ring, two five-membered sila-cyclic ring ($C_4Si$) encapsulated molecular type nanoribbon structures were found. Such structures are probably formed through sequential processes involving debromination, C–C coupling, dehydrogenation, and C–Si coupling of nanoribbon segments and Si atoms. Another structure was most likely formed through sequential coupling reactions of nanoribbon segments and Si atoms. Flat nanoribbon structures were found. There are no bright spots in the STM topography and no characteristic contrast in the dI/dV map. This suggests that the Br atoms have already been desorbed from the structure in the product. The above observations demonstrate a method for obtaining low-dimensional Si incorporated nanostructures by direct bonding on the surface. This methodology also shows the possibility of dealing with heavy group 14 elements in the synthetic chemistry at surfaces. In other words, it could be extended to the synthesis of nanostructures incorporating heavy elements such as germanium. This is expected to provide additional flexibility for the resulting electronic structures.

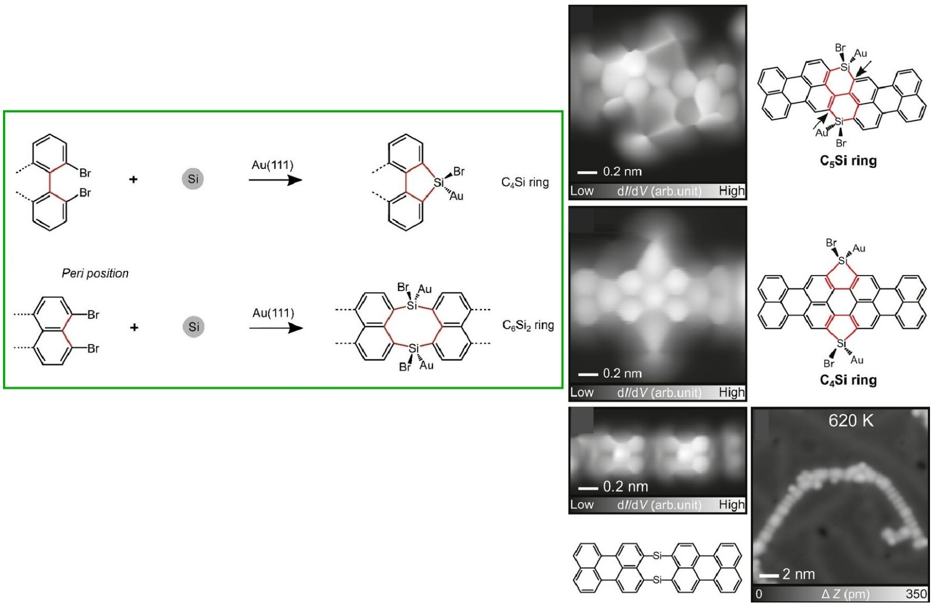

**Figure 2.** Reaction of bromo-substituted molecules with silicon atoms on Au(111) with high-resolution constant height dI/dV maps of various segments. Reproduced under terms of the CC-BY license.[56] 2024, K. Sun, L. Kurki, O. J. Silveira, T. Nishiuchi, T. Kubo, A. S. Foster, S. Kawai, published by Wiley-VCH.

Acenes are a unique class of polycyclic aromatic hydrocarbons. They have potential applications in organic electronics. Elongated acene molecules are also attractive targets for surface synthesis. A comprehensive understanding of the fundamental properties of higher acenes requires nanoarchitectonics of longer homologues. Bettinger, Tonner-Zech, Gottfried, and co-workers have demonstrated tridecacene synthesis through atomically manipulated nanoarchitectonics on the Au(111) surface (Figure 3).[57] The synthesis process involved rearomatization of stable hexahydro-tolitheno-tridecacene precursors by multi-step manipulation in a low-temperature STM, including a three-dimensional structural transformation step and a three-step removal step of the etheno-bridges by tip-assisted carbon-carbon bond dissociation. Initial manipulation of the molecular conformation is essential to enable the formation of the desired product. The intentionally synthesized tridecacene was observed by STM/STS and examined by ab initio calculations. According to spin-polarized density functional theory calculations, the electron configuration of tridecacene is an antiferromagnetic open-shell ground state in the gas phase system. On the other hand, tridecacene physisorbed on an Au(111) surface has a significantly reduced open-shell nature. Interaction with the surface decreases the magnetization of tridecacene. The gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is reduced compared to the gas phase. Therefore, the relative energy to the nonmagnetic state is reduced. The influence of the Au(111) substrate on the physical properties of long acenes is significant, indicating that nanoarchitectonics of solid surfaces is a major key for the application of long acenes.

The introduction of non-benzenoid motifs into graphene nanostructures greatly affects their properties. Such structural nanoarchitectonics is very attractive for carbon-based electronics. However, the impact of specific nonbenzenoid structures on the properties of graphene needs to be further investigated. Biswas et al. have synthesized a surface of non-benzenoid nanographene with different combinations of pentagonal and heptagonal rings (Figure 4).[58] Different nanographenes were obtained under ultra-high vacuum conditions via oxidative ring closure of methyl substituents, rearrangement reactions, and bonding reactions by thermal activation on the Au(111) surface. Their structures and electronic properties were investigated using STM/STS. Further computational investigations were also carried out. Upon thermal activation of the precursor on an Au(111) surface, two major nanographene products were detected. Insights into the reaction mechanisms responsible for their origin were obtained. There, the fundamental catalytic role of a single gold adatom in the oxidative ring-closing reaction was revealed. Nanographene encapsulating two azulene units formed by the oxidative ring-closing reaction of methyl substituents exhibited an antiferromagnetic ground state. This antiferromagnetic ground state is an open-shell singlet. It had a very high magnetic exchange coupling among the non-benzenoid-containing nanographenes. The other major product was nanographene encapsulating one azulene unit and one Stone-Wales defect formed by a combination of oxidative ring-closing and skeletal ring rearrangement reactions. This nanographene is in a closed shell

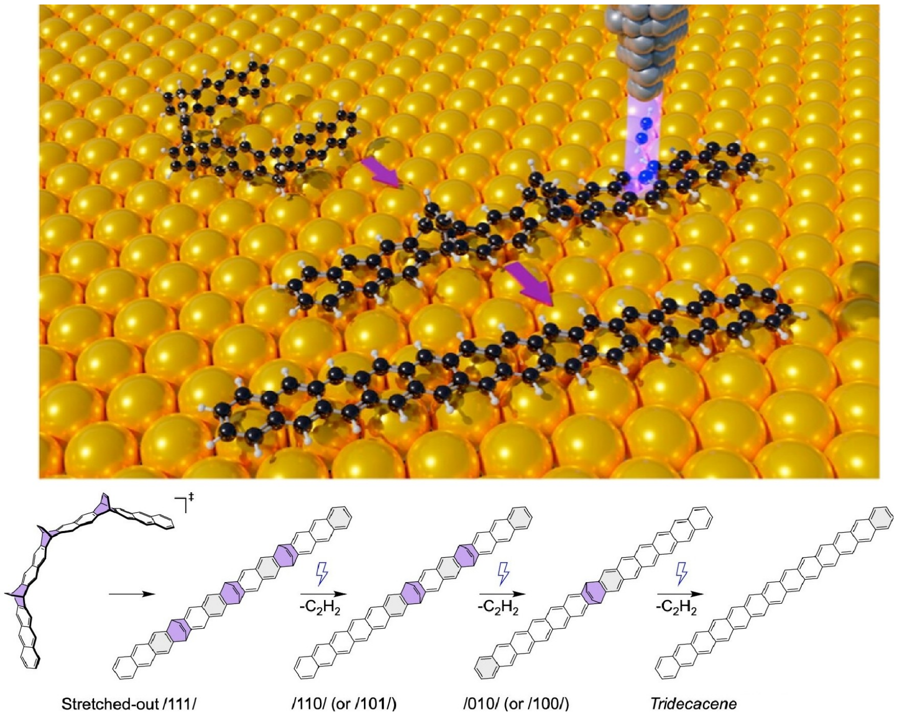

**Figure 3.** Tridecacene synthesis through atomically manipulated nanoarchitectonics on the Au(111) surface. Reproduced under terms of the CC-BY license.[57] 2024, Z. Ruan, J. Schramm, J. B. Bauer, T. Naumann, H. F. Bettinger, R. Tonner-Zech, J. M. Gottfried, published by American Chemical Socirty.

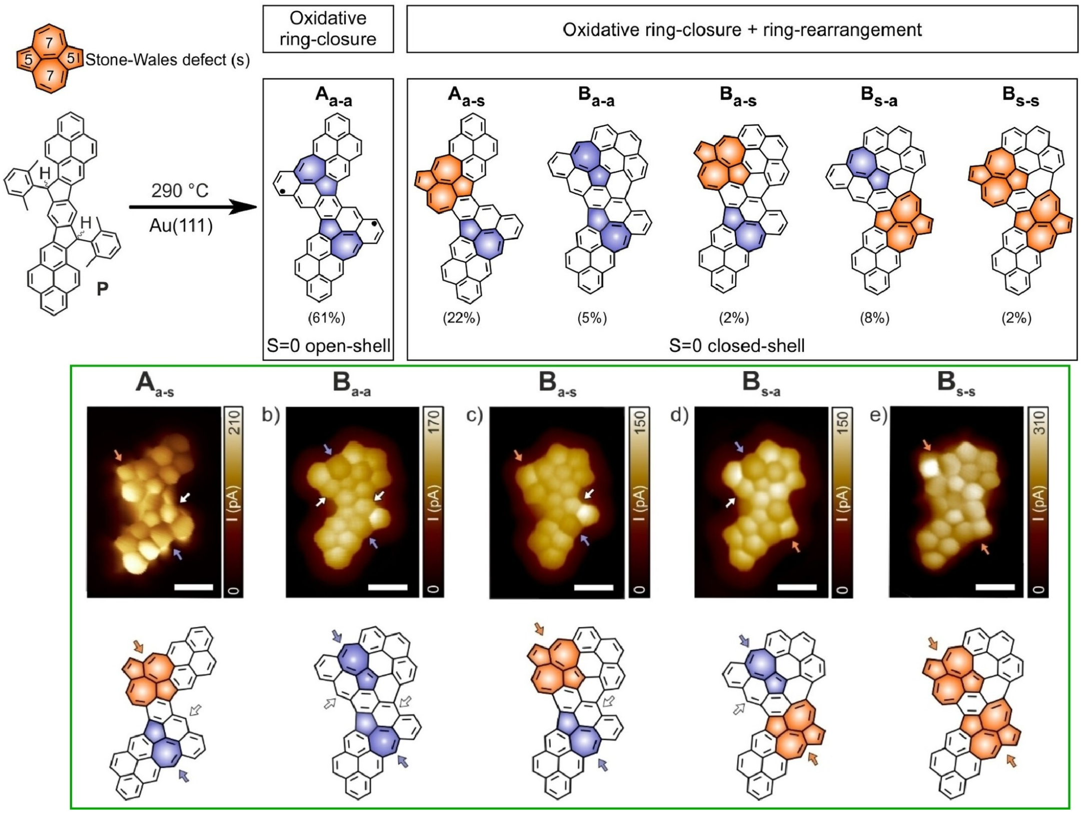

**Figure 4.** On-surface synthesis of nonbenzenoid nanographene with different combinations of pentagonal and heptagonal rings under ultra-high vacuum conditions via oxidative ring closure of methyl substituents, rearrangement reactions, and bonding reactions by thermal activation on the Au(111) surface. Reproduced under terms of the CC-BY license.[58] 2024, K. Biswas, Q. Chen, S. Obermann, J. Ma, D. Soler-Polo, J. Melidonie, A. Barragán, A. Sánchez-Grande, K. Lauwaet, J. M. Gallego, R. Miranda, D. Écija, P. Jelínek, X. Feng, J. I. Urgel, published by Wiley-VCH. All scale bars = 0.5 nm.

configuration. In addition, byproducts with a closed-shell configuration resulting from a combination of ring-closing and rearrangement reactions were also obtained. The observation of a series of reactions is also useful for exploring monoatomic gold catalysis in surface synthesis.

The design and synthesis of supramolecular organic radical cages and frameworks produce interesting material properties. Potential applications include (photo)redox catalysts and sensors. Alternatively, the structures are useful for the investigation of host-guest spin-spin interactions. However, organic radical molecules are generally highly reactive, and the synthesis of supramolecular radical assemblies is generally difficult. Sánchez-Grande, Curiel, Jelínek, and co-workers achieved surface synthesis of pure organic supramolecular radical frameworks by combining supramolecular chemistry with surface chemistry on Au(111) (Figure 5),[59] where a tripodal precursor functionalized with a 7-azaindole group was used. This precursor, 1,3,5-tris(7-methyl-α-carboline-6-yl)benzene, is designed to have appropriately positioned methyl groups that promote subsequent cyclodehydrogenation on the surface and hydrogen bond donor and acceptor sites that induce supramolecular self-assembly. One gold atom on the surface was used as a catalyst to form radical molecular products consisting of a radical core based on π-extended fluoradene. The radical products self-assemble through hydrogen bonding. The result is the formation of extended two-dimensional domains arranged in a Kagome honeycomb lattice. Magnetic properties over a wider region are investigated to corroborate the long-range magnetic ordering. Constant height STM images of different overviews of the Kagome honeycomb phase were measured at low bias voltages. The results indicate that the magnetism is a phenomenon that extends throughout the supramolecular assembly. Characteristic Kondo resonances were also observed in the dI/dV spectra obtained over a series of seven neighboring molecules. These properties are indicative of the monoradical properties of all molecules on the assembly extended to hundreds of nanometers. This series of studies can be described as an interdisciplinary study combining supramolecular chemistry, π-magnetism, and surface synthesis. It contributes to the development of supramolecular organic radical chemistry. Considering a broad target, this research is expected to have important applications in catalytic redox reactions, sensors, and quantum technology.

In artificial electron Kagome lattices, exotic supersymmetries may be obtained from the electronic potential landscape. The nanoarchitectonics of such structures is also an attractive research target. Ma, Wang, and co-workers reported a method for constructing a variety of electron Kagome lattices by utilizing surface synthesis of halogen hydrogen-bonded organic frameworks (Figure 6).[60] As a demonstration of the method-

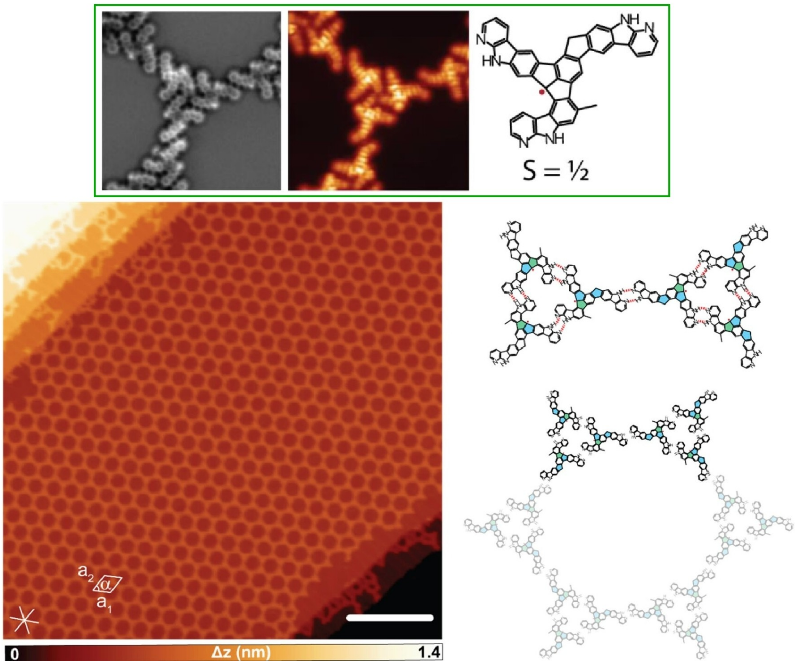

**Figure 5.** Surface synthesis of pure organic supramolecular radical frameworks by combining supramolecular chemistry with surface chemistry on Au(111), where a tripodal precursor functionalized with a 7-azaindole group, 1,3,5-tris(7-methyl-α-carboline-6-yl)benzene, is designed to have hydrogen bond donor and acceptor sites for induce supramolecular self-assembly. Reproduced under terms of the CC-BY license.[59] 2024, F. Frezza, A. Matěj, A. Sánchez-Grande, M. Carrera, P. Mutombo, M. Kumar, D. Curiel, P. Jelínek, published by American Chemical Socirty. Scale bar = 31 nm.

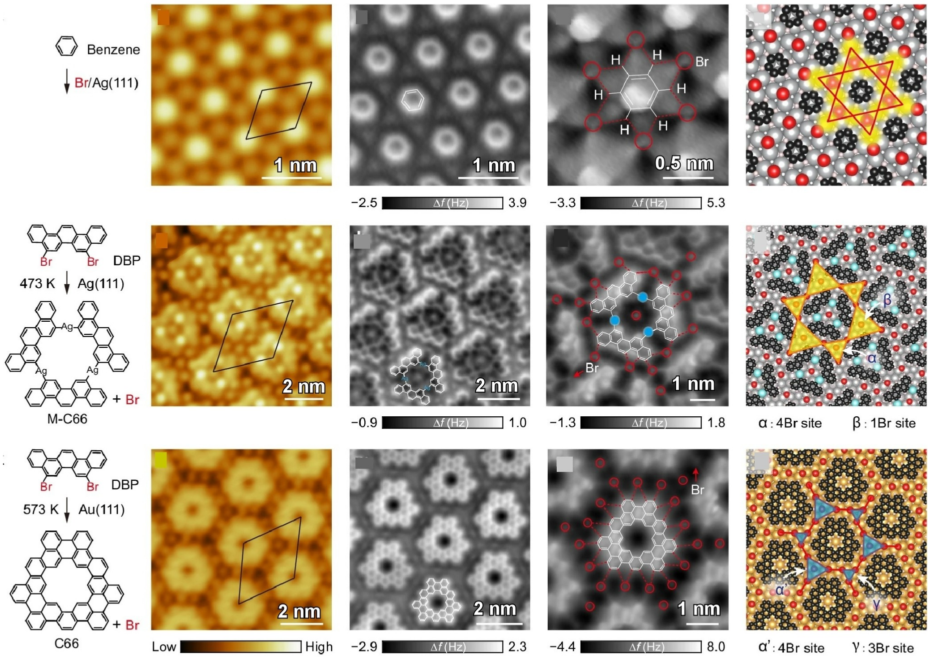

**Figure 6.** A method for constructing a variety of electron Kagome lattices by utilizing surface synthesis of halogen hydrogen-bonded organic frameworks synthesized on Ag(111) and Au(111) surfaces. Reproduced under terms of the CC-BY license.[60] 2024, R. Yin, X. Zhu, Q. Fu, T. Hu, L. Wan, Y. Wu, Y. Liang, Z. Wang, Z.-L. Qiu, Y.-Z. Tan, C. Ma, S. Tan, W. Hu, B. Li, Z. F. Wang, J. Yan, B. Wang, published by Springer-Nature.

ology, several halogen hydrogen-bonded organic frameworks were synthesized on Ag(111) and Au(111) surfaces. As one proof of concept, a benzene molecule was first used as a building block. STM and non-contact-AFM images show that each benzene molecule is surrounded by 6 Br atoms and stabilized by 12 Br·H bonds. In this supramolecular assembly, a benzene/Br/Ag(111) superlattice is formed. This structure was also reproduced by structural modeling using DFT simulations. The 5,8-dibromopicene molecules were also annealed at 473 K and 573 K on Ag(111) and Au(111) surfaces, respectively. The resulting quasi-hexagonal organometallic trimers and porous nanographene were obtained. Thus, topological edge states and charge ordering appeared from regular Kagome lattices to breathing Kagome lattices to chiral breathing diatomic-Kagome lattices. The applicability of this methodology to a wide range of lattices is demonstrated. In addition, the domain size of Kagome lattices could be increased up to more than 100 nm. Porous structures capable of periodic embedding of individual metal atoms, trimerized metal atoms, and other functional groups are possible. This property could result in atomically precise surface synthesized nanoarchitectonics and progress to practical multifunctionality. It could also be a reliable way to realize electron Kagome lattices for quantum state engineering. It has obvious advantages such as scale-up properties and atomic precision.

Nanoarchitectonics on solid surfaces is not limited to molecular manipulation as typified by on-surface synthesis. Of course, structural control and observation of inorganic nanomaterials are also actively pursued as nanoarchitectonics on solid surfaces.[61] For example, the Au/$TiO_2$ system is a commonly used model for functional nano-interfaces. It is also a typical nano gold catalyst. In particular, its crystalline shape is important for functional nano-interfaces. Tada et al. prepared an Au/Brookite $TiO_2$ catalyst active for low-temperature CO oxidation and performed TEM observations of its interface structure (Figure 7).[62] Gold nanoparticles were adsorbed on Brookite $TiO_2$ (101). Au nanoparticles of 2–5 nm in diameter and larger nanoparticles of about 10 nm were observed. Since Au nanoparticles of this smaller diameter on $TiO_2$ have higher catalytic activity, the interface structure between Au particles of 1–5 nanometer size and Brookite $TiO_2$ was analyzed. Specifically, analysis of the crystal lattice spacing and crossing angles reveals an Au(111)// Brookite (101) orientation relationship at the nano-interface. DFT calculations reveal that Brookite $TiO_2$ (101) can adsorb Au atoms more strongly than other $TiO_2$ surfaces. In Au/Brookite $TiO_2$, stabilization is achieved through surface complex formation. This example demonstrates that even stoichiometric, non-polar surfaces without defect sites or doping can be used to immobilize Au atoms and perform catalytic nanoarchitectonics.

## 3. At Liquid Surface

Like solid surfaces, liquid surfaces are also good playing sites for nanoarchitectonics.[63] Compared to solid surfaces, liquid surfaces are more mobile, and thus high-resolution structural observation is not always easy. On the other hand, the high fluidity offers many possibilities for structure fabrication by nanoarchitectonics. In this case, the interaction between components in the liquid surface is important. Liquid surfaces can have significantly increased interactions between molecules. For example, it has been experimentally[64] and theoretically[65] demonstrated that molecular recognitions through hydrogen bonding and other interactions at the air-water interface are much more efficient than those in water.[66] In addition, liquid surfaces are molecular in thickness, but macroscopic in size and freedom in the lateral directions. This feature also makes it possible to control molecules by macroscopic motion at liquid surfaces.[67] Using monolayers at the air-water interface, molecular machines can be manipulated by macroscopic movements, similar to the motions of hands.[68] These ideas have been utilized in various studies. The following section presents some examples of recent work on various nanoarchitectonics approaches at the liquid surface.

Two-dimensional ordered monolayers formed at the air-water interface are known as Langmuir monolayers as a field for nanoarchitectonics on liquid surfaces. In order to obtain a uniform and high-quality film structure as a Langmuir film, it is important that the constituent molecules are suitable. Factors such as the balance between hydrophilicity and hydrophobicity of the molecular species, the geometry to give the applicable molecular orientation, and the use of intermolecular interactions can support two-dimensional assemblies. In a developing process of amphiphiles suitable for monolayers, Naota, Mori, and co-workers considered a new category of amphiphiles called coordination amphiphiles (Figure 8).[69] Specifically, the optical properties and molecular dynamics of salicylaldiminato- and β-(iminomethyl)azolato-complexes with long chain structures were studied based on their self-assembling properties. The complexes have a square coordination structure, but may also exhibit chiral functions by modification of substituents. In the case of arched complexes, the linker length is also an important parameter. For monolayer formation, the topology of

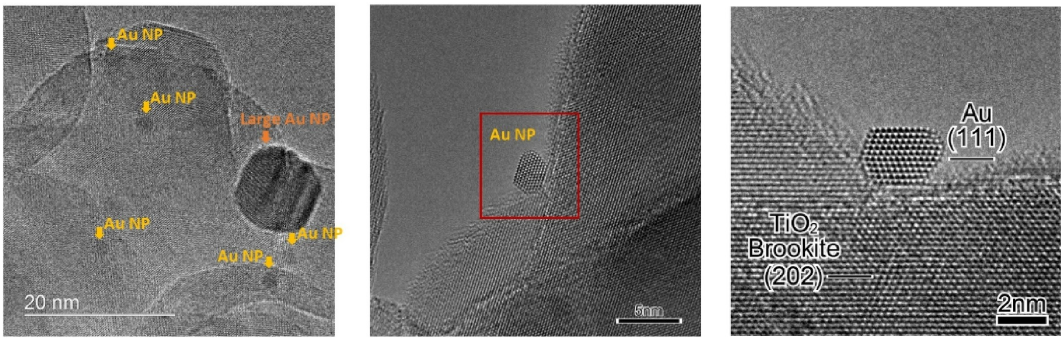

**Figure 7.** TEM observations of Au/Brookite TiO2 catalyst: TEM image at low magnification (left), TEM image at atomic resolution (middle), and enlarged image (right). Reproduced with permission.[62] 2023, Oxford University Press.

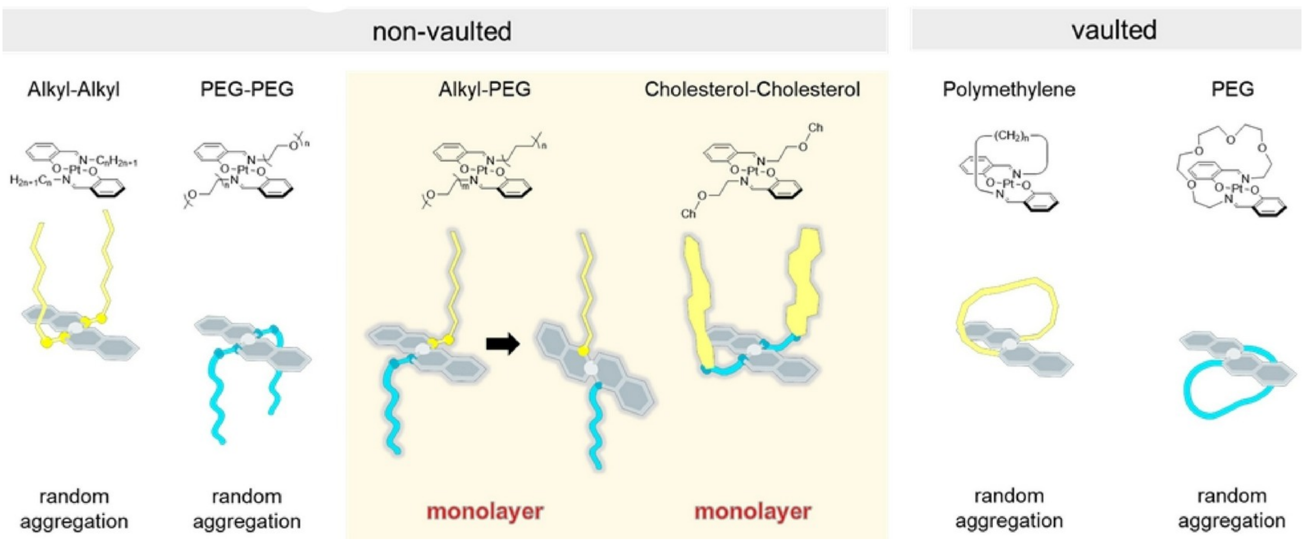

**Figure 8.** Various coordination amphiphiles: their structures and assembling modes. Reproduced with permission.[69] 2022, Oxford University Press.

the alkyl chain is also important. The topology of molecules based on non-vaulted or vaulted structures was also found to have a significant effect on monolayer formation. These results provide important information for the development of asymmetric functional complexes that take advantage of the interface-specific asymmetry.

Recognition of biological substances such as amino acids,[70] peptides,[71] sugars,[72] nucleotides,[73] and the others[74] has been investigated based on enhanced hydrogen bonding at the air-water interface. Recognition of various cations has also been performed.[75] In comparison, recognition systems for anions in aqueous media relevant to biological and environmental systems are still limited.[76] Anions are involved in effective molecular interactions with biological membranes and proteins. Based on this, various chemical reactions, molecular recognition, and transport are precisely and selectively controlled by anion recognition. Akamatsu, Sakai, and co-workers explored anion binding through anion-π interactions in Langmuir monolayers of amphiphilic naphthalenediimide derivatives (Figure 9).[77] At the air-water interface, the addition of anions to the aqueous phase increased the molecular area of the Langmuir monolayer. In particular, anions with high hydration energies related to electron density bound to naphthalene diimide derivatives with a stoichiometry of 1:1 and exhibited large binding constants. Better anion responses were observed in weakly packed monolayers formed by amphiphilic naphthalene diimide derivatives with bromine groups. In contrast, $NO_3^-$ binding was markedly enhanced in the highly packed monolayers. Anion recognition was found to depend not only on the affinity of the host molecule for inclusion, but also on the arrangement of the interaction sites. In order to tune the bonding strength and side chains, the naphthalene diimide backbone also offers synthetic flexibility to introduce electron-withdrawing or electron-donating groups and to adjust membrane properties and molecular orientation. By optimizing these properties, the strength of interactions and selectivity for anions can be controlled. The capture of anions in such electron-deficient aromatic compounds may also lead to doping and compositional techniques for n-type semiconductors. These findings would also contribute to interfacial nanoarchitectonics for device applications.

Monolayer nanoarchitectonics at the air-water interface can create fields for specific molecular and ion recognition. Such behavior is difficult to observe directly with techniques such as probe microscopy. On the other hand, spectral methods such as infrared spectroscopy are powerful for analyzing such mobile interfaces.[78] Kim and co-workers have used 1,2-dipalmitoyl-3-trimethylammonium-propane monolayers with choline groups

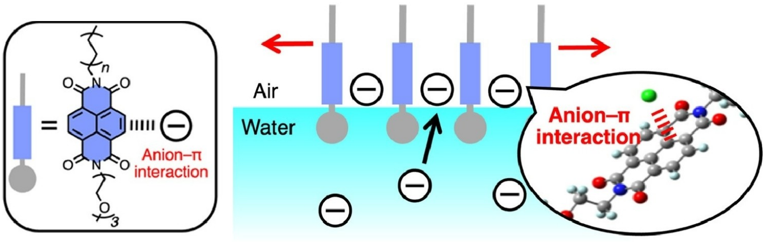

**Figure 9.** Anion binding through anion-π interactions in Langmuir monolayers of amphiphilic naphthalenediimide derivatives. Reproduced with permission.[77] 2023, American Chemical Society.

to analyze the molecular structure, intermolecular interactions, and molecular recognition at the air-water interface.[79] The interaction of aromatic ring molecules (indole, phenol, benzylamine) with the monolayer was investigated using sum-frequency vibrational spectroscopy at the air-water interface. When an aromatic molecule of about 120 Å$^2$ per molecule is introduced into the aqueous phase, a sum-frequency signal appears due to molecular adsorption. This behavior was used to investigate the adsorption of aromatic ring molecules in the aqueous phase on the choline headgroup of 1,2-dipalmitoyl-3-trimethylammonium-propane monolayers via cation-π interactions. After the addition of aromatic molecules to the subphase, the OH intensity increased rapidly and the CH peaks of 1,2-dipalmitoyl-3-trimethylammonium-propane and aromatic ring molecules appeared. Changes in surface pressure and occupied area also confirmed the presence of some interactions. Unlike 1,2-dipalmitoyl-3-trimethylammonium-propane, dipalmitoylphosphatidylcholine did not show a rapid increase in signal intensity after addition of the indole molecule. The zwitterionic surfactant molecule, dipalmitoylphosphatidylcholine, showed a weaker interaction than the cationic 1,2-dipalmitoyl-3-trimethylammonium-propane molecule.

Molecular chirality often plays an important role in nanoarchitectonics of precisely controlled and highly ordered molecular assemblies.[80] Monolayers at the air-water interface also provide a good medium for studying interactions based on the chirality of their constituent molecules. Negi et al. investigated the behavior of monolayers with chiral centers at hydrophilic sites.[81] Specifically, they synthesized 1-[1-(6-stearyl)pyrenyl]ethanol, a novel amphiphilic molecule containing a secondary alcohol moiety as a chiral backbone. After chiral separation of the synthesized molecule, the monolayer properties of the racemic (±)- and chiral (S)-(−)-forms at the air-water interface were investigated in detail. The (±)-mixture formed a monolayer like a racemic solid solution. On the other hand, the (S)-(−)-isomer showed the cooperative action of the chiral steric factor with the face-to-face association of the pyrene ring. The resulting structure-controlled monolayers are a combination of π-π stacking and chirality as interaction elements. By combining chirality with other molecular interactions in artificial systems, molecular assemblies with more precisely controlled functions may be nanoarchitectonically created.

As shown in the above example, chiral monolayers formed on the water surface are a very useful venue for studying the relationship between chirality and the structure of molecular assemblies. Negi et al. designed 2,2′-bis(octadecyloxy)-1,1′-binaphthalene-6,6′-dicarboxylic acid and their monolayer properties were investigated (Figure 10).[82] This molecule has axial chirality derived from the binaphthyl group. The axial chirality derived from the binaphthyl group has a larger asymmetric space than the comventional chirality. This axial chirality is expected to have a pronounced effect on the structure of the monolayer. Further intermolecular interactions are also expected since the molecule has two COOH groups in the binaphthyl moiety. In the case of the (±)-racemic form, AFM results suggest the formation of a racemic compound-like monolayer due to heterochiral recognition. π-A isotherm and Brewster angle microscopy observations suggest the formation of a solid monolayer in the (±)-racemic form. The π-π stacking between naphthyl rings and the strong van der Waals interactions between the long alkyl chains are probably responsible for this solid membrane formation. The states of the mixed monolayers were computationally investigated for 1:1 molecular pairs of (R)-isomers and (S)-isomers. The naphthyl rings of each enantiomer face each other to form π-π stacking. The long alkyl chains are close to each other so as to maximize

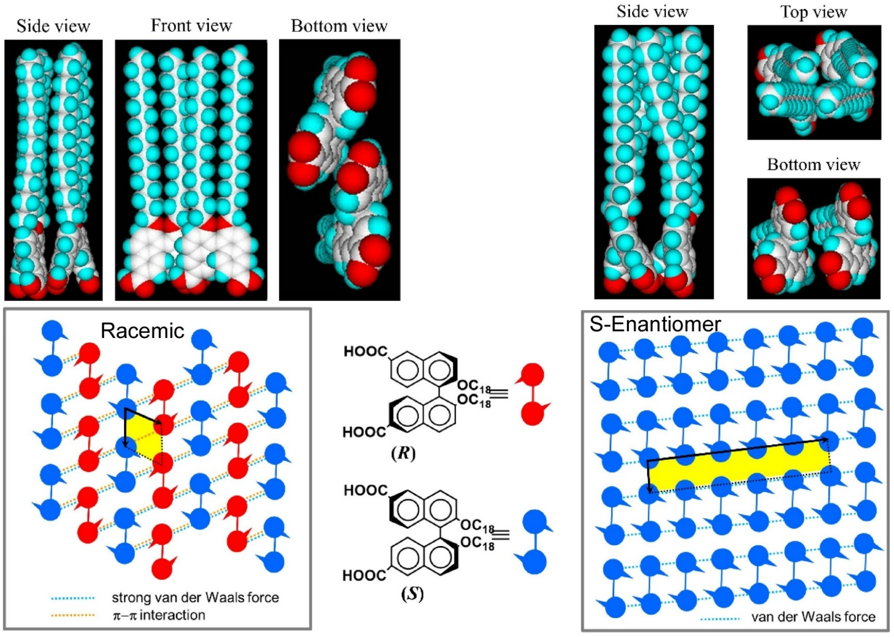

**Figure 10.** Monolayer structure models of 2,2′-bis(octadecyloxy)-1,1′-binaphthalene-6,6′-dicarboxylic acid: racemic mixture and S-enantiomer. Reproduced with permission.[82] 2023, Oxford University Press.

van der Waals interactions. In general, a solid monolayer is formed in the (±)-racemic form, where a stable structure without steric hindrance is formed. On the other hand, in the case of (S)-enantiomers, a characteristic structural pattern with alkyl chains regularly arranged in one-dimensional direction was observed in AFM images. Examination of the molecular model predicted that each naphthyl ring of the binaphthyl moiety is oriented in the same direction. In this case, the dimer units overlap in the same manner to form the structure. As a result, a one-dimensional columnar structure as seen in the AFM image is expected to be formed. Molecular modeling suggests that in the (S)-enantiomer, the steric hindrance of the long alkyl chain causes the distance increase between the naphthyl rings, where $\pi$-$\pi$ stacking cannot be effectively formed and they cannot associate closely together. Since strong intermolecular forces do not work, the monolayer expands due to intermolecular electrostatic repulsion caused by the dissociation of carboxyl groups. The results of this study also show that the successful combination of various chiral frameworks and intermolecular interactions can lead to the development of more precise two-dimensional nanoarchitectonics.

Metal nanoparticles are known to exhibit a variety of properties not observed in bulk materials. Localized surface plasmon resonance induced by strong light-metal interactions is one notable feature.[83] Localized surface plasmon resonance has the ability to enhance fluorescence and Raman signals. Such properties are sensitive to the surrounding environment, and thus can be used as sensing and imaging materials for estimation of environmental conditions. In addition, signals can be enhanced by plasmonic coupling effects arising from the densely assembled structure of metallic nanoparticles. The fabrication of plasmonic nanoparticle films is an attractive target for two-dimensional nanoarchitectonics. Mitomo, Ijiro, and co-workers have investigated the accumulation of metal nanoparticle cubes coated with oligo(ethylene glycol)-linked alkanethiol ligands at the air-water interface (Figure 11).[84] The oligo(ethylene glycol) moiety was prepared to give a temperature-responsive hydrophilic/hydrophobic transition via hydration/dehydration. Accordingly, the properties of the self-assembled and nanoarchitectonized plasmonic nanofilms with respect to temperature were investigated. To this end, silver nanocube films self-assembled on a water surface were transferred onto a solid substrate modified with hydrophobic molecules. Scanning electron microscopic (SEM) observation of the transferred thin film structure on the substrate revealed that the cube structure formed a well-packed lattice structure. Hysteresis was observed in the color change of the film. When the substrate with the silver nanocube film attached was immersed in a cold buffer solution, it showed a reddish orange color. When the substrate was taken from the cold solution, it also showed a reddish-orange color. On the other hand, when the substrate was taken from the solution after immersion in the hot solution, it immediately turned reddish purple. This different color change involves a temperature-dependent hydrophilicity/hydrophobicity change. The difference may be attributed to the difference in surface wettability via this difference. Another advantage is that the colored film was stable in solution for more than a week at both high and low temperatures. The plasmonic nanocube sheets have potential applications in nanoimaging, surface-enhanced Raman scattering (SERS) detection, or regenerative medical engineering such as cell sheets.

The creation of two-dimensional arrays of single molecule magnets is an attractive research target. This nanoarchitectonics structure is necessary for the development of devices with ultra-high-density magnetic memory based on molecular spintronics. Horii and co-workers investigated two-dimensional single-molecule magnet-based MOF structures using the LB method (Figure 12).[85] First, a series of phthalocyaninato-porphyrinato-terbium(III) double-decker single-molecule magnets were synthesized. Then, they were reacted with Pd$^{2+}$ ions at the air-water interface to nanoarchitectonically fabricate two-dimensional single molecule magnet-based MOFs. This study shows that the structure and magnetism of the films can be systematically tuned by introducing appropriate substituents. The magnetic relaxation times of the prepared MOFs increased with increasing alkoxy chain length. As a result, the magnetic interactions that induce magnetic relaxation are suppressed. This method, which combines long alkoxy substituents with bond formation at the air-liquid interface, is an effective way to develop functions from a spintronics point of view. It is a useful method to construct highly oriented single molecule magnet nanosheets with increased magnetic relaxation time. It is also promising for single molecule magnet-based magnetic memory.

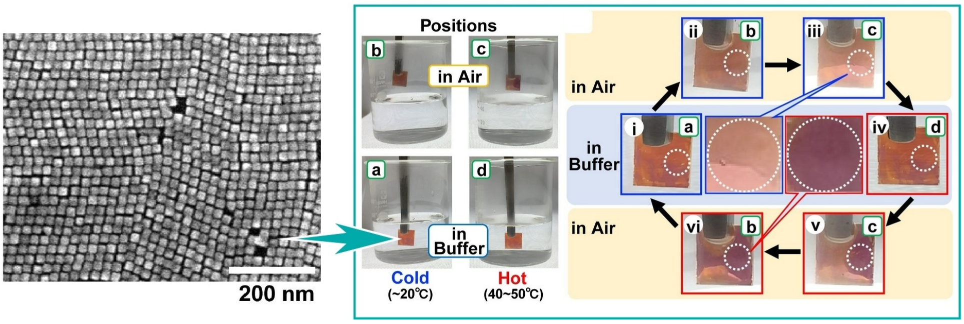

**Figure 11.** Accumulated monolayer of metal nanoparticle cubes coated with oligo(ethylene glycol)-linked alkanethiol ligands (left) and color change hysteresis upon immersion into cold and hot solutions. Reproduced with permission.[84] 2022, Oxford University Press.

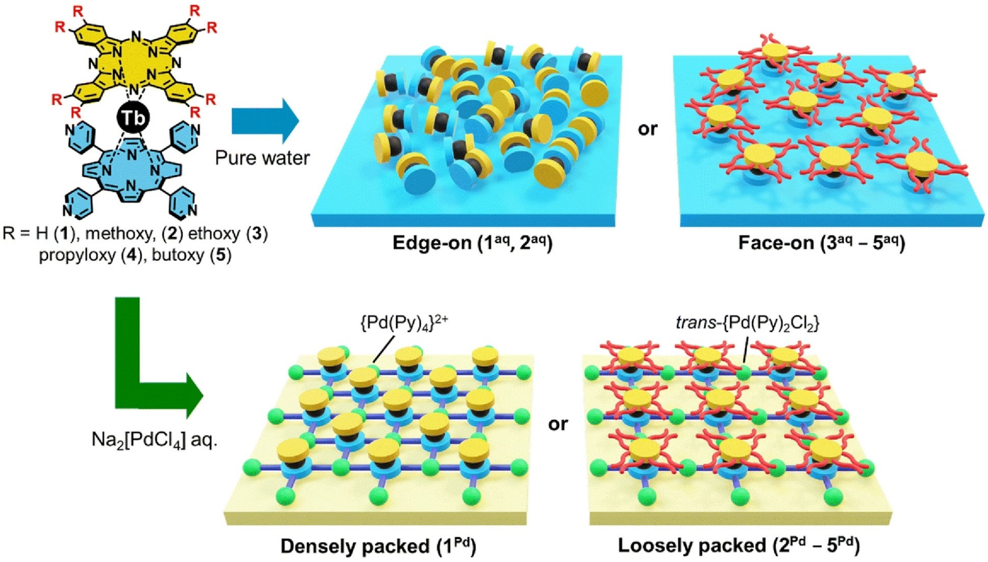

**Figure 12.** Two-dimensional single-molecule magnet-based MOF structures using the LB method where phthalocyaninato-porphyrinato-terbium(III) double-decker single-molecule magnets were reacted with $Pd^{2+}$ ions. Reproduced with permission.[85] 2024, Royal Society of Chemistry.

Incorporating single molecule magnets into a more rigid two-dimensional lattice, MOF, suppresses the molecular vibrations that cause spin-lattice relaxation. This contributes to the improved properties of single molecule magnets. Thus, the correlation between the steric factor of individual single molecule magnets and the arrangement of single molecule magnets in thin films is important for spintronics functionality development. It is crucial for improving the performance of single molecule magnet thin films based on nanoarchitectonics of two-dimensional thin films.

MOFs, which are constructed by coordination bonds between metal ions and organic ligands, are a powerful method for nanoarchitectonics of liquid interfaces.[86] They are valuable structures that not only provide a regular arrangement of specific functional groups, but also uniform nanopores. To obtain high quality MOFs, experimental know-how is also required. In particular, the expected functionality of MOF nanosheets, including electrical conduction, also depends on their structural control. For example, control of structural properties such as lateral size, thickness, crystallinity, orientation, and morphology is important. However, their regulation has not yet been fully achieved. Makiura and co-workers focused on the effect of spreading solvents on the preparation of MOF thin films on the water surface.[87] In the synthesis procedure, a 2,3,6,7,10,11-hexaaminotriphenylene solution is spread over an aqueous $Ni^{2+}$ solution. The ligand reacts with $Ni^{2+}$ at the air-water interface to form MOF nanosheets composed of $Ni^{2+}$ and 2,3,6,7,10,11-hexaiminotriphenylene. They focused on the type of solvent in the ligand diffusion solution for the difference. Solvents with different polarities and boiling points, methanol and *N*,*N*-dimethylformamide, were considered. Better results for macroscopic morphological uniformity were obtained with *N*,*N*-dimethylformamide. This is because *N*,*N*-dimethylformamide, with its higher polarity, is less volatile, and it easily binds to the amino groups of the ligands, facilitating the formation of coordination connections and the growth of MOF nanosheets. Further optimization of the interfacial nanoarchitectonics method is important to obtain two-dimensional MOF structures for practical use.

Makiura and co-workers also examined other factors. By varying the concentration of the ligand diffusion solution, they examined structural changes at the air-water interface of similar MOF nanosheets (Figure 13).[88] The concentration of ligands acts as a factor in crystal formation through both chemical reactions and intermolecular interactions. Changes in chemical composition, crystal orientation, lateral size, thickness, roughness, and morphology were investigated. Systematic increase in the concentration of ligand leads to an increase in the lateral size and thickness of the nanosheets. On the other hand, the complete alignment and preferential orientation of the nanosheets are maintained. Higher concentrations effectively increase the number of molecular stacks due to $\pi$-$\pi$ interactions, increasing the thickness of the MOF nanosheets from about 3 nm–about 7 nm. However, an increase in surface roughness and a decrease in orientation were observed with even higher concentrations of the solution. This can be interpreted as a result of the rapid evaporation of the solvent in the solution, which resulted in diverse and non-uniform interfacial conditions. MOFs miniaturized into nanosheets could act as the ultimate thin functional component in nanodevices. Such nanosheet MOFs exhibit unique properties rarely seen in bulk MOFs. Practical nanoarchitectonics for precise control of such nanosheet MOF structures is a necessary process for nanodevice research and the development of novel applications.

The water interface is not only a medium for the creation of precise structures at the molecular level as described above, but also a place for the expression of functions of nanoarchitectonized materials. In the following example, an example is given for the use of functional materials for possible practical uses at the air-water interface. The deterioration of the global

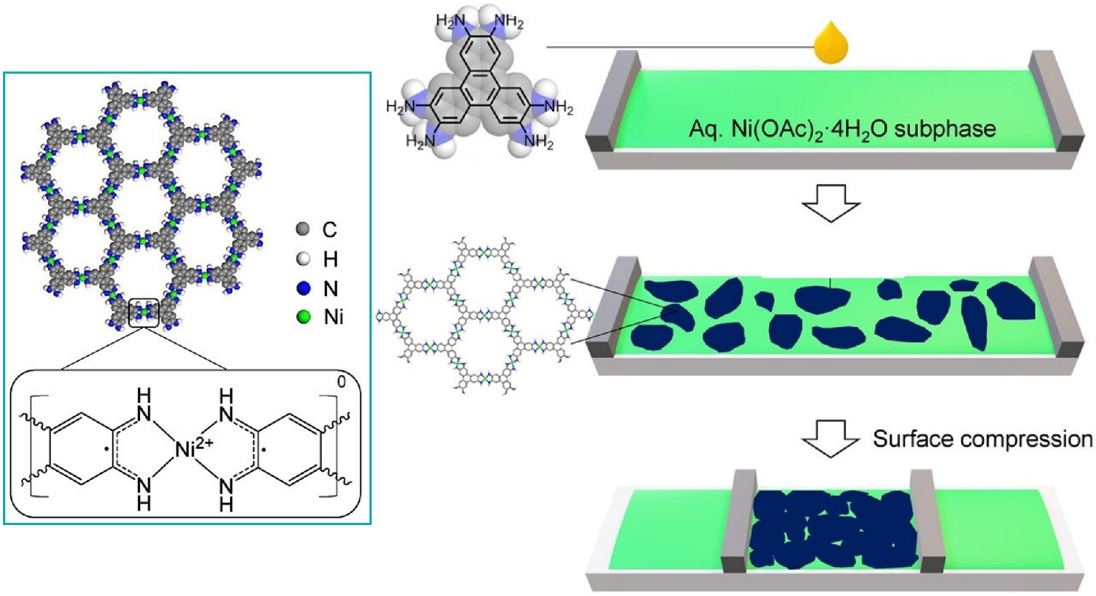

**Figure 13.** Assembly of MOF nanosheets, composed of 2,3,6,7,10,11-hexaiminotriphenylene and N$^{i2+}$ ion, at the air/liquid interface. Reproduced with permission.[88] 2023, American Chemical Society.

environment is a serious problem, especially the lack of fresh water is an urgent issue to be solved. Among several methodologies, freshwater production by interfacial steam generation using solar heat is a very green approach that utilizes inexhaustible solar energy. Li, Xu, and coworkers created porous wood modified with polyaniline and applied it for interfacial vapor production (Figure 14).[89] Hydrogen bonds are formed between the nitrogen moieties of polyaniline and the hydroxyl groups of cellulose, immobilizing the polyaniline into the wood material. As a sunlight application, the polyaniline/wood material exhibited almost full spectrum light absorption covering a wide spectral range from 250–2500 nm. As a result, it produces water vapor at a high evaporation rate. In addition, the structure by wood is high robust. It is a robust and low-cost evaporator that can be used for water purification. It is expected to be suitable for continuous operation in seawater and various contaminated water environments.

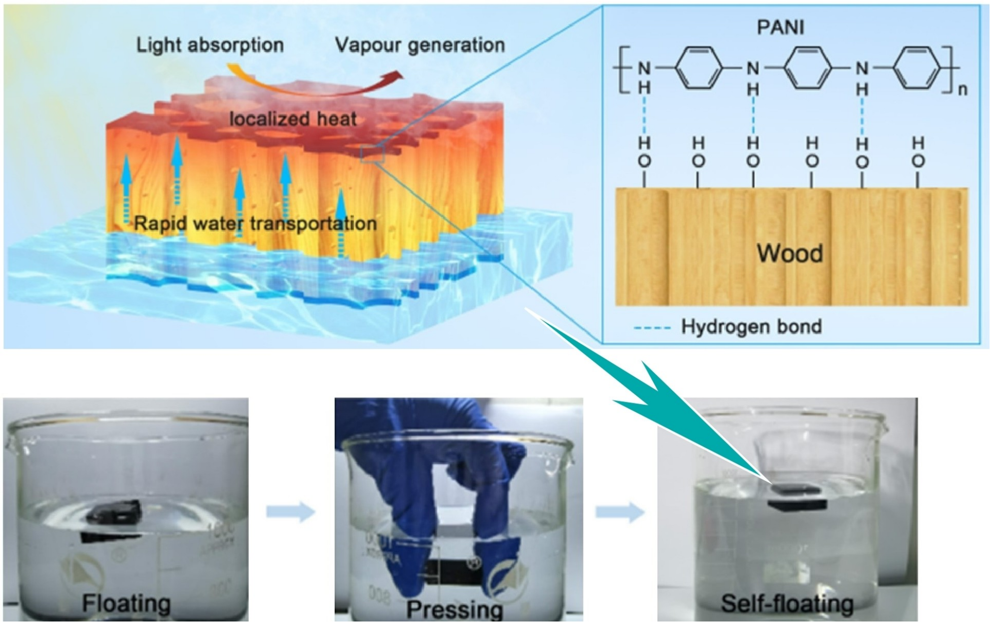

**Figure 14.** Porous wood piece modified with polyaniline for interfacial vapor production: structure (top) and floating behaviour (bottom): Reproduced with permission.[89] 2023, Oxford University Press.

## 4. Summary and Perspective

In nanoarchitectonics, nano-units (atoms, molecules, and nano-objects) interact and react to create functional materials. Ideally, such functional structures are precisely fabricated in a three-dimensional space. However, such structural control and fabrication are not always easy. A realistic methodology to control such structures is the use of interfacial environments.

As shown in examples listed in this paper, in solid interfacial environments, molecular structures can be precisely observed and analyzed with theoretical calculations. The presented examples are shortly summarized here. Solid surfaces are a prime site for nanoarchitectonics at the molecular level. Molecules interact with each other in specific orientations, and selective molecular coupling and polymerization occur. It is also possible to observe these phenomena in detail. Such studies combine scanning tunneling microscopy and spectroscopy with density functional theory calculations to examine the details of nanoarchitectonics at the molecular level. Spin-polarized density-functional theory calculations of the magnetic properties of nanoarchitectonized molecules on solid surfaces are investigated. Surface synthesis of pure organic supramolecular radical frameworks is achieved by combining supramolecular chemistry with surface chemistry. This work has important applications in catalytic redox reactions, sensors, and quantum technology. Artificial electron Kagome lattices at solid surfaces have also shown the potential for exotic supersymmetry from electronic potential landscapes. Single atomic catalysis in surface synthesis to form these special brews can also be highly explored. Not only molecular structures, but also structural control and observation of inorganic nanomaterials are being actively pursued as nanoarchitectonics on solid interfaces. The immobilization of gold atoms on stoichiometric, non-polar surfaces without defect sites or doping is also being explored for its catalytic function. Nanoarchitectonics of solid surfaces has the potential to pave the way for cutting-edge functionality and science based on advanced observation and analysis.

Liquid surfaces are more kinetic and dynamic than solid interfaces, but high-resolution structural observation is not always easy. On the other hand, the high fluidity offers many possibilities for structure fabrication by nanoarchitectonics. The interaction between components in the liquid interface is important in this process. Below shortly, the selected examples are summarized. Langmuir monolayers at the air-water interface is one of typical media. The search for suitable molecular structures for interfacial monolayers and the sensing of important prizes such as anions are also being investigated. The successful combination of various chiral frameworks and intermolecular interactions can lead to the development of more precise two-dimensional nanoarchitectonics. Spectral methods such as infrared spectroscopy are powerful for analyzing interfaces. The fabrication of plasmonic nanoparticle films and the formation of two-dimensional single-molecule magnet MOF structures have been demonstrated. The latter is particularly useful for developing devices with ultra-high-density magnetic memory based on molecular spintronics. Along with the development of these advanced features, fundamental aspects are also being investigated. MOF thin films are promising structures for nanoarchitectonics on liquid surfaces. There are also detailed studies of the effects of the solvent and concentration of the developing solution on the control of structural properties such as lateral size, thickness, crystallinity, orientation, and morphology of MOF thin films in order to produce higher quality MOF thin films. Not only these functional molecules and nanomaterials, but also material systems are studied at the liquid interface. A material study, an interfacial evaporator made of porous wood modified with polyaniline, is also being conducted on the water surface. It is suitable for continuous operation in seawater and various contaminated water environments as a practical material. Although nanoarchitectonics at the liquid interface is inferior to solid interfaces in terms of ultra-precise structural control and microscopic observation, it has advantages in terms of freedom of interaction and diversity of components. It is a more suitable environment for the development of functionalities.

As seen in these example summary, the scope of interest in nanoarchitectonics at interfaces can range from state-of-the-art molecular manipulation to realistic and practical applications such as freshwater production. This is due to the creation of specific interactions at interfaces, an environment that is both expansive and constrained in its range of motion. In actual functional material development, material development may not be limited to interfacial materials. There is a need to advance the knowledge gained from interfacial nanoarchitectonics to more practical three-dimensional material structures. One practical approach is to develop multilayer structures such as layered construction. Suitability of nanoarchitectonics concepts for layer-by-layer adsorption[90] and Langmuir-Blodgett multilayering[91] has already been discussed in the other review articles.

We must also challenge three-dimensional integral nanoarchitectonics, which is more complex and multifunctional than multilayered two-dimensional systems. However, the choices of materials and construction strategies, including components, two-dimensional layers, and integral modes, are diverse, and approaches based on experience and theory may not be able to keep up. In other words, an artificial intelligence approach may be necessary since materials design and creation by machine learning is becoming widely used.[92] Indeed, the need for collaboration between nanoarchitectonics and materials informatics is being discussed.[93] It is very significant that interfacial nanoarchitectonics, which is able to collaborate with detailed basic science, contributes to the development of practical functional material systems through the methodology of materials informatics. It is wonderful that nanoarchitectonics is advancing as a method of material production for human development, while aiming at the ultimate form in the concept of "method for everything.

Other aspects such as approach to mass production and biocompatibility must also be satisfied to get more uses in human society. The interface field is considered to be very useful in this regard. At the interface, it is expected to be possible to create an elaborate structure with a nanosize thickness but a size that is large enough to be used in practical applications. The interfacial membrane structure is also a good material for biocompatibility. Soft two-dimensional tissues should be able to become densely packed structures in the living body if the surface structure is well designed. This review paper describes how nanoarchitectonics at the interface of solids and liquids can be useful from the basic field at the molecular level to practical materials. The introduction of layered structure methodology, artificial intelligence, membrane engineering for mass production, and the pursuit of biocompatibility will lead to further developments. Of course, the continuing contributions of chemistry and physics developments in such arenas will be well expected. From this viewpoint, recalling existing areas into nanoarchitectonics strategy would be fruitful. For example, polymers and block-copolymers, as self-assembling nano-units able to provide well defined nanostructured films in nanoarchitectonics approaches as seen in fine structure tuning with solvent annealing, breath figure, substrate guided, and wrinkling processes.[94] Even old yet relevant seminal work of Alan Turing on morphogenesis may have meaningful contributions.[95] Such continuous developments create the intersection of nanoarchitectonics with other scientific fields with analyzing the environmental sustainability of nanoarchitectonics materials production and application,

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## Conflict of Interests

The authors declare no conflict of interest.

**Keywords:** Interface · Interaction · Liquid · Nanoarchitectonics · Solid

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